Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans: Their Concentrations and Profiles in Sediments in the Tama River, Japan

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Surface sediments were collected from eight sampling points, representing upper, mid- and downstream regions, of the Tama River, to obtain background information on the polychlorinated dibenzo-*p*-dioxin/dibenzofuran (PCDD/ DF) levels, profiles and transport in this river. The sediment profiles of PCDD/DF were strongly dependent on the sampling points, with total PCDD/DF levels ranging from 27.0 to 231.6 pg/g dry weight (mean value, 90.7 pg/g) and the I-TEQ values ranging from 0.05 to 2.8 pg/g (mean value, 1.2 pg/g). Two maxima in the PCDD/DF concentrations were observed for the sediment samples taken from stations 3 (midstream) and 7 (upstream) in this river, although none for the samples from downstream (industrial area). Sediment samples taken from the midstream near waste water discharges and a municipal solid waste (MSW) incinerator plant showed high TEQ values of 0.5 to 1.2 and 13.0 pg/g, respectively, indicating a potential PCDD/DF source in this river. In contrast, the PCDD/DF concentrations in the sediment samples taken from five tributaries flowing into the midstream region were very low, indicating no PCDD/DF impact into the studied areas. These data suggest a multiplicity of sources ranging from agricultural activities to urban activities such as emission gas from MSW incinerators and effluents from wastewater treatment plants.

Key words —— polychlorinated dibenzo-*p*-dioxin, polychlorinated dibenzofuran, surface sediment, Tama River

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofuran (PCDF) are ubiquitous environmental pollutants. Chemical production, the chlorine bleaching and disinfection process, and the combustion process are the three primary environmental sources of PCDD/DF.[1] Because of the high toxicity of some individual PCDD/DF, it is important to understand their environmental behavior of transport, deposition and sink. A lot of work has been done on their emission by incineration and transport by air.[2,3] Cuzczwa and Hites demonstrated that atmospheric transport is the major source of airborne PCDD/DF to the Great Lakes.[2] However, source reconciliation studies based on atmospheric release estimates can only account for approximately 10% of the environmental load of PCDD/DF.[4] PCDD/DF are highly lipophilic, poorly soluble, have low volatility and adsorb strongly to particles and surfaces; thus, they are immobile once they are incorporated into the sedimentary sink.[5] Emission of PCDD/DF into water is not well investigated and has not been analyzed with the same intensity as air emissions of these substances.[6]

Three major rivers drain into Tokyo Bay, 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 wastewaters, 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. The increase in pollution by organic matter [biochemical oxygen demand (BOD), over

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7 mg/l] in the Tama River is critical, and the use of this river as a source of potable water has been sharply reduced since 1970. Although the major inorganic components, *i.e.* heavy metals, total-N, total-P and organic components [*i.e.* chemical oxygen demand (COD) and BOD] in the Tama River have been well characterized,[7] specific organic components including PCDD/DF and their behavior are still not well understood.[8-11] Thus, the purpose of this study was to show the regional changes in 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 inputs.

MATERIALS 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 and July 1993. To avoid contamination all utensils and containers were scrupulously cleaned and rinsed with deionized and distilled water and then 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 a municipal solid waste (MSW) incinerator or wastewater discharges in the midstream of this river during May to Oct. 1994. Table 1 summarizes the information concerning each sampling station.

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 h by ultrasonic extraction. The toluene extract was concentrated nearly to dryness and dissolved in 30 ml of *n*-hexane. The *n*-hexane layer was washed with conc. sulphuric acid (10 ml) in a separate funnel and, if necessary, this was repeated to the remove the remaining color in the extract. After washing with distilled water (50 ml) three times and drying over anhydrous sodium sulfate, the *n*-hexane layer was evaporated to 1 ml by rotary evaporation at 60℃ for the next clean-up procedure.

