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Emission of polybrominated diphenyl ethers (PBDEs) in use of electric/electronic equipment and recycling of e-waste in Korea

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HIGHLIGHTS

- Rear TV covers produced before the year 2000 contained high concentration of PBDEs.
- The concentrations present in the refrigerator components are lower than TV covers.
- The highest atmospheric concentration was detected in the process of dismantling TV.
- Emission factors varied according to the type of E-waste in recycling process.

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ABSTRACT

The emission rates of polybrominated diphenyl ethers (PBDEs) from electric/electronic products during their use and disposal were estimated. E-wastes, including televisions and refrigerators, gathered at recycling centers were also analyzed to estimate their emissions. The average concentrations of PBDEs in TV rear covers produced before and after the year 2000 were 145,027 mg/kg and 14,049 mg/kg, respectively. The PBDEs concentration in TV front covers was lower than the concentration in TV rear covers. The concentration in the components of the refrigerator samples ranged from ND to 445 mg/kg. We estimated the atmospheric emissions of PBDEs based on the concentrations. The annual emissions from TV rear covers produced before 2000 were calculated to be approximately 162.1 kg and after 2000, the annual emissions were 18.7 kg. Refrigerators showed the lowest annual emissions of PBDEs (0.7 kg). The atmospheric concentrations were also measured to calculate emissions generated during the recycling process. The highest concentration was 16.86 ng/m^3 emitted from the TV sets during the dismantling process. The concentrations of PBDEs generated in the plastic processing field ranged from 2.05 to 5.43 ng/m^3 depending on the products, and ambient air in open-air yards showed concentrations in the range of 0.32 to 5.55 ng/m^3. Emission factors for the recycling process were calculated using the observed concentrations. The estimated emissions according to the emission factors ranged from 0.3×10^{-1} to 90.3 kg/year for open-air yards and from 0.1×10^{-1} to 292.7 kg/year for the dismantling and crushing processes of TV set, depending on the production year.

1. Introduction

Most plastics used in electrical and electronic equipment such as televisions, washing machines and refrigerators contain a variety of flame retardants. Flame retardants are physically and chemically derived materials that consist of organic compounds containing carbon, hydrogen and oxygen rendered incombustible by additives (Covaci et al., 2011). Some PBDEs were recently banned in the Fourth Meeting of the Conference of the Parties to the Stockholm Convention, although the PBDEs possess extensive industrial applications and are widely used (Stockholm Convention, 2009).

Diphenyl ether molecules contain ten hydrogen atoms, any of which can be exchanged with bromine to result in 209 possible congeners (Alaee et al., 2003). Major commercial PBDEs include deca-BDE (decabromodiphenyl ether), octa-BDE (octabromodiphenyl ether) and penta-BDE (pentabromodiphenyl ether) (Sjödin, 2000). These compounds are highly bioaccumulative and are classified as endocrine disruptors that cause reproductive disorders and hepatotoxicity (US EPA, 2008a,b,c,d).

The use of brominated flame retardants causes the worst effects on the environment. The European Union (EU) therefore decided to ban

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the use of penta-BDE and octa-BDE (Birnbaum and Staskal, 2004). The production and use of these two BDEs were prohibited worldwide in the 1990s (Cischem, 2009). The EU regulations 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 environmental and health effects (Cischem, 2009). Until 2006, a wide array of products made in the Republic of Korea such as computers, TV sets and automobiles used brominated flame retardants (MOE of Korea, 2010). Environmental regulations in Korea have restricted the use of brominated flame retardants since 2006 (Business Service Center for Global Environmental Regulation, 2010). Due to their human toxicity and environmental issues, many countries have conducted research and studies relative to effective management of PBDEs.

The Ministry of Environment of Korea has calculated the emissions for some deca-BDE emissions only during manufacturing, and the data available on the emissions of PBDEs to the atmosphere of Korea are therefore very limited (Korea NIER, 2011). However, Japan has presented data on the national emissions and emission factors for PBDEs emitted during the life cycle of PBDEs-containing products from production to disposal (Sakai et al., 2006). The Ministry of the Environment of Japan showed that emissions from the recycling process accounted for 32% of the total atmospheric emissions from waste electrical and electronic equipment (MOE of Japan, 2003). However, there is a lack of studies assessing the impact of e-waste recycling (Tsydenova and Bengtsson, 2011). To the best of our knowledge, there is especially no report available concerning emissions of PBDEs released during the use of appliances or from the recycling process for e-waste in the Republic of Korea. Hard data on emissions in the indoor environment at e-waste recycling facilities are required to support risk assessment and establish some guidelines that seem to be lacking at present (Tsydenova and Bengtsson, 2011).

In this study, TV sets and washing machine were used as the key discarded home appliances to investigate the characteristics of PBDEs by year of production and by component. The atmospheric concentrations were also measured during the recycling process of e-waste and used to calculate the emission factors. These two results were then used to estimate the PBDEs emissions generated during the life cycle of products, especially at the time of use and recycling, which accounts for high release levels.

