Historical Contribution of Different Sources to Environmental Dioxin Pollution Estimated from the Lake Shinji Sediment Core

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Introduction

A significant portion of dioxins accumulated in surface aquatic sediment in Japan was indicated to have originated from agrochemicals, especially pentachlorophenol (PCP) and chloronitrofen (CNP)[(1)]. Since these chemicals were used extensively as paddy field herbicides in the past, their present contribution to pollution may be less than that in the past. Thus, it is of interest to estimate their historical contribution to environmental dioxin pollution. In this study, we analyzed dioxins in a dated sediment core taken from Lake Shinji which receives effluent from agricultural land and some local towns. A total of more than 80 gas chromatographic peaks corresponding to individual congeners or groups of congeners were quantified in order to perform a detailed statistical analysis.

Materials and Methods

Sediment core: A sediment core sample was taken from the western part of Lake Shinji, Shimane Prefecture, 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/year by the Pb-210 method and 0.25 g/cm^2/year by the Cs-137 method[(2)]. Both estimates were similar and the value obtained using the Pb method was used in this study.

Dioxin analysis: After the addition of ^{13}C-labeled internal standards, dried sediment disks (about 4 g) were Soxhlet-extracted with toluene for 20 hours. They then were treated by alkaline hydrolysis and concentrated sulfuric acid. They were further cleaned using a series of silica gel, aluminum and carbon columns. The final PCDD/F and coplanar PCB fractions were concentrated to 25 μl and spiked with ^{13}C-labeled recovery standards for HRGC/HRMS analysis. Both DB-5 and DB-17 columns (J&W Scientific) were used for quantification.

Results

Dioxins in the sediment core: More than 80 gas chromatographic peaks corresponding to the individual tetra- through octa-chlorinated PCDD/F congeners or groups of congeners were quantified using the DB-5 column. All the 2378-chlorine-substituted congeners were quantified using both DB-5 and DB-17 columns. Some of the results are shown in Table 1.

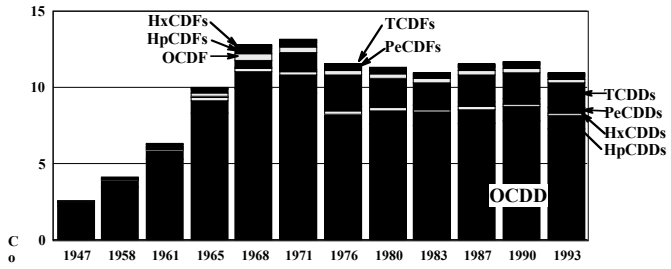
Table 1. Dioxin concentrations in Lake Shinji sediment core (pg/g dry sediment or pg TEQ/g dry sediment)

e 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
ed 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 Age	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
s	20.1	32.5	25.4	36.0	398	1040	2050	1670	1480	1780	1740	1640
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
Ds	13.3	18.1	18.6	36.7	99.5	206	333	299	286	331	325	319
,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
,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
,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
Ds	58.9	87.1	112	156	191	213	195	196	170	176	186	169
4,6,7,8-HpCDD	77.8	142	225	350	471	469	360	358	363	371	381	362
Ds	230	390	567	872	1120	1120	921	883	891	920	957	898
)	2250	3530	5340	8320	9960	9700	7350	7600	7540	7670	7800	7310
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
s	6.0	10.9	12.0	10.7	39.6	65.8	113.4	83.5	76.7	94.5	91.5	86.1
,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
,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
Fs	4.4	9.3	14.2	15.2	36.9	46.6	58.3	50.2	46.3	55.0	54.3	56.7
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
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
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
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
Fs	6.4	23.2	54.1	100	147	133	116	108	104	118	114	114
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
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
Fs	6.8	37.0	98.2	203	355	291	199	214	190	198	209	188
	7.6	41.2	107	264	485	399	266	269	246	249	266	238
PCDD/Fs	2600	4180	6350	10000	12800	13200	11600	11400	11000	11600	11700	11000
*	4.75	8.00	12.2	19.6	25.1	25.6	21.1	21.3	21.0	22.2	22.3	21.6
TEQ	3.02	5.25	7.96	12.8	17.1	17.9	15.6	15.7	15.6	16.8	16.5	16.4

ulated using the I-TEFs (WHO/ICPS, 1988). ** Calculated using the TEFs for human (WHO, 1998)

stic increase in the total PCDD/F concentration in sediment occurred during 1945-1970 followed by a small decrease during 1994 (Figure 1). The major components that increased during 1945-1970 were OCDD and HpCDD congeners, which are known ities of PCP[3]. They decreased during 1972-1976 but have remained at the same level since 1980. The period between 1972 and corresponds well to the period during which PCP use declined rapidly in Japan (1970-1972). In contrast to the highly chlorinated ıs, TCDDs, PeCDDs and TCDFs (especially 1368-TCDD, 1379-TCDD, 12368-PeCDD, 12379-PeCDD and 2468-TCDF) sed during 1964-1977 but have since remained at the same level. These congeners are reported to be the major impurities of). The period from 1964 to 1977 corresponds well with the period from 1966 to 1972 during which the use of CNP in Japan sed rapidly.

