CURRENT STATUS OF POLYBROMINATED DIBENZO-p-DIOXINS AND FRANS (PBDD/DFs) EMISSIONS IN JAPAN

Ota S. [1], Aizawa H. [1], Kondo Y. [1], Takigami H. [2], Hirai Y. [3], Sakai S. [3]

[1] Ministry of the Environment, 1-2-2 Kasumigaseki, Chiyoda-ku, Tokyo 100-8975, Japan
[2] National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaragi 305-8506, Japan
[3] Environmental Preservation Center, Kyoto University, Yoshidahonmachi, Sakyo-ku, Kyoto 606-8501, Japan

Abstract

Since 2002, the Ministry of the Environment of Japan (MOE) has conducted a series of field studies to survey the emissions of polybrominated dibenzo-*p*-dioxins and furans (PBDD/DFs) and related compounds from several industrial processes involving brominated flame retardant (BFRs). The present studies have revealed that high levels of PBDD/DFs were detected at 10^4-10^5ng/m^{3}N levels in the emission gas released from production facilities of flame-retarded plastics and processing facilities of flame retardants; and at 10^5pg/L levels in the effluents at the main wastewater outlets in production facilities of flame-retarded plastics and manufacturing facilities of flame-retarded textiles. In addition, high emission of BFRs, in particular polybrominated diphenyl ethers (PBDEs), has been found at the facilities in which we detected high concentrations of PBDD/DFs. These results suggest that the emission of PBDD/DFs is closely associated with those of BFRs (mainly PBDEs).

Introduction

Although there have been growing concerns on the influence of PBDD/DFs (related substances of polychlorinated dibenzo-*p*-dioxins and furans, PCDD/DFs) on the environment and human health, little is known about the emission sources of these compounds. The Law Concerning Special Measures against Dioxins of Japan requires the government to promote "the research and study of brominated dioxins (e.g., PBDD/DFs) with regard to the extent of their effects on human health, the process of generation, etc". It also states the necessity of the governmental measures based on the survey results. Therefore, MOE has investigated to establish a method for measuring PBDD/DFs since 1998, and prepared the Provisional Survey Method for PBDD/DFs in 2002[1]. According to this Provisional Survey Method, MOE has conducted a series of field studies to survey the emission of PBDD/DFs and related compounds from industrial processes involving BFRs. It is important for the global community to share the knowledge on PBDD/DFs sources and their estimated emission, in order to consider the way to reduce the total emission of PBDD/DFs. Here we report the survey results on the current status of PBDD/DFs emissions in Japan.

Materials and Methods

Investigated facilities

World Health Organization (WHO) published IPCS Environmental Health Criteria on PBDD/DFs and reported possible sources of PBDD/DFs[2]. Among the candidates, facilities producing or using several BFRs and post-consumer secondary sources were selected as major sources of PBDD/DFs in this survey. Table 1 summarizes the facilities surveyed from 2002 to 2006.

Sampling and analysis

Sampling and analyses were conducted according to the Provisional Survey Method for PBDD/DFs[1].

Emission gases were collected with absorption filters, pots, and columns at the exhaust outlets of processes in each facility where PBDD/DFs may be produced. The samples were then extracted in toluene. Effluents were sampled at the drain outlets of processes where PBDD/DFs may be generated. Effluent samples were also collected at the main wastewater outlets of the effluent after the remediation. The sample liquid was then filtered after adding of ^{13}C-labeled internal standards. The filtrates and residues were extracted by Soxhlet extractors in dichloromethane and toluene, respectively.

To measure PBDD/DFs, the extract was further cleaned up by multilayer silica gel- and active carbon-impregnated silica gel-columns. We added the ^{13}C-labeled internal standards to the extracts for a syringe spike. Quantitative detection of PBDD/DFs was performed by a high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS; the electron impact ionization method, mass resolutions >10,000) with ^{13}C-labeled internal standards.

For BFRs, PBDEs are measured and quantified by HRGC/HRMS, basically according to the above-mentioned pretreatment method. Tetrabromobisphenol-A (TBBPA) was ethyl-derivatized, and analyzed by HRGC/HRMS (resolution: >10,000, electronic ionization method). For hexabromocyclododecane (HBCD), the samples were first cleaned up through a florigil column, and then measured by liquid chromatography-mass spectrometry (LC/MS) to separate α, β, γ -isomers. In these analyses, ^{13}C-labeled internal standards were also added to the extracts for a syringe spike

Since PBDD/DFs and BFRs are potentially photo- and thermo-fragile, all samples were handled under dark and appropriate temperature conditions.

