THE MONITORING OF DIOXINS IN FISH AND SHELLFISH FROM TOKYO BAY

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Abstract
Levels of dioxins in fish and shellfish from Tokyo bay were estimated to monitor their safety regarding consumption from fiscal 1999 to 2005. In fiscal 2005, the average accumulated dioxins levels were 4.37 pg-TEQ/g in fish and 0.23 pg-TEQ/g in shellfish. The percentage contribution of coplanar-PCBs (Co-PCBs) to total dioxins ranged from 74.1 to 86.3 %, which might reflect the pollution of Tokyo bay with Co-PCBs in the past. The average daily intake of dioxins by Tokyo residents estimated from the levels in fish and shellfish was equivalent to 2.43 pg-TEQ/kg bw/day in fiscal 2005, apparently below the Tolerable Daily Intake (TDI) of 4 pg-TEQ/kg bw/day, if the fish and shellfish from Tokyo bay were consumed raw without cooking. It is necessary to continue monitoring dioxins in fish and shellfish from Tokyo bay.

Introduction
Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and coplanar polychlorinated biphenyls (Co-PCBs), known as "dioxins", were measured to investigate dioxins exposure in Tokyo residents. The Tolerable Daily Intake (TDI) of dioxins (PCDDs and PCDFs, including Co-PCBs) is less than 4 pg-TEQ/kg bw/day. The total daily intake of dioxins through diet, water, air, and soil was 1.57 pg-TEQ/kg bw/day, with 98 % of the total exposure (1.54 pg-TEQ/kg bw/day) being through the diet in Tokyo residents in fiscal 2005.[1]
Tokyo bay is a closed-water area, which contains the large city of Tokyo. Along the coast, there are a port, factories, and landfills, etc. On the other hand, as Tokyo bay supports rich fish and shellfish resources with a high popularity for so-called Edo-mae fish and shellfish, fish and shellfish are commonly taken from Tokyo bay. In the present study, we investigated contamination by dioxins since fiscal 1999 in order to secure the safety of fish and shellfish and the health of the residents of Tokyo.[1-3]

Materials and Methods
The sample species of fish were striped mullet, sea bass, conger eel, marbled sole, Japanese gizzard shad, and common brackish goby were captured at three sites in Tokyo bay, and those of shellfish were short-neck clam and blue mussel were collected at two sites. The edible parts of fish and shellfish were minced, and, after alkaline decomposition, samples were extracted three times with *n*-hexane, and extracts were concentrated. Then, sulfuric acid-processing and clean-up were conducted, and samples were subjected to high resolution GC/MS measurement.
Analyses were performed using an HP 6890 PLUS gas chromatograph (Hewlett-Packard) coupled to an Autospec-Ultima mass spectrometer (Micromass). The combination of capillary columns used in this study was as follows: a BPX-DXN (0.25 mm x 60 m, SGE) to determine PCDDs and PCDFs, and an HT-8 (0.25 mm x 30 m, SGE) to determine Co-PCBs. The mass spectrometer was operated in the electron impact ionization mode using selected ion monitoring (SIM) at a minimum resolution of 10,000 (10 % valley).
Calculation of the 2,3,7,8-TCDD toxicity equivalency quantity (TEQ) of the dioxins analogues in analyzed samples was carried out on the basis of the Toxic Equivalency Factor (TEF) by the WHO.

Results and Discussion
The yearly levels of dioxins in fish and shellfish are shown in Figure 1. Those were expressed as pg-TEQ per g wet weight (Figure 1-A) and pg-TEQ per g fat (Figure 1-B).
Striped mullet: The sum of dioxins in striped mullet was 4.14 pg-TEQ/g wet weight in fiscal 1999, and 4.90 pg-TEQ/g wet weight in fiscal 2005, that is, values per g wet weight were about the same. On the other hand, the values expressed per g fat were decreased from 158 pg-TEQ/g fat in fiscal 1999 to 120 pg-TEQ/g fat in fiscal 2005.
Sea bass: Dioxins in sea bass showed a decreasing tendency year by year after fiscal 1999. This was particularly conspicuous when these values were expressed per g fat.

