Emission factors of Polybrominated diphenyl ethers (PBDEs) from plastics processing and recycling facilities

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Introduction

With regard to polybrominated diphenyl ether (PBDE), there is few scientific knowledge on the emission patterns into the environment and exposure pathways to humans, and basic information is insufficient to consider what measures effective are. For the purpose of promoting risk reduction of target substances more effectively and efficiently, it is desirable to comprehend accurately the causal chain from the target substances utilization to the risk intake, and to evaluate the measures covering the whole applications of target substances. As the existing researches on the PBDE emission inventory, there are EU risk assessment report (European Chemical Bureau 2000, 2002, 2003), Danish EPA (1999), Palm et al.(2002) and Alcock et al. (2003). In addition, emissions of DecaBDE are published in TRI (Toxic Release Inventory) of US EPA. However, the primary information of the previous inventories is often the same and estimations based on the measured values are few.

In light of the situation, PBDE emission concentrations from processing facilities of flame retardant plastics and recycling facilities of home electric appliances are measured in practice to presume material flow of PBDE and to estimate emission factors and inventories from each phase of life cycles. The validities of emission factors are examined in comparison to measured values of atmospheric depositions surroundings, which are close to sources.

Materials and Methods

Methods to add flame retardants to plastics are classified roughly into compounding and processing. Flame retardant components and main components of plastics (polycarbonate, polystyrene and the like) are blended in the compounding process and end-products are shaped by extruder in the processing. In a survey on emissions of brominated compounds conducted by the Ministry of the Environment (2003), PBDE concentrations in the flue gases and ambient atmosphere from 9 manufacturing facilities of flame retardant plastics were measured.

In terms of recycling electric appliance products, it is common to collect metals after dismantling and recover heat from plastic materials. In this study, the dismantling and recycling processes are principally targeted for consideration. There are approximately 40 electric appliance recycling facilities in Japan where about 10 millions products from a total of four items; air conditioner, TV, refrigerator and washing machine, are annually treated. The treated TVs are approx. 3 to 3.5 millions per year, which mean about a half or one-third of the estimated waste TVs of 7 ~ 9 millions per year in Japan are treated in this route. It is estimated that the rest of those are exported as secondhand appliances. The Ministry of the Environment (2003) measured PBDE concentrations in flue gases, working environments and ambient surroundings from 7 facilities of electric appliance recycling plants.

An apparatus made of amber-colored glass or covered with aluminum foil to prevent photolysis of brominated compounds was used for the analysis. Solid samples were Soxhlet extracted. The bulk deposition samples (which consisted of rainwater containing a small amount of solid material) and rain samples were filtered, the residue was Soxhlet extracted with toluene, and the filtrate was liquid-liquid extracted with dichloromethane. The extracts were concentrated and cleaned up by using multilayer silica gel column chromatography ($AgNO_3$-silica / H_2SO_4-silica / KOH-silica). The final extracts were concentrated and analyzed by using HRGC/HRMS.

Results and Discussion

The results of measuring flue gas concentrations in the manufacturing facilities of flame retardant plastics (6 facilities, 11 points) are shown in Table 1. In 3 facilities with measured values of flue gas emissions, BDE-209 emissions per facility were calculated and they were 0.22~6.2g/year. Given capacities of extruder and

concentrations of flame retardants in resin (refer to notes to the table), emission factors per PBDE utilization were estimated to be 3×10^{-7}~5×10^{-9}.

Table 1: Emission Factors of PBDE (BDE-209) from Manufacturing Process of Flame Retardant Resin

Plants	Points of measuring	Concentrations in flue gas	Amounts of flue gas	Estimates of PBDE emission		PBDE emission factors	
		□BDE-209□ ng/m^3	m^3/hr	(□plant□ mg/hr	(□plant□ g/year	Case1	Case 2
P-1	Extruder Outlet	38	—	-	-	-	-
P-1	General Outlet	170	—	-	-	-	-
P-2	Extruder Outlet	150	—	-	-	-	-
P-2	General Outlet	33	12,500	0.41	3.6	1.7E-07	8.3E-08
P-3	Extruder Outlet	33	—	-	-	-	-
P-3	General Outlet	5.3	4,800	0.025	0.22	1.0E-08	5.1E-09
A-1	Extruder Outlet	45	—	-	-	-	-
A-2	Extruder Outlet	18	—	-	-	-	-
A-2	General Outlet	110	6,400	0.70	6.2	2.8E-07	1.4E-07
A-3	Extruder Outlet	11	—	-	-	-	-
A-3	General Outlet	0.72	—	-	-	-	-

