Time Trends of PCDDs/DFs in Sediments from Osaka Bay and Lake Biwa

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Introduction

The emission of PCDDs/DFs into the environment from various sources including municipal solid waste incineration has been a pressing problem in our society. Recently traces of the situation of PCDDs/DFs contamination in the soil, air, and in mother's milk have been reported. However, very little research has focused on the analysis of PCDDs/DFs contamination by using sediment core in Japan. In Europe and the U.S., several investigations on this subject have already been conducted. The processes of PCDDs/DFs contamination from the past through to the present have been recognized, and effective measures for their control have been outlined. Regarding this research the time trends in levels, patterns and profiles of PCDDs/DFs were analyzed from sediment core samples taken from Osaka Bay and Lake Biwa. This paper reported our new findings on the processes of past PCDDs/DFs.

Material and Methods

Sediment core samples were taken from three points in Osaka Bay: the coast of the Yodo River, the coast of Kobe City, and the south of the Kansai International Airport and from two points in Lake Biwa (the northern and the southern parts). The reasons as to why we chose these areas for sampling are as follows:

- The coast of the Yodo River is considered to be affected by the activities in the urban area and the water phase of the Yodo River
- The coast of Kobe City is affected by the activities in the urban area
- To the south of the Kansai International Airport there are no specific sources
- The northern part of Lake Biwa is considered to be less affected by man-made pollution due

to the low population density

- The southern part of Lake Biwa is considered to be more affected by man-made pollution in comparison to the northern part.

The sediment cores were sampled by divers using a plastic cylinder 10 cm in diameter and 1.2~1.5 m in length at a depth of 5~18 m. These samples were immediately refrigerated and later sliced into 2 cm-thick disks, and then air-dried for two days after which they were analyzed for traces of PCDDs/DFs. In the analysis of PCDDs/DFs, 10 core disks were equally chosen from each sediment core, following the "Manual for Standard Measurement and Analysis of PCDDs/DFs[1]". They were dated by the ^{210}Pb method[2] which is a method using a radio nucleotide: the sedimentation rate is calculated from the concentration variation of ^{210}Pb, which is a fallout formed by radioactive decay through ^{222}Rn from ^{238}U in the earth crust, from which the age is then estimated. The half-life of ^{210}Pb is 22.2 years. Using this method the deposition date retroactive to 100 years ago can be measured, and this method is fairly suitable for sediments from lakes and inland seas where the deposition velocity is relatively high. The deposition velocity was 900 mg/cm^2·year (23.3 mm/year) on the coast of the Yodo River, whereas the velocities in the northern and southern parts of Lake Biwa were 186 mg/cm^2·year (2.6 mm/year) and 152 mg/cm^2·year (4.7 mm/year) respectively.

Results and Discussion

Figure 1 shows the time trends of PCDDs/DFs in the sediment core from the coast of the Yodo River. Figures 2 and 3 represent the time trends of PCDDs/DFs in the sediment cores from the northern and southern parts of Lake Biwa respectively. The time trends in sediment cores from Osaka Bay were considerably different from those taken from Lake Biwa. They were also slightly different in stations of Osaka Bay and in two stations of Lake Biwa. First of all, looking at the time trends of PCDDs/DFs in sediment cores from Osaka Bay, shown in Figure 1, the concentration doubled during the latter half of the 1960s through to the beginning of the 1980s. The peak input occurred in 1993. Following this period, the concentration level became slightly lower and is presently stabilized. However, during this period, the homologue and congener profiles had not changed, which means that PCDDs/DFs have been being released from the same kinds of sources since the latter half of the 1960s. Regarding other stations in Osaka Bay, the necessity of reinvestigation is under discussion because the results of the ^{210}Pb method suggested the possibility of deposit disturbance. However, except at the surface level, no variation in the PCDDs/DFs concentration levels have been observed since the 1950s.

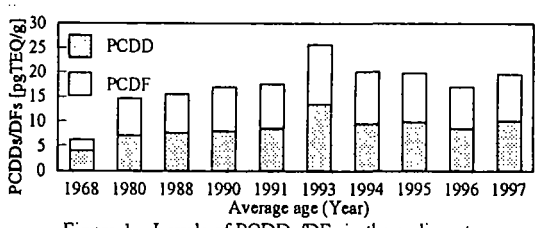

Figure 1 Levels of PCDDs/DFs in the sediment core from the coast of Yodo River

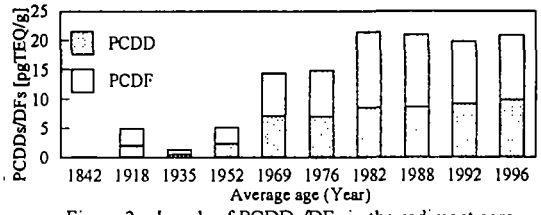

Figure 2 Levels of PCDDs/DFs in the sediment core from the northern part of Lake Biwa

On the other hand, in the northern part of Lake Biwa, the PCDDs/DFs concentration level increased from the latter half of the 1960s to the middle of the 1970s. It hit its peak input level at the beginning of the 1980s, and has since leveled off.