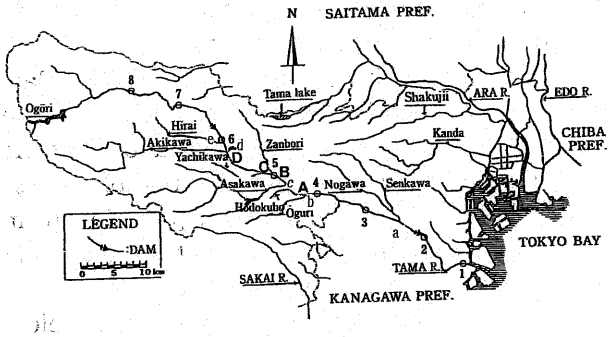

Fig. 1. Location of Sampling Sites in the Tama River

1, Daishi; 2, Maruko; 3, Tamasuido; 4, Koremasa; 5, Hino; 6, Nagata; 7, Ayumi; 8, Kawai. A, Minamitama; B, Kitatama; C, Nishiki-cho; D, Tama-oh.

Clean-up of the above extracts was performed on a multi-layer column (15 mm × 30 cm) and an alumina column (10 mm × 30 cm) systems, according to the literature[12] with minor modifications. The multi-layer column was prepared by packing with anhydrous sodium sulfate (10 g)/22% (w/w) H_2SO_4–silica gel (8 g)/44%(w/w) H_2SO_4–silica gel (7 g)/silica gel (2 g)/2% (w/w) KOH–silica gel (5 g)/silica gel (2 g)/10%(w/w) $AgNO_3$–silica gel (5 g)/silica gel (2 g). The extract was eluted gently with *n*-hexane (150 ml) to remove organic interferences and then the eluate was concentrated to 1 ml using a rotary evaporator at 60℃. The concentrate was poured onto the alumina column (30 g alumina of Merck activate 1 and 5 g of silica gel) and separated into PCBs and dioxin fractions with the first eluent of 2% dichloromethane in *n*-hexane (150 ml) and the second eluent of 50% dichloromethane in *n*-hexane (200 ml), respectively. Both fractions were then concentrated nearly to dryness using a rotary evaporator at 40℃ and dissolved into 100μl of toluene for GC-MS analyses.

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 × 0.25 mm i.d., 0.20 μm film thickness) coupled to a JEOL JMS-SX102 A mass spectrometor. HRGC-HRMS was operated under the following conditions. GC operating conditions: oven temp., 100℃ (2 min hold) → 210℃ (20℃/min) → 250℃ (2℃/min and 45 min hold); injection temp., 250℃; carrier gas (He), 0.8 ml/min (25 psi); sample injection, splitless 1μl. MS conditions: ionization method, electron impact (EI); ionization energy, 70 eV; ionization current, 600 μA; interface temp., 280℃; ion source temp., 280℃; resolving power, 10000.

Quantitative determination was performed by the absolute calibration-curve method using the relative response factor previously obtained from the standard mixture solution. The quality of the data was ensured by regular control of resolution, perfor-

mance, and sensitivity of the instruments as well as by regular checks for instrument blanks and method blanks. We used the I-TEF/89 system[13] to calculate the toxic equivalents (TEQ). Recovery data were obtained by spiking sediment samples 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%.

RESULTS AND DISCUSSION

Sediment Profiles of PCDD/DF

To obtain background information on PCDD/DF levels and profiles in the Tama River, toluene extracts of eight surface sediments taken from upper, mid- and downstream of this river (Fig. 1 and Table 1) were analyzed by HRGC-HRMS. Figure 2 shows the HRGC-HRMS traces of tetra-(TCDD/F), penta- (PeCDD/F) and hexa-chlorinated dibenzo-*p*-dioxins and dibenzofurans (HxCDD/F) in the sediments sampled at station 1 of the river. 2,3,7,8- substituted PCDD/DF congeners, except for octachlorodibenzofuran (OCDF), were detected in all samples collected. Highly toxic 2,3,7,8-TCDD was quantified in five (stations 1, 3, 6, 7 and 8) of the eight sediments, but at concentrations much lower than those detected for other TCDD isomers. Comparatively high toxic 1,2,3,7,8-PeCDD was also quantified in three (stations 1, 2, and 8) of the eight sediment samples.

