EMISSIONS INVENTORY OF POLYBROMINATED DIPHENYL ETHERS (PBDEs) ON A HOMOLOGUE BASIS

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Introduction

Emissions of Polybrominated Diphenyl Ethers (PBDEs), a class of brominated flame retardants, into the environment were estimated over their entire life cycle, from their production and use to their recycling and waste management, in order to provide information for their risk control. A previous estimated inventory focused only on deca-brominated diphenyl ether (DBDE)[1)]. The present aims to estimate mono- to deca-brominated diphenyl ether homologues.

Materials and Methods

To estimate the material flow of PBDEs in Japan, we set the emission factor and the level of activity at each stage of their life cycle and estimated their emission inventory. In this study, the following processes were considered: the manufacture of flame retardants[2)], the processing of flame-retardant resins [3)], the processing of flame-retardant fiber [4)], the use of final products containing PBDEs (primarily home electric appliances)[5-7)], the dismantling and crushing of home electric appliances[3, 8)], RDF (Refuese Derived Fuel) molding[5)], the crushing of bulky electrical waste[9)], incineration [10)], gasification [10)], the melting of automotive shredder residue (ASR)[9)], and open uncontrolled combustion[11)]. Emission factors were estimated from the monitoring data for individual sources, if any were available. If no actual monitoring data was available, default values used in previous risk assessments were applied[12-15)].

Results and Discussion

Table 1 shows the emission factors of PBDEs on a homologue basis at each stage of their life cycle, and Figure 1 shows the distribution of PBDE homologues in emissions from each source. The distribution of the homologues reveals TeBDEs, lower-brominated DEs, in the dismantling and crushing of home appliances for recycling. Since lower-brominated DEs have been used as flame retardants in Japan in the past, it is conceivable that waste products containing lower-brominated DEs are now in the recycling process. It can be seen from the distribution of homologues in open burning that OcBDEs are dominant. In contrast, DeBDE is dominant in all homologue distributions for other emission factors in the product life cycle.

Table 2 shows the maximum, minimum, and representative emission factors associated with each PBDE, the activity levels, and the resulting estimated release into the environment, at each stage in the product life cycle. Atmospheric emissions of PBDEs were estimated to be about 780 kg/year. Their emission from open burning accounts for about 90% of the total emission. Excluding open-burning emissions, atmospheric emissions were

