Comprehensive Analysis of Dioxin and co-PCB Behaviors in Lake Shinji Basin

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Abstract

Based on the dioxin (PCDD/DF) and coplanar PCB (co-PCB) analyses of a dated sediment core, fish and shellfish collected from Lake Shinji as well as other related published information, the past and present states of dioxin pollution in the Lake Shinji Basin were described.

The dioxin concentration and profile recorded in the sediment core showed that the pollution originating from PCP and CNP herbicides was severe in the 1960s and 1970s. From the decrease of dioxin deposition in the lake after intensive herbicide use, the dioxins accumulated in the soil of the basin was estimated to have decreased by 0.9 – 1.4% per year or a half-life of 50 – 77 years, indicating that dioxin run-off from agricultural fields would continue for a long time in the basin. The contributions of PCP, CNP and incineration to the TEQ concentration in the present surface sediment of the lake were estimated to be about 60, 10 and 30%, respectively.

A rough estimate of the contribution of PCB formulation and incineration to the non-ortho-PCB pollution in the sediment core indicated that PCP formulation increased its share during the 1960s and 1970s when it was produced and used. Its share was about half the total co-PCB-concentration in recent sediment.

The contributions of the various sources to dioxins accumulated in the aquatic organisms in the lake were different from those in the sediment due to the preferential bioaccumulation of dioxin and PCB congeners. While the contribution of PCP formulation to total TEQ decreased from around 60% in the sediment to 20 – 30% in organisms, co-PCB from incineration and PCB formulations increased from abut 2 % in sediment to about 40 - 50% in organisms. The

incineration derived PCB-TEQ was estimated to be in a similar range as the incineration derived PCDD/DF-TEQ in organisms while the former was only 4 % of the latter in the sediment.

1. Introduction

In the two previous workshops, I presented evidence that past agricultural use of herbicides is one of the major causes of the present environmental dioxin pollution in Japan. The evidence presented consisted of the results of analyses of present surficial aquatic sediments as well as the estimated time trends of dioxin emissions from major sources. During the last year, we have concentrated our efforts on determining whether the past pollution is indeed recorded in the environmental samples and aquatic biota. These data are presented by the other members in this workshop. In this paper, I will summarize all the results and present a holistic view of the state of the Lake Shinji Basin. Although I am solely responsible for this summary and interpretation of the data, the data themselves are the fruit of cooperation of the many people listed in the acknowledgments.

2. Data acquisition

2.1 *Sediment core from Lake Shinji*

A sediment core was sampled from the western part of Lake Shinji, Shimane Prefecture in 1994 and dated by the Pb-210 and Cs-137 methods by Kanai (Geological Survey of Japan) and his co-workers (Kanai *et al.*, 1998). Dioxin (PCDD/DF) and coplanar PCB (co-PCB) concentrations in the core were measured by Yao and Ogura (Masunaga *et al.*, 1999; Yao *et al.*, 1999).

2.2 *Biological samples from Lake Shinji*

The biological samples were collected from Lake Shinji by Yamamuro (Geological Survey of Japan) and her co-workers. The dioxin and co-PCB concentrations of these samples were measured by Kang (Kang *et al.*, 1999).

3. Analysis and discussion of the data obtained from Lake Shinji Study

3.1 *Trends of dioxin pollution recorded in the sediment core*

Total dioxin concentration in the dated sediment core increased gradually from the 1940s to 1950s and then increased rapidly during the 1960s (Fig. 1). 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

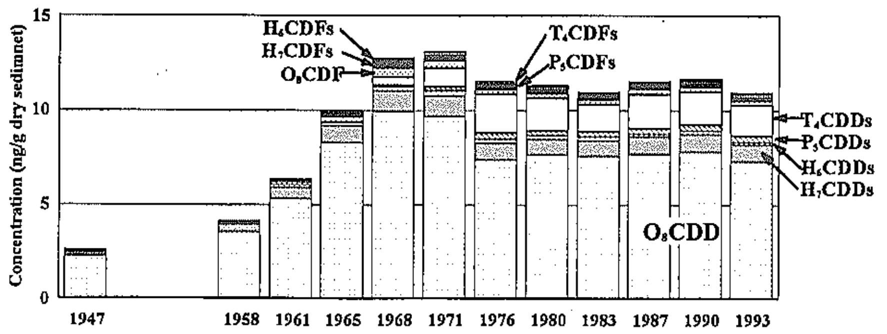

Fig. 1. Trends of dioxin concentration in dated Lake Shinji sediment core

T_4CDDs increased.

