CONGENER PROFILES OF PCDDs, PCDFs, AND COPLANAR-PCBs IN SEDIMENT FROM LAKE SUWA IN JAPAN

Yoshinori Ikenaka[1], Heesoo Eun[2], Eiki Watanabe[2], Yuichi Miyabara[1]

[1]Research and Education Center for Inlandwater Environment, Shinshu University, 5-2-4 Kogandori, Suwa, Nagano, 392-0027, Japan

[2]National Institute for Agro-Environmental Sciences, 3-1-3, kannondai, Tsukuba, Ibaraki, 305-8604, Japan

Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and coplanar PCBs (Co-PCBs) have strong toxicity, therefore health effects and sources of these compounds have been actively studied. Major sources of PCDDs, PCDFs, and Co-PCBs are among other chemical synthetics, municipal incineration and chlorine bleaching. The source of PCDDs, PCDFs, and Co-PCBs can be identified by its congener profile[1)].

Lake Suwa (36°3'N, 138°5'E) is a shallow eutrophic lake located in central Japan with average depth of 4.0 m and maximum depth of 6.3 m. Its surface and drainage area is 13.3 and 531 km^2, respectively. About 12 % of drainage area is utilized as agricultural purpose, and about 10 % is commercial and residential area. Various artificial pollutants drain into lake through the rivers, and accumulate in the lake sediment. Especially, PCDDs, PCDFs, and Co-PCBs tend to be adsorbed to fine particles and persisted in sediment for a long period since they are hydrophobic and persistent pollutants. Thus, lake sediment can be good sample representing the chemical pollution of drainage area. According to the governmental investigation, the total concentrations of PCDDs, PCDFs, and Co-PCBs were 30~60 pg-TEQ/dry-g in sediment of Lake Suwa. However, there is no information on their main sources in the drainage area of Lake Suwa.

In the present study, we investigated congener profiles of PCDDs, PCDFs, and Co-PCBs in the sediment from Lake Suwa, and elucidate the sources of dioxins. We also investigated dioxins in

river sediment, suspended particulate matter (SPM), and soil of paddy field and road dust in the drainage area.

Materials and Methods

To measure the concentration of PCDDs, PCDFs, and Co-PCBs, sediment was collected using Ekman grab from Lake Suwa and river in the drainage area. The soil of paddy field was also collected. Collected samples were air-dried in the laboratory at room temperature (20). SPM was collected using high - volume air sampler near the lake. Each sample was weighed, and Soxhlet extracted with toluene for 19 hours. These extracts were spiked with ^{13}C-PCDDs, PCDFs, and Co-PCBs isomers as internal standards. Then, it was cleaned-up by silica gel column and activated carbon column chromatography. n-Hexane was used to elute the PCDDs, PCDFs, and Co-PCBs fraction from a silica gel column. Mono-ortho PCBs and di-ortho PCBs were eluted with dichloromethane/n-hexane (25/75, v/v), and non-ortho PCBs, PCDDs and PCDFs were eluted with toluene from the activated carbon column. Each eluent was concentrated under nitrogen gas stream. Then we analyzed these compounds by HRGC/HRMS (Agilent 6890 plus/Micromass Autospec-Ultima), equipped with capillary columns (SP-2331; Te-HxCDDs/DFs, DB-5/MS; Hp-OCDDs/DFs and Co-PCBs).

Results and Discussion

1: Sources of PCDDs and PCDFs

Total PCDDs and PCDFs concentrations in lake sediment, river sediment, paddy field soil and road dust were 31.4 ± 6.5 pg-TEQ/dry-g, 1.9 ± 1.5 pg-TEQ/dry-g, 21.3 pg-TEQ/dry-g and 2.8 pg-TEQ/dry-g, respectively. Congener profiles of PCDDs and PCDFs of those samples were shown in Figure 1. The Dominant congeners were 1,2,3,6,8-PeCDD and 2,4,6,8-TeCDF in lake sediment and paddy field soil. It was reported that they were dominant congener in the impurity of chloronitrophen (CNP) [2)], which had been widely used in paddy field as herbicide in the past in Japan. These profiles indicate that major source of PCDDs and PCDFs of Lake Suwa is the impurity of CNP. On the other hand, congener profile of the river sediment was different from the lake sediment, and rather similar to the road dust (Figure.1). This river flows through the

