

DISTRIBUTION AND CHARACTERIZATION OF POLYBROMINATED DIPHENYL ETHERS IN PARTICLE AND GAS PHASE OF INDOOR AIR

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are representative additive type brominated flame retardants. Three types of commercial products, penta-BDEs (c-Penta-BDEs), octa-BDEs (c-Octa-BDEs) and deca-BDEs (c-Deca-BDEs), and they have been widely in use in plastic, computer, television, textile, automobile, etc¹. Additive type flame retardants have better flame retardant characters and they are cheaper than reaction type products. These chemicals leak out easily by heat and/or pressure during manufacture, use and disposal, causing environmental pollution.

In general, PBDEs have similar chemical characteristics and structures as polychlorinated biphenyls (PCBs), which extensively contaminate the environment and biota. PBDEs have been known to affect neural development, thyroid function, reproduction and also found to enhance cancer risk in animal experiments^{1,2}. Tetra- to hepta-BDEs were designated as the “New POPs” compounds in the Stockholm convention which was promulgated in 2009³.

Contamination by higher molecular weight PBDE congeners (e.g., deca-BDE), which is less bioavailable for animals and human, has been reported in recent years^{4,5}. The presence of higher-BDE congeners in human indicates that dust ingestion may be a significant exposure pathway for human⁶. In one of our our previous studies,⁷ higher-BDE congeners were also found in house dust samples collected from Korea.

In the present study, in order to clarify the origin of PBDEs in house dust and their possible exposure by inhalation, we investigated the concentration levels and the congener patterns of PBDEs in indoor air using the Andersen air sampler (floating dust) and alumina adsorption filter (gas phase), and discuss their distribution and characteristics in the particle and gas phases of indoor air.

2. Materials and methods

2.1. Sampling of particle and gas phase in indoor air

2.2.1 Sampling location

For the analysis of indoor PBDEs, four air samples were collected from (1) office (area: 104 m²; No. of PC: 17; No. of duplicator: 1), (2) laboratory (area: 117 m²; No. of GC and LC/MS: 8) and (3) computer room (area: 268 m²; No. of PC: 80; computers were produced in 2009) of Ehime University and also from behind a (4) TV set (test for identifying the sources of PBDEs; TV was made in Japan in 1990).

2.2.2 Air sampling

We collected particle and gas phase samples by the Andersen air sampler (AN-200[®]; Tokyo. Dylec Co., Japan) between October 2012 and February 2013. Indoor particle and gas phase samples were collected for 2 or 3 days with 28 L/min of air flow. Particle phase samples were classified into nine particle size phases (> 11 μm; 11 ~ 7.0 μm; 7.0 ~ 4.7 μm; 4.7 ~ 3.3 μm; 3.3 ~ 2.1 μm; 2.1 ~ 1.1 μm; 1.1 ~ 0.65 μm; 0.65 ~ 0.43 μm; < 0.43 μm). Gas phase samples were also collected using the alumina adsorption filter (Dioana filter[®]; Miura Co., Japan) which was connected to the outlet of the Andersen air sampler. The alumina adsorption filter was maintained at 100 °C during the sampling period. The collected particle and gas phase samples were reclassified into 6 groups (I to VI group) as shown in Fig. 1.

2.2. Analysis of PBDEs in particle and gas phases of indoor air

Twenty seven congeners of mono- to deca-BDEs in particle and gas phase samples were analyzed. All samples were extracted in a Soxhlet installation using 150 ml of toluene for 8hr (more than 100 cycles) after spiking with ¹³C₁₂-labelled standards (1000 pg, MBDE-MXE-STK; Wellington Laboratories, Canada). Clean-up was carried

out by multi-layer silica gel column chromatography, and the final PBDEs fraction was eluted with 180 mL of 10 % dichloromethane/*n*-hexane. The eluant were concentrated to approximately 50 μ l after spiking with $^{13}\text{C}_{12}$ -labelled standard substances (1000 pg; BFR-ISS-STK; Wellington Laboratories, Canada) for instrumental analysis. The 27 congeners of PBDEs in the eluates were measured using the HRGC (6890N series gas chromatography; Agilent Technologies, USA) and HRMS (JMS-800D high resolution mass spectrometer; JEOL, Japan) equipped with DB-5HT capillary column (15 m, 0.25 mm i.d., 0.1 μ m film thickness; J & W Scientific, USA).

