# Flux and Characteristics of Atmospheric PCDD/DF Deposition in the Kanto Region

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## Abstract

Flux and characteristics of atmospheric deposition for polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/DFs) were investigated at four locations in the Kanto region to reveal the levels of these air-transported contaminant compounds, their sources and their atmospheric behavior. Deposition fluxes were higher in winter than in summer. Total PCDD/DF annual deposition fluxes ranged from 450 to 1,300 ng/m$^2$/year and the toxic equivalent (TEQ) fluxes ranged from 5.7 to 17 ng-TEQ/m$^2$/year. Based on the air concentrations in Tokyo measured in a previous study, average and high deposition fluxes in Tokyo urban area were estimated to be 25 and 53 ng-TEQ/m$^2$/year, respectively. From these results, total annual TEQ deposition flux throughout the entire Kanto region was estimated to range from 180 to 1700 g-TEQ/year, while the estimated total annual emission from municipal solid waste incinerators (MSWIs) in the Kanto region was approximately 800g-TEQ/year. Although these estimates include a degree of uncertainty, it is implied that MSWI is a major emission source. In spite of the variety of homologue profiles, the isomer profiles of depositions were similar to those of combustion emissions and Tokyo urban soil. This result suggests that the PCDD/DFs in both depositions and Tokyo soil are derived from combustion emissions, and the isomer profile is stable in air and soil. On the other hand, the PCDD/DFs in the sediments of Tokyo Bay and paddy field could be derived not only from combustion emissions, but also from other sources. The contribution of Co-PCBs to total TEQ is significant in certain locations.

## 1. Introduction

Some congeners of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are known to have high toxicity. These compounds emitted into the atmosphere as by-products from various thermal processes are transported in air over long distances and are distributed into various environmental components. Atmospheric deposition is considered to be the major pathway for the input of these compounds into the biosphere.

According to a rough annual emission estimation of PCDD/DFs in Japan (Hiraoka and Okajima, 1994), the amount of total annual emission is estimated to be from 4.0 to 8.4 kg, with the contribution of municipal solid waste incinerators (MSWIs) being about 75 to 90%. However, since this estimation was based on limited information, their sources and the amount of emissions remains questionable.

In this study, the flux and characteristics of PCDD/DFs in atmospheric deposition were investigated to reveal the levels of these air-transported contaminant compounds, their sources and their atmospheric behavior. Moreover, since coplanar polychlorinated biphenyls (Co-PCBs) have dioxin-like toxicity, the contribution of Co-PCBs to total toxic equivalent (TEQ) for atmospheric deposition was also investigated.

## 2. Experimental

### 2.1 *Sampling locations*

Atmospheric deposition sampling locations are shown in Fig. 1. Sampling points in Tokyo and Yokohama were located in urban areas, the point in Tsukuba was located in a suburban area and the point in Tanzawa was located on a mountain summit.

### 2.2 *Sample collection*

Dry and wet deposition samples were collected in stainless steel pots with an inner diameter of 30 cm and a height of 30 cm (see Fig. 2). The pots were placed so that their tops were 120 cm above the ground. Before sampling, enough water was added to the pots to cover the bottom surface with a thin layer of water. Because the presence of water can make the deposition process more efficient, it is preferable to have water present at all times.

The sampling period was approximately one to two months in December 1996 - March 1998.