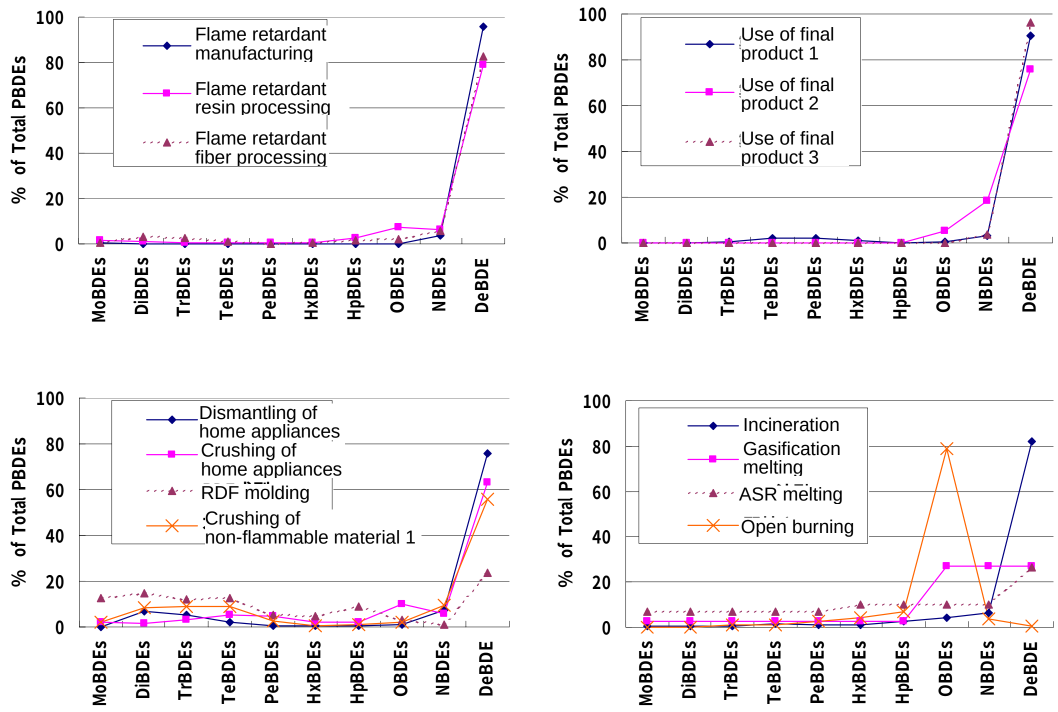

Figure 1. Distribution of homologues for the respective life-cycle stages

Table 1. Atmospheric emission inventory of PBDEs

Process	Emission Factor (g/g-DBDE)											Range*4 (g/g-DBDE)	
	MoBDEs	DiBDEs	TrBDEs	TeBDEs	PeBDEs	HxBDEs	HpBDEs	OBDEs	NoBDEs	DeBDE	PBDEs	min	max
DBDE Production	3.4E-07	5.4E-08	8.7E-09	1.5E-09	3.0E-10	4.6E-11	2.6E-11	1.1E-07	2.4E-06	6.7E-05	7.0E-05	-	-
Flame Retarded Fabric Processing (Air)	4.0E-09	2.9E-08	2.4E-08	8.6E-09	2.1E-09	4.9E-09	1.3E-08	2.0E-08	5.0E-08	7.5E-07	9.1E-07	-	-
Flame Retarded Fabric Processing (Water)	3.3E-12	8.5E-08	6.4E-08	2.6E-09	1.5E-09	1.5E-08	1.4E-07	2.8E-06	5.6E-05	1.0E-02	1.0E-02		
Flame Retarded Resin Processing	1.2E-09	8.7E-10	5.0E-10	2.6E-10	3.4E-10	5.1E-10	1.8E-09	4.9E-09	4.2E-09	5.4E-08	6.8E-08	2.7E-09	1.8E-07
Use of Final Products*1	-	8.4E-11	1.4E-09	9.3E-09	1.2E-08	5.3E-09	8.0E-10	2.9E-09	1.6E-08	4.4E-07	4.9E-07	1.4E-07	6.4E-07
Open Fire*2	6.2E-05	2.0E-04	1.1E-03	1.2E-03	2.5E-03	4.0E-03	6.5E-03	7.4E-02	3.5E-03	5.0E-04	9.1E-02	-	-
Dismantling & Crusshing of TVs	4.3E-11	1.8E-09	1.6E-09	1.3E-09	6.4E-10	5.5E-10	4.5E-10	1.1E-09	1.1E-08	1.1E-07	1.3E-07	1.0E-08	4.5E-06
Crushing of Bulky Waste	4.0E-09	5.9E-09	2.6E-09	3.6E-09	1.8E-09	5.6E-09	1.5E-08	1.6E-08	4.5E-08	5.2E-07	7.2E-07	2.5E-07	2.1E-06
Material Recycling*3	1.2E-09	8.7E-10	5.0E-10	2.6E-10	3.4E-10	5.1E-10	1.8E-09	4.9E-09	4.2E-09	5.4E-08	6.8E-08	2.7E-09	1.8E-07
Incineration	-	1.2E-08	1.8E-08	3.2E-08	2.4E-08	2.0E-08	3.4E-08	2.8E-08	8.7E-08	1.4E-06	1.7E-06	1.4E-07	1.5E-05
ASR Melting	-	-	-	-	-	-	-	-	-	-	5.7E-08	-	-
Open Burning	6.2E-05	2.0E-04	1.1E-03	1.2E-03	2.5E-03	4.0E-03	6.5E-03	7.4E-02	3.5E-03	5.0E-04	9.1E-02	-	-

*1: Emission factors corresponding toproduct use are expressed as g/(g-DBDE·year)
*2: Same emission factors as open burning
*3: Same emission factors as flame-retarded resin
*4: Maximum and minimum of PBDE emission factors

estimated to be between 90 and 157 kg/year, and the atmospheric emissions of PBDEs were the highest in the manufacture of flame retardants, followed by the use of the final products containing PBDEs.

