Levels and Features of PCDDs, PCDFs and Co-PCBs in River and Coastal Sediments

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1.Introduction

In recent years, polychlorinated dibendo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) have been found in many countries and are considered as the most hazardous man-made chemicals for environmental animals and human beings. Non-ortho coplanar polychlorinated biphenyl (Co-PCB) is also known to be similar in structure and toxicity to PCDD and PCDF. It is the most toxic among the polychlorinated biphenyl (PCB) congeners. Recently, Co-PCB was found in environmental and animal samples as well as PCDD and PCDF[1,2]. Little information is available on the environmental contamination in Japan by those compounds. In the present study, the concentrations of PCDDs, PCDFs and Co-PCBs in river and coastal sediments were measured for assessment of their contribution to environmental pollution. Subsequently, the distribution of their congeners and the regional difference of their levels were investigated. The findings of these studies are described herein.

2. Experiment

Sample

Twenty three sediment samples were collected from 14 rivers and 6 sediment samples were taken from 3 coasts around Fukuoka Prefecture. Of these samples, 9 sediments collected from a urban river and a rural river were used for studying the regional difference of the levels of pollutants. All samples were collected between April and December in 1993 in Fukuoka Prefecture, Japan. All samples were dried at room temperature and passed through a 1mm sieve after crushing manually.

Analysis

An aliquot of 20g of dried sediment sample was extracted with 30% acetone in toluene by using Soxhlet extractor for 16 hours. The extract was treated with 0.5N sodium hydroxide and sulfuric acid after spiking with ^{13}C-labeled PCDDs, PCDFs and Co-PCBs. Subsequently, the solution was cleaned up using activated silica, silver nitrate silica and activated charcoal silica column (10mm internal diameter X 300mm length).

The amounts of PCDDs, PCDFs and Co-PCBs were determined using a Finnigan Mat 90 high resolution mass spectrometer equipped with a Varian 3400 gas chromatograph. In GC/MS analysis, two columns were used. A column for PCDD and PCDF ranging from tetra to hexachloro congeners was SP-2331 (Supelco, 0.25mm x 60m). Another column for PCDD, PCDF ranging from hepta to octachloro congeners and Co-PCBs was MPS-50 (Quadrex, 0.25mm x 25m). The analyzer in a mass spectrometer was used in the selected ion monitoring mode. The resolving power was 7000-10000.

3. Results and Discussion

Concentrations of PCDDs, PCDFs and Co-PCBs

PCDDs, PCDFs and Co-PCBs were found in all sediment samples. The average concentrations of total PCDDs, total PCDFs and total Co-PCBs in all sediments were 9300, 1100 and 110 (pg/g, dry base), respectively. The magnitude of amount of these chemicals was in the order of total PCDDs>total PCDFs>total Co-PCBs in both river and coastal sediments. The concentration of total PCDDs was about eight times higher than that of other chemicals and that of total PCDFs was ten times higher than that of total Co-PCBs. The levels of all these compounds in the river sediments were higher than those in the coastal sediments. These levels of PCDDs and PCDFs are similar to those in the sediments of the Hudson River[3].

Distribution of PCDD, PCDF and Co-PCB congeners

Figures 1-3 show the average concentrations of their congeners. The magnitude of the concentrations of their congeners in river sediments was in the order of OCDD>TeCDD>HpCDD>PeCDD>HxCDD for PCDDs, OCDF>HpCDF>HxCDF> TeCDF>PeCDF for PCDF and TeCoCB> PeCoCB> HxCoCB for Co-PCBs, respectively. However, in the case of coastal sediments, the order of those of PCDFs was HpCDF>OCDF>HxCDF>TeCDF>PeCDF. The concentrations of octachloro congeners were higher than those of any other congener in both dioxin and dibenzofuran series, while the level of OCDF was much lower than that of OCDD. The concentrations of PCDFs increased gradually with the number of chlorine atoms. In dioxin series, the concentrations of OCDD and TeCDD were dominant. Taking the levels of OCDD and TeCDD into consideration, there was a possibility that they might have derived from PCDDs as a by-product in chlorinated herbicides applied previously. The profiles of PCDD, PCDF and Co-PCB congeners are fairly different from those in the soils[2,4].

Regional difference in river sediments

Figures 4-6 show the concentrations of PCDDs, PCDFs and Co-PCBs in sediments at lower and upper reach of two rivers (each in urban and rural area). The concentration of these compounds in the lower reach where the sediment is polluted with domestic, industrial waste water and pesticide was much higher than that in the less polluted upper reach. The distribution of these contaminants would be influenced not only by the regional difference of the river but also by the kind of sediment.

4. Conclusion

1. The profiles of PCDD, PCDF and Co-PCB congeners in the sediments are fairly different from those observed in the soils.
2. PCDDs, PCDFs and Co-PCBs in river and coastal sediments may have derived from chlorinated pesticide applied previously together with the atmospheric dispersion of combustion-derived particles.
3. The level of concentrations of PCDDs, PCDFs and Co-PCBs in the sediments was in the order of lower reach > coast> upper reach.

