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Identifying Sources and Mass Balance of Dioxin Pollution in Lake Shinji Basin, Japan

SHIGEKI MASUNAGA,^{*,†,‡} YUAN YAO,^{†,‡}
ISAMU OGURA,[†] SATOSHI NAKAI,[†]
YUTAKA KANAI,[§]
MASUMI YAMAMURO,[§] AND
JUNKO NAKANISHI^{†,‡}

*Institute of Environmental Science and Technology,
Yokohama National University, 79-7 Tokiwadai,
Hodogaya-ku, Yokohama 240-8501, Japan, CREST, Japan
Science and Technology Corporation, Kawaguchi,
Kawaguchi 332-0012, Japan, and Geological Survey of Japan,
1-1-3 Higashi, Tsukuba 305-8567, Japan*

On the basis of congener-specific analysis of dioxins in a dated sediment core, the sources and behavior of dioxins in Lake Shinji Basin, Japan, were estimated. The dioxins in the core showed that their deposition in the lake increased rapidly during the 1960s, peaked in the early 1970s, and then decreased gradually. Principal component analysis of the congener-specific data showed that three major sources existed: pentachlorophenol (PCP), chloronitrophen (CNP), and combustion. PCP and CNP are paddy field herbicides used extensively in the basin. The time trends of source contributions were estimated by multiple regression analysis using the source profiles. The results revealed that dioxin emission from PCP and CNP herbicides was high in the 1960s and the early 1970s, respectively. The contributions from PCP, CNP, and combustion in recent surface sediment were about 68, 16, and 16% in terms of total amount of dioxins. From the decreasing trend of dioxin deposition in the lake after extensive herbicide use, the amount of dioxins that accumulated in the agricultural soil in the basin was estimated to have decreased by about 2%/yr or a half-life of about 35 yr, indicating that dioxin runoff from agricultural fields would continue for a long time.

Introduction

To better understand the current status of dioxin pollution, the historical trend of the pollution has been investigated using sediment cores (1–5) and stored biological materials such as plant (6, 7), food (8), and human blood and milk samples (9, 10). Collectively, these studies revealed that dioxin levels in both the environment and the biota increased during the earlier part of the 1900s and peaked between the 1960s and 1980s (11). Sediment cores from remote lakes in Germany and Finland, however, showed increasing trends of dioxin pollution until recent years (4, 5). Biological samples including stored human milk also indicated increasing and then decreasing trends during the 20th century (8–10). These

results indicate that dioxin pollution is now in remediation. However, the causes of these trends have not yet been completely clarified. To select effective countermeasures against dioxin pollution, the contribution of different sources to the current trends must be investigated.

The proposed major sources of dioxins, among others, are the combustion of various materials, the production and use of chlorinated organic compounds, and the bleaching of pulp and paper. Czuczwa and Hites suggested that the historical increase in the amount of dioxin in sediments from Lake Huron was similar to the trends in the production, use, and disposal of chlorinated organic compounds (1). Kjeller and Rappe (2) analyzed sediment cores from the Baltic Sea and suggested that the combustion of coal, wood, and peat was the major source from 1882 to 1962 and that pentachlorophenol was the main contributor from 1970 to 1985. The trend of atmospheric dioxin deposition estimated from stored soil and herbage in the U.K. also indicated that both combustion and use of chlorinated aromatics were the main contributors (6, 7). These studies used homologue or congener dioxin profiles to discuss the contribution of dioxin sources. However, these results were qualitative. To better describe the differences in dioxin profiles, principal component analysis of homologue- or congener-specific data has often been carried out, and the differences among media, sites, and contributions from different sources have been discussed (12–16). In those studies, however, the quantitative estimations of source contribution have rarely been accomplished (17).

In this study, we estimated the historical contributions from different sources based on the detailed congener-specific dioxin profiles obtained from the sediment core. Following a preliminary study (18), we assumed that dioxins as agrochemical impurities are a relatively important source of dioxin in Japan. Thus, we selected Lake Shinji located in a rural area as the site for study.

Materials and Methods

Study Area. Lake Shinji is located in a rural area along the coast of the Japan Sea on Japan's main island (Figure 1). Its 1227 km² wide basin consists of about 88% forest, 9% paddy (rice), and 2% vegetable fields. River Hii, the largest river in the basin, flows into the lake on its western side.

Sediment Core. A sediment core sample was taken from the western part of the lake near the mouth of River Hii in 1994. The core was sliced into 1-cm-thick disks, and the average sedimentation rates were estimated to be 0.26 g cm⁻² yr⁻¹ using the Pb-210 method and 0.25 g cm⁻² yr⁻¹ using the Cs-137 method (19). Both estimates were quite similar; thus, the value obtained using the Pb-210 method was adopted in this study.

