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Brominated and organophosphate flame retardants in selected consumer products on the Japanese market in 2008

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ABSTRACT

The concentrations of traditional brominated flame retardants (BFRs) and organophosphate flame retardants (OPFRs) in new consumer products, including electronic equipment, curtains, wallpaper, and building materials, on the Japanese market in 2008 were investigated. Although some components of the electronic equipment contained bromine at concentrations on the order of percent by weight, as indicated by X-ray fluorescence analysis, the bromine content could not be fully accounted for by the BFRs analyzed in this study, which included polybrominated diphenylethers, decabromodiphenyl ethane, tetrabromobisphenol A, polybromophenols, and hexabromocyclododecanes. These results suggest the use of alternative BFRs such as newly developed formulations derived from tribromophenol, tetrabromobisphenol A, or both. Among the 11 OPFRs analyzed, triphenylphosphate was present at the highest concentrations in all the products investigated, which suggests the use of condensed-type OPFRs as alternative flame retardants, because they contain triphenylphosphate as an impurity. Tripropylphosphate was not detected in any samples; and trimethylphosphate, tributyl tris(2-butoxyethyl)phosphate, and tris(1,3-dichloro-2-propyl)phosphate were detected in only some components and at low concentrations. Note that all the consumer products evaluated in this study also contained traditional BFRs in amounts that were inadequate to impart flame retardancy, which implies the incorporation of recycled plastic materials containing BFRs that are of global concern.

1. Introduction

There is growing concern about the potential for human exposure to brominated flame retardants (BFRs), which are present in commonly used articles such as electronic equipment, household furnishings, building materials, and car interiors. In the absence of any internationally standardized approach to information sharing regarding the presence of these chemicals in such articles, some jurisdictions have created information disclosure requirements. One of the innovative measures with international influence is the Restriction of Hazardous Substances (RoHS) Directive (Directive 2002/95/EC), which entered into force in 2006 in the European Union (EU) [1]. Under the directive, new electrical and electronic equipment containing more than agreed-upon levels of hazardous metals (Pb, Hg, Cd, Cr^{6+}) and two types of BFRs [polybrominated diphenylethers (PBDEs) and polybrominated biphenyls (PBBs)] are banned from the EU market. Even the RoHS Directive is in force only in EU, all the companies in other parts of the world including Japan who are exporting the products, components, and materials to EU are also required to respond to this restriction. Within Japan, since 2006, it is mandatory for the specific electronic products to label the presence of the substances restricted by the RoHS Directive if one contains more than agreed-upon levels. Owing to the phase-out of PBDEs, an increasing number of organophosphate flame retardants (OPFRs) and alternative BFRs are being used around the world and are consequently being introduced into the environment. However, determining which flame retardant formulations are currently being used in high volumes to meet flammability standards is difficult because information about the use of such formulations in consumer products is usually not publicly available.

Recently, the BFR concentrations in house dust samples were found to vary widely [2–4], and clearly higher concentrations were observed in indoor air than in outdoor air [3]. From the viewpoint of indoor pollution, we recently demonstrated an increase in BFR concentrations in indoor air when products treated with flame retardants, such as televisions (TVs), personal computers, and textile products, were installed in a room [5]. Furthermore, by means of an emissions test using small containers, we confirmed the emission of BFRs from flame-retarded curtains even at room temperature [6]. The results of a series of investigations [5,6] led us to conclude that consumer products frequently used by the public are important sources of human exposure to BFRs.

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Table 1
Target compounds and analytical standards[a] used in this study.

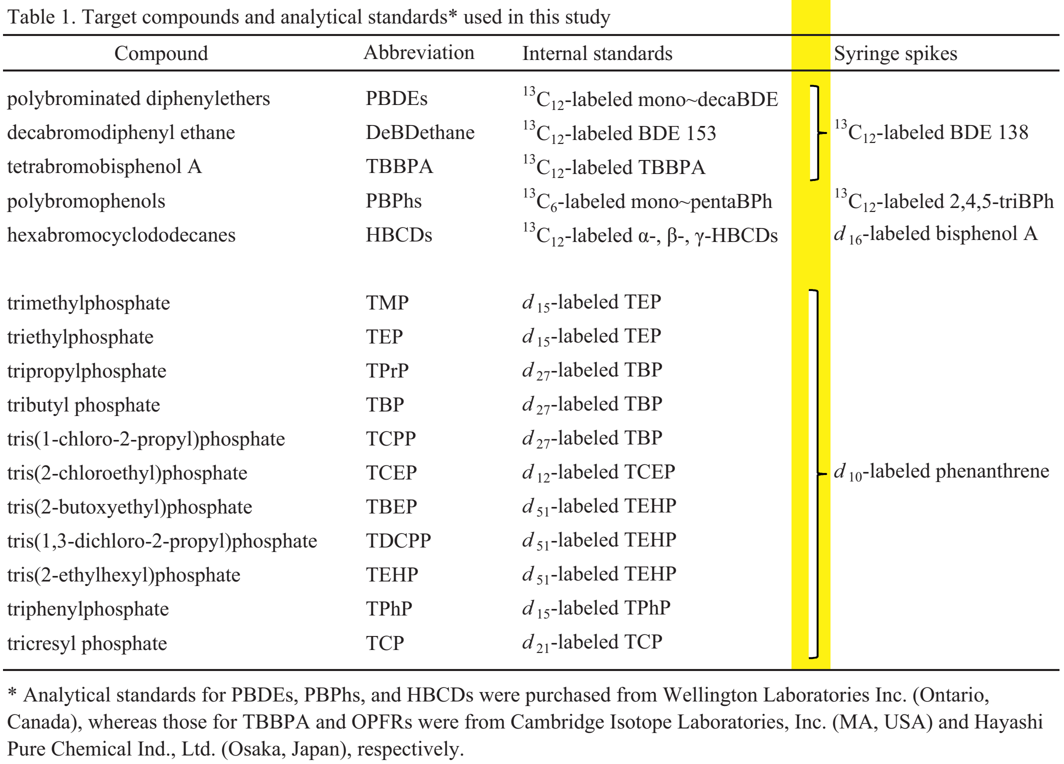


Table 1. Target compounds and analytical standards* used in this study

Compound	Abbreviation	Internal standards	Syringe spikes
polybrominated diphenylethers	PBDEs	$^{13}C_{12}$-labeled mono~decaBDE	$^{13}C_{12}$-labeled BDE 138
decabromodiphenyl ethane	DeBDethane	$^{13}C_{12}$-labeled BDE 153	
tetrabromobisphenol A	TBBPA	$^{13}C_{12}$-labeled TBBPA	
polybromophenols	PBPhs	$^{13}C_6$-labeled mono~pentaBPh	$^{13}C_{12}$-labeled 2,4,5-triBPh
hexabromocyclododecanes	HBCDs	$^{13}C_{12}$-labeled α-, β-, γ-HBCDs	d_{16}-labeled bisphenol A
trimethylphosphate	TMP	d_{15}-labeled TEP	d_{10}-labeled phenanthrene
triethylphosphate	TEP	d_{15}-labeled TEP	
tripropylphosphate	TPrP	d_{27}-labeled TBP	
tributyl phosphate	TBP	d_{27}-labeled TBP	
tris(1-chloro-2-propyl)phosphate	TCPP	d_{27}-labeled TBP	
tris(2-chloroethyl)phosphate	TCEP	d_{12}-labeled TCEP	
tris(2-butoxyethyl)phosphate	TBEP	d_{51}-labeled TEHP	
tris(1,3-dichloro-2-propyl)phosphate	TDCPP	d_{51}-labeled TEHP	
tris(2-ethylhexyl)phosphate	TEHP	d_{51}-labeled TEHP	
triphenylphosphate	TPhP	d_{15}-labeled TPhP	
tricresyl phosphate	TCP	d_{21}-labeled TCP	