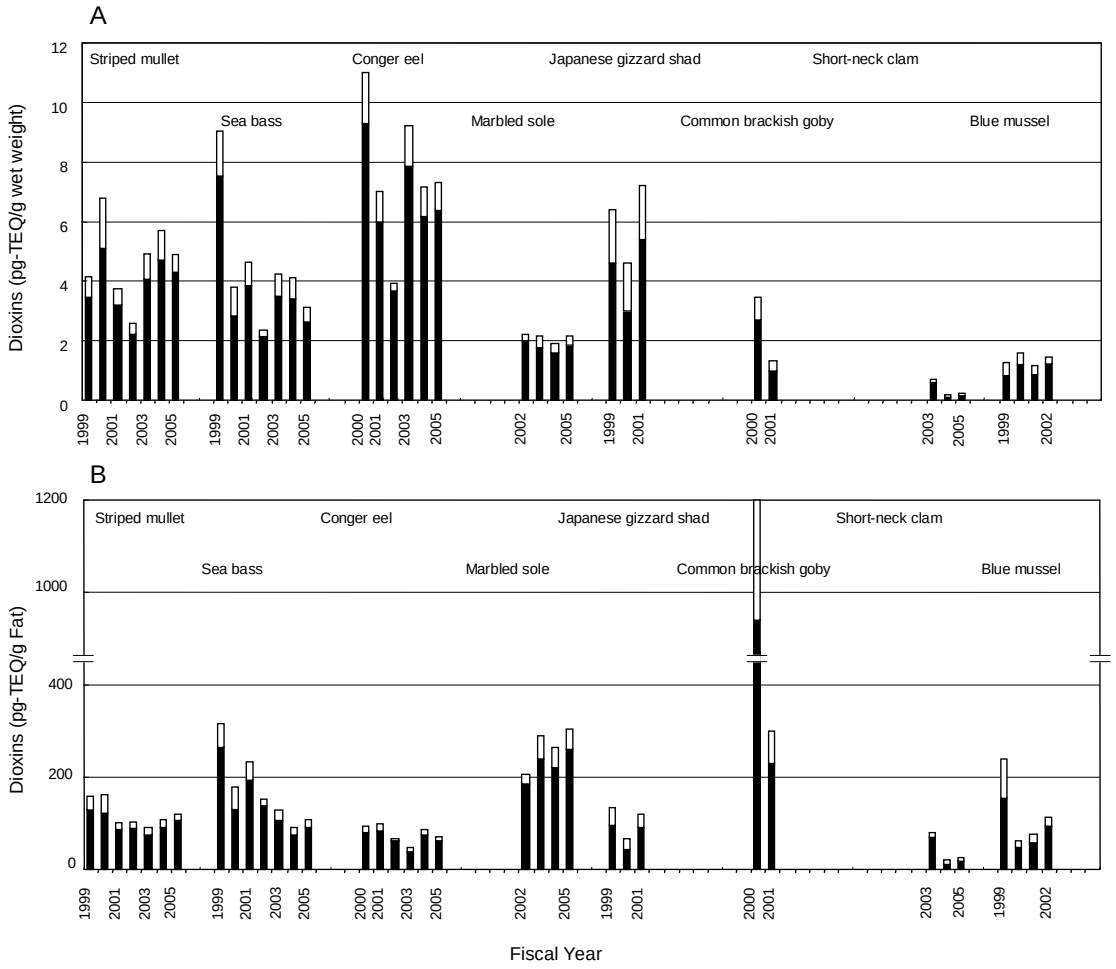

Figure 1 Dioxins contamination of fish and shellfish in Tokyo bay.
A is shown per g wet weight, B per g fat. □: PCDDs plus PCDFs; ■: Co-PCBs.

