PC-11

CHARACTERISTICS OF ISOMERIC PATTERN FOR ORGANIC CHLORINATED COMPOUNDS IN ENVIRONMENT

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ABSTRACT

PCB and relevant chlorinated organic compounds in environmental samples were analyzed by high-resolution GC/ECD and GC/MS-SIM. The sea-sediments were investigated in the lateral and vertical direction, and individual PCB congeners were evaluated. The distribution of chemical substances was expressed by three-dimensional graph. The distribution of these compounds in the Harimanada Inland Sea are investigated. The levels of these compounds in the sea-water, sea-sediment, plankton and atmosphere were monitored isomer-specifically, and compared with commercial PCB and industrial chlordane. Residual isomeric pattern of these compounds in the sediment and plankton reflects the general abundance of isomer component of their commercial products.

KEYWORDS

PCB; PCT; Chlordane; atmosphere; water; sediment; plankton; GC/MS; isomer specific analysis;

EXPERIMENTAL

Sample collection

Water, sediment and biological samples were collected from the monitoring area in the Harimanada Inland Sea. Water samples were collected with a pail, sediment with a Smith-McIntyre dredge and biological sample with a plankton-net. Air samples were collected at urban area in Kobe with a high volume air sampler.

Sample preparation

Pesticide-grade solvents were used in all extractions and cleanup steps. Water samples were extracted with n-hexane, and sediment and plankton were first saponificated, then extracted with n-hexane. Air sample which collected by high volume air sampler were extracted with acetone/n-hexane(1/1) by Soxhlet extractor. The extract was concentrated to 1-ml by using Kuderna-Danish (KD) evaporator.

Cleanup

Two grams of silica gel were filled in a 50cm x 1cm ϕ glass column with n-hexane. One ml condensed extract was put on the silica gel column and eluted with n-hexane. The first 200 ml of eluate was collected, and shaken with copper powder to remove sulfur. The eluate was concentrated to 1 ml for GC/MS analysis.

GC/MS analysis
The sample was analyzed with GC/MS-SIM using a 30m x 0.25mm ϕ ULTRA-2(SPB-1). GC conditions used were: carrier gas helium 10 psi;temperature program 50°C(1 min) to 200°C at the rate of 30°C/min, then 5°C/min to 250°C. MS conditions used were:ionization EI mode, 280 °C, 70eV, 300 μA. PCB Monitoring ion:222.000; 223.998; 255.961; 257.959; 289.922; 291.920; 323.883; 325.881; 357.844; 359.842; 393.803; 395.800; 427.764; 429.761; 461.725; 463.722

RESULT AND DISCUSSION

Commercial PCB are complex mixture of chlorinated biphenyls having specified chlorine content, and associated with over 110 resolved peaks (Nakano et al., 1987a) in GC/MS analysis. Industrial chlordane is also mixture of chlordane isomers (Nakano et al.,1987b). Data are presented for PCB congeners in vapor, particulates, sediment, and plankton. Fig. 1 shows characteristic GC/MS-SIM chromatograms of PCB congeners in the various samples. Residual isomeric pattern of PCB and chlordane in the sediment and plankton reflects the general abundance of isomer component in the commercial products.