Case 1□It is assumed as capacity of extruder 50 kg/hr and PBDE contents of 5% in resin. They are equivalent to 22 ton/year.

Case 2□It is assumed as capacity of extruder 50 kg/hr and PBDE contents of 10% in resin. They are equivalent to 44 ton/year.

As primary information concerning emissions from application process of flame retardants to resin, there are (1) EU Technical Guidance Document (1996) and (2) UCD (1994, 1998). Default lists of emission factors per variety of production process and vapor pressure were indicated and the emission factor was 10^{-4} order. The estimated values of emission factors in this study were at least approx. 3 orders lower than the previous emission factors. Meanwhile, since estimating emissions on the basis of measurements were not conducted in previous studies, the relation of estimated emission factors and atmospheric deposition is focused on.

PBDE emitted into the air are transported by ways of wet/dry depositions and advection, and partly destructed by photolysis. It is expected that PBDE depositions are smaller than PBDE emissions from facilities. When PBDE emissions are extraordinary low in comparison with PBDE amounts in deposition, it means that there are sources of PBDE other than the flue gas outlet. When the

estimated emissions from respective facilities were divided by the PBDE depositions that measured within the sites of facilities, they were equivalent to areas with a radius of 10~50m (Table 2). They were nearly the same distances of the sampling points of bulk depositions. Moreover, it can be considered that there is the possibility of existence of PBDE sources other than each facility measured at the flue gas outlet.

Table 2: Relation of PBDE Emissions and Bulk Deposition from Manufacturing Process of Flame Retardant Resin

Plant No.	PBDE emissions	Bulk Deposition	Deposit area	Deposit radius	Distance	Concentrations in air
	estimates		Calculated values	Calculated values		Reference
	mg/hr	ng/m^2/day	m^2	m	M	ng/m^3
P-1/A-1	-	2,000	-	-	60	41
P-2	0.41	28,000	354	11	20	7.0
P-3	0.025	93	6,565	46	-	0.051
A-2	0.70	2,800	6,034	44	-	0.40
A-3	-	450	-	-	-	0.31
E-2	-	570	-	-	-	0.32
E-3	-	600	-	-	-	0.16

Distance□ □Distance between flue gas outlet and measuring points of atmospheric deposition

PBDE emissions per facility were 0.38~2.2g/year calculated from flue gas concentrations and flue gas amounts from electric appliance recycling facilities (Table3). It was estimated that PBDE emissions from electric appliance recycling process of overall Japan were 15~88g/year and emission factors were 2.5×10^{-9}~2.9 x 10^{-7}. However, it should be aware that PBDE emission factors were calculated in only 5 facilities out of 7 facilities with measured values of PBDE concentrations in flue gas. That is because that flue gas amounts from the rest of 2 facilities (R-5, R-6) have not been reported, whereas the flue gas concentrations from the 2 facilities were 1~2 orders higher than the other facilities and it may be afraid the emission factors are underestimated.

In terms of the previous researches, there were no examples that PBDE emissions from electric appliance recycling process were estimated. EU Risk Assessment Report, as a similar process of electric appliance recycling, estimated the generation of “scrap” in the disposal (dismantling) process of flame retardant products. Grounds for estimation, which is the same as emissions in the process of utilization, are from a draft of Risk Assessment report on de-(2-ethylhexyl) phthalate (DEHP). It is assumed that waste products of 2 % are emitted into the

environment, of which 75 % are into the soil, 0.1 % into the atmosphere and 24.9% into the water system. The emission factor is 2 x 10^{-5} . Tamade et al.(2002) conducted a measurement on mass balance of PBDE, TBBP-A and PBDD/DF in the electric appliance recycling plants, which comprised of the processes of crushing, sorting, making compressed pieces of fuel and the process of combusting fuel. PBDE inputs to the processes of crushing and sorting were 21 kg/hr and emissions into flue gas system were 0.058 mg/hr at BF outlet and 1.2 mg/hr in the combustion air at the latter incinerator. If the amounts in the combustion air as well are assumed to be emitted into the environment, PBDE emission factors in the processes of destruction and sorting are 6×10^{-8}.

