# PBDE EMISSIONS IN RECYCLING CENTER OF E-WASTE

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## Introduction

Polybrominated diphenyl ethers (PBDEs) is the most widely used brominated flame retardants (BFRs) which are a group of bromine containing organic compounds which are added to several polymers used in plastics, textiles, and other materials to prevent or retard the spread of fires[1]. PBDEs have been used extensively as three formulations: decabromodiphenylether (deca-BDE), octabromodiphenylether (octa-BDE), and pentabromo-diphenylether (penta-BDE). However, the use of brominated flame retardants causes the worst effect on environment due to which the European Union (EU) decided to ban the use of penta-BDE and octa-BDE. Thus, the production and use of the two BDEs is prohibited worldwide in 1990'[2]. The EU regulation such as the RoHS (Restriction of the use of Hazardous Substances in electrical and electronic equipment) and the WEEE (Waste Electrical and Electronic Equipment) banned the use of PBDEs due to their harmful effect[2]. Until 2006, a wide array of products made in the Republic of Korea such as computers, TVs and automobiles used brominated flame retardants[3]. Environmental regulations of Korea have restricted the use of brominated flame retardants since 2006. Due to their human toxicity and environmental issues, many countries have conducted research and studies about effective management of PBDEs. For the emission of PBDEs, Japan had already calculated the emission factors and the emissions in the environment of flame retardants during the product life cycle from production to disposal of PBDEs. Ministry of the Environment of Japan showed that emissions from the recycling process account for 32% out of the total atmospheric emissions of waste electrical and electronic equipment [4]. In most cases, emission factors used in previous studies are based on expert judgments or laboratory experiments to estimate the emissions. They are not based on field studies because field studies do not always supply sufficient information to derive an emission factor[5]. In this study, we did calculate the emissions through the field studies in recycling centers of e-waste

## Materials and methods

Taking the consideration of the processing volume and targeted products, four RCs termed as RC1, RC2, RC3 and RC4 were selected for conducting air-borne samples from their recycling processes. RC1and RC2 conduct the recycling processes of TVs while RC3 mainly recycles refrigerators and air-conditioner. RC4 is recycling the small appliances. The air samples were collected from the areas such as dismantling and crushing/plastic segregation (Fig. 1).

