

Environmental Levels (Air and Soil) of Other Organohalogenes and Dioxins P304

Halogenated Dibenzo-*p*-Dioxins and –Dibenzofurans in Atmospheric Deposition in an Urban Area (Osaka) in Japan

Isao Watanabe and Masahiro Ugawa

Osaka Prefectural Institute of Public Health, 1-3-69 Nakamichi, Higashinari-ku, Osaka 537-0025, Japan

Introduction

Recently considerable amounts of polychlorinated dibenzo-*p*-dioxins and –dibenzofurans (PCDDs and PCDFs) have been found in environmental samples such as soil collected in the vicinities of some municipal and industrial waste incinerators in Japan. Therefore, there is still great social concern in Japan over PCDD/DFs pollution of the environment and human exposure. The Japanese Government lately announced a guideline for reduction of PCDD/DFs emission into the environment according to which their total emissions in 2002 will decrease to about 10% of those in 1997. Atmospheric deposition is considered to be the major pathway for PCDD/DFs from various sources to the earth's surface. Therefore, surveillance of PCDD/DFs in atmospheric deposition, as well as in the effluent gas from waste incinerators, is useful for the study on PCDD/DFs emission.

In this research, PCDD/DFs, together with bromine-containing dioxins such as brominated and bromopolychlorinated congeners (PBDD/DFs and PXDD/DFs), in atmospheric deposition were determined at an urban area, Osaka, which is an area in Japan relatively heavily polluted by PCDD/DFs. Furthermore, these halogenated dioxins were measured in other selected environmental samples, such as airborne dust, roof dust and soil, for the prediction of PCDD/DFs fate in the environment.

Materials and Methods

1. Samples

- (1) Atmospheric deposition: Total depositions, including dry and wet depositions, were collected in several enamel beakers (24cm inner diameter, 24cm height) on the roof of Osaka Prefectural Institute of Public Health (about 20m above the ground, 34:40:37N,135:32:16E). The collection period for a sample was one month. The beakers held water to the depth of about 2cm during the sample collection period for preventing loss of deposition once collected. Investigation period was from April 1995 to November 1998 (excluding May 1996 to March 1997)
- (2) Airborne dust: Airborne dust was collected on a quartz fiber filter using a high volume air sampler at a flow rate of about 700ml/min. for 24 hours. Sampling was also carried out on the roof of our institute building from April 1997 to November 1997. All crude extracts of airborne dust samples were combined to one sample.

- (3) Roof dust: Dust soil deposited on the roof of our institute was collected in December 1998

Environmental Levels (Air and Soil) of Other Organohalogenes and Dioxins P304

(N=1). A greater part of this dust was composed of fine particles like soil.

- (4) Soil: A soil sample was collected from a 0-5cm layer at Osaka Castle Park in July 1998 (34:41:00N, 135:31:00E) (N=1).

2. Extraction and cleanup

A deposition sample (rain water containing a small amount of solid) was filtered through a glass fiber filter (0.6µm, 90mm). After filtration, the aqueous layer was extracted with C18 solid phase cartridge (Empore Disk, 90mm). The filter and disk of a sample were simultaneously soaked with acetone and then Soxhlet extracted with toluene for over 20 hours. The quartz fiber filters of airborne dust samples were also Soxhlet extracted. For roof dust and soil, after grinding, particles smaller than 0.7mm were used for the analysis. These samples were also Soxhlet extracted. The crude extract of each sample was cleaned up according to the procedure described in our previous report⁴⁾. Briefly, the extract was treated with concentrated sulfuric acid several times and cleaned up using a multi-layer column (AgNO₃-silica/H₂SO₄-silica/KOH-silica). Then the eluate was passed through a neutral alumina column. To avoid photodegradation of PBDD/DFs and PXDD/DFs during analysis, amber colored glasswares were used.

3 GC/MS analysis

A HP-5890 series II equipped with a DB-5MS column (30m x 0.25mm, 0.25µm film thickness. J&W) was employed for the analysis of PCDD/DFs, PBDD/DFs (tetra- to hexa-substituted congeners) and PXDD/DFs (hexa- to octa-substituted PXDFs were not analyzed because of lack of analytical standards). The following conditions were used: injector temperature: 280C; carrier gas: He at a head pressure of 15 psi; injection mode: splitless; oven temperature: 130C(2min.) to 230C at a rate of 15C/min. and then to 300C at a rate of 4C/min.(15 min.). Congener analysis of 2,3,7,8-sustituted PCDD/DFs were carried out using SP2331 column (60m x 0.25mm, 0.20µm film thickness. Supelco). The HRMS used was JEOL-JMS700 (Tokyo, Japan). The SIM conditions were as follows: ion source mode: EI; ion source temperature: 290 C; electron energy: 50 eV; postacceleration detector: 10kV; resolution: about 10000. The two most intensive mass numbers were chosen for monitoring of molecular ion cluster.

