Characterization and Determination of PCDDs and PCDFs in Sediments in the Tama River

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Introduction

Polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofuran (PCDF) are ubiquitous environmental pollutants. Chemical production, chlorine bleaching and disinfection process, and combustion process are the three primary sources of PCDD/DF to the environment (1). Because of the high toxicity of some individual PCDD/DF, it is important to understand their environmental behavior, such as transport, deposition and sink
Three major rivers drain into Tokyo Bay, Japan , namely the Edo, Ara and Tama Rivers. Each has been used for agricultural, recreational and domestic purposes, including as a source of potable water. Particularly in the Tama River, pollution from industrial and domestic waste waters, including heavy metals and organic contaminants, has increased over the last 30 years due to the development of industries and population increases in this area. Although the major inorganic components, i.e. heavy metals, total-N, total-P and organic components in the Tama River have been well characterized (2), specific organic components including PCDD/DF, and their behavior are still not well understood (3). Thus, the purpose of this study is to show the regional changes in the concentrations and compositions of PCDD/DF in the Tama River. These findings provide background information that will be useful in assessing the health implications and trends of PCDD/DF behavior in this river, and in others of similar anthropogenic imputs.

Material and Methods

Sample collection: Sediment samples were collected from the Tama River at eight sampling stations 1 to 8 (Fig. 1), representing upper, mid- and downstream of the river, during June to July 1993. To avoid contamination all utensils and containers were scrupulously cleaned and rinsed with deionaized and distilled water and subsequently with acetone before use. A stainless steel box was employed and all surface sediments (depth 0-5 cm) were taken at the middle of the river. Additional sediment samples were collected from five tributaries of a to e and stations A to D (Fig. 1) near municipal solid waste (MSW) incinerator or waste

water discharges in the midstream of this river during May to Oct. 1994.

Analytical Procedure: The sediment samples were dried in glass jars for 1 day at 60 ℃ to complete dryness. The dried samples were crushed in a steel blender and sieved; only the fraction < 2 mm was analyzed. Each powdered sample (50 g) was extracted with 300 ml of toluene for 12 hours by ultrasonic extraction. The toluene extract was concentrated to nearly dryness and dissolved in 30 ml of n-hexane. The n-hexane layer was washed with conc. sulfic acid (10 ml) in a separately funnel and this was repeated, if it is necessary to remove remaining color in the extract. After washing with distilled water (50 ml) triplicate and then drying over anhydrous sodium sulfate, the n-hexane layer was evaporated to 1 ml by means of rotary evaporation at 60 ℃ for next procedure. Clean up of these extracts were performed on a multi-layer column (15 mm x 30 cm) and an alumina column (10 mm x 30 cm) systems, according to the literature (4) with minor modifications.

The purified PCDD/DF extracts were analyzed by HRGC-HRMS on a Hewlett packard 5890 II gas chromatograph fitted with a Supelco SP2331 fused-silica capillary column (60 m x 0.25 mm I.D., 0.20 μ m film thickness) coupled to JEOL JMS-SX102 A mass spectrometor. Quantitative determination was performed by the absolute calibration- curve method using relative response factor previously obtained from standard mixture solution.

The quality of the data was ensured by regular control of resolution, performance, and sensitivity of the instruments as well as regular checks for instrument blanks and method blanks. We used the I-TEF/89 system(5) to calculate the toxic equivalents (TEQ).

Recovery data were obtained by spiking sediment sample with 1,2,3,4-tetrachlorodibenzo-p-dioxin (TCDD), 2,3,7,8-TCDD, octachlorodibenzo-p-dioxin (OCDD) and carrying them through the entire analytical procedure. The recovery of these compounds in all cases ranged from 70 to 110%.

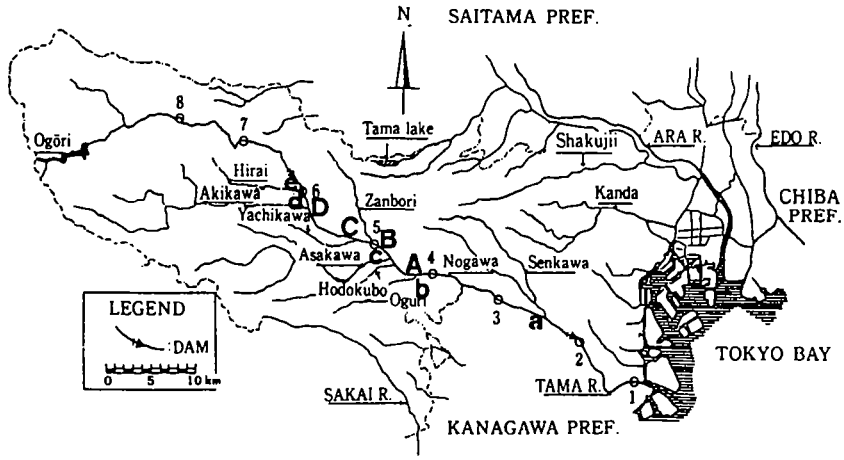

Fig. 1. Location of sampling sites in the Tama River
1: Daishi, 2: Maruko, 3: Tamasuido, 4: Koremasa, 5: Hino, 6: Nagata, 7: Ayumi, 8: Kawai, A: Minami Tama, B: Kita Tama, C: Nishiki-cho, D: Tama-oh.

