Polybrominated and Mixed Polybromo/chlorinated Dibenzo-*p*-dioxins and -Dibenzofurans in the Japanese Environment

Isao WATANABE
Osaka Prefectural Institute of Public Health, 1-3-69 Nakamichi, Higashinari-ku, Osaka 537, Japan
Masahide KAWANO and Ryo TATSUKAWA
Department of Life Environment Conservation, Ehime University, 3-5-7 Tarumi, Matsuyama 790, Japan

1. INTRODUCTION

Polybrominated and mixed polybromo/chlorinated dibenzo-*p*-dioxins and -dibenzofurans (PBDD/DF and PXDD/DF) in addition to polychlorinated dibenzo-*p*-dioxin and -dibenzofurans (PCDD/DF) have been reported to be present in fly ash from municipal waste incinerators (MWI)[1-4]. Considerable amounts of PBDD/DF are known to be produced by the pyrolysis of some organobrominated flame retardants such as polybrominated biphenyl ethers (PBBE)[5,6]. One possible formation of PXDD/DF would be the chlorine exchange of bromine in PBDD/DF produced first in the incinerator[7]. Another possible formation of these compounds would be the bromination of PCDD/DF during incineration[2]. In addition, PBDD/DF and PXDD/DF has also been recognized to be produced from another sources such as automobile traffic[8].

The toxicity data available for PBDD/DF and PXDD/DF suggest that they have similar toxicological properties to those of PCDD/DF[9]. Therefore, PBDD/DF and PXDD/DF in addition to PCDD/DF has also become a matter of concern because of the new environmental problems arising out of these compounds in the world. However, very few information is available on their occurrence, distribution, dynamic and fate in the environment for the prediction of their environmental effects.

In this experiment, the determination of PBDD/DF and PXDD/DF as well as PCDD/DF was attempted in the airborne dust collected from an urban area in Osaka, which is relatively highly polluted area by PCBs and PCDD/DF in Japan[10]. These pollutants were also analyzed in selected water, sediment and fish samples collected from the rivers in Osaka city and from Osaka Bay. In this report, the occurrence and distribution of PBDD/DF and PXDD/DF in the Japanese environment were described and discussed.

2. EXPERIMENTAL

(1) Samples

(a) Airborne dust: Seven airborne dust samples were collected at Osaka, Japan, from August 1993 to July 1994. Airborne dust was collected on a quartz filter using a high volume air sampler at a flow rate of about 700ml/min. for 24 hours. **(b) Water:** Two water samples were collected at the down stream of two rivers in Osaka city and two sea water were collected at Osaka Bay in 1994. **(c) Sediment:** Two sediments were collected by means of a dredger from upper sediment layer at the two rivers in Osaka city and three marine

sediments were also collected at Osaka Bay in 1994. **(d) Fish:** Two crucians and two gray mullet were collected at the down stream of two rivers in Osaka city in 1993.

(2) Extraction and cleanup

A filter sample of airborne dust was Soxhlet extracted using 150 ml of dichloromethan for over 20 hours. A water sample (10 - 20L) was extracted with n-hexane (100ml/1L-water) after addition of small amount of acetone (30ml/1L-water) using a separation funnel. A dried sediment sample (15 -20g) was extracted with a Soxhlet apparatus by 150ml of a mixture of acetone and n-hexane (1:1). An edible fish meat sample (20 -30g) was homogenized and extracted with 100ml of acetone and then with 100ml of hexane using a Polytron^{R} homogenizer. The each crude extracts of air, water, sediment and fish was transferred to n-hexane and spiked internal standards of ^{13}C-2378-T_4CDD/DF (2 ng each), ^{13}C-O_8CDD/DF (2 ng each) and ^{13}C-2378-T_4BDD(2.5 ng), respectively. The crude hexane extract was cleaned up according to the procedure described in our previous report[11]. To avoid photodegradation of PBDD/DF and PXDD/DF during analysis, amber color glasswares were used.

