

**EMISSIONS OF BROMINATED FLAME RETARDANTS FROM TV SETS**Hirai Y<sup>1</sup>, Sakai S<sup>1</sup>, Sato K<sup>2</sup>, Hayakawa K<sup>2</sup>, Shiozaki K<sup>2</sup><sup>1</sup> Environmental Preservation Center, Kyoto University, Yoshida Hon-machi, Sakyo-ku, Kyoto, 606-8501, Japan  
<sup>2</sup> Kaneka Techno Research, Settsu, Osaka, 566-0072, Japan**Introduction**

Recent studies have shown that PBDEs are detected in house dust samples. One of the possible sources is the electric home appliance such as TVs.<sup>1</sup> Several studies were conducted to characterize the emission of brominated flame retardants from electric appliances by chamber test method.<sup>2,3</sup> However the emission of PBDEs from this process are not fully understood. The purpose of this study was to estimate the emission factor of PBDEs from the TVs during their use.

**Materials and Methods***Description of TVs*

Three waste TV sets, which were confirmed by their model number to contain PBDEs in their casings, were obtained from a home appliance recycling facility in Japan. All three TVs were made in 1992 by a Japanese manufacturer; the CRT size was 21" (measured diagonally); the mass of back casing was 1.5 kg/unit. After all chamber tests were completed, the TVs were returned to the recycling facility and were processed according to Home Appliance Recycling Law in Japan.

*Test chamber parameters*

A VOC-emission chamber (Espec, VOC-020) was used for emission measurements. The volume of the chamber was 2.0 m<sup>3</sup> and the dimensions were 2.0m (w) x 1.1m (h) x 0.91 m (d). The inner walls of the chamber were made of SUS. The input air was purified by HEPA filter and then moistened so that the relative humidity was controlled at 50%. The chamber was kept at 28 °C during the test period. Gas sampling device for dioxin sampling (JIS K0311) was used for collecting the chamber outlet air.

Four emission tests including one blank test were performed. Table 1 shows the conditions of the four tests. The test periods were 48 h (blank, TV1), 144 h (TV2) and 0 h (TV3). In TV3, only the wipe sample of chamber floor was collected. To avoid the direct contact of the TVs and the chamber floor, the TVs were put on a seat made of SUS. During the test period, the TVs were turned on to simulate the actual situation. Temperature of the TV casing was about 40 °C at the end of the test period.

Table 1: Parameters for chamber tests

Test ID	Test samples	Chamber volume (m <sup>3</sup> )	Air flow rate (m <sup>3</sup> /h)	Test period (h)	Sampling volume (m <sup>3</sup> )
Blank	blank	2	1	48	48
TV1	Three TVs	2	1	48	48
TV2	Three TVs	2	1	144	144
TV3	Three TVs	2	1	0	*

\* Chamber outlet air was not sampled. Only wipe sample was collected.

*Sampling procedure*

Before the first chamber test, all TVs were opened and visible dusts inside the TVs were collected as much as possible. The dust sample (1.23g) was analyzed for PBDEs. The casings were reattached to the TVs, and were wiped with wet towel. Before each test, the TV seat and chamber walls were cleaned by hexane. Before the blank, TV1 and TV2 test, the chamber was baked out at 105 °C for 24 hours, then the temperature was set at 28 °C and the outlet air blank for each test was sampled for 48 hours (Blank, TV1) or 144 hours (TV2). Then,

## Brominated Compounds - Sources and environmental levels

the three TVs were put in the chamber, air was introduced and the air passed through the chamber. The chamber outlet air was not sampled during the first two hours after setting the TVs. Then, outlet air was sampled for 48 or 144 hours. After removing the TVs, inner chamber walls (including floor and ceiling) and TV screens were wiped using glass fiber filters with hexane. The air samples and wipe samples were analyzed for PBDEs. After all tests were completed, TV casing (12.5g) was sampled.

### *Chemical analysis*

The air samples were extracted in a soxhlet extractor (solids) and by liquid-liquid extraction in a separation funnel (liquids). The wipe samples were extracted by supersonic extraction in hexane. TV casing and TV dust samples were extracted by dissolution/precipitation method. The crude extracts were cleaned up by using multilayer silica gel column chromatography for PBDE analysis. The final extracts were concentrated and analyzed by HRGC/HRMS.