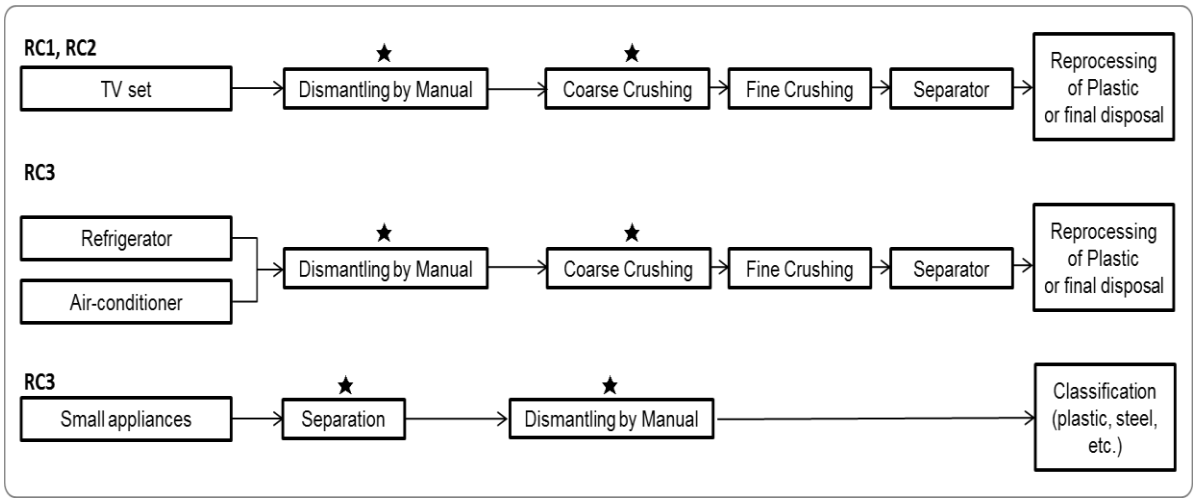


Fig. 1. Air-borne sampling points in the 4 recycling centers

The analysis of the atmospheric samples was conducted according to US EPA 1614 and the official standard test method of POPs in Korea published by the Ministry of Environment of the Republic of Korea in 2007. In the extraction process, the collected samples were added in Soxhlet thimble filter followed by the addition of 1~5 ng of 11 surrogated standards ($^{13}$C-labeled BDEs) for recovery correction and extracted using 300 mL toluene for 16 hours. After bringing the concentrated extract volume up to 2 mL, the total amount was eluted with n-hexane and sulfate solutions. Then it was washed two or three times with a hexane solution and the collected n-hexane layer was dehydrated. Final volume of the dehydrated solution was purified using multi-layer silica gel column (filled with neutral-base-neutral-acid-neutral) and alumina column chromatography. For the purpose of calculating the samples recovery rate, a C-labeled BDE-138 internal standard solution (2ng) was added prior to instrumental analysis. The analysis was conducted in EI-SIM (Electron Impact-Selective Ion Monitoring) mode with HRGC/HRMS(High Resolution Gas Chromatography/ High Resolution Mass Spectrometry) at resolution limit over 10,000 (10% valley) using a DB-5HT (15 m × 0.25 mm i.d., 0.1 μm, J&W Scientific) column.

## Results and discussion

### 1. Atmospheric concentration and distribution of PBDEs

Table 1 shows the results on the atmospheric concentrations obtained from RC1 and RC2 in which TV is being treated mainly. In RC1, the area for crushing in summer had the highest concentration of 48,874 pg/m$^3$, followed by the dismantling in summer. RC1 had the lower concentrations compared to RC1 and it had 1,727 pg/m$^3$ and 3,251 pg/m$^3$ in the area for crushing and dismantling respectively in summer.

**Table 1. Atmospheric concentration (pg/m$^3$) and homologue ratio in RC1 and RC2**

| Homologue | RC1 | | | | RC2 | | | |
|---|---|---|---|---|---|---|---|---|
| | Dismantling | | Crushing | | Dismantling | | Crushing | |
| | summer | autumn | summer | autumn | summer | autumn | summer | autumn |
| Tetra-BDE | 193 (0.9%) | 167 (1.0%) | 530 (1.1%) | 505 (2.7%) | 95 (2.9%) | 268 (3.7%) | 47 (2.7%) | 99 (13.2%) |
| Penta-BDE | 374 (1.8%) | 676 (3.9%) | 1,782 (3.7%) | 2,503 (13.5%) | 280 (8.6%) | 506 (7.1%) | 36 (2.1%) | 44 (5.9%) |
| Hexa-BDE | 427 (2.1%) | 773 (4.5%) | 1,570 (3.2%) | 1,554 (8.4%) | 96 (3.0%) | 215 (3.0%) | 13 (0.8%) | 59 (7.9%) |
| Hepta-BDE | 1,329 (6.4%) | 1,893 (11.0%) | 5,539 (11.4%) | 3,317 (17.8%) | 116 (3.6%) | 442 (6.2%) | 41 (2.4%) | 52 (6.9%) |
| Octa-BDEs | 614 (3.0%) | 1,559 (9.1%) | 1,886 (3.9%) | 1,279 (6.9%) | 58 (1.8%) | 269 (3.8%) | 30 (1.8%) | 38 (5.1%) |
| Nona-BDEs | 3,049 (14.7%) | 4,946 (28.8%) | 9,437 (19.3%) | 3,585 (19.3%) | 341 (10.5%) | 925 (12.9%) | 257 (14.9%) | 1431 (19.1%) |
| Deca-BDE | 14,762 (71.2) | 7,159 (41.7%) | 28,040 (19.3%) | 5,845 (31.4%) | 2,266 (69.7%) | 4,523 (63.3%) | 1,303 (75.4%) | 314 (41.9%) |
| Total PBDEs | 20,747 | 17,172 | 48,784 | 18,588 | 3,251 | 7,149 | 1,728 | 749 |