Figure 1. Dioxin concentration in dated Lake Shinji sediment core



ipal component analysis: To identify the possible sources of dioxin in the sediment, principal component analysis was performed a correlation matrix calculated from congener-specific data (83 GC peaks as variables and 12 slices of sediment core as cases). sis after the varimax rotation yielded three major principal components (PCs) (Table 2). Based on the characteristic congeners in PC, PC-1 and PC-2 were judged to be impurities of PCP and CNP, respectively. It was not possible to attribute PC-3 to any n sources confidently; however, PC-3 might correspond to another major dioxin generator, incineration. The principal onent scores of all PCs are shown in Figure 2. The component score of PC-1 increased during the 1960s and reached its num in around 1970. The component score of PC-2 follows the same trend as that of PC-1 but with a delay of several years. The iors of PC-1 and PC-2 were in accordance with the amounts of PCP and CNP used in Japan, respectively.

Table 2. Results of principal component analysis with varimax rotation

	PC-1	PC-2	PC-3
oportion (%)	46.9	31.8	16.3
ımulative proportion (%)	46.9	78.7	95.1
ıaracteristic congeners	OCDD, HpCDDs,	2468-TCDF,	some TCDDs &
ongeners with high	OCDF,	1368/1379-TCDD,	TCDFs,
factor loading)	most of HpCDFs	12368-PeCDD	12469/12369-PeCDD

ated trends of different dioxin source contributions: Based on the result of PC analysis, we assumed that PCP, CNP and ration (atmospheric deposition) are the three major sources of dioxin in Lake Shinji. Their contributions to pollution in sediment estimated by multiple regression analysis using congener profiles of dioxin impurities in PCP[3] and CNP[3] and of

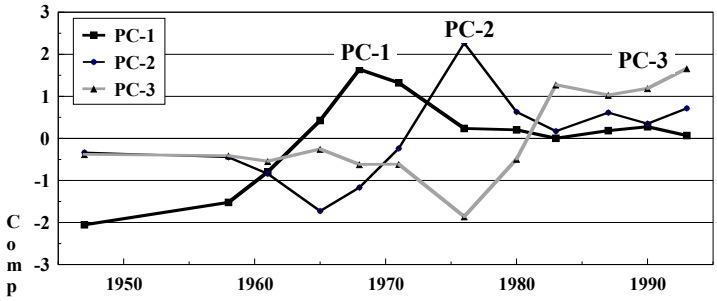


Figure 2. Component scores of three principal components (PCs)

pheric dioxin deposition. For atmospheric deposition, data obtained in the Kanto area[4] were used because of the lack of ner-specific data in this area. The result indicated that PCP had been the greatest contributor to aquatic sediment pollution since '50s (Figure 3). The contribution from CNP began in the 1970s. Atmospheric deposition increased during the 1950s and 1960s ıbsequently leveled off.

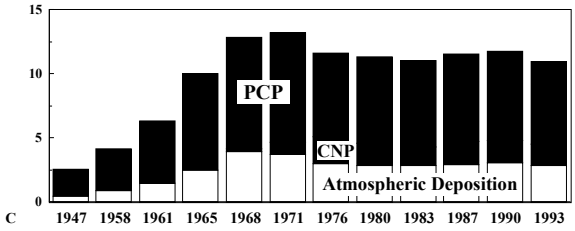


Figure 3. Contributions of different sources to dioxin pollution in sediment core

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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
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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/Fs	2600	4180	6350	10000	12800	13200	11600	11400	11000	11600	11700	11000
I-TEQ*	4.75	8.00	12.2	19.6	25.1	25.6	21.1	21.3	21.0	22.2	22.3	21.6
WHO-TEQ	3.02	5.25	7.96	12.8	17.1	17.9	15.6	15.7	15.6	16.8	16.5	16.4

* Calculated using the I-TEFs (WHO/ICPS, 1988). ** Calculated using the TEFs for human (WHO, 1998)

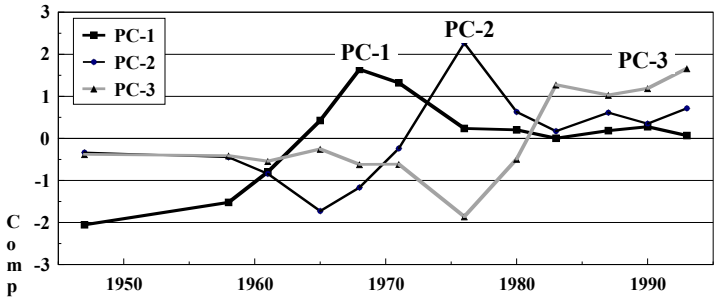

Figure 2. Component scores of three principal components (PCs)

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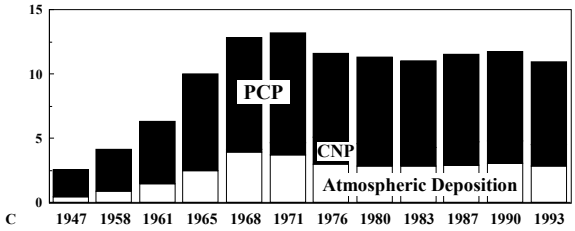

Figure 3. Contributions of different sources to dioxin pollution in sediment core

Discussion and Conclusion

Detailed analysis of a dated sediment core showed that dioxin input to aquatic sediment increased in accordance with PCP and CNP use. The input did not significantly decrease even after the decline of their use, indicating that dioxins remaining in agricultural land continued to run off and pollute the aquatic environment. A discrepancy between the contributions of different sources presented here and those estimated from the dioxin source inventory[5] was noted. This may be due partly to the limitation of the present statistical analysis based on data consisting of a very wide range of concentrations (very high concentration of OCDD and low concentration of many other congeners).

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