TRANSPORTATION OF PCDD/Fs AND DIOXIN-LIKE PCBs BY RIVERS INTO TOKYO BAY, JAPAN

Norihiro Kobayashi¹, Shigeki Masunaga¹, Yutaka Kameda¹, Yoshimichi Hanai¹ and Junko Nakanishi¹²

1 Graduate School of Environment & Information Sciences, Yokohama National University, 79-7 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, JAPAN
2 Research Center for Chemical Risk Management, National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, 305-8569, JAPAN

Introduction
Environmental pollution by PCDD/Fs and dioxin-like PCBs is a public concern in recent years. In Japan, as main human exposure pathway is consumption of fish and shellfishes¹, investigation of aquatic environment is very important. However, concentrations in river water and seawater are generally extremely low, and data on these environmental media are very limited. In this study, PCDD/Fs and dioxin-like PCBs were measured in seawater in the Tokyo Bay and in six major rivers that flow into the Tokyo Bay. TEQ distributions and homologue compositions are reported. Moreover, the amount of PCDD/Fs transportation by these 6 rivers was estimated, using the monitoring data of river water flows² and suspended solid (SS) concentrations.

Methods and Materials
Sample Collection and analysis
River water samples were collected at 6 stations in 6 different rivers (Edo River (n=1), Naka River (n=1), Ara River (n=1), Sumida River (n=1), Tama River (n=3) and Tsurumi River (n=7)) from April 2001 to March 2003. And seawater samples were collected at 3 stations from the Tokyo Bay in December 2002 and March 2003. Seawater samples were collected at surface layer (-0.5 m) and bottom layer (-10 m or -20 m) in each sampling station. Locations of the sampling stations are shown in Fig. 1.
About 100-200 L of river and seawater was collected by a water pump, then immediately filtered by a filtering device (DS690, GL Science). In this device, particle phase PCDD/Fs and dioxin-like PCBs were trapped in glass fiber filter (GFF, 293mm Φ, pore size 0.5µm) and dissolved phase PCDD/Fs and dioxin-like PCBs, which went through GFF, were trapped in polyurethane foam (PUF, 100mmΦ×50mm×4). After filtering, GFF and PUF were added $^{13}$C-labeled internal standards, then Soxhlet-extracted with toluene for 16 hours. And then, they were cleaned by a H$_2$SO$_4$ silica gel column and fractionated by an active carbon column. The final PCDD/Fs and dioxin-like PCBs fraction was spiked with $^{13}$C-labeled recovery standards for HRGC/MS analysis. All 1-8Cl PCDD/F and 12 dioxin-like PCB (IUPAC No. 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189) congeners were analyzed in this study. 4-8 Cl PCDD/Fs and dioxin-like PCBs were quantified by a DB-5 column, and 1-3 Cl PCDD/Fs were quantified by a SP-2331 column.

Results and Discussion

**TEQ distributions in river and seawater**

TEQ values (including 12 dioxin-like PCB congeners) in river and seawater samples are shown in Fig. 2. In both particulate and dissolved phase PCDD/Fs and dioxin-like PCBs, river water had several to dozens times higher TEQ compared with the Tokyo Bay seawater. It can be assumed that PCDD/Fs and dioxin-like PCBs carried by the river were diluted by seawater, resulting in low concentration in the Tokyo Bay. In particulate phase PCDD/Fs and dioxin-like PCBs in seawater, differences in TEQ were not observed among stations except for the surface layer of the St. A, which is located in front of the mouths of large rivers. Thus, particulate phase PCDD/Fs and dioxin-like PCBs in the river deposits immediately after the river water flowed into the bay. On the other hand, TEQ in dissolved phase PCDD/Fs did not differ among sampling points. From these results, it is considered that dissolved phase PCDD/Fs and dioxin-like PCBs transported from the river is immediately diluted with seawater, revealing no marked variation in the bay.

**Homologue Concentrations**

Fig. 3 shows PCDD/Fs homologue concentrations in several river water and seawater samples. In Naka River (Fig. 3-B) and Ara River (Fig. 3-C), OCDD was the most abundant homologue, while...
Di (Cl₂) CDDs was the most abundant homologue in Tama River (Fig. 3-C) and Tsurumi River (Fig. 3-F). Edo River’s homologue profile (Fig. 3-A) was in between of these two profiles. In seawater, DiCDDs was the most abundant homologue in every sampling station except for the lower layer of St. A. It is considered that these differences in homologue profiles were the results of differences in contributions of sources. Source identification using congener profiles was described in the other paper submitted to dioxin 2003.

*Fig. 3: Average PCDD/Fs homologue concentrations of river water and seawater samples. Both are expressed in pg/L.*

**Estimation of amount of PCDD/Fs transportation by rivers**
Using measured concentrations, amounts of PCDD/Fs transportation by each river to the Tokyo Bay in 2001 were estimated. Daily amount of particulate phase PCDD/Fs was estimated by multiplying daily SS concentration by the average PCDD/Fs concentration per SS (pg/g). Daily amount of dissolved phase PCDD/Fs was estimated by multiplying daily river water discharge by the average PCDD/Fs concentration (pg/L). And the total amounts of PCDD/Fs in 2001 were summed from these estimated daily amounts. It was estimated that 2700 g (particulate phase) and
740 g (dissolved phase) of total 1-8 Cl PCDD/Fs were transported by these six rivers in 2001. Judging from river water discharge, it is considered that rivers other than these 6 rivers have little influences to the whole amount that was transported into the Tokyo Bay. Converted into TEQ (including 12 dioxin-like PCB congeners), it was estimated that 7.2 g-TEQ (particulate phase) and 0.61 g-TEQ (dissolved phase) were transported in 2001.

The amounts of each PCDD/F homologue transported by the rivers are shown in Fig 4. It was estimated that OCDD was the most transported homologue (1500 g/year). Assuming that there are no sources other than river water and the transported PCDD/Fs by the rivers are immediately diluted in the Tokyo Bay, homologue profile shown in Fig. 4 should be in agreement with homologue profiles of seawater in the Tokyo Bay (Fig.3-G, H, I, J, K, L). However, all of homologue profiles of seawater except for the bottom layer of St. A (Fig. 3-J) had the high percentage of lower chlorinated PCDD/Fs, especially DiCDDs, and the percentage of OCDD was not high. Thus, higher chlorinated PCDD/Fs, such as OCDD, might not have carried to the mouths of rivers, or even if they are carried, they have deposited immediately after entering the bay and they are not transported to a distance. These results are consistent with the results of TEQ distributions in Tokyo Bay (Fig. 2), because higher chlorinated PCDD/Fs are mostly existed as a particulate phase.

![Fig. 4: Total amount of PCDD/Fs transportation for each homologue.](image)

**Acknowledgements**

This work has been supported by Grant-in-aid for the Creation of Innovations through Business-Academic-Public Sector Cooperation (No. 12323) and the 21st Century COE Program "Bio-Eco Environmental Risk Management", Japanese Ministry of Education, Culture, Sports, Science and Technology.

**References**