To identify the possible sources of dioxin, principal component analysis (PCA) using a correlation matrix 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 after varimax rotation 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 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 can 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 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 measured in this project (Masunaga and Nakanishi, 1999). This average composition was slightly modified to adjust its homologue profile to be similar to the one indicated in the PCA without changing its isomer profile within each homologue. The congener profile of CNP was determined based on the weighted average of five CNP formulations measured in this project (Masunaga and Nakanishi, 1999). The weight was based on the trend of the amount of use. For incineration sources, atmospheric deposition measured in the Kanto area was used due to the lack of conger-specific data for the Lake Shinji region (Ogura *et al.*, 1999). The results of the multiple regression analysis are shown in Fig. 2 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 standard error of atmospheric deposition was larger than those of other sources, probably because of the lack of conspicuous congeners in its congener profile.

The contributions in terms of WHO-TEQ were estimated using the TEQ/PCDD&DF ratio in each source profile. The results are shown in Fig. 3. The estimated trend of total TEQ corresponded well with the observed TEQ in sediment; however, it was 2 – 3 times greater than the observed TEQ. This discrepancy showed that the congener profiles used in this study did not completely match those in the field. This was unavoidable because of 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 were about 60%, 10% and 30%, respectively.

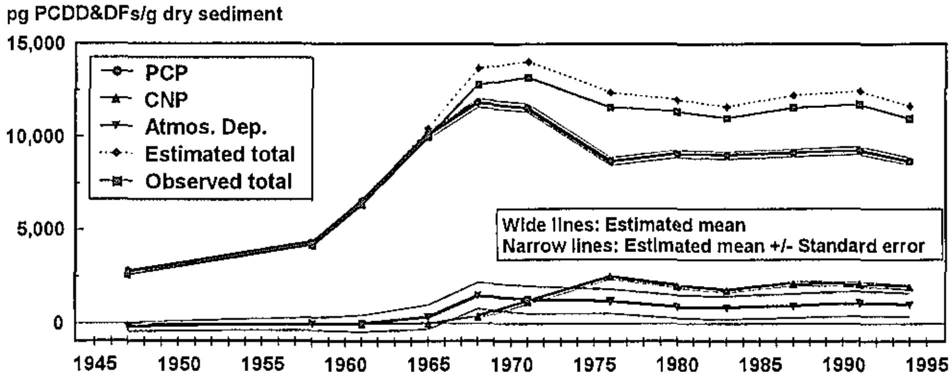

Fig. 2. Contributions of different sources to PCDD/DF concentration in Lake Shinji sediment

Atmos. Dep.= Atmospheric deposition = incineration sources

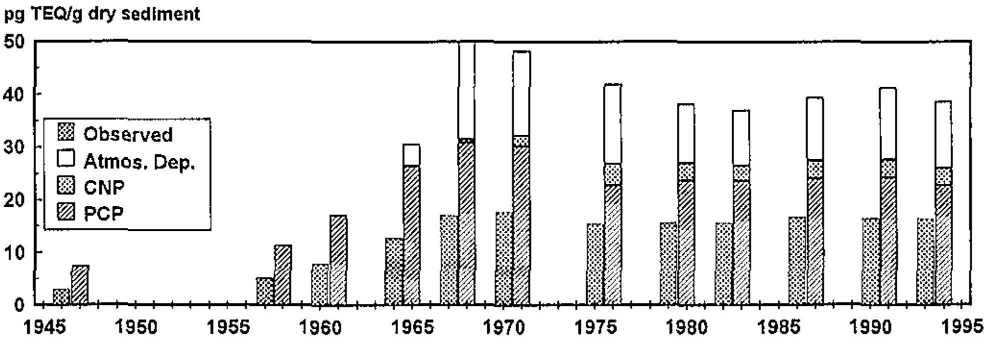

Fig. 3. Contributions of different sources to TEQ concentration in Lake Shinji sediment