PCDD/DF congener profiles in surface sediments taken from the Tama River are illustrated in Fig. 3. All sediment samples were dominated by PCDD and the ratios of PCDD to PCDF ranged from 3 (station 3) to 20 (station 5). In general, no characterized pattern was observed for PCDF congener in any of the sediment samples collected. In contrast, PCDD congener profiles in these samples taken from stations 1 to 6 of this river were very similar, with an increase in the concentrations from TCDD to OCDD. Total PCDD concentrations (mean value of six samples) accounted for 71.5% and 21.7% of OCDD and heptachloro-dibenzo-*p*-dioxin (HpCDD), respectively. Similar PCDD congener patterns as described above have been found for surface soil

Table 1. Description of Sampling Sites Selected in the Tama River, Japan

Code	Site name	Distance (km)[a]	Remarks	Site description/pollution source
Tama River				
Site 1	Daishi Bd.	3.8	Sludge	Industrial impact
Site 2	Maruko Bd.	14.0	Sand	Industrial impact
Site 3	Tamasuido Bd.	25.0	Sludge	Urban and industrial impact
Site 4	Koremasa Bd.	34.0	Sand	Urban and industrial impact
Site 5	Hino Bd.	43.0	Sand	Urban impact
Site 6	Nagata Bd.	54.0	Sand	Urban impact
Site 7	Ayumi Bd.	64.0	Sand	Agricultural impact
Site 8	Kawai	78.0	Sand	Agricultural impact
Tributary				
Site a	Nogawa stream		Sand	Urban impact
Site b	Oguri stream		Sand	Urban impact
Site c	Asakawa stream		Sand	Urban impact and agricultural impact
Site d	Akikawa stream		Sand	Agricultural impact
Site e	Hirai stream		Sand	Agricultural impact
Urban activity				
Site A	Minamitama	35.0	Clay	Wastewater discharge and MSW incinerator
Site B	Kitatama	38.0	Sand	Wastewater discharge
Site C	Nishiki-cho	43.5	Sand	Wastewater discharge
Site D	Tama-oh	48.0	Sand	Wastewater discharge

a) Distance from the river mouth.

