Dynamics of PCDDs/DFs and Coplanar-PCBs in Aquatic Food Chains from Lake Shinji and Tokyo bay.

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Abstract

The contamination levels of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/DFs) and coplanar-polychlorinated biphenyls (coplanar-PCBs) were determined in aquatic organisms from Lake Shinji and Tokyo bay. In addition, the various biological samples were analyzed for stable nitrogen isotope ratios, which are used as a variable for quantifying trophic levels on the aquatic food chains. In the aquatic food chains of Lake Shinji and Tokyo bay, the total concentrations of coplanar- PCBs increased with increasing trophic position. On the other hand, the relationship between the PCDD/DF concentrations and trophic level was not clear, however, dioxin levels were positively correlated with trophic levels for lower-chlorinated congeners and negatively correlated for higher-chlorinated congeners.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/DFs) and coplanar-polychlorinated biphenyls (coplanar-PCBs) are highly persistent toxic compounds. These persistent lipophillic and hydrophobic organic chemicals are pervasive in the environment and biomagnify readily in the food chain. Therefore many studies have revealed that they are found in all compartments of environmental media, including air, water, soil, sediments, animals and humans (Schecter et al., 1989; Broman et al., 1991; Oehme et al., 1995; Brzuzy and Hites, 1996).

Naturally, almost all animals and humans in Japan have been, and continue to be exposed to these substances. Adequate understanding of the contamination state and bioaccumulation pathways in freshwater and marine biota is an important issue, because fish and shellfish consumption is a significant cause of exposure of these substances in Japanese populations (Miyata, 1991). Water, sediment and food in the aquatic environment are potential reservoirs of PCDDs/DFs and coplanar-PCBs for aquatic organisms. In general, waterborne uptake is not an important pathway for most aquatic organisms because of the low concentrations of these compounds dissolved in the water relative to those in food. Persistent organic contaminant dynamics models and tropho-dynamic examination of distribution patterns of these compounds in water and organisms at different trophic levels have also indicated that dietary uptake is the more important bioaccumulation pathway (Thomann, 1981 ; Oliver and Niimi, 1988). Some studies indicate that uptake from contaminated sediments is another pathway for benthic organisms (Stein et al., 1987)

Stable isotopes of carbon, and nitrogen have been used as tracers in examining the trophic relationship and origins of prey in aquatic food webs (Wada and Hattori, 1991). The most commonly used stable isotopes in aquatic food chain research are ^{13}C and ^{15}N. In general, the metabolic processes in animals enrich the heavier isotopes relative to the lighter ones. The $^{15}N/^{14}N$ ratio ($\delta^{15}N$) generally increases by 3 to 5‰ from prey to predator. Several investigators have reported that biomagnification of organochlorinated compounds is significantly correlated to stable nitrogen isotope ratio. Broman et al. (1992) indicated that the three most toxic 2,3,7,8-substituted isomers were biomagnified in Baltic food webs, whereas OCDD/DF decreased with increasing trophic level in the aquatic food chains. On the other hand, Borgå et al. (1998) found a good relation between total PCB, total DDT and trophic levels, as defined by $\delta^{15}N$ in Norwegian arctic food webs. Based on this information, we have determined trophic levels in aquatic food chains from two different areas of investigation, namely, Lake Shinji and Tokyo bay. Furthermore, we present the contamination levels of PCDD/DFs and coplanar-PCBs and their relationship to stable nitrogen isotope ratios in aquatic food webs. The objectives of the present study were to quantify the contamination state and accumulation profiles of PCDDs/DFs and coplanar-PCBs in aquatic organisms from Lake Shinji and Tokyo bay. This study also aimed to inquire into the biomagnification phenomenon of PCDDs/DFs and coplanar-PCBs through the food chains.

2. Materials and Methods

2.1 Sample Collection

All biological samples were collected in Lake Shinji from November 1994 to December 1995 and in Tokyo bay from November 1998. Information on the species collected, size, lipid content and stable nitrogen isotope ratio of samples are shown in Table 1. Polychaetes were collected in

benthic grab samples, rinsed, and frozen. Fish and bivalve samples were collected using trawling and gill nets at several sampling sites. We collected dead tufted ducks accidentally caught in fishing gill nets in Lake Shinji. Immediately after collection, all samples were transported to the laboratory on dry ice and stored at -20℃ in a deep freezer until further analysis.

Table 1. Details of biological samples collected from Lake Shinji and Tokyo bay.

