RESIDUE PROFILES OF PCBs IN SEDIMENT AND PADDY SOIL AND THEIR BEHAVIOR IN THE LOWER BASIN

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Abstract

The concentrations of mono- to deca-chlorinated biphenyls in sediment and soil collected from the Toyano lagoon and the Kameda basin in the lower area of the major rivers in Niigata city, Japan, was congener-specifically determined and then discussed.

The level of polychlorinated biphenyls (PCBs) in the lower layers of the sediment core estimated approximately 30 years ago was one of the highest levels ever detected in Japan. Considering the good agreement between the temporal trend of concentration and the period of PCB product use in Japan, it is believed that the PCB products themselves are the cause of the high PCB concentration in the sediment.

The homologue and congener profiles of the paddy soil, surface sediment, and sediment core revealed varied patterns. It is suggested that route by which accumulation occurred in each medium was also different. Particularly, it is considered that recent deposition in each medium occurred via specific routes after the PCB discharge into the environment.

Introduction

In Japan, polychlorinated biphenyls (PCBs) toxicity had become a social issue in the latter 1960s, and the production, import, and use of PCBs have been prohibited since the early 1970s.

On the other hand, it was discovered that certain PCBs continue to persist in the environment. The widespread environmental persistence of PCBs is well known. Waters contaminated by PCBs particularly affect fish and aquatic biota. In the previous study, we discovered that sedimental polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/DFs) and PCBs affect fish, and the effect of sedimental PCBs on fish is greater than that of PCDD/DFs[1)]. However, the land used for the study had been used mostly for agricultural purposes and was not subjected to a direct input of PCBs

The aims of this study are to investigate the PCBs in the paddy soil and the sediment that was obtained from the same basin, to examine the source of the PCBs in each area, and clarify the behavior of PCBs present in the waters by using residue profiles.

Materials and Methods

Description of the sampling area

The paddy soil samples were collected from the Kameda basin in January 2004, and the surface sediment samples were obtained from the Toyano lagoon in December 2003.

The paddy soil was collected at a depth of approximately within 15 cm below the rice field surface. The surface sediment samples were collected using an Ekman-Birge type bottom sampler. In December 2000, the sediment core, which was a cylindrical sample with a diameter of 20 cm and a length of 80 cm, was collected from the northern part of the Toyano Lagoon. Figure 1 illustrates the sampling site and the number of samples collected.

The Kameda basin and the Toyano lagoon are present in suburban Niigata city and in the lower basin of the Shinano River and the Agano River. The area of the Kameda basin is 11,000 ha. Agricultural land account for approximately 40% of Kameda basin and 85% of it is paddy field.

The area of the Toyano lagoon is approximately 160 ha, and it receives water flow from the paddy fields irrigated by the Shinano River and Agano River and wastewater from households in the northern area of the city.

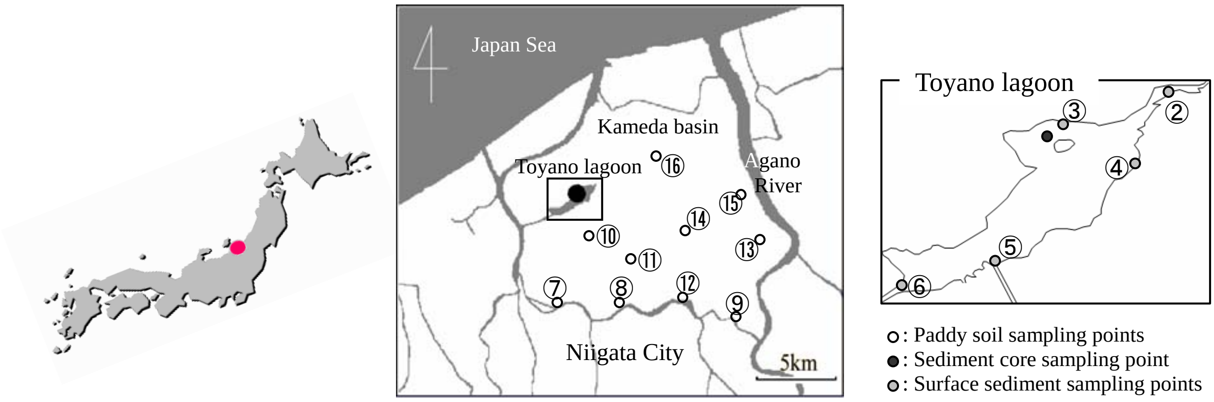

Figure 1 Map of the field study site. Niigata plain, Kameda basin, Toyano lagoon; location of each sampling station is indicated. (Paddy soil, n = 10; Sediment core, n = 1; Surface sediment, n = 5)

Determination of PCB concentration and sedimentation rate

The sample core was sliced into 2-cm thick disks. The average sedimentation rate was measured to be 0.32 g cm^{-2} $year^{-1}$ by using the Pb-210 and Cs-137 methods.

