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 retardants2), the processing of flame-retardant resins3), the processing of flame-retardant fiber4), the use of final products containing PBDEs (primarily home electric appliances5-7), the dismantling and crushing of home electric appliances3,8), RDF (Refuse Derived Fuel) molding5), the crushing of bulky electrical waste9), incineration10), gasification10), the melting of automotive shredder residue (ASR)9), and open uncontrolled combustion11). 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 applied12-15).

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
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)

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

*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) 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, the total floor area burnt out by fires in Japan in 2004 was 1.574 million m². The total floor space in buildings in Japan has been assumed to be 7 billion m², 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/m² 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. 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.

References
2) European Commission (1993): Techno-economic study on the reduction of industrial emissions to air, discharges to water, and the generation of wastes from the production, processing, and destruction (by incineration) of brominated flame retardants: final report: document
13) Palm, A; Cousins, IT; Mackay, D; Tysklind, M; Metcalfe, C; Alaee, M (2002): Assessing the environmental fate of chemicals of emerging concern: a case study of the polybrominated diphenyl ethers. Environmental Pollution 117(2), 195–213