SURVEY ON POLLUTION OF DIOXIN AND RELATED COMPOUNDS MONITORED BY BLUE MUSSEL AS A BIOLOGICAL INDICATOR AT 24 COASTAL AREAS IN JAPAN

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OBJECTIVES

It is well known that the blue mussel is an effective biological indicator for studying the distribution of the enviromental pollutants because the inhabiting area extends over widely and it settles at the same spots.[1)]

Authors already studied the pollution distribution of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in the blue mussels from 4 marine coastal water in Japan[2)], but in that study the level of dissolution for each detailed isomers was considered unsatisfactory for enough evaluation due to a low resolution ability (600) of the mass spectrometer used for it.

In this study the samples were collected much more widely over the coastal areas from northern to southern Japan. In addition due to using the mass spectrometer of higher resolution ability, the detailed distributions of congeners were made clear regarding PCDDs and PCDFs as well as non-ortho and mono-ortho chlorine substituted coplanar PCBs (abbreviated as non-ortho Co-PCBs and mono-ortho Co-PCBs), both of which are treated as the dioxin related compounds.

SAMPLING

Samples of blue mussel were collected from 24 coastal areas over northern Japan (Hokkaido) to southern (Okinawa) during a period from December 3, 1992 to June 13, 1993. The average length of examined shellfish was in the range from 3.26 to 9.09cm and the average weight of content including muscle and viscera was in the range from 0.72 to 9.50g.

EXTRACTION AND ANALYTICAL PROCEDURE

After the shellfish sample was washed, the content was taken out and homogenized by ultra-disperser.

Then, after being added with $^{13}C_{12}$-labeled PCDD, PCDF and coplanar PCB isomers, the

homogenized sample was digested with 0.5N KOH-ethanol solution. After extraction with n-hexane, the concentrated solutions were dehydrated over anhydrous sodium sulfate and purified by multi-layer column containing $AgNO_3$-silica/H_2SO_4-silica/KOH-silica.

Above the eluate was chromatographed into three fractions on alumina column with successive eluents of 0.1%, 2% and 50% methylene chloride in n-hexane. The first and second fractions were analyzed for total amount of PCBs by a Shimadzu GC-8A gas chromatograph with ^{63}Ni electron capture detector (ECD).

After studying to find the optimum conditions for separating non-ortho Co-PCBs from mono-ortho Co-PCBs by gas chromatography, the second and third fractions were analyzed for PCDDs, PCDFs and coplanar PCBs in an electron impact-single ion monitoring mode at a resolution of 10,000 using a Hewlett Packard 5890 Series II gas chromatograph-JEOL SX102A mass spectrometer.

RESULTS AND DISCUSSION

Results of analysis regarding the concentration of PCDDs and PCDFs showed the average values of 247.5 ppt and 74.0 ppt on all samples respectively, and the concentration of PCDDs was observed to be higher than that of PCDFs at each area. These both concentrations had the tendency of higher level at urban areas than local ones. However a higher concentration of PCDDs was observed for some local country areas and this was surmised to be caused from the contamination by the herbicide CNP(4-nitrophenyl 2,4,6-trichlorobiphenyl ether) because their congeners found out in this study are mainly composed of 1,3,6,8-TCDD and 1,3,7,9-TCDD[3].

Fig.1 shows the average congener ratios of PCDDs, PCDFs and Co-PCBs, indicating the main pollutants to be TCDDs with the level of 63.5% in PCDDs and TCDFs with 59.3% in PCDFs.