2. Materials and methods

2.1. Collection and preparation of samples

Among all the TV parts, the front and rear covers are supposed to contain the major portion of the flame retardants, especially PBDEs (Japan NIES, 2011; Tamade et al., 2002). Crushed TV sets produced during the early 1980s and the mid-2000s were collected from the recycling center, and the details are presented in Table 1. Refrigerator samples produced during the year 2002 (before the regulation came into effect) were collected. These refrigerators were disassembled into components to study the different flame retardants used in each part. These samples were collected from the recycling center.

Only home appliances (TV sets, refrigerators, washing machines and air conditioners) are being recycled in domestic recycling centers. Korea has seven recycling centers, and the weight of TV sets, refrigerators, washing machines and air conditioners collected at these recycling centers is approximately 15.5×10^3 t, 45.4×10^3 t, 23.6×10^3 t and 2.2×10^3 t, respectively. TV sets and refrigerators account for more than 57% of the appliances entering recycling facilities. Researchers have previously reported that the PBDE contents of TV sets are very high (Sakai et al., 2006). Based upon the highest quantities of target products (TV sets, refrigerators, washing machines, etc.) entering recycling facilities and previous results, two recycling centers termed 'A-RC' and 'B-RC' were selected for the sampling. When compared to the total number of recycling centers in Korea, the collected appliances from the two selected recycling centers account for 32% of the contents of the seven domestic recycling centers, and only three recycling centers are dealing with TV sets, with approximately 35% at A-RC.

Air samples were collected from areas such as dismantling, crushing/plastic segregation and the open-air yard containing the piles of the waste products at A-RC (Fig. 1). At B-RC, the sampling was performed at the crushing/plastic segregation area and the open-air yard but not at the dismantling area (because of practical difficulties). Some background samples were also collected from the B-RC area boundary, located approximately 100 m from the working area. A-RC and B-RC are approximately 82 km away. For sampling, a high volume air sampler (HVAS) (Model HV-1000F, SIBATA Inc.) was installed at three locations at each of the two RCs (A-RC and B-RC) in October 2012. Particles were collected by passing air through a quartz fiber filter with a size of 203 × 245 mm. Pollutants in the gas phase were collected on polyurethane foam (PUF), diameter 85 mm and thickness 50 mm. Samples were collected for an average sampling period of 48 h. The mean flow rate for each sample collected was approximately 1000 L/min.

2.2. Analysis

The plastic samples selected for analysis were cut into approximately 5 mm × 5 mm pieces, infused with liquefied nitrogen, frozen for 1 min, and then turned into particles less than 1 mm in size using VSRM (Variable Speed Rotor Mill). The IEC 62321 method was used to analyze the PBDEs contained in the TV covers and refrigerator plastics that were sampled (IEC, 2008). Approximately 20 μL of internal standard (CB-209; 10 μg/mL) and 100 mL of toluene were added to 0.1 g of powdered sample, and the sample was extracted for 30 min using a supersonic wave extractor. The sample was subjected to instrumental analysis after adjusting the total volume of the solvent lost during extraction and filtering. PBDEs were determined by gas chromatography/mass spectrometry (GC/MS) in the selected ion monitoring (SIM) mode using a DB5-HT column (15 m × 0.25 mm i.d., 0.1 μm, J&W Scientific). The sample was analyzed for thirteen isomers (BDE-3, BDE-15, BDE-33, BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, BDE-203, BDE-206, and BDE-209).

The analysis of the atmospheric samples was performed according to US EPA Method 1614 (US EPA, 2007), and the official standard method for testing POPs in Korea published by the Ministry of Environment of the Republic of Korea (MOE of Korea, 2007). In the extraction process, particulate and gas phase samples were extracted together. The samples were added to a soxhlet extraction thimble followed by the addition of 1–5 ng of eleven surrogate standards (^{13}C-labeled BDEs) for recovery correction. The spiked samples were extracted using 300 mL toluene for 16 h. After bringing the concentrated extract volume up to 2 mL, the total volume was washed with *n*-hexane and sulfate solutions. Then, the extract was washed two or three times with a hexane cleaning solution, and the collected *n*-hexane layer was dried. The final volume of the dried solution was purified using a multi-layer silica gel column (filled with neutral-base–neutral-acid–neutral layers) and an alumina chromatographic column. To calculate the sample recovery, a C-labeled BDE-138 internal standard solution (2 ng) was added prior to instrumental analysis. The analysis was conducted in Electron Ionisation-Selected Ion Monitoring (EI-SIM) mode with High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) at a resolution over 10,000 (10% valley) using a DB-5HT (15 m × 0.25 mm i.d., 0.1 μm, J&W Scientific) column. The 37 isomers analyzed in the atmospheric samples were: mono-BDE (BDE-3), di-BDE (BDE-7, BDE-15), tri-BDE (BDE-17, BDE-28), tetra-BDE (BDE-47, BDE-49, BDE-66, BDE-71, BDE-77), penta-BDE (BDE-85, BDE-99, BDE-100, BDE-119, BDE-126), hexa-BDE (BDE-138, BDE-153, BDE-154, BDE-156), hepta-BDE (BDE-183,

Table 1
PBDEs concentrations (mg/kg) of plastics from TVs and refrigerators.