Results and Discussion

PBDD/DFs

The measurement data for PBDD/DFs in emissions from the facilities are shown in Table 2 (the emission gas) and Table 3 (the effluents). Toxicity equivalency factor (TEF) for PBDD/DFs has not been available to date. Thus, we assumed the toxicity of PBDD/DFs to be equivalent to other chlorinated counterparts. The toxicity equivalent (TEQ) value is estimated from the actual PBDD/DFs concentrations and the WHO-TEF (1998) of PCDD/DFs.

We detected PBDD/DFs in the emission gas from all types of the facilities, although there is a rather broad variation in concentration. In particular, high concentrations of PBDD/DFs were often observed at the facilities producing flame-retarded plastics (up to 140,000 ng/m^{3}N; 23,000 ng/m^{3}N, in average, at extruder outlets) and those processing flame retardants (tribromophenol (TBP)) (up to 24,000 ng/m^{3}N; 8,100ng/m^{3}N, in average). PBDD/DFs were detected at most at a 10 ng/m^{3}N order in other facilities, such as the recycling facilities of home electric appliances, the manufacturing facilities of flame-retarded textiles, and the sewage treatment terminal facilities. High TEQ values (maximum 33 ng-TEQ/m^{3}N; 3.9ng-TEQ/m^{3}N in average) have sometimes been observed at the molding facilities of flame-retarded plastics.

We also detected PBDD/DFs in the effluents of all types of the facilities. High concentrations of PBDD/DFs (10^5-10^6 pg/L orders at the highest level) were observed in the process water from the recycling facilities of home electric appliances, the facilities producing flame-retarded plastics, and those processing flame retardants (TBP and DeBDE). PBDD/DFs were also detected up to a 10^5pg/L order in the effluents collected at the main wastewater outlets in the production facilities of flame-retarded plastics and the manufacturing facilities of flame-retarded textiles. The concentrations of PBDD/DFs in the process water were higher than those in the effluents collected at the main wastewater outlets, except for the samples from the production facilities of flame-retarded plastics. These data suggest that conventional effluent treatments are effective for removal of PBDD/DFs. High TEQs values (10-10^2 pg-TEQ/L orders at the highest level) have been sometimes observed at the main wastewater outlets in the facilities for flame-retarded textile manufacturing, flame-retarded

plastics molding, and flame retardants (DeBDE) processing.

The mean PBDD/DFs concentrations in emission gases from the facilities involving BFRs in this survey were maximum 10^5-fold higher compared to the data in municipal waste combustors reported by Wyrzykowska B. et al. (from undetectable levels to 7.17ng/dscm, 0.46ng/dscm in average)[3].

The procedure for this survey has been modified by taking into account the higher molecular masses of PBDD/DFs than those of PCDD/DFs and their heat-/photo-instability, as described in Wyrzykowska B. et al [3]. We have also employed parallel confirmation studies by different organizations. The reason for the higher levels of PBDD/DFs in this survey compared to the previous studies may be that the facilities examined in this survey were those dealing with BFRs that directly involve the emissions of PBDDs/DFs.

BFRs

The concentrations of BFRs (PBDEs, TBBPA and HBCD) in the emission gas and effluent are shown in Table 4 and 5, respectively. We have detected high concentrations of PBDEs in the emission gas from the molding facilities of flame-retarded plastics (up to $2.1x10^6$ ng/m^{3}N; $2.7x10^5$ ng/m^{3}N in average). The TBBPA concentration was up to $6.2x10^5$ ng/m^{3}N ($1.3x10^5$ ng/m^{3}N in average) at the main outlets of the production facilities of flame-retarded plastics, and was up to $5.4x10^5$ ng/m^{3}N ($1.8x10^5$ ng/m^{3}N in average) at the processing facilities of flame retardants (TBP). The HBCD concentration was at most $3.7x\ 10^6$ ng/m^{3}N ($7.4x10^5$ ng/m^{3}N in average) at the manufacturing facilities of flame-retarded textiles.

