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Sources, Distribution, and Inflow Pattern of Dioxins in the Bottom Sediment of Lake Suwa, Japan

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Dioxins [Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and coplanar polychlorinated biphenyls (co-PCBs)] are persistent organic chemicals that have low vapor pressure and water solubility. Thus, they tend to be associated with fine particles, and these particles drain into lakes through rivers and finally accumulate in the lake sediment. Therefore, lake sediment is considered to reflect the current status of dioxin contamination in its drainage area.

In Japan, there have been a number of studies of dioxin pollution using lake sediment (Kang *et al.* 2002; Masunaga *et al.* 2001 (a); (b); Sakurai *et al.* 1996; Sakurai *et al.* 1998). These studies indicated that the major sources of PCDDs and PCDFs were impurities from agrochemicals, especially herbicide pentachlorophenol (PCP) and chloronitrophen (CNP). In addition, the major sources of co-PCBs were commercial PCB products, such as KC300 and KC400.

We also determined the vertical distributions of dioxins in sediment from Lake Suwa, which is a shallow eutrophic lake in Japan (Ikenaka *et al.* 2005). Marked increases in the concentrations of dioxins were observed in the 1960s, which reached their maximum levels in the 1970s, and the major sources were considered to be PCP, CNP, and commercial PCB products. On the other hand, no information is available about the horizontal distributions of dioxins in Lake Suwa. It is important to determine the horizontal and vertical distributions of dioxins to elucidate the sources, distribution, and inflow patterns of these pollutants to allow the development of effective countermeasures, such as environmental purification.

In the present study, we investigated the horizontal distributions of dioxins in Lake Suwa bottom sediment. We also investigated dioxins in river sediment, soil of paddy fields, and air of the drainage area. In addition, we estimated the present status of dioxin pollution and elucidated the sources, distribution, and inflow patterns of dioxins in Lake Suwa.

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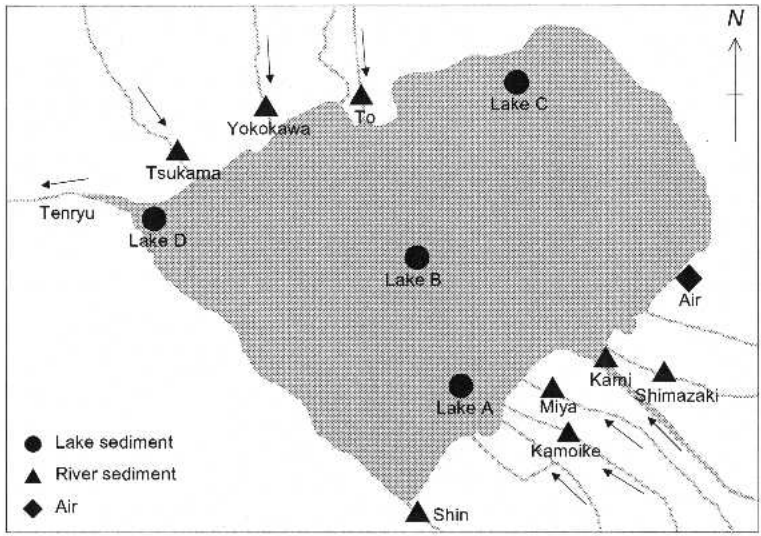

Figure 1. Map of Lake Suwa and sampling stations.

MATERIALS AND METHODS

Lake Suwa is located in a rural mountainous area in Japan (36° 3'N, 138°5'E) and has an average depth of 4.0 m and a maximum depth of 6.3 m. Its surface and drainage areas are 13.3 and 531 km^2, respectively. About 12% of the drainage area is utilized for agricultural purposes, about 10% is given over to commercial and residential areas, and the rest is forest. The area around Lake Suwa is known for silk production in former times, and for mechanical and electrical industries in recent times.

