

Environmental Levels in Sediment, Sewage, Sludge and Food

Influential Factors on Time Trends of PCDDs/DFs in Sediments

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1. Introduction

In 1997, analysis of PCDDs/DFs in sediments over time in Osaka Bay and Lake Biwa were performed. We observed that the PCDDs/DFs concentration in every sediment core dramatically increased after the middle of the 20th century and was recently stabilized or slightly less. According to the evaluation of homologue profiles, PCDDs/DFs formation was considered to be due to multiple pollution from combustion sources and herbicides containing organic chlorine compounds, such as PCP and CNP¹⁾. Here the influence of various factors including types of sources and the load to the environment on time trends of PCDDs/DFs in sediment cores from the coast of Kobe City in Osaka Bay was investigated, in addition to measurements of PCDDs/DFs in a background area in Japan.

2. Experimental Methods

Columnar sediment cores were sampled from lakes and inland seas using an acrylic pipe 1.2 m in length. These samples were sliced into 2 cm thick disks, and then, in which the concentrations of PCDDs/DFs and PCBs were quantitatively measured. They were dated using the ²¹⁰Pb method. The sedimentation rate was calculated from the concentration variation of ²¹⁰Pb contained in sediment core samples. PCDDs/DFs and PCBs analysis and the theory of the ²¹⁰Pb method are precisely described in our former report.

Sediment core samples were taken from the coast of Kobe City in Osaka Bay and Shiraike Pond (Niigata prefecture) in August 1997, July and September 1998 and March 1999. Shiraike Pond was chosen as a background as it is located in mountainous region (altitude: 1100 m) and there is no definite pollution sources of PCDDs/DFs in the surrounding area. Sediment core samples and surface samples of sediment cores were taken from the coast of Kobe City where large-scale fires occurred during Great Hanshin Earthquake, which damaged the area of Kobe city in January 17, 1995. The surface sediment core samples were taken at a depth of 10 cm using a Smith-Mackintire type sediment sampler.

3. Results and Discussion

3.1 Background trend

Figure 1 shows the trend of PCDDs/DFs sedimentation in Shiraike Pond. The sedimentation rate is now under measurement, but it is thought to be very low. It was confirmed that the concentrations in surface sediment core samples (maximum: 1100 pg/g, 7.6 pg-TEQ/g) were slightly higher than those in other samples. As a whole, the concentrations have been at low level of 65~170 pg/g (0.13~0.38 pg-TEQ/g). Since plants were found in the uppermost sediment layers, it is considered that plants containing PCDDs/DFs have possibly influenced on the concentration in the sediment core. The PCDDs level was higher than that of PCDFs and levels of OCDD and TCDDs were outstandingly high ratio in the homologue distribution profiles.