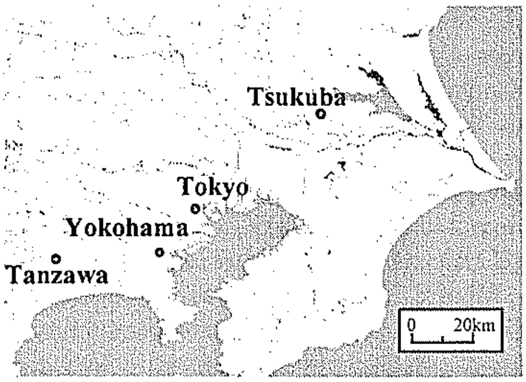

Fig. 1. Sampling Locations

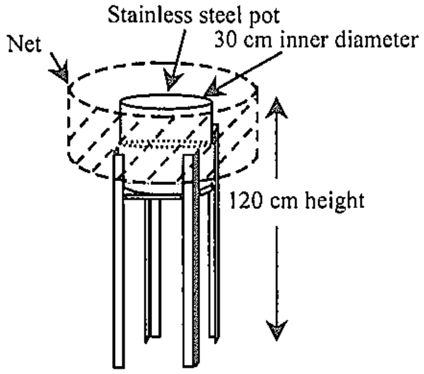

Fig. 2. Sampling equipment for dry and wet deposition

### 2.3 *Sample Analysis*

Samples were filtered through a glass fiber filter and a solid phase (octadecyl bonded phase) extraction disk. After the addition of a mixture of $^{13}$C-PCDD/DF (or $^{13}$C-PCDD/DF/B) internal standards, the filter and disk were extracted with toluene using a Soxhlet/Dean-Stark extractor for 16 hours. The extracts were treated with concentrated sulfuric acid and cleaned using silica gel column chromatography. PCDD/DFs and non-ortho Co-PCBs were divided from mono-ortho Co-PCBs and other PCBs using activated-carbon-impregnated silica gel column chromatography. These final extracts were concentrated and analyzed using high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS; HP6890 GC and VG Autospec-Ultima). The mass spectrometer was operated in the EI mode at a resolution R>10,000 (5% valley). Tetra- to octa-chlorinated PCDD/DF congeners were measured. These 136 congeners were separated into 84 peaks using a DB-5 column (60 m, J&W Scientific). A DB-17 column (60 m, J&W Scientific) was used to quantitate 2,3,7,8-substituted compounds that were not separable on the DB-5 column. Non-ortho Co-PCBs (PCB-77, 81, 126 and 169 (IUPAC No.)) and mono-ortho Co-PCBs (PCB-105 114, 118, 123, 156, 157, 167 and 189 (IUPAC No.)) were also quantitated with the DB-5 column.

## 3. Results and Discussion

### 3.1 *Deposition flux of PCDD/DFs*

Total PCDD/DF deposition fluxes and the corresponding I-TEQ (international toxic equivalent) fluxes are shown in Fig. 3.

Based on seasonal average fluxes, annual average deposition fluxes were estimated to be 1300, 970, 1200 and 450 ng/m$^2$/year, and the annual average TEQ fluxes were estimated to be 17, 11, 8.6 and 5.7 ng-TEQ/m$^2$/year for Tokyo, Yokohama, Tsukuba and Tanzawa, respectively. The deposition fluxes for Tokyo and Kawasaki in the Kanto region reported by the Environment Agency of Japan (1998) were both 29 ng-TEQ/m$^2$/year. Although these fluxes were measured only once in March, they were slightly higher than our results. In this study, the deposition flux in Tokyo was the highest among the sampling points, but it could be less than the background level for urban areas.

Ambient air concentrations for 19 urban sites and 1 rural site in Tokyo were reported by The Tokyo Metropolitan Research Institute for Environmental Protection. The concentration investigated near our deposition sampling point in Tokyo was about two-thirds the average concentration for 19 urban sites, about one-third the highest concentration among 19 urban sites, and about twice the level of the rural concentration. Based on the assumption that deposition flux is proportional to the concentration in air, the average and the high deposition fluxes in Tokyo urban area were estimated to be 25 and 53 ng-TEQ/m$^2$/year, respectively, and the deposition flux in Tokyo rural area was estimated to be 8.0 ng-TEQ/m$^2$/year.

From the results above, the deposition flux in the Kanto region was estimated to range from 5.7 to 53 ng-TEQ/m$^2$/year, while total deposition flux in the entire Kanto region (32,419 km$^2$) was estimated to range from 180 to 1700 g-TEQ/year. In addition, using the PCDD/DF emission data from the Ministry of Health and Welfare of Japan, total annual emission from MSWIs in the Kanto region was estimated to be approximately 800 g-TEQ/year (Ogura, 1998). Comparison of the estimated total emission with the estimated flux range implies that MSWI is a major emission source. Because of the transport of PCDD/DF emissions into outside of the Kanto region, high deposition in local areas near incinerators, and degradation in the environment, other sources should not be neglected.