Analysis of Dioxins and Coplanar PCBs. After the addition of ¹³C-labeled internal standards, dried sediment disks (about 4 g) were extracted with toluene in a Soxhlet apparatus for 20 h. They were then subjected to alkaline hydrolysis followed by concentrated sulfuric acid treatment. They were further purified using a series of silica gel, alumina, and carbon columns. The final dioxin and coplanar PCB fractions were concentrated to 25 μ L and spiked with ¹³C-labeled recovery standards for HRGC/HRMS (Micromass Autospec-Ultima) analysis. Both DB-5 and DB-17 GC columns (J&W Scientific) were used for the quantification of polychlorinated dibenzop-dioxins and polychlorinated dibenzofurans (PCDD/DFs), and a DB-5 column was used for coplanar polychlorinated biphenyls (co-PCBs). The average recoveries were 74.6 \pm 10.5% for 2,3,7,8-congeners and 72.8 \pm 13.9% for co-PCBs.

* Corresponding author e-mail: masunaga@kan.ynu.ac.jp; telephone: 81-45-339-4352; fax: 81-45-339-4373.

[†] Yokohama National University.

[‡] Japan Science and Technology Corporation.

[§] Geological Survey of Japan.

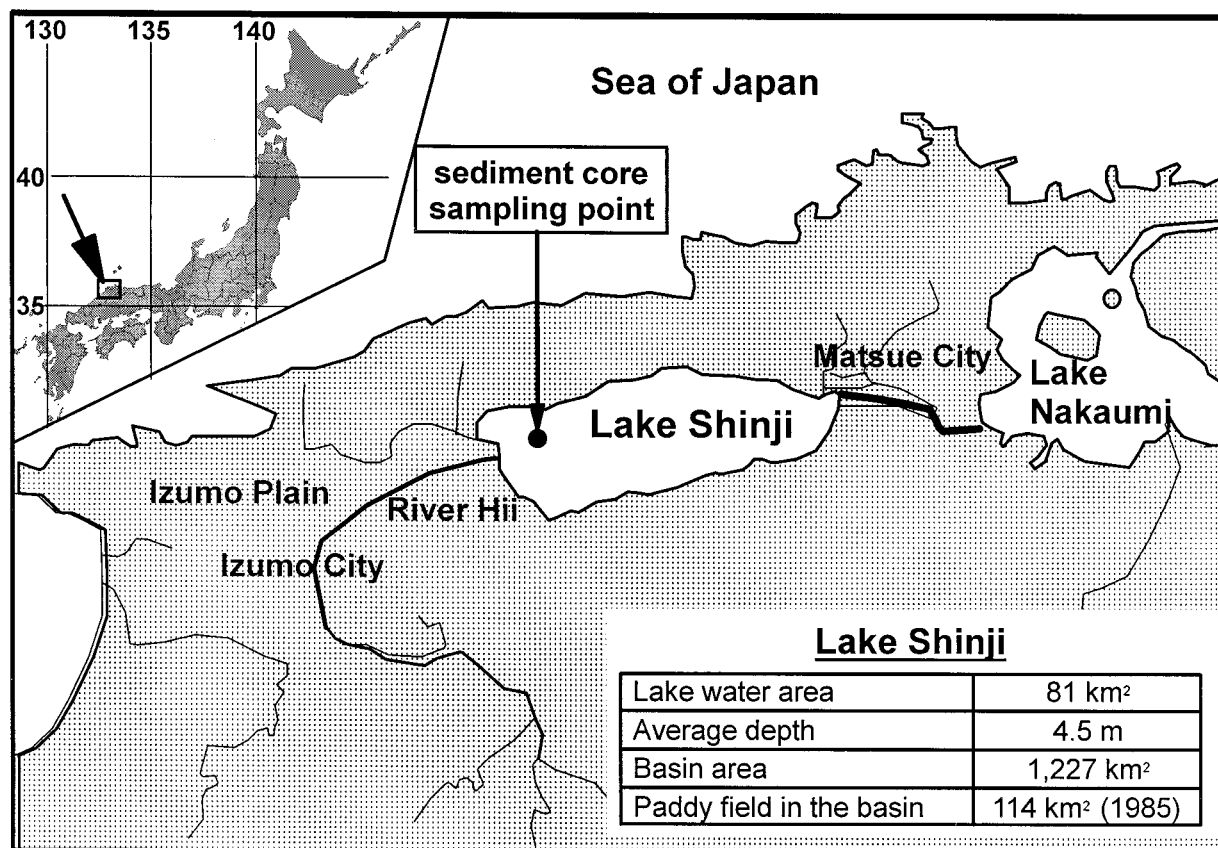


FIGURE 1. Map of Lake Shinji and the sampling point.

Statistical Analysis. Principal component analysis (PCA) and multiple regression analysis (MRA) of the data were performed using software packages such as Statistica (Stat-Soft, Inc.).