The samples were air-dried before the analysis. The sediment samples were ground into fine powder. The paddy soil was sifted using a 2-mm mesh sieve. Samples of dry weight 10 – 60 g were used for the analysis. The analytical method applied was in accordance with the manual of the Japanese Ministry of Environment.

After the addition of ^{13}C-labeled internal standards, each sample was extracted using a Soxhlet apparatus with 300 ml toluene for 16 h. During the extraction, the sulfur present in the sediment was removed using copper tips. Subsequently, the samples were subjected to sulfuric acid oxidation. Sample clean-up included chromatography on silica and active carbon-impregnated silica gels.

Identification and quantification of PCBs was performed by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC-HRMS; Hewlett Packard HP6890/JEOL JMS-700). Two hundred nine congeners of PCBs were separated and were quantified as 170 gas chromatographic peaks.

Results and Discussion

Sediment core concentrations and temporal trend

The concentrations of PCBs along with the estimated sedimentation age for each sliced core are presented in Figure 2. The minimum, maximum, average, and central PCBs concentrations were measured to be 2.2, 1200, 260 and 69 ng/g dry weight in the sediment core, respectively. The PCBs concentration of the sediment present in the Toyano lagoon was higher than the average concentration of 7.3 ng/g dry weight that was obtained in an investigation of the sediment by the Japan Environment Association[2)]. The PCBs concentrations in the lower layers of the sediment core was one of the highest levels ever reported in Japan with regard to the sediment present in rivers and lakes. The PCBs concentrations obtained after 1990 were approximately 10 times higher than the reported average.

In the late 1960s, the homologue concentration of PCBs significantly increased, maximized in approximately 1973 and/or 1975, decreased after the mid-1970s, and stabilized after the 1990s. The contribution of the homologue to the total concentration was similar in all the time periods. The sum of 3CBs, 4CBs, and 5CBs accounted for from 71% to 91% of the total concentration.

One of the sources of the present PCBs pollution is PCBs products that were used in the past. In Japan, production of PCBs began in 1954, and a large amount of PCBs were utilized. The period of peak usage was around 1970. The temporal trend for PCBs concentrations in the sediment core was in good agreement with the production date, reflecting the use of the products.

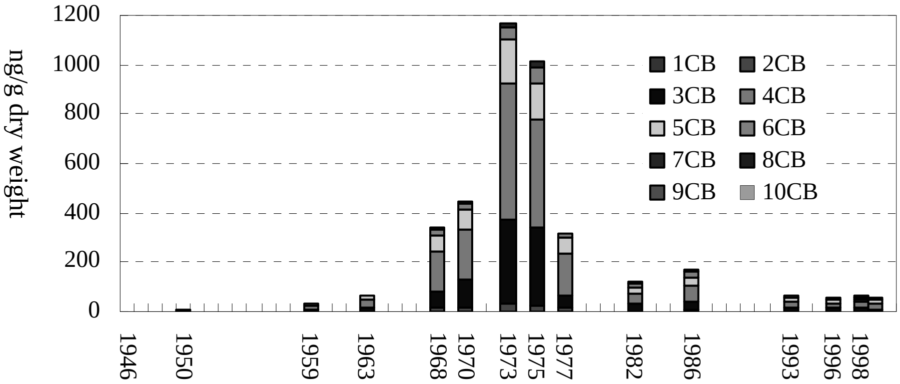

Figure 2 Temporal trend of PCBs concentration in the sediment core of Toyano lagoon.

Paddy soil and surface sediment concentrations

Table 1 lists the concentrations of PCBs present in the paddy soil and the surface sediment. The minimum, maximum, and average PCBs concentrations in the paddy soil were measured to be 1.7, 5.6, and 3.0 ng/g dry weight, respectively.

Both the range and average were comparable to or higher than the results obtained for the paddy soil collected from the Akita prefecture[3)]. The homologue profile and concentrations indicated the specific distribution of each sample; however, a constant tendency could not be found in the Kameda basin.

Comparison of concentrations between each paddy soil and sediment

The PCBs concentrations in the sediment were higher than those in the paddy soil for both the lower layers and the surface. PCBs accumulate in the sediment and soil via certain deposition routes from various media, including atmospheric deposition. However, the difference in concentrations could not be explained only by the route of atmospheric deposition because the Kameda basin and the Toyano lagoon are almost in the same region. There are a number of small channels in the Kameda basin that enable waste water collection from the paddy field. It is considered that these channels accumulate PCBs in their sediment. The sediment from a small channel is usually supplied to the lagoon by water flow and floods. Thus, the potential influence of the small channel as a source of contamination to the Toyano lagoon was indicated the by difference in concentrations between the paddy soil and the sediment in this.