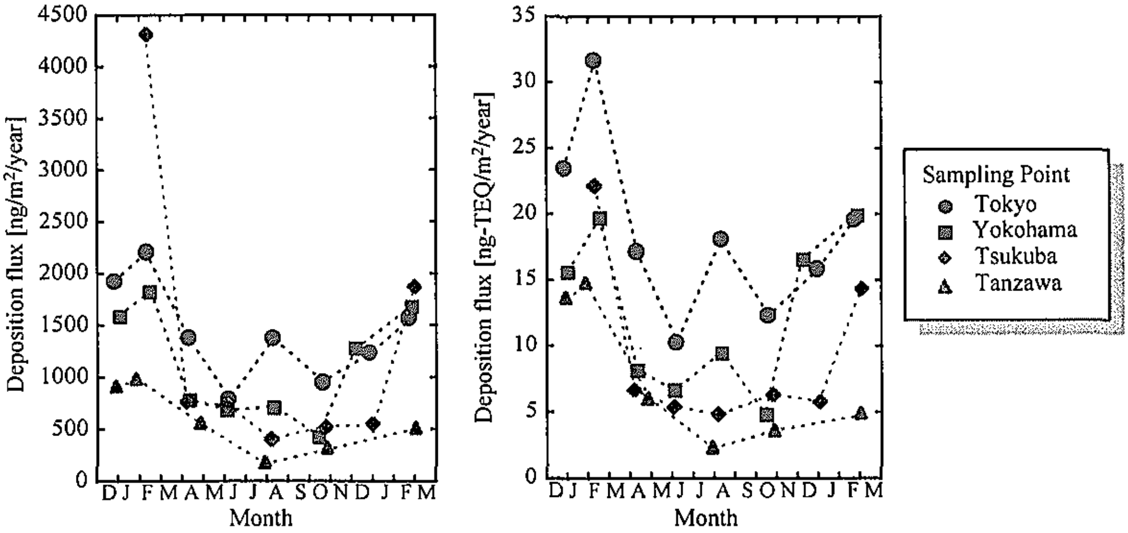

Fig. 3. Deposition fluxes of PCDD/DFs
Left: actual fluxes; right: corresponding I-TEQ fluxes.

### 3.2 *Homologue profile of PCDD/DFs*

Homologue profiles of deposition samples are shown in Fig. 4 which also shows the homologue profiles of emissions from two MSWIs and two industrial waste incinerators (IWIs) (the extracts were given), sediments of Tokyo Bay and paddy field, and urban soil of Tokyo (Sakurai, 1997).

The homologue profiles for the depositions were characterized by an almost uniform homologue. The homologue profiles for the combustion emissions varied among samples. The homologue profiles for combustion emissions are influenced by the type of incinerator, operation, emission controls and type of waste burned (Hiraoka, 1990). In spite of the variety of homologue profiles for combustion emissions, the homologue profiles for the depositions were similar regardless of sampling location and sampling season. The reason could be that the homologue profiles for deposition depend on atmospheric behavior such as degradation, vapor-particle partition and deposition process.

Most of the investigations for sinks have shown that sinks had homologue profiles dominated by OCDD (e.g., Brzuzy and Hites, 1996). Sakurai (1997) reported that most of the sediment in Tokyo Bay and the urban soil in Tokyo also had homologue profiles dominated by OCDD, although the homologue profile of sediment for the paddy field was dominated by TCDD which could be derived from CNP. The reason for the difference between deposition and sinks might result from the degradation occurring after deposition and/or the contribution of previous contaminants.

