Possibility of Transfer of Brominated Flame Retardants onto Dust from Components of Television Sets

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Introduction

Recent studies have revealed that brominated flame retardants (BFRs) and brominated dibenzo-*p*-dioxins/dibenzofurans (PBDD/DFs) are detected in dust samples in the home and working environment (Sjödin et al. 2004, Fabrellas et al. 2005, Stapleton et al. 2005, Wilford et al. 2005, Julander et al. 2005, Suzuki et al. 2006). It has been suggested that indoor exposure via air and dust is important pathways by which people (especially young children) accumulate the brominated compounds. Possible sources are the home/office electric appliances such as television (TV) sets, computers and fabric products etc. However, little is known about the transfer mechanism of those brominated compounds onto dust from such residential/office use products. In this study, we focused on TV sets with high polybrominated diphenyl ether (PBDE) concentrations considered in their housing rear cabinets. We collected inside dust and TV set components (housing front cabinet, rear cabinet and circuit board) from five TV sets used in Japan and measured BFRs {i.e., PBDEs, tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD)} and PBDD/DFs. Our objectives were as follows:

- to examine relationships between the concentrations of the brominated compounds in TV inside dust and the above three components.
- to discuss migration possibility of the brominated compounds to dust from the components in the TV inside microenvironments.

Materials and Methods

Five waste TV sets, which were being used until 2005 and were accepted as a trade-in, were obtained from an electrical store in Japan (Table 1). TV inside dust, housing front cabinet, rear cabinet and circuit board samples were collected from each waste TV set. Dust was collected by vacuuming the inside of each TV set until sufficient mass (> 200 mg) was collected on a glass fiber filter. The target substances in TV cabinet and dust samples were extracted by dissolution/precipitation method. The

crude extracts were cleaned up by using multilayer silica gel column chromatography for PBDE analysis (followed by additional activated carbon chromatography for PBDD/DF analysis). For analyzing TBBPA, the crude extracts were derivatized (ethylated) and cleaned up by florisil column chromatography, while only florisil column chromatography was needed for HBCD analysis. The final extracts were concentrated and analyzed for PBDD/DFs, PBDEs and TBBPA by HRGC/HRMS and for HBCD by LC/MS .

Table 1 Information on five waste TV sets sampled.

Sample	Manufacturer	Year of manufacture	CRT size	Inside dust amount (g)	Sample amount of circuit board and cabinets (g)
1	A	1989	29	2.2	all > 5.0
2	A	1991	14	0.57	all > 5.0
3	B	1994	14	0.22	all > 5.0
4	C	1997	20	1.6	all > 5.0
5	D	1998	21	2.4	all > 5.0

Results and Discussion

TV set components. The concentrations of the brominated compounds in TV set components are presented in Table 2. The concentrations of ΣPBDDs (460 ng/g as a mean value) detected were highest in circuit board samples, where TetraBDDs dominated the pattern of PBDDs. Differently, those of PBDFs, PBDEs and TBBPA (9600 ng/g, 48000 μg/g and 19000 μg/g as mean values, respectively) were all highest in rear cabinets. OctaBDF dominated the pattern in the PBDF-abundant rear cabinet samples (samples 2, 3 and 4). More than 10%(w/w) of DecaBDE was detected from two rear cabinets (samples 2 and 4) and one front cabinet (sample 4), while 9.7%(w/w) of TBBPA was present in one rear cabinet (sample 3) instead of DecaBDE. Circuit board contained comparatively high concentrations of PBDEs (4500 μg/g as a mean value). In the circuit board samples 4 and 5 with high PBDE sum of 250 and 22000 μg/g, respectively, TetraBDEs and PentaBDEs were the major homologues. The detection of HBCD was not pronounced for the component samples compared to other investigated compounds.

When conducting multiple linear regression analysis using the analytical data for all the components of five TV sets, statistically significant positive relationship was obtained between log-normalized ΣPBDE and ΣPBDF concentrations (R^2 > 0.80), which suggests occurrence of PBDFs in TV set components be highly associated with PBDEs.

TV inside dust samples. Table 2 also summarizes the levels of the brominated compounds in TV inside dust samples. ΣPBDF and ΣPBDE concentrations in dust samples were in the range of 180-650 ng/g (mean 410 ng/g) and 67-500 μg/g (mean 300 μg/g), respectively. For all the samples, the patterns of PBDFs were dominated by Octa and HeptaBDF, while those of PBDEs were by DecaBDE

(additionally Tetra and PentaBDEs for sample 5). As compared with previous reports on house dust (Sjödin et al. 2004, Fabrellas et al. 2005, Stapleton et al. 2005, Wilford et al. 2005, Julander et al. 2005, Suzuki et al. 2006), the levels in the TV inside dusts were two to three orders of magnitude higher compared to those in house dust samples in Japan, North America and European countries in terms with PBDEs, and two orders higher than those in house dust samples in Japan in terms with PBDFs (Suzuki et al. 2006). Such specifically high ΣPBDF and ΣPBDE concentrations in TV inside dust are consistent with previous data for dust in TV sets manufactured during 1980's and 1990's (Tamade et al. 2002). Our results strongly suggest the brominated compounds are transferred from TV components onto dust and are not significantly influenced by other factors such as contents in the room where the TV sets were placed.