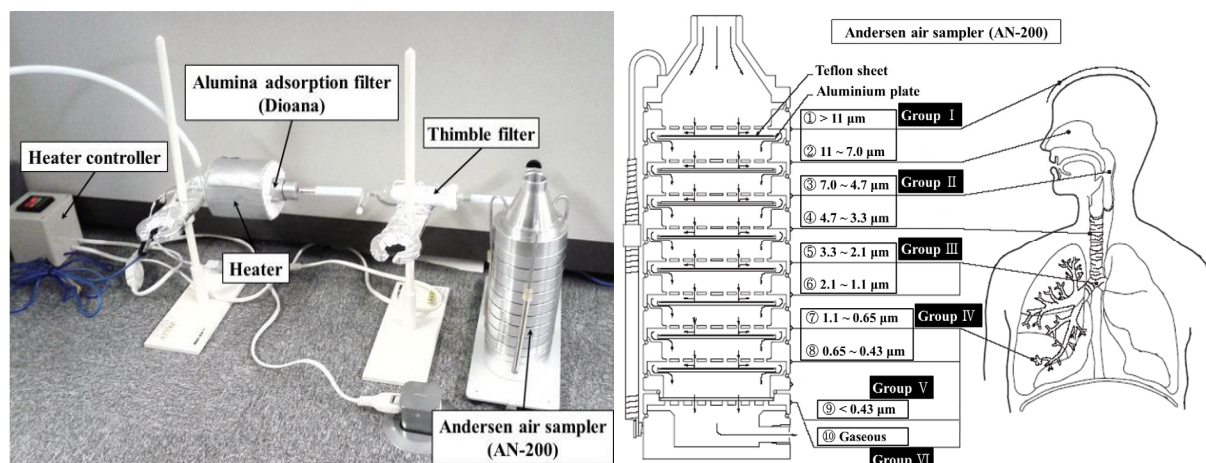


Fig. 1. Schematic representation of the particle and gas phase samples in Andersen air sampler

2.3. Quality Control/Quality Assurance

For checking contaminations by the solvent, glassware, equipments and other interfering substances, one blank sample was analyzed along with a set of six samples. No PBDE congener was detected in these blanks. The average recovery rates of the $^{13}\text{C}_{12}$ -labelled standard substances were 60.6 ± 12.0 % for mono- to hepta-BDE and 81.1 ± 11.8 % for octa- to deca-BDE. The limit of detection (LOD) was defined as three times the standard deviation of the measured values for each PBDE standard in blank tests, that had ranged from 0.01 ~ 0.10 pg/m^3 for mono- to hepta-BDE and 0.08 ~ 0.32 pg/m^3 for octa- to deca-BDE. Levels below LOD were represented “ND” (not detected), in this study.

Adsorption and debromination tests using the alumina adsorption filter were also conducted as follows. The Andersen air sampler was installed in a clean room, and ran for 3 days under the same conditions as actual sampling. The standard substances of PBDEs were spiked in the thimble filter for adsorption test, and also spiked in the alumina adsorption filter for debromination test.

Table 1. Recovery rates (%) for adsorption and debromination test of PBDEs in the alumina adsorption filter

$^{13}\text{C}_{12}$ -labelled standard substance	Adsorption test (3 days)		Debromination test (3 days)
	Thimble filter (%)	Alumina adsorption filter (%)	Alumina adsorption filter (%)
#3-MoBDE	0.0	78.3	70.4
#15-DiBDE	0.0	92.4	77.6
#28-TriBDE	0.0	98.7	82.1
#47-TeBDE	3.58	94.5	88.8
#99-PeBDE	30.8	57.3	102
#154-HxBDE	94.3	9.66	70.7
#153-HxBDE	101	4.22	74.6
#183-HpBDE	98.3	1.36	78.4
#197-OcBDE	80.3	5.91	78.6
#207-NoBDE	103	0.0	97.0
#209-DeBDE	81.9	0.0	80.4

3. Results and discussion

3.1 Recovery rates in adsorption and debromination test

The results of the adsorption and debromination tests in alumina adsorption filter are shown in Table 1. Most of the mono- to penta-BDE were found to be adsorbed on the alumina adsorption filter, while most of the hexa- to deca-BDE were recoverable from the thimble filter, which indicates that lower-BDEs volatilized from the thimble filter, and then adsorbed to the alumina adsorption filter. In addition, the results of debromination test during the sampling periods of 3 days exhibited relatively high recovery rates of the standards of PBDEs, especially higher -BDEs. These results indicate that the sampling apparatus and equipments and chemicals used in this study are suitable for accurate analysis of PBDEs.