Sampling area	Species	Common name	Scientific name	*n*	Analyzed tissue	Sample wt. (g)	Lipid content (%)	δ^{15}N (‰)
Shinji Lake	Waterfowl	tufted duck	*Aythya fuligula*	5	Muscle	895.5	12.7	13.5±0.3
	Fish	sea bass	*Lateolabrax japonicus*	3	Whole	122.3	28.8	14.8±0.5
		gizzard shad	*Konosirus punctatus*	2	Whole	126.7	30.7	12.6±0.8
		large-eyed herring	*Sardinella zunasi*	1[*2*]	Whole	9.1	15.2	12.4
		goby	*Acanthogobius flavimanus*	1[*2*]	Whole	24.4	10	11.9
	Bivalve	shijimi clam	*Corbicula japonica*	3[*10*]	Soft tissue	-	5.8	11.1±0.3
Tokyo Bay	Fish	sea bass	*Lateolabrax japonicus*	2	Whole	611.1	23.9	17.7±0.04
		gizzard shad	*Konosirus punctatus*	2	Whole	171.7	22.7	14.5±0.01
		stone flounder	*Platichthys stellatus*	2	Whole	771.3	11.6	14.8±0.13
		dab	*Limanda yokohamae*	1	Whole	660	9.8	13.5
		stingray	*Dasyatis akajei*	1	Whole	140.9	13.3	15.9
	Bivalve	littleneck clam	*Ruditapes philippinarum*	1[5]	Soft tissue	2.3	10.0	12.0
		hard-shell clam	*Chloromytilus viridis*	1[12]	Soft tissue	2.1	11.8	11.7
		mactridae	*Mactra chinensis*	1[6]	Soft tissue	6.1	5.2	11.9
	Polychaete		*Paraprionospio sp. Type A*	1	Whole	-	5.2	12.9

Figures in parentheses indicate the number of samples pooled.

2.2 Stable nitrogen isotope analysis

Stable nitrogen isotope analysis was performed on individual biological samples. Fats in the biological samples were removed with 50% ethanol in benzene. These samples were dried using a vacuum dryer at 30℃, and then ground to a fine powder. Subsequently, samples were set in an elemental analyzer, then sealed under vacuum and combusted at 650℃. Nitrogen gas was then carried through the interface (ConFlo Ⅱ, Finnigan MAT) and analyzed using a mass spectrometer (Delta plus, Finnigan MAT). Stable isotope ratios are expressed by δ as parts per thousand according to

$$\delta^{15}\mathrm{N} = \{(R_{sample} / R_{standard}) - 1\} \times 1000\ (‰),$$

where R is the corresponding ratio $^{15}\mathrm{N}/^{14}\mathrm{N}$ and $R_{standard}$ for $^{15}\mathrm{N}$ is atmospheric nitrogen.

2.3 Determination of PCDDs/DFs and coplanar-PCBs

Approximately 20g of muscle of tufted ducks collected from lake Shinji was homogenized, freeze-dried and extracted with a Soxhlet apparatus for 12 h with 500 m*l* of dichloromethane. The whole body of the fish and shelled soft tissue of each species of bivalves were used for the Soxhlet extraction following the same steps as above. The extract was then concentrated to about 10 m*l* with a Kuderna-Danish concentrator. The final extract was transferred into a separatory funnel containing 300 m*l* of *n*-hexane and cleaned with concentrated sulfuric acid. A total of

sixteen ^{13}C-labelled 2,3,7,8-chlorine-substituted PCDDs/DFs and four ^{13}C-labelled non-*ortho*-substituted CBs were used as internal standards, spiked to the hexane extract prior to sulfuric acid treatment. The extract was then passed through 2 g of silica gel packed in a glass column and eluted with 130 ml of 10% dichloromethane in hexane. The extract was next passed through 5 g alumina packed in a glass column. The extract was then passed through a carbon column packed with 1 g of activated carbon-impregnated silica gel. The first fraction eluted with 20 mL of 25% dichloromethane in hexane was discarded. The second fraction eluted with 250 mL of toluene contained 2,3,7,8-substituted PCDDs and PCDFs and non-*ortho* coplanar PCB congeners 81, 77, 126 and 169.

PCDDs/DFs and non-*ortho* coplanar PCBs were analyzed using a HRGC-HRMS. A Hewlett-Packard 6890 GC connected to an Autospec Ultima (VG) was used. PCDD and PCDF congeners were separated on a DB-5 capillary column coated at 0.25 μm (60 m x 0.25 mm i.d.). The column oven temperature was programmed from 160°C (3 min) to 200°C at a rate of 40°C/min with a 2 min holding time, and to 310°C at 2°C/min, with a holding time of 1 min. Injector and transfer line/ion source temperatures were held at 280 and 250°C, respectively. The mass spectrometer was operated at an EI energy of 40 eV and the ion current was 600 μA. PCDD/DF congeners were monitored by SIM at the two most intensive ions at the molecular ion cluster. Recoveries of ^{13}C-labelled PCDD and PCDF congeners through the analytical procedure ranged from 63 to 90%. The reported concentrations were not corrected for the recoveries of internal standard. Concentrations of certain PCDD/DF congeners were confirmed using the DB-17 (60 m x 0.25 mm i.d., 0.25 μm film thickness) column. Non-*ortho* PCBs were separated on a DB-5 capillary column coated at 0.25 μm (60 m x 0.25 mm i.d.) and analyzed using a SIM mode.