Table 3: PBDE Emission Factors from Recycling Process of Electric Appliance

Plant No.	Concentrations in flue gas	Flue gas amounts	Estimates of PBDE emissions			PBDE emission factors	
	□BDE-209□		(1 plant□	(□plant□	(Domestic 40 plants)	a	b
	ng/m^3	m^3/hr	mg/hr	g/year	g/year	6000 ton	300 ton
R-1	1.9	22,800	0.043	0.38	15	2.5E-09	5.1E-08
R-2	13	13,500	0.18	1.5	61	1.0E-08	2.0E-07
R-3	24	3,100	0.074	0.65	26	4.3E-09	8.7E-08
R-4	38	6,610	0.25	2.2	88	1.5E-08	2.9E-07
R-5	1400	-	-	-	-	-	-
R-6	630	-	-	-	-	-	-
R-7	8.7	9,350	0.081	0.71	29	4.8E-09	9.5E-08

a: PBDE influx into electric appliance recycling facility is assumed as 6000 ton/year. (the amounts were the same as domestic demands approx. 10 years ago)

b: PBDE influx into electric appliance recycling facility is assumed as 300 ton/year. □TV casing materials from 3 millions TVs□

Estimates of emission factors (2.5×10^{-9}~2.9×10^{-7})in this study are mostly equivalent to the emission factors (6×10^{-8}) based on a report of Tamade et al.(2002). Meanwhile, these are 2 orders and over less than the estimates (2×10^{-5}) in the EU risk assessment report. The latter is based on the estimation by other substances (DEHP) and it can be an assessment on the conservative side.

On the basis of measured results of the atmospheric deposition from electric appliance recycling facilities, a relation of PBDE emissions and deposition has been examined in the same manner as manufacturing facilities of flame retardant plastics (Table 4). With the assumption that the area is a circle, the radiuses are approximately 10~60m. The measuring points of deposit dust are about 20~100m away from flue gas outlet and both orders are largely matched. This means that most of the PBDE in the flue gas emitted from facilities are remained within the facilities sites. Taking into consideration that the average wind speed at the measuring points were 2~3 m/sec, the retention period after being emitted into the atmosphere are very short; several tens of seconds. From the measuring results of bulk deposition, it can be estimated that there are PBDE sources other than the electric appliance recycling process on which targeted in this study.

Table 4: Relationship of PBDE emissions and bulk deposit from home appliance recycling process

Plant No.	PBDE emissions estimates	Bulk Deposition	Deposit area	Deposit radius	Distance	Atmospheric concentration Reference
	mg/hr	ng/m^2/day	m^2	m	m	ng/m^3
R-1	0.043	460	2,260	27	30	0.43
R-2	0.18	410	10,273	57	70	0.48
R-3	0.074	460	3,882	35	80	0.36
R-4	0.25	17,000	355	11	20	1.8
R-5	-	540	-	-	100	0.37
R-6	-	2,500	-	-	60	0.99
R-7	0.081	390	5,006	40	100	0.69

Distance: Distance between flue gas outlet and the measuring points of atmospheric deposition

Estimated results (maximum value) of emissions based on the measurement of flue gas concentrations at sources were 0.7 kg/year (emission factor 3×10^{-7}) in the manufacturing process of flame retardant resin such as casing materials, and 2 kg/year (3×10^{-7}) from the electric appliance recycling facilities and 18 kg/year(3×10^{-6}) from incinerator. Those were approx. 2 orders less than the emissions estimated from environmental concentrations (Hirai et al.) and the significance of sources that have not been comprehended yet were indicated.

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