POLYBROMINATED DIPHENYL ETHERS (PBDEs), POLYBROMINATED DIOXINS/FURNAS (PBDD/Fs) AND MONOBROMO-POLYCHLORINATED DIOXINS/FURANS (MoBPXDD/Fs) IN ATMOSPHERE AND BULK DEPOSITION IN KYOTO, JAPAN

Kenichi Hayakawa[1], Hiroshi Takatsuki[2], Isao Watanabe[3], Shin-ichi Sakai[4]

[1]Kaneka Techno Research Co. Ltd. (1-8 Takasagocho-miyamaecho, Takasago, Hyogo, 676-8688, Japan)
[2]Environment Preservation Center, Kyoto University (Yoshidahonmachi, Sakyo-ku, Kyoto, 606-8501, Japan)
[3]Osaka Prefectural Institute of Public Health (1-3-69 Nakamichi, Higashinari-ku, Osaka, 537-0025, Japan)
[4]National Institute for Environmental Studies (16-2 Onogawa, Tsukuba, Ibaraki, 305-8506, Japan)

Introduction

Polybrominated diphenyl ethers (PBDEs) are flame retardants that are added to plastics to prevent fires. The estimated demand for decabromo diphenyl ether (deca-BDE) products in Japan[1,2] was 10000 t in 1990 and 2800 t in 2000. PBDEs have been known to cause environmental pollution since the 1980s[3-6]. Polybrominated dioxins/furans (PBDD/Fs) forms by thermolysis or combustion of PBDEs[7]. In 1998, Norén and Meironyté[8-10] reported that the PBDEs level in human milk of Swedish women increased exponentially from 1972 to 1997. Recently, numerous studies on environmental pollution from PBDEs and PBDE toxicity have been published[1,7,11-14], but there is little information on PBDEs in the atmosphere and their bulk deposition. The purpose of this study was to determine PBDE levels in the atmospheric environment.

Methods and Materials

Sampling

Samples were collected at Kyoto University. Atmospheric samples were collected with a high-volume air sampler equipped with a glass fiber filter (GFF) and three polyurethane foam plugs (PUF). Bulk deposition samples were collected with a glass funnel and a glass bottle. Rain samples were collected with a glass funnel and an amber-colored glass bottle by an automatic rain sampler (a device that detects rainfall and then opens the cover of the funnel). Surface soil (0~5cm) sample was collected at the same sampling point as the air samples.

Analysis

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 (GFF, PUF and soil) 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 cleanup procedure was conducted as specified for PCDD/Fs[15]. 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

Concentrations are shown in Table 1.

		Atmosphere [pg/m^3]					Bulk deposition [pg/m^2/d]			Rain [pg/m^2/d]			Soil [pg/g]
		Aug. 17-24 2000	Aug. 24-31 2000	Jan. 22-29 2001	Jan.29 -Feb.5 2001	Sep. 4-7 2001	Aug. 17-31 2000	Jan.29 -Feb.5 2001	Sep. 4-18 2001	Aug. 17-31 2000	Jan.26 -Feb.5 2001	Sep. 4-18 2001	Aug. 17 2000
PBDEs	BDE-47	23	1.3	0.59	0.78	1.1	9700	1000	560	4100	100	150	21
	BDE-99	20	1.2	0.44	0.64	0.38	12000	920	520	6600	52	190	22
	BDE-153	1.9	0.97	0.071	0.13	<0.3	2400	150	100	1500	150	<120	25
	BDE-183	2.4	4.9	0.14	0.19	<0.3	4500	150	<60	500	1000	<120	120
	BDE-209	15	48	<1.5	<1.5	3.7	1500000	24000	8300	6500	1500	20000	9100
	ΣPBDEs [1]	80	65	4.4	6.5	12	1600000	28000	11000	26000	4000	21000	9500
PBDD/Fs	Σ1~3Br [2]	10	3.3	1.2	1.6	1.9	890	90	130	270	33	19	81
	Σ4~6Br [3]	2.3	0.53	0.57	1.1	0.25	1300	77	13	460	29	60	200
MoBPXDD/Fs	Σ3~7Cl [4]	0.34	0.13	0.36	0.61	0.013	9.4	32	27	11	ND	27	52
PCDD/Fs	Σ4~8Cl [5]	6.0	3.6	3.7	7.8	5.2	1600	880	NA [6]	850	410	NA [6]	540
	TEQ	0.075	0.044	0.059	0.11	0.034	22	13	NA [6]	9.1	3.8	NA [6]	11

1) Sum of mono- to deca-brominated homologues 2) Sum of mono- to tri-brominated homologues
3) Sum of tetra- to hexa-brominated homologues 4) Sum of tetra- to octa-halogenatad homologues
5) Sum of tetra- to octa-chlorinated homologues 6) Not analysed

Homologue profiles of PBDEs

BDE-209 was predominant in bulk deposition and soil samples, where it accounted for more than 75 % of all PBDEs (SPBDEs). In the atmosphere, BDE-209 was detected in 3 of 5 samples, and the ratio of BDE-209 to SPBDEs was smaller than those in the bulk deposition and soil samples. This result is different from those of studies conducted in North America. Strandberg et al.[16] reported that BDE-47 and -99 were detected and BDE-209 was scarcely detected in the atmosphere near the Great Lakes. Alaee et al.[17] reported that in the atmosphere over the Arctic or the Great Lakes, tetra- to hexa-BDEs were observed, whereas octa- to deca-BDEs were not detected. The differences in atmospheric PBDE profiles may reflect differences in the demand for PBDE products in the respective regions. For example, penta-BDE products are more in demand in the Americas than in Asia[18] (Table 2).