Results and Discussion

Dioxin Homologues and 2,3,7,8-Substituted Congeners in the Sediment Core. More than 80 gas chromatographic peaks corresponding to individual tetra- through octachlorinated PCDD/DF congeners or groups of congeners were quantified using the DB-5 column. For 2,3,7,8-chlorine-substituted congeners that could not be separated using the DB-5 column, a DB-17 column was used for quantification. The results of 2,3,7,8-substituted PCDD/DF congener, homologue, and coplanar PCB (co-PCB) concentrations are shown in Table 1. A drastic increase in the concentration of total PCDD/DF congeners in the sediment core occurred during 1945–1970, followed by a small decrease during 1972–1994 (Figure 2). The major components that increased in concentration during 1945–1970 were OCDD and HpCDD congeners. They decreased during 1972–1976 and have remained at relatively the same level since 1980. The homologues that showed similar trends included OCDF, HpCDFs, and HxCDFs. In contrast to the highly chlorinated dioxins, TeCDDs, PeCDDs, and TeCDFs increased in concentration during 1964–1976, reached their maximum around 1976, and decreased slightly thereafter.

When each of the 2,3,7,8-congeners was examined, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, and 1,2,3,4,7,8,9-HpCDF were found to have their maximum concentrations around 1968 and belonged to the highly chlorinated group. Congeners 1,2,3,6,7,8-HxCDF and 2,3,7,8-TCDF showed a trend intermediate to those of highly chlorinated and lowly chlorinated groups, indicating that they may belong to both groups.

Principal Component Analysis of Dioxin Congeners in the Sediment Core. To investigate the cause of this trend, all individual and cluster congeners separated using the DB-5 column were quantified (see Supporting Information, Table S1). A total of 78 gas chromatographic peaks (excluding the peaks below the detection limit in any sediment layer) and 12 slices of the sediment core were regarded as variables and as cases, respectively, and PCA was performed. As the number of cases was smaller than the number of variables, congener-specific data were transformed into a correlation matrix, and the matrix was used as input data for PCA. The analysis revealed three major principal components (PCs) after varimax rotation (Table 2 and Supporting Information, Table S2). The cumulative proportion of the three PCs was more than 95%. Thus, it was shown that these three components could explain most of the dioxin variation in the sediment core.

Characteristic congeners in PC-1 that had high factor loadings were OCDD, all the HpCDD isomers, OCDF, and most of HpCDF isomers. These corresponded well with the impurities in pentachlorophenol (PCP) (20). PCP was used extensively as a herbicide in paddy fields during 1955–1974 in Japan. Characteristic congeners in PC-2 were 2,4,6,8-TeCDF, 1,3,6,8-TeCDD, 1,3,7,9-TeCDD, 1,2,3,6,8-PeCDD, and 1,3,6,7,8-PeCDD. Other penta- and hexachlorinated dioxin congeners with 1,3,6,8- or 1,3,7,9-chlorine substitutions also had relatively high factor loadings (>0.7). These agreed well with the impurities in chloronitrophen (CNP) (20) that was used extensively as a paddy field herbicide in Japan. The characteristics of PC-3 were not as outstanding. However, almost all congeners with factor loadings higher than 0.5 belonged to tetra- and pentachlorinated PCDDs and PCDFs. As relatively uniform isomer distribution and less chlorinated PCDD/DFs are characteristics of combustion sources (21), we assumed that PC-3 represents the atmospheric input of dioxins originating from combustion sources.