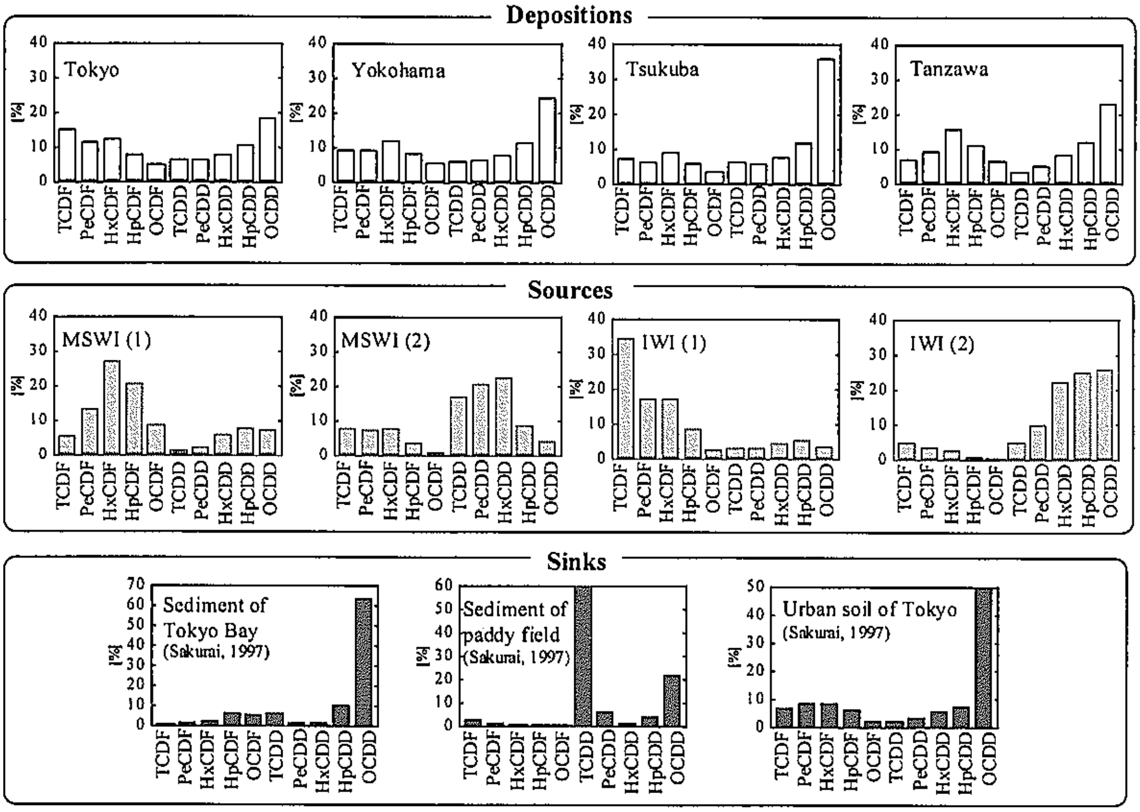

Fig. 4. Homologue profiles

Depositions are the average of the samples for each location analyzed in this study. Sources are incinerator emissions of which the extracts were given and analyzed by the method of this study. Sinks are sediments and soil reported by Sakurai (1997)

### 3.3 *Isomer profile of PCDD/DFs*

In spite of the variety of homologue profiles, the isomer distribution within each homologue is expected to be almost stable in the environment because physical and chemical properties primarily depend on the degree of chlorination and the structural differences between PCDDs and PCDFs. Observations of the isomer profile could reveal the contribution of various emission sources. Therefore, the isomer distribution within each homologue was examined. The isomer profile was based on the 84 DB-5-separated peaks. The proportions of isomer or isomer cluster values to the total