Sample	Year of production/items	BDE-153	BDE-183	BDE-203	BDE-206	BDE-209	Total PBDEs
Rear TV cover	1983	ND	ND	ND	8223	121,834	130,058
	1988	ND	ND	22	10,570	142,293	152,885
	1989	ND	12,324	8738	13,238	120,128	154,428
	1990	ND	ND	523	10,054	118,196	128,773
	1991	ND	ND	ND	11,822	143,229	155,051
	1995	ND	ND	224	14,068	143,812	158,104
	1997	ND	ND	ND	11,029	124,861	135,891
	2000	ND	ND	ND	ND	42	42
	2002	ND	ND	ND	ND	570	570
	2005	ND	ND	ND	285	41,340	41,625
Front TV cover	1988	ND	13	4	50	463	530
	1989	ND	ND	ND	86	2210	2296
	1991	ND	6	10	33	194	243
	1997	ND	ND	ND	ND	265	265
	2001	ND	ND	ND	ND	70	70
Refrigerator	Lamp cover	ND	ND	ND	ND	40	40
	Upper housing cover	ND	33	94	ND	318	445
	PCB cover	ND	ND	ND	ND	27	27
	Bottom refrigerator cover	ND	ND	ND	ND	23	23
	Inner shelves	2	ND	ND	ND	17	19
	Beverage shelves	ND	ND	ND	ND	ND	ND
	Vegetable shelves	ND	ND	ND	ND	ND	ND
	Inner housing cover	6	ND	ND	ND	146	152
	Compressor cover	ND	22	ND	ND	60	82

ND: not detected, which is treated as zero when calculate total concentration.

BDE-184, BDE-191), octa-BDE (BDE-196, BDE-197), nona-BDE (BDE-206, BDE-207), and deca-BDE (BDE-209).

2.3. Quality control

The recovery of decachlorobiphenyl (CB-209) among the PBDEs present in plastics in the electrical and electronic equipment ranged from 92% to 105% (97%, on average), and the method detection limits (MDLs), defined as the average concentration in the blank sample plus 3× the standard deviation for BDE-3, BDE-15, BDE-28, BDE-47, BDE-99, BDE-153, BDE-154, BDE-183, BDE-197, BDE-207, and BDE-209 were in the range of 1–5 mg/kg. The Relative Standard Deviation (RSD) for the nine homogeneous reference plastic materials (RM; 3 of ABS material, 3 of PBT material and 3 of PC material) was ±3.76%, which indicates the repeatability of an assay. The average recovery of the eleven ^{13}C-labeled isomers included in the analysis of PBDEs among the atmospheric samples ranged from 45% to 107%, within the range of 25–50% set by EPA Method 1614. The MDLs for various congeners (the signal/noise (S/N) >3) ranged from 0.01 to 10 pg/m^3 and the same for each congener is presented in Table 2.

2.4. Estimation of emissions

In most cases, emission factors for estimated emissions used in previous studies were based on expert judgment or laboratory experiments. The emission factors were not based on field studies because field studies do not always supply sufficient information to derive an emission factor (Sakai et al., 2006). However, the emission factors from field studies in which measured concentration and facility information are involved will be more applicable for estimating the emissions. In this study, two methods have been used for calculating emissions of PBDEs from electric/electronic equipment and recycling e-waste. For emission estimation during the recycling of e-waste, we did field studies.

First, for estimating emissions by using the appliances, the vapor pressure of PBDEs was used, as shown in Eq. (a). This method has

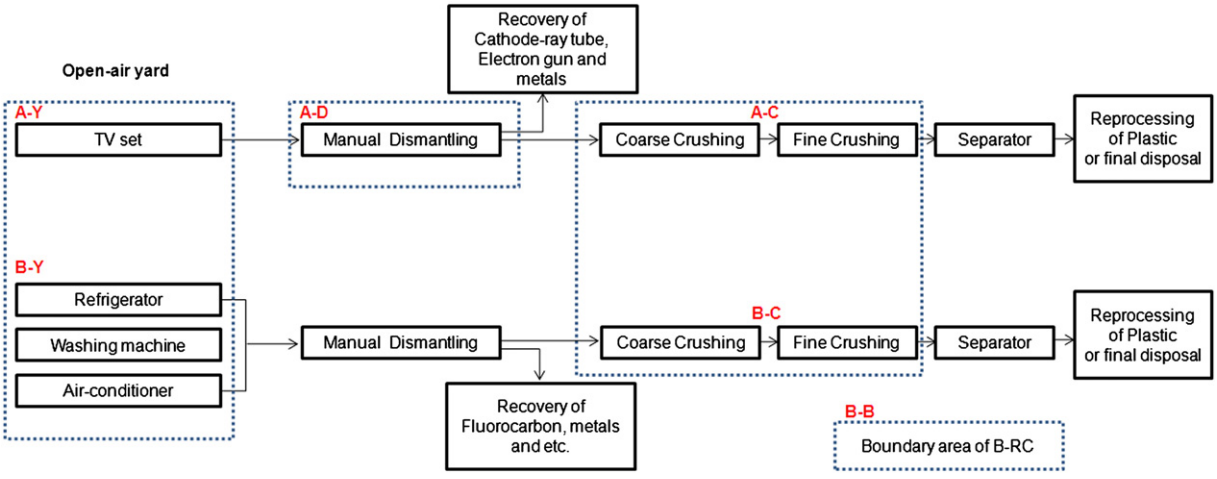

Fig. 1. Atmospheric sampling points at the recycling center.

