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SOURCE IDENTIFICATION OF PCDD/FS AND DIOXIN-LIKE PCBS IN RIVERS FLOWING INTO THE TOKYO BAY, JAPAN

Norihiro Kobayashi[1], Shigeki Masunaga[1] and Junko Nakanishi[1, 2]

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

In recent years, environmental pollution by PCDD/Fs and dioxin-like PCBs is a public concern. As main human exposure pathway is consumption of fish and shellfishes [1)] in Japan, investigation of aquatic environment is very important. However, concentrations in river water and seawater are generally extremely low, and data on these environmental mediums 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, concentrations and compositions were reported and the amount of PCDD/Fs and dioxin-like PCBs transportation by these 6 rivers was estimated in the other paper submitted in Dioxin 2003 [2)]. In this paper, source identification of PCDD/Fs and dioxin-like PCBs are presented. Moreover, amount of PCDD/Fs and dioxin-like PCBs transportation by each source were estimated. There are few reports which estimate quantitatively the contributions of sources in an environmental medium. However, in order to develop effective countermeasures against dioxin pollution, information about contributions of different PCDD/F and dioxin-like PCB sources to the environmental medium is necessary.

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

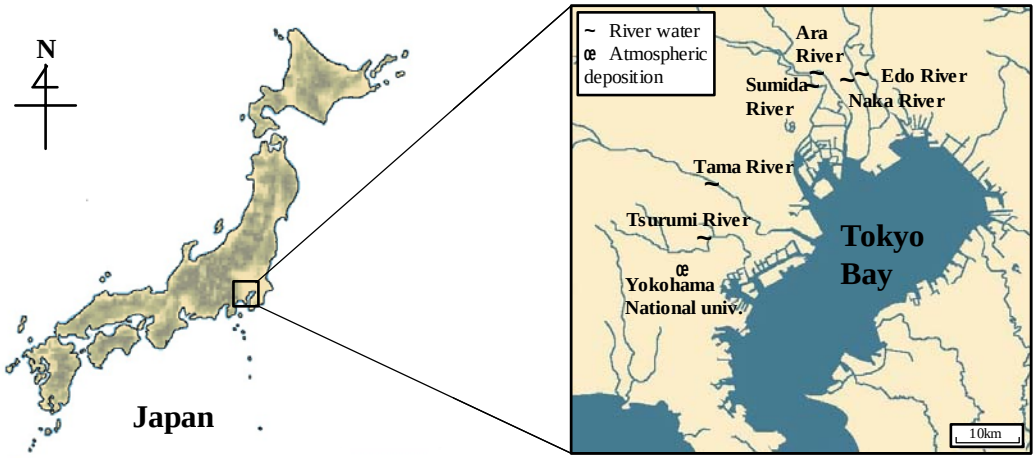

Fig. 1: Locations of the sampling stations.

April 2001 to March 2003. And Atmospheric deposition samples were collected at the Yokohama National University from June 2001 to March. 2002 (n=7). Locations of the sampling stations are shown in Fig. 1. The details of sampling and analytical procedures were reported in the other paper submitted to Dioxin 2003 [2] and atmospheric deposition samples were also analysed by the same method used for river water and seawater samples, and hence the details were not given.

Results and Discussion

Comparison of congener profiles of river water and atmospheric depositions

Fig. 2 shows average congener profiles of several river water samples and atmospheric depositions. Congener profiles are shown in percentage in each homologue. MoCDDs, DiCDDs, OCDD and OCDF are not shown in Fig. 2, because only one congener was in existence or detected in these homologues. Congener profiles in river water were basically similar to those of atmospheric depositions. Thus, it is assumed that PCDD/Fs in river water are mainly influenced by the atmospheric depositions originating from combustion sources. Several congeners, however, showed significantly higher proportions within each homologue compared with atmospheric depositions. For example, 1,2,4,6,8,9-HxCDF, 1,2,3,4,6,8,9-HpCDF, 1,3,6,8-TeCDD, 1,3,7,9-TeCDD and 1,2,3,6,8-PeCDD showed higher proportions, especially in Ara River, Naka River (not shown) and Sumida River (not shown). These results are explained by the influences from impurity of the PCP and CNP [3], which were heavily used in Japan as herbicides. And 2,4,8-TrCDF, 1,3,9/2,3,7-TrCDD, 1,2,8-TrCDD and 1,2,3,7/1,2,3,8-TeCDD showed higher proportions, especially in Tama River and Tsurumi River (not shown). It is reported that these congeners existed as the impurity of triclosan (Irgasan DP300) [4), 5), 6), 7)], which is widely used as germicides