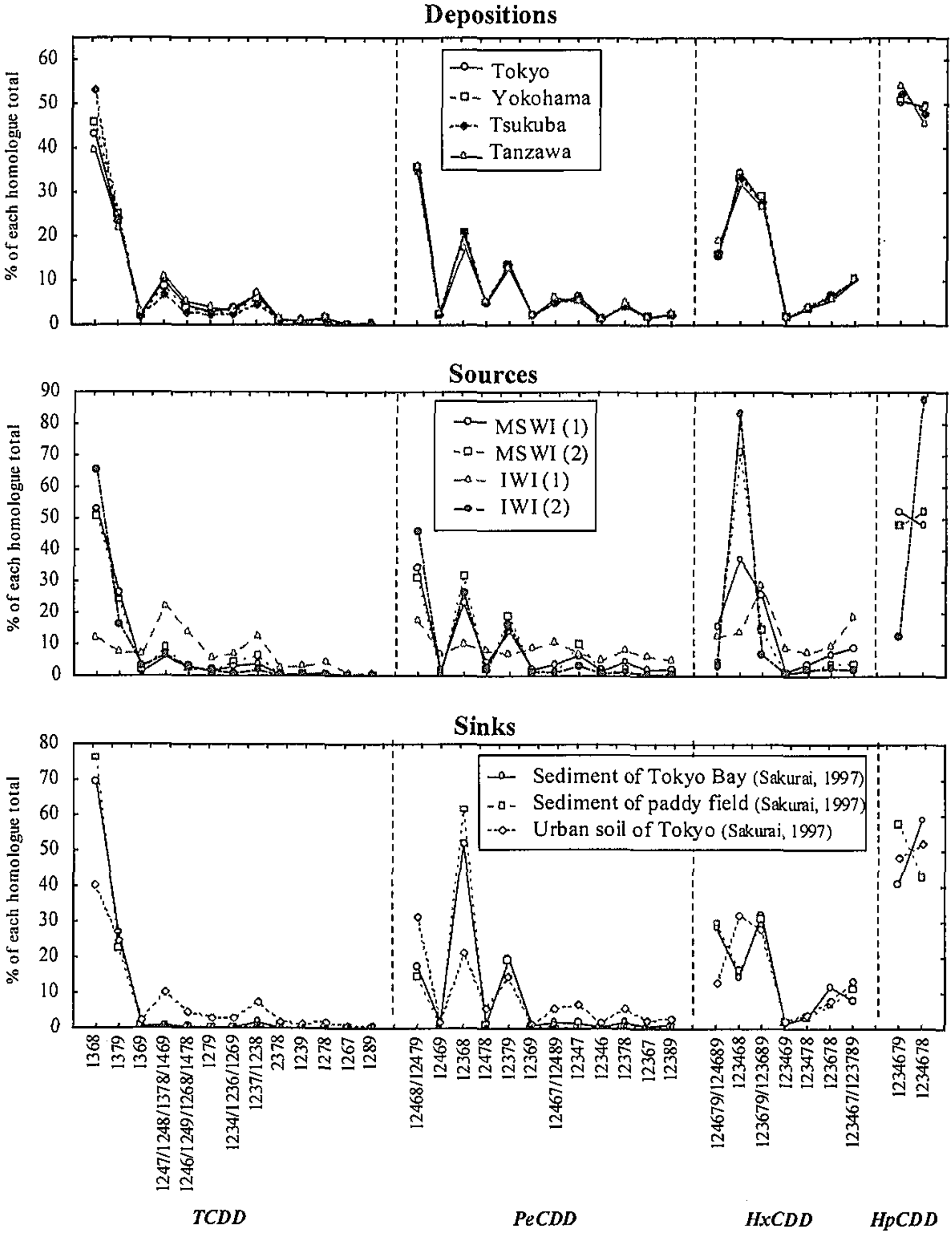

Fig. 5. Isomer profiles for PCDDs

The isomers or isomer clusters are plotted in the order of gas-chromatographic elution and by the ratio to the corresponding homologue total value. Isomer cluster which co-elutes on DB-5 is expressed by '/'. Depositions are the average of the samples for each location analyzed in this study. Sources are incinerator emissions of which the extracts were given and analyzed by the method of this study. Sinks are sediments and soil reported by Sakurai (1997)

