BEHAVIORS OF DIOXINS IN LAKE SHINJI BASIN DURING THE PAST 50 YEARS

Shigeki Masunaga[1,2], Yuan Yao[1,2], Isamu Ogura[1], Yutaka Kanai[3], Masumi Yamamuro[3], Junko Nakanishi l[1,2]

[1] Institute of Environmental Science and Technology, Yokohama National University, Yokohama 240-8501, Japan
[2] CREST, Japan-Science and Technology Corporation, Kawaguchi 332-0012, Japan.
[3] Geological Survey of Japan, 1-1-3 Higashi, Tsukuba, Ibaraki 305-8567, Japan

Introduction

A dated sediment core collected from Lake Shinji, Japan was analyzed and detailed isomer profiles were obtained [1].. In this paper, we have further analyzed the results to obtain a holistic view of the dioxin behaviors in the Lake Shinji Basin.

Materials and Methods

A sediment core was sampled from the western part of Lake Shinji, Shimane Prefecture, Japan in 1994 (Fig. 1) and dated by the Pb-210 and Cs-137 methods[2]. Detailed congener specific dioxin (PCDD/DF) and coplanar PCB (co-PCB) analysis was condcuted[1].

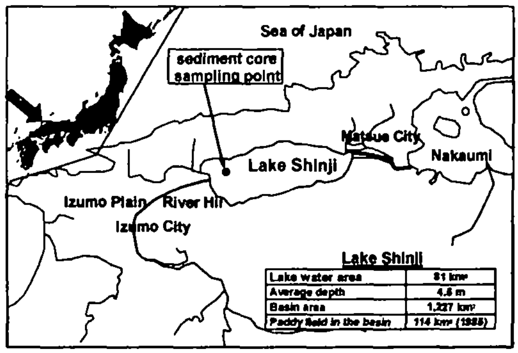

Fig.1. Sampling point in Lake Shinji

Results and Discussion

Trends of dioxin pollution recorded in the sediment core: Total dioxin concentration in the sediment core increased gradually from the 1940s to 1950s and then increased rapidly during the 1960s (Fig. 2). It decreased slightly in the early 1970s and then leveled off. The rapid increase during the 1960s is due mainly to O_8CDD and partly to H_7CDDs. The concentration of O_8CDD decreased in the early 1970s while that of T_4CDDs increased.

To identify the possible sources of dioxin, principal component analysis (PCA) was applied to congener-specific data (83 GC peaks corresponding to an individual or group of congeners as variables and 12 sliced disks of sediment core as cases). The PCA yielded three major principal components (PCs) (Table 1). Based on the characteristic congeners in each PC, PC-1 and PC-2 were judged to be the

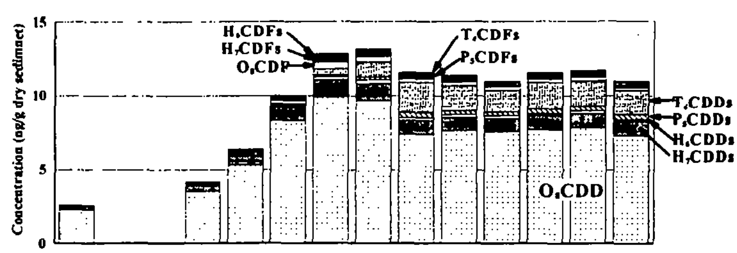

Fig. 2. Trends of dioxins in the dated Lake Shinji sediment core

impurities of pentachlorophenol (PCP) and chloronitrophen (CNP), respectively. Both PCP and CNP were used as paddy field herbicides in Japan. PC-3 did not match any known sources perfectly, however, it could be attributed to another major dioxin source, incineration (thermal process), because its T_4CDD, P_5CDF, T_4CDF and P_5CDF congeners had relatively high factor loadings. Thus PCP, CNP and incineration (atmospheric deposition) were found to be the three major sources of dioxin in the Lake Shinji sediment.

Table 1. 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)	O_8CDD, H_7CDDs, O_8CDF, most of H_7CDFs	2468-T_4CDF, 1368/1379-T_4CDD, 12368-P_5CDD	some T_4CDDs & T_4CDFs, 12469/12369-P_5CDD

