BROMINATED FLAME RETARDANTS AND RELATED SUBSTANCES IN THE INTERIOR MATERIALS AND CABIN DUSTS OF END-OF-LIFE VEHICLES COLLECTED IN JAPAN

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Introduction

In Japan, the Law for the Recycling of End-Of-Life Vehicles (ELV) started in January 2005. Before the enforcement of the law, automobile shredding residue (ASR) was mostly landfilled. Because of the limited availability of final disposal sites, as well as to prevent illegal dumping and improper treatment of ELVs, the low intends to define appropriate roles among related parties to promote sound treatment and recycling of ELVs. This law requires manufacturers to retrieve fluorocarbons (refrigerant gas), airbags, and ASR from ELVs and to properly recycle the remaining materials. When people buy a new car a recycling fee has to be paid by owner as deposit, and then when the car become ELV, the fee is used for recycling. After the enforcement of the recycling law, recycling rate of ASR increased drastically, and the current total recycling rate is about 95% by weight.

In the meantime, the behavior of hazardous substances during ELV recycling and ASR treatment remain to be elucidated as a critical issue. So far, the studies on persistent organic pollutants (POPs) including brominated flame retardants (BFRs) in ASR are limited. To establish suitable methods for ASR treatment, detailed analysis of hazardous substances in ELV components should be conducted, and their risk in the recycling process should be examined. From a viewpoint of human exposure to chemicals from car interiors during usage, unintentional ingestion of indoor dust is an important pathway. Since car interiors usually require flame-retardant materials, the exposure to BFRs may be higher in in-vehicle compare to other common indoor environments.

From this background, the aims of this study were 1) to identify the use of BFRs including polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs) in car interiors distributed in the Japanese market, and 2) to reveal the accumulation profiles of BFR in car dust and their migration from materials to dust.

Materials and methods

A total of 40 ELVs manufactured during 1993 and 2004 were investigated at an ELV-dismantling plant in Japan. For comparison, 5 currently-used vehicles (CUVs) manufactured during 2008 and 2012 were also involved in this study. Interior materials/components including dashboard, door trim panel, automotive headliner, car seat fabric, seat polyurethane foam (PUF), plastic parts of car seats, floor covering, floor mat, and soundproof material were collected from each vehicle. First, a screening survey of bromine (Br) in each material/component was conducted by using a handheld X-ray fluorescence (XRF) analyzer (Innov-X Alpha 6500, Innov-X Systems, MA, USA) with RoHS/WEEE mode and analytical time was set at 30 seconds. The materials/components containing more than 0.1% by weight of Br were selected for further chemical analysis. They were crushed into homogeneous small pieces and then pulverized to a fine powder with a freezer mill prior to the ultrasonic extraction with toluene.

Cabin dust samples were collected separately from ‘the entire surface of floor (floor dust)’ and ‘the upper surface of front and rear seats and dashboard (seat dust)’ in 41 cars including both ELVs and CUVs. They were collected using a vacuum cleaner, to which a nylon sock with a 25 μm mesh size was inserted into the nozzle of the device to retain the dust. Prior to extraction, samples were sieved through a 250 μm mesh, weighed, and stored in the cold dark place.

Identification and quantification of PBDEs and polybrominated dibenzo-*p*-dioxins and furans (PBDD/Fs) were performed by a HRGC-HRMS whereas HBCD diastereomers were analyzed by using a LC-MS/MS.

Results and discussion

Interior materials/components

The XRF survey showed that 32 out of 515 materials/components investigated (6.2% of the total) contained more than 0.1% by weight of Br (Figure 1), indicating that the use of BFRs in ELV is limited. No correlation was observed between the year of manufacture and the Br contents in the cars. Among 32 samples, seat fabric contributed the most, 60% of the total, followed by floor covering. High Br contents were not found in dashboard, floor mat, and plastic parts of car seats. The results of XRF screening of Br suggest that seat fabric and floor covering are likely the main source of BFRs accumulated in ASR.

Among 32 materials/components exceeding 0.1% by weight of Br, 27 samples employed for further chemical analysis. Subsequent analysis by mass spectrometry confirmed that 16 samples were treated with either the technical PBDEs or HBCDs; this result indicates the use of alternative BFRs in the rest of 11 samples (Table 1). The congener and isomer profiles of PBDEs indicated that 12 samples including 9 seat fabric samples were DecaBDE-treated materials. Only a set of seat fabric and PUF collected from a foreign car (ELV-10) were found to be treated with the PentaBDE technical mixture. High HBCD contents were found in only 2 floor covering samples (none of seat fabric). According to Japan Automobile Manufacturers Association, the replacement of HBCDs in car interior fabric is steadily carried out and the use of HBCDs has abolished totally in the vehicles manufactured after April 2010.

PBDFs were concurrently detected in the car interior samples containing more than 100 mg/kg of PBDEs (Table 1), possibly because of their presence in the technical mixtures of PBDEs. Octa-BDF was the predominant congener found in DecaBDE-treated materials, whereas contribution of tri- to penta-BDFs to the total PBDFs were particularly prominent in the case of PentaBDE-treated seat fabric and PUF.