* Analytical standards for PBDEs, PBPhs, and HBCDs were purchased from Wellington Laboratories Inc. (Ontario, Canada), whereas those for TBBPA and OPFRs were from Cambridge Isotope Laboratories, Inc. (MA, USA) and Hayashi Pure Chemical Ind., Ltd. (Osaka, Japan), respectively.

[a] Analytical standards for PBDEs, PBPhs, and HBCDs were purchased from Wellington Laboratories Inc. (Ontario, Canada), whereas those for TBBPA and OPFRs were from Cambridge Isotope Laboratories, Inc. (MA, USA) and Hayashi Pure Chemical Ind., Ltd. (Osaka, Japan), respectively.

Although there is a strong need for an international strategy for proper management of hazardous chemicals including flame retardants in the articles on the market, information on the chemical contents of such items is scarce. Therefore, in this study, we determined the concentrations of traditional BFRs and OPFRs in selected new consumer products on the Japanese market: the major components of two TVs and a laptop computer, as well as curtains, electrical outlets, wallpaper, and building materials.

2. Materials and methods

2.1. Sample collection

In February 2008, we used a handheld X-ray fluorescence (XRF) analyzer (Innov-X Alpha 6500, Innov-X Systems, MA, USA) at an electronic appliance store in Tsukuba City, Ibaraki Prefecture, Japan to survey the substances contained in the housing of new electronic equipment. Prior to use, the handheld XRF was standardized by the peak positions of iron and molybdenum, the peak width at half height of manganese, and the total count of SUS316. Then, the screening survey was conducted with RoHS/WEEE mode and analytical time was set at 30 s. On the basis of the bromine (Br) and phosphorus (P) contents, we selected two liquid crystal display TVs (LCD TV-1 and -2) and a laptop computer (all produced by leading Japanese companies) as target articles for the study. The purchased items were dismantled manually, and the element concentrations at several spots on the surface of each component were determined with the handheld XRF analyzer.

Using the results of the XRF analysis for Br and P contents, we selected 17 component samples for further chemical analysis. From the LCD TVs, we selected the front and rear covers, the printed circuit boards (PC boards) for the power supply and the fluorescent tube, a composite sample of the remaining PC boards (other PC boards), and the outermost part of the LCD panel. The PC boards for the power supply and fluorescent tube of LCD TV-1 were separate, whereas those of LCD TV-2 were of an all-in-one type. From the laptop, the bottom of the chassis, the keyboard top, PC boards, a cooling fan, a speaker, an AC adapter, and the outermost part of the LCD panel were selected. All the PC boards in the laptop were combined into one composite sample. Because the cooling fan and speaker were too small to be subjected to chemical analysis separately, these two components were combined for further analysis. Surface projections on the PC boards from the TVs and the laptop were removed as much as possible. Plastic materials from each component, except the PC boards, were subjected to chemical analysis.

In addition to the electronic equipment, two types of flame-retarded curtains, two electrical outlets, two extruded polystyrene (XPS) insulation boards used in the building and construction industry, and four kinds of wallpaper were included in the survey because these products are potential indoor sources of flame retardants. All products were bought new in retail stores in Tsukuba City, Ibaraki Prefecture, Japan in 2008.

2.2. Sample preparation and chemical analysis

The selected components were crushed into homogeneous small pieces and then pulverized to a fine powder with a freezer mill prior to extraction.

Samples other than curtains and insulation boards were ultrasonically extracted with toluene. During ultrasonic extraction, ice was put in the water bath to prevent a temperature increase. After ultrasonication, the samples including TV covers, cooling fan and speaker of the laptop, and electronic outlets were almost completely dissolved in toluene, but for the others the insoluble particles remained as residues. Because XPS is readily soluble in toluene, ultrasonication was not conducted for insulation boards. For curtain samples, the target substances were extracted by Soxhlet extraction with toluene for 16 h. A portion of the toluene extract

Table 2
Comparison of PBDE concentrations (ng/g) in the polymer samples obtained by using different methods of extraction.

		Composite sample of PC boards						Rice cooker-1		Rice cooker-2		Computer mouse	
		Ultrasonic ($n = 3$)		SE-100 ($n = 3$)		Soxhlet ($n = 3$)		Ultrasonic ($n = 1$)	SE-100 ($n = 1$)	Ultrasonic ($n = 1$)	SE-100 ($n = 1$)	Ultrasonic ($n = 1$)	SE-100 ($n = 1$)
		Average	RSD (%)	Average	RSD (%)	Average	RSD (%)						
monoBDE	#3	1.0	4	1.1	6	1.0	8	130	140	62	56	370	370
diBDE	#7	0.40	10	0.42	7	0.40	6	99	100	32	33	75	89
diBDE	#15	6.2	6	6.1	5	5.9	3	960	990	320	310	290	310
triBDE	#17	10	4	9.8	5	9.5	1	1200	1300	270	260	290	300
triBDE	#28	49	4	47	4	45	4	5500	5700	1100	1100	410	440
tetraBDE	#49	100	3	93	3	89	2	8800	9600	1200	1200	340	350
tetraBDE	#71	1.3	23	1.2	10	1.5	29	250	290	41	40	15	15
tetraBDE	#47	1100	4	1000	4	1000	0.4	15,000	15,000	1600	1500	530	560
tetraBDE	#66	110	5	110	3	100	6	10,000	11,000	1100	1100	250	240
tetraBDE	#77	7.0	5	6.2	2	6.1	2	830	820	81	57	41	39
pentaBDE	#100	230	5	220	5	230	2	790	810	71	68	27	30
pentaBDE	#119	5.2	6	4.8	5	4.3	8	460	430	53	38	ND	ND
pentaBDE	#99	1600	4	1500	7	1600	2	12,000	13,000	960	920	250	260
pentaBDE	#85	67	3	63	6	65	4	570	570	36	39	ND	14
pentaBDE	#126	ND		ND		ND		ND	ND	ND	ND	ND	7.4
hexaBDE	#138	23	2	21	4	22	4	150	160	11	12	10	11
hexaBDE	#154	120	4	120	7	120	1	730	750	58	55	46	50
hexaBDE	#153	210	2	200	6	200	2	1800	1800	120	120	70	76
heptaBDE	#184	2.1	6	2.0	21	2.3	1	78	76	8.3	6.2	17	19
heptaBDE	#183	94	3	98	2	96	3	250	240	30	29	97	110
heptaBDE	#191	2.7	18	3.0	5	2.7	10	56	50	3.1	5.2	18	17
octaBDE	#196	47	6	47	4	55	7	140	130	14	13	54	54
octaBDE	#197	47	4	49	5	50	7	200	180	20	18	65	67
nonaBDE	#207	1000	10	1200	3	1400	8	960	770	55	47	260	160
nonaBDE	#206	700	13	770	3	900	8	600	560	31	33	78	91
decaBDE	#209	16,000	7	17,000	1	16,000	2	11,000	11,000	300	280	550	830
Homolog groups													
monoBDEs		1.9	4	2.0	13	1.9	6	270	270	120	100	800	750
diBDEs		12	5	11	4	11	1	2200	2300	760	750	1300	1400
triBDEs		95	3	90	4	87	3	14,000	14,000	2800	2800	1600	1700
tetraBDEs		1300	4	1300	4	1300	1	40,000	41,000	4500	4400	1400	1400
pentaBDEs		2000	4	1900	7	1900	2	19,000	19,000	1500	1400	460	510
hexaBDEs		380	3	360	6	370	2	3500	3600	250	230	240	300
heptaBDEs		110	5	120	1	110	4	950	930	96	93	290	300
octaBDEs		150	3	150	5	170	7	890	850	92	84	290	290
nonaBDEs		2400	11	2600	3	3200	7	2100	1800	120	110	330	330
decaBDE		16,000	7	17,000	1	16,000	2	11,000	11,000	300	280	550	830
Total PBDEs		22,000	7	24,000	0.7	23,000	2	94,000	96,000	11,000	10,000	7300	7900