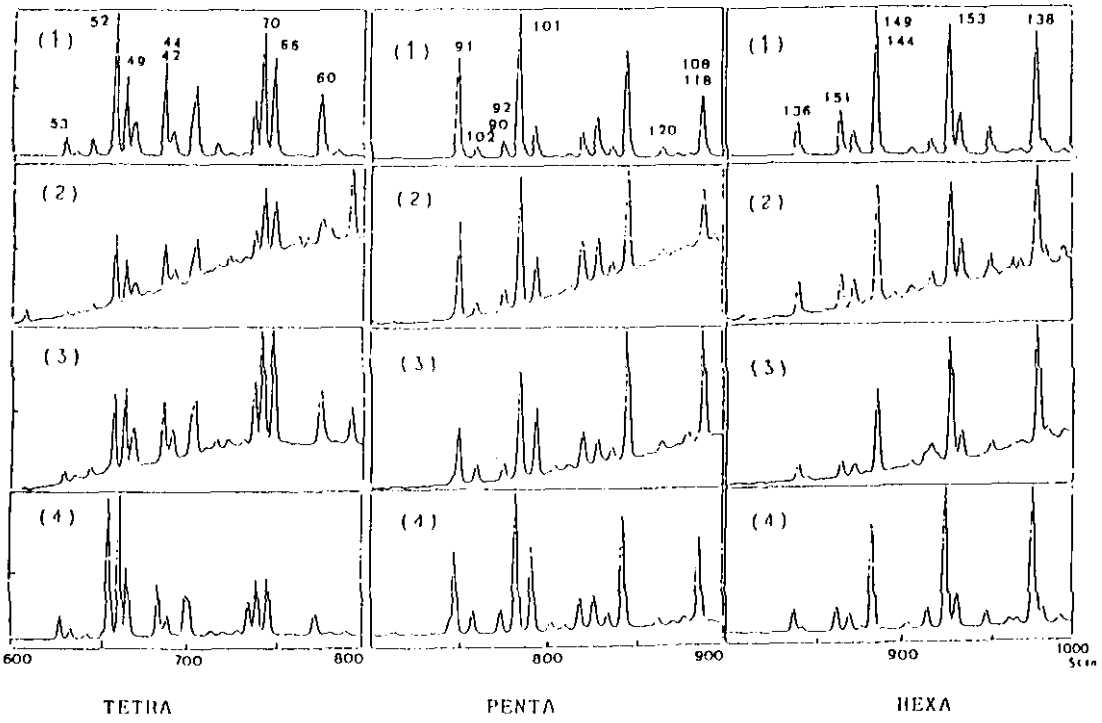


Fig. 1 GC/MS-SIM chromatograms of PCBs in the environmental samples.
(1) Equivalent mixture of Kanechlor (KC-300,400,500,600=1:1:1:1)
(2) Urban air (vapor) (3) Sediment (4) Plankton (IUPAC No.)

Thirty monitoring ions of PCBs were analyzed simultaneously by SIM using magnetic field switching technique. This rapid analytical method was developed to determine for each congener in environmental samples. Thousand sediment samples were collected over 15 years. Isomer specific analysis showed that the PCB composition in sediments reflect historical input with different usage

into each local site.
A similarity in isomeric pattern of PCBs (Swackhamer et al., 1988) and chlordanes was seen between in technical product and environmental samples (Muir et al., 1988). PCB in the surficial sediment were also analyzed considering the following factors : physical and chemical property of the sediment, distance from the source, bottom topography, and tidal effect. As the result, it is elucidated that the fine particle is playing an important role in the diffusion of contaminants. The PCT/PCB ratio increased as the percentage chlorine of the PCB composition in sediments increased. It was considered that "constant flows" affect the diffusion of PCB, and that the difference in contamination patterns between each sea area results from bottom topography and tidal effect.
Twenty sediment cores from the Harimanada Inland Sea were collected to investigate environmental fate and transport of contaminants historically. The sedimentary profiles of PCBs corresponding with historical input record. were exactly similar to production and consumption data. The PCB production and the concentrations of the total PCB are plotted versus sediment depth and age in Fig.2. The total PCB concentration peak for a single core close to the source occurs sharply in the sediment of 20cm depth. The peak became wider, as the distance from the source increases. If it is assumed that time lag for the diffusion is negligible, it is possible to estimate the sedimentation rate roughly. Its rate at the sampling site close to the PCB source was estimated about 17 mm/year, and the rates at each sea area range between 6 and 17 mm/year. These rates agreed approximately with the values obtained by 210 Pb method.
The typical congeners (Nakano et al.,1988) selected for the comparison were as follows : No.18,No.31/28,No.44,No.49,No.52,No.66,No.91,No.101,No.118,No.138, No.149,No.153,No.180(IUPAC No.). As a result of comparing the ratio of typical congeners observed in this study, it was possible to consider that the congener distributions were similar between PCB products and environmental samples.

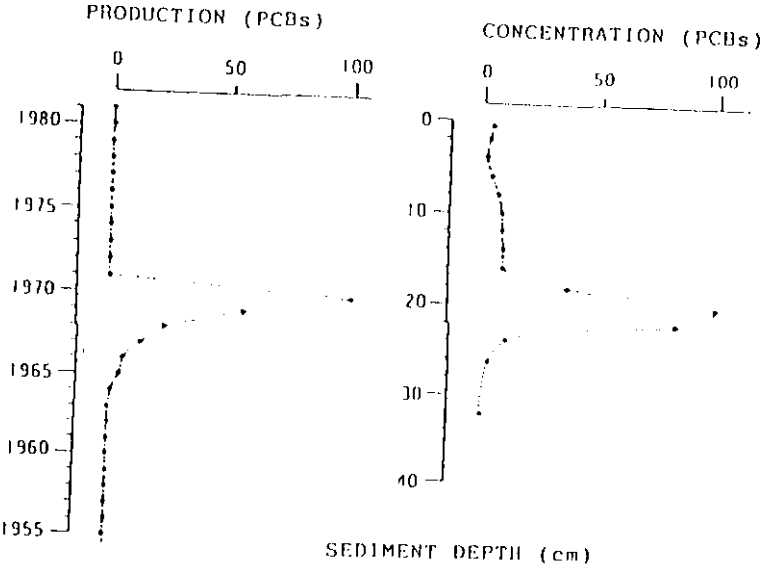


Fig. 2. PCBs concentrations versus sediment depth and age for the core.

CONCLUSION

PCBs were analyzed simultaneously by GC/MS-SIM. The PCB composition in sediments reflect historical input. The fine particle is playing an important role in the diffusion of contaminants. It was considered that

"constant flows" affect the diffusion of PCB, and that the difference in contamination patterns between each sea area results from bottom topography and tidal effect.
The sedimentary profiles of PCBs corresponding with historical input record were exactly similar to production and consumption data. The sedimentation rate at sampling site close to the PCB source was estimated about 17 mm/year. The congener distributions were similar between PCB products and environmental samples.
Detailed studies on the behavior of PCBs in environment must be requested to evaluate the transfer and diffusion of individual congeners inter-matrices.

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