The bottom sediment samples were collected from 4 sampling stations (Lake A, Lake B, Lake C, Lake D) using an Ekman-Berge dredge from Lake Suwa on 29 July 2002, and 8 sampling stations (Tsukama, Yokokawa, To, Shimazaki, Kami, Miya, Kamoike, Shin) from rivers in the drainage area on 1 May 2003 (Fig. 1). The soils of paddy fields in the drainage area were also collected from 5 sampling stations (Paddy A, Paddy B, Paddy C, Paddy D, Paddy E) on 16 April 2003. Air (gas and particles) of the drainage area were collected 6 times (Air A, Air B, Air C, Air D, Air E, Air F) using a high-volume air sampler (Sibata HV-1000F) during the period November 2002 – February 2003. With the exception of air samples, the collected samples were air-dried in the laboratory at room temperature. The dry weight of each sample was measured after 12 h of drying in an oven at 105°C, and ignition loss (IL) was measured after 3 h of heating in an oven at 600°C.

Each sample was treated according to the method described by Miyabara *et al.* (1999). Briefly, samples of approximately 20 g of sediment were air-dried at

Table 1. Concentration of dioxins and ignition loss (IL) in sediment, soil and air samples.

		PCDDs	PCDFs	co-PCBs	IL
		ng/g-dry (pg-TEQ)	ng/g-dry (pg-TEQ)	ng/g-dry (pg-TEQ)	%
Lake	Lake A	18.31 (18.18)	0.98 (6.26)	1.19 (0.90)	17.78
	Lake B	23.98 (24.89)	1.02 (7.70)	1.60 (1.20)	16.98
	Lake C	13.99 (20.40)	1.40 (13.89)	2.32 (1.84)	15.87
	Lake D	0.51 (0.76)	0.05 (0.60)	0.33 (0.17)	3.93
River	Tsukama	0.12 (0.61)	0.06 (1.07)	0.19 (0.27)	1.91
	Yokokawa	0.26 (1.32)	0.12 (1.90)	2.44 (1.38)	5.15
	To	0.16 (0.50)	0.04 (0.54)	0.04 (0.11)	3.56
	Shimazaki	22.12 (27.90)	1.17 (8.05)	1.52 (1.43)	13.90
	Kami	1.07 (1.73)	0.03 (0.36)	0.01 (0.02)	1.73
	Miya	0.43 (0.57)	0.02 (0.18)	0.02 (0.02)	1.66
	Kamoike	19.18 (26.50)	2.10 (14.08)	0.61 (1.33)	8.15
	Shin	2.47 (3.98)	0.26 (2.12)	0.67 (0.45)	14.27
Paddy field	Paddy A	122.19 (87.87)	53.32 (14.51)	0.43 (0.63)	13.28
	Paddy B	81.18 (63.84)	3.95 (12.71)	0.54 (0.19)	10.72
	Paddy C	47.77 (58.06)	1.40 (4.97)	0.09 (0.11)	15.46
	Paddy D	50.23 (37.42)	1.57 (5.35)	0.09 (0.19)	16.89
	Paddy E	68.05 (79.96)	2.22 (8.60)	0.08 (0.17)	16.26
		pg/m^3 (pg-TEQ)	pg/m^3 (pg-TEQ)	pg/m^3 (pg-TEQ)	
Air	Air A	2.30 (13.62)	3.36 (24.61)	0.90 (1.28)	
	Air B	1.56 (16.81)	2.33 (28.57)	0.92 (1.77)	
	Air C	4.42 (29.13)	3.58 (52.08)	1.51 (3.45)	
	Air D	5.97 (20.37)	3.58 (32.97)	1.18 (2.95)	
	Air E	3.21 (9.54)	1.76 (11.06)	2.48 (3.99)	
	Air F	2.84 (30.54)	2.03 (18.94)	1.79 (6.64)	

room temperature and Soxhlet extracted with toluene for 18 h. After extraction, ^{13}C-labeled PCDDs/DFs and co-PCBs were spiked as internal standards (Wellington Laboratories, Ont. Canada). Then, the extract was cleaned up and fractionated by silica gel and activated carbon column chromatography. The amounts of dioxins were measured by HRGC/HRMS (Agilent 6890 plus/Micromass Autospec-Ultima) equipped with capillary columns (Supelco SP-2331 for Te-HxCDDs/DFs, Agilent DB-5/MS for Hp-OCDDs/DFs and co-PCBs).

Data were analyzed with the non-parametric Kruskal-Wallis and Mann-Whitney tests. Classification of each sample was performed by cluster analysis according to Euclidean distance, on the basis of standardized values of each dioxin congener. PCP and CNP data used in the cluster analysis were referenced from the data of Masunaga *et al.* (2001) (a).