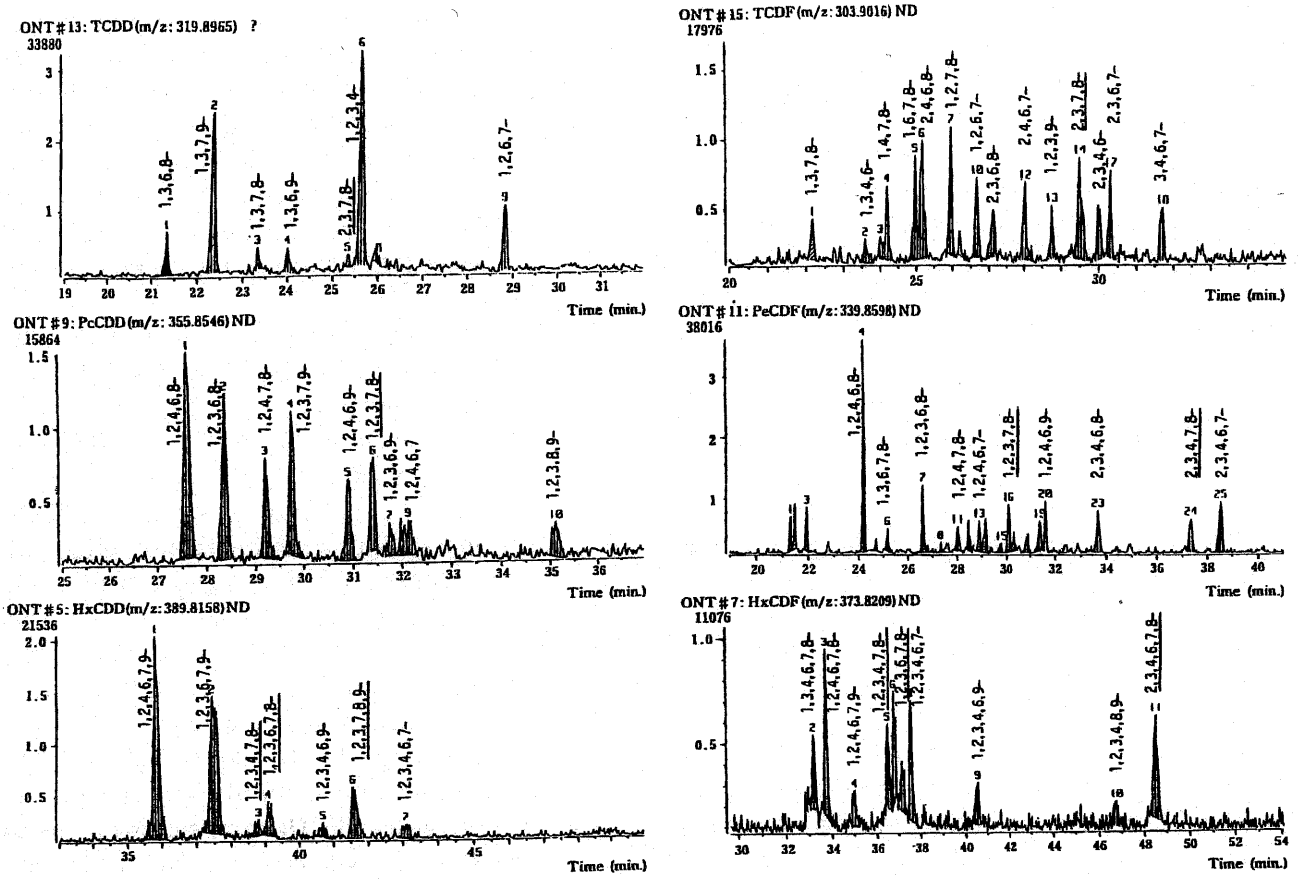

Fig. 2. Isomer Patterns of Tetra-, Penta- and Hexachlorinated Dibenzo-*p*-dioxins/dibenzofurans in the Surface sediment Sampled at Site 1