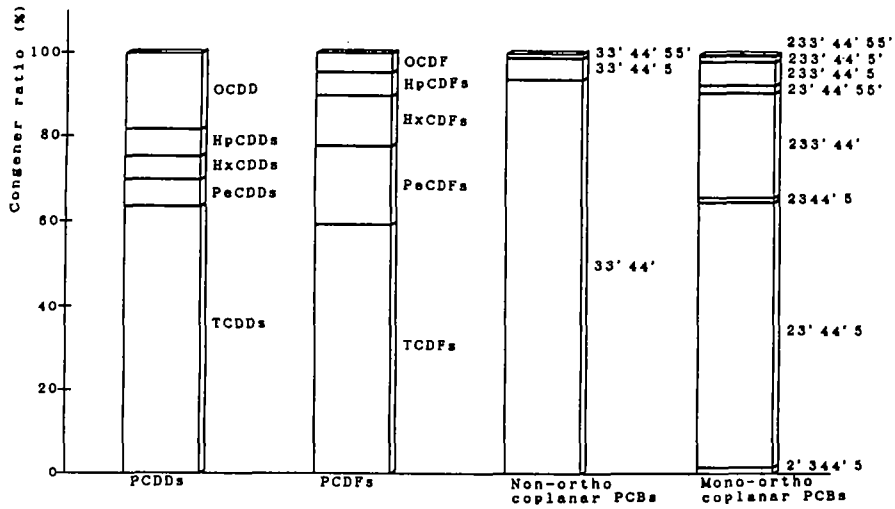

Fig.1 Average congener ratios of PCDDs,PCDFs and coplanar PCBs in blue mussel from 24 coastal areas in Japan

Regarding Co-PCBs, their concentrations showed the much higher values than those of PCDDs and PCDFs. The averages on all samples for mono-ortho Co-PCBs and non-ortho Co-PCBs were 1998 and 435.2 ppt respectively, and the tendency of higher level for mono-ortho Co-PCBs than

non-ortho ones was observed at all areas, showing the ratio of mono-ortho versus non-ortho Co-PCBs to be in the range of 1.21 to 29.8. Furthermore the level of total Co-PCBs was generally higher at the urban than country areas, that is, the contamination degree showed a close relationship with the industrial and commercial activities as well as in the case of PCDDs and PCDFs.

Fig.1 also illustrates that the main isomers of Co-PCBs were 3,3',4,4'-TeCB with the ratios of 93.8% in mono-ortho Co-PCBs, and 2,3',4,4',5-PeCB with 64.0% and 2,3,3',4,4'-PeCB with 25.0% in mono-ortho Co-PCBs.

Meanwhile the existing ratios of non-ortho and mono-ortho Co-PCBs occupied in PCBs were found to be in approximately constant levels with $0.8 \pm 0.5\%$ and $4.0 \pm 2.2\%$, respectively, for all tested places.

Fig.2 shows the average level of the TCDD toxicity equivalency quantities (TEQ) of PCDDs, PCDFs, mono-ortho and non-ortho Co-PCBs at each sampling place, and the main pollutant affecting the total level was confirmed to be non-ortho PCBs. In general, this level had a tendency of relatively higher values at urban zones comparing to the country areas, showing the highest value to be 36.22pg/g at Osaka.

Futhermore the accumulation of the dioxin related compounds in the blue mussels was also studied from the view of the dependency of a content of pollutants on the length of blue mussel inhabited at the same spots. The concentration of PCDDs showed a decreasing tendency with the increasing of the shell length, but this phenomenon was slighter in the case of PCDFs. Regarding Co-PCBs, the total concentration stayed approximately at the same level with no connection to the length of the samples, though it was observed that it's level was extremely high in samples with shell length less than 3cm.

On the other hand, the composition ratios of PCDDs and PCDFs in the sum of PCDDs plus PCDFs were nearly constant (average: 85.7 and 14.3%, respectively) with no relation to the sample size and the areas. Observing the congener ratios of PCDDs and PCDFs, tetra and penta chlorides showed an increasing tendency relating to the length increasing, whereas octa chloride tended to decrease depending on the growth of mussel. Although this reason remains unclear at present, it is considered that the kind of feed of blue mussel changes on the growing stage and that the transfer of lower chlorinated congeners from intestinal tract into the body tends to be more active than those of higher chlorinated ones.