RESULTS AND DISCUSSION

Table 1 shows the concentrations of dioxins in each sample. The concentrations of dioxins in sediment or soil from Lake Suwa, rivers, and paddy fields were 16.4±11.0 (mean±SD) ng/g-dry (24.2±15.8 pg-TEQ/g-dry), 6.1±9.8 ng/g-dry (10.8±16.5 pg-TEQ/g-dry), and 77.2±32.1 ng/g-dry (74.9±23.1 pg-TEQ/g-dry),

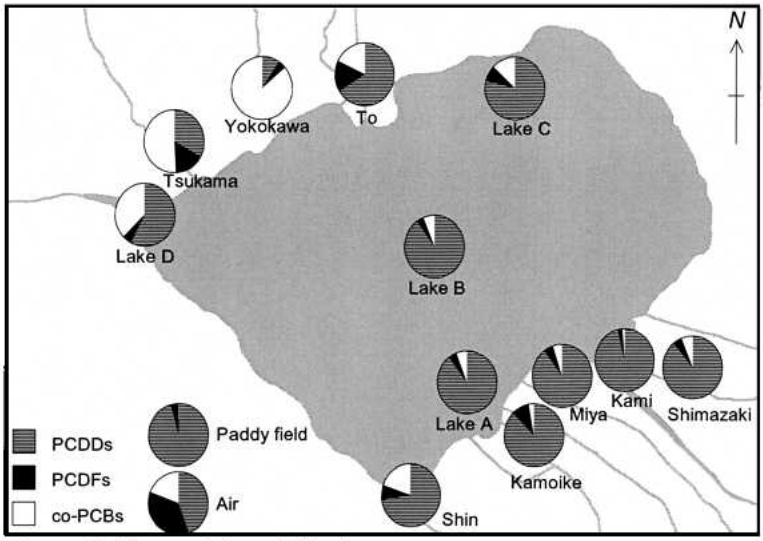

Figure 2. Composition of dioxins.

respectively. The concentration of dioxins in air samples from the drainage area was 7.6±1.8 pg/m^3 (0.05±0.02 pg-TEQ/m^3). The concentrations of dioxins in paddy field soil were significantly higher than those in lake sediment ($p = 0.0002$) and river sediment ($p < 0.0001$). Thus, paddy fields were considered to be reservoirs of dioxins in the drainage area of Lake Suwa.

Fig. 2 shows the compositions of dioxins in each sample. In Lake Suwa bottom sediment, PCDDs were the major components accounting for about 80% of the total dioxin concentration. The ratio of PCDFs and co-PCBs tended to be high in Lake C and Lake D, located on the north side of Lake Suwa, as compared to Lake A and Lake B. In river sediment, congener profiles were different between north and south sides. On the south side (Kami, Miya, Shin, Kamoike, Shimazaki), PCDDs were the major components accounting for about 80% of the total dioxin concentration. On the other hand, on the north side (Yokokawa, To, Tsukama), the ratio of co-PCBs was significantly higher as compared to the south side ($p = 0.03$). Especially in Tsukama and Yokokawa, the ratio of co-PCBs was more than 50% of the total dioxin concentration. In paddy field soil, PCDDs accounted for about 95% of the total dioxin concentration, while co-PCBs accounted for less than 1%. In air samples, the ratios of PCDDs, PCDFs, and co-PCBs were 44, 36, and 19%, respectively.

To identify the sources of PCDDs/DFs in each sample, cluster analysis was performed (Fig. 3). We divided each sample into two groups, cluster A and cluster B. Cluster A included lake sediment, paddy field soil, river sediment (south side: Kami, Miya, Shin, Kamoike, Shimazaki), PCP and CNP, while cluster B included river sediment (north side: Yokokawa, To, Tsukama) and air. The results indicated that the major source of PCDDs/DFs in the sediment of Lake Suwa at present