ND, not detected.

of all the samples was added dropwise to hexane to precipitate the dissolved polymer matrix. Then the precipitate was filtered off. To analyze the 5 BFRs and 11 OPFRs listed in Table 1, we divided all the hexane extracts into 4 aliquots, each of which was spiked with appropriate ^{13}C- or deuterium-labeled internal standards (Table 1). They were subsequently purified as follows.

For analysis of PBDEs, one of the four aliquots was cleaned up by means of a multilayer silica gel column, which consisted of silica gel, 2% (w/w) KOH/silica gel, 44% (w/w) H_2SO_4/silica gel, and 22% (w/w) H_2SO_4/silica gel. The column was eluted with 5% dichloromethane/hexane. For analysis of brominated phenols, including tetrabromobisphenol A (TBBPA) and polybromophenols (PBPhs), an aliquot was derivatized (ethylated) and then cleaned up on a Florisil column eluted with 4% diethyl ether/hexane. For hexabromocyclododecane (HBCD) analysis, an aliquot was subjected to H_2SO_4 treatment and cleaned up on Florisil column eluted by 30% diethyl ether/hexane. For OPFR analysis, an aliquot was passed through a Florisil column, which was eluted sequentially with 10% acetone/hexane and 2% methanol/dichloromethane. Each eluate was concentrated, and the appropriate syringe spike as shown in Table 1 was added prior to instrumental analysis.

PBDEs, TBBPA, PBPhs, and OPFRs were analyzed by high-resolution gas chromatograph (Agilent 6890N, CA, USA) coupled with high-resolution mass spectrometry (AutoSpec Ultima, Micromass, Manchester, UK; or JMS-700 MStation, JEOL, Japan) in selected-ion-monitoring mode. An HP-5MS column (30 m × 0.25 mm i.d. × 0.15 μm) was used for the analysis of PBPhs, mono–heptaBDEs, and OPFRs, whereas an HP-5MS column (30 m × 0.25 mm i.d. × 0.25 μm) and a DB-5MS column (15 m × 0.25 mm i.d. × 0.10 μm) were used for the analysis of TBBPA and octa–decaBDE, respectively. Twelve PBDE congeners (BDE 15, BDE 33/28/16, BDE 47, BDE 99, BDE 100, BDE 153, BDE 154, BDE 175/183, BDE 209), 19 PBPh congeners (2-monoBPh, 3/4-monoBPh, 2,6-diBPh, 2,5/3,5-diBPh, 2,4-diBPh, 3,4-diBPh, 2,3-diBPh, 2,4,6-triBPh, 2,3,6-triBPh, 2,4,5-triBPh, 2,3,5-triBPh, 3,4,5-triBPh, 2,3,4-triBPh, 2,3,4,5-tetraBPh, 2,3,4,6-tetraBPh, 2,3,5,6-tetraBPh, pentaBPh), TBBPA, and OPFRs were identified and quantified by the isotope dilution method using the appropriate ^{13}C- or deuterium-labeled internal standards. Decabromodiphenyl ethane (DeBDethane) concentrations in some of the key samples were semi-quantified using the eluate prepared for PBDE analysis. In addition, unknown peaks that matched the isotopic ratios of the primary and secondary ions of PBDEs in authentic standards were quantified by using the response factor for the same homolog group. Total concentrations of each group of PBDE homologs (mono- to decaBDE) and PBPh homologs (mono- to pentaBPh) were determined on the basis of the total area of all standard-assigned and potential peaks of the corresponding homolog group.

For HBCDs, the concentrations of the 3 diastereomers (α-, β-, and γ-HBCD) were determined with a liquid chromatograph equipped with a mass spectrometer (1100 Series, Agilent). Separation of α-, β-, and γ-HBCDs was achieved by using a 150 mm × 2.1 mm i.d. Develosil C30-UG-5 column (Nomura Chemical Co., Ltd., Japan) at a column temperature of 40 °C. The gradient mobile phase consisted of ammonium acetate solution (A) and acetonitrile (B). The flow rate was set at 0.2 mL/min. The gradient program started at an initial composition of 50:50 A/B (v/v), which was held for 1 min before the composition was changed to 0:100 A/B over 10 min. This composition was held for 10 min. All diastereomers were quantified using the isotope dilution method on the basis of the responses from the corresponding ^{13}C-labeled isomers.

2.3. Quality assurance and quality control (QA/QC)

Samples were analyzed using established laboratory QA/QC procedures. All analytical processes for BFRs and OPFRs were conducted under 'UV-cutoff' conditions. Recoveries of the ^{13}C- or deuterium-labeled internal standards added to samples were: PBDEs 65–100%, TBBPA 70–85%, PBPhs 70–100%, HBCDs 75–90%, and OPFRs 70–100%. Concentrations of all the target compounds were below detection limits in method blanks for the analysis procedures, except BDE 209 (0.04 ng/g) and triphenylphosphate (TPhP, 0.4 ng/g).