Table 2 shows the results on the atmospheric concentrations obtained from RC3 and RC4 in which refrigerator and small appliances are being treated mainly. The crushing and dismantling area in autumn in RC were 4,399 and 18,712 pg/m$^3$ respectively. RC4 which conducts the recycling processes of small appliances was a little bit lower than others. The similar type of our research was conducted which measured the atmospheric concentrations of the e-waste in the dismantling area in a previous study. Their results showed that the concentrations near the area ranged between 506 pg/m$^3$ and 1,662 pg/m$^3$ in China [6]. Fig. 2 also showed the various concentrations (720 to 170,000 pg/m$^3$) present among the different plastic recycling centers at Japan[4]. Compared with urban and industrial area in other countries, these values were higher[7, 8].

**Table 2. Atmospheric concentration (pg/m$^3$) and homologues ratio in RC3 and RC4**

| Homologue | RC3 | | | | RC4 | | | |
|---|---|---|---|---|---|---|---|---|
| | Dismantling | | Crushing | | Dismantling | | Classification | |
| | summer | autumn | summer | autumn | summer | autumn | summer | autumn |
| Tetra-BDE | 46 (1.3%) | 249 (1.3%) | 117 (3.7%) | 102 (2.3%) | 30 (0.7%) | 29 (2.1%) | 63 (1.6%) | 24 (3.1%) |
| Penta-BDE | 82 (2.3%) | 632 (3.4%) | 114 (3.6%) | 203 (4.6%) | 35 (0.8%) | 15 (1.1%) | 60 (1.5%) | 14 (1.9%) |
| Hexa-BDE | 35 (1.0%) | 1,124 (6.0%) | 27 (0.9%) | 38 (0.9%) | 15 (0.3%) | 8 (0.5%) | 29 (0.7%) | 11 (1.4%) |
| Hepta-BDE | 118 (3.3%) | 2,404 (12.8%) | 44 (1.4%) | 100 (2.3%) | 58 (1.3%) | 27 (1.9%) | 138 (3.5%) | 19 (2.4%) |
| Octa-BDE | 101 (2.8%) | 2,940 (15.7%) | 40 (1.3%) | 157 (3.6%) | 44 (1.0%) | 22 (1.5%) | 98 (2.5%) | 15 (1.9%) |
| Nona-BDE | 510 (14.1%) | 5,483 (29.3%) | 480 (15.3%) | 1,051 (23.9%) | 548 (12.3%) | 166 (11.8%) | 642 (16.1%) | 141 (18.3%) |
| Deca-BDE | 2,721 (75.3%) | 5,881 (31.4%) | 2,309 (73.8%) | 2,748 (62.5%) | 3,714 (83.6%) | 1,136 (80.9%) | 2,950 (74.1%) | 550 (71.0%) |
| Total PBDEs | 3,612 | 18,712 | 3,130.43 | 4,399 | 4,444 | 1,404 | 3,981 | 774 |

When it comes to distribution of homologues, it showed that air samples of RC1 contained 1.4% tetra-BDE, 5.7% penta-BDE, 4.5% hexa-BDE, 11.7% hepta-BDE, 5.7% octa-BDE, 20.5% deca-BDE and 50.4% deca-BDE as average value. The homologue ratio of RC2 was similar to the RC1. In RC2, It showed that air samples in RC1and RC2 contained less than 3% tetra-BDE~hexa-BDE, 14.3%~14.6% nona-DBE and 62.6%～77.4% deca-BDE as average value. The technical penta-BDE products (DE-71 and Bromkal 70-5DE) contains higher ratio of tetra-BDE other than penta-BDE[9]. Though the technical octa-BDE products varied with different company products (DE-79 and Bromkal 79-8DE), it mainly contains hepta, octa and nona-BDE. However, the technical deca-BDE products (Saytex and Bromkal) contains more than 90% of deca-BDE[9]. Therefore it was assumed that the deca-BDE containing technical deca-BDE products had a large influence on the PBDEs generated during the e-waste recycling process.

