

The Releases of PBDD/DFs from the Flame-retarded Textile Manufacturing Facilities

Shizuko Ota¹, Yoshiyuki Kondo¹, Tohru Miyazaki², Hidetaka Takigami³, Yasuhiro Hirai⁴, Shin-ichi Sakai⁴

¹ Ministry of the Environment, 1-2-2 Kasumigaseki, Chiyoda-ku, Tokyo 100-8975, Japan

² Nittech Research Corporation, 1 Fujicho, Hirohata-ku, Himeji, Hyogo 671-1123, Japan

³ National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba, Ibaragi 305-8506, Japan

⁴ Kyoto University, Yoshidahonmachi, Sakyo-ku, Kyoto 606-8501, Japan

Introduction

Since 2002, the Ministry of the Environment of Japan (MOEJ) 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), which reported as possible sources of PBDD/DFs in IPCS Environmental Health Criteria on PBDD/DFs published by World Health Organization (WHO)¹.

These studies² have revealed that high levels of PBDD/DFs were detected at 10^4 - 10^5 ng/m³N levels in the emission gas released from production facilities of flame-retarded plastics and processing facilities of flame retardants; and at 10^5 pg/L levels in the effluents at the main wastewater outlets in production facilities of flame-retarded plastics and manufacturing facilities of flame-retarded textiles.

This paper reports the releases of PBDD/DFs from flame-retarded textile manufacturing facilities.

Materials and Methods

Investigated facilities and sample media

The following three facilities were investigated: two textile manufacturing facilities using HBCD as a flame retardant (B-1 and B-3) and one textile manufacturing facility using DeBDE and HBCD as flame retardants (B-2).

Sample media are as follows:

2003: emission gas, effluents, working environment air, ambient air, dust fall, environment water, sediments, BFRs, and products

2005: effluents

2006: effluents, sludge, effluents from the small-scale test machine, BFRs, and dyes

2007: effluents, effluents from the test machine, BFRs, and dyes

Sampling and analysis

Sampling and analyses were conducted according to the Provisional Survey Method for PBDD/DFs³.

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 ¹³C-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 ¹³C-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 ¹³C-labeled internal standards.

For BFRs, PBDEs are measured and quantified by HRGC/HRMS, basically according to the above-mentioned pretreatment 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, ¹³C-labeled internal standards were also added to the extracts for a syringe spike.

Results and Discussion

We focus on the survey results of the emission gases and effluents in this paper.

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.

Emission gases

The concentrations of PBDD/DFs in emission gases are shown in Table 1.

Compared with the other BFRs-related facilities' results, relatively high concentrations of PBDD/DFs were observed in emission gases from the backing process of B-2(13ng/m³N, 0.11ng-TEQ/m³N) and the finishing process after dyeing and flame retarding of B-3(10ng/m³N, 0.21ng-TEQ/m³N)).

Table 1: Concentrations of PBDD/DFs in emission gases (2003)

Process	Detection frequency	Actual concentration(ng/m ³ N)		TEQ*(ng-TEQ/m ³ N)	
		Average	Range	Average	Range
Preparatory Set (B-1,2)	2/2	0.082	0.063-0.10	0.0001	0-0.0002
Backing (B-2)	1/1	13	13	0.11	0.11
Thermal fusion bonding (B-2)	1/1	0.31	0.31	0.0012	0.0012
Finishing Set (B-1,2,3)	2/3	3.4	ND-10	0.070	0-0.21

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

Effluents

The concentrations of PBDD/DFs in effluents are shown in Table2.

In 2003, we measured PBDD/DFs in dyeing process water and wastewater after the treatment. The higher concentrations of PBDD/DFs were detected in wastewater after the treatment than in dyeing process water. This result suggested the possibility that PBDD/DFs were produced from processes other than dyeing and/or flame retarding.