Table 2. Concentrations (pg/m³) and distribution ratios (%) of PBDEs in particle and gas phase

	Total	Particle phase (I to V group)					Gas phase
	Group I to VI (>11~Gas)	Group I (>11~7.0 μm)	Group II (7.0~3.3 μm)	Group III (3.3~1.1 μm)	Group IV (1.1~0.43 μm)	Group V (< 0.43 μm)	Group VI (Gas)
Office	Con. (%)	Con. (%)	Con. (%)	Con. (%)	Con. (%)	Con. (%)	Con. (%)
BDE-15	2.03 (7.69)	0.010 (0.35)	0.012 (0.40)	0.011 (0.64)	0.014 (0.35)	0.067 (1.11)	1.91 (22.4)
BDE-28	1.01 (3.84)	0.024 (0.85)	0.019 (0.61)	0.015 (0.87)	0.016 (0.38)	0.155 (2.55)	0.785 (9.19)
BDE-47	1.55 (5.87)	0.041 (1.43)	0.040 (1.32)	0.038 (2.17)	0.043 (1.03)	1.27 (21.0)	0.113 (1.32)
BDE-183	1.62 (6.14)	0.085 (3.01)	0.063 (2.03)	0.056 (3.22)	0.143 (3.46)	0.495 (8.16)	0.778 (9.11)
BDE-209	12.1 (45.8)	2.14 (75.5)	1.84 (60.1)	0.857 (49.2)	2.62 (63.3)	1.86 (30.6)	2.78 (32.5)
Σlower-BDEs ^a	8.07 (30.6)	0.159 (5.63)	0.154 (5.03)	0.145 (8.35)	0.270 (6.51)	2.80 (46.1)	4.55 (53.2)
Σhigher-BDEs ^b	18.3 (69.4)	2.67 (94.4)	2.91 (95.0)	1.60 (91.6)	3.87 (93.5)	3.27 (53.9)	4.00 (46.8)
Σtotal-BDEs ^c	26.4	2.83	3.07	1.74	4.14	6.07	8.54
Laboratory							
BDE-15	3.85 (6.89)	0.033 (0.54)	0.040 (0.72)	0.045 (1.49)	0.019 (0.30)	0.115 (0.58)	3.60 (24.0)
BDE-28	3.53 (6.31)	0.056 (0.90)	0.071 (1.28)	0.102 (3.36)	0.055 (0.86)	0.693 (3.51)	2.55 (17.0)
BDE-47	11.6 (20.8)	0.295 (4.72)	0.317 (5.71)	0.246 (8.09)	0.484 (7.58)	10.1 (51.0)	0.238 (1.59)
BDE-183	0.817 (1.46)	0.069 (1.10)	0.083 (1.50)	0.036 (1.18)	0.106 (1.66)	0.339 (1.72)	0.184 (1.23)
BDE-209	19.3 (34.4)	3.49 (55.8)	3.33 (59.8)	1.47 (48.4)	4.09 (64.1)	4.04 (20.5)	2.85 (19.0)
Σlower-BDEs	25.4 (45.4)	0.469 (7.51)	0.512 (9.20)	0.444 (14.6)	0.947 (14.8)	13.5 (68.6)	9.50 (63.5)
Σhigher-BDEs	30.5 (54.6)	5.78 (92.5)	5.05 (90.8)	2.59 (85.4)	5.44 (85.2)	6.19 (31.4)	5.47 (36.5)
Σtotal-BDEs	55.9	6.25	5.56	3.04	6.39	19.7	15.0
Computer room							
BDE-15	11.3 (28.1)	0.073 (5.34)	0.069 (5.49)	0.134 (8.18)	0.053 (2.76)	1.070 (7.02)	9.88 (52.7)
BDE-28	8.02 (19.9)	0.082 (5.97)	0.137 (11.0)	0.488 (29.7)	0.087 (4.52)	6.182 (40.5)	1.04 (5.55)
BDE-47	1.22 (3.04)	0.060 (4.38)	0.046 (3.68)	0.076 (4.64)	0.056 (2.90)	0.940 (6.16)	0.041 (0.22)
BDE-183	1.46 (3.63)	0.116 (8.43)	ND	0.090 (5.50)	0.222 (11.5)	0.801 (5.25)	0.231 (1.23)
BDE-209	5.38 (13.4)	0.836 (60.7)	0.446 (35.7)	0.681 (41.4)	1.02 (53.0)	1.97 (12.9)	0.431 (2.30)
Σlower-BDEs	31.9 (79.3)	0.332 (24.1)	0.332 (26.5)	0.963 (58.6)	0.418 (21.7)	12.1 (79.0)	17.8 (94.9)
Σhigher-BDEs	8.30 (20.7)	1.04 (75.9)	0.919 (73.5)	0.681 (41.4)	1.51 (78.3)	3.20 (21.0)	0.951 (5.08)
Σtotal-BDEs	40.2	1.38	1.25	1.64	1.93	15.3	18.7
TV							
BDE-15	15.9 (19.8)	0.070 (6.58)	0.060 (4.54)	0.065 (5.53)	0.067 (1.74)	0.597 (1.95)	15.0 (36.0)
BDE-28	32.5 (40.5)	0.236 (22.3)	0.227 (17.1)	0.277 (23.5)	0.302 (6.62)	11.4 (37.3)	20.1 (48.2)
BDE-47	5.90 (7.34)	0.148 (14.0)	0.155 (11.7)	0.196 (16.7)	0.426 (9.35)	4.96 (16.2)	0.015 (0.04)
BDE-183	3.22 (4.00)	0.083 (7.83)	0.037 (2.78)	0.083 (7.04)	0.919 (20.1)	2.05 (6.71)	0.045 (0.11)
BDE-209	4.06 (5.06)	0.354 (33.4)	0.723 (54.4)	0.397 (33.8)	1.043 (22.9)	1.17 (3.83)	0.376 (0.90)
Σlower-BDEs	74.2 (92.3)	0.705 (66.6)	0.606 (45.6)	0.777 (66.2)	2.61 (57.1)	28.3 (92.6)	41.3 (98.9)
Σhigher-BDEs	6.16 (7.67)	0.354 (33.4)	0.723 (54.4)	0.397 (33.8)	1.96 (42.9)	2.28 (7.45)	0.460 (1.10)
Σtotal-BDEs	80.4	1.06	1.33	1.17	4.56	30.5	41.7