We have also detected high concentrations of PBDEs in the effluents collected at main wastewater outlets of the manufacturing facilities of flame-retarded textiles (up to $6.2x10^6$ ng/L; $2.1x10^6$ ng/L in average). TBBPA was maximum $3.7\ x10^4$ ng/L ($7.9\ x10^3$ ng/L in average) at the production facilities of flame-retarded plastics. HBCD was maximum $2.0x10^6$ ng/L ($1.2x10^6$ ng/L in average) at the manufacturing facilities of flame-retarded textiles.

As in the case of PBDD/DFs, the mean PBDEs concentrations of the emission gases in this survey were maximum 10^4-fold higher than the report by Wyrzykowska B. et al (25 ng/dscm in average (1.62-312 ng/dscm)[3]. In addition, the mean PBDEs concentrations were also higher than the previous data concerning indoor air at recycling plants (12-70 ng/m^3 of DeBDE)[4] and river water in China (0.344-68 ng/L)[5].

Correlation between PBDD/DFs and BFRs

The data in Table 2- 5 indicate that the facilities handling high concentrations of BFRs also exhibit high concentrations of PBDD/DFs emission. For example, there is strong correlation between PBDD/DFs and PBDEs concentrations in the emissions gas at the molding facilities of flame-retarded plastics (Fig. 1), and in the effluents at the manufacturing facilities of flame-retarded textiles (Fig. 2).

Indeed, the correlation coefficients between the concentrations of PBDD/DFs and PBDEs are very high: 0.8580 and 0.9164 in the molding facilities of flame-retarded plastics and the manufacturing facilities of flame-retarded textiles, respectively.

In this survey, PBDD/DFs were detected as contaminants in the flame-retarded materials (DeBDE and HBCD) used in the manufacturing facilities of flame-retarded textiles (data not shown). In addition, it is reported in the Environment Health Criteria on PBDD/DFs that the gases from burning electronics devices and heated DeBDE in polymer bases produce high concentrations of PBDFs (11-1,700 μg/m^3 and maximum 39,300mg/kg, respectively)[2].

All these led us to conclude that the emissions of BFRs have significant relationship with those of PBDD/DFs.

Future prospects

MOE has been preparing to set up a provisional emission inventory of PBDD/DFs, based on the results of the present surveys. The systematic emission inventory of PBDD/DFs is a new and original approach in the world. We believe that continuation of this type of survey will lead to the development of measures to reduce PBDD/DFs emissions in the future.

Acknowledgements

We are grateful for all the facilities in support of our survey.

References

1. Ministry of the Environment; Provisional Survey Method for Polybrominated Dibenzo-*p*-dioxins and Polybrominated Dibenzofurans (2002) (in Japanese). http://www.env.go.jp/air/report/h14-03/index.html
2. World Health Organization; IPCS Environmental Health Criteria 205 (1998)
3. Wyrzykowska B., Gullett B.K., Tabor D. and Touati A. *Organohalogen Compounds.*2008; 70: 65.
4. Destaillats H., Maddalena R.L., Singer B.C., Hodgson A.T. and McKone T.E. *Atmospheric Environment* 2008; 42:1371.
5. Guan Y., Wang J., Ni H. and Zeng E. *Environ. Sci. Technol.* 2007 ;41: 5641.
6. Ministry of the Environment; Report on Results of Survey of Current Brominated Dioxins Emissions (2002-2006) (in Japanese). http://www.env.go.jp/chemi/dioxin/chosa/shuki.html

Table 1. Facilities surveyed in 2002-2006[6]

Year of surveys	Facilities surveyed	Related BFRs	Number of facilities
2002	Recycling facilities of home electric appliances (TVs)		7
	Production facilities of flame-retarded plastics (PS polymers, ABS polymers or epoxy polymers)		8
2003	Production facilities of flame retardants	TBBPA,TBBPA polycarbonate oligomer	2
	Manufacturing facilities of flame-retarded textiles	DeBDE, HBCD	3
2004	Molding facilities of flame-retarded plastics	DeBDE	6
	Sewage treatment facilities (located in industrialized urban areas)		3
2005	Processing facilities of flame retardants (TBP)	2,4,6-TBP	3
2006	Processing facilities of flame retardants (DeBDE)	DeBDE	2

Table 2. Detection levels of PBDDs/DFs in major emission gas sources[6]