In 2005, we measured PBDD/DFs in each effluent line. The higher concentrations of PBDD/DFs were detected in wastewater after the treatment than in process water and wastewater before the treatment in B-1and B-3. In B-2, the concentration of PBDD/DFs in wastewater after the treatment was lower than those in process water including DeBDE drain and in wastewater before the treatment, although it was higher than that of HBCD using process water.

In 2006, we collected wastewater samples before and after the treatment in B-1 and B-3 considering the timing of sampling. We also collected solution in the aeration tanks and measured PBDD/DFs in the solution separating suspended solids and dissolved matter. In the aeration tanks, the

concentration of PBDD/DFs in suspended solids (SS) was higher than that in dissolved matter and PBDD/DFs seemed to be absorbed suspended solids and circulate in the aeration tanks.

In 2007, we analyzed wastewaters after the treatment in B-1, B-2 and B-3 separating suspended solids and dissolved matter. In these three facilities, the concentrations of PBDD/DFs in wastewater after the treatment were higher than those before the treatment and the ratio of the suspended solids in the whole wastewaters after the treatment was about 60-90%.

Table 2: Concentrations of PBDD/DFs in effluents (2003, 2005, 2006 and 2007)

Facility	Year	Sampling Points	Detection frequency	Actual concentration(pg/L)		TEQ*(pg-TEQ/L)	
				Average	Range	Average	Range
B-1	2003	Dyeing process water	1/1	4.4	4.4	0	0
		Wastewater before the treatment	1/1	2,000	2,000	6.6	6.6
		Wastewater after the treatment	1/1	320	320	3.6	3.6
	2005	Process water(HBCD)	1/1	510	510	3.0	3.0
		Process water	2/2	2,600	610-4,500	11	1.5-21
		Wastewater after the treatment	2/2	131,000	11,000-250,000	630	57-1,200
	2006	Wastewater before the treatment	2/2	1,200	400-2,000	5.9	3.7-8.1
		Aeration tank(SS)	4/4	12,000	9,100-14,000	92	59-110
		Aeration tank(dissolved)	1/4	45	ND-180	0.0045	0-0.018
	2007	Wastewater after the treatment	2/2	600	95-1,100	1.0	0.37-1.7
		Wastewater before the treatment	2/2	980	560-1,400	4.0	1.3-6.6
		Wastewater after the treatment	2/2	190	91-280	0.39	0.21-0.57
Wastewater after treatment(SS)		2/2	54	10-98	0.21	0.08-0.33	
Wastewater after the treatment(dissolved)		2/2	12	8.0-15	0.09	0.07-0.10	
B-2	2003	Dyeing process water	1/1	180	180	1.3	1.3
		Wastewater after the treatment	1/1	170,000	170,000	130	130
	2005	Process water(HBCD)	1/1	630	630	2.2	2.2
		Process water	2/2	480,000	460,000-490,000	480	360-590
		Wastewater before the treatment	1/1	95,000	95,000	250	250
	2007	Wastewater after the treatment	1/1	85,000	85,000	290	290
		Wastewater before the treatment	2/2	33,000	28,000-37,000	47	31-63
		Wastewater after the treatment (SS)	2/2	33,000	32,000-33,000	52	45-59
		Wastewater after the treatment (dissolved)	2/2	3,600	3,100-4,000	3.0	2.6-3.3
B-3	2003	Process water(HBCD)	1/1	1,500	1,500	1.4	1.4
		Process water (non-treatment)	0/1	ND	ND	0	0
		Wastewater after the treatment	1/1	70,000	70,000	97	97
	2005	Process water(HBCD)	1/1	270	270	1.4	1.4
		Process water	1/1	890	890	4.0	4.0
		Wastewater before the treatment	1/1	3,900	3,900	7.2	7.2
	2006	Wastewater after the treatment	1/1	10,000	10,000	26	26
		Wastewater before the treatment	2/2	150,000	25,000-270,000	730	150-1,300
		Aeration tank (SS)	3/3	370,000	200,000-460,000	780	720-810
		Aeration tank (dissolved)	3/3	710	530-880	2.4	1.9-2.7
	2007	Wastewater after the treatment	2/2	4,500	4,300-4,700	18	16-19
		Wastewater before the treatment	2/2	17,000	14,000-19,000	34	25-43
Wastewater after the treatment (SS)		2/2	9,200	8,800-9,600	13	12-14	
Wastewater after the treatment (dissolved)		2/2	3,200	3,100-3,300	12	8.2-15	

*:TEQ values of PBDD/DFs were calculated using WHO-TEF(1998) of PCDD/DFs. **: ND means "not detected."