3.2 *Behavior and mass balance of dioxin in Lake Shinji Basin*

In order to estimate the dioxin input to the Lake Shinji Basin, the amount of herbicide used in the basin was calculated from the herbicide shipment data to Shimane Prefecture (Ministry of Agriculture, Forestry and Fishery, 1958-1996) and the ratio of paddy field areas in Shimane Prefecture to that in Lake Shinji Basin (Fig. 4). The arithmetic mean of dioxin concentrations in PCP reported worldwide and the time trend change of dioxin concentration in CNP were used to calculate the dioxin load to the basin. The historical trend of dioxin deposition in the sediment of Lake Shinji was also calculated from the core data, assuming that the dioxin concentration in sediment was uniform all over the lake but that the sedimentation rate differed depending on the part of the lake (Kanai *et al.*, 1998). 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 Figs. 5 and 6.

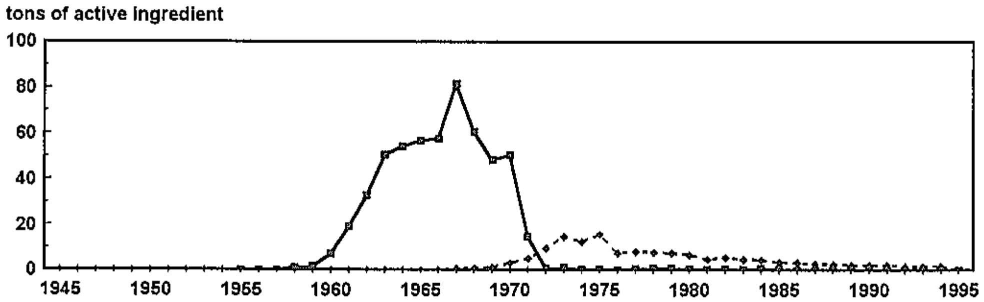

Fig. 4. Amount of PCP and CNP herbicides used in Lake Shinji Basin (active ingredient)

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. 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 shown in Fig. 5. 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. 6). The trends of cumulative TEQ input and sediment deposition corresponded to each other very well although the increase of deposition occurred a 2 – 3 years of 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 the trend of deposition in sediment, the dioxins in the soil in the Lake Shinji 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 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).

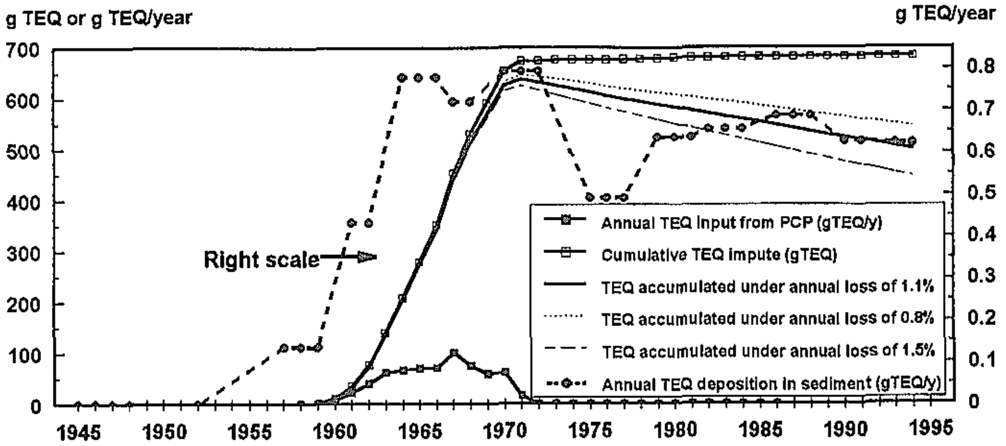

Fig. 5. Estimated trends of TEQ deposition in bottom sediment of Lake Shinji and TEQ input to and accumulation in the basin through PCP herbicide use (WHO-TEQ)

Follow left scale except for 'Annual TEQ deposition in sediment'.