Facilities surveyed		Detection frequency[a)]	Actual concentration		Toxicity equivalent value[b)]	
			Average value (ng/m^3_N)	Concentration range (ng/m^3_N)	Average value ($ng\text{-}TEQ/m^3_N$)	Range ($ng\text{-}TEQ/m^3_N$)
Recycling facilities of home electric appliances		4/7	2.4	ND～12	0.017	0～0.11
Production facilities of flame-retarded plastics	Extruder outlet	6/6	23,000	0.81～140,000	0.0025	0～0.0059
	Main outlet	5/5	980	0.011～4,900	0.0036	0～0.018
Production facilities of flame retardants		5/5	0.12	0.012～0.18	0.00022	0～0.0006
Manufacturing facilities of flame-retarded textiles		6/7	3.4	ND～13	0.046	0～0.21
Molding facilities of flame-retarded plastics		6/9	860	ND～7,100	3.9	0～33
Sewage treatment facilities	Deodorization device entrance	2/3	0.023	ND～0.047	0.011	0～0.023
	Deodorization device exit	0/3	0	ND	0	0
	Incinerator	1/3	0.013	ND～0.039	0	0
Processing facilities of flame retardants (TBP)		3/3	8,100	1.5～24,000	0.0013	0.00033～0.011
Processing facilities of flame retardants (DeBDE)		6/6	6.5	0.16～13	0.0061	0～0.0039

a) Detection frequency: Number of measured sites for which substance was detected/total number of measured sites at the surveyed facility

b) TEQ values of PBDD/DFs were calculated using WHO-TEF(1998) of PCDD/DFs

Table 3. Detected levels of PBDDs/DFs in major effluent sources[6]

Facilities surveyed		Detection frequency[a)]	Actual concentration		Toxicity equivalent value[b)]	
			Average value (pg/L)	Concentration range (pg/L)	Average value (pg-TEQ/L)	Range (pg-TEQ/L)
Recycling facilities of home electric appliances	Process water etc.	1/1	27	27	0.22	0.22
	Process water etc. (SS)	1/1	4,100	4,100	25	25
	Gray water	6/6	5,600	790～14,000	31	2.5～65
	Process water	1/1	140,000	140,000	420	420
Production facilities of flame-retarded plastics	Other process etc.	13/13	68,000	7.6～820,000	7.3	0.067～74
	Main wastewater outlet	6/6	32,000	2.0～190,000	1.5	0～8.5
Production facilities of flame retardants	Other process etc.	2/2	69,000	8,000～130,000	24	0～48
	Main wastewater outlet	2/2	460	280～630	0.92	0.54～1.3
Manufacturing facilities of flame-retarded textiles	Other process etc.	4/5	740	ND～2,000	2.3	0～6.6
	Main wastewater outlet	3/3	80,000	320～170,000	77	3.6～130
Molding facilities of flame-retarded plastics	Other process etc.	3/4	2,400	ND～9,200	16	0～63
	Main wastewater outlet	4/6	600	ND～3,000	2.8	0～14
Sewage treatment facilities	influent water	3/3	5,300	110～13,000	26	0.25～63
	primary sedimentation tank effluent water	2/3	1,900	ND～5,700	10	0～30
	final sedimentation tank effluent water	1/3	370	ND～1,100	0.63	0～1.9
	final effluent	1/3	470	ND～1,400	0.73	0～2.2
Processing facilities of flame retardants (TBP)	Process water	2/2	650,000	220～1,300,000	0.34	0.29～0.40
	Main wastewater outlet	3/3	30	14～55	0.062	0.022～0.096
Processing facilities of flame retardants (DeBDE)	Process water	1/1	220,000	220,000	360	360
	Main wastewater outlet	2/2	2,600	340～4,900	14	0.69～27

a) Detection frequency: Number of measured sites for which substance was detected/total number of measured sites at the surveyed facility

b) TEQ values of PBDD/DFs were calculated using WHO-TEF(1998) of PCDD/DFs

Table 4. Detected levels of BFRs in major emission gas sources[6]