Results and Discussion

1. PCDD/DFs, PBDD/DFs and PXDD/DFs in atmospheric deposition

The occurrence of PXDD/DFs and tri- to hexa-substituted PBDFs in the airborne dust collected in the Osaka area has been reported in our previous work⁴⁾. In this study, PXDD/DFs and PBDFs, in addition to PCDD/DFs, were also found in atmospheric deposition samples. Figure 1 shows homologue profiles of these halogenated dioxins for atmospheric deposition, airborne dust, roof dust and soil samples. Levels and composition of these halogenated dioxins detected in atmospheric deposition varied in the samples. PCDDs were dominant in all samples, and bromine-containing dioxins such as PXDD/DFs and PBDFs were minor components. It is noticeable that the samples having higher levels of PCDDs contained a relatively lower contribution of PCDFs in atmospheric deposition. For example, the deposition collected in September 1998, which contained high levels of PCDDs, showed a lower ratio of PCDFs to PCDDs than those collected in August

1998. The homologue profile of halogenated dioxins in the deposition is expected to be essentially

Environmental Levels (Air and Soil) of Other Organohalogenes and Dioxins P304

similar to those in the air or airborne dust, i.e., total-PCDDs < total-PCDFs. However, the dioxin homologue profile of the September 1998 deposition showed total-PCDDs dominant and significantly resembles those of roof dust and soil, as shown in Figure 1. It is suggested that possibly the dioxins in the deposition samples of September 1998 came largely from those in particles such as roof dust and soil. The PCDD/DFs levels in roof dust and soil were 430 and 220 pg-TEQ/g(dry), respectively, which were significantly higher than those in soils collected in rural areas in Japan. Therefore, the blowing up of dust and soil particles to the atmosphere by wind may be one of the factors for PCDD/DFs deposition flux. Especially, in urban areas in which the greater part of the earth's surface is covered with paved roads and buildings, this factor might be important.

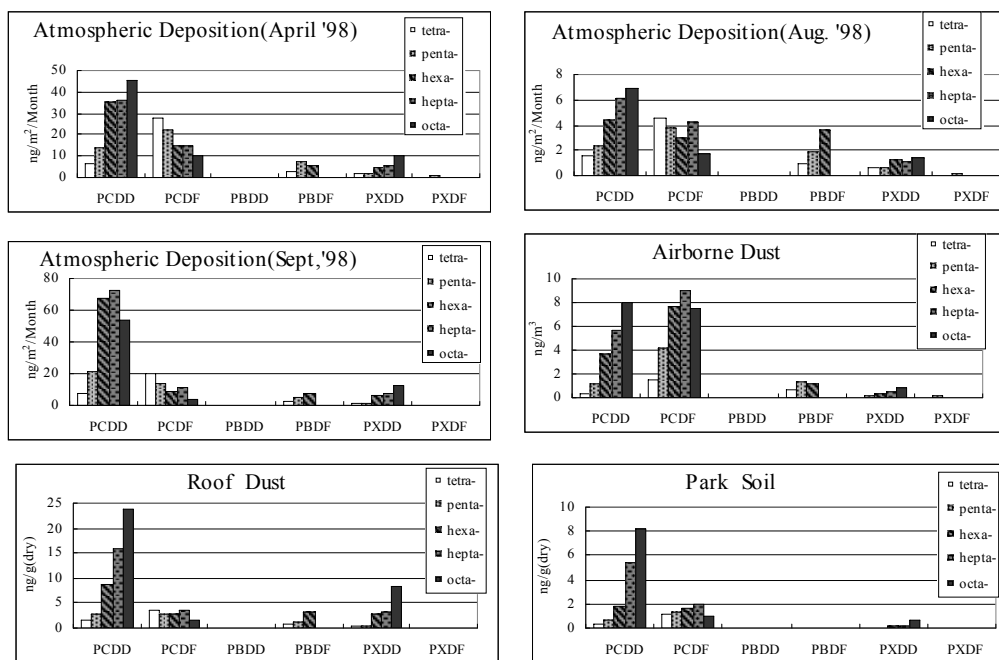


Figure 1. Polyhalogenated dioxin homologue profiles in atmospheric deposition, airborne dust, roof dust and soil collected in Osaka, Japan. (PBDD/DFs: determined tetra- to hexa-substituted homologues, PXDFs: determined tetra- and penta-substituted homologues)