Table 2
Atmospheric concentrations (pg/m^3) of PBDEs at the recycling centers.

Isomer	MDL	A-RC			B-RC		
		A-Y	A-D	A-C	B-Y	B-C	B-B
49-TeBDE	0.01	1.571	5.108	0.577	0.504	1.109	0.125
71-TeBDE	0.01	0.108	0.187	0.034	0.111	0.123	0.023
47-TeBDE	0.01	11.213	26.590	3.352	13.620	17.450	1.812
66-TeBDE	0.01	1.500	4.437	0.522	0.417	0.990	0.080
77-TeBDE	0.01	0.216	0.748	0.132	0.049	0.132	0.013
100-PeBDE	0.01	15.901	183.758	6.113	1.667	10.972	0.418
119-PeBDE	0.01	1.189	9.692	0.494	0.081	0.224	ND
99-PeBDE	0.01	39.102	246.796	17.776	6.215	70.761	1.135
85-PeBDE	0.01	0.494	1.067	0.108	0.195	2.393	0.019
126-PeBDE	0.01	0.091	0.863	0.132	0.061	0.064	0.012
154-HxBDE	0.05	7.955	78.031	7.935	0.664	10.036	0.255
153-HxBDE	0.05	19.142	133.048	20.152	1.432	21.538	0.427
138-HxBDE	0.05	0.950	2.828	0.550	0.189	2.478	0.065
156-HxBDE	0.05	0.147	0.462	ND	0.086	0.081	ND
184-HpBDE	0.1	1.344	7.259	3.486	0.358	0.827	0.130
183-HpBDE	0.1	73.565	473.858	89.046	4.929	46.881	1.074
191-HpBDE	0.1	0.849	4.147	1.442	0.284	0.613	ND
196-OcBDE	1	32.943	95.558	42.528	3.727	25.223	1.105
197-OcBDE	1	45.844	190.804	56.271	3.745	34.848	1.001
206-NoBDE	2	294.940	880.360	327.083	20.720	92.377	4.327
207-NoBDE	2	348.628	819.663	514.343	25.024	120.696	7.276
209-DeBDE	10	4656.179	13,695.359	4337.584	237.459	1591.659	58.180
PBDEs		5553.873	16,860.621	5429.661	321.536	2051.477	77.477

ND: not detected, which is treated as zero when calculating total concentration.
A-Y: open-air yard of A-RC; A-D: dismantling line of A-RC; A-C: crushing area of A-RC; B-Y: open-air yard of B-RC; B-C: crushing area of B-RC; B-B:boundary of B-RC.

been proposed for calculating the amounts of PBDEs volatilized from the product over the service life (Prevedouros et al., 2004; US EPA 2010).

$$\text{Percentage loss due to volatilisation}(\%) = \left(1.1 \times 10^{6}\right) \times V_p \times N \qquad (a)$$

where

V_p vapor pressure of the PBDE flame retardant, mm Hg at 21 °C
N service life of the flame retarded product in years.

Measuring a reliable V_P is a challenging past in the above estimation method. The value used in this study is 4.3×10^{-6} Pa (3.23×10^{-8} mm Hg at 21 °C) by Cetin and Odabasi (2007).

For estimating emissions from recycling of e-waste, we calculated the emission factor, which is the ratio of PBDEs released to air to the total amount of PBDEs used in appliances like TV sets, refrigerators, etc., calculated using Eq. (b) (Sakai et al., 2006). We estimated the emission factors using the measured PBDE concentration from the recycling process.

$$\text{Emission factor}(g/g) = \text{PBDE output}/\text{PBDE input} \qquad (b)$$

where

PBDEs input (ng/m^3) number of products disposed × weight of plastic in each product (kg/product) × content of PBDEs in the plastic (mg/kg) × 10^{-3} × dimensions of the working place $(m^3)^{-1}$
PBDEs output (g/m^3) PBDEs concentration in the atmosphere measured inside recycling facility (ng/m^3) × 10^{-6}

3. Results and discussion

3.1. PBDEs concentrations of e-waste

Table 1 shows the PBDEs concentrations in the plastics used in TV sets and refrigerators produced between 1983 and 2005. The concentrations of the isomers tetra-BDE (tetrabromodiphenyl ether) to hexa-BDE (hexabromodiphenyl ether) were below detectable limits and thus are not presented in Table 1. As for e-waste, PBDE concentrations in TV front covers ranged from 70 to 2296 mg/kg. The TV rear covers were assumed to be the most contaminated with PBDEs among the plastics in TV sets, and the results by production year were 128,773 to158,104 mg/kg (average = 145,027 mg/kg, n = 7) during the period of 1983–1997, 42 mg/kg (n = 1) for the year 2000, 570 mg/kg (n = 1) for the year 2002, and 41,625 mg/kg (n = 1) for the year 2005. The PBDE concentrations present in the TV rear covers declined drastically after the year 2000. The EU and numerous countries began to prohibit and restrict the use of penta-BDE, octa-BDE and deca-BDE in early 2004 (Business Service Center for Global Environmental Regulation, 2010). The PBDEs concentrations were low in products produced in the early 2000s (before the Korean regulation was framed) due to the influence of international regulations on use of PBDEs (Janssen, 2005). Manufacturers in Germany and the Netherlands voluntarily started to restrict the use of PBDEs in 1989 (Cischem, 2009). The Organisation for Economic Cooperation and Development (OECD) began to establish partnerships with the industry in 1995 in an effort to reduce PBDEs (Business Service Center for Global Environmental Regulation, 2010). These movements or activities in the global community seem to have affected the use of PBDEs in Korea.