(3) GC/MS analysis

HRGC/HRMS analysis was carried out using a Shimadzu GC 14A equipped with a DB-5 column (60m x 0.25mm i.d., 0.1μm film thickness, J$W) for the analysis of PBDD/DF, PXDD/DF, PCDD/DF and PBBE(tetra- to hexa-substituted congeners), as described in our previous report[11]. The detector was a Shimadzy-Kratos Concept 1S (Kyoto, Japan). Although most of analytical standards of monobromo-PXDD/DF were not available, semiquantitation of monobromo-PXDD/DF was made by assuming that the SIM responses of penta-, hexa-, hepta- and octa-substituted congeners were 1/2, 1/3, 1/5 and 1/5 of monobromotrichloro-PXDD/DF, respectively, since the response ratio of penta-, hexa, hepta and octa-PCDD/DF to tetra-PCDD/DF was roughly 1/2, 1/3, 1/5 and 1/5 in our GC/MS system. However semiquantitation of dibromo-PXDD/DF was not made because that their levels in the samples were seemed to be extremely low. A Shimadzu GC 15A connected with an electron capture detector (ECD,^{63}Ni) and a DB-1 column (15m x 0.25mm i.d., 0.25 μm film thickness, J&W) was used to determine decabromobiphenyl ether (DBBE).

3. RESULTS AND DISCUSSION

(1) PBDD/DF and PXDD/DF determination in the airborne dust

The occurrence of tri- to hexa-substituted PBDF and PBBE in the air samples collected at an urban area of Japan, Osaka, has been reported in our previous work[11,12]. In the present study, mono- and dibromo-PXDD/DF in addition to PBDF were also found in the airborne dust. However, few PBDD was found in the air samples in this time also. PBDD/DF and a part of PXDD/DF found in airborne dust were estimated to be the by-products of the pyrolysis of PBBE because of the presence of large amount of PBBE, DBBE dominant, in the air. Since most standards of PXDD/DF are not available, the confirmation of PXDD/DF found in the sample was conducted by comparing theoretical accurate masses with those calculated by a mass peak profile method with a 200 ppm sweep at 10000 resolution. The very close agreement between theoretical and observed masses by the mass peak profile method for ions of mono- and dibromo-PXDD/DF was obtained ,as shown in Table 1.

(2) PBDD/DF and PXDD/DF levels in the environmental samples.

Table 2 shows the levels of PBDD/DF, monobromo-PXDD/DF, PCDD/DF and PBBE in airborne dusts, river and marine sediments and fish. The PCDD/DF levels obtained in this study are comparable to the urban area results reported by the Environmental Agency of Japan[13,14]. The levels of PBDF (tetra- to hexa-substituted congeners) in the airborne dust was also almost the same as those reported in our previous work[12].

Table 1. Accurate masses calculated by the mass peak profile method for mono- and dibromo-PXDD/DF in the airborne dust.