TABLE 1. Dioxin and co-PCB Concentrations in Lake Shinji Sediment Core^a

core depth (cm)	25–26	20–21	18–19	16–17	14–15	12–13	10–11	8–9	6–7	4–5	2–3	0–1
dated by Pb-210	1945–1948	1957–1959	1961–1962	1964–1966	1967–1968	1970–1972	1975–1977	1979–1981	1982–1984	1986–1988	1990–1991	1993–1994
mean date	1947	1958	1961	1965	1968	1971	1976	1980	1983	1987	1990	1993
2,3,7,8-TCDD	0.1	0.1	0.1	0.2	0.0	0.3	0.4	0.5	0.4	0.4	0.5	0.5
TCDDs	20.1	32.5	25.4	36.0	398	1040	2050	1670	1480	1780	1740	1640
1,2,3,7,8-PeCDD	0.6	0.9	1.3	2.0	2.6	2.8	2.7	3.0	3.1	3.5	3.0	3.1
PeCDDs	13.3	18.1	18.6	36.7	99.5	206	333	299	286	331	325	319
1,2,3,4,7,8-HxCDD	1.4	2.2	3.3	5.3	7.1	7.2	6.3	6.2	6.0	6.2	6.3	6.3
1,2,3,6,7,8-HxCDD	2.7	5.1	8.0	12.8	15.6	16.2	14.1	13.8	13.6	14.2	14.6	14.1
1,2,3,7,8,9-HxCDD	4.1	6.3	8.9	13.9	16.6	18.1	14.7	14.9	13.2	15.1	15.9	14.8
HxCDDs	58.9	87.1	112	156	191	213	195	196	170	176	186	169
1,2,3,4,6,7,8-HpCDD	77.8	142	225	350	471	469	360	358	363	371	381	362
HpCDDs	230	390	567	872	1,120	1,120	921	883	891	920	957	898
OCDD	2,250	3,530	5,340	8,320	9,960	9,700	7,350	7,600	7,540	7,670	7,800	7,310
2,3,7,8-TCDF	0.6	1.6	1.4	1.4	2.2	2.6	1.9	1.9	1.7	1.9	1.9	1.9
TCDFs	6.0	10.9	12.0	10.7	39.6	65.8	113.4	83.5	76.7	94.5	91.5	86.1
1,2,3,7,8-PeCDF	0.4	0.6	0.7	1.1	1.4	1.9	2.0	1.9	1.9	2.2	2.1	2.1
2,3,4,7,8-PeCDF	0.3	0.6	0.7	1.0	1.5	2.0	2.3	2.1	2.1	2.6	2.4	2.7
PeCDFs	4.4	9.3	14.2	15.2	36.9	46.6	58.3	50.2	46.3	55.0	54.3	56.7
1,2,3,4,7,8-HxCDF	0.7	2.1	4.1	7.8	11.4	9.8	8.2	7.9	7.6	8.3	8.4	8.1
1,2,3,6,7,8-HxCDF	0.5	1.2	2.3	4.3	5.5	6.6	5.8	5.5	5.7	6.2	6.1	5.7
2,3,4,6,7,8-HxCDF	0.5	1.0	1.8	3.3	5.3	6.1	8.0	7.5	8.3	9.1	8.6	9.4
1,2,3,7,8,9-HxCDF	0.1	0.2	0.3	0.6	0.7	0.9	0.8	0.7	0.8	1.0	0.7	0.9
HxCDFs	6.4	23.2	54.1	100	147	133	116	108	104	118	114	114
1,2,3,4,6,7,8-HpCDF	3.3	14.1	35.6	75.1	127	107	74.4	76.4	73.7	77.3	77.8	76.6
1,2,3,4,7,8,9-HpCDF	0.5	1.5	3.8	8.3	13.6	11.7	8.4	8.5	8.4	8.5	9.4	8.4
HpCDFs	6.8	37.0	98.2	203	355	291	199	214	190	198	209	188
OCDF	7.6	41.2	107	264	485	399	266	269	246	249	266	238
total PCDD/DFs	2,600	4,180	6,350	10,000	12,800	13,200	11,600	11,400	11,000	11,600	11,700	11,000
<i>WHO-TEQ (PCDD/DFs)^b</i>	3.0	5.2	8.0	12.8	17.1	17.9	15.6	15.7	15.6	16.8	16.5	16.4
<i>I-TEQ (PCDD/DFs)^c</i>	4.7	8.0	12.2	19.6	25.1	25.6	21.1	21.3	21.0	22.2	22.3	21.6
CB-77	6.4	40.6	64.8	151	218	211	86.7	89.5	69.3	76.7	82.0	73.0
CB-81	0.4	0.9	1.2	2.4	5.1	5.0	3.1	3.1	2.8	3.4	3.3	3.4
CB-126	0.8	1.9	2.3	4.5	10.7	10.6	6.9	7.4	6.9	8.5	8.0	8.9
CB-169	0.3	0.3	0.3	0.3	1.0	0.9	1.3	1.3	1.3	2.2	1.6	1.8
total non-ortho-PCBs	7.8	43.7	68.5	151	234	227	97.9	101	80.3	90.7	94.9	87.1
<i>WHO-TEQ (co-PCBs)^b</i>	0.08	0.20	0.24	0.47	1.10	1.09	0.71	0.77	0.71	0.87	0.83	0.91
<i>WHO-TEQ (PCDD/DFs + co-PCBs)^b</i>	3.1	5.4	8.2	12.8	18.2	19.0	16.3	16.5	16.3	17.7	17.3	17.3

^a pg/g dry sediment or pg TEQ/g dry sediment. ^b Calculated using the WHO-TEFs for human (WHO, 1998). ^c Calculated using the I-TEFs (WHO/ICPS, 1988).