Though all the samples possess the same congener pattern, the concentrations of PBDEs found in the TV rear covers were significantly higher than in any other samples. The concentration of BDE-209 (accounting for 90% of technical deca-BDE products) was the highest among the isomers with a range of 118,196–143,812 mg/kg (accounting for 78–100% of the total PBDEs) before 2000. Next, BDE-206 and -207 were also observed in significant concentrations but far less than BDE-209 and accounted for 4.5–6.4% and 4.9–9.5% of total PBDEs, respectively. BDE-206 and -207 were known to be present as impurities in both technical PBDE products such as technical deca-BDE products and technical octa-BDE products, whereas the impurity (%) of BDE-207 in technical octa-BDE products (11.2–11.5%) is much greater than technical deca-BDE products (0.2–4.1%). Moreover the concentration of BDE-183 in technical octa-BDE products was reported to be in the range of 13–42% (La Guardia et al., 2006). Approximately

12,324 mg/kg of BDE-183 accounted for 8% of the total PBDEs found in appliances produced in 1989. Therefore, not only technical deca-BDE products but also technical octa-BDE products might have been used in some appliances produced before 2000. This study could not obtain many samples of appliances produced in the 1980s, and only one of the three available samples was confirmed to contain BDE-183. The concentration of penta-BDE was not detected in the samples collected for this study.

The concentrations of PBDEs in parts of the refrigerator samples ranged from ND to 445 mg/kg. The compressor covers of the sampled refrigerators were expected to contain a high concentration of PBDEs because of heat generation. We also observed that the housing covers on the upper side of the refrigerators had a higher concentration. Our data showed that plastics used for compressor covers typically consist of regular ABS (acrylonitile butadiene styrene) and flame-retardant ABS and that regular ABS is sufficient to retard flames. Our research confirmed that flame-retardant ABS was used only in some of the premium product lines.

3.2. PBDEs generated in the process of recycling e-waste

Table 2 shows the results for the atmospheric concentrations obtained from recycling centers. In A-RC, the area for manual dismantling had the highest concentration of 16.86 ng/m^3, followed by the area for the open-air yard (5.55 ng/m^3) and finally the area for crushing/segregating plastics (5.43 ng/m^3). B-RC had lower concentrations compared to A-RC and had 2.05 ng/m^3 in the area for crushing/segregating plastics and 0.32 ng/m^3 in the open-air yard. These results correlate strongly with the PBDEs concentrations obtained in Section 3.1. Because A-RC handles TVs containing many PBDEs, the concentrations were expected to be relatively high in the processing area and the open-air yard. The PBDEs concentrations present in the open yard (where TVs are stacked) at A-RC were 15 times higher than the concentrations at B-RC. The PBDEs concentrations in products were confirmed to have a direct impact on the atmospheric concentrations. The concentration of the B-RC background sample (B-V) was 77.48 pg/m^3, lower than for the processing area. However, a previous study (Choi et al., 2008) reported the analysis of PBDEs in the atmosphere near a steel-making plant in Korea and found concentrations in the range of 9.0–61.6 (average = 25.2) pg/m^3 (Fig. 2). As shown in Fig. 2, research similar to our research was conducted to measure the atmospheric concentrations near the e-waste dismantling area in China. Their results showed that the Σ_{13} PBDE concentrations near the e-waste dismantling area were in the range of 100.7–2765.8 pg/m^3, out of which BDE-209 ranged from 76.7 to 2087.3 pg/m^3 (Han et al, 2009). Fig. 2 also showed the various concentrations of BDE-209 (720 to 170,000 pg/m^3) present among the different plastic recycling centers (R-1 to R-5) in Japan (Sakai et al., 2006). Compared with urban and industrial areas in other countries, these values were higher (Agrell et al., 2004; Cetin and Odabasi, 2008).

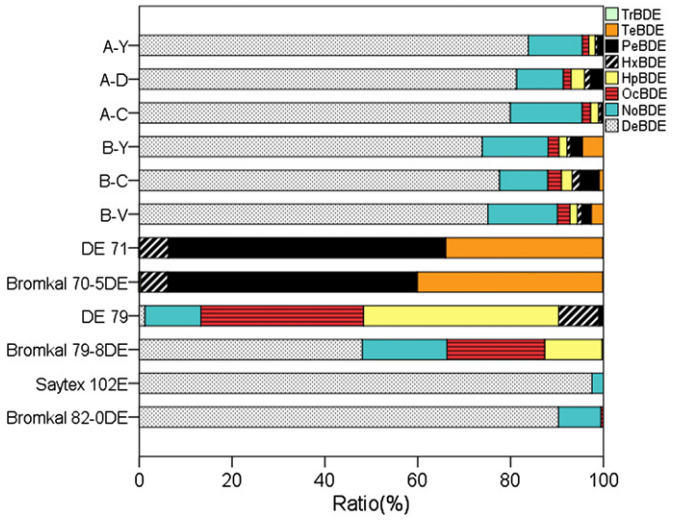

Fig. 3. Comparison of PBDE isomer pattern in the atmospheric samples from the recycling process with technical PBDE products (DE 71 and Bromkal 70-5DE are the technical penta-BDE products. DE 79 and Bromkal 79-8DE are the technical octa-BDE products. Saytex 102E and Bromkal 82-0DE are the technical deca-BDE products).