The contributions of the three sources to the sediment pollution were estimated by multiple regression analysis (MRA) using the congener profiles of PCP, CNP and atmospheric deposition. The congener profile for PCP was constructed based on the average congener composition of four PCP formulations produced in Japan[3] with slight modification to adjust its homologue profile. The congener profile of CNP was determined based on the average of five CNP formulations weighted by their representing amount of production[3]. For incineration sources, atmospheric deposition measured in the Kanto area, Japan was used due to the lack of data for the Lake Shinji region[4]. The results of the MRA are shown in Fig. 3 with the standard error ranges. The dioxin concentration originating from PCP peaked in the late 1960s and decreased slightly in the 1970s. Although the contribution of PCP was estimated to be 100% for the year 1947, this can be regarded as the background contamination level because PCP had not yet been used in those days. The dioxins from CNP increased in the early 1970s and then leveled off. Those from atmospheric deposition (incineration sources) increased in the late 1960s and then leveled off. The contributions in terms of WHO-TEQ were estimated using the TEQ/PCDD&DF ratio in each source profile. The estimated trend of total TEQ corresponded well with the observed TEQ trend in sediment; however, it was 2 - 3 times greater than the observed TEQ. The discrepancy might be due to the large uncertainties in source profile data and the possible changes of dioxin composition in the environment. The contributions of PCP, CNP and atmospheric deposition in the recent sediment in terms of WHO-TEQ were about 60%, 10% and 30%, respectively.

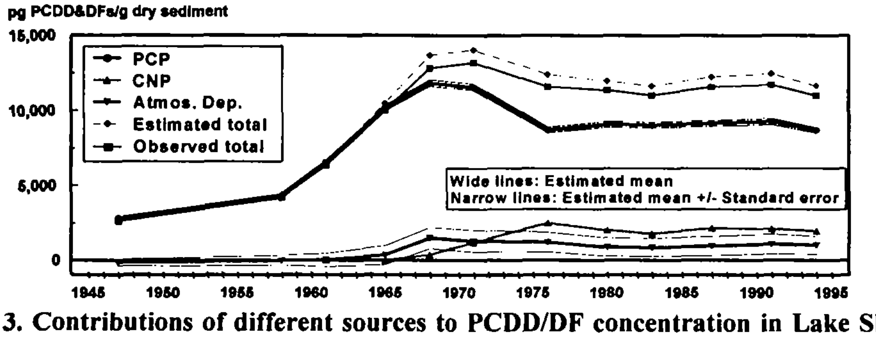

Fig. 3. Contributions of different sources to PCDD/DF concentration in Lake Shinji sediment core. (Atmos. Dep.= Atmospheric deposition = incineration sources)

***Behavior and mass balance of dioxin in Lake Shinji Basin*:** The amounts of dioxin input to the basin from herbicides were estimated from the amounts of herbicides used[5] and their dioxin contents. The arithmetic mean of dioxin concentrations in PCP reported worldwide and the time trend change of dioxin concentration in CNP were used. The historical trend of dioxin deposition in the bottom sediment of the lake was also calculated assuming that the dioxin concentrations in sediments were spacially uniform over the lake but that the sedimentation rates differed[2]. The trends of dioxin input to the basin and deposition in bottom sediment from PCP and CNP in terms of WHO-TEQ are shown in Fig. 4. The trends of dioxin input, accumulation in the basin and deposition in sediment from PCP showed that deposition in sediment increased several years ahead of PCP use (Fig. 4-(A)). This may be due to an error in core dating, the vertical mixing of sediment, and/or a higher run-off rate during the period of herbicide application. However, the trends of cumulative input and annual deposition appeared to be very similar. Assuming that annual deposition was proportional to the amount of dioxin present in the agricultural field in the basin, the annual loss rate of dioxin present in the basin was estimated so that the simulated decrease of dioxin in the basin would be parallel to the annual deposition. The simulation indicated that dioxin in the basin decreased at a rate of about 1.1%/year. A similar analysis was conducted for CNP (Fig. 4-(B)). The trends of cumulative TEQ input and sediment deposition corresponded to each other very well although the increase of deposition occurred 2 - 3 years ahead of the increase of input. Under the same assumptions as in the case of PCP, the annual loss of dioxin from the soil in the basin was estimated to be around 0.9%/year, which was close to that for PCP. Based on these, the dioxins in the soil in the basin were estimated to be lost at a rate of 0.9 - 1.4 %/year (loss rates of PCDD/DFs for PCP and CNP were estimated to be 1.4 and 1.1 %/year, respectively) or a half-life of 50 - 77 years. The loss mechanism may include run-off, volatilization, degradation, and burial (covering of surface soil due to a change in land use).