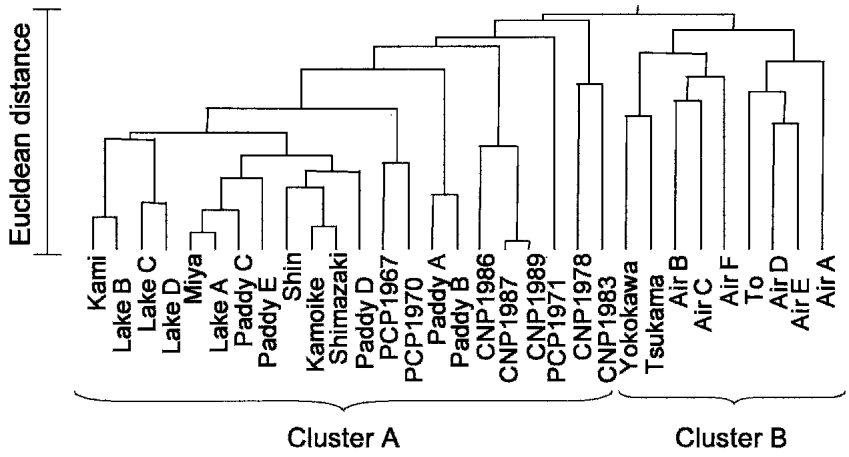

Figure 3. Cluster analysis of each sample based on the Euclidean distance method.

were impurities of PCP and CNP, which flowed mainly into the south side of the lake, where paddy fields are located. On the other hand, the north side of the lake was affected mainly by dioxins from the air. Dioxin congeners in the air were mainly lower chlorinated PCDFs that were mainly produced in the combustion process (Iino *et al.* 2001). Thus, the major source of PCDDs/DFs on the north side of the lake was considered to be combustion as there are few paddy fields on the north side, and the contributions of combustion and of PCP and CNP were stronger and weaker, respectively, as compared to the south side.

Concentration of co-PCBs was significantly higher on the north as compared to the south side of the lake. This indicated that co-PCBs flowed into the lake from the north side. The congener profiles of co-PCBs were similar among all samples, and major congeners were 2,3',4,4',5-PeCB (IUPAC #118), 2,3,3',4,4'-PeCB (#105), 3,3',4,4'-TeCB (#77), and 2,3'4,4',5,5'-HxCB (#167). These congeners were major components of PCB products, such as KC 300 and KC 400 (Sather *et al.* 2001). These results suggested that the major sources of co-PCBs in the bottom sediment from Lake Suwa were commercial PCB products.

As shown in Fig. 4, there was a strong relationship between dioxin concentrations and IL in lake and river sediment. IL is an indicator of organic matter in the sediment. Thus, it was considered that dioxins tend to be adsorbed to fine particles, and are then transferred and accumulated in the organic matter-rich sediment.

The results of the present study revealed the present status of dioxin pollution, sources, and inflow patterns of dioxins in Lake Suwa. In summary, PCDDs/DFs flowed into Lake Suwa mainly from the south side, and the major source was

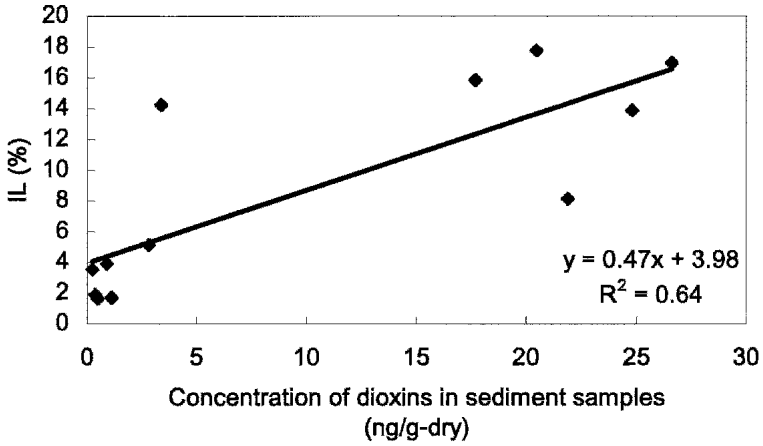

Figure 4. Relationship between concentration of dioxins and ignition loss (IL) in sediment samples.

thought to be the PCP and CNP impurities. Co-PCBs flowed into Lake Suwa mainly from the north side, and their major source was thought to be commercial PCB products. These results indicated that the major sources of dioxins were chemical products that were used widely in Japan more than 20 years ago. PCDDs/DFs and PCBs remain in various parts of drainage areas, and flow continuously into the aquatic environment despite the application ban of PCP, CNP, and PCB. After draining into the aquatic environment, dioxins tend to be transferred with fine particles and accumulate in the sediment, which is rich in organic matter.

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