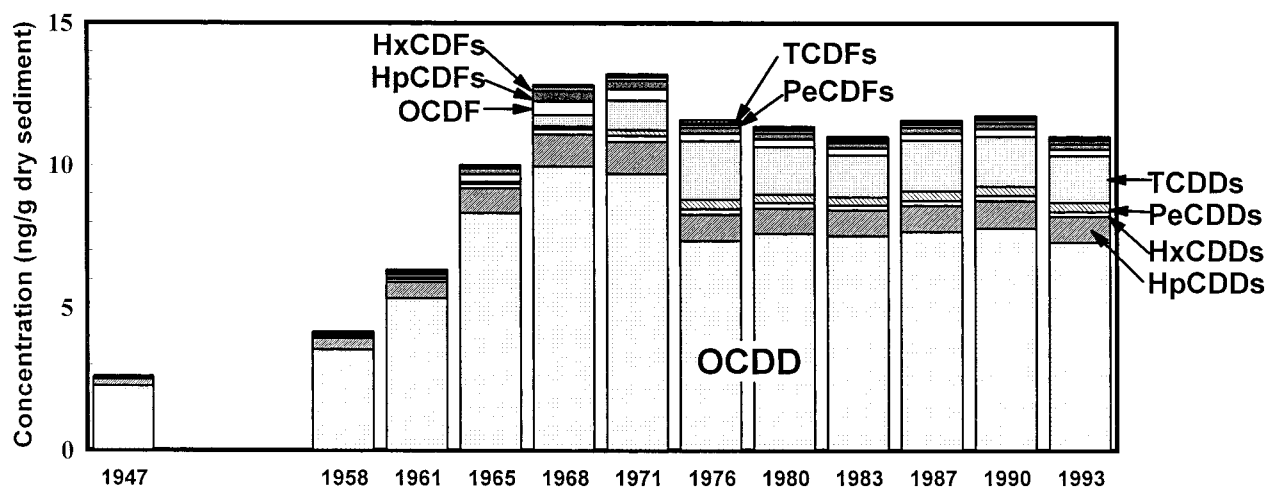


FIGURE 2. Trend of dioxin concentration in the dated Lake Shinji sediment core.

TABLE 2. Results of Principal Component Analysis with Varimax Rotation

	PC-1	PC-2	PC-3
proportion (%)	46.9	31.8	16.3
cumulative proportion (%)	46.9	78.7	95.1
characteristic congeners (congeners with high factor loading)	OCDD, HpCDDs, OCDF, most of HpCDFs	2,4,6,8-TeCDF, 1,3,6,8-TeCDD, 1,3,7,9-TeCDD, 1,2,3,6,8-PeCDD 1,3,6,7,8-PeCDD	some TeCDDs, some TeCDFs, some PeCDDs

Estimated Contributions of Different Dioxin Sources.

On the basis of the results of PCA, we assumed that PCP, CNP, and atmospheric deposition from combustion sources had been the three major sources of dioxins in Lake Shinji. The percentage contribution calculated by PCA does not represent the real concentration of dioxins because a correlation matrix was used as input data. Therefore, we decided to estimate their contributions by MRA using the dioxin congener profiles of the three sources. In MRA, dioxin impurities from PCP, CNP, and atmospheric deposition from combustion were regarded as independent variables, and dioxin concentrations in sliced sediment disks were regarded as dependent variables. The input data for the independent variables are obtained as follows. The average dioxin profile of four Japanese PCP formulations (20) was used as the input for PCP. The average concentration of five CNP formulations (20) weighted by the amount of production represented by each sample based on its date of production was used for CNP. Because of the lack of appropriate congener-specific data for atmospheric deposition in the study area, atmospheric deposition measured in the Kanto area of Japan (22) was used. These input data are provided as Supporting Information, Table S3.

MRA was carried out for each isomer group because the environmental behavior of dioxins differs based on the differences in the basic molecular structure and the number of substituted chlorines; however, it does not substantially differ between isomers due to the similarity in their physical characteristics. Thus, MRA was repeated for the following eight groups: TeCDDs, PeCDDs, HxCDDs, HxCDDs + HpCDDs + OCDD, TeCDFs, PeCDFs, HxCDFs, and HpCDFs + OCDF. As the number of congeners belonging to HxCDDs and OCDD was only three, they were analyzed in combination with HxCDDs. Similarly, HpCDFs and OCDF were combined into one group. Thus, the regression coefficients for the three sources were obtained for those eight groups separately. Then source apportioning was carried out using the regression coefficients for the eight groups. The results obtained were

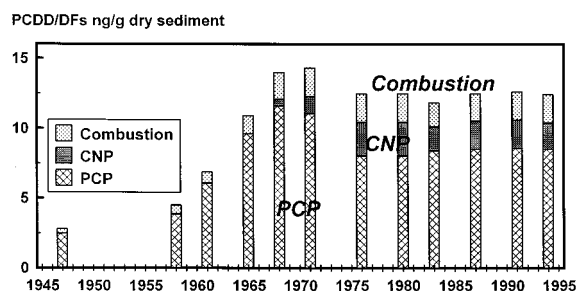


FIGURE 3. Contributions from different sources to dioxin pollution in Lake Shinji sediment core in terms of PCDD/DFs.

summed, and the contribution of the three sources in terms of total PCDD/DFs was calculated for each slice of the sediment core.

The final results indicated that PCP had been the greatest contributor to aquatic sediment pollution since the 1950s (Figure 3). Its contribution peaked in the late 1960s and declined thereafter. The contribution from CNP started in the late 1960s and peaked in the 1970s. These time trends corresponded very well with the period of use of these herbicides in the basin. Contributions from combustion increased during the 1950s and 1960s and subsequently leveled off. The contributions from PCP, CNP, and combustion in recent surface sediments were about 68, 16, and 16%, respectively.