Fig. 3 shows the distribution of isomers present in the atmospheric samples in the two RCs with the technical PBDEs products. This study showed that air samples contained less than 3% tetra-BDE–octa-BDE, 10–15% nona-DBE and 74–81% deca-BDE. The technical penta-BDE products (DE-71 and Bromkal 70-5DE) contain higher ratios of tetra-BDE compared to penta-BDE. Though the technical octa-BDE products were produced from different companies (DE-79 and Bromkal 79-8DE), the products contain mainly hepta-, octa- and nona-BDE. However, the technical deca-BDE products (Saytex and Bromkal) contain more than 90% BDE-209. Therefore, the BDE-209 containing technical deca-BDE products had a large influence on the PBDEs generated during the e-waste recycling process. In the isomer distribution observed in TV rear covers and refrigerators, BDE-209 was 93% and 89% on average, respectively, compared with the air where BDE-209 was 74–81%. There is

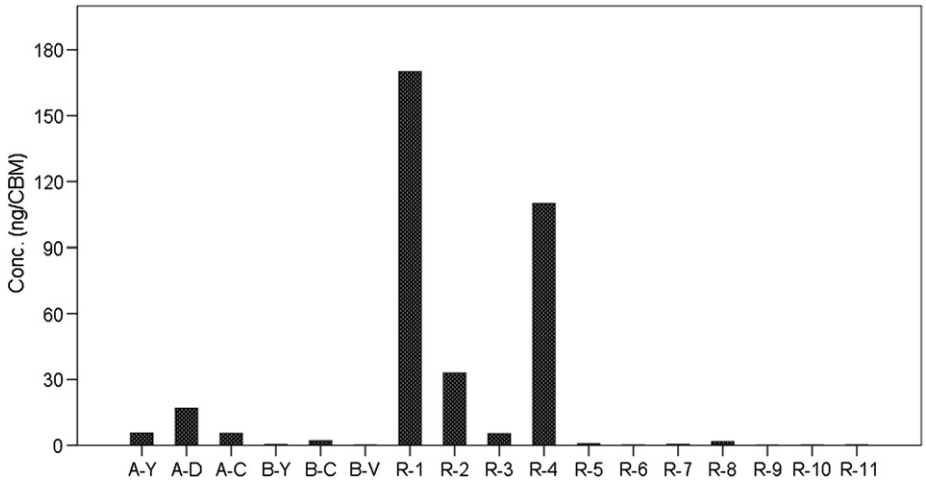

Fig. 2. Comparison between the atmospheric concentrations of PBDEs according to different studies in various places: R-1 to R-5 (plastic recycling process in Japan); R-6 (near the iron and steel plant in Republic of Korea); R-7 to R-8 (near the e-waste dismantling area in China); R-9 (urban area in Sweden); R-10 (urban area in Turkey); R-11 (industrial area in Turkey).

the possibility that the degradation of highly brominated PBDEs during the recycling process was responsible for the production of BDE-209, as suggested in a previous study (Huang et al., 2010; Bezares-Cruz et al., 2004).

3.3. Estimated emissions of PBDEs during the use and recycling process of e-waste

3.3.1. Emissions of PBDEs during its use

The vapor pressure approach was used to calculate the amount of PBDEs that could have volatilized into the indoor air and the value of V_P measured by Cetin and Odabisi (2007) was used as mentioned in Section 2.4. We used only the vapor pressure of BDE-209 based on the distribution of isomers of PBDEs in the e-waste that was analyzed in this study. N is the average numbers of years the TV sets and refrigerators were used, 7.33 and 7.69, respectively, based on the research report published in Korea (MOE of Korea, 2009). With these factors, 0.26% was calculated to be lost by volatilization for the duration of 7.33 years. As much as 0.036% of the BDE-209 concentration present in the products was emitted into the atmosphere per mass unit every year. Based on the available statistics in Korea, the annual domestic demands for TV sets were 2,329,000 and 2,506,000, respectively, before and after 2000 (KOSIS, 1995–2008). In the case of refrigerators, the annual domestic demand was 4,422,000 in 2002 (KOSIS, 1995–2008). The average plastic content in the products used for the study was estimated as 1.5 kg/product in a TV set and 5 kg/product in a refrigerator. Finally, using the measured BDE-209 concentration in plastics of the TV rear cover and refrigerator, emission of PBDEs had been calculated. As shown in Table 3, we estimate that approximately 162.1 kg/year of BDE-209 contained in the TV rear covers produced before 2000 was emitted to the atmosphere, and that for products recently produced (after the current regulations), the estimated emissions were approximately 18.7 kg/year. Comparatively, refrigerators were shown to be relatively low in PBDEs and to contribute 0.7 kg/year.