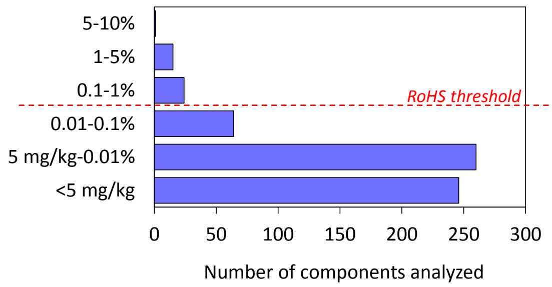

Figure 1. Br contents in ELV interior materials

Table 1. Concentrations (mg/kg) of total Br, PBDEs, HBCDs, and PBDD/Fs in the ELV interior materials

	n	ID	Br	PBDEs	HBCDs	PBDD/Fs
Seat fabric	16	ELV-03	50,000	78,000	<LOD	32
		ELV-39	45,000	62,000	<LOD	22
		ELV-24	41,000	52,000	11	23
		ELV-07	34,000	46,000	50	31
		ELV-27	34,000	49,000	0.46	32
		ELV-11	34,000	43,000	<LOD	28
		ELV-31	34,000	48,000	<LOD	41
		ELV-04	32,000	45,000	<LOD	34
		ELV-42	23,000	26,000	0.21	14
		ELV-10	5,600	5,500	<LOD	5.2
		ELV-46	5,400	<LOD	<LOD	<LOD
		ELV-01	5,200	<LOD	<LOD	<LOD
		ELV-43	4,500	7.0	1.8	<LOD
		ELV-32	3,700	110	0.15	0.044
		ELV-47	3,000	0.040	<LOD	<LOD
		ELV-29	2,600	100	<LOD	0.078
Floor covering	4	ELV-43	14,000	2.2	13,000	<LOD
		ELV-32	5,500	6,700	<LOD	2.2
		ELV-25	4,500	16	3,000	<LOD
		ELV-11	<LOD	16	<LOD	<LOD
Soundproof material	3	ELV-11	6,000	6,600	<LOD	2.4
		ELV-40	2,100	820	<LOD	0.32
		ELV-40	1,200	11	<LOD	<LOD
Seat PUF	2	ELV-10	38,000	52,000	0.17	3.4
		ELV-15	2,000	3.4	<LOD	<LOD
Headliner	1	ELV-30	5,600	8,200	<LOD	2.0
Door trim fabric	1	ELV-44	4,200	0.025	450	<LOD

Table 2. Concentrations of BFRs and PBDD/Fs in car dust (mg/kg; median and range)

	n	PBDEs	HBCDs	PBDD/Fs	Reference
Floor dust	36	4.5 (0.53-440)	0.50 (0.026-66)	0.024 (0.0021-0.17)	This study
Seat dust	36	11 (0.96-170)	0.49 (0.081-37)	0.053 (0.0061-1.7)	This study
Czech Republic	27	0.21 (<LOQ-34)	0.057 (<LOQ-0.24)	NA	Ref 1
Sweden	4	1.4 (0.054-30)	0.054 (0.0068-0.17)	NA	Ref 2
UK	14	200 (30-850)	9.2 (1.2-24)	NA	Ref 3
USA	60	48 (4.4-3,600)	NA	NA	Ref 4
USA	66	9.9 (0.91-350)	NA	NA	Ref 5

Cabin dust

BFRs and PBDD/Fs were detected in all the cabin dust samples analyzed (Table 2). It should be noted that the PBDEs and HBCDs were also detected in dust taken from vehicles that did not contain any BFRs in the main interior materials. This result suggests that pollution sources of BFRs in the car may also include the interior materials having small surface areas, in-car devices such as audio, navigation systems, child seat, *etc*. Those are outside the scope of this study, as well as soil from outside taken into the vehicles. There is also a possibility that BFRs were emitted from internal devices including printed circuit boards and eventually have migrated to the dust. When comparing BFR concentrations in the cabin dust from other countries, the levels observed in this study were higher than those found in Czech Republic[1] and Sweden[2], and within the range of reported values from UK[3] and USA[4,5] (Table 2).

In general, BFR concentrations found in seat dust were higher than those in the corresponding floor dust samples (Table 2). Among the floor dust, the highest concentrations of PBDEs and HBCDs were found in the samples collected from ELV-32 and ELV-43 in floor coverings which were treated with the technical DecaBDE and HBCDs, respectively (Table 1). The profiles of HBCD isomers and PBDE congeners in the floor dust did not correspond with those observed in floor materials. Relatively more volatile compounds tended to accumulate into dust. These observations imply that BFRs in floor dust may contain abraded particles of floor coverings and migration of BFRs emitted from treated materials to dust. As for the seat dust, however, the samples collected from ELVs using DecaBDE-treated materials as seat fabric did not show apparently higher PBDE concentrations. Further investigation should be conducted to reveal the migration behavior of BFRs from treated materials to dust.

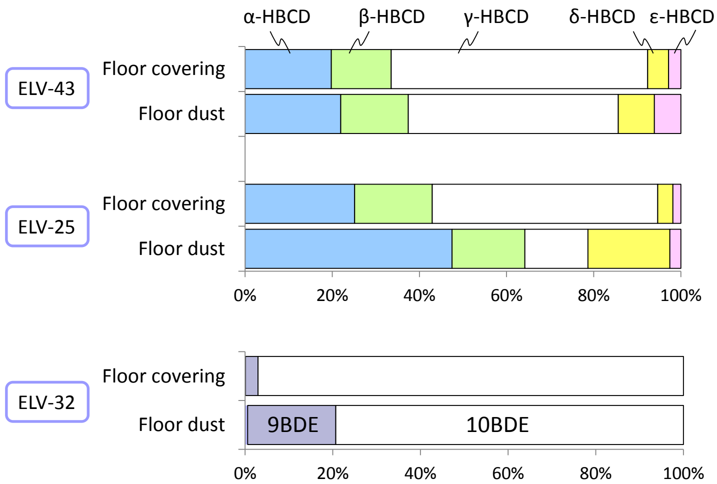

Figure 2. The congener and isomer profiles of BFRs in the floor covering and dust collected from ELVs

Acknowledgements
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