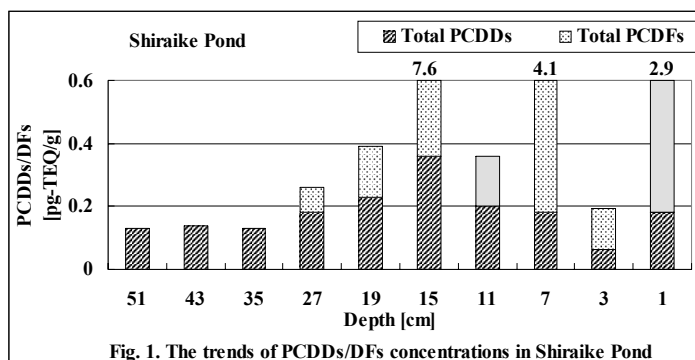


Fig. 1. The trends of PCDDs/DFs concentrations in Shiraike Pond

Compared with the analysis

of time trends and homologue distributions conducted in other countries, in the case of the Five Lakes in the U.S.²⁾, PCDDs/DFs concentrations in Siskiwit and Outer Island, where are remote from urban areas and affected by airborne contamination, were between 300 and 1100 pg/g, which are higher than those in Shiraike Pond. The PCDDs/DFs level in Lake Siskiwit increased from 1954 to 1980 and then slightly decreased. The level in Outer Island has been stable since 1937. The homologue distribution profiles in these two areas show high levels of highly chlorinated PCDDs. High PCDDs/DFs concentration levels at 1.98~63.7 pg-TEQ/g (average: 18.7 pg-TEQ/g) were detected in 27 surface sediment core samples taken from lakes remote from urban areas in the southern part of the Mississippi state³⁾. Their homologue profiles also showed that the levels of OCDD and HpCDDs were remarkably high. In Lake Baikal⁴⁾ in Russia, PCDDs/DFs levels were between 0.03 and 0.05 pg-TEQ/g in the surface sediment layer samples taken from the northern unpopulated area which is less affected by man-made pollution. These levels are lower by one digit than those in Shiraike Pond. Although the background levels of Shiraike Pond are very low, further investigation on the trend over time is necessary.

Environmental Levels in Sediment, Sewage, Sludge and Food

3.2 Trend of PCDDs/DFs in the coast of Kobe City in Osaka Bay

Figures 2 and 3 show that the trends of PCDDs/DFs concentrations in Core A sampled from a station 2.2 km from land in 1997 and in Core B sampled from a station 2.6 km from land in 1998, respectively.

All PCDDs/DFs concentrations in Core A samples were in the range of 1.3~2.1 ng/g (7.1~12.3 pg-TEQ/g) except those in surface layer samples, although the sampling stations are close to the large city of Kobe. The concentrations in Core B samples were also in the range of 2.1~2.5 ng/g (8.8~11 pg-TEQ/g) until 1990, but the levels in samples of recent sediment layers had slightly increased to 2.5~2.7 ng/g (15~18 pg-TEQ/g). In particular, TEQ values had obviously increased. High levels of PCDDs/DFs in

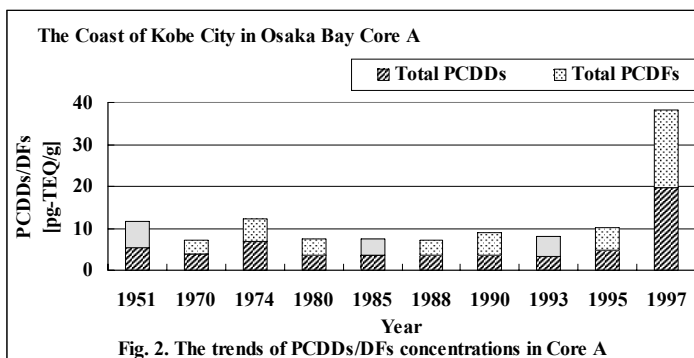


Fig. 2. The trends of PCDDs/DFs concentrations in Core A

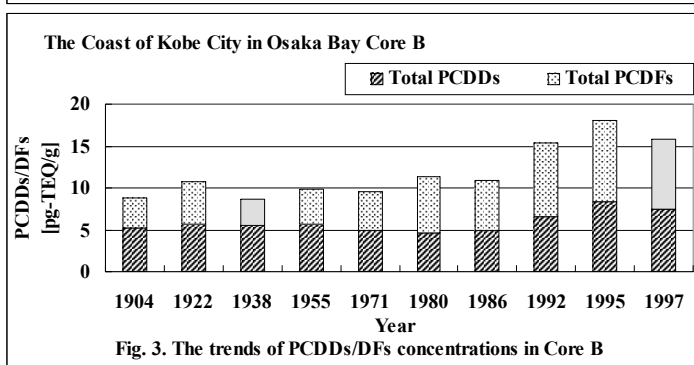


Fig. 3. The trends of PCDDs/DFs concentrations in Core B

recent sediment layers are considered to be due to the increase in furans levels. Tidal disturbances are thought to be the reason for no changes in the levels in sediment cores before 1990 - 1995. The homologue profiles in Core A and Core B showed that the levels of OCDD were highest and followed by HpCDDs. Furans were also detected in all homologues at a low level, which means the possible sources are combustion and herbicides including PCP.

Concentrations of both PCDDs/DFs were at the same level in Core A and Core B. Their sampling stations are thought to be affected by the same sources. Compared to the levels in Shiraike Pond as a background, the levels in Core A and Core B were one or two digits higher, although they are not specifically higher than those in sediment samples of internal bays. These results indicate that the magnitude and type of PCDDs/DFs pollution in the coast of Kobe City is greatly influenced by human-activities-oriented combustion and herbicides.