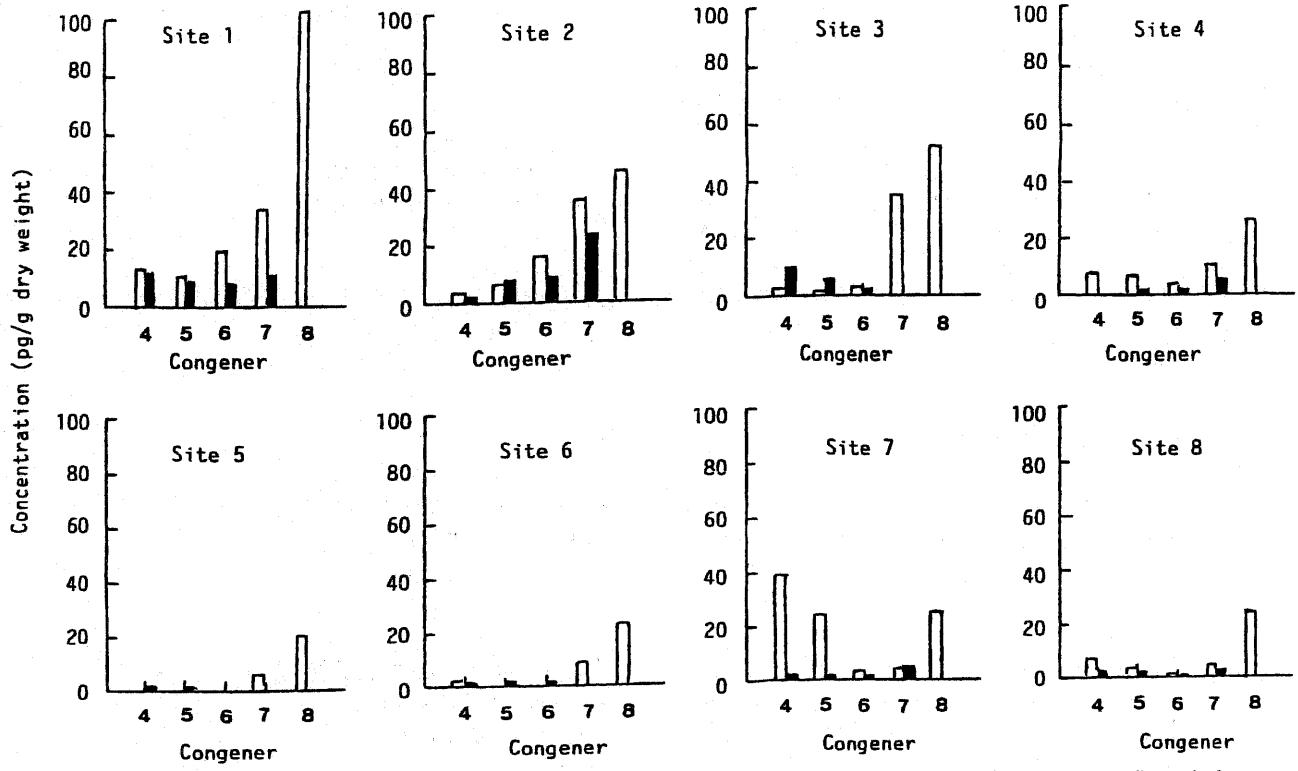

Fig. 3. Congener Patterns of Polychlorinated Dibenzo-*p*-dioxins /furans in the Surface Sediments Sampled.
Open bars, PCDD ; closed bars, PCDF.

samples[14] contaminated with emission gas from MSW incinerators and their fly ash samples[15] in Japan. Thus, it seems that the midstream region of the Tama River is contaminated with PCDD/DF in emission gas from MSW incinerators and effluents from wastewater treatment plants.

In addition, surface sediments taken from stations 7 and 8 (upstream) of the river showed a similar PCDD/DF congener pattern. In these sediments the concentrations decline from TCDD to HxCDD and increase again from HxCDD to OCDD. The sediment sample collected from station 7 showed a predominance of TCDD isomers and 33% of these compounds were PCDD concentrations. A similar PCDD congener pattern as described above has been found for sediment sampled from the water treatment system.[16,17] Therefore, it seems that the upstream region of the Tama River is contaminated with PCDD/DF mainly from two sources, agricultural activity and water treatment plants.

Distribution of PCDD/DF and I-TEQ in the Tama River

There are two main dams in the Tama River, Den-enchofu and Hamura, between stations 2 and 3, and stations 6 and 7, respectively (Fig. 1). Therefore, this river is divisible into three regions in terms of water quality : upstream (relatively clean, BOD≦1 mg/l), midstream (heavily polluted, BOD≦6 mg/l) and downstream (moderately polluted with a tidal effect, BOD≦3 mg/l). In the midstream, relatively polluted water is diluted with clean water from the Akikawa stream near station 6 and then polluted again heavily by industrial and domestic effluents through the Asakawa, Nogawa and other small streams between stations 3 and 6. At the present time, it is known that over 80% of the BOD in this river is loaded with effluents from domestic wastewater through these small streams flowing into the river.

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

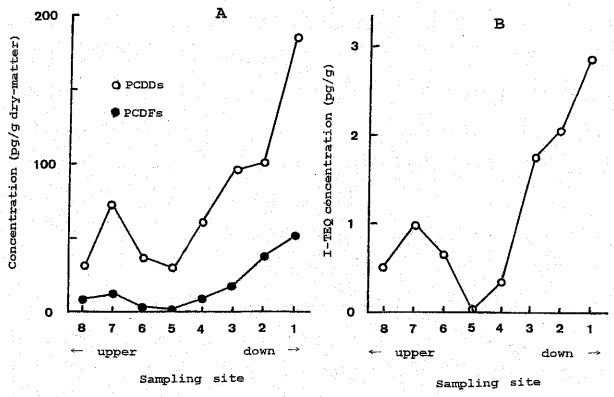

Fig. 4. Distribution of Total Polychlorinated Dibenzo-*p*-dioxins /furans (A) and International Toxic Equivalents (I-TEQ) (B) in the Surface Sediments Sampled

In addition, two maxima in the PCDD/DF levels in the sediment samples can be seen in Fig. 4, except for the samples taken from the downstream (industrial area) in this river. As mentioned above, two 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, their aggregation forming larger particles and then their deposit onto surface sediment at stations 3 and 7, respectively. The pollution levels of PCDD/DF in the surface sediments from 12 rivers in Japan were reported by the Japan Environment Agency in 1995.[18] The TEQ of PCDD/DF ranged widely from 0.02 to 24 pg/g I-TEQ. Compared with those findings, the concentrations of PCDD/DF in the Tama River were relatively lower than those in heavily contaminated rivers in Japan.

