Flux and Characteristics of Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in Atmospheric Deposition

Isamu Ogura

Yokohama National University, 79-7 Tokiwadai, Hodogaya-ku, Yokohama, Kanagawa 240-8501, JAPAN

Abstract

Flux and characteristics of PCDD/PCDFs in atmospheric deposition are investigated in order to reveal air-transported contamination levels of these compounds and their atmospheric behavior. Total PCDD/PCDF deposition fluxes ranged from 2.0 to 6.0 ng/m²/day and the TEQ values ranged from 23 to 89 pg/m²/day in Tokyo, Yokohama and Tanzawa. Homologue profiles of PCDD/PCDF deposition varied among samples, but all isomer profiles of PCDD/PCDF deposition were very similar. As a possible explanation of these results, we can consider that isomer profiles of depositions were primarily determined by isomer profiles of emissions from incineration processes, and are relatively stable in air and soil. The result of the comparison between dry and wet depositions suggests that deposition mechanisms for each homologue differ between wet and dry depositions.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are known to have strong toxicity. These compounds are emitted into the atmosphere as by-products from various thermal processes, such as municipal solid waste incineration, and industrial activities. In Japan, over 70% of municipal solid waste is incinerated. The amount of municipal solid waste in Japan is significantly higher compared with those in other countries (Hiraoka and Okajima, 1994). These compounds have been transported in air over long distances and are distributed in various environmental components. Since atmospheric deposition is considered to be the major pathway for the input of PCDD/PCDFs into the biosphere, it is essential to understand their deposition flux and mechanisms. In this study, the flux and

characteristics of PCDD/PCDFs in atmospheric deposition are investigated in order to reveal air-transported contamination levels of these compounds and their atmospheric behavior.

2. Experimental

2.1 Sampling locations

Sampling locations of atmospheric deposition are shown in Fig.1. Sampling points in Tokyo and Yokohama are located in urban areas, the point in Tsukuba is located in a suburban area and the point in Tanzawa is located on a mountaintop. These sampling points, which are situated far from potential sources, were selected to represent the ambient level for each location.
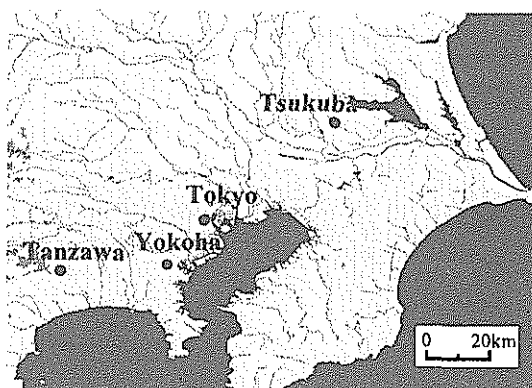

Fig.1. Sampling Locations

2.2 Sample collection

Dry and wet deposition samples were collected in stainless steel pots with 30 cm inner diameter and 30 cm height (see Fig.2, left). The top of the pots was 120 cm above the ground. At the start of sampling, water was added into the pots such that the bottom surface was covered with a thin layer of water. The reason for this is that the efficiency of deposition collection may be influenced by the presence of water, so it is preferable to have water present at all times.

Wet deposition samples were collected with the rain sampler that consisted of a glass funnel with a 45 cm inner diameter and a glass bottle (see Fig.2, right). When the rain sensor detects rain, the cover on the funnel is opened, then rainwater is collected and stored.
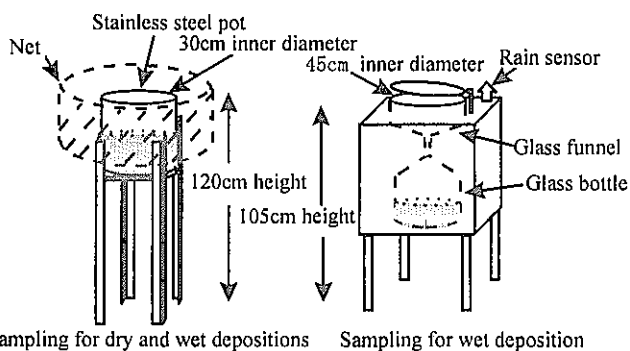
The sampling period was approximately one or two months.