### **Results and Discussion**

Table 1 shows the amount of PBDEs in chamber outlet air, chamber walls (wipe sample) and TV screens (wipe sample). The PBDE levels of outlet air blanks for each test (results not shown) were similar to that of Blank air. In all wipe samples, DBDE was the dominant congener.

The total amounts of  $\Sigma$ PBDEs released from the TVs (sum of air sample and wipe samples) were 9,000 ng (TV1, 24h), 3,900 ng (TV2, 144h) and 610 ng (TV3, 0h) respectively. Contrary to our initial expectation, the test periods were not correlated with  $\Sigma$ PBDE emissions (Fig. 1). This may be caused by the depletion of mobile dusts in the TVs. The same TVs were used for all three tests. If mobile fraction of dusts were released in TV1 test, then less mobile fraction of dusts would be available in TV2 test, which would result in smaller emission of dusts in TV2. This hypothesis is consistent with the observation that the emissions of higher-brominated diphenyl ethers did not correlate with the test periods but the emissions of lower-brominated diphenyl ethers correlated with the test periods (Fig. 1).

Figure 2 shows the distribution of PBDEs among different samples in emission chamber tests TV1 and TV2. In both TV1 and TV2, lower brominated diphenyl ethers were found in chamber outlet air. On the other hand, higher brominated diphenyl ethers were found in wipe samples of TV screens. This distribution suggests the importance of physico-chemical parameters in the emission of PBDEs from the TVs.

Emission factors were calculated for TV1 and TV2 by dividing the total emission with PBDE content in TV casings and the test periods. The emission factors were  $4.8 \times 10^{-6}$  (1/year) for TV1 and  $7.1 \times 10^{-7}$  (1/year) for TV2. These emission factors were within the range of or slightly higher than our previous estimate for PBDE emission factors ( $2.1 \times 10^{-7} - 8.9 \times 10^{-7}$  (1/year)) based on the amount of dust inside the TVs and the years after the production.<sup>1</sup>

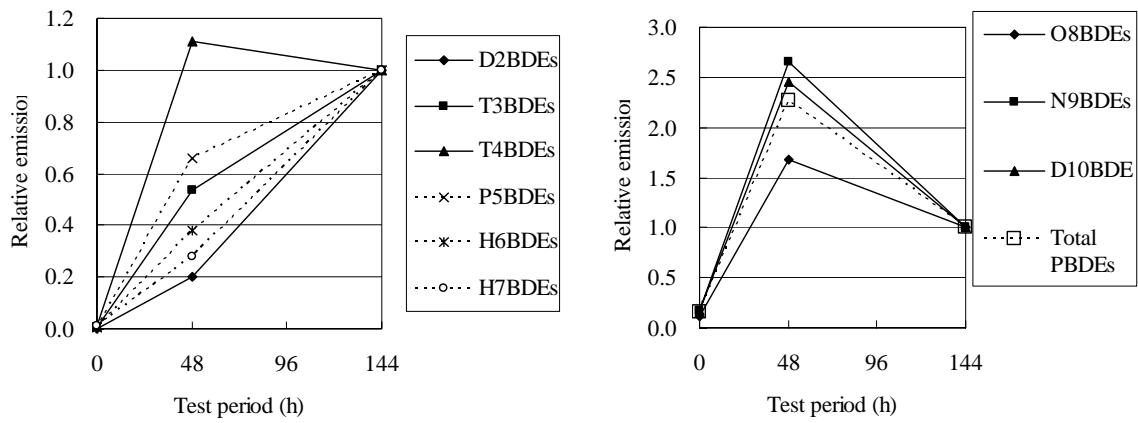
### **Acknowledgements**

The authors thank the recycling facility for providing the waste TV samples.