Compound	Composition	Accurate mass (theoretical value)	Accurate mass (experimental value)	error (ppm)
Bromotetrachloro-DD	$C_{12}H_3O_2{}^{35}Cl_3{}^{37}Cl_1{}^{79}Br_1$	399.8041	399.8016	- 6.3
	$C_{12}H_3O_2{}^{35}Cl_4{}^{81}Br_1$	399.8051	399.8016	- 8.8
Bromopentachloro-DD	$C_{12}H_2O_2{}^{35}Cl_4{}^{37}Cl_1{}^{79}Br_1$	433.7651	433.7640	- 2.5
	$C_{12}H_2O_2{}^{35}Cl_5{}^{81}Br_1$	433.7662	433.7640	- 5.1
Bromohexachloro-DD	$C_{12}H_1O_2{}^{35}Cl_5{}^{37}Cl_1{}^{79}Br_1$	467.7262	467.7274	2.6
	$C_{12}H_1O_2{}^{35}Cl_6{}^{81}Br_1$	467.7272	467.7274	0.4
Bromoheptachloro-DD	$C_{12}O_2{}^{35}Cl_5{}^{37}Cl_2{}^{79}Br_1$	503.6843	503.6861	3.6
	$C_{12}O_2{}^{35}Cl_6{}^{37}Cl_1{}^{81}Br_1$	503.6853	503.6861	1.6
Dibromotetrachloro-DD	$C_{12}H_2O_2{}^{35}Cl_3{}^{37}Cl_1{}^{79}Br_1{}^{81}Br_1$	479.7127	479.7122	- 1.0
	$C_{12}H_2O_2{}^{35}Cl_4{}^{81}Br_2$	479.7137	479.7122	- 3.1
Dibromopentachloro-DD	$C_{12}H_1O_2{}^{35}Cl_3{}^{37}Cl_2{}^{79}Br_2$	513.6727	513.6743	3.1
	$C_{12}H_1O_2{}^{35}Cl_4{}^{37}Cl_1{}^{79}Br_1{}^{81}Br_1$	513.6737	513.6743	1.2
Dibromohexachloro-DD	$C_{12}O_2{}^{35}Cl_4{}^{37}Cl_2{}^{79}Br_2$	547.6337	547.6301	- 6.6
	$C_{12}O_2{}^{35}Cl_5{}^{37}Cl_1{}^{79}Br_1{}^{81}Br_1$	547.6348	547.6301	- 8.6

Table 2. PBDD/DF, PXDD/DF, PCDD/DF and PBBE levels in airborne dust, sediment and fish collected at an urban area in Osaka, Japan.

Sample	Compound	Concentration						
		tetra-	penta-	hexa-	hepta-	octa-	deca-	total
Airborne	PCDD	ND - 0.37	0.61 - 4.0	2.6-16	3.5-27	2.8-24		9.6-71
Dust	PCDF	0.3-2.8	1.9-14	6.2-47	7.3-78	3.2-51		20-193
N=7	PBDD	ND	ND	ND	NA	NA		ND
pg/m^3	PBDF	0.5-2.8	1.0-6.5	0.6-8.0	NA	NA		4.2-17
	PXDD	ND	(ND-1)	(1-6)	(1-10)	(0.6-5)		(4-22)
	PXDF	ND-0.3	0.2-2.3	(0.8-7)	(0.7-8)	(0.1-5)		(2-23)
	PBBE	1.2-7.1	1.7-6.1	2.1-46	NA	NA	83-3060	88-3100
Sediment	PCDD	0.01-0.04	0.07-0.12	0.28-0.60	0.48-1.9	0.6-7.0		1.5-9.4
N=5	PCDF	0.03-0.08	0.08-0.15	0.18-0.31	0.3-0.53	0.03-0.21		0.68-1.1
μg/kg•dry	PBDD	ND-0.006	ND	ND	NA	NA		ND-0.006
	PBDF	0.01-0.04	0.007-0.13	0.01-0.20	NA	NA		0.03-0.37
	PXDD	ND	(ND-0.02)	(ND-0.1)	(ND-0.3)	(0.05-0.1)		(0.06-0.5)
	PXDF	ND	ND-0.01	(ND-0.04)	(ND-0.07)	(ND-0.01)		(ND-0.1)
	PBBE	NA	NA	NA	NA	NA	54-390	54-390
Fish	PCDD	0.004-0.03	0.008-0.05	0.007-0.06	0.018-0.08	ND-0.005		0.04-0.22
N=4	PCDF	0.007-0.10	0.009-0.06	ND-0.033	ND-0.011	ND		0.02-0.20
μg/kg•wet	PBDD	ND	ND	ND	NA	NA		ND
	PBDF	ND	ND	ND	NA	NA		ND
	PXDD	ND	ND	ND	ND	ND		ND
	PXDF	ND	ND	ND	ND	ND		ND
	PBBE	6.3-89	0.62-9.4	0.72-17	NA	NA	ND	7.7-104

ND: not detected, NA: not analyzed.
Values in parenthesis are obtained by the semiquantitative calculation described in the text.