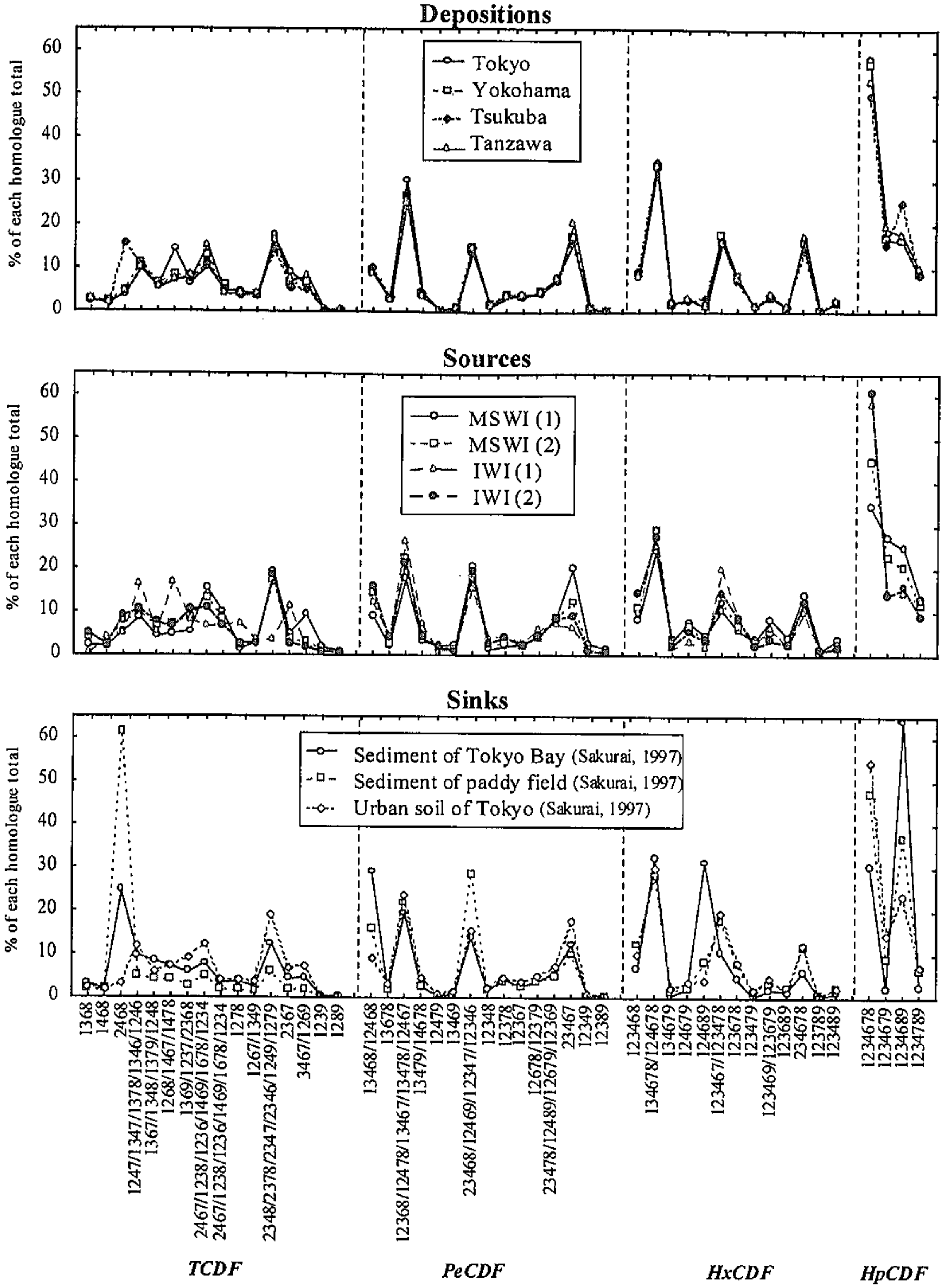

Fig. 6. Isomer profiles for PCDFs

The isomers or isomer clusters are plotted in the order of gas-chromatographic elution and by the ratio to the corresponding homologue total value. Isomer cluster which co-elutes on DB-5 is expressed by '/'. Depositions are the average of the samples for each location analyzed in this study. Sources are incinerator emissions of which the extracts were given and analyzed by the method of this study. Sinks are sediments and soil reported by Sakurai (1997) isomer value within each homologue were used to compensate for the homologue-dependent difference. The average PCDD/DF isomer profiles of depositions for each location are shown in Fig. 5 and 6. The isomer profiles of sources and sinks are also shown.

The isomer profiles in all depositions were very similar regardless of sampling location and sampling season, except the winter samples for Tsukuba, in which some congeners (1,3,6,8-TCDD, 2,4,6,8-TCDF, 1,2,4,6,8,9-HxCDF and 1,2,3,4,6,8,9-HpCDF) were peculiar.

Compared to the similarity of the isomer profiles for depositions, isomer profiles of combustion emissions varied slightly among each other. The isomer profiles of depositions were very similar to that of MSWI (1). It is hard to conclude that the reason for the similarity in the isomer profiles for depositions could result from a uniform combustion or atmospheric behavior. Hoewver, the isomer profiles of depositions match those of combustion emissions.

The isomer profile of the urban soil in Tokyo was very similar to those of depositions, suggesting that PCDD/DFs in the urban soil are derived from the deposition of combustion emissions and are stable in air and soil. On the other hand, the isomer profiles of the sediment in Tokyo Bay and the paddy field showed that the proportions of some congeners (1,3,6,8-TCDD, 1,3,7,9-TCDD, 1,2,3,6,8-PeCDD, 1,2,3,7,9-PeCDD, 1,2,4,6,7,9/1,2,4,6,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, 2,4,6,8-TCDF, 1,3,4,6,8/1,2,4,6,8-PeCDD, 1,2,4,6,8,9-HxCDF and 1,2,3,4,6,8,9-HpCDF) were greatly difference from those of the depositions. Some of these congeners agree with the major congeners of the impurities in herbicides, such as CNP (1,3,5-trichloro-2-(4-nitrophenoxy) benzene) (Yamagishi *et al.*, 1981) and PCP (pentachlorophenol) (Hagenmaier and Brunner, 1987). Thus, PCDD/DFs in the sediments could be derived not only from the deposition of combustion emissions, but also from other sources.