Effects of Urban Activities on PCDD/DF Pollution in the Midstream Region

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 HRGC-HRMS determinations

of PCDD/DF in four sediments are summarized in Table 2. 2,3,7,8- substituted PCDD/DF congeners were detected in all samples collected from stations A to D of the midstream region. Higher concentrations of 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF as well as high I-TEQ values were also observed for the sediment from station A.

PCDD/DF concentrations between 86.1 and 889 pg/g (dry weight) and I-TEQ values ranging from 0.8 to 13 pg/g were found in sediment samples (Table 2). The highest concentration of PCDD/DF as well as TEQ value was observed for sediment from station A near the MSW incinerator plant plus municipal wastewater discharge. This concentration was about 15 times higher than that observed for the sample of station 4 which is at a distance of 1 km from station A. The PCDD/DF concentration (264 pg/g) in sediment taken from station C near municipal wastewater discharges was also about 10 times higher than 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 wastewater discharges in the midstream of the Tama River.

Table 2. PCDD/DF Concentrations in Sediment Samples Collected from the Midstream of the Tama River near MSW Incinerator and Municipal Wastewater Discharges

PCDD/DF	Concentration (pg/g, dry weight)			
	Site A	Site B	Site C	Site D
2,3,7,8-TCDD	0.9	0.1	ND	0.2
sum TCDD	44.0	5.0	4.4	2.0
1,2,3,7,8-PeCDD	3.6	0.4	0.4	ND
sum PeCDD	82.0	7.0	31.0	2.0
1,2,3,4,7,8-HxCDD	4.2	0.5	0.2	ND
1,2,3,7,8,9-HxCDD	5.2	0.8	1.6	0.9
1,2,3,6,7,8-HxCDD	8.6	1.2	2.5	ND
sum HxCDD	209.0	8.0	7.0	2.0
1,2,3,4,6,7,8-HpCDD	69.0	9.0	3.0	4.0
sumHpCDD	140.0	12.0	3.0	12.0
OCDD	255.0	48.0	140.0	50.0
2,3,7,8-TCDF	10.0	0.6	0.3	0.1
sum TCDF	82.0	10.0	1.0	5.0
1,2,3,7,8-PeCDF	7.0	1.0	0.2	ND
2,3,4,7,8-PeCDF	10.0	1.0	0.2	0.1
sum PeCDF	39.0	13.0	2.0	7.0
1,2,3,4,7,8-HxCDF	0.2	1.3	ND	ND
1,2,3,6,7,8-HxCDF	0.4	1.5	ND	ND
2,3,4,6,7,8-HxCDF	10.0	3.6	0.7	3.9
1,2,3,7,8,9-HxCDF	0.7	0.5	0.1	ND
sum HxCDF	20.0	83.0	1.0	4.0
1,2,3,4,7,8,9-HpCDF	2.6	0.8	0.2	ND
1,2,3,4,6,7,8-HpCDF	4.4	9.5	1.2	0.1
sum HpCDF	10.0	11.0	2.0	0.1
OCDF	38.0	30.0	73.0	2.0
I-TEQ	13.0	1.2	1.1	0.8

In conclusions, the Tama River is divisible into three regions by two main dams: upstream (agricultural impacts), midstream (urban impacts) and downstream (industrial impacts). All sediment samples were dominated by PCDD and the ratios of PCDD to PCDF were ranged from 3 to 20. Although the PCDD/DF levels and the congener patterns were dependent on the sampling points, the sediment profiles of PCDD/DF in mid- and downstream of the river were very similar, with an increase in the concentrations from TCDD to OCDD. Except for samples from downstream, two maxima in the PCDD/DF concentrations as well as the TEQ values can be seen in sediments taken just from the upper part of each of the two main dams. Higher concentrations of PCDD/DF as well as TEQ values were also observed for sediment samples taken from midstream near the MSW incinerator facility and municipal wastewater discharges. The total concentrations of PCDD/DF in surface sediments taken from the Tama River seem to be somewhat lower than in other rivers of Japan, suggesting a multiplicity of sources ranging from agricultural, urban and industrial activities.

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