Monobromo-PXDD/DF (tetra- to octa-substituted congeners) in this airborne dust were roughly estimated 1/10 - 1/4 of PCDD/DF in the same samples, as shown in Table 2. The ratios of PXDD/DF to PCDD/DF in the air samples are resemble to those in fly ash reported in earlier works[1-4]. PBDF and monobromo-PXDD/DF were also found in the sediment samples though their levels are very low compared to PCDD/DF levels in the same samples. No PBDF and no PXDD/DF was found in water and fish samples though PCDD/DF and PBBE were detected in these samples. Wiberg[15] has reported that PBDD/DF and PXDD/DF were absent in biological samples such as salmon and osprey in Sweden, though PCDD/DF were present in significantly higher levels. The results obtained in fish in this study are consistent with those of Swedish study. Absence of PBDD/DF and PXDD/DF in biota might be due to their low bioaccumulation potential in addition to low transportable and labile properties[11] in the environment compared to those of PCDD/DF.

4. CONCLUSION

On the basis of these results obtained , it could be concluded tentatively that the environmental effects of PBDD/DF and PXDD/DF are not serious in the Japanese environment at present because of their low levels in the environment. However, discharge of PBBE to the environment might be increased in proportion to the rapidly consumption of these compounds in last decade in Japan. Therefore, a continuous survey on PBDD/DF and PXDD/DF in addition to PCDD/DF in Japanese environment is recommended in and around the pollution sources such as the MWI.

5. REFERENCES

1) Schwind K.H., J. Hosseinpour and H. Thoma (1988): Chemosphere **17**, 1875-1844
2) Sovocool G.W., J.R. Donnelly, W.D. Munslow, T.L. Vonnahme, N.J. Nunn, Y. Tondeur and P.K. Mitchum (1989): Chemosphere **18**, 193-200
3) Harless R.L., R.G. Lewis, D.D. McDaniel and A.E. Dupuy (1989): Chemosphere **18**, 201-208
4) Chatkittikunwong W. and C.S. Creaser (1994): Chemosphere **29**, 559-566
5) Buser H.R. (1986): Environ. Sci. Technol. **20**, 404-408
6) Thoma H., G. Hauschulz, E. Knorr and O. Hutzinger (1987): Chemosphere **16**, 277-285
7) Luijk R., C. Dorland, P. Smit, J. Jansen and H.A.J. Govers (1994): Chemosphere **28**, 1299-1309
8) Bacher R., U. Riehle, M. Swerev and K. Ballschmiter (1991): Chemosphere **23**, 1151-1171
9) Schulz-Schalge T., E. Koch, K.H. Schwind, O. Hutzinger and D. Neubert (1991): Chemosphere **23**, 1925-1931
10) Miyata H., O. Aozasa, K. Yamamori, A. Fujiwara and Y. Yasuda (1994): Dioxin '94, Vol. **20**, 187-190
11) Watanabe I., M. Kawano and R. Tatsukawa (1994): Dioxin '94, Vol **19**, 235-238
12) Watanabe I., M. Kawano, Y.Wang, Y. Chen and R. Tatsukawa (1992): Dioxin '92, Vol **9**, 309-312
13)The Environmental Agency report on the surveillance of PCDD/PCDF levels in atmospheric air in FY 1990 in Japan. (Nov. 25, 1991)(Japanese)
14) The Environmental Agency of Japan (1994): Chemicals in the environment - Report on environmental survey and wildlife monitoring of chemicals in FY 1993, (Dec. 1994) (Japanese)
15) Wibreg K., C. Rappe and P. Haglund (1992): Chemosphere **24**, 1431-1439