Table 2 Concentrations of the brominated compounds in dust and components of five waste TV sets.

Compounds	Unit	Dust (n = 5)			Circuit board (n = 5)			Front cabinet (n = 5)			Rear cabinet (n = 5)		
		mean[a]	range	no quant.[b]	mean[a]	range	no quant.[b]	mean[a]	range	no quant.[b]	mean[a]	range	no quant.[b]
PBDDs (4-8Br)	ng/g	8	0.67-15	5	460	4.1-1100	5	1.6	<0.15-1.6	1	16	<0.15-48	2
PBDFs (4-8Br)	ng/g	410	180-650	5	300	1.8-1400	5	170	0.41-720	5	9600	0.56-44000	5
PBDEs (1-10Br)	μg/g	300	67-560	5	4500	2.4-22000	5	30000	0.76-150000	5	48000	1.5-130000	5
TBBPA	μg/g	240	5.5-680	5	280	7.9-1300	5	20	0.24-67	5	19000	0.12-97000	5
HBCD	μg/g	2.8	<0.4-2.8	1	<0.3	<0.3	0	0.38	<0.03-0.38	1	2.2	<0.03-2.2	1

[a] Mean of quantitated samples. [b] Number of samples quantitated.

Migration possibility from the components to dust. As possible mechanisms of transfer of the brominated compounds onto dust, vaporization, migration and sink (adsorption) effects have to be taken into account in the TV inside microenvironments. Emission sources could be identified by comparing congener patterns and concentrations among dust and component samples, though physicochemical properties such as vapor pressure and hydrophobicity differ according to congeners.

The profiles of BFRs present in the TV inside dust were compared with those in the plastic components for the two TV sets investigated (samples 2 and 4). PBDE patterns in dust from TV set sample 4 were dominated by DecaBDE, which is quite similar to those in front and rear cabinets, suggesting the PBDEs in dust derived from cabinet samples. On the other hand, PBDE patterns in dust from sample 2 were quite different from those in cabinet samples with respect to lower BDE parts. Lower BDEs (Di- to HexaBDEs) were clearly influenced by those in circuit board. These results indicate concentrations of the brominated compounds could be influenced by various components and more detailed study are needed to quantitatively estimate contribution rates from inner components

and outer environment of TV sets.

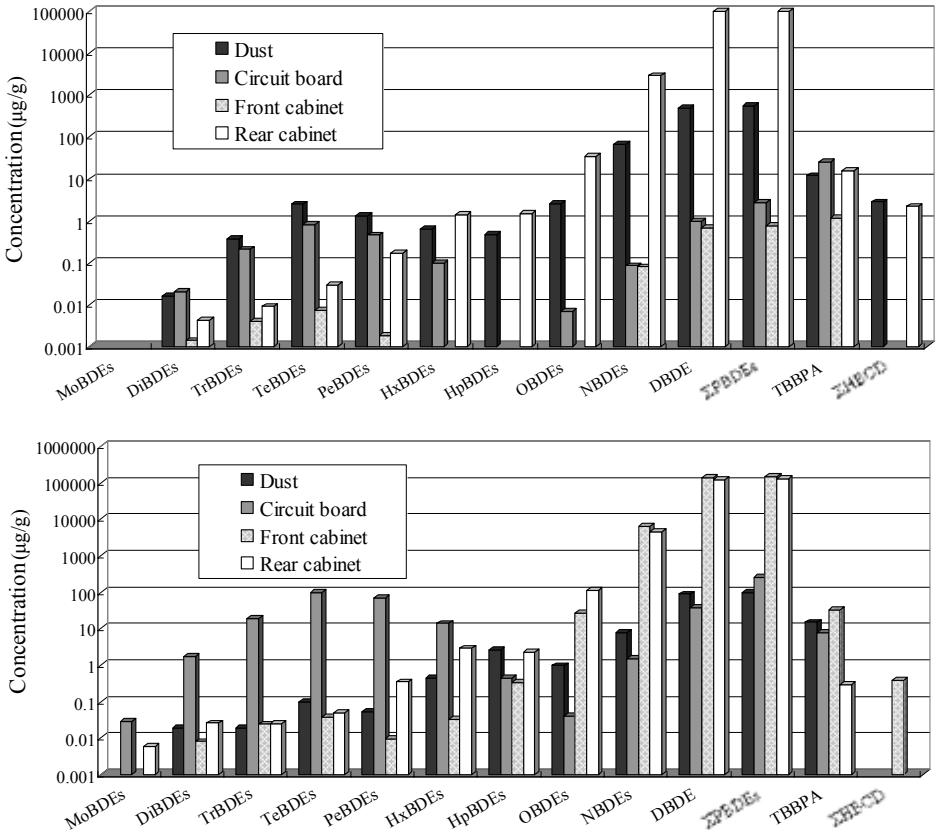

Figure 1 The differences in concentration (μg/g) of BFRs for TV inside dust and plastic component samples. TV set sample 2 (upper) and sample 4 (lower).

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