To verify the extraction efficiency of our analytical method for flame retardants in polymer samples which are insoluble in toluene, we conducted triplicate analysis of PBDE contents in a composite sample of waste PC boards using three different methods of extraction—ultrasonic, High Speed Solvent Extractor (SE-100, Mitsubishi Chemical Analytech Co., Ltd., Japan), and Soxhlet extraction with toluene. Further, outer plastic parts of two rice cookers and a computer mouse (they were also insoluble in toluene) were employed for chemical analysis of PBDEs using ultrasonic and SE-100 extraction. All of these samples were collected from end-of-life articles. They were pulverized to a fine powder prior to extraction and the crude extracts were cleaned up by using same procedure. The results obtained by ultrasonic extraction favorably compared with other extraction methods (see Table 2), indicating that additive flame retardants like PBDEs can be sufficiently extracted from pulverized polymer by ultrasonication with toluene even when they are not completely dissolved.

3. Results and discussion

3.1. TVs and laptop computer

3.1.1. Handheld XRF analysis

The maximum concentrations of total Br detected by XRF analysis in the components of the TVs and the laptop are shown in Tables 3–5. Because the handheld XRF analyzer used in this study has poor sensitivity to light elements such as P, the P concentrations obtained with this analyzer were used only as a rough indication of whether a component contained very high concentrations of OPFRs. The XRF analysis indicated that LCD TV-1 contained more than 10% by weight of Br in its covers, which indicates that some sort of BFR was used in the TV. LCD TV-2 and the laptop were selected as target articles of this study because we expected that OPFRs were used in their housings instead of BFRs from the results of the XRF analysis.

3.1.2. BFRs

Subsequent analysis by mass spectrometry confirmed that BFRs were present in all three electronic articles (Tables 3–5). There were large differences between the BFR concentrations and congener profiles of the various samples. The PBDE concentrations were below the threshold limit (1000 mg/kg) specified by the RoHS Directive in all the components investigated in the present study. The congener and isomer profiles of PBDEs, PBPhs, and HBCDs are shown in Figs. 1–3, respectively. Although some of the components contained Br at concentrations on the order of percent by weight, the Br content cannot be fully accounted for by the 5 BFRs we analyzed; this result indicates the use of alternative BFRs. Recently, Bantelmann et al. conducted an extensive survey of BFR contents in wide range of industrial and consumer products on the Swiss market, and they also revealed the predominant use of alternative BFRs other than PBDEs, PBBs, HBCDs, and TBBPA [7].

In the rear and front covers of LCD TV-1, the BFR present at the highest concentrations was DeBDethane (130 and 92 μg/g, respectively), followed by PBDEs and PBPhs (Table 3). However, the DeBDethane concentration was far lower than the concentrations of additive flame retardants generally added intentionally to flammable polymers (5–20% by weight). According to Sellström and Jansson [8], even if TBBPA, which is reactive, was used as a flame retardant for polymers, a substantial amount of unreacted TBBPA would remain in the end products. Therefore, our results strongly suggest the use of BFRs other than the 5 BFRs we analyzed. 2,4,6-TriBPh was the only one of the 6 triBPh isomers that was detected in appreciable quantities in the covers of LCD TV-1 (detailed data for individual samples are available in the Supporting information; see Table S1), and 2,4,6-triBPh accounted for approximately 90% of the total PBPhs (Fig. 2). These results suggest that BFRs derived from 2,4,6-triBPh may have been used. It is known that 2,4,6-triBPh is not always used directly as a flame retardant; it is mostly used as an intermediate in the preparation of products such as 1,2-bis(2,4,6-tribromphenoxy)ethane and 2,4,6-tris-(2,4,6-tribromophenoxy)-1,3,5-triazine, and as an end-cap for TBBPA derivatives including TBBPA epoxy/carbonate oligomer [9,10]. The structures for these compounds are presented in Fig. 4. So far, 2,4,6-TriBPh has been detected at concentrations up to 0.05% by weight in some of these BFR formulations [11]. If 10% by weight of the BFR above were added to a polymer, roughly 50,000 ng/g of 2,4,6-triBPh could be expected to be present as an impurity or an unreacted intermediate. We believe that it is unlikely that any type of TBBPA oligomer was added to the covers of LCD TV-1 because TBBPA was detected at the low concentrations of 68 and 92 ng/g in the rear and front covers, respectively (Table 3).

We assumed that TBBPA or its derivatives were used in the composite sample consisting of the cooling fan and the laptop speaker. Of all the brominated compounds, TBBPA showed the highest concentration (approximately 1.0% by weight), followed by PBPhs and DeBDethane (Table 5). Considering the fact that a variety of TBBPA-derived flame retardants have been widely used in recent years [10], we believe that the TBBPA detected in this sample was an impurity or an unreacted compound derived from the raw materials. In the AC adapter of the laptop, only small amounts of the target BFRs were detected, even though the Br content of this sample was about 0.5% by weight. This result suggests that alternative BFRs were the primary flame retardants used in this component.

Comparison of the profiles of the PBDE homologs indicated that decaBDE (i.e., BDE 209) was the predominant congener, accounting for 73–98% of the total PBDEs in all the components of the TVs and the laptop, except for the front cover of LCD TV-2, in which tetraBDE and pentaBDE were present in high proportions (44% and 33% of the total PBDEs, respectively; Fig. 1). This result indicates that the latest electronic equipment on the Japanese market is influenced mostly by the decaBDE technical mixture, even if they are treated by alternative flame retardants.

Table 3
Concentrations (ng/g) of brominated compounds and phosphates in LCD TV-1.

	Rear cover	Front cover	Power board	PC board for fluorescent	Other PC boards	LCD panel
PBDEs	14,000	14,000	15	54	59	2.4
DeBDethane	130,000	92,000	1100	770	36	na
TBBPA	68	92	90	890	87	7.3
PBPhs	5700	4600	980	1200	730	33
HBCDs	<0.5	6.1	130	680	<0.5	1.9
Total Br (XRF)	140,000,000	130,000,000	130,000	23,000,000	24,000,000	<18,000
TMP	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
TEP	0.50	3.0	3.6	1.1	0.70	6.3
TPrP	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
TBP	16	11	3.4	1.8	2.1	2.5
TCPP	10	14	52	16	23	4.0
TCEP	7.0	4.0	<4	4.0	9.0	<4
TBEP	<80	<80	<80	<80	<80	<80
TDCPP	<2	<2	<2	<2	<2	<2
TEHP	2.7	17	<0.9	5.7	<0.9	<0.9
TPhP	1100	2400	6,700,000	320,000	1,600,000	1,200,000
TCP	180	370	4,500,000	140,000	480	54

na, no data available.

Table 4
Concentrations (ng/g) of brominated compounds and phosphates in LCD TV-2.

	Rear cover	Front cover	PC board for power supply and fluorescent	Other PC boards	LCD panel
PBDEs	32	540	13	45	5.4
DeBDethane	na	na	2400	380	na
TBBPA	15	21	840	74	8.7
PBPhs	41	65	250	120	4.8
HBCDs	53	40	400	3.9	<0.5
Total Br (XRF)	<1000	<1000	42,000,000	90,000,000	<20,000
TMP	<0.3	<0.3	<0.3	<0.3	<0.3
TEP	0.40	0.40	190	0.40	0.30
TPrP	<0.5	<0.5	<0.5	<0.5	<0.5
TBP	2.1	2.3	7.7	1.9	1.5
TCPP	4.0	9.0	5.5	26	4.0
TCEP	<4	<4	5.5	7.0	<4
TBEP	<80	<80	<80	<80	<80
TDCPP	<2	<2	<2	<2	<2
TEHP	<0.9	80	<0.9	<0.9	<0.9
TPhP	600,000	940,000	14,000,000	870	1,200,000
TCP	47	140	84,000	72	110

Table 5
Concentrations (ng/g) of brominated compounds and phosphates in the laptop computer.

