

Emission factors of PBDD/DFs and PBDEs from textile processing and BFR production, and the tentative PBDEs emission inventory

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Introduction

The Japanese Ministry of the Environment has been undertaken a project^{1,2} to characterize releases of polybrominated dibenzo-p-dioxins and -dibenzofurans (PBDD/DFs), polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) from the production, processing, recycling and disposal of brominated flame retardants (BFRs). In the last conference we reported the estimated emissions from manufacturing process of flame retardant resin such as casing materials, the electric appliance recycling facilities and incinerators³. This paper reports the releases of PBDD/DFs and PBDEs from two BFRs production facilities and three textile processing facilities. The tentative emission inventory of DBDE is also estimated with the new measurement trials.

Materials and Methods

The following five facilities were investigated: TBBP-A production facility (A-1), TBBP-A polycarbonate oligomer production facility (A-2), textile processing facility that uses HBCD as a flame retardant (B-1), textile processing facility that uses HBCD and DBDE as flame retardants (B-2) and textile processing facility that uses HBCD as a flame retardant (B-3).

Flue gas, wastewater, indoor air, ambient air, and atmospheric deposition samples were collected at the five facilities. Water and sediment samples were collected at two points for each facility. River water and sediment samples were collected upstream (riverU) and downstream (riverD) of B-2 and B-3. Sea water and sediment samples were collected 0-100 m away (sea1) and 800-3000 m away (sea2) from the wastewater discharge points of A-1, A-2, and B-1. Textile samples after processing and BFR samples (HBCD and DBDE) were collected at B-1, B-2 and B-3.

In all samples, PBDD/DFs (Br4-8) and Br1ClxDD/DFs (Cl3-7) were measured. PBDEs and HBCD were measured in samples from the textile processing facilities (B-1, B-2, and B-3). The analytical methods are described in the full report².

Results and Discussion

The respective PBDD/DF concentrations in the flue gas and the wastewater from the BFR production facilities were 12-180 pg/m³N (n=5, mean value 120 pg/m³N) and 280-630 pg/l. The PBDD/DF concentrations in samples from the textile processing facilities were between ND-13,000 pg/m³N (n=6, mean value 3,400 pg/m³N) and 320-170,000 pg/l (Table 1).

Figure 1 shows that the PBDD/DF concentrations in river and seawater samples in this study were higher than those in the water samples collected from the monitoring areas⁴. The concentrations of PBDD/DFs in the downstream sample of B-2 facility were more than 100 times higher than those in the upstream sample, indicating the effect of wastewater release from the B-2 facility.

The \sum PBDD/DF concentrations and \sum PBDE concentrations in wastewater samples from the textile processing facilities were correlated significantly (Spearman's rank order correlation coefficient = 0.976; $p < 0.01$), whereas the \sum PBDD/DF concentrations and HBCD concentrations were not correlated significantly. These results suggest that

the PBDD/DFs in the wastewater from the textile processing facility originated from the DBDE used as the flame retardant.

Table 2 shows the mass balance of PBDEs and PBDD/DFs in the textile processing facility (B-2). The estimated release factors of PBDEs to the wastewater and air were 1×10^{-2} and 1×10^{-6} , respectively. The \sum PBDD/DFs (150 mg/batch) output was slightly greater than the input of \sum PBDD/DFs (94 mg/batch), suggesting the possibility of PBDD/DF formation during textile processing with DBDE.

Emission factors of each process and the estimated emissions were shown in Table 3. Estimated result of air emissions from textile processing was 0.1 kg/year, which was lower than other sources. Open burning has a maximum estimate of emission, 2.3 ton/year as total PBDEs and 13 kg/year as DBDE, which has the same magnitude of emission potential as the controlled combustion of 18 kg DBDE annually⁵. The tentative total emission of DBDE, 0.12 – 25 ton/year, has a wide variation of two orders of magnitude and therefore the significance of sources that have not been comprehended yet were indicated.

References

1. Ministry of the Environment (2003): Survey on PBDD/DF emissions in FY 2002
2. Ministry of the Environment (2005): Survey on PBDD/DF emissions in FY 2003
3. Sakai, S., Hirai, Y., Ohta, S., Sudo, K. (2004): Emission factors of Polybrominated diphenyl ethers (PBDEs) from plastics processing and recycling facilities, Organohalogen Compounds
4. Ministry of the Environment (2005): Survey on PBDD/DF monitoring in FY 2003
5. Hirai, Y., Kida, A., Sakai, S. (2005): Emission factors of PCDD/DFs and PBDE by landfill fire simulation, this conference.

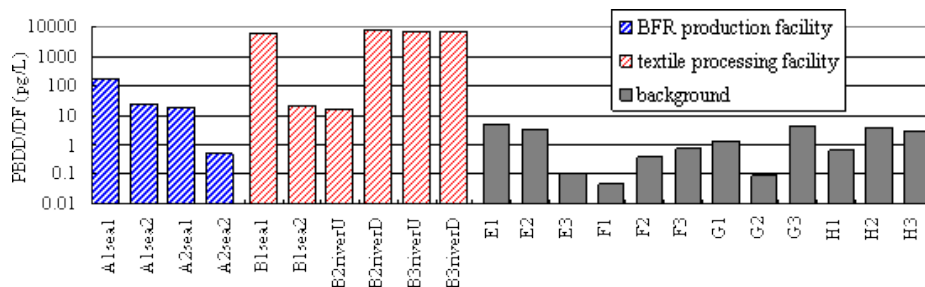


Fig. 1: Concentration of PBDD/DFs in water.