3. Results and Discussion

3.1 *Trophic level characterization with stable nitrogen isotopes*

The value of δ^{15}N in the two different food chains studied are illustrated in Table 1 and Figure 1. In the case of Lake Shinji food chains, the values of δ^{15}N varied from a low value of 11.1 ‰ in shijimi clam to a high value of 14.8 ‰ in sea bass. The tufted ducks, which had consumed mainly bivalves (*i.e.*, shijimi clams) in a restricted wintering area (Yamamuro et al. 1998),

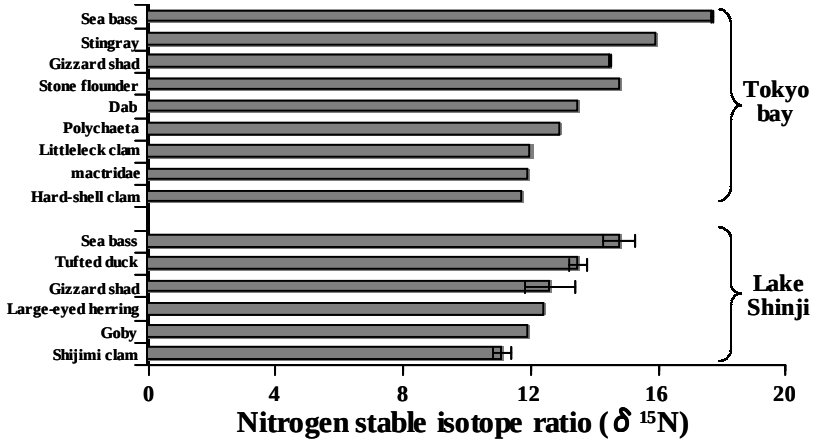

Fig. 1. Mean values of δ^{15}N in aquatic food chains from Lake shinji and Tokyo Bay.

were found to have an average $\delta^{15}N$ value of 13.5 ‰, which is an increase in $\delta^{15}N$ of 2.4 ‰ compared to shijimi clam. On the other hand, the values of $\delta^{15}N$ in Tokyo bay food chains ranged from 11.7 ‰ for hard-shell clam to 17.7 ‰ in sea bass. The $\delta^{15}N$ values of littleneck clam, hard-shell clam and mactridae indicated similar trophic levels. The stone flounder and dab feed mainly on polychaetes and bivalves in the Tokyo bay food chain. In general, it is known that sea bass consumes small fish and crustaceans based on stomach-content analysis. In the two different food chains, it was confirmed that sea bass is the top consumer, as indicated by their high stable nitrogen isotope ratios.

3.2 *Contamination level and characterization of PCDDs/DFs and coplanar-PCBs*

PCDD/DF and coplanar-PCB congeners were detected in all biological samples in this study. The residue levels of individual congeners and the isomers of PCDD/DF in biological samples from Lake Shinji and Tokyo bay are listed in Tables 2 and 3, respectively. In the case of Lake Shinji, the increasing amounts of total PCDDs/DFs were detected in all biological samples in the following order : shijimi clam > tufted duck > large-eyed herring > gizzard shad > sea bass >

Table 2. Isomer-specific concentrations (pg/g dry wt. basis) of PCDD/DFs in biological samples collected from Lake Shinji.

