

Flux and Characteristics of Atmospheric Deposition of PCDD/Fs and Coplanar PCBs in the Kanto Region, Japan

Isamu Ogura*, Shigeki Masunaga*[†] and Junko Nakanishi*[†]

* Institute of Environmental Science and Technology, Yokohama National University
79-7 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

[†] CREST, Japan Science and Technology Corporation
4-1-8 Honcho, Kawaguchi, Saitama 322-0012, Japan

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and coplanar polychlorinated biphenyls (Co-PCBs) are emitted into the atmosphere as by-products of a variety of thermal processes, such as municipal solid waste incineration and industrial activities. The amount of waste incinerated in Japan is very high compared with those in other countries [1] and consequently, the ambient air concentrations are relatively high [2]. The Kanto region, which includes the Tokyo metropolitan area and its surrounding areas, is considered to be one of the most polluted areas in Japan because of the high incidence of anthropogenic activities. In this study, since atmospheric deposition is considered to be the major pathway to the biosphere, we investigated the atmospheric deposition of PCDDs, PCDFs and Co-PCBs in the Kanto region to elucidate their fluxes, sources and atmospheric behavior.

Materials and Methods

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.

Dry and wet deposition samples were collected in stainless steel pots (see Fig. 2). Before sampling, enough water to cover the bottom with a thin layer was added to the pots. 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 the period of December 1996 - March 1998.

Samples were filtered through a glass fiber filter and a solid phase extraction disk (C₁₈). After the addition of a mixture of ¹³C-labeled 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. The extracts were divided into the fraction of PCDD/Fs and non-ortho Co-PCBs and the fraction of mono-ortho Co-PCBs and other PCBs using activated-carbon-impregnated silica gel column chromatography. These final extracts were concentrated and analyzed using GC/MS (HP6890 GC and VG



Fig. 1. Sampling locations

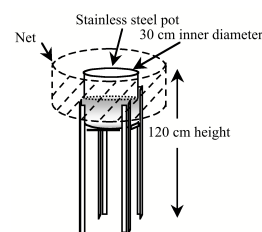


Fig. 2. Sampling equipment

Autospec-Ultima). Tetra- to octa-chlorinated PCDD/F 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 and mono-ortho Co-PCBs were also quantitated with the DB-5 column.

Results and Discussion

Deposition flux of PCDD/Fs

Total PCDD/F deposition fluxes and the corresponding I-TEQ fluxes are shown in Fig. 3. The deposition flux was higher in winter than in summer. Based on seasonal average fluxes, annual average deposition fluxes were calculated to be 1300, 970, 1200 and 450 ng/m²/year, and the annual average TEQ fluxes were calculated to be 17, 11, 8.6 and 5.7 ng-TEQ/m²/year for Tokyo, Yokohama, Tsukuba and Tanzawa, respectively.

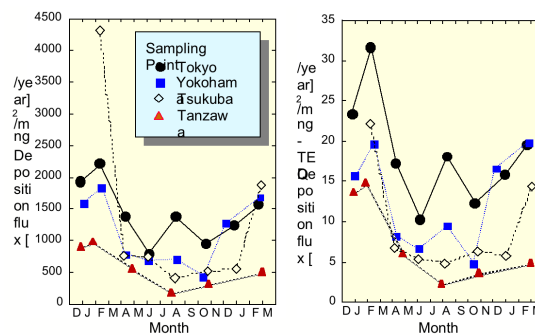
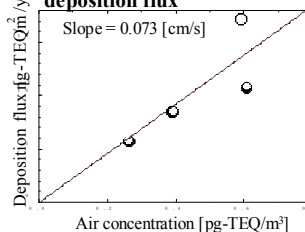


Fig. 3. Deposition fluxes of PCDD/Fs

Fig. 4. Air concentration versus deposition flux



Since air concentrations have not been investigated at our deposition sampling points, those investigated near our deposition sampling points by the municipalities [2-6] were substituted in order to examine the relation between annual average air concentration and annual average deposition flux (Fig. 4). Based on the approximation that deposition flux is proportional to the air concentration, the apparent deposition velocity (the ratio of the deposition flux to the air concentration) was roughly estimated to be 0.073 cm/s. The air concentrations in the Kanto region ranged from 0.055 to 1.5 pg-TEQ/m³ for the 81 data points which were measured at least twice, in summer and winter, by municipalities [2-9]. Using the apparent deposition velocity of 0.073 cm/s, the deposition fluxes corresponding to the air concentrations indicated above were estimated to range from 1.3 to 35 ng-TEQ/m²/year.

