

## Accumulation of PCDD/DFs and PCBs in Fish in Toyano Lagoon in Niigata Prefecture

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## Introduction

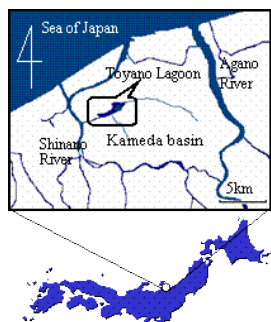


Fig. 1 Sampling Site.

The Japanese eats rice as main food. Niigata Prefecture has a lot of paddy field where a lot of agrochemicals has been used. Masunaga et al. reported that agrochemicals such as penta-chlorophenol (PCP) and chloronitrophen (CNP) used nationwide in paddy fields of Japan in the past contained dioxins as impurities<sup>1</sup>. Therefore, the Toyano lagoon sediment in Niigata Prefecture and its surrounding paddy soils were investigated. It was found that parts of PCP- and CNP-derived dioxins still remained now<sup>2</sup>. The concentration of dioxins that accumulated in the sediment of the lagoon was higher than other regions of Japan.

In this study, dioxin in fish that lived in the Toyano lagoon was investigated, the accumulation properties of the dioxin in each fish species were made clear, and the effects of the sedimental dioxin on the fish were examined.

## Materials and Method

## Samples

*Carassius cucuieri* (Hera-crucian), *Cyprinus carpio* (Carp) and *Micropterus salmoides* (black bass) were collected in the Toyano lagoon from October 2001 to November 2003. Toyano Lagoon is located in a suburban area in Niigata City, between the lower basin of the Shinano River and Agano River in Niigata Plain (Fig.1). Toyano Lagoon receives water

flow from paddy fields that are irrigated by the Shinano and Agano Rivers, and wastewater from households in northern city area. The sediment samples collected in December 2000 and February 2003 was used in this study.

Carp and Hera-crucian eat a benthos and a phytoplankton, respectively. On the other hand, because the black bass eat a fish as food, the trophic levels are higher than the carp and Hera-crucian. Table 1 showed details of the fish sampled and analyzed.

## Analytical method

Each sample was separated into muscle and internal organs tissue, homogenized, and analyzed. After freeze-dry, followed by the addition of <sup>13</sup>C-labeled internal standards, each sample was Soxhlet-extracted with toluene for 16 h. The percentage of lipid in the sample tissue was measured using 10 % of the extract. The remainder of the extract (90%) was treated by sulfuric acid for oxidation. Then sample cleanup was made using chromatography on silica gel, aluminum oxide and active-carbon-impregnated silica gel. Identification and quantification of PCDD/DFs and Co-PCBs were performed by HRGC-HRMS (Hewlett Packard HP6890/JEOL JMS-700). 136 PCDD/DFs congeners (from tetrachloro- to octachloro-) were separated and quantified as 83 gas chromatographic peaks. On the other hand, 209 congeners of PCBs were also quantified as 170 peak groups.

Table 1 Details of fish samples caught in Toyano lagoon

Common name	n	Sample length <sup>a</sup> (cm)	Sample weight <sup>b</sup> (g)	Lipid content (%)
Hera-crucian	6	34.1 (31.5-36.5)	655 (464-804)	2.81 (1.25-4.36)
Carp	6	42.7 (39.8-46.0)	1047 (762-1450)	2.72 (0.61-8.73)
Black bass	3 <sup>a</sup>	36.8 (35.0-40.1)	872 (691-1210)	4.67 (2.65-6.72)

<sup>a</sup> Values in parentheses indicate the minimum and maximum.

<sup>b</sup> PCDD/DFs was analyzed only for two samples among the three.

## Result and discussion

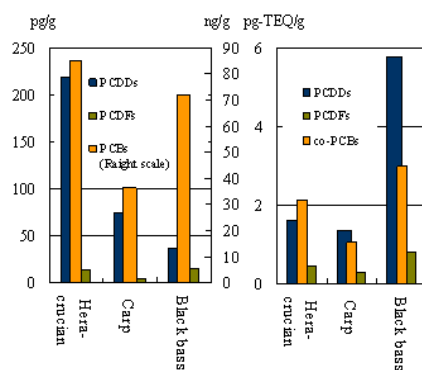


Fig. 2 Accumulation property between each samples

## Comparison between PCDD/DFs and PCBs

## 1) Accumulation property

The minimum, maximum and average TEQ concentration was 1.30, 8.08 and 4.18 in Hera-crucian, 0.97, 4.21 and 2.70 in carp, 9.24, 9.89 and 9.56 in black

bass, respectively. The ratio of co-PCB to total dioxins amounted to about 40% on the average. In contrast, the ratio of PCBs in sediment was about 2.8% on the average.