Large-scale fires and the inadequate treatment of collapsed housing and waste materials caused by Great Hanshin Earthquake in January 1995⁵⁾ are specific factors causing changes in the time trend.

Environmental Levels in Sediment, Sewage, Sludge and Food

In this regard, the high concentration of PCDDs/DFs in the 2 cm uppermost layer of Core A (5.4 ng/g, 38 pg-TEQ/g) in 1997 is notable. In Core B, a peak similar to the outstanding one in Core A was not observed, however an increase in the concentrations in the recent sediment layers was identified.

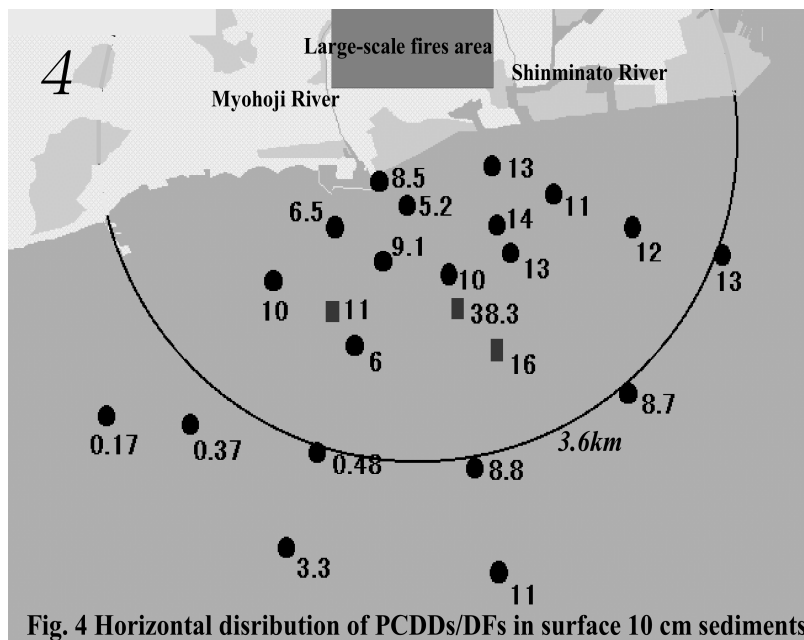


Fig. 4 Horizontal distribution of PCDDs/DFs in surface 10 cm sediments

PCDDs/DFs concentrations in the surface 10 cm sediment cores from the coast of Kobe City, shown in Figure 4, were almost same at the level of 10~15 pg-TEQ/g. The high level found in the 2-cm uppermost layer of Core A was not observed. The curved line in Figure 4 shows the outline of the expansion area of rain at 8 mm/hr rainfall on average, which was calculated by the Nitta method⁶⁾ taking into account the Shinminato River, the Myohoji River and a trunk line of the rain inflow as a route of the rain outflow. Since the left side of the outline experiences tidal influence, the concentrations are lower than those in other stations. Simulation of the spread of PCDDs/DFs from the fire area was implemented, taking the wind direction and firing conditions when fires broke out into account. High concentrations were expected in the southwestern part of the burnt-down area, but actually the high levels were observed in the southeastern area, as shown in Figure 4.

In the sediment cores of the coast of Kobe City, PCDDs/DFs accumulate under the influence of rivers, tides and the air. Particularly in samples taken from stations located in the influential area of rivers, PCDDs/DFs concentrations are at the almost same level, between 10 and 15 pg-TEQ/g. One of the uppermost layer of 1997 had the high concentration of PCDDs/DFs, 38.3 pg-TEQ/g. The level of highly chlorinated PCDDs/DFs was outstandingly high and furans was detected in all kinds of homologues. Furans levels have increased recently. The fires are therefore regarded as a factor which has increased the levels of PCDDs/DFs in sediment cores.

Environmental Levels in Sediment, Sewage, Sludge and Food

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Environmental Levels in Sediment, Sewage, Sludge and Food