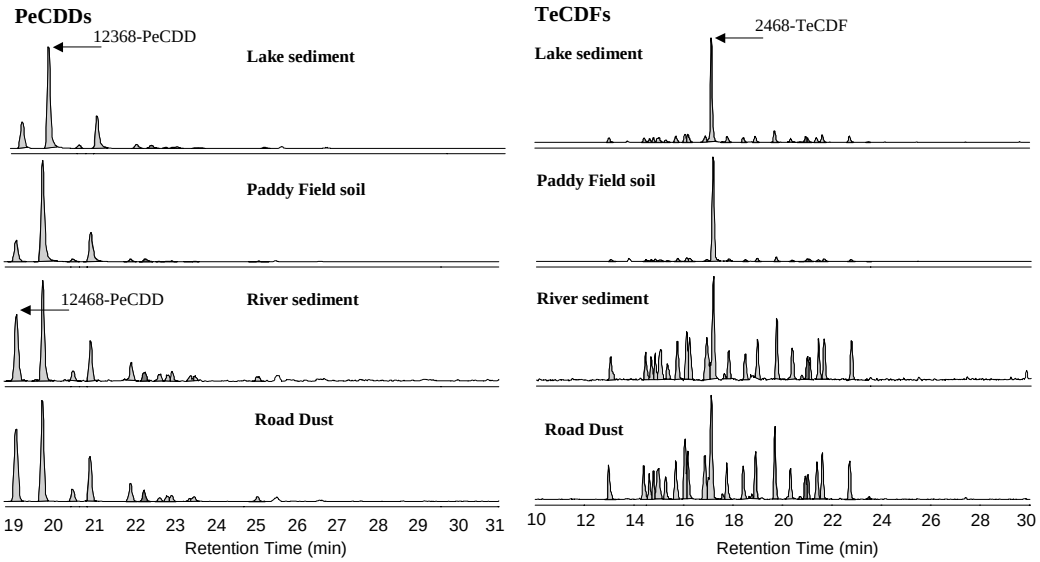

Figure 1. Chromatogram of PeCDDs and TeCDFs in lake sediment, paddy field soil, river sediment and road dust.

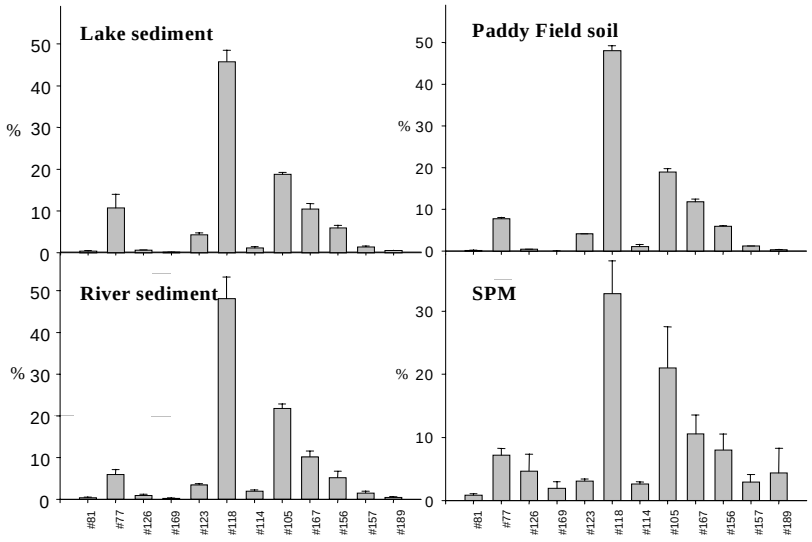

Figure 2. Congener profile of Co-PCBs in lake sediment, paddy field soil, river sediment and SPM.

commercial and residential area in the northern part of the lake, and there are few paddy fields in this

area. The congener profile of the river sediment and the road dust may be reflected by other source of dioxins such as combustion process (municipal incineration and/or automobile).

2: Sources of Co-PCBs

The concentrations of Co-PCBs in the lake sediment, river sediment, paddy field soil and SPM were 1.9±1.5 pg-TEQ/dry-g, 0.2±0.1 pg-TEQ/dry-g, 1.0 pg-TEQ/dry-g and 0.002±0.004 pg-TEQ/m^3, respectively. The congener profiles of Co-PCBs were shown in Figure 2. It showed that PCB #118 was dominantly detected in these samples. The PCB #118 is known as dominant Co-PCBs congener in Kanechlor products[3, 4]. The result suggests that source of Co-PCBs at the drainage area is Kanechlor.

From the present result, major sources of PCDDs, PCDFs, and Co-PCBs in the sediment of lake Suwa are thought to be the impurity of CNP and Kanechlor, which had been used in the past. However, the use of those chemicals was prohibited in the 1980's. Our results show that dioxins still have persisted in soil and sediment in Lake Suwa and its drainage area.

References

1. Masunaga S, Takada H, Sakurai K, and Nakanishi J. (2001) Geochemistry 35, 159-168.
2. Masunaga S, Takada H, and Nakanishi J. (2001) Chemosphere, 44, 873-8.
3. Iimura F, Sasaki Y, Tukui K, Yoshioka H, Higashino K, Takeda N and Kasai T. (2002) Journal of Environmental Chemistry, 12, 343-352.
4. Sakai S, Deguchi S and Takatuki H. (2002) Journal of Environmental Chemistry, 15, 361-376.