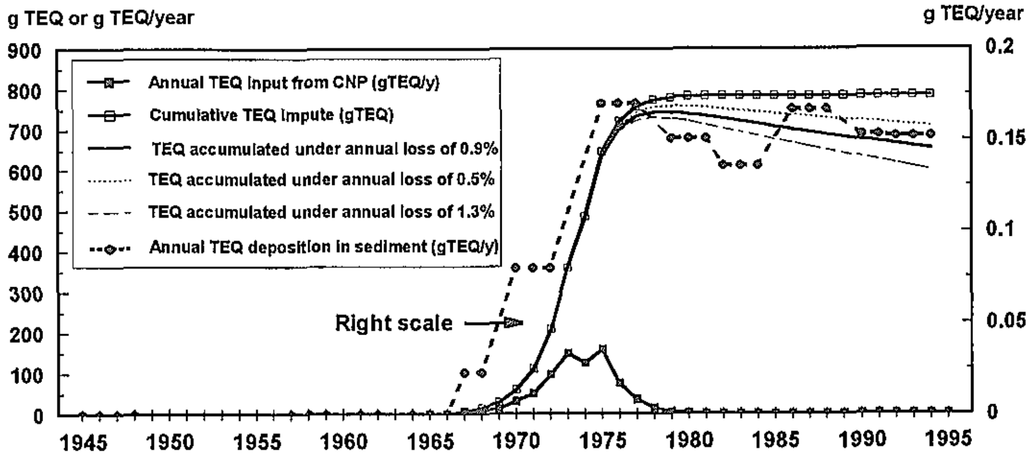

Fig. 6. Estimated trends of TEQ deposition in bottom sediment of Lake Shinji and TEQ input to and accumulation in the basin through CNP herbicide use (WHO-TEQ)

Follow left scale except for 'Annual TEQ deposition in sediment'.

The mass balance of dioxin during the past 50 years (1945-1994) is summarized in Table 2. While the amount of PCDD/DF input to the basin from PCP was estimated to be slightly greater than that 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. The weighted average TEQ concentration in CNP used in this study might have been up to five times too high relative to that in PCP.

Table 2. Estimated total dioxin input to the basin and total dioxin deposition in the sediment of Lake Shinji during 1945-1994

	PCP	B.G.[1]	CNP	Air.Dep.[2]	Total
PCDD/DFs					
Input to the basin (kg)	610	-	480	23[3]	1,100
Loss from the basin (kg)	200	-	100	-	-
Accumulated in sediment[4] (kg)	22	18	5.3	3.3	48
Accumulated in the lake / Input (%)	3.5	-	1.1	15	4.4
Accumulated in the lake / Loss (%)	11	-	5.3	-	-
PCDD/DF-WHO-TEQ					
Input to the basin (g TEQ)	680	-	780	330[3]	1,800
Loss from the basin (kg)	180	-	140	-	-
Accumulated in sediment[4] (g TEQ)	22	22	3.7	17	65
Accumulated in the lake / Input (%)	3.3	-	0.5	5.2	3.7
Accumulated in the lake / Loss (%)	12	-	2.5	-	-

[1] Background dioxin deposition in sediment. [2] Atmospheric deposition = incineration sources.
[3] Estimated based on Environment Agency's atmospheric deposition monitoring data of 1998.
[4] Estimated from the sediment core data in this study.

3.3 *Discussion on non-ortho-PCBs in the Lake Shinji Basin*

Since all-congener analysis of PCBs in sediment was not performed, the application of PCA to the data for source identification was judged to be inappropriate. Thus, a simpler analysis was conducted assuming that PCB formulation and incineration were the only two major sources of co-PCB pollution.

The trends for non-ortho-PCBs in the sediment core are shown in Fig. 7. While congeners, CB-77, CB-81 and CB-126, exhibited peaks in the late 1960s, reflecting the period of production and use of PCB formulation (Kanechlor), congener CB-169 did not show any elevation during the same period. In order to confirm that PCB formulations were not the major source of CB-169, the amount of each PCB congener produced was estimated based on the concentration in Kanechlor (Takasuga *et al.*, 1995) and the amount of production. Fig. 8 shows the results as well as the emission from other sources. Although values of emission from waste incineration are not reliable due to the limited data, incineration was indicated to be a greater source of CB-169