These estimations were based only on the products sampled in this study. According to the survey conducted by the Korean Ministry of Environment on the flame retardant, approximately 7834 t of deca-BDE was used in Korea as of 2003. Applying this value to the percentage loss due to volatilization (%), we calculated that approximately 3.0 t of deca-BDE was released into the atmosphere. When this information was applied to the data for imports (the official statistics of technical deca-BDE product imported to Korea in 2003 was 14,895 t, approximately twice the value released by the Ministry of Environment), BDE-209 emissions to the environment were calculated to be approximately 5.7 t in 2003.

3.3.2. Estimated emissions of PBDEs during the recycling process

The emission factor was calculated based on the atmospheric concentrations analyzed in this study during the recycling process. Table 4 shows the basic information needed to calculate the input PBDEs emitted at A-RC and B-RC during the two-day measurement period and the input data mentioned. Table 5 shows the emission factors by product year. Because the PBDEs concentrations of all TV sets, refrigerators, etc. entering facilities could not be measured exactly, to estimate the emissions by PBDEs concentration, we suggested use of a scenario by product year. At A-RC treating TV sets, the emission factor in the TV dismantling line was in the range of 8.67×10^{-10}–2.69×10^{-6} (average = 4.84×10^{-7}), while the emission factor in the area of the crushing process was in range of 9.48×10^{-11}–2.94×10^{-7} (average = 5.29×10^{-8}), lower than the TV dismantling line, an unexpected result. In the area of the open-air yard, the emission factor was very similar to the TV dismantling line, an average of 1.49×10^{-7}. The open-air yard area is close to the TV dismantling line in nearly the same space, and this proximity may be the reason why the emission factors are similar. Emission factor varied widely depending on the production years. For the production year 2002, emission factor at TV dismantling line and crushing area was 1.99×10^{-7} and 2.17×10^{-8} respectively, whereas the emission factor for the production years 1983–1997, they were 8.67×10^{-10} and 9.48×10^{-11} respectively. For this reason, an exact measurement of PBDEs in the appliances is needed. For the refrigerator produced in the year 2002, the emission factor in the area of crushing process and open-air yard was 6.97×10^{-8} and 1.04×10^{-8} respectively. As per earlier studies related to the emission factor calculation during the recycling process of home appliances, the emission factors were calculated to be 6×10^{-8} by Tamade et al. (2002) and 8×10^{-9}–5×10^{-6} by Sakai et al. (2006).

We assumed several factors/parameters because the measurement activity in the field was limited to a certain extent. For these reasons, estimation of emissions is subject to uncertainties in this study because (i) emission factors can be highly variable, depending on conditions, surroundings at the working places, production year of appliances, etc.; and (ii) inadequate information is available, such as the amount of PBDE consumption in Korea and the facility data for calculating emission factor from RCs. So, this study clearly needs to be improved to determine more accurate values of the emission factors. We are now performing the measurement of the rest of the five RCs and other appliances including small WEEE (waste

Table 4
Input information from recycling center for calculation of emission factors.

	A-RC	B-RC
Disposed volume (the number of products) for two days	1778	1479
Weight of plastics (kg/product)	1.5	5
Contents of PBDEs in plastics (mg/kg)[a]	145,027	88
Final PBDEs input (ng)[b]	3.87×10^{14}	6.51×10^{11}
TV dismantling area (m^3)	17,921.4	–
Dimension of the area for crushing and selecting plastics (m^3)	6079	17,640
Open-air yard (m^3)[c]	16,800	16,800

[a] Average concentration of TVs produced before 2000 and average concentration of nine components of the refrigerator.
[b] PBDE input (ng) = the number of products × weight of plastics (kg/product) × content of PBDEs in plastics (mg/kg) × 10^6.
[c] The dimensions of the open-air yards in the two recycling centers actually differ, but they were not confirmed and the same dimensions were applied to both centers. Another assumption was that the open-air yards are closed although they are partly open.

Table 3
Emissions for BDE-209 in the environment while using TV set and refrigerator.

	Percentage loss due to volatilization (%)	Percentage loss due to volatilization (%/year)	BDE-209 contents (mg/kg)	Annual domestic demand (the number of products)	Atmospheric emissions (kg/year)
TVs produced before 2000	0.26[a]	0.036	130.622	2,329,000[b]	162.133
TVs produced after 2000	0.26[a]	0.036	13,984	2,506,000[c]	18.677
Refrigerators produced in 2002	0.27[d]	0.036	88	4,422,000	0.691

[a] $1.1 \times 10^6 \times V_p$ (3.23 mm Hg) × N (7.33 year).
[b] Mean value of annual domestic demand from 1995 to 1999.
[c] Mean value of annual domestic demand from 2000 to 2008.
[d] $1.1 \times 10^6 \times V_p$ (3.23 mm Hg) × N (7.69 year).

Table 5
Calculated emission factors and emissions for PBDEs in the recycling process.