Homologue profiles of PBDD/Fs and MoBPXDD/Fs

In all samples, PBDFs were predominant and PBDDs were detected only at trace levels. Heptabromo- and octabromo-DD/Fs were not detected in any samples. Monobromo-polychlorinated dioxins and furans (MoBPXDDs and MoBPXDFs, respectively) were present at the same levels in the atmosphere. Watanabe et al.[19] reported PBDD/Fs and MoBPXDD/Fs in airborne dust in Osaka, Japan. Homologue profiles in the present study were similar to those found by Watanabe et al.[19]

Atmospheric gas-particle partitioning

The proportion of the atmospheric particulate phase of PCDD/Fs is known to increase with increasing chlorine number and to be higher in winter than in summer.[20] In the present study of the brominated compounds (Table 3), as with PCDD/Fs, the proportion of the atmospheric particulate phase increased with increasing halogen number, and the proportion was higher in samples collected in winter than in those collected in summer. Furthermore, the proportion in PBDFs was higher than in PCDFs with the same halogen number. Also, the proportion in PBDEs was lower than in PBDFs with the same bromine number.

Table 3. Atmospheric gas-particle partitioning: Relative particulate-phase concentrations [%].

	Aug. 17-24 2000	Aug. 24-31 2000	Jan. 22-29 2001	Jan.29 -Feb.5 2001
T3BDEs	<	<	3.0	5.1
T4BDEs	<	<	34	55
P5BDEs	3.8	<	86	92
H6BDEs	26	<	>	>
H7BDEs	>	19	>	>
D2BDFs	1.4	1.4	1.9	2.1
T3BDFs	5.3	5.9	32	42
T4BDFs	26	33	95	96
P5BDFs	71	83	>	>
H6BDFs	72	>	>	>
MoBT3CDDs	<	<	16	44
MoBT4CDDs	<	<	>	>
MoBP5CDDs	63	52	>	>
MoBH6CDDs	>	>	>	>
MoBH7CDDs	>	>	>	>
MoBT3CDFs	<	<	29	44
MoBT4CDFs	23	<	92	93
MoBP5CDFs	63		>	>
MoBH6CDFs	>	>	>	>
MoBH7CDFs	>	>	>	>
T4CDDs	5.5	5.2	15	12
P5CDDs	24	22	78	72
H6CDDs	47	43	98	98
H7CDDs	85	80	>	>
O8CDD	96	95	>	>
T4CDFs	6.2	4.8	14	15
P5CDFs	20	14	68	70
H6CDFs	43	38	96	97
H7CDFs	76	73	99.2	99.6
O8CDF	92	95	>	>

< : Particulate phase conc. was below the limit of quantitation (LOQ).
> : Gaseous phase conc. was below the LOQ.
blank : Conc. of both phases were below the LOQ.

Table 2. Estimated world market demand for PBDEs in 1999 by region (metric tons)[18].

	Europe	Americas	Asia
Deca-BDE	7,500	24,300	23,000
Octa-BDE	450	1,375	2,000
Penta-BDE	210	8,290	--

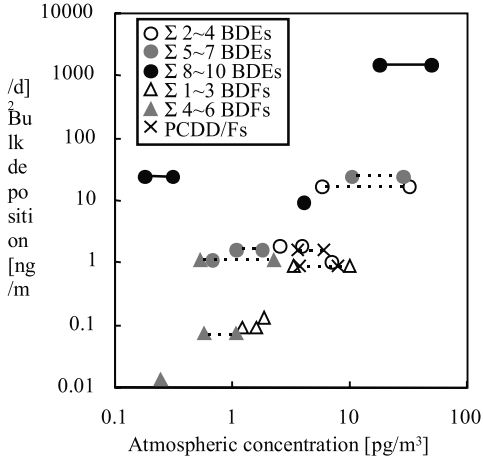

Figure 1. Bulk deposition vs. atmospheric concentrations. The atmospheric concentration is the sum of the gaseous and particulate-phase concentrations.

Correlation between bulk depositions and atmospheric concentrations

Bulk depositions correlate positively with atmospheric concentrations except in the case of the sum of octa- to deca-BDEs (Figure 1).