These results were transformed into toxic equivalent (WHO-TEQ) using the congener composition of each source. The transformed results are presented in Figure 4. The calculated trend of TEQ corresponded well with that observed in the sediment core. However, the calculated results were 1.5–1.7 times higher than the observed TEQ. The discrepancy was rather small considering the unavoidable errors in the calculation, such as possible changes in dioxin composition in the environment due to transformation and degradation,

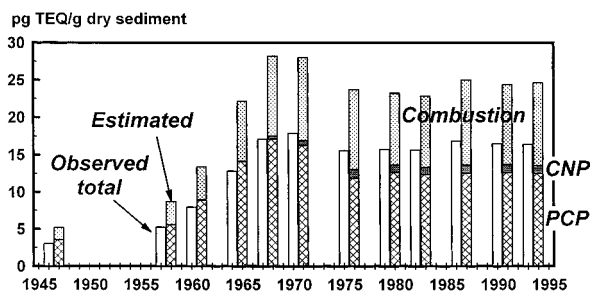


FIGURE 4. Contributions from different sources to dioxin pollution in Lake Shinji sediment core in terms of WHO-TEQ. Observed total: analytical results. Estimated: contributions from three sources in terms of WHO-TEQ, calculated by the transformation of the results in terms of PCDD/DFs

and also large errors in the source profile data due to the limited number of source samples analyzed. The contributions from PCP, CNP, and combustion in the recent sediment were about 52, 4, and 44% in terms of WHO-TEQ, respectively. The contribution from combustion increased while that from CNP decreased as compared to the results in terms of PCDD/DFs.

Dioxin Mass Balance in Lake Shinji Basin. To understand the behavior and mass balance of dioxin in Lake Shinji Basin, the amounts of dioxin input to and deposition in the lake basin were examined. First, the amount of herbicides used in the basin was calculated based on the data of herbicide shipments to Shimane Prefecture (23) and the ratio of paddy field areas in Shimane Prefecture to that in Lake Shinji Basin. Then, the arithmetic mean of dioxin concentrations in PCP reported worldwide and the change in trend over time of dioxin concentration in CNP (20) were used to calculate dioxin input to the basin. The historical trends of dioxin deposition in the sediment of Lake Shinji were also calculated from the core data presented in this study, assuming that dioxin concentration in sediments was uniform all over the lake but that the sedimentation rate differed depending on the part of the lake (19). The trends of annual dioxin input to the basin and deposition in the bottom sediments from PCP and CNP are shown in Figures 5 and 6, respectively.

The trends of annual input, cumulative input to the basin and deposition in sediments of dioxin from PCP showed that deposition in sediments increased several years ahead of PCP use (Figure 5). This may be due to an error in core dating, the vertical mixing of the sediment, and/or a higher runoff rate during the period of herbicide application. However, the trends of cumulative input and annual deposition appear to be very similar. As a primary estimate, it is possible to assume that the amount of annual dioxin loss from the paddy field is proportional to the amount of dioxin present in the field and that the annual amount of dioxin deposition in the lake is proportional to the amount of dioxin loss from the field. Thus, it can be assumed that annual deposition is proportional to the amount of dioxin present in agricultural fields in the basin. If the annual loss rate of dioxin from the field were constant over the past 50 yr, which is the average annual loss rate, the trend of the amount of dioxin in the field could be simulated using this average annual loss rate. The simulated trends at different annual loss rates (1.5, 1.9, and 2.4%/yr) are shown in Figure 5. Among these, the one at an annual loss rate of 1.9%/yr best fit the trend of dioxin deposition in the lake. Therefore, this simulation indicated that the amount of dioxin in the basin decreased at a rate of about 1.9%/yr. A similar analysis was conducted for CNP (Figure 6). The trends of cumulative PCDD/DFs input and deposition in sediments corresponded very well, although the increase in deposition occurred 2–3 yr ahead of the increase in the input. Under the same assumptions as those for the case of PCP, the annual loss of dioxin from the soil in the basin was estimated to be approximately 2.0%/yr, which was very similar to that of PCP.

On the basis of the trend of deposition in sediments, dioxins in the soil in Lake Shinji Basin were estimated to be lost at a rate of about 2%/yr or a half-life of about 35 yr. The loss mechanism may include runoff, volatilization, degradation, and burial (covering of surface soil due to a change in land use). Although vertical mixing in the sediment has been pointed out to be minimal in Lake Shinji (19, 24), the estimated loss rate from the soil in the basin could be underestimated due to possible vertical mixing. Thus, the