Conger eel: The examination of dioxins in conger eel started from fiscal 2000. The contamination level was the highest among fish examined when expressed per g wet weight, whereas it was one of the lowest when expressed per g fat.
Marbled sole: The examination of dioxins in marbled sole started from fiscal 2002. Levels did not fluctuate so much from year to year.
Japanese gizzard shad: The examination was carried out from fiscal 1999 to 2001. Dioxins levels were relatively high, showing 6.4, 4.6, and 7.2 pg-TEQ/g wet weight in fiscal 1999, 2000, and 2001, respectively, whereas those obtained per g fat were low.
Common brackish goby: Dioxins levels in common brackish goby were examined in fiscal 2000 and 2001. The life span of common brackish goby, inhabiting areas near sediment, is usually 1 year. Its contamination levels were 3.45 and 1.32 pg-TEQ/g wet weight in 2000 and 2001, respectively. However, those per g fat were extremely high, being 1207 and 300 pg-TEQ/g fat, respectively, showing the highest concentration among the species examined. There might be a tendency whereby fish with a low fat content throughout the whole body, such as in common brackish goby, exhibit high levels of dioxins when expressed per g fat.
Short-neck clam: A large amount of short-neck clams were caught in Tokyo bay and consumed by residents of Tokyo. Therefore, the species has been an object of examination since fiscal 2003. Short-neck clam inhabits areas near sediment, and was assumed to be more contaminated with chemicals than fish. In fiscal 2003, the

Table 1 Dioxins contamination of water and sediment in Tokyo bay in fiscal 2005.[4]

		Dioxins	PCDDs+PCDFs	Co-PCBs
Water	Ave.	0.21	0.17	0.038
(pg-TEQ/L)	Max.	0.96	0.78	0.19
(n = 8)	Min.	0.068	0.064	0.0041
Sediment	Ave.	22	19.3	2.7
(pg-TEQ/g)	Max.	51	46	4.8
(n = 8)	Min.	10	8.7	0.62

average level of dioxins was relatively high, because a high level at one site raised the mean value (data not shown).

Blue mussel: Blue mussel was examined from fiscal 1999 to 2002, and the dioxins levels were in the range of 1.18 - 1.58 pg-TEQ/g wet weight. The ratios of PCDDs plus PCDFs to Co-PCBs were higher than those of fish. Shellfish might show a tendency to be more contaminated with PCDDs and PCDFs compared with fish. Especially, 7-chloride and 8-chloride forms of PCDDs and PCDFs were abundantly detected. These data suggest that shellfish exhibit different characteristics of bioaccumulation from those of fish.

Seawater and sediments obtained at eight sites in Tokyo bay were also examined for dioxins contamination in fiscal 2005 (Table 1).[4] The average level of dioxins in water was 0.21 pg-TEQ/L (PCDDs plus PCDFs: 0.17 pg-TEQ/L, and Co-PCBs: 0.038 pg-TEQ/L), and that in sediment was 22 pg-TEQ/g (PCDDs plus PCDFs: 19.3 pg-TEQ/g, and Co-PCBs: 2.7 pg-TEQ/g). The amount of Co-PCBs in seawater and sediment accounted for 12.3 % and 18.1 % of the total dioxins, respectively. There might be a tendency whereby Co-PCBs highly accumulate in fish and shellfish despite there being abundant PCDDs and PCDFs in ambient seawater, indicating that fish and shellfish selectively incorporate more Co-PCBs than PCDDs and PCDFs.

Daily intake of dioxins in residents of Tokyo was equivalent to 1.57 pg-TEQ/kg bw/day in fiscal 2005,[1] whereas its value in fiscal 1999 was 2.32 pg-TEQ/kg bw/day.[5] This would indicate that dioxins in fish and shellfish from Tokyo bay seemed to be gradually decreased. Residents of Tokyo consume a lot of fish, which accounts for not less than 80 % of dioxins of total exposure.[1] If the dioxins contamination levels in fish and shellfish are decreased, the intake of dioxins will be eventually reduced.

Measures to prevent the emission of dioxins were formulated by the “Law Concerning Special Measures against Dioxins” (The Dioxins Law), and they were effective to reduce environmental contamination levels. However, dioxins contaminating fish and shellfish in Tokyo bay are hard to degrade. They are likely to bioaccumulate, and highly toxic, and they are the targets of “Stockholm Convention on Persistent Organic Pollutants” (POPs Treaty), which comprises measures to eliminate or reduce the release of POPs into the environment with international cooperation. The implementation of a management system to investigate the levels of environmental contamination is required. Therefore, in view of the data presented here, it is necessary to continue monitoring dioxins in fish and shellfish in Tokyo bay.

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