5. References

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2. Y. Ohsaki and T. Matsueda (1994) : Levels, Features and a Source of Non-ortho Coplanar Polychlorinated Biphenyl in Soil. Chemosphere, 28, 47-56.
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4. Y. Ohsaki, T. Matsueda and Y. Kurokawa (1992) : Level of Concentrations of PCDDs and PCDFs in Soil. J. Environ. Chem., 2, 523-531.

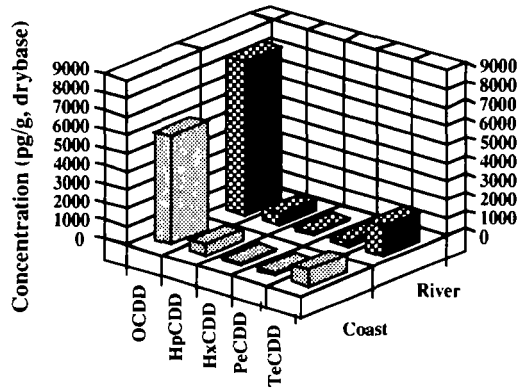

Fig. 1 Concentrations and distribution of PCDD congeners in river and coastal sediments

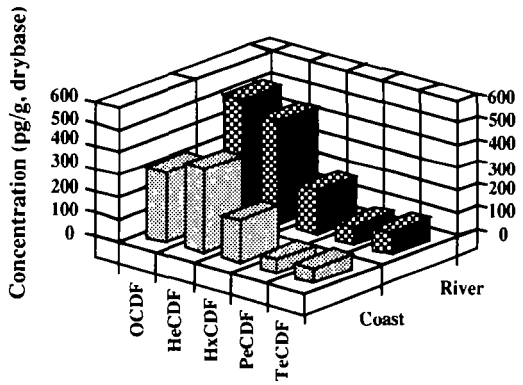

Fig. 2 Concentrations and distribution of PCDF congeners in river and coastal sediments

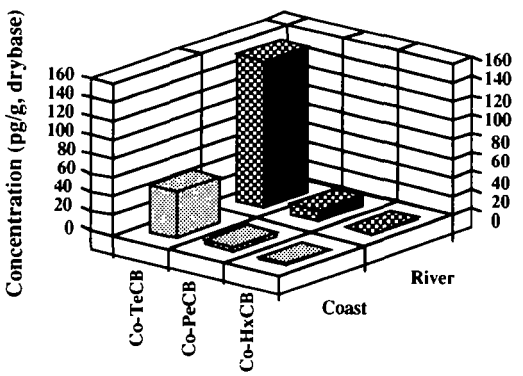

Fig. 3 Concentrations and distribution of Co-PCB congeners in river and coastal sediments

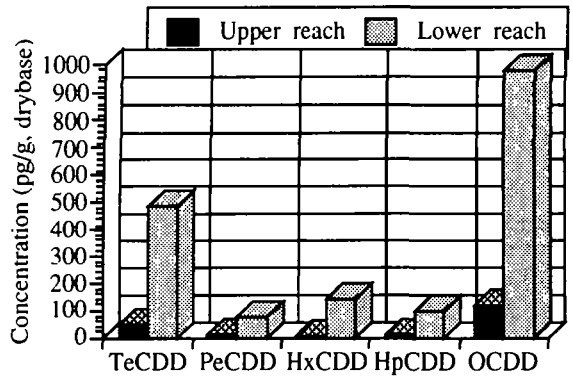

Fig. 4 Concentrations and distribution of PCDD congeners in river sediments at upper and lower reach

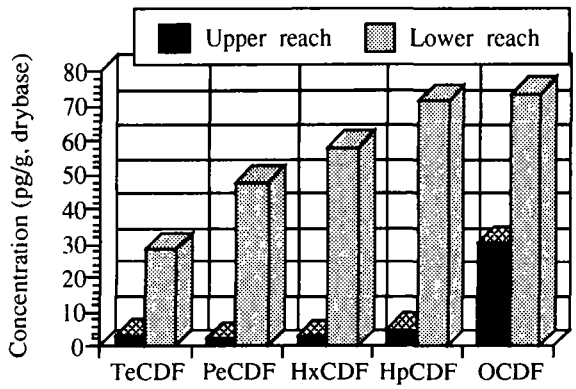

Fig. 5 Concentrations and distribution of PCDF congeners in river sediments at upper and lower reach

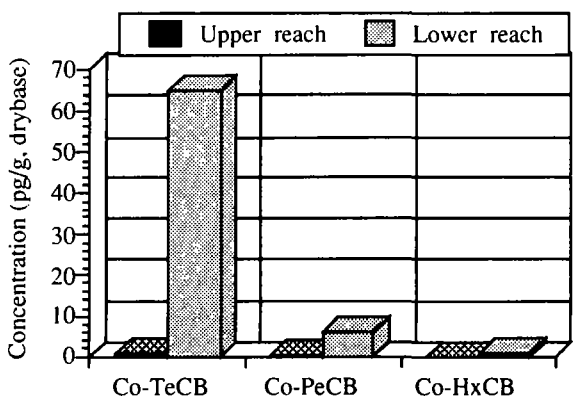

Fig. 6 Concentrations and distribution of Co-PCB congeners in river sediments at upper and lower reach