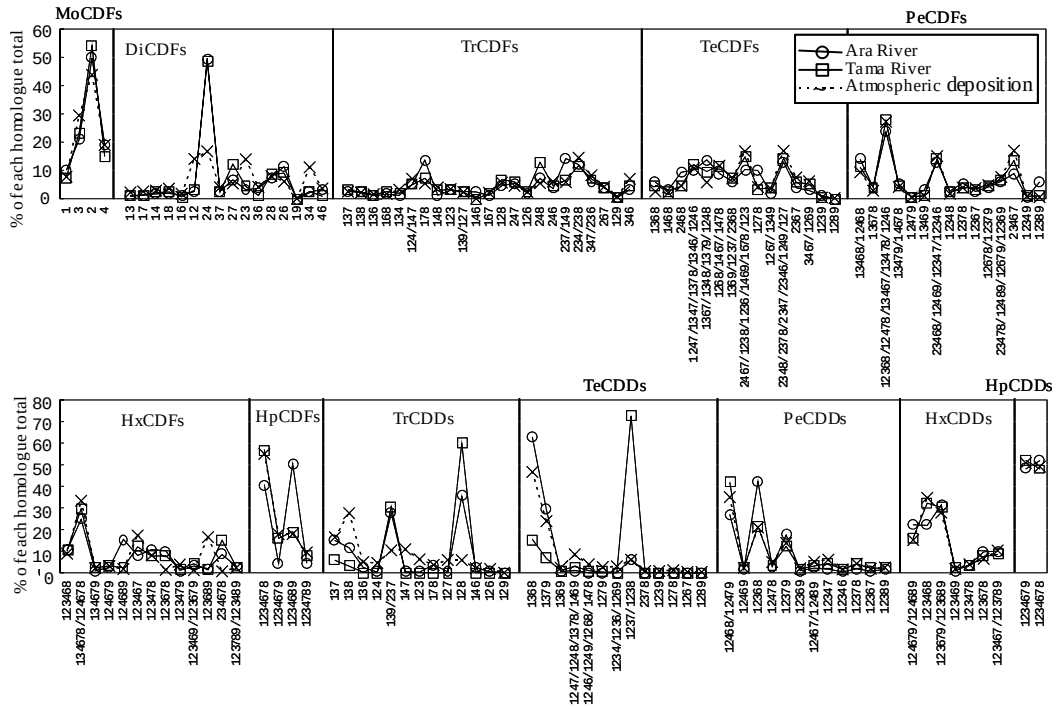

Fig. 2: Average congener profiles of the river water and the atmospheric depositions. The proportions of a congener or congener cluster within each homologue are plotted according to the order of gas-chromatographic elution of SP-2331 (1-3 Cl) or DB-5 (4-7 Cl).

and antiseptics. However, there is no report that triclosan includes 2,3,7,8-substituted PCDD/Fs congeners. Thus, influences of triclosan to TEQ may be negligible. To estimate the contributions of these sources to total TEQ in river water, chemical mass balance (CMB) approach was used in this study.

Estimation of contributions of sources by a chemical mass balance (CMB) approach

The contributions (S_j) of sources j to river water were estimated by minimizing χ^2, as shown by equation 1.

$$\chi^2 = \sum_{i=1}^{k} \left(\frac{1}{C_i} \left(C_i - \sum_{j=1}^{p} a_{ij} S_j \right) \right)^2 \qquad (1)$$

Where a_{ij} is the mass fraction of congener i for source j, k is the number of congeners, and p is the number of sources. The details of this method were described by Ogura et al. [8]. Contributions of sources to measured congener profiles in river water were first determined for each 4-8 Cl PCDD/F homologue and they were summed. It was assumed that incineration emission and impurity of agrochemicals (PCP and CNP) are the sources of PCDD/Fs in river water in Japan. As substitutes for PCDD/F congener profiles of incinerator emissions of PCDD/Fs, those of atmospheric depositions obtained from this study were used in this estimation. Congener profiles of impurity of agrochemicals were obtained from the concentrations of PCDD/Fs congeners in PCP and CNP reported by Masunaga et al. [3]. Congener profiles of dioxin-like PCB sources used in this estimation were the same to those reported by Ogura et al. [8].