	Chassis	Keyboard top	PC boards	Cooling fan and speaker	AC adapter	LCD panel
PBDEs	68	130	70	4800	6.9	6.7
DeBDethane	670	na	37	19,000	na	na
TBBPA	2700	1400	800	9,500,000	81	110
PBPhs	600	260	180	110,000	44	32
HBCDs	210	4.4	1.4	610	<0.5	<0.5
Total Br (XRF)	490,000	<2000	80,000,000	95,000,000	4,900,000	23,000
TMP	<0.3	0.70	<0.3	0.50	<0.3	<0.3
TEP	6.0	17	56	30	1.1	13
TPrP	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
TBP	1.6	1.8	4.4	1.8	1.3	1.2
TCPP	100	11	34	4.0	150	12
TCEP	16	<4	14	120	<4	<4
TBEP	<80	<80	<80	<80	<80	<80
TDCPP	<2	<2	9.0	14	35	<2
TEHP	130	190	<0.9	26	1300	<0.9
TPhP	170,000	500,000	560	42,000	1800	2,600,000
TCP	390	28	43	3600	17	130

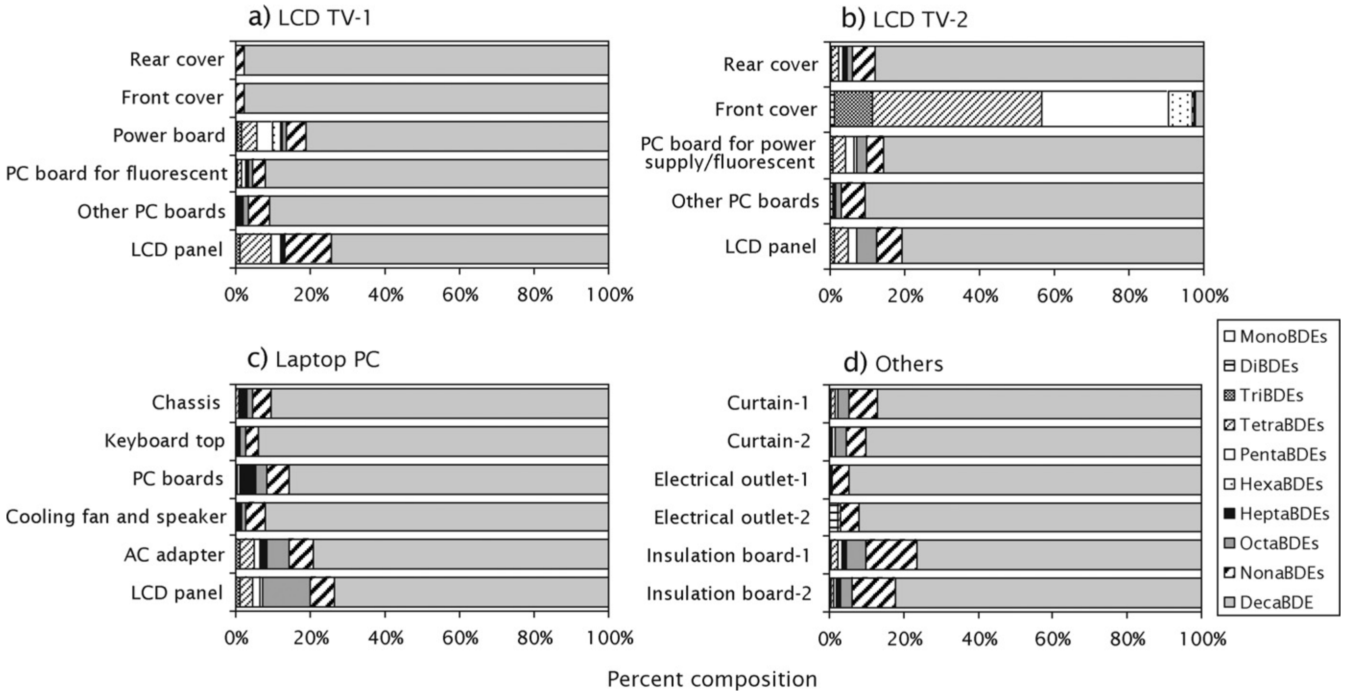


Fig. 1. Profiles of PBDE homologs in the LCD TVs (a and b), the laptop (c), and other consumer products (d) in Japan.

As for HBCDs, the α-diastereomer was the major HBCD in most samples (Fig. 3), although γ-HBCD always formed the majority (>75%) of the technical mixtures of HBCDs with smaller amount of the other two diastereomers being present [12]. Previously, we found that α-HBCD was the major isomer in textile products treated with the technical mixtures of HBCDs, owing to thermal isomerization of γ-HBCD to the α-diastereomer during heat treatment of flame-retarded products during manufacturing [13]. In the present study, HBCDs were generally the most minor BFRs in the components we tested, including 5 samples in which the HBCD concentrations were lower than the detection limit (Tables 3–5). Nevertheless, it is important to note that α-HBCD is the predominant diastereomer in commonly used home electronic appliances because this fact is essential for understanding HBCD accumulation behavior in the indoor environment and also in biota, including humans.

Note that all the samples analyzed in this study contained traditional BFRs in amounts that were inadequate to impart flame retardancy. A plausible explanation for this observation is that some of the components were manufactured using recycled plastic