On the basis of the above results, total deposition flux in the entire Kanto region (32,419 km²) was estimated to range from 41 to 1100 g-TEQ/year. In addition, using the PCDD/F 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 [10]. The roughly estimated flux did not contradict the estimated emission from MSWIs.

The contribution of Co-PCBs to total TEQ

For some samples, Co-PCBs were analyzed in addition to PCDD/Fs. The contributions of PCDD/Fs, non-ortho Co-PCBs and mono-ortho Co-PCBs to total TEQ are shown in Fig. 5. The fractions of Co-PCBs for Yokohama, Tsukuba and Tanzawa were less than 10% of the 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/F TEQ. According to previous studies, most of the fractions of Co-PCBs for MSWI emission and ambient air were less than 10% of the total TEQ [11-13]. The high fraction of Co-PCBs for Tokyo might be due to specific sources, such as commercial PCBs and combustion of a particular type of waste. Therefore, it is concluded that

the contribution of Co-PCBs to the 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 the total non-ortho Co-PCB TEQ.

Homologue and isomer profiles of PCDD/Fs

Homologue profiles of the annual average depositions at each location are shown in Fig. 6. In spite of the variety of homologue profiles for combustion emissions [14], 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. Comparing the depositions and soil, most investigations have shown that soils had homologue profiles dominated by OCDD [15], while those of the depositions were characterized by an almost uniform homologue.

Next, we examined the isomer distribution within each homologue. The isomer profile was based on the DB-5-separated peaks, except for OCDD/F which include only one isomer. The proportions of isomer or isomer cluster values to the total isomer value within each homologue were used to compensate for the homologue-dependent difference. The isomer profiles in all depositions were similar regardless of sampling location and sampling season. The average isomer profile for the depositions was compared with those for exhaust gas from a MSWI [10] and for soil in Tokyo [16] (Fig. 7). All isomer profiles were very similar, in spite of the different homologue profiles. Thus, we can conclude that all isomers within each homologue can behave identically in air and soil. This is a reasonable assertion because physical and chemical properties primarily depend on the degree of chlorination and the structural differences between PCDDs and PCDFs.

It is considered that isomer distribution patterns are characteristic for the formation of PCDD/Fs in thermal reactions, but all isomer profiles from various incinerators were not necessarily similar [17]. Further research is required in order to improve the elucidation of the contribution of various emission sources.

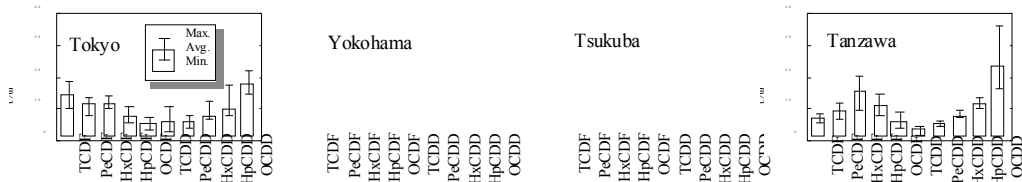


Fig. 6. Homologue profiles of deposition

Acknowledgement

This work has been supported by CREST (Core Research for Evolutional Science and Technology) of the Japan Science and Technology Corporation (JST).

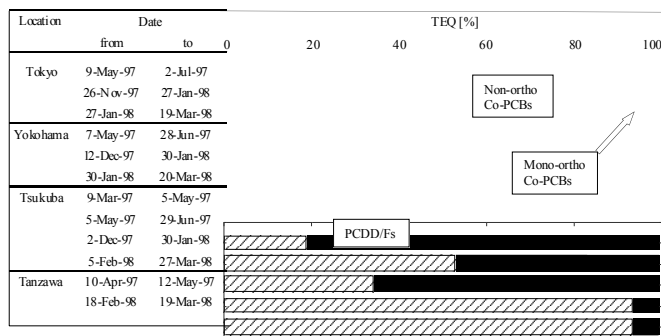


Fig. 5. The contributions of PCDD/Fs, non-ortho Co-PCBs and mono-ortho Co-PCBs to total TEQ

TEF of WHO (1997) was used for Co-PCBs, while International TEF was used for PCDD/Fs. Some congeners of mono-ortho Co-PCBs were not independent peaks, therefore these values are overestimated.