In Fig. 2, the black bass showed a high TEQ concentration while Carp and Hera-crucian showed a high absolute amount of PCDD/DFs. It follows that the black bass is easy to accumulate the lower chlorinated 2378-substituted congener most of which TEQ are high.

## 2) Correlation with Lipid content

A good correlation was found between 2378-T4CDD concentrations and the lipid content ( $r$  is 0.936), whereas O8CDD was not correlated with the lipid content ( $r$  is 0.001). It is suggested that lower chlorinated 2378-substituted congener easily accumulate in the lipid, and that to accumulate of higher chlorinated congener does not accumulate easily.

The concentration of every PCBs rose as the amount of lipid content increased.

**Effects of dioxin in the sediment**

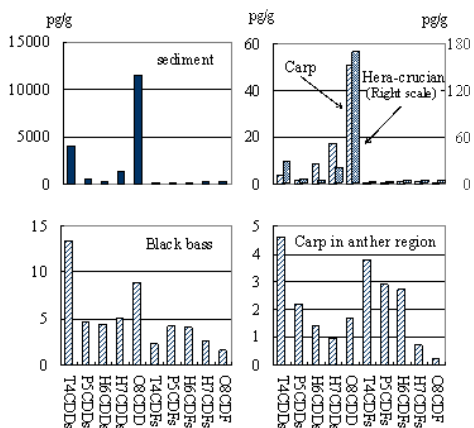


Fig 3 Comparison homologous distribution between each fish species and sediment

In Fig. 3, the distribution of PCDD/DFs of the sediment Toyano lagoon was compared with that of PCDD/DFs of fish lived there and another regions. The PCDD/DFs distribution of the sediment was similar with that of Carp and Hera-crucian of the Toyano lagoon. But that of Carp caught in another area showed different one. It was suggested that Carp and Hera-crucian of the Toyano lagoon have been influenced from the sediment. The relationship was found to some extent in the black bass. The extent of the influence of dioxin in the sediment on fish was different according to the fish's food habit.

The biota-sediment accumulation factor (BSAF) values are calculated in order to elucidate the relationship between concentration of PCDD/DFs and PCBs in biota and sediment. Figure 4 shows the BSAF of black bass. BSAF of PCBs was larger than that of PCDD/DFs. It was suggested that the influence of PCBs in the sediment on the fish is larger than PCDD/DFs. As BSAF shows the relation between the sediment and fish, the bioaccumulation occurs easily between fishes if this value is large. BSAF was large at lower chlorinated 2378-substituted congener.

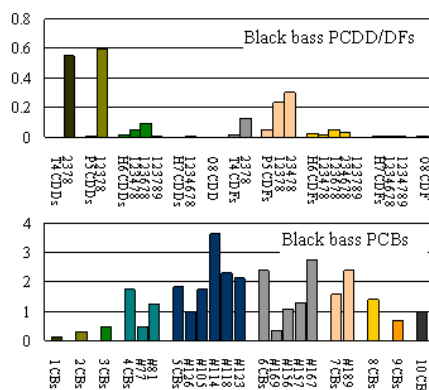


Fig.4 The BSAF value of 2,3,7,8-, substituted PCDD/DFs, homologue of PCDD/DFs, co-PCBs and homologue of PCBs for Black bass.

The effects of the sediment on fishes were different according to congener and the fish species. These effects may also originate from the different in trophic level and the bioaccumulation.

**References**

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- Sakai, M., Kajihara, H., Fukumura, K., Kobayashi, Ohizumi, M., Takahashi, Y., Nakadaira, H. and Yamamoto, M.: Time trends and source for dioxins in sediments in a large-scale rice production area, Niigata, Japan. *Organohalogen Compounds*, 57, 11-14 (2002)