Correlations among brominated compounds in the atmosphere

The relationships among atmospheric concentrations of PBDEs, PBDD/Fs, MoBPXDD/Fs, and PCDD/Fs are shown in Figure 2. The MoBPXDD/F level correlates positively with that of PCDD/Fs, and PBDD/F levels correlate positively with the sum of di- to hepta-BDE levels. This relationship between MoBPXDD/Fs and PCDD/Fs has been previously observed in waste incineration samples. For example, Yoneda et al.[21] investigated the emission of brominated dioxins during municipal and industrial solid waste incineration in Japan and reported that the MoBPXDD/F level was correlated with the PCDD/F level in emission gas and that MoBPXDD/Fs levels were about 10 %~20 % PCDD/F levels. In addition, we[22] previously combusted waste television casings and resin pellets containing brominated flame retardants in a rotary kiln furnace and found a correlation between MoBPXDD/F levels and PCDD/F levels in the waste gas before gas treatment.

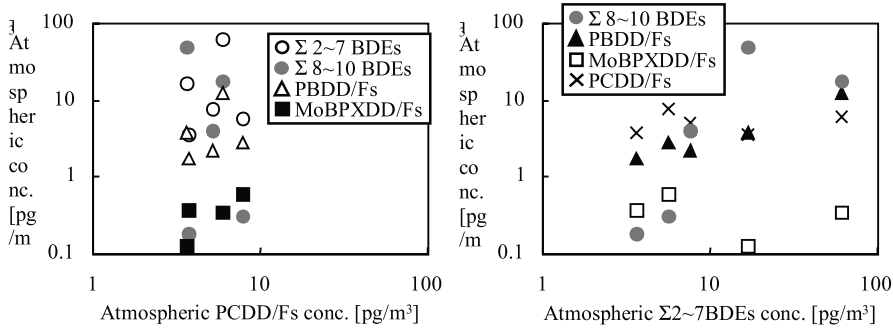

Figure 2. Relationships among PBDEs, PBDD/Fs, MoBPXDD/Fs, and PCDD/Fs in the atmosphere.

References

1. Watanabe, I. and Kawano, M. (1997) Proceedings of IEA-ISWMG/JWRF Seminar on Integrated Solid Waste Management, pp.11-1~11-12, Sep.24-25, Kyoto
2. Kagaku Kogyo Nippo Co. Ltd. (2001) *Kagaku Kogyo Nenkan 2001* (in Japanese)
3. Andersson, O. and Blomkvist, G. (1981) *Chemosphere*, 10, 1051-1060
4. Watanabe, I., Kashimoto, T. and Tatsukawa, R. (1986) *Bull.Enviorn.Contam.Toxicol.*, 36, 839-842
5. Watanabe, I., Kashimoto, T. and Tatsukawa, R. (1987) *Chemosphere*, 16, 2389-2396
6. Jansson, B., Asplund, L. and Olsson, M. (1987) *Chemosphere*, 16, 2343-2349
7. WHO (1994) *Environmental Health Criteria 162*, WHO, International Programme on Chemical Safety, Geneva
8. Norén, K. and Meironyté, D. (1998) *Organohalogen Compounds*, 38, 1-4
9. Norén, K. and Meironyté, D. (2000) *Chemosphere*, 40, 1111-1123
10. Meironyté, D. and Norén, K. (2001) Proceedings of the 2nd International Workshop on Brominated Flame Retardants, pp.303-305, May 14-16, Stockholm
11. Pijnenburg, A. M. C. M., Everts, J. W., de Boer, J. and Boon, J. P. (1995) *Rev.Environ.Contam.Toxicol.*, 141, 1-26
12. Rahman, F., Langford, K. H., Scrimshaw, M. D. and Lester, J. N. (2001) *Sci.Total Environ.*, **275**, 1-17
13. Darnerud,P.O., Eriksen,G.S., Jóhannesson,T., Larsen,P.B. and Viluksela,M.(2001) *Environ. Health Perspect.*, 49-68
14. de Wit,C.A.(2002) *Chemosphere*, 46, 583-624
15. JIS (Japan Industrial Standards) K0312 (1999)
16. Strandberg, B., Dodder, N. G., Basu, I. and Hites, R. A. (2001) *Environ.Sci.Technol.*, 35, 1078-1083
17. Alaee, M., Cannon, C., Muir, D., Blanchard, P., Brice, K. and Fellin, P. (2001) *Organohalogen Compounds*, 52, 26-29
18. Bromine Science and Environmental Forum, «An introduction to brominated frame retardants», 19 October 2000, obtained from the internet (http://www.bsef.com/)
19. Watanabe, I., Kawano, M. and Tatsukawa, R. (1995) *Organohalogen Compounds*, 24, 337-340
20. Harrad, S. J. (1998) in: *Atmospheric Particles*, (Harrison, R. M. and van Grieken, R. E., Eds) pp.233-251, John Willey & Sons, ISBN 0471959359
21. Yoneda, K., Tani, A., Morita, M. and Sakai, S. (2001) Proceedings of the 10th Conference of Environmental Chemistry, pp.106-107, May 23-25, Matsuyama (in Japanese)
22. Sakai,S., Watanabe,J., Honda,Y., Takatsuki,H., Aoki,I., Futamatsu,M. and Shiozaki,K. (2001) *Chemosphere*, 42, 519-531