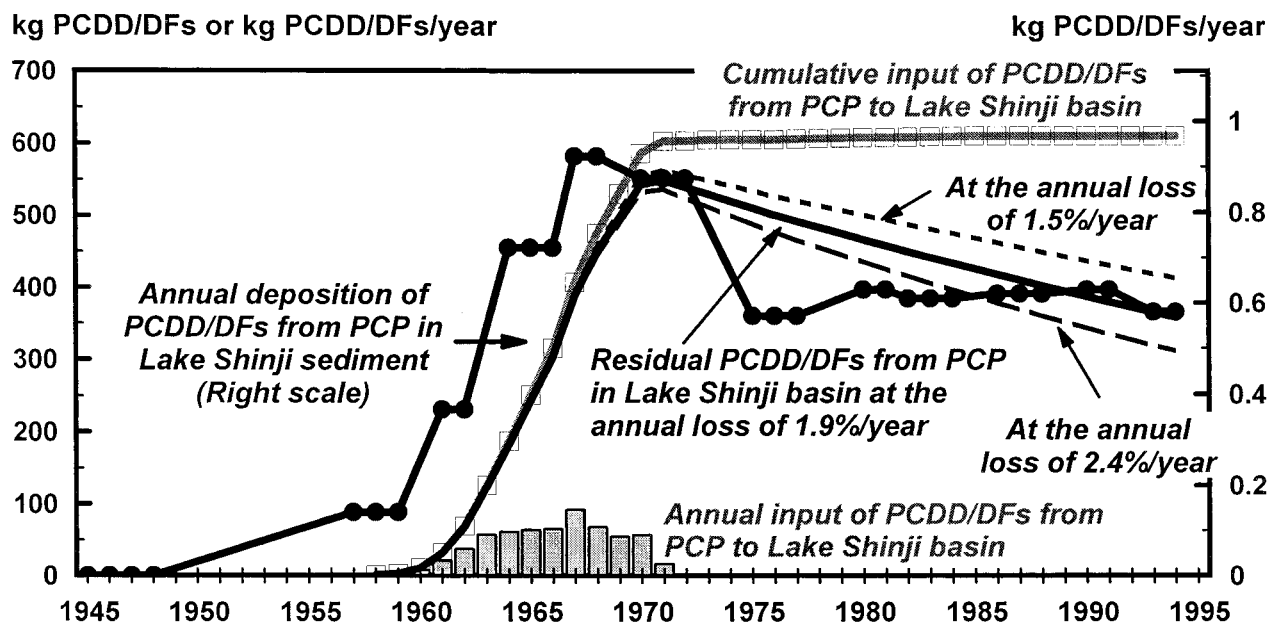


FIGURE 5. Trend of PCP-originated dioxin input to and deposition in Lake Shinji basin: (●) annual deposition of PCDD/DFs from PCP in Lake Shinji sediment (kg of PCDD/DFs/yr) (right scale); (□) cumulative input of PCDD/DFs from PCP to Lake Shinji basin (kg of PCDD/DFs) (left scale); (---, —, and —) residual PCDD/DFs from PCP in Lake Shinji basin estimated at the annual loss rates of 1.5, 1.9, and 2.4%/yr, respectively (kg of PCDD/DFs /yr) (left scale).