Contributions of sources to river water samples

Fig. 3 shows the results of source contribution of PCDD/Fs and dioxin-like PCBs, which were combined and converted to TEQ. Differences between measured TEQ values and TEQ values predicted by a CMB were interpreted as the contributions of unknown sources of PCDD/Fs and dioxin-like PCBs. In Tama River and Tsurumi River, it was estimated that more than 85% of total TEQ originated from combustion source. While, in other 4 rivers, contributions of other sources except for the combustion were higher than Tama River and Tsurumi River. Especially in Sumida River, contribution of combustion source was less than 50%. Differences in the land use in the river basin might be reflected in the result of estimation.

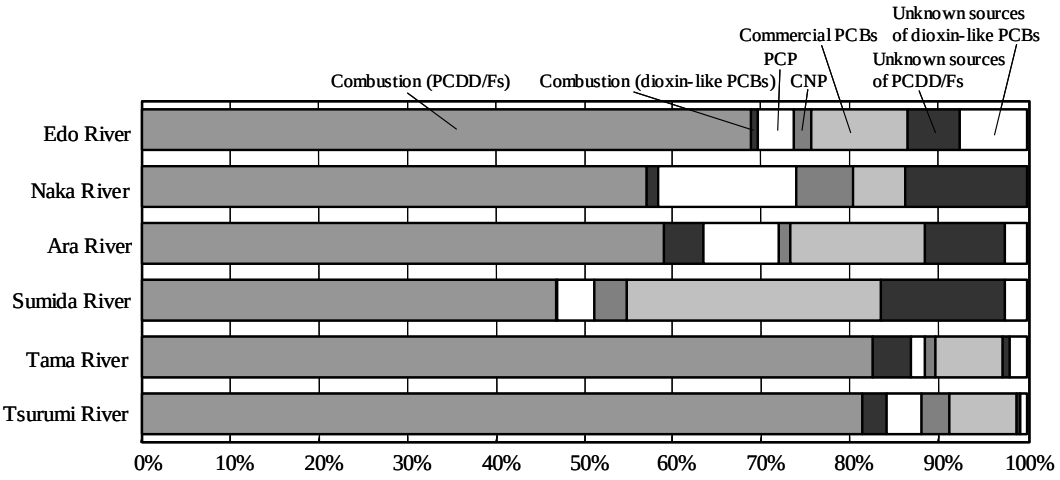

Fig. 3: Contributions of different sources to river water.

In the other paper submitted to dioxin 2003 [2], we estimated the amount and TEQ of PCDD/Fs and dioxin-like PCBs transportation to Tokyo Bay by these rivers in recent years. 7.8 g-TEQ (including 12 dioxin-like PCB congeners) were transported by sum of these 6 rivers in 2001. Based on this result, TEQ of PCDD/Fs and dioxin-like PCBs transportation by each source were estimated, assuming that contributions of sources in the same river are constant in recent year. Fig. 4 shows estimated contribution of each source to total TEQ as the sum of these 6 rivers transported to the Tokyo Bay. It was estimated that combustion source accounted most for total TEQ (64%) and 5.0 g-TEQ were transported to the Tokyo Bay. And it was also estimated that PCP, CNP and commercial PCBs accounted for 23 % (1.8 g-TEQ) of total TEQ of transportation and they were found to be still transported by rivers although they have been prohibited to use for the past several years (CNP), two decades (PCP) and three decades (commercial PCBs). These results show that PCDD/Fs and dioxin-like PCBs from these sources will not decline soon and continue to be transported in the future.

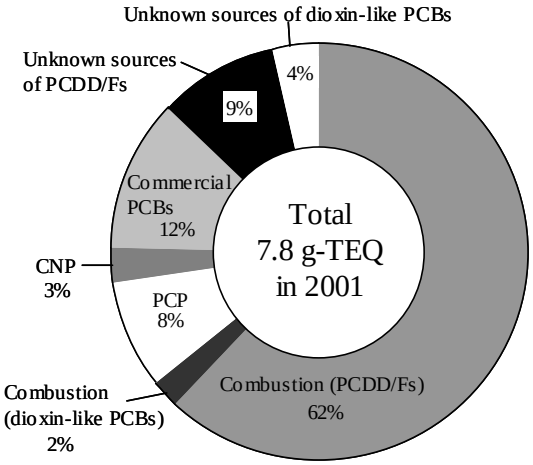

Fig. 4: Contributions of sources to the total TEQ of PCDD/Fs and dioxin-like PCBs transportation.

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