**2. PBDEs emissions from recycling centers of e-waste**

In order to estimate the emissions of PBDEs, The emission factor was calculated based on the atmospheric concentrations analyzed in this study during the recycling process. The method derived by previous study was used for calculating the emission factor, using the concentrations measured in the field[5]. According to this method, the emission factor (g/g) = Output PBDEs/Input PBDEs. Input PBDEs were calculated as follows: PBDEs Input (ng) = Disposed volume ×Weight of plastics × content of PBDEs in plastics × $10^6$. Where, Disposed volume is No of units disposed, Weight of plastics = Wt of plastics present in each unit (kg), content of PBDEs in plastics = Calculated concentration of PBDE in plastics (mg/kg), the concentrations of PBDEs in the output were based on the PBDEs in the atmosphere measured inside the recycling center.

Table 3 shows the results on emission factors and estimated amounts of emission. At RC1 and RC2 are treating TV sets, the emission factors in the TV dismantling line was in the range of $1.87\times10^{-7}$-$5.67\times10^{-7}$ (average=$3.08\times10^{-7}$), while the emission factors in the area of the crushing process were $2.70\times10^{-9}$ and $2.35\times10^{-6}$ respectively. The emission factors of RC3 were not low due to the low input-PBDEs compared to the output-PBDEs from the atmosphere in RC1 and RC2, indicating that the emission factor can be affected, depending on the concentration of PBDEs. For this reason, an exact measurement of PBDEs in the appliances is needed. The emission factor in RC4 in which is treating small appliances was in range of $2.91\times10^{-8}$~$8.29\times10^{-8}$ (average=$6.82\times10^{-8}$) in dismantling and classification area. As per earlier studies related to the emission factor calculation during the recycling process of home appliances, the emission factors were calculated to be $6\times10^{-8}$ by Tamade et al. [10] and $8\times10^{-9}$-$5\times10^{-6}$ by Sakai et al.[5]. The emission factor was used to estimate the emissions generated during the recycling process as shown Table 3.

**Table 3. Estimated emissions of PBDEs during recycling process**

| Facility | area | season | emission factor (g/g) | emissions (g/year) |
|---|---|---|---|---|
| RC1 | Dismantling | summer | 2.26E-07 | 4,086 |
| | | autumn | 1.87E-07 | 3,382 |
| | Crushing | autumn | 2.70E-09 | 49 |
| RC2 | Dismantling | summer | 5.67E-07 | 10,276 |
| | | autumn | 2.50E-07 | 4,455 |
| | Crushing | autumn | 2.35E-06 | 42,527 |
| RC3 | Dismantling | summer | 1.29E-07 | 3,248 |
| | | autumn | 6.72E-07 | 16,827 |
| | Crushing | summer | 6.14E-08 | 1,538 |
| | | autumn | 8.63E-08 | 2,162 |
| RC4 | Dismantling | summer | 8.29E-08 | 133 |
| | Classification | summer | 9.25E-08 | 148 |
| | | autumn | 2.92E-08 | 47 |

This emission factors were used to estimate the emission amount during recycling process. For RC1 and RC2 TV recycling centers, in which TV is being recycled mainly, the emissions were estimated 49~42,527 g/year in dismantling and crushing areas. The emissions of RC3 and RC4 RC3 and RC4, in which refrigerator and small appliances are recycled mainly, were in range of 47~16,827 g/year . We assumed several factors and parameters as the measurement activity in the field was limited to a certain extent. The more precise emission factors can be calculated if more data were collected from a wide variety of locations of recycling facilities in Korea and if the relevant information was applied more appropriately.

**Acknowledgements:**
The authors are thankful to the Ministry of Environment, Republic of Korea for funding the project.

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