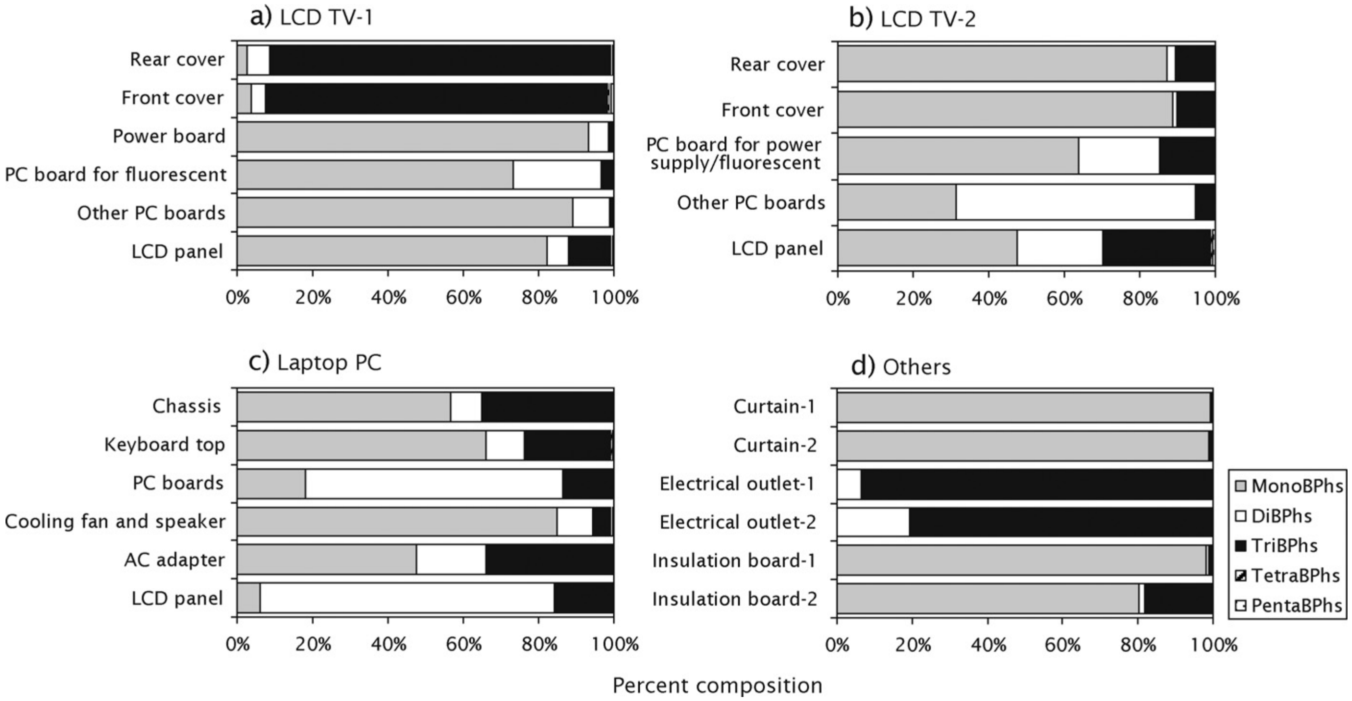


Fig. 2. Profiles of PBPh homologs in the LCD TVs (a and b), the laptop (c), and other consumer products (d) in Japan.

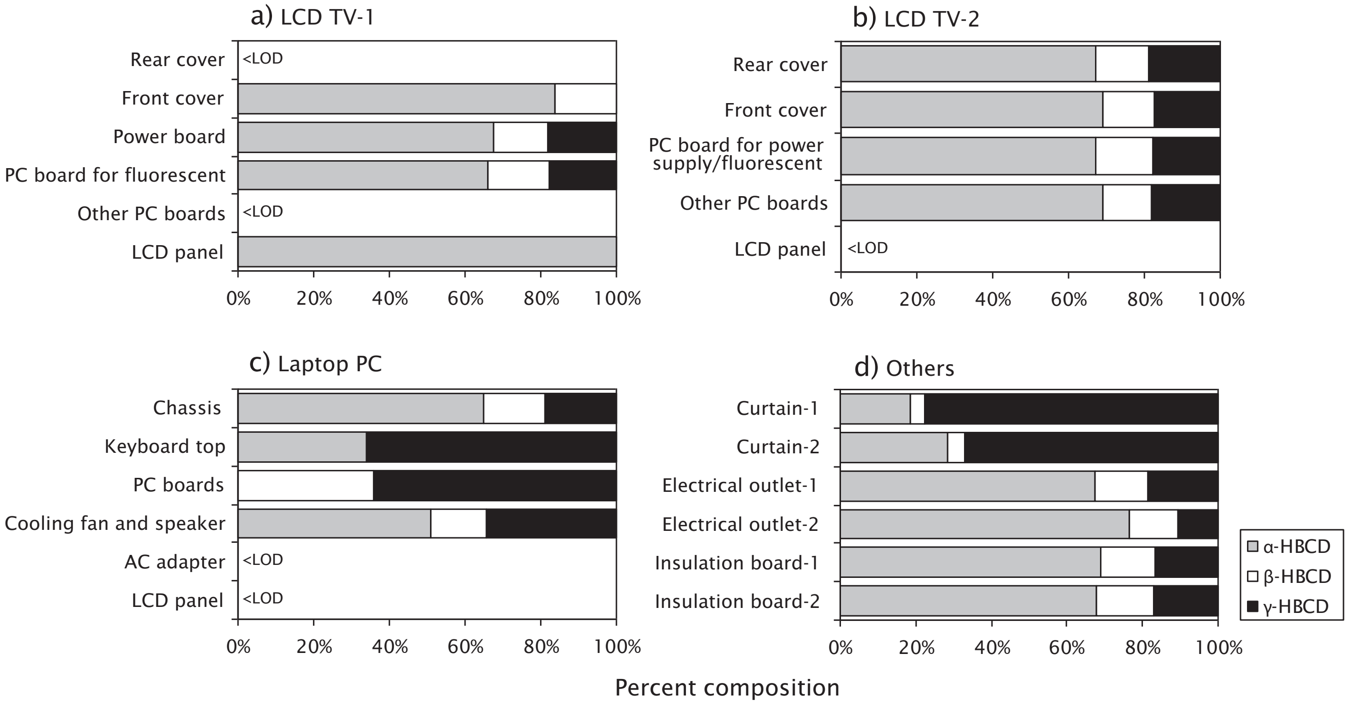


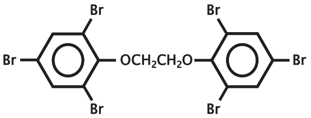
Fig. 3. Profiles of HBCD diastereomers in the LCD TVs (a and b), the laptop (c), and other consumer products (d) in Japan.

materials that contained certain BFRs such as PBDEs. In addition, the articles may have been unintentionally contaminated by those BFRs because they were fabricated on manufacturing lines shared with BFR-treated articles.

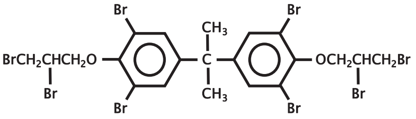
3.1.3. *OPFRs*

Among the 11 OPFRs we analyzed, TPhP showed the highest concentrations in all the components, with concentrations ranging from 560 to 14,000,000 ng/g (Tables 3–5). Tripropylphosphate and tris(2-butoxyethyl)phosphate (TBEP) were not detected in any samples, and trimethylphosphate and tris(1,3-dichloro-2-propylphosphate) were detected in only some of the components of the laptop at low concentrations. The profile of OPFR concentrations in this study differed from the profiles in floor dust of a hotel in Japan [14]: TBEP was the predominant compound in the dust, which indicates a difference in the potential sources. TBEP is generally used as a plasticizer in rubber and plastics, and it aids in floor polish formation and leveling and improves gloss. Because

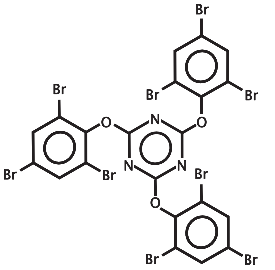
1,2- bis(2,4,6- tribromphenoxy)ethane
(CAS No. 37853- 59- 1)