Results and Discussion

Sediment profiles of PCDD/DF: In order to obtain background information about PCDD/DF levels and profiles in the Tama River, toluene extracts of eight surface sediments taken from upper, mid- and downstream of the Tama River were analyzed by means of HRGC/HRMS. 2,3,7,8-substituted PCDD/DF congeners, except for octachlorodibenzofuran (OCDF), were detected in all samples collected from the river. Highly toxic 2,3,7,8- TCDD was quantified in five (stations 1, 3, 6, 7 and 8) of the eight sediments, but its concentrations were very lower than those detected for other TCDD isomers. Comparatively high toxic 1,2,3,7,8-PeCDD were also quantified in three (stations 1, 2, and 8) of the eight sediments. All sediment samples were dominated by PCDD and the ratios of PCDD to PCDF were ranged from 3 (station 3) to 20 (station 5). In general, no characterized pattern was observed for PCDF congener in all sediment samples collected. In contrast, PCDD congener profiles in these samples taken from the stations 1 to 6 of this river were very similar, with an increase in the concentrations from TCDD to OCDD. OCDD and heptachlorodibenzo-p-dioxin (HpCDD) were composed of 71.5% and 21.7% in total PCDD concentrations (mean value of six samples), respectively. In addition, surface sediments taken from the stations 7 and 8 (upstream) of the Tama river showed similar PCDD/DF congener pattern. In these sediments the concentrations decline from TCDD to HxCDD and increase again from HxCDDs to OCDD. The sediment sample collected from the station 7 showed a predominance of TCDD isomers and these compounds were composed of 33% in the total PCDD concentrations.

Distribution of PCDD/DF and TEQ in the Tama River: Figure 2 shows the distribution of total PCDD/DF concentrations as well as the TEQ values in eight surface sediments sampled at the middle of the river. The total PCDD/DF concentrations in these sediments were ranged from 27.0 to 231.6 pg/g dry weight (mean value, 90.7 pg/g) depending on the sampling point. The TEQ values in these sediments calculated from the measurements of each 2,3,7,8-substituted PCDD/DF levels were ranged from 0.05 to 2.8 pg/g with a mean value of 1.2 pg/g. High PCDD/ DF levels as well as the TEQ values were found for sediments collected from the stations 1, 2 , 3 and 7, whereas low values were observed from samples collected from the stations 4 to 6 (midstream) and 8 (upstream).

In addition, two maxima in the PCDD/DF levels in the sediment samples can be seen in Fig. 2, except for the samples taken from the downstream (industrial area) in this river. Two main dams, Den-enchofu and Hamura, have been constructed between stations 2 and 3, and stations 6 and 7 (Fig. 1), respectively. Therefore, the presence of two maxima in the PCDD/DF concentrations in this river may be accounted for by transport of the particulates associated with PCDD/DF from each upper part, aggregation forming larger particles and then deposit of them onto surface sediment at the stations 3 and 7, respectively. The pollution levels of PCDD/DF in the surface sediments from 12 rivers in Japan were reported by Japan Environment Agency in 1995 (5). The TEQ of PCDD/DF was in a wide range of < 0.02 to 24 pg/g TEQ. As compared with those findings, the concentrations of PCDD/DF in the Tama River was relatively lower than that in heavily contaminated river in Japan.

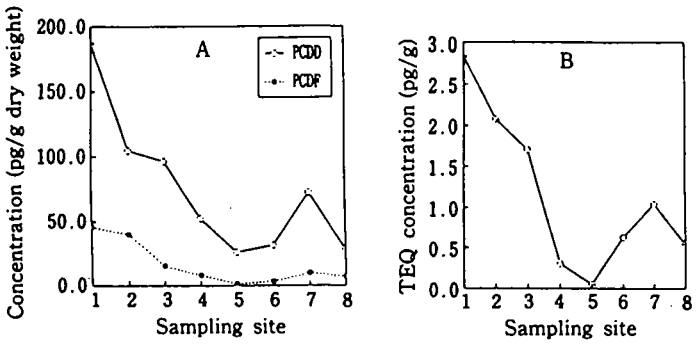

Fig. 2. Distribution of total PCDD/DF (A) and international toxic equivalents (TEQ) (B) in surface sediments sampled at the middle of the Tama River

Effects of urban activities on the PCDD/DF pollution in the midstream region: In order to obtain further information about PCDD/DF pollution in the midstream of the Tama River, surface sediments taken from stations A to D and the junction of the river with five tributaries were analyzed for their profiles and levels of PCDD/DF. The highest concentration of PCDD/DF (889 pg/g) as well as the TEQ value (13.0 pg/g) was observed for sediment from station A near MSW incinerator plant plus municipal waste water discharge. This concentration was about 15 times higher than that observed for the sample of station 4 where is down at a distance of 1 km from the station A. The PCDD/DF concentration (264 pg/g) and the TEQ (1.1 pg/g) in sediment taken from station C near municipal waste water discharges was also about 10 times higher as compared with that found for the sample of station 5. However, the PCDD/DF levels in sediments taken from five tributaries of a to e were very low, indicating no contribution of PCDD/DF impact into the river. These findings suggest a multiplicity of sources ranging from emission gas from MSW incinerator to waste water discharges in the midstream of the Tama River.

Acknowledgements

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