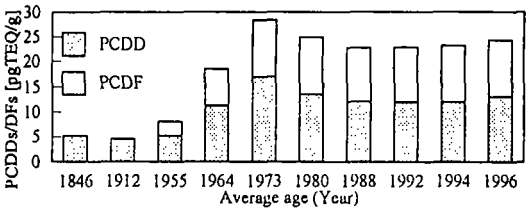

Figure 3 Levels of PCDDs/DFs in the sediment core from the southern part of Lake Biwa

In the southern part of Lake Biwa, the variation of PCDDs/DFs concentration was not observed for the 1840 ~ 1910 period. Furans were first detected in the sediment core sample corresponding to 1955, at which point the concentration level increased slightly. The level of concentration in the sediment core sample corresponding to 1964 increased drastically, and it reached a peak input level around 1980, as shown in Figure 3. And is now stabilized after having lowered slightly.

These data showed that the period of increase in PCDDs/DFs level in the northern part of Lake Biwa coincided with that in the southern part.

Figure 4 shows the homologue profiles of the 4 sediment core samples taken from the northern part of Lake Biwa in order of age (note the use of different scales of the concentration axis in these charts). In the 1935 sediment core sample, the PCDDs/DFs level was higher than that in the 1842 sediment core sample, and respectively the levels of TCDD and furans were higher as well. Moreover, in the 1969 sediment core sample, the total concentration and the ratio of TCDD in total were very high. In the 1996 sediment core sample, the ratio of TCDD increased slightly, but the entire distribution level was not much different from that of 1969. In particular, considering the TEQ values in the southern part of Lake Biwa, as shown in Figure 3, the OCDD-dominated increase of TEQ values coincided, along with the increase of PCDFs. These increased levels might have been due to the increase of PCDFs emissions from incineration and the presence of OCDD in the PCP (Pentachloro phenol) preservative.

The primary components were analyzed by the homologue profiles in the sediment cores from Osaka Bay and from Lake Biwa. Compared to the homologue profiles from the existing PCDDs/DFs sources, it became evident that the sediment cores from 3 stations in the Osaka Bay area have mainly been influenced by combustion-derived PCDDs/DFs. The sediment cores from 2 stations in the Lake Biwa area have been affected not only by the combustion-derived contaminants but also by CNP (Chloronitrofen, 4-nitrophenyl 2,4,6-trichlorophenyl ether) - derived PCDDs/DFs.

Investigations on this subject were conducted in Europe and the U.S. In comparison to the analysis of those sediment cores sampled in areas remote from specific contamination sources, the PCDDs/DFs levels in the uppermost sediment layers in Osaka Bay and in Lake Biwa are equivalent to the middle- or high-level contamination in Europe and the U.S. According to the investigations of PCDDs/DFs levels in sediment cores from Europe and the U.S., these levels hit a peak input level during the 1970s through to the 1980s, and they have been decreasing since due to various measures implemented for wastes, including agricultural chemicals and wastewater from chemical plants[3),4)].

In Japan the recent dioxin measures are expected to lower the PCDDs/DFs emission levels in the environment and in sediment. On the other hand, the high-level 1,3,6,8-TCDD, 1,3,7,9-TCDD

and OCDD, which are the PCDDs/DFs contained in herbicides and preservatives, such as CNP and PCP, have been detected in recently deposed sediment cores from Lake Biwa. This indicates that the PCDDs/DFs released in the environment in the past cannot be reduced soon, and the input of PCDDs/DFs into the environment is still continuing. In the future, the PCDDs/DFs level in the environment is expected to be lowered by a reduction in the direct release of MSW incineration gases into the environment.

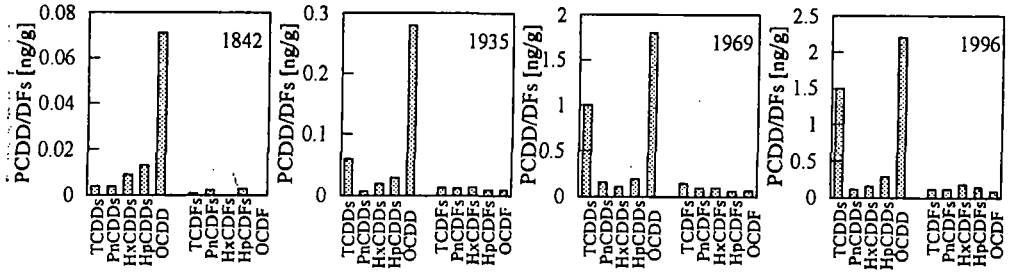

Figure 4 Homologue profiles in the sediment core from the northern part of Lake Biwa

Conclusion

1. This investigation clarified the time trends of PCDDs/DFs in sediment cores from Lake Biwa from around 1850 to the present. PCDDs/DFs were already detected in Lake Biwa around 1850. The PCDDs/DFs level began to be high around 1950, and rapidly rose in the 1960s. It reached to a peak during the 1980s to the 1990s, and the level has been stable since.
2. Due to the high rate of sedimentation in Osaka Bay, we could only observe the time trends for deposition from around 1950 to the present. From this, the time trends corresponding to the increase in total PCDDs/DFs were identified.
3. In the samples from Lake Biwa, the homologue distribution of PCDDs/DFs was observed. This observation shows that this area has had an influence of herbicides and preservatives, such as CNP and PCP, in addition to incineration.

References

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