The activity level for open burning was set as follows. Assuming the life of products containing PBDEs is 10 years, about 5,000 tons of the DeBDE produced in Japan over the past 10 years would have been disposed of by

Table 2. Atmospheric emission factors, activity levels, and emissions (kg/y)

Process	Emission Factors (g-PBDEs/g-DBDE) Rep.	min	max	Activity		Total PBDEs Rep.	min	max
DBDE Production	7.0E-05	-	-	1,030	ton/year	72	-	-
Flame Retarded Fabric Processing (Air)	9.1E-07	-	-	600	ton/year	0.54	-	-
Flame Retarded Resin Processing	6.8E-08	2.7E-09	1.8E-07	1,400	ton/year	0.095	0.0038	0.25
Use of Final Products*1	4.9E-07	1.4E-07	6.4E-07	33,000	ton/year	16	4.6	21
Open Fire*2	9.1E-02	-	-	7	ton/year	640	-	-
Dismantle and Crusshing of TVs	1.3E-07	1.0E-08	4.5E-06	770	ton/year	0.10	0.0077	3.5
Crushing of Bulky Waste	7.2E-07	2.5E-07	2.1E-06	3,320	ton/year	2.4	0.82	7.0
Material Recycling*3	6.8E-08	2.7E-09	1.8E-07	100	ton/year	0.0068	0.00027	0.018
Incineration	1.7E-06	1.4E-07	1.5E-05	2,300	ton/year	4.0	0.32	35
ASR Melting	5.7E-08	-	-	140	ton/year	0.0080	-	-
Open Burning	9.1E-02	-	-	0.5	ton/year	46	-	-
Total						781		

*1：Emission factors corresponding to product use are expressed as g/(g-DBDE・year)
*2：Same emission factors as open burning
*3：Same emission factors as flame-retardant resin
*4：Maximum and minimum of PBDE emission factors

now. If the proportion of this DeBDE disposed of by open burning is taken to be the same as the proportion of total municipal solid waste (51.61 M tons in 2003) disposed of by self-disposal (170,000 tons)[16] multiplied by the concentration of DeBDE in municipal solid waste (3,000 ng-DeBDE/g-waste), then the annual inflow of DeBDE into open burning would amount to about 500 kg. However, since self-disposal of municipal waste includes compost from kitchen organic waste, the actual outdoor incineration rate is probably not as high as this. Therefore, 500 kg of DeBDE incinerated in the open air was set as the maximum. Open fires can be thought of as uncontrolled combustion as well as open burning. According to the Fire and Disaster Management Agency[17], the total floor area burnt out by fires in Japan in 2004 was 1.574 million m^2. The total floor space in buildings in Japan has been assumed to be 7 billion m^2 [18], which would mean that the burnt ratio can be calculated to be 0.02% annually. When this ratio is multiplied by the total DeBDE stock of 33,000 tons, the amount of DeBDE burnt out is 7 tons/year. Alternatively, if the waste per unit area of floor space is taken as 1 ton/m^2 and the DeBDE concentration in the waste is 3,000 ng-DeBDE/g-waste, as it is for bulky electrical waste, the amount of DeBDE burnt out by fires would amount to about 5 tons/year. To obtain the emission factor for PBDEs in the open-burning process, the results of the study conducted by Hirai were applied[11]. In that study, an uncontrolled-combustion experiment was conducted on the supposition of an open-burning process. The atmospheric emission factor corresponding to the input of PBDEs was 9.1 x 10^{-2}. However, it is anticipated that these values will vary significantly depending on the setting for the concentration of PBDEs in the waste. For the estimated range of PBDEs emissions, the processes of incineration and gasification gave rise to a wide range of values corresponding to the extended range of the activity levels; this also applied to the processing of flame-retardant resin and the crushing of home electric appliances and nonflammable products. Since open burning has a high emission factor, a small difference in the activity level has a high impact on the emission of PBDEs. Furthermore, the release into water media from the processing of flame-retardant fabric was estimated to be 6,000 kg/year more than the corresponding air emissions. Therefore it is conjectured that the one of the major sources of DeBDE in rivers and coastal areas is derived from the release of wastewater from flame-retardant fabric processing plants. The emissions from these processes in the life cycle of DeBDE require further study.

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