In cases of Co-PCBs, it was observed that the composing ratios of non-ortho and mono-ortho Co- PCBs in the total Co-PCBs at the same place were nearly in the constant levels unrelating with the growth of mussel, and the congener ratios of both the chemicals stay also approximately at same values

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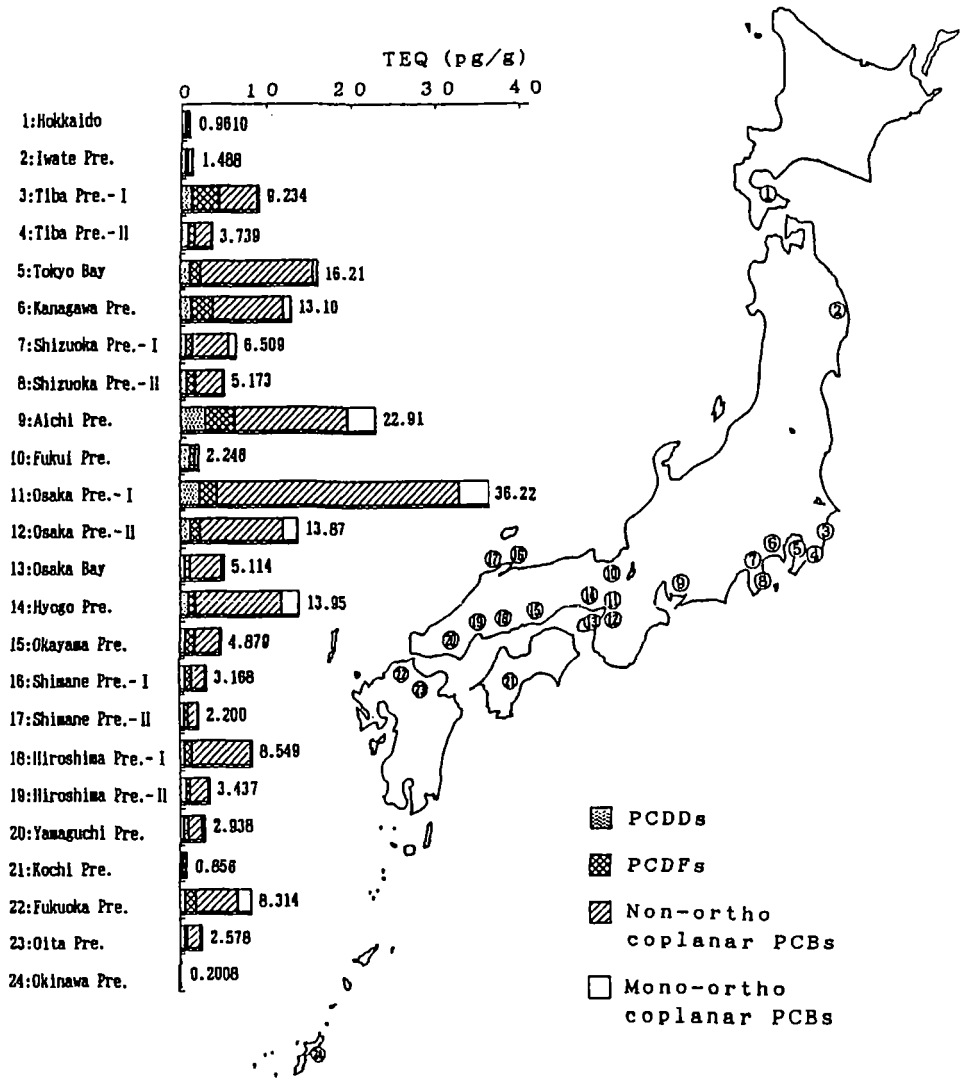

Fig.2 TEQ(pg/g) of 2,3,7,8-chlorine substituted PCDDs and PCDFs, and coplanar PCBs in blue mussel from 24 coastal areas in Japan