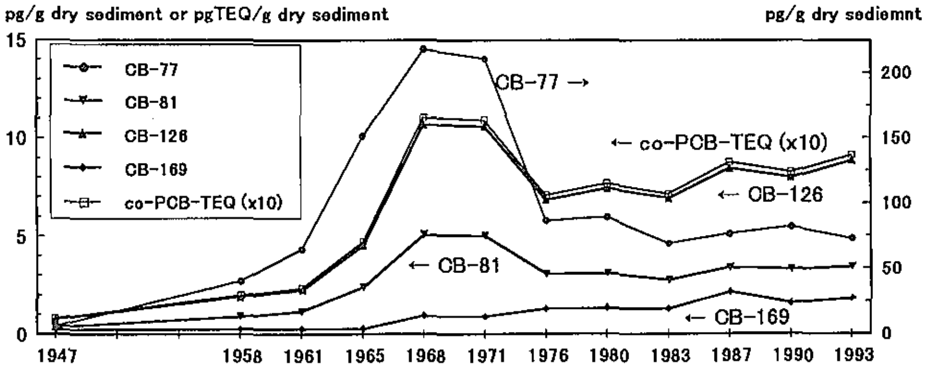

Fig. 7. Non-ortho-PCB concentrations in the dated Lake Shinji sediment core
Follow left scale except for CB-77.

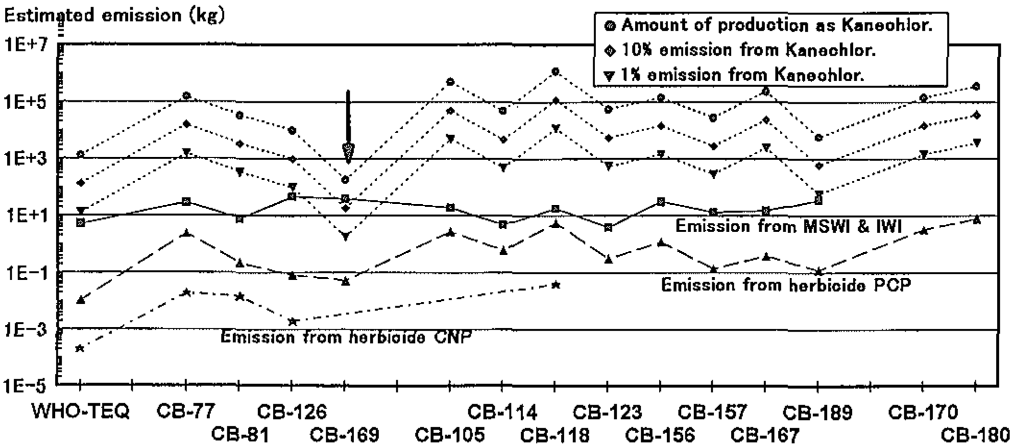

Fig. 8. Environmental input of PCB congeners from different sources over the past 40 years in Japan

The coplanar PCB concentration data used for estimation: Kanechlor: Takasuga *et al.*, 1995; Municipal solid waste incineration (MSWI): Sakai *et al.*, 1999; Herbicides: Masunaga *et al.*, 2000.

than PCB formulations and herbicides. Since TEFs for CB-126 and CB-169 are much larger than those for other PCB congeners, these two congeners are usually the top two contributors to total PCB-TEQ. Thus, co-PCB pollution in terms of TEQ can be roughly discussed based on only CB-126 and CB-169. As CB-126/PCB-169 ratios were very large for most Kanechlor formulations and about 2.7 ± 0.7 for atmospheric deposition in the Kanto area, excluding the data with significant influence of PCB formulations (Ogura *et al.*, 1999), the assumption that CB-169 came totally from incineration sources can be justified. Thus, the contribution of incineration to PCB-TEQ could be roughly calculated using the CB-169 concentration and average CB-126/CB-169 ratio for incineration sources. The results are presented in Fig. 9 and show that incineration contributed most of the co-PCB-TEQ in sediment core in the 1950s, but its contribution declined to about 20% in the 1960s and then increased to about 50% after the late 1970s. Although this is a rough estimate of the co-PCB pollution, it should be noted that nearly half of the present co-PCB-TEQ in Lake Shinji sediment was indicated to have originated from PCBs produced in the past.