Facilities surveyed		PBDEs concentration		TBBPA concentration		HBCD concentration	
		Average value (ng/m^3_N)	Concentration range (ng/m^3_N)	Average value (ng/m^3_N)	Concentration range (ng/m^3_N)	Average value (ng/m^3_N)	Concentration range (ng/m^3_N)
Recycling facilities of home electric appliances		360	3.9～1,400	110	13～300	-	-
Production facilities of flame-retarded plastics	Extruder outlet	69	22～170	62,000	540～350,000	-	-
	Main outlet	83	1.0～230	130,000	3.1～620,000	-	-
Manufacturing facilities of flame-retarded textiles		2,400	16～9,000	550	8.6～2,400	740,000	46～3,700,000
Molding facilities of flame-retarded plastics		270,000	16～2,100,000	4.2	0.84～12	110	6.8～790
Sewage treatment facilities	Deodorization device entrance	130	110～160	1.8	1.4～2.2	19	ND～39
	Deodorization device exit	13	6.7～19	1.8	1.3～2.1	31	ND～79
	Incinerator	88	14～230	4.0	3.3～5.1	36	6.6～78
Processing facilities of flame retardants (TBP)		5,200	310～10,000	180,000	940～540,000	690	580～790

Table 5. Detected levels of BFRs in major effluent sources[6]

Facilities surveyed		PBDEs concentration		TBBPA concentration		HBCD concentration	
		Average value (ng/L)	Concentration range (ng/L)	Average value (ng/L)	Concentration range (ng/L)	Average value (ng/L)	Concentration range (ng/L)
Recycling facilities of home electric appliances	Gray water	610	110～1,800	780	18～2,600	-	-
	Process water	190,000	190,000	25,000	25,000	-	-
Production facilities of flame-retarded plastics	Other process etc.	670	0.85～7,600	18,000	6.7～220,000	-	-
	Main wastewater outlet	380	0.15～1,900	7,900	9.4～37,000	-	-
Manufacturing facilities of flame-retarded textiles	Other process etc.	1500	1.2～6,500	64	5.5～170	150,000,000	5700～530,000,000
	Main wastewater outlet	2,100,000	1,900～6,200,000	440	61～710	1,200,000	180,000～2,000,000
Molding facilities of flame-retarded plastics	Other process etc.	230	3.6～440	3.8	0.16～11	0.99	0.50～1.3
	Main wastewater outlet	710	2.4～4,200	1.5	0.15～6.7	2.5	ND～5.0
Sewage treatment facilities	influent water	160,000	140～490,000	10	6.7～11	5,700	11～17,000
	primary sedimentation tank effluent water	33,000	13～100,000	3.3	2.0～4.1	210	9.7～620
	final sedimentation tank effluent water	5,300	3.9～16,000	0.45	0.34～0.56	400	1.6～1,200
	final effluent	6,000	3.2～18,000	0.86	0.33～1.4	400	2.9～1,200
Processing facilities of flame retardants (TBP)	Process water	100	8.4～200	1,400,000	490～2,700,000	110	17～200
	Main wastewater outlet	5.0	4.1～5.9	130	12～270	8.1	1.9～16

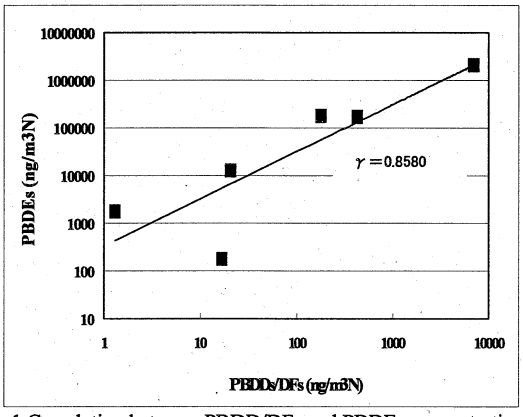

Fig.1 Correlation between PBDD/DFs and PBDEs concentrations (Molding facilities of flame-retarded plastics: emission gas)

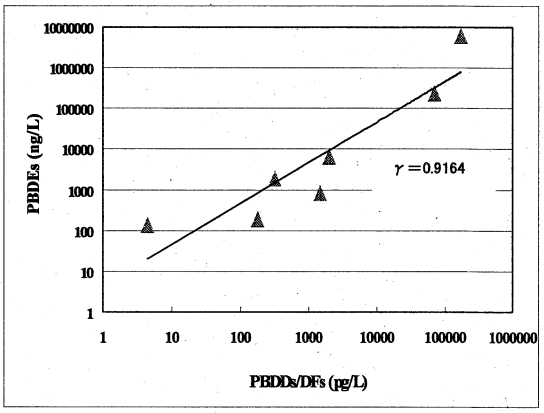

Fig.2 Correlation between PBDD/DFs and PBDEs concentrations (Manufacturing facilities of flame-retarded textile: effluent)