The mass balance of dioxin during the past 50 years (1945-1994) is summarized in Fig. 5. The amount of PCDD/DF input to the basin from PCP was estimated to be slightly greater than that

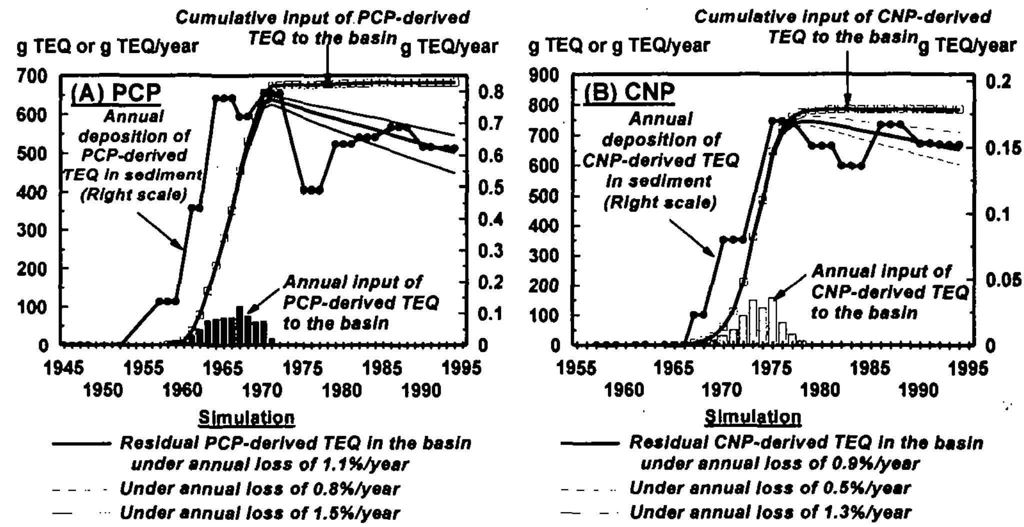

Fig. 4. Estimated trends of TEQ deposition in bottom sediment of Lake Shinji and TEQ input to and accumulation in the basin through the use of PCP (A) and CNP (B)

from CNP, the amount of PCP-derived PCDD/DF lost from the soil in the basin was estimated to be twice as much as that from CNP. This difference may be due to the difference in the application history of the two herbicides (PCP was used prior to CNP). The ratios of accumulation in the lake sediment against loss for the two herbicides differed by twofold. The ratios are expected to be close to each other if the environmental behavior of dioxins from the two herbicides were similar. Thus, this difference might be partly due to an error in the estimation of dioxin concentration in the herbicides. In terms of WHO-TEQ, the ratio for PCP was estimated to be nearly five times larger than that for CNP.

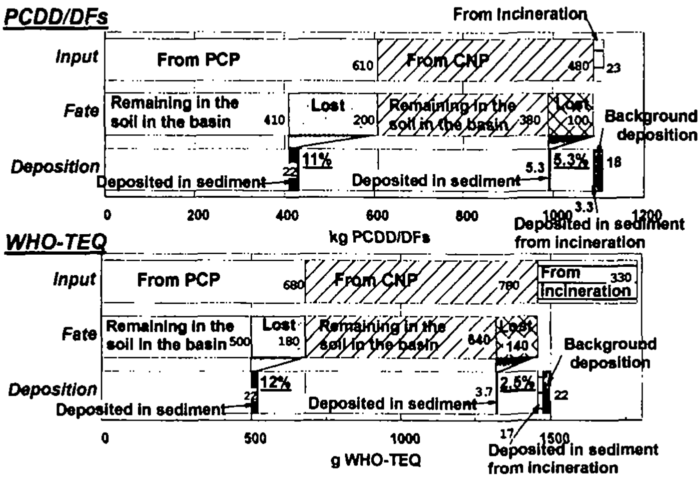

Fig. 5. Estimated input and fate of dioxins originating from PCP and CNP in Lake Shinji basin during 1945-1994.

Conclusions

The analysis of a dated Lake Shinji sediment core revealed that dioxin pollution from PCP and CNP herbicides was severe in the 1960s and 1970s. On the basis of the decrease of dioxin deposition in the lake after the period of intensive herbicide use, accumulated dioxin in the soil of the lake basin was estimated to have decreased at 0.9 - 1.4% per year or a half-life of 50 - 77 years. Thus, dioxin run-off from agricultural fields will continue for a long time in the basin.

Acknowledgments

This research was supported by CREST of the Japan Science and Technology Corporation.

References

1. Masunaga, S., Yao, Y., Ogura, I., Nakai, S., Kanai, Y., Yamamuro, M., and Nakanishi, J. (1999) Organohalogen Compounds 43, 383-386.
2. Kanai, Y., Inouchi, Y., Yamamuro, M., Tokuoka, T. (1998) Chikyukagaku (Geochemistry) 32, 71-85.
3. Masunaga, S., Nakanishi, J. (1999) Organohalogen Compounds 41, 41-44.
4. Ogura, I., Masunaga, S., Nakanishi, J. (1999) Organohalogen Compounds 41, 443-446.
5. Ministry of Agriculture, Forestry and Fishery (1958-1996) Noyaku Yoran, Nihon Shokubutsu-Boueki Kyokai.