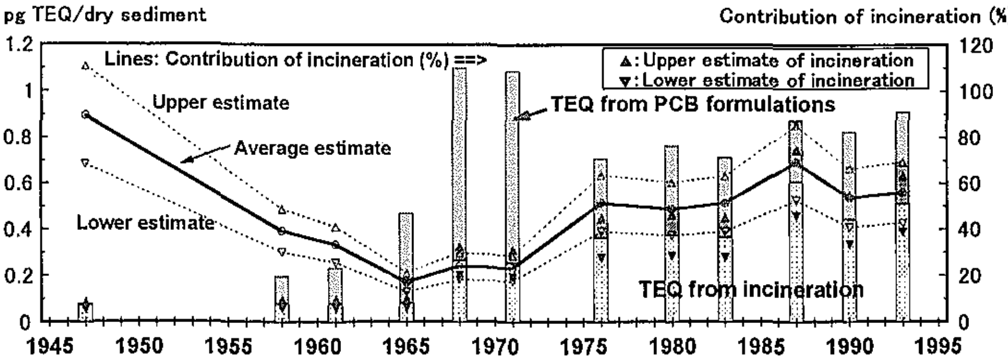

Fig. 9. Estimated contribution of incineration and PCB formulation to co-PCB-TEQ in the Lake Shinji sediment core

TEQ was calculated based on four non-ortho-PCB congeners.

3.4 *Discussion on contamination of fish and shellfish in Lake Shinji*

Based on the above analysis of the contributions of the different sources to sediment pollution and the reported contamination of fish (sea bass = suzuki) and shellfish (corbicula = shijimi) in the lake (Kang *et al.*, 1999), the transfer of dioxins from sediment to biota will be discussed. Assuming that contamination in aquatic organisms reflects the contamination in surface sediment and that bioavailability of each dioxin and co-PCB congener does not change irrespective of their original sources, namely, PCP, CNP, PCB or incineration, the contributions of different sources in organisms were calculated. The results are presented in Fig. 10 for corbiculas and sea basses caught in the lake. While PCP-derived PCDD/DF was the largest contributor to the total TEQ in surface sediment, its contribution in organisms decreased to 1/2 – 1/3. Coplanar PCBs, which were minor contributor in sediment (about 2 %) constituted about half the total TEQ in organisms. Incineration contributed nearly 60 % of the total TEQ in fish and shellfish.

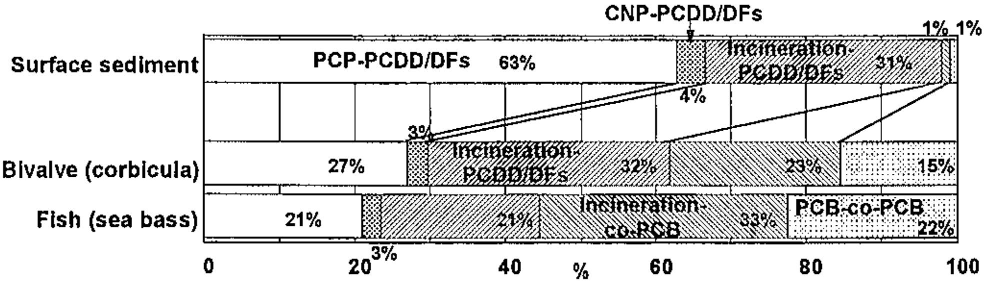

Fig. 10. Contribution of different sources to total TEQ in fish and shellfish from Lake Shinji

4. Conclusions

The analysis of a dated sediment core revealed that dioxin pollution from PCP and CNP herbicides was severer in the 1960s and 1970s than at present in Lake Shinji . On the basis of the decrease of dioxin deposition in the lake after the period of intensive herbicide use, the decrease of accumulated dioxin in the soil of the lake basin was estimated to be 0.9 – 1.4% per year or a half-life of 50 – 77 years, indicating that dioxin run-off from agricultural fields will continue for a long time in the Lake Shinji Basin. The contributions of PCP, CNP and incineration to the TEQ concentration in the recent sediment of Lake Shinji were estimated to be about 60, 10 and 30%, respectively.

A rough estimate of the contribution of PCB formulations and incineration to the non-ortho-PCB pollution in the sediment core indicated that PCP formulation increased its share during the 1960s and 1970s when it was produced and used. Its share was about half the total TEQ for recent sediment.

In the aquatic organisms in the lake, the contributions of sources were different from those in the sediment due to the preferential bioaccumulation of dioxin and PCB congeners. While the PCP contribution to total TEQ decreased from around 60% in the sediment to 20 - 30% in organisms, co-PCB from incineration and PCB formulations increased from about 2% in sediment to nearly 50% in organisms. The results also indicate that reduction of incineration sources is expected to contribute to the reduction of PCDD/DF-TEQ and PCB-TEQ in fish and shellfish to a similar extent.

5. Acknowledgments

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