### 3.4 *Influence of atmospheric phenomena on deposition flux*

The deposition flux was higher in winter than in summer. This trend was similar to that reported in other studies (Hiester *et al.*, 1993; Fiedler *et al.*, 1997). Assuming that there is no seasonal change in the amount of emission, then the deposition flux could be influenced mainly by ambient temperature.

The vapor-particle partition of less chlorinated PCDD/DFs varies with seasonal temperature, while more chlorinated PCDD/DFs are primarily present as particle-bound materials in all seasons (Eitzer and Hites, 1989). Because the degradation of PCDD/DFs in the vapor phase could be more efficient than that in the particle-bound phase (Kwok *et al.*, 1995; Koester and Hites, 1992 a) and because deposition flux of PCDD/DFs in the particle-bound phase could be more efficient than that in the vapor phase, the deposition flux could be largely dependent on particle-bound PCDD/DFs. Therefore, the fluxes of less chlorinated PCDD/DFs are expected to be more variable with seasonal temperature than those of more chlorinated PCDD/DFs.

Eitzer and Hites (1989) indicated that the logarithm of vapor-particle partition for a PCDD/DF congener is almost proportional to reciprocal temperature. Assuming that vapor-phase deposition is negligible, PCDD/DF concentration in air is distributed lognormally, and deposition flux is proportional to particle phase PCDD/DF concentration, the logarithm of the flux is proportional to reciprocal temperature. Fig. 7 shows a plot of the logarithm of each homologue flux versus 1000/T for eight samples measured in Yokohama.

Both the slope of the regression line and the correlation coefficient ($r$) generally decreased as the degree of chlorination increased. The results for the other locations showed similar trends. These results were consistent with the expected difference in the variation among homologues.

On the other hand, it was found that the fluxes of more chlorinated PCDD/DFs, which are primarily present as particle-bound phase in all seasons, also increased as temperature decreased. The reasons for enhanced deposition for all homologues in winter could be the high probability of occurrence of inversion layers and reduction in the extent of the atmosphere. Mizuno *et al.* (1990) reported that these phenomena contributed to the enhanced atmospheric SPM concentration in the Kanto region in winter.

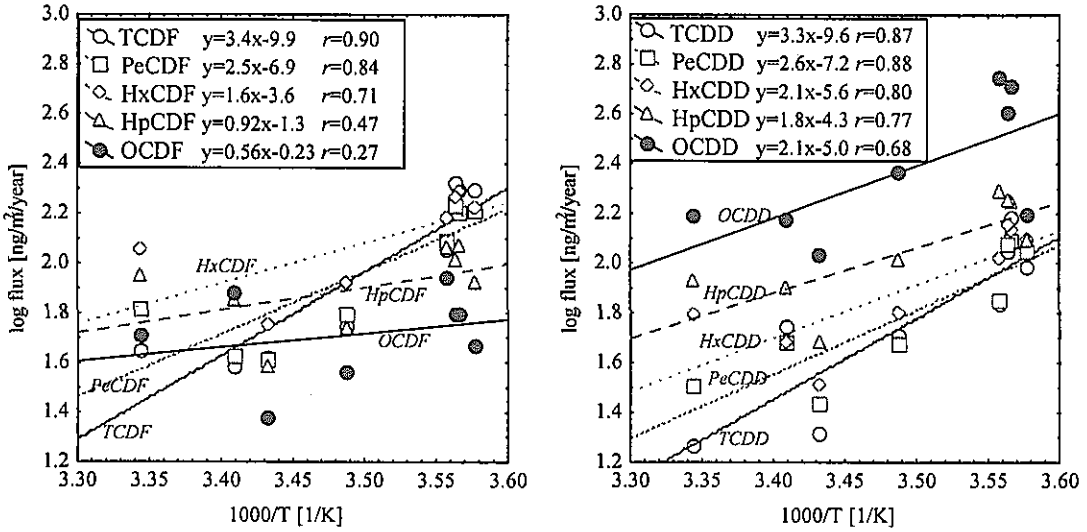

Fig. 7. Influence of ambient temperature on deposition flux

Left: PCDFs; right: PCDDs. This figure shows the plot of the logarithm of each homologue flux versus 1000/T (the average temperature during each sampling period) for eight samples measured in Yokohama.