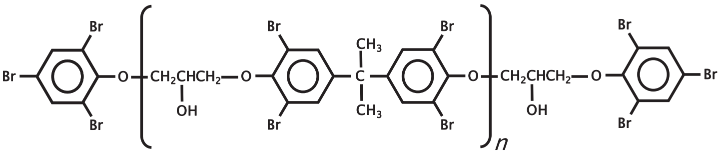
TBBPA bis(2,3- dibromopropyl ether)
(CAS No. 21850- 44- 2)



2,4,6- tris- (2,4,6- tribromophenoxy)- 1,3,5- triazine
(CAS No. 25713- 60- 4)



TBBPA brominated epoxy oligomer end- capped with triBPh
(CAS No. 139638- 58- 7/135229- 48- 0)



TBBPA carbonate oligomer end- capped with triBPh
(CAS No. 71342- 77- 3)

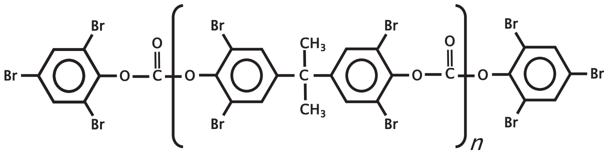
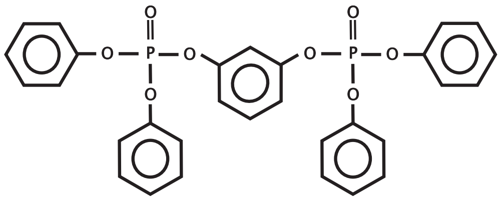


Fig. 4. Chemical structures of principal BFRs derived from 2,4,6-triBPh and/or TBBPA.

Resorcinol bis(diphenyl phosphate) (RDP)
(CAS No. 57583- 54- 7, 125997- 21- 9)



Bisphenol- A bis(diphenyl phosphate) (BDP)
(CAS No. 5945- 33- 5, 181028- 79- 5)

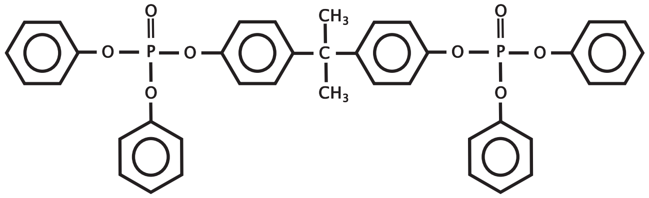


Fig. 5. Chemical structures of principal condensed-type PFRs.

commercially available floor finish products contain TBEP as a plasticizer (0.5–8% by weight) [15], it is a plausible source of floor dust samples.

In stark contrast to the covers of LCD TV-1, the covers of LCD TV-2 exhibited total Br concentrations that were lower than the detection limit of the XRF instrument, and subsequent mass spectrometry analysis indicated that TPhP was the predominant phosphate compound (Table 4). These results indicate that OPFR were used in this item. As was the case for LCD TV-2, the TPhP concentration was also the highest in the bottom of the chassis and the keyboard top of the laptop (Table 5). However, it is quite unlikely that TPhP itself was used as a flame retardant in these components, because the addition of percent order concentrations of OPFRs by weight is generally required for sufficient flame retardancy [16,17]. It is highly possible that condensed-type OPFRs, such as resorcinol bis(diphenyl phosphate) and bisphenol A bis(diphenyl phosphate), whose general structures are shown in Fig. 5, were applied to these articles, because there formulations contain approximately 3–5% by weight of TPhP as an impurity [18]. Condensed-type OPFRs are high-molecular-weight compounds with extremely low volatility compared to their monomer, TPhP [19]. To reduce indoor emissions of flame retardants from the articles, consumption of condensed-type OPFRs has risen dramatically over the past decade in Japan [20]. In addition, a recent study revealed that one of the replacements for the pentaBDE formulation for polyurethane foam, Firemaster 550, contains TPhP as a major component (18% by weight) [21]. Because this technical mixture also contains brominated compounds (~40% by weight), the possibility that Firemaster 550 was used in the chassis of the laptop, which also contained substantial concentrations of Br, cannot be ruled out.

Because PC boards are assembled from numerous plastic and metallic parts, we could not determine the concentrations of flame retardants only in the polymer used for laminating the board. Among the BFRs and OPFRs analyzed, TPhP and tricresyl phosphate were the two dominant compounds detected in 4 out of the 6 PC board samples (power supply board, PC board for the fluorescent tube, other PC boards of LCD TV-1, and PC board for power supply and the fluorescent tube of LCD TV-2) (Tables 3 and 4). The highest concentration of TPhP – up to 1.4% by weight – was found in the PC board for the power supply and the fluorescent tube of LCD TV-2. Conversely, OPFRs including TPhP were present in relatively small amounts in the other PC boards of LCD TV-2 (Table 4) and the PC boards of the laptop (Table 5). Because noncondensed-type OPFRs evaporate easily and are not stable to hydrolysis, it is unlikely that they are extensively used for components like PC boards, which will be subjected to high temperatures. However, our results imply that some type of OPFRs was used in PC boards as flame retardants or plasticizers. It is highly probable that condensed-type OPFRs were added to the polymer used to laminate the boards because the stability of OPFRs has been greatly improved. There is also the possibility that alternative phosphorus–bromine flame retardants such as Firemaster 550 were used in the PC boards evaluated in this study, because the total Br contents of the boards were at concentrations on the order of percent by weight, except in the power board of LCD TV-1 though any PC board samples contained remarkably high concentrations of the 5 BFRs we analyzed.

In the LCD panels, TPhP was also the predominant compound detected, with concentrations ranging from 0.12 to 0.26% by weight (Tables 3–5). For such panels, TPhP is thought to be used not only as a flame retardant but also as a plasticizer for optical triacetyl cellulose (TAC) films, which are widely used as protective films for polarizers in LCDs. These films contain TPhP as a plasticizer at concentrations on the order of percent by weight [22]. The outermost part of the LCD panel analyzed in this study consisted of several layers of sheets glued together, which means that some of them will be the TAC film.

Recently, two different mechanisms for transfer of flame retardants from consumer products to indoor dust were reported: physical processes (e.g., abrasion, weathering) and volatilization [23,24]. Considering that dust is the primary route for human intake of chemicals from consumer products, it is not enough to replace chemicals of concern with high-molecular-weight compounds that are less volatile; assessment of the risk of the alternative chemicals themselves is also required.