A good relationship between PCDDs and PXDDs levels in the atmospheric deposition was observed ($r^2=0.85$). This phenomenon suggested that PXDDs might have been produced

Environmental Levels (Air and Soil) of Other Organohalogenes and Dioxins P304

simultaneously along with PCDDs by *de novo* synthesis during incineration of waste. The ratio of PXDDs to PCDDs in the atmospheric deposition resembled those in airborne dust and roof dust as shown in Figure 1. Bromine-containing dioxins such as PXDD/DFs and PBDD/DFs are considered to be labile compared to PCDD/DFs in the environment. However, the similar ratio of PXDDs to PCDDs in these samples suggests that PCDD/DFs as well as PXDDs absorbed on particles might be resistant to degradation/photolysis in the atmospheric environment.

2. Deposition flux of PCDD/DFs.

Table 1 shows the deposition flux (pg-TEQ/m²/day) of PCDDs and PCDFs in the two periods from April 1995 to April 1996 and from April 1996 to March 1997. As described above, the samples showing high contributions of PCDDs in total-PCDD/DFs are considered to be highly influenced by soil and roof dust particles. Therefore, samples which have high PCDDs contributions, i.e., PCDDs-TEQ > PCDFs-TEQ, were excluded in the calculation of average deposition flux of PCDD/DFs. Average deposition flux of PCDD/DFs was about 80pg-TEQ/m²/day in the former period and about 50pg-TEQ/m²/day in the latter period. Therefore, a decreasing tendency of PCDD/DFs flux was noted, though there is no statistical difference. Consequently, PCDD/DFs emission to the environment in Osaka in 1998 is estimated to have decreased to 60-70% of that in 1995.

The PCDD/DFs deposition flux (50-80 pg-TEQ/m²/day) obtained in Osaka in this experiment was significantly higher than that reported in rural and semi-rural areas i.e., 6-30pg-TEQ/m²/day, and was similar to those in other urban areas in Japan such as Tokyo¹⁻³).

The atmospheric deposition flux of PCDD/DFs may vary depending on sampling methods, sites, weather conditions, and effect of dust and soil particles. PXDD/DFs may convert into more stable PCDD/DF by reductive debromination in the environment. Therefore, further investigation of the atmospheric deposition of PXDD/DFs, as well as PCDD/DFs, is needed.

References

1. Seike, N., Matsuda, M., Kawano, M. and Wakimoto, T.: J. Environmental Chemistry of Japan, **1998**, 8, 23 (in Japanese)
2. Ogura, I.: Proceedings of 1st International Workshop on Risk Evaluation and Management of Chemicals, Yokohama, **1998**, pp67-74
3. Environmental Agency of Japan: in the report on the results of monitoring for air pollution compounds in 1997 (July 16, 1998, in Japanese)
4. Watanabe, I., Kawano, M. and Tatsukawa, R.: Organohalogen Compounds. **1995**, 24, 337

Environmental Levels (Air and Soil) of Other Organohalogen and Dioxins P304

Table 1. Deposition flux of PCDD/DFs (I-TEQ)

Sample	PCDDs-TEQ pg/m ² /day	PCDFs-TEQ pg/m ² /day	total-TEQ pg/m ² /day	Sample	PCDDs-TEQ pg/m ² /day	PCDFs-TEQ pg/m ² /day	total-TEQ pg/m ² /day
Apr-95	18	43	61	Apr-97	12	31	43
May-95	13	34	48	May-97	73	55	128
Jun-95	10	43	53	Jun-97	15	32	47
Jul-95	18	41	59	Jul-97	32	43	75
Aug-95	27	52	79	Aug-97	11	28	39
Sep-95	57	55	112	Sep-97	30	42	72
Oct-95	76	98	174	Oct-97	14	19	33
Nov-95	27	39	66	Nov-97	51	45	95
Dec-95	44	74	118	Dec-97	39	57	96
Jan-96	20	40	60	Jan-98	8	23	31
Feb-96	33	51	85	Feb-98	NA	NA	NA
Mar-96	35	56	91	Mar-98	7	23	30
Apr-96	111	62	173	Apr-98	26	49	75
				May-98	23	30	53
				Jun-98	20	33	54
				Jul-98	5	10	15
				Aug-98	4	11	15
				Sep-98	58	35	94
Average*	29	52	81	Average*	18	31	48
stdev*	18	19	37	std*	11	14	35

NA: not analyzed

*Average and stdev.: excluded samples showing PCDDs-TEQ>PCDFs-TEQ