Table 1 Minimum, maximum, and average concentrations (ng/g dry weight) of total and homologue PCBs in the soil of paddy fields and surface sediment collected in the Kameda basin and Toyano lagoon.

	Paddy soil n = 10	Surface sediment n = 5
1CB	0.017 － 0.32 (0.084)	0.0029 － 0.64 (0.20)
2CB	0.035 － 0.69 (0.17)	0.018 － 3.2 (0.83)
3CB	0.061 － 0.75 (0.26)	0.074 － 31 (7.3)
4CB	0.24 － 1.4 (0.74)	0.12 － 87 (20)
5CB	0.31 － 1.6 (0.73)	0.068 － 16 (8.7)
6CB	0.25 － 1.3 (0.65)	0.047 － 16 (4.2)
7CB	0.081 － 0.32 (0.18)	0.030 － 4.3 (1.1)
8CB	0.017 － 0.079 (0.048)	0.0057 － 1.3 (0.33)
9CB	0.0077 － 0.37 (0.052)	0.0011 － 0.16 (0.045)
10CB	0.0096 － 0.18 （0.055）	0.00078 － 0.083 (0.027)
Total PCBs	1.7 － 5.6 (3.0)	0.35 － 180 (43)

Homologue and congener composition in sediment and soil

Figure 3 lists the average of the homologue contribution ratio for the surface sediment and the paddy soil. The homologue compositions of the PCBs in the Toyano lagoon sediment were similar. The presence of 4CBs was predominant, and 3CBs and 5CBs were the major contributors to the PCBs. On the other hand, the homologue composition of PCBs in the Kameda basin paddy soil sample revealed a tendency to differ from each other. A Here, 4CBs, 5CBs, and 6CBs were the major contributors. The tendency from 3CBs to 7CBs exhibited that the composition of the paddy soil was biased to high chlorine.

Figure 4 illustrates the contribution ratio for each homologue to KC300, KC400, KC500, and KC600. These PCB products were mainly used in Japan. The homologue composition of KC400 and the sediment was similar; though the contribution rate of 4CBs was different between KC400 and the sediment. The past PCB products, especially the effect of KC400 significantly remained in the sediment, and the possibility of still keeping the composition was suggested.

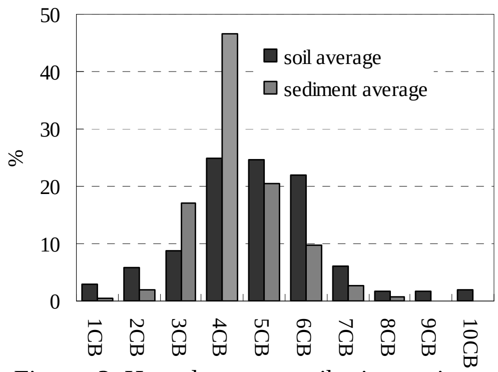

Figure 3 Homologue contribution ratios of sediment surface and paddy fields

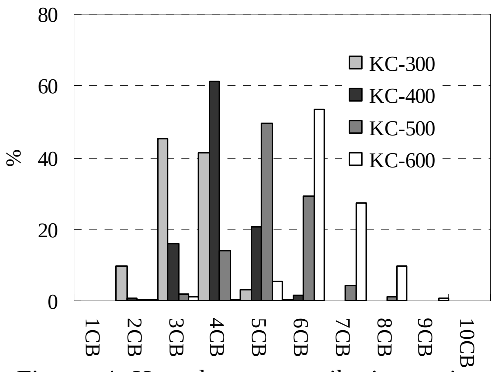

Figure 4 Homologue contribution ratios of each PCB product

The tendencies of the congener profiles in each homologue were similar at most sampling points of the surface sediment and paddy soil. However, the congener profiles in the homologue of the sediment core varied depending upon the sedimentation age. Particularly, certain layers, which were deposited from 1968 to 1977, that estimated effecting PCB products was showed different tendency. The profiles in each homologue of these layers were similar to these of PCB products. But surface layers that were deposited after 1977 show different profiles from PCB products. This tendency was observed significantly in the lower chlorinated congener. It is suggested that transformation and/or degradation in the lower chlorinated congener were caused by physical properties of these congeners after discharged in the environment.

Surface sediment of the core samples was deposited after the use of the PCB products was discontinued. The accumulation pattern for the core surface, sediment surfaces, and paddy soil was not a direct effect of the PCB products. It is suggested that these profiles appeared after the deposition by each media occurring via specific routes after the PCBs were discharged in the environment.

Acknowledgements

This work was supported by a research grant from Sasaki Environmental Technical Promoting Foundation.

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