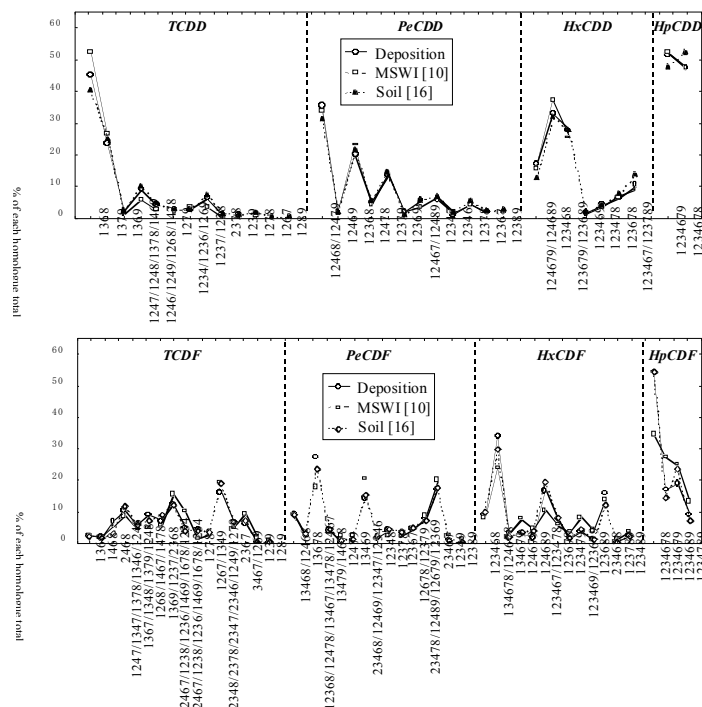


Fig. 7. Isomer Profiles for deposition, MSWI and soil

References

1. Hiraoka, M. and Okajima, S.: *Organohalogen Compounds* **19**, 275-291 (1994)
2. Environmental Agency of Japan: *Web site*, <http://www.eic.or.jp/kisha/199812/53574.html> (1998)
3. The Tokyo Metropolitan Research Institute for Environmental Protection: *Web site*, <http://www.kankyoken.koto.tokyo.jp> (1999)
4. The City of Yokohama: *Web site*, <http://www.city.yokohama.jp/me/cplan/epb/kanshi/press/diox9811.htm> (1999)
5. Kanagawa Environ. Research Center: *Web site*, <http://www.fsinet.or.jp/~k-center/release/199903/24-01.htm> (1999)
6. Ibaraki Prefecture: *Web site*, <http://www.pref.ibaraki.jp/reports/kankyo/pcdh10/> (1999)
7. The City of Chiba: *Web site*, <http://www.city.chiba.jp/env/taiki/dioxine.html> (1999)
8. Chiba Prefecture: *Web site*, <http://www.pref.chiba.jp/DailyLife/News/taikichosa9811-j.html> (1998)
9. The City of Tokorozawa: *Web site*, <http://www.city.tokorozawa.saitama.jp/Town/daioxin/paper0605/01.html> (1998)
10. Ogura, I.: *Proc. of the 1st International Workshop on Risk Evaluation and Management of Chemicals* (1998)
11. Kurokawa, Y., Matsueda, T., Nakamura, M., Takada, S. and Fukamachi, K.: *Chemosphere* **32**, 491-500 (1996)
12. Miyata, H, Aozasa, O., Mase, Y., Ohta, S., Khono, S. and Asada, S.: *Chemosphere* **29**, 2097-2105 (1994)
13. Sakai, S., Hiraoka, M., Takeda, N. and Shiozaki, K.: *Organohalogen Compounds* **20**, 309-313 (1994)
14. Hiraoka, M.: *Waste Management Research* **1**, 20-37 (1990)
15. Brzuzy, L. P. and Hites, R. A.: *Environ. Sci. Technol* **30**, 1797-1804 (1996)
16. Sakurai, T., Suzuki, N., Masunaga, S. and Nakanishi, J.: *Chemosphere* **37**, 2211-2224 (1998)
17. Weber, R. and Hagenmaier, H.: *Chemosphere* **38**, 2643-2654 (1999)