Deposition flux is also expected to be influenced by the amount of rainfall since most particles containing pollutants are washed out of the atmosphere by rain. The deposition fluxes observed for each homologue were inversely correlated with the amount of rainfall, regardless of the exclusion of temperature difference. Koester and Hites (1992 b) reported that the particle-bound PCDD/DF concentrations in the rain collected were inversely correlated with the amount of rainfall, the reason was thought to be that most particle which contain pollutants are washed out of the atmosphere at the beginning of the rain event. Thus, it is difficult to conclude that deposition flux is correlated with the amount of rainfall.

### 3.5 *The contribution of Co-PCBs to total TEQ*

For some samples, Co-PCBs were analyzed in addition to PCDD/DFs. The cotributions of PCDD/DFs, non-ortho Co-PCBs and mono-ortho Co-PCBs to total TEQ are shown in Fig. 8.

The fractions of Co-PCBs for Yokohama, Tsukuba and Tanzawa were less than 10% of total TEQ, however, the fractions of Co-PCBs for Tokyo were relatively high, and the total Co-PCB TEQ for Tokyo was almost equal to or more than the total PCDD/DF TEQ. According to previous limited investigations, the most of fractions of Co-PCBs for MSWI emission and ambient air were less than 10% of total TEQ (Sakai *et al.*, 1994; Miyata *et al.*, 1994; Kurokawa *et al.*, 1996; Environmental Agency of Japan, 1998). The high fraction of Co-PCBs for Tokyo might be derived from particular sources, such as commercial PCBs and combustion of a particular type of waste. Therefore, it is concluded that the contribution of Co-PCBs to total TEQ is significant in certain locations.

The majority of total Co-PCB TEQ was confirmed to be contributed by non-ortho Co-PCBs in which the fraction of PCB-126 ranged from 94 to 97% of total non-ortho Co-PCB TEQ.

## 4. Acknowledgements

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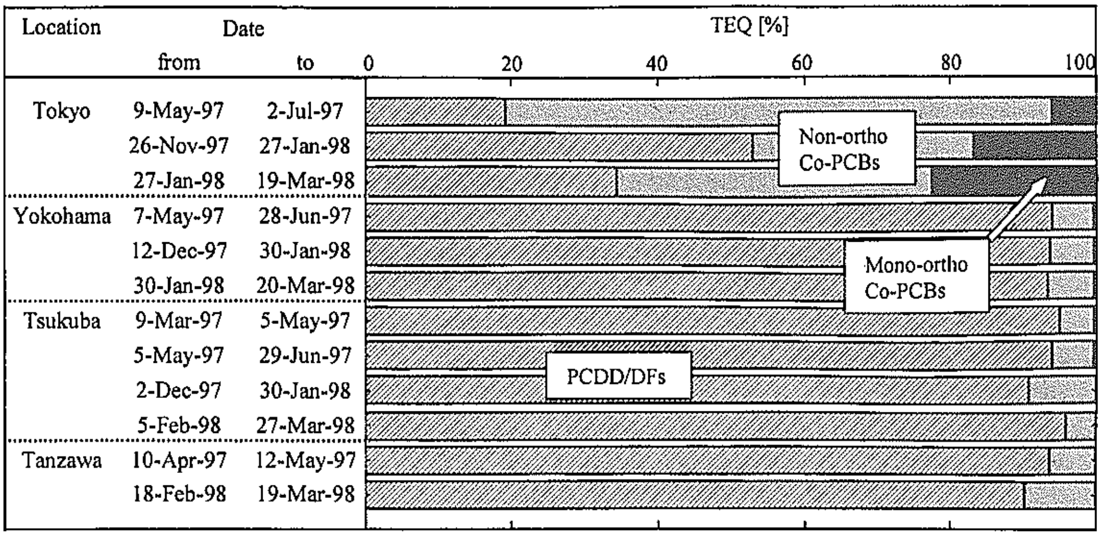

Fig. 8. The contributions of PCDD/DFs, non-ortho Co-PCBs and mono-ortho Co-PCBs to total TEQ
TEF of WHO (1997) was used for Co-PCBs, while International TEF was used for PCDD/DFs. Some congeners of mono-ortho Co-PCBs were not independent peaks, therefore these values would be overestimated.

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