Table 1: Concentrations of BFRs and PBDD/DFs in wastewater from textile processing.

	plant wastewater	B1		B2		B3		
		from dyeing	before treatment	after treatment	from dyeing	after treatment	from dyeing	after treatment
BDE-47	ng/L	ND	0.16	0.055	3.6	1.2	0.86	2.6
BDE-99	ng/L	0.061	0.08	0.046	0.033	0.79	0.36	0.84
BDE-100	ng/L	0.013	0.074	0.037	0.12	0.13	0.074	0.093
BDE-153	ng/L	0.023	0.82	0.44	0.23	7.9	0.11	4.8
BDE-154	ng/L	ND	0.32	0.21	ND	0.94	0.052	0.87
M1BDE	ng/L	ND	ND	ND	ND	ND	ND	ND
D2BDE	ng/L	ND	ND	0.11	17	52	7.6	1.4
T3BDE	ng/L	ND	0.17	0.31	16	39	8.1	2.8
T4BDE	ng/L	ND	0.32	0.092	4.4	1.6	0.92	5.5
P5BDE	ng/L	0.074	0.19	0.082	0.15	0.94	0.43	0.97
H6BDE	ng/L	0.023	1.8	0.99	0.23	9.3	0.16	6.4
H7BDE	ng/L	0.02	1.2	0.53	0.65	85	0.88	2.9
O8BDE	ng/L	0.2	7.7	2.0	0.99	1,700	1.0	80
N9BDE	ng/L	21	600	170	3.4	34,000	11	3,400
D10BDE	ng/L	120	5,900	1,800	150	6,200,000	810	230,000
PBDEs	ng/L	140	6,500	1,900	190	6,200,000	840	240,000
HBCD	mg/L	530	1.4	0.18	3.6	2.0	190	1.4
PBDDs	pg/L	1.7	3.2	6.2	10	17,000	11	960
PBDFs	pg/L	2.7	2,000	310	170	150,000	1,500	69,000

Table 2: Mass balance of PBDEs and PBDD/DFs in plant B2

	volume per batch	concentration		amount per batch	
		PBDEs	PBDD/DFs	PBDEs	PBDD/DFs
textile	300 kg *1	0 mg/g *3	0 ng/g *3	0 kg *5	0 mg *5
PBDE	130kg *8	200 mg/g *4	720 ng/g *4	26.0 kg *6	94 mg *5
HBCD	6kg *1	0.027 mg/g *4	0.18 ng/g *4	160 mg *5	0.0011 mg *5
water	21,000 L *1	4.4 ng/L *4	0 pg/L *4	0.092 mg *5	0 mg *5
total input				26.0 kg	94 mg
product	360 kg *1	69 mg/g *1	390 ng/g *4	25 kg *5	140 mg *5
water release	42,000 L *8	6.2 mg/L *4	170 ng/L *4	0.26 kg *7	7.1 mg *5
air emission 1	1,086 m ³ *2	1,600 ng/m ³ *4	0.063 ng/m ³ *4	1.7 mg *5	70 ng *5
air emission 2	3,392 m ³ *2	6,300 ng/m ³ *4	13 ng/m ³ *4	21 mg *5	0.04 mg *5
air emission 3		n.a. 130 ng/m ³ *4		n.a	n.a.
solid waste	n.a.	n.a.		0.78 kg *7	n.a.
total output				26.0 kg	148 mg

n.a.: not available; *1: Information obtained from the facility; *2: (flue gas flow rate) × (operation time per batch); 0.6 h for preset, 0.8 h for backing; *3: Assumption; *4: Measured concentrations; *5: (volume per batch) × (concentration of

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PBDE);*6: PBDE in product/0.96; *7: PBDE input x 0.01for wastewater; PBDE input x 0.03 for solid waste; *8: (amount of PBDE)/(concentration of PBDE)

Table 3: Air emission factors of DBDE and the estimated annual emission

Processes	Air emission factors	References	Activity	PBDE emission*1	
BFRs poduction	7.0E-05-/-	EC (1993)	1,200ton/year	0.084	ton/year
Polymer processing	5.0E-04-/-	TGD (1996)	2,200ton/year	1.1	ton/year
	2.0E-04-/-	UCD (1994)	2,200ton/year	0.44	ton/year
	3.0E-07-/-	Our last estimate	2,200ton/year	0.00066	ton/year
Textile processing	9.0E-07-/-	This time	110ton/year	0.0001	ton/year
Products use	3.8E-04-/year	UCD (1994)	60,000ton	23	ton/year
	1.0E-05-/year	Breivik et al. (2002)	60,000ton	0.60	ton/year
	2.0E-06-/year	ECB (2000b)	60,000ton	0.12	ton/year
	1.0E-06-/year	Our last estimate	60,000ton	0.060	ton/year
	3.2E-07-/year	Ball et al. (1991)	60,000ton	0.019	ton/year
WEEE Recycling and Crushing	2.0E-05-/-	ECB (2000b)	6,000ton/year	0.12	ton/year
Controlled combustion	3.0E-07-/-	Our last estimate	6,000ton/year	0.0018	ton/year
Open burning	1.0E-04-/-	Danish EPA (1999)	6,000ton/year	0.6	ton/year
	3.0E-06-/-	Our last estimate	6,000ton/year	0.018	ton/year
	9.1E-02-/-	This time(Σ PBDE)	~26ton/year	~2.3	ton/year
	5.0E-04-/-	This time(DeBDE)	~26ton/year	~0.013	ton/year
Total				0.12 – 25	ton/year

*1 PBDE emission = Air emission factors x Activity