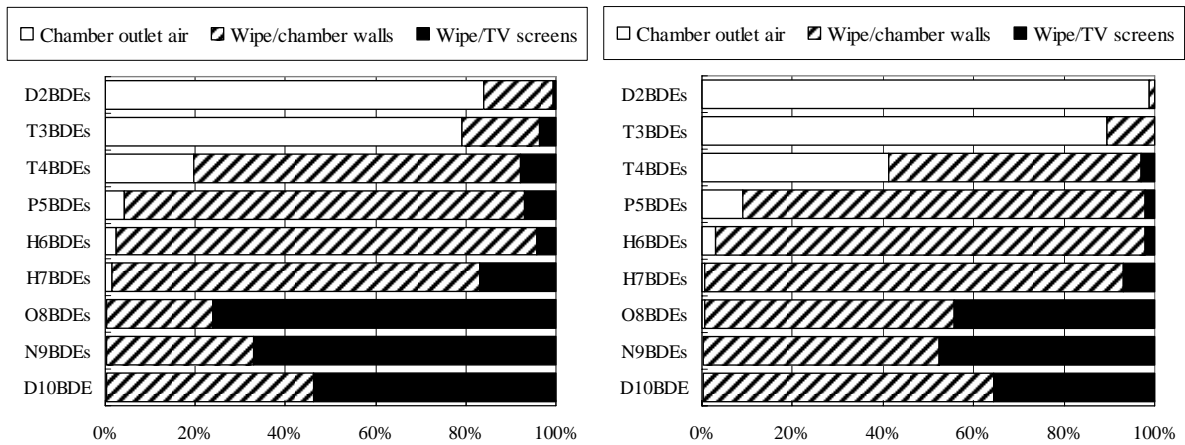
### **References**

1. Sakai, S.; Hirai, Y.; Aizawa, H.; Ota, S.; Muroishi, Y. (2006) *Journal of Material Cycles and Waste Management* 8(1), 56-62
2. Herrmann, T.; Ball, M.; Rothenbacher, K.; Wesselmann, M. (2003) *Organohalogen Compounds* 61, 259-262
3. Kemmlin, S.; Hahn, O.; Jann, O. (2003) *Atmospheric Environment* 37(39-40), 5485-5493

# Brominated Compounds - Sources and environmental levels



**Figure 1: Relative emission of PBDEs and test period for TV1, TV2 and TV3 tests.**



**Figure 2: Distribution of PBDE homologues among different samples in emission chamber tests TV1 (left) and TV2 (right).**

**Table 2: Amount of PBDEs in chamber outlet air, chamber walls (wipe sample) and TV screens (wipe sample) and concentration of PBDEs in TV casings and dusts inside the TVs.**

Test ID	Blank		TV1			TV2			TV3	-	
Sample	Air	Wipe/ chamber	Air	Wipe/ chamber	Wipe/ TV screens	Air	Wipe/ chamber	Wipe/ TV screens	Wipe/ chamber	TV casing	Dusts in TV
Unit	ng	ng	ng	ng	ng	ng	ng	ng	ng	mg/kg	mg/kg
M1BDEs	ND	ND	0.29	ND	ND	26	ND	ND	ND	ND	ND
D2BDEs	(0.01)	(0.01)	2.4	(0.44)	(0.02)	14	0.15	(0.01)	(0.01)	ND	ND
T3BDEs	0.35	(0.13)	4.0	0.86	0.19	8.4	1	ND	(0.05)	ND	0.0055
T4BDEs	0.33	0.86	4.3	16	1.7	8.2	11	0.62	0.19	0.024	0.051
P5BDEs	(0.12)	1.0	0.91	19	1.5	2.9	29	0.66	0.17	0.29	0.058
H6BDEs	(0.03)	(0.32)	2.2	86	3.9	7.2	230	4.9	1.0	2.3	0.44
H7BDEs	ND	ND	0.16	8.6	1.8	(0.26)	35	2.6	0.33	3.3	0.38
O8BDEs	(0.20)	(0.39)	0.25	18	58	(0.27)	25	20	5.3	18	0.79
N9BDEs	2.4	2.1	2.5	400	820	1.2	240	220	77	4,100	20
D10BDE	18	10	14	3500	4100	5.3	2000	1100	530	72,000	200
Total PBDEs	21	15	31	4000	5000	75	2600	1300	610	76,000	220