Fig.2. Sampling equipment for PCDD/PCDFs in atmospheric deposition

2.3 *Sample Analysis*

The sample was filtered through a glass fiber filter. The particle fraction was extracted using a Soxhlet extractor with acetone for 16 hours and toluene for 16 hours sequentially, and the aqueous filtrate was shaken with methylene chloride. All extracts were combined. After the addition of a mixture of ^{13}C-PCDD/PCDF internal standards, the extract was treated with concentrated sulfuric acid and cleaned using a series of silica gel, alumina and activated-carbon-impregnated silica gel column chromatography. The final extract was concentrated and analyzed using high-resolution gas chromatography / high- resolution mass spectrometry (HRGC/HRMS; HP6890 GC and VG Autospec-Ultima). We measured tetra- to octa-chlorinated PCDD/PCDFs isomers. These 136 isomers were separated into 87 peaks using a DB-5 GC column (60 m, J&W Scientific). A DB-17 GC column (60 m, J&W Scientific) was used to quantitate 2,3,7,8-substituted compounds that were not separable on DB-5. The mass spectrometer was operated in the EI mode at a resolution R>10,000 (10% valley).

3. Results and Discussion

3.1 *Deposition flux*

Total PCDD/PCDF deposition fluxes are shown in Fig.3, left. Tsukuba samples still remain to be analyzed. The corresponding I-TEQ values are also shown to the right in Fig.3, but TEQ values for PCBs are not included.

From our measurements, the total PCDD/PCDF deposition fluxes ranged from 2.0 to 6.0 ng/m²/day and the TEQ values ranged from 23 to 89 pg/m²/day. Fig.3 indicates that deposition fluxes in the winter were higher in the order of Tokyo, Yokohama, and Tanzawa. The deposition flux for Tanzawa was approximately half the fluxes for Tokyo and Yokohama. The TEQ value of the flux for Tokyo was again the highest of all. There was no significant difference between the values for Yokohama and Tanzawa. Moreover, there was no distinct difference between the fluxes for urban areas in Tokyo/Yokohama and for the rural area in Tanzawa. Based on the observations above , we believe that PCDD/PCDFs are widespread.
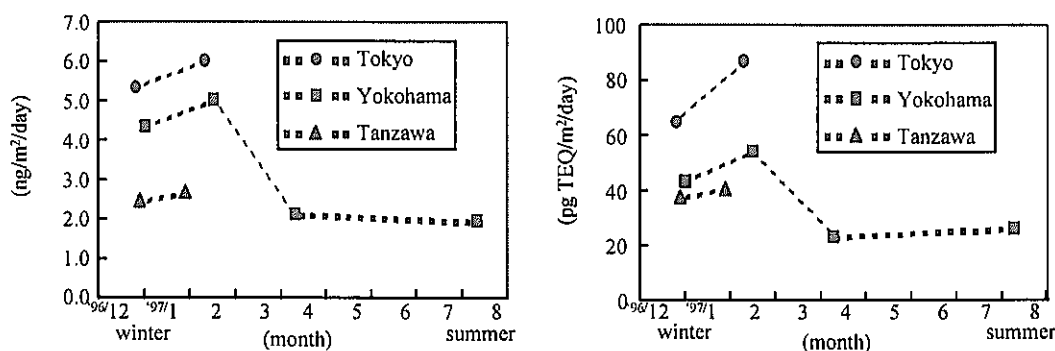
Fig.3. Deposition fluxes of PCDD/PCDFs

Left, actual values ; right, corresponding I-TEQ values

For the results in Yokohama, the deposition flux was higher in the winter than in the summer. There are other studies that show results similar to our result (Hiester *et al.*, 1993 and Fiedler *et al.*, 1997). The reason for this might be that the deposition of particle-bound PCDD/PCDFs is enhanced in the winter because more atmospheric PCDD/PCDFs are bound to particles at lower temperatures (Koester and Hites, 1992).