3.2. *Curtains*

We studied the contents and profiles of flame retardants in textile products treated by principal BFRs including HBCDs and decaBDE [13]. In the present study, we selected two flame-retarded curtains with low Br contents (as verified by XRF analysis), expecting to confirm the use of OPFRs. Among BFRs and OPFRs analyzed, TPhP was the compound detected at the highest concentration in curtain-1 and -2, followed by HBCDs and tricresyl phosphate (Table 6). These results indicate that the replacement of HBCDs by OPFRs in textile products is under way (The Japanese government has classified HBCDs as a Type I Monitoring Chemical Substance as specified by the Law Concerning the Evaluation of Chemical Substances and Regulation of Their Manufacture, etc.). Because TPhP concentrations did not exceed 0.1% by weight, we suggest that the curtains were made flame retardant by means of condensed-type OPFRs such as resorcinol bis(diphenyl phosphate) and bisphenol A bis(diphenyl phosphate) and that TPhP was present as an impurity. Interestingly, HBCDs were also detected at relatively high concentrations, with the largest proportion made up by the γ-diastereomer (Fig. 3); this result differs from results observed for textiles treated by HBCDs, in which α-HBCD is the predominant isomer [13]. The current results suggest the combined application of both OPFRs and HBCDs or unintentional contamination by HBCDs due to the sharing of manufacturing lines.

3.3. *Electrical outlets*

The Br contents of two electrical outlets investigated were 3.9 and 6.3% by weight, respectively (Table 6), and these values indicate that some type of BFR was used in these products. PBPhs

Table 6
Concentrations (ng/g) of brominated compounds and phosphates in curtains, electrical outlets, and insulation boards.

	Curtain-1	Curtain-2	Electrical outlet-1	Electrical outlet-2	Insulation board-1	Insulation board-2
PBDEs	7.4	9.1	97	33	63	220
DeBDethane	na	na	320	6100	na	na
TBBPA	21	16	340	15,000	22	22
PBPhs	860	1800	5200	36,000	4400	330
HBCDs	130,000	180,000	800	240	23,000,000	18,000,000
Total Br (XRF)	110,000	210,000	39,000,000	63,000,000	19,000,000	21,000,000
TMP	<0.3	<0.3	<0.3	<0.7	<0.3	<0.3
TEP	<0.1	<0.1	0.50	1.4	11	5.7
TPrP	<0.5	<0.5	<0.5	<1	<0.5	<0.5
TBP	1600	1300	2.7	5.0	8.8	4.8
TCPP	<3	<3	85	12	28	37
TCEP	4.0	6.0	4.0	<8	9.0	10
TBEP	<80	<80	<80	<200	890	140
TDCPP	<2	<2	<2	<5	<2	6.0
TEHP	<0.9	<0.9	<0.9	<2	<0.9	6.4
TPhP	820,000	840,000	12,000	630	8700	5300
TCP	4900	190,000	24	53	190	570

Table 7
Concentrations (ng/g) of brominated compounds and phosphates in wallpaper.

	Wallpaper-1	Wallpaper-2	Wallpaper-3	Wallpaper-4
PBDEs	3.1	14	6.6	7.3
DeBDethane	na	na	na	na
TBBPA	13	24	20	16
PBPhs	110	110	52	65
HBCDs	210	290	130	340
Total Br (XRF)	<2000	<2000	na	na
TMP	<0.3	<0.3	<3	<3
TEP	1.1	1.3	4.0	3.0
TPrP	<0.5	<0.5	<5	<5
TBP	7.1	6.0	60	40
TCPP	78	100	60	90
TCEP	15	<4	60	80
TBEP	<80	<80	<800	<800
TDCPP	<2	<2	<20	<20
TEHP	3.9	8.7	27	80
TPhP	230	140	1500	1800
TCP	94	95	660	740

were the predominant compounds among the 5 BFRs analyzed, followed by TBBPA and DeBDethane. 2,4,6-TriBPh was the only isomer detected in appreciable quantities among the triBPh isomers identified in electrical outlet-1 and -2 (Table S4), and 2,4,6-triBPh was also the predominant isomer among the PBPhs, contributing more than 80% of the total PBPhs (Fig. 2). Therefore, as was the case for the chassis of LCD TV-1, it is conceivable that BFRs derived from 2,4,6-triBPh, such as 1,2-bis(2,4,6-tribromphenoxy)ethane and 2,4,6-tris-(2,4,6-tribromophenoxy)-1,3,5-triazine, or from TBBPA derivatives, including the TBBPA epoxy/carbonate oligomer (Fig. 4), were used. Of course, it is not possible to obtain a complete picture owing to the small number of tested products, but the use of flame retardants in electrical outlets to prevent fire arising from dust accumulated between the plug and the wall outlet is probably common. Thus, these devices may also be sources of flame retardant emissions to the indoor environment.

3.4. Insulating boards

As expected, HBCDs were present at high concentrations in XPS insulation board-1 and -2 (2.3 and 1.8% by weight, respectively; Table 6). For these items, the Br content detected by the handheld XRF could be clearly explained by the intentional use of HBCDs. Nevertheless, other compounds, such as PBPhs, TPhP, and TBEP, were detected in both samples at more than trace levels, which suggests contamination during the manufacturing process. As for HBCD profiles, the α-diastereomer was present in the highest proportion, accounting for approximately 70% of the total HBCDs (Fig. 3). This observation indicates thermal isomerization of γ-HBCD in the technical mixture to the α-diastereomer during the process for manufacturing of XPS, because the extruder must be operated at temperatures exceeding 200 °C; this temperature is much higher than the temperature at which the thermal rearrangement of the HBCD diastereomers occurs (160 °C) [25]. Because insulation boards do not face the inside of a room, HBCD emissions from these building materials may not be as important as emissions from other products present in a room. Instead, further research is required for evaluation of the release of HBCDs from construction and demolition waste (including insulation boards) into the ambient environment after their disposal.

3.5. Wallpaper

The BFRs and OPFRs detected in the wallpaper samples are listed in Table 7. TPhP was the most prevalent compound in the wallpaper samples, with concentrations ranging from 230 to 1800 ng/g, except for wallpaper-2, in which HBCDs predominated. No compounds were detected at concentrations sufficient to impart adequate fire retardancy, which implies that these products were not treated with any flame retardants. Because all the wallpapers we selected for this study were made from poly(vinyl chloride), which itself has flame retardancy, they might not have required treatment with BFRs or OPFRs. Our results suggest that wallpaper is not likely to be an important source of indoor pollution by flame retardants.

4. Conclusions

The results of this study indicate that the type of flame retardants used in consumer products on the Japanese market is shifting in response to domestic and international regulations. However, further risk assessment is imperative for answering the recurring question of whether alternative flame retardants (including BFRs derived from 2,4,6-triBPh and TBBPA, and condensed-type OPFRs) are safer than traditional retardants from the viewpoint of human and environmental health and safety. In addition, we must carefully consider that all the samples analyzed in this study contained traditional BFRs in amounts inadequate to impart flame retardancy, which suggests that recycling and re-use of end-of-life electronic products might be important pathways by which these BFRs find their way into new products.

A new European Union law REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals), which entered into force in 2007, requires stakeholders to make every effort to share data on the properties of chemical substances used. From the perspective of verifying the effect of implementation of controls and filling the information gap, however, studies to identify and determine the concentrations of substances actually contained in various articles are important. Further studies are required for the development of methods for quantitative analysis of alternative flame retardants. Because consumers are unable to protect themselves from hazards posed by toxic substances in articles at present, an internationally standardized approach to information sharing about chemicals in articles including recycled products should be developed.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.06.043.

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