DISTRIBUTION AND SOURCE OF PCDD/Fs AND Co-PCBs IN THE TONE RIVER AREA, JAPAN

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Introduction

Since dioxins (polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs), and coplanar polychlorinated biphenyls (Co-PCBs)) are well known as toxic environmental pollutants, many researches with regard to probe of their formation mechanisms or estimation of their emitting sources have been aggressively studied all over the world. Mainly, combustion processes such as municipal incinerator could form PCDD/Fs in Japan [1)]. Furthermore, it is well known that their formation has also close relation to agricultural operation, that is, some PCDD/Fs are contained in a kind of pesticide as impurities [2, 3)]. Pentachlorophenol (PCP) and chloronitrophen (CNP), which could be contained them as impurities, are typical pesticides. These pesticides are a kind of herbicide widely used in Japanese paddy field in the past, and the use of them could cause the environmental pollution by PCDD/Fs. Therefore, it is extremely important to understand estimation of their emitting sources and their behavior in agro-environmental media.

The Tone River was selected for the present study on contamination by dioxins. It has the second longest river and the largest area of the basin in Japan. Especially, the lower part of the river, which corresponds to the area of about 90 km from Toride City (Ibaraki Prefecture) to Choshi City (Chiba

Prefecture), has extensive paddy fields. Furthermore, Kashima industrial area is located on the north of the basin.

In the present study, we investigate the actual circumstances of pollution by dioxins in the lower part of the river, and estimate their emitting sources based on the distribution and patterns of dioxins in samples obtained from each sampling point.

Materials and Methods

All PCDD/Fs and Co-PCBs used as internal, recovery and calibration standards were purchased from Wellington Laboratories (Guelph, Ontario, Canada). All other chemical used were for organic trace analysis and were obtained from Kanto Kagaku (Tokyo, Japan).

Collected sediment samples were air-dried. On the other hand, water samples were filtrated and concentrated on glass filter and C_{18} solid phase extraction disk. These were Soxhlet extracted with toluene for more than 16 hrs. After concentration of the extracts, the residues were applied to multi-layer silica gel column and to active carbon column. *n*-Hexane was used to elute dioxins from the multi-layer silica gel column. Dichloromethane/*n*-hexane (1:3, v/v) was used to collect mono-*ortho* Co-PCBs and toluene was used to collect non-*ortho* PCBs, PCDD/Fs. Finally, each fraction was concentrated under nitrogen stream.

Identification and quantification were performed using HR-GC/MS. Separation was achieved on a HP 5890/5971 instrument equipped with a DB-5MS for PCDD/Fs with 7 and 8 chlorine atoms, and Co-PCBs or SP2331 column for PCDD/Fs with 4, 5, and 6 chlorine atoms with a 1 µL splitless injection.

Results and Discussion

For the purpose of the present study, two sampling points were selected. The first sampling point is located on this side of meeting of three rivers, the Tone River (T), the Hitachi-Tone River (HT), and the Kurobe River (K) and the second sampling point is located near the Tone Kamone Bridge (TK). Firstly, congener profiles of dioxins in sediment and water samples collected from these rivers were analyzed. As shown in Figure 1, in the congener profiles of TeCDDs, 1,3,6,8-TeCDD and 1,3,7,9-TeCDD were significantly detected. It is well known that these TeCDDs are contained as impurities in herbicide CNP [2, 3]. Although congener profiles of TeCDDs originated from combustion processes are nearly similar to them, it is difficult to affirm that it is pollution originated from impurities in these pesticides. In the case of the congener profiles of TeCDFs, there are great differences between these emitting sources. Especially, in the congener profiles originated from impurities in pesticides, 2,4,6,8-TeCDF was significantly detected. The congener profiles of TeCDFs in three rivers were considered based on the finding. Consequently, we confirmed the congener profiles originated from combustion processes in the sediment sample (HT) and water samples (HT and T) (Figure 2). On the other hand, we confirmed the congener profiles originated from impurities. Since the industrial area (Kashima) is situated on north of the sampling point, it was suggested that a cause of dioxin emission is due to be exhaust from the industrial establishments. Next, the sediment and the water samples collected from the second sampling point were also similarly analyzed. The congener profiles were nearly similar to ones originated from impurities.

In summary, the congener profiles of dioxins in each sample collected from each sampling point reflect the environment around the lower part of the Tone River selected in this study. It was suggested that the actual circumstances of pollution by dioxins in aqueous animals live in each river are understood, and then it is essential to inspect the environmental behavior in the Tone River and the related rivers around it in the future.

Acknowledgement

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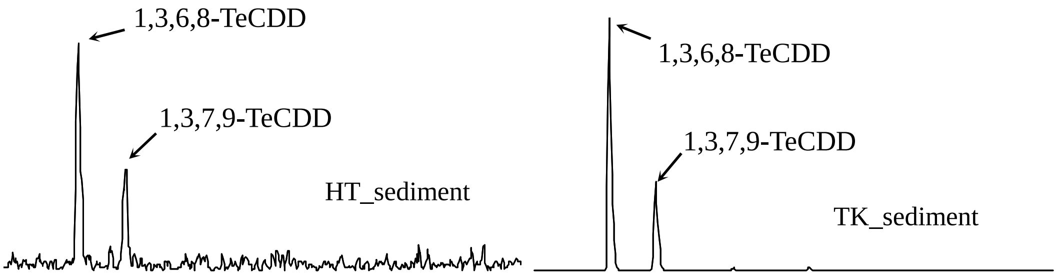

Figure 1. Congener profiles of TeCDDs in sediment samples.

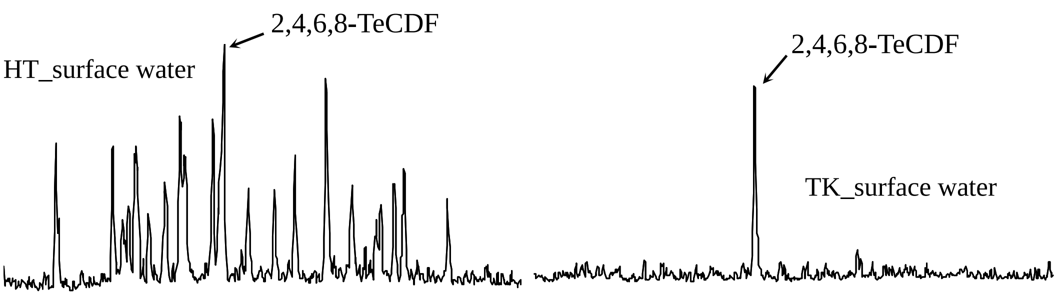

Figure 2. Congener profiles of TeCDFs in surface water samples.