Kurokawa *et al.* (1992) reported that total PCDD/PCDF deposition fluxes ranged from 1.2 to 3.3 ng/m²/day and the TEQ values ranged from 9.6 to 38 pg/m²/day for April to September in Hakata, Japan. Although these fluxes are less than the results of our measurements, it is reasonable to say that both results are of the same order if considering seasonal differences.

Based on our results, the total annual deposition flux in the Kanto region is estimated to be from 270 to 1000 g TEQ. On the other hand, using the PCDD/PCDF emission data from the Ministry of Health and Welfare of Japan, the total annual emission from municipal solid waste incineration in the Kanto region is estimated to be approximately 800 g TEQ*. The two calculated values are of the same order.

*The annual PCDD/PCDF emission in each prefecture was estimated using

$$E = \frac{A}{\sum_i M_i} \times \sum_i (M_i \times C_i) \times 5000 \times 10^9 ,$$

where E is the annual emission of PCDD/PCDFs in a prefecture (g TEQ/year), A is the amount of waste incinerated in 1994/5 (ton/year), M_i is the maximum amount of waste incinerated in one day by incinerator i (ton/day) and C_i is the concentration of PCDD/PCDFs in the exhaust gas from incinerator i (ng TEQ/Nm³). The volume of exhaust gas is regarded to be 5000 Nm³ per ton of waste incinerated.

3.2 Homologue profile and isomer profile

Homologue profiles of deposition samples are shown in Fig.4. Homologues of the deposition samples were evenly distributed compared with that of Tokyo soil in which OCDD was dominant (Sakurai *et al.*, 1996). The proportion of lower chlorinated homologues were higher in Tokyo than in Yokohama and Tanzawa. In Tanzawa, total PCDF flux was higher than total PCDD flux. Samples in Yokohama were measured through three seasons. The profiles varied slightly from season to season. The profile for the winter ('96/12/16-'97/1/17) was similar to the Tokyo soil profile (Sakurai *et al.*, 1996). The profile in the summer ('97/7/18-8/29) showed that the PCDF concentrations were relatively high. The Yokohama deposition profile ('97/7/18-8/29), Tanzawa deposition profiles, and Yokohama wet deposition profile ('97/12/16-'97/1/17) exhibit homologue profiles similar to that for typical municipal waste incinerator emissions reported by Brzuzy and Hites (1996).

The homologue profiles varied among samples. This could be influenced by seasonal and site-specific factors such as temperature, rainfall and amount of particles.
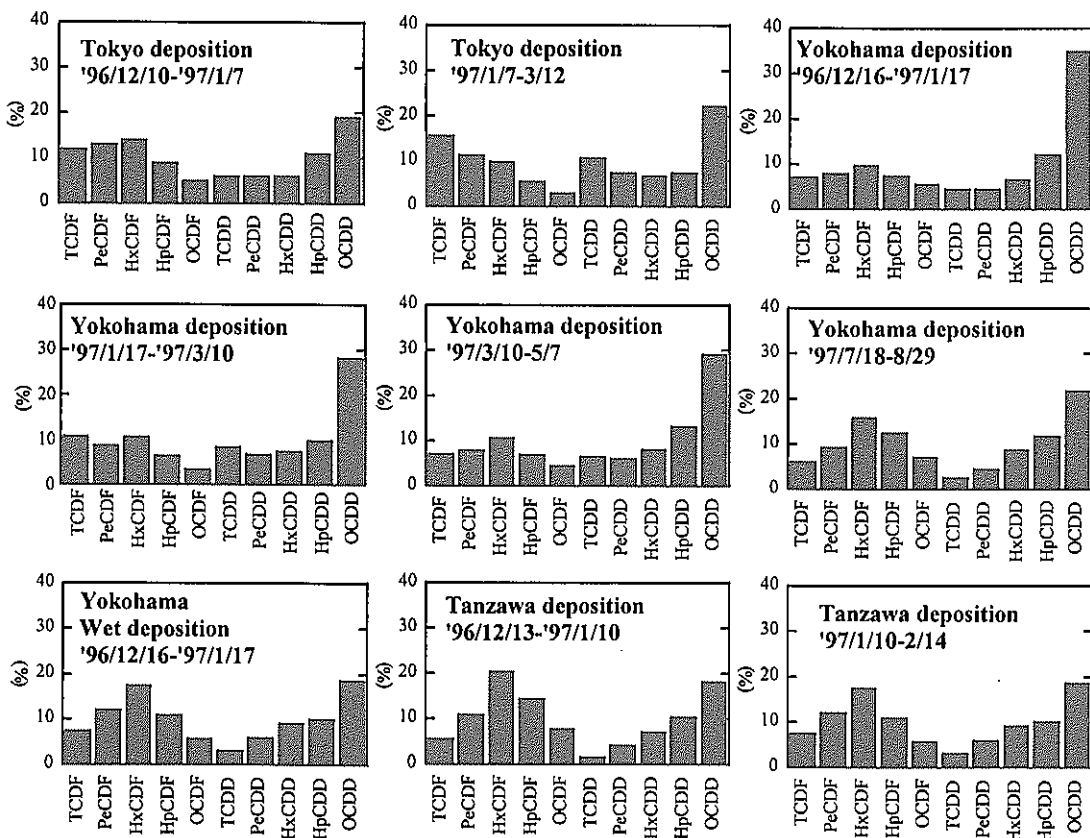