BFRs and dyes

The concentrations of PBDD/DFs and PBDEs in BFRs and dyes used in the facilities are shown in Table 3. We have detected higher concentrations of PBDD/DFs in DeBDE than in HBCD and dyes.

Table 3: Concentrations of PBDD/DFs and PBDEs in BFRs and Dyes

Facility	B-1		B-2		B-3			B-3		
BFRs(year)	HBCD (2003)	HBCD (2007)	HBCD (2003)	HBCD (2007)	DeBDE (2003)	DeBDE (2006)	DeBDE (2007)	HBCD (2003)	HBCD (2006)	HBCD (2007)
PBDD/DFs(ng/g)	0.13	0.50	0.18	ND	720	1,200	11,000	9.0	ND	0.06
PBDEs(ng/g)	40,000	5,300	27,000	10	2.0x10 ⁸	4.5x10 ⁸	3.6x10 ⁸	16,000	3,100	13
Facility	B-1			B-3			* ND : not detected			
Dyes(year)	Dye A Azo(Black) (2007)	Dye B Azo(Orange) (2007)	Dye C Azo(Orange) (2007)	Dye A Azo(Black) (2006)	Dye B Quinone (Blue) (2006)					
PBDD/DFs(ng/g)	2.9	3.7	4.2	1.8	0.55					
PBDEs(ng/g)	17	130	49	640	230					

Dyeing test machine

In order to determine the source of PBDD/DFs, we conducted several tests using the dyeing test machine in 2007 (Table 4).

PBDD/DFs were not detected in effluents after dyeing using Dye A(azo dye(black)) or Dye B(azo dye(orange)). On the other hand, PBDD/DFs were detected in low level in effluent after the dyeing process with Dye B followed by the flame retarding by HBCD. We could not see a clear difference of PBDEs concentrations between Dye A and Dye B in the effluent. PBDEs concentrations in the effluent after flame retarding by HBCD were about fifteen times higher than those before that process. These results suggest PBDD/DFs in the effluent may be mainly due to impurities in HBCD.

Table 4: Concentration of PBDD/DFs and PBDEs in effluents from the dyeing test machine (2007)

Sample	Dye(B-1)	PBDD/DFs		PBDEs (ng/L)
		Actual concentration(pg/L)	TEQ*(pg-TEQ/L)	
Effluent after dyeing	Dye A	ND	0	6.3
	Dye B	ND	0	7.8
Effluent after flame retarding by HBCD	Dye A	ND	0	110
	Dye B	90	0.009	100

*:TEQ values of PBDD/DFs were calculated using WHO-TEF(1998) of PCDD/DFs.**: ND means "not detected."

Conclusion

PBDD/DFs were detected in high concentration in effluents from the flame-retarded textile manufacturing facilities and the presence of PBDD/DFs was closely associated with PBDEs, though the detailed mechanism of emission of PBDD/DFs is yet to be solved.

Acknowledgement

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

References

1. World Health Organization.1998. IPCS Environmental Health Criteria 205
2. Ministry of the Environment. 2002-2008. Report on Results of Survey of Current Brominated Dioxins Emissions (in Japanese)
<http://www.env.go.jp/chemi/dioxin/chosa/shuki.html>
3. Ministry of the Environment. 2002. Provisional Survey Method for Polybrominated Dibenzo-*p*-dioxins and Polybrominated Dibenzofurans (in Japanese)
<http://www.env.go.jp/air/report/h14-03/index.html>