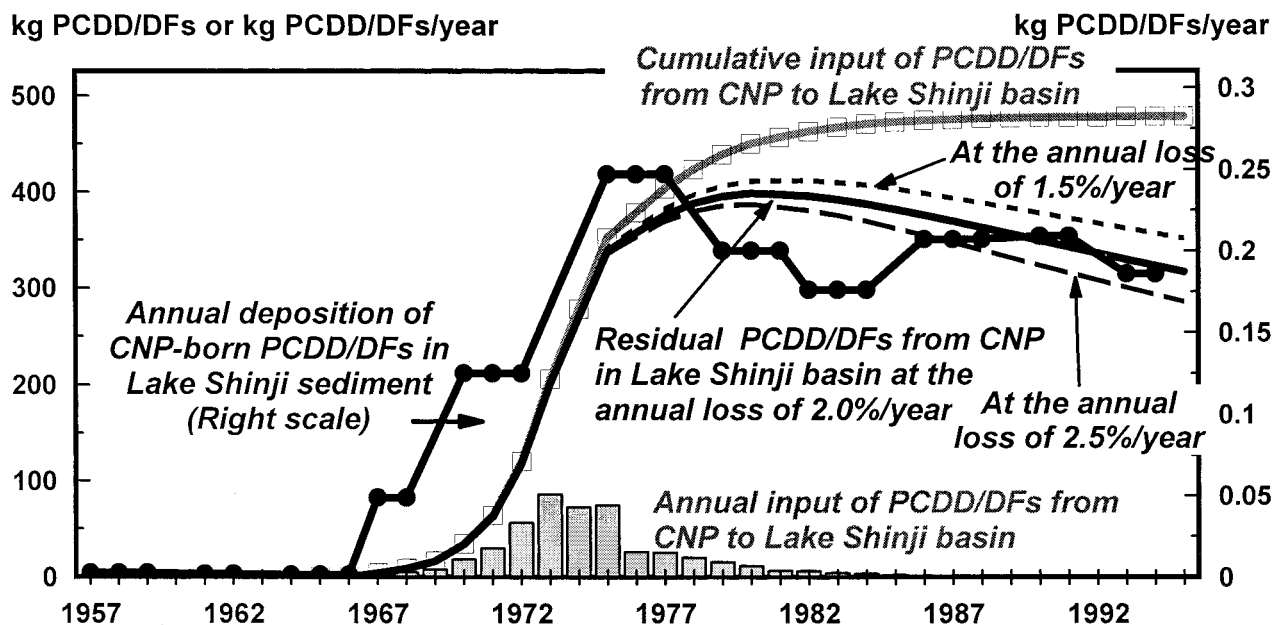


FIGURE 6. Trend of CNP-originated dioxin input to and deposition in Lake Shinji basin: (●) annual deposition of PCDD/DFs from CNP in Lake Shinji sediment (kg of PCDD/DFs/yr) (right scale); (□) cumulative input of PCDD/DFs from CNP to Lake Shinji basin (kg of PCDD/DFs) (left scale); (- - -, —, and - · -) residual PCDD/DFs from CNP in Lake Shinji basin estimated at the annual loss rates of 1.5, 2.0, and 2.5%/yr, respectively (kg of PCDD/DFs/yr) (left scale).

TABLE 3. Dioxin Mass Balance in Lake Shinji Basin during the Past 50 Years (1945–1994)

	sources	input to soil	remaining in soil	lost from soil	deposition to lake sediment	ratio of lost/input (%)	ratio of deposition/lost (%)
PCDD/DFs (kg)	PCP	610	360	250	36	41	14
	CNP	480	320	160	5.1	32	3
	combustion	23 ^b	a	a	7.0	a	a
WHO-TEQ (g TEQ)	PCP	680	420	260	37	38	14
	CNP	780	650	130	2.0	17	2
	combustion	330 ^b	a	a	27	a	a

^a No data available. ^b Estimated using the atmospheric deposition data measured in 1998.

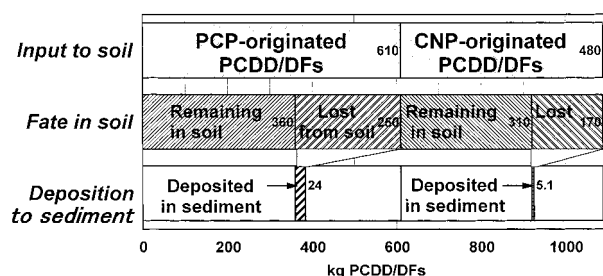


FIGURE 7. Mass balance of PCDD/DFs originating from PCP and CNP in Lake Shinji basin during the past 50 yr (1945–1994).

loss rate estimated here should be regarded as the lower limit of estimation.

In this simulation, the mass balance of PCP- and CNP-originated dioxins during the past 50 yr (1945–1994) was calculated, and the results are shown in Figure 7 in terms of PCDD/DFs and in Table 3 in terms of WHO-TEQ. The ratio of the amount of dioxins lost from soil to that of the input was higher for PCP than for CNP. This difference was considered to be due to differences in the application history of the two herbicides: PCP was used prior to CNP by about 10 yr and PCP dioxins had a greater chance of runoff than CNP dioxins. On the other hand, the ratios of the amount of dioxins deposited in the lake sediment to that lost from the basin for the two herbicides differed by 7-fold. The ratios were expected to be close to each other if the environmental

behavior of the dioxins from the two sources was similar. The difference may be mainly due to errors in the estimation of average dioxin concentration in the herbicides. This cannot be avoided because of the large variation in dioxin concentration from different formulations. The contribution from the different environmental behaviors of dioxins from the two herbicides however cannot be ruled out because the homologue profiles of the two herbicides are quite different.

The estimated mass balance showed that dioxins released into the environment as herbicide impurities remained in the agricultural field for a long time and gradually flowed into the aquatic environment. More than half of the dioxins released were indicated to remain in the soil of the lake basin.

Discussion. In this study, the historical trends of sources, behavior, and mass balance of dioxins in Lake Shinji Basin were successfully estimated by statistical analyses of the detailed congener-specific data of a dated sediment core. Although there is much uncertainty in the obtained results, especially in the mass balance estimation, due to the fluctuation of dioxin content in agrochemical formulations and other environmental factors, congener-specific analysis is a powerful tool for the study of the environmental behavior of dioxins. The results obtained showed that dioxin input to the basin as an herbicide impurity was high during the 1960s and 1970s and that a large part of the dioxin input still remained in the soil of the basin. From the declining trend of dioxin deposition in the bottom sediment, the loss rate of dioxins from the terrestrial part of the basin was estimated

to be about 2%/yr. This value should be regarded as the lower limit of estimation considering the possibility of vertical mixing of the sediment. The remaining dioxins in the paddy field will continue to run off and pollute the aquatic environment, which, in turn, will pollute the aquatic food chain of the lake in the future. Because PCP and CNP were used extensively as herbicides nationwide in Japan, this situation is expected to be ubiquitous all over the country. Considering this, the current Japanese government's effort to reduce dioxin emissions from combustion sources may not be as effective as measures to reduce exposure over a short-term period, since about half of the dioxin intake by Japanese is through fish and shellfish consumption.

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Supporting Information Available

Three tables showing the result of congener-specific analysis of the sediment core, factor loadings obtained by PCA, and source dioxin profiles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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