Fig.4. Homologue profiles of deposition samples

We now examine the isomer distribution in each homologue. Isomer profiles were based on the 87 DB-5-separated peaks. The ratios of isomer or isomer cluster values to total isomer value in the corresponding homologue were used in order to neglect the homologue-dependent difference.

Isomer profiles for Tokyo deposition ('96/12/10-'97/1/7), Yokohama deposition ('96/12/16-'97/1/17) and Tanzawa deposition ('96/12/13-'97/1/10) are shown in Fig.5. All isomer profiles were very similar. Moreover, all correlation coefficients for each isomer profile in all samples were above 0.97, which means that isomer profiles in all samples are very similar. A possible explanation for this could be the similar emission patterns of similar sources.
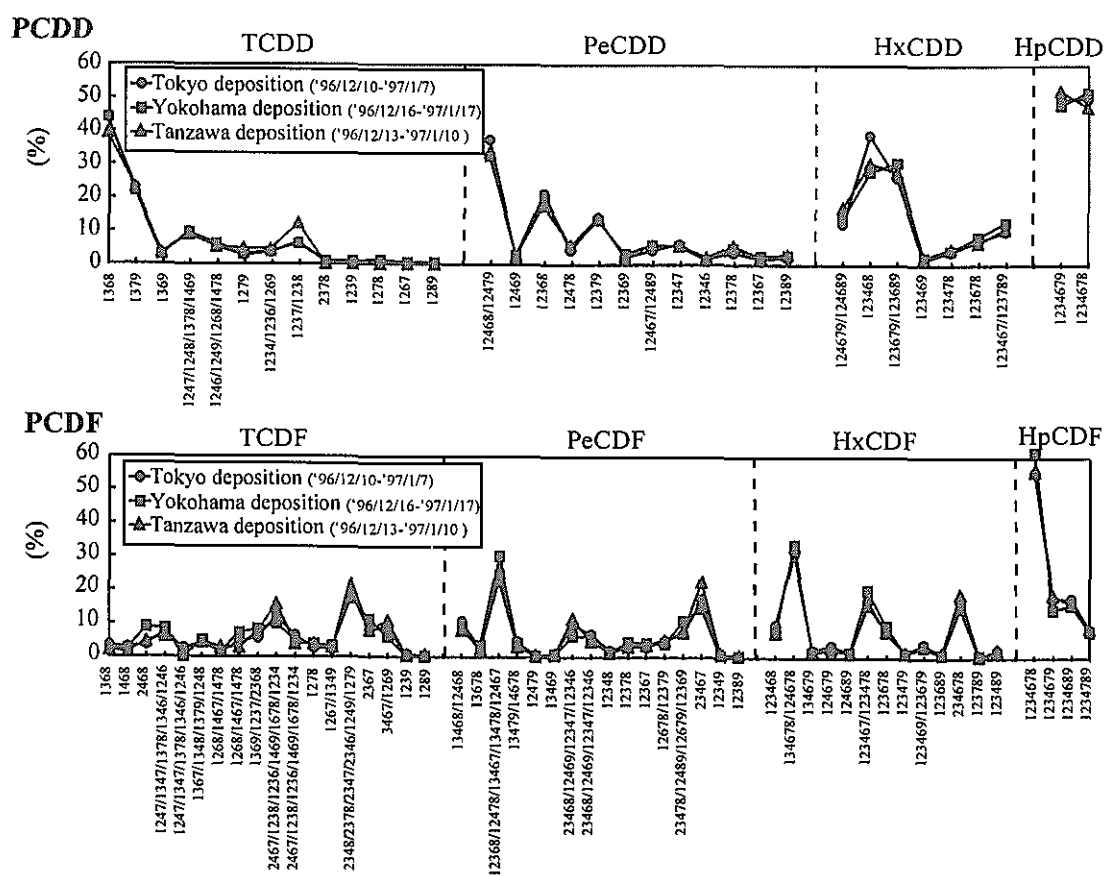