Facility	point	Scenario by product year	Input-PBDEs (ng/m^3/2 days)	Output-PBDEs (ng/m^3/2 days)	Emission factor (g/g)	Emission (kg/year)[a]
A-RC	TV dismantling line	1983–1997	1.94×10^{10}	16.86	8.67×10^{-10}	0.094
		2000–2005	0.21×10^{10}	16.86	8.10×10^{-9}	0.880
		1983–2005	1.42×10^{10}	16.86	1.18×10^{-9}	0.129
		2000	6.26×10^{6}	16.86	2.69×10^{-6}	292.727
		2002	8.49×10^{7}	16.86	1.99×10^{-7}	21.581
		2005	6.15×10^{9}	16.86	2.74×10^{-9}	0.298
	Crushing area	1983–1997	5.73×10^{10}	5.43	9.48×10^{-11}	0.010
		2000–2005	0.61×10^{10}	5.43	8.85×10^{-10}	0.096
		1983–2005	4.20×10^{10}	5.43	1.29×10^{-10}	0.014
		2000	1.85×10^{7}	5.43	2.94×10^{-7}	31.980
		2002	2.50×10^{8}	5.43	2.17×10^{-8}	2.358
		2005	1.81×10^{10}	5.43	2.99×10^{-10}	0.033
	Open-air yard	1983–1997	2.07×10^{10}	5.55	2.68×10^{-10}	0.029
		2000–2005	0.22×10^{10}	5.55	2.50×10^{-9}	0.272
		1983–2005	1.52×10^{10}	5.55	3.66×10^{-10}	0.040
		2000	6.68×10^{6}	5.55	8.31×10^{-7}	90.331
		2002	9.06×10^{7}	5.55	6.13×10^{-8}	6.660
		2005	6.56×10^{9}	5.55	8.46×10^{-10}	0.092
B-RC	Crushing area	2002	2.94×10^{7}	2.05	6.97×10^{-8}	0.003
	Open-air yard	2002	3.09×10^{7}	0.32	1.04×10^{-8}	0.910

[a] For calculating the emission, we used the amount of appliance entering the seven recycling facilities as per the latest data available (KECO, 2008).

electrical and electronic equipment) to obtain more precise calculated emission factors. Within a few years, we expect to improve uncertainties of the values for parameters related with PBDE emission during use and recycling of appliances.

The emission factor was used to estimate the emissions generated during the recycling process. In 2008, 550,602 TV sets, 761,185 refrigerators and 444,884 washing machines were conveyed to the seven recycling centers in Korea (KECO, 2008). Applying these values to the emission factors presented in Table 5, the TV sets emitted approximately 0.3×10^{-1}–90.3 kg of PBDEs per year due to storing in the open-air yard. The process for the crushing including dismantling by hands of TVs emits approximately 0.1×10^{-1}–292.7 kg of PBDEs per year. For refrigerators (B-RC), the emissions were estimated to be approximately 0.3×10^{-2} kg/year in the crushing process, whereas in the open-air yard, the emissions of PBDEs were quite high at 0.9 kg/year. The possibility of higher concentrations in the B-RC open-air yard may be also due to the recycling of various electrical and electronic equipment such as washing machines and air conditioners apart from refrigerators. In this study, the PBDE concentration of washing machine and air conditioners was not carried out and thus we could not be able to justify that the refrigerators alone account for higher emission. Ministry of the Environment of Japan had determined the deca-BDE concentration in the atmosphere during the recycling process to be approximately 9.24 kg/year in 2003. In this study, we estimated emissions only for TV sets and refrigerators. If a detailed study is carried out on the emissions generated in the recycling processes of all types of e-waste, the total atmospheric emissions can be estimated accurately.

4. Conclusions

This study was conducted to investigate the concentrations of PBDE emissions in Korea from the actual waste electrical and electronic equipment and to estimate and measure the atmospheric concentrations encountered during the recycling process. We concluded the following:

(i) The average concentration of PBDEs in TV rear covers produced before the year 2000 was 145,027 mg/kg whereas the average concentration of PBDEs in TV rear covers produced after the year 2000 was 14,079 mg/kg. The emissions from the TV rear covers produced before and after the year 2000 were 162.1 kg/year and 18.7 kg/year, respectively. The concentrations of PBDEs present in the components of refrigerator samples and its emissions were lower than that of TV sets.

(ii) We found that the highest concentration of emissions was obtained during the dismantling process of TV sets (16.83 ng/m^3). The emission factors were calculated based on the field data and found to be 8.67×10^{-10} to 2.69×10^{-6} in the TV set dismantling area and 9.48×10^{-11} to 2.94×10^{-7} at the area for crushing and plastic segregation of TV sets and refrigerator. These emission factors were used to estimate the emissions that were found to be 0.3×10^{-1}–90.3 kg/year in the open-air yard, depending on the recycled products, and 0.1×10^{-1}–292.7 kg/year for the dismantling and crushing processes of TV sets.

(iii) From the study, we observed that B-RC storage area was very high when compared to its boundary area. The storing in the open environment may be a possible reason for the high concentration. So it can be recommended to store the products in a closed environment to maintain the stability of the temperature and to avoid possible volatilization of PBDEs. The study also concludes that the TV sets manufactured before 2000 possesses high concentration of PBDEs, hence the recycling centers were not able to minimize the atmospheric emission. So the government can take necessary steps to control the volatilization of PBDEs in these centers while recycling the TV sets manufactured before 2000.

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