Σlower-BDEs^a: sum of mono- to hepta-BDEs.

Σhigher-BDEs^b: sum of octa- to deca-BDEs.

Σtotal-BDEs^c: sum of mono- to deca-BDEs.

3.2. Concentration levels and congener profiles of PBDEs in each sampling place

The concentrations of major PBDEs congeners, Σ lower-BDEs (mono- to hepta-BDE), Σ higher-BDEs (octa- to deca-BDE) and Σ total-BDEs, in particle and gas phase samples collected from office, laboratory, computer room and behind TV are shown in Table 2. The highest concentration of Σ total-BDEs was found in the sample collected from behind the TV set (80.4 pg/m³), followed by laboratory (55.9 pg/m³), computer room (40.2 pg/m³), and Office (26.4 pg/m³) samples.

The Σ higher-BDEs, especially BDE-209 were the predominant congeners in the laboratory and office samples. In contrast, among Σ lower-BDEs, BDE-15 and BDE-28 were especially dominant in the computer room and behind TV, and their distribution was different from those in the laboratory and office. Considering the use of penta-BDE mixtures in computer and TV as flame retardants, the differences in congener distribution in the present study may be attributed to the usage of different PBDEs products in electronic equipment (computer and/or TV).

3.3. Characterization of PBDEs in particle and gas phase samples

Concentrations and congener distributions of PBDEs in each particle size are shown in Table 2. Except for the samples from behind TV, distribution ratios of Σ higher-BDEs were relatively high in the particle phase samples of I to IV group, and particularly, BDE-209 was a predominant congener. In contrast, Σ lower-BDEs showed the highest distribution ratio in gas phase (Group VI), with predominant congeners of BDE-15 and BDE-28. Furthermore, almost all the PBDE congeners were detected in the < 0.43 μ m phase (Group V), and the distribution pattern in this group showed an intermediate composition between particle (Group I-IV) and gas phase (Group VI). These observations indicate that the distribution of semi-volatile organic compounds (SVOCs) such as PBDEs between particle and gas phase will be associated with octanol-air partition coefficient (K_{oa})⁸⁾.

Meanwhile, it was thought that the congeners such as hexa- to deca-BDE were not derived from gas phase. However, these congeners were detected even in the gas phase collected from each sampling place and so, based on the results in the adsorption test of higher-BDE standards, it can be presumed that the ultra-fine particles that have passed through the thimble filter adsorbed to the alumina adsorption filter.

It has been reported that PBDEs are released into the air by the use of electronic equipment⁹⁾. These compounds are released through volatilization in the form of gas and/or aerosol by the rise in temperature during the operation of electronic equipment, and then it may be adsorbed to the air dust.

With respect to the exposure pathway of PBDEs to human *via* house dust, PBDEs in the floating dusts in the air are likely to be a major source. In addition, BDE-209 was found in human specimens at relatively high frequency of the detection, and also detected in particle (3.3 ~ < 0.43 μ m) and gas phases which are inhaled by bronchia and/or alveolus (Fig.1). In present study, we conclude that inhalation through lungs is important an exposure pathway of PBDEs, in particular, BDE-209 for human, and also a detailed estimation of the daily intake of PBDEs are needed.

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