Fig.5. Isomer profiles of deposition samples

We compared isomer profiles of our result with other isomer profiles. The isomer profile of the Tokyo soil (Sakurai et al., 1996) was very similar to those of all deposition samples ($r \geqq$ 0.98). The isomer profile of exhaust gas from a municipal solid waste incinerator in Kanagawa (the extract was given by courtesy of Urano and Kato) almost agree with those of all deposition samples (r=0.92~0.98).

Based on the examination above, we can conclude that isomer profiles of depositions were primarily determined by isomer profiles of emissions from incineration processes, and are relatively stable in air and soil. However, homologue profiles varied among samples. Thus it is reasonable to say that all isomers in the corresponding homologues could behave identically in air and soil. In other words, the environmental behavior of PCDD/PCDFs might depend on the degree of chlorination and structural differences between PCDDs and PCDFs.

Judging from the above, the observations of homologue profiles might lead to the elucidation of their atmospheric behavior. In the same way, the observations of isomer profiles could lead to the elucidation of the contribution of various emission sources.

More work is needed to improve the above results. It is essential to compare deposition profiles with many other emission profiles for all isomers or isomer clusters.

3.3 Wet Deposition

The wet deposition flux and the total (dry and wet) deposition flux for Yokohama ('96/12/16-'97/1/7) are shown in Table 1. The homologue profiles are shown in Fig.4. The wet deposition includes both wet-derived deposition and dry-derived deposition during rain. It is reasonable to say that the wet deposition here is mostly wet-derived deposition. The ratios of the wet deposition to the total deposition among homologues were different. Compared to dry deposition, wet deposition had a stronger effect on the depositions of HxCDF and HpCDF, and a weaker effect on the deposition of OCDD. On the other hand, the isomer profiles in wet deposition and total deposition showed good agreement ($r=0.98$).

The results above suggest that deposition mechanisms for each homologue differ between wet and dry depositions. Due to the limited number of samples, detailed discussion was difficult. Further analysis is required for greater clarification.

Table 1. Total (wet+dry) deposition and wet deposition

	Total ($ng/m^2/day$)	Wet ($ng/m^2/day$)	Wet/Total (%)
TCDF	0.31	0.08	25.9
PeCDF	0.34	0.11	31.6
HxCDF	0.42	0.17	39.8
HpCDF	0.32	0.13	39.7
OCDF	0.24	0.07	30.4
TCDD	0.19	0.04	19.2
PeCDD	0.19	0.05	24.0
HxCDD	0.29	0.07	23.5
HpCDD	0.53	0.08	15.3
OCDD	1.52	0.15	9.8
ΣPCDF	1.62	0.55	34.0
ΣPCDD	2.73	0.38	14.0
ΣPCDD/PCDF	4.35	0.93	21.5

Total: Yokohama Deposition '96/12/16-'97/1/17
Wet: Yokohama Wet Deposition '96/12/16-'97/1/17

4. Acknowledgements

5. References

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