Species	Waterfowl	Fish				Bivalve
Isomer	Tufted duck	Sea bass	Gizzard shad	Large-eyed herring	Goby	Shijimi clam
2,3,7,8-TeCDD	0.39 ± 0.25	0.43 ± 0.34	0.63 ± 0.39	ND	0.37	ND
Other TeCDD	103 ± 42.8	13.1 ± 11.2	10.2 ± 3.57	24.6	5.66	324 ± 147
1,2,3,7,8-PeCDD	1.91 ± 1.42	1.71 ± 1.71	4.05 ± 3.35	0.73	0.98	0.24 ± 0.24
Other PeCDD	3.18 ± 1.42	0.31 ± 0.40	0.13 ± 0.18	1.48	ND	23.3 ± 9.00
1,2,3,4,7,8-HxCDD	0.64 ± 0.17	0.45 ± 0.51	1.42 ± 0.80	0.17	0.45	0.30 ± 0.04
1,2,3,6,7,8-HxCDD	1.30 ± 0.34	1.63 ± 1.69	3.45 ± 2.28	1.72	1.24	0.92 ± 0.13
1,2,3,7,8,9-HxCDD	0.18 ± 0.04	0.21 ± 0.21	1.21 ± 0.81	0.42	0.2	0.31 ± 0.09
Other HxCDD	0.74 ± 0.29	0.12 ± 0.12	0.26 ± 0.20	0.23	0.08	5.36 ± 4.01
1,2,3,4,6,7,8-HpCDD	0.62 ± 0.21	1.01 ± 1.10	4.65 ± 1.95	2.39	0.08	6.11 ± 4.14
Other HpCDD	0.21 ± 0.20	0.16 ± 0.21	0.25 ± 0.35	1.29	ND	10.4 ± 3.32
OCDD	2.90 ± 0.97	4.03 ± 1.62	11.2 ± 6.06	10.2	3.75	120 ± 54.3
Total PCDDs	115 ± 42.1	23.2 ± 18.6	37.4 ± 12.8	43.3	12.8	491 ± 211
2,3,7,8-TeCDF	3.99 ± 2.74	3.82 ± 4.16	1.66 ± 0.08	1.86	2.62	0.78 ± 0.14
Other TeCDF	11.0 ± 6.43	0.96 ± 0.61	1.38 ± 0.80	2.37	0.09	17.9 ± 11.9
1,2,3,7,8-PeCDF	0.75 ± 0.26	0.59 ± 0.58	0.98 ± 0.48	0.75	0.54	0.11 ± 0.19
2,3,4,7,8-PeCDF	3.06 ± 1.26	2.31 ± 2.44	3.95 ± 2.78	0.83	2.17	0.72 ± 0.04
Other PeCDF	7.74 ± 1.56	1.44 ± 1.16	0.88 ± 0.18	2.96	0.83	5.82 ± 2.22
1,2,3,4,7,8-HxCDF	0.39 ± 0.10	0.40 ± 0.40	0.88 ± 0.50	0.47	0.46	0.37 ± 0.04
1,2,3,6,7,8-HxCDF	0.32 ± 0.09	0.36 ± 0.33	0.77 ± 0.40	0.54	0.46	0.36 ± 0.02
2,3,4,6,7,8-HxCDF	0.54 ± 0.22	0.52 ± 0.49	2.12 ± 1.07	1.29	0.52	0.51 ± 0.45
1,2,3,7,8,9-HxCDF	ND	ND	0.07 ± 0.10	0.08	ND	ND
Other HxCDF	1.02 ± 0.34	1.21 ± 1.44	1.30 ± 0.36	1.37	0.14	3.36 ± 1.28
1,2,3,4,6,7,8-HpCDF	0.10 ± 0.10	0.38 ± 0.36	0.92 ± 0.34	1.16	ND	1.24 ± 1.07
1,2,3,4,7,8,9-HpCDF	0.02 ± 0.03	0.07 ± 0.08	0.11 ± 0.16	ND	0.11	0.23 ± 0.03
Other HpCDF	0.08 ± 0.11	0.54 ± 0.59	0.26 ± 0.37	1.41	0.38	2.05 ± 0.49
OCDF	0.2±0.16	0.34 ± 0.34	0.36 ± 0.51	0.88	ND	2.13 ± 1.54
Total PCDFs	29.3 ± 8.6	12.9 ± 12.9	15.6 ± 6.24	16	8.32	35.6 ± 17.6
∑ PCDDs/DFs-TEQ	4.62 ± 2.08	4.09 ± 4.1	7.9 ± 5.79	1.88	3.06	1.16 ± 0.1

goby. The mean concentrations on a dry weight basis of total PCDDs/DFs determined from the various species were 21 pg/g for goby, 35 pg/g (rang ; 15 ~ 72 pg/g) for sea bass, 52 pg/g (39 ~ 65 pg/g) for gizzard shad, 58 pg/g for large-eyed herring, 140 pg/g (83 ~ 200 pg/g) for tufted duck and 530 pg/g (310 ~ 760 pg/g) for shijimi clam. On the other hand, the amount of total PCDDs/DFs in organisms from Tokyo bay were found to increase in the order of polychaete > hard-shell clam > littleneck clam > mactridae > dab > stingray > gizzard shad > sea bass > stone flounder. The concentrations of total PCDDs/DFs determined from the aquatic organisms in Tokyo bay were 62 pg/g for stone flounder, 74 pg/g (67 ~ 81 pg/g) for sea bass, 79 pg/g (48 ~ 110 pg/g) for gizzard shad, 108 pg/g for stingray, 149 pg/g for dab, 322 pg/g for mactridae, 398 pg/g for littleneck clam, 799 pg/g for hard-shell clam and 2700 pg/g for polychaete.

Table 3. Isomer-specific concentrations (pg/g dry wt. basis) of PCDD/DFs in biological samples collected from Tokyo bay.

Species	Fish					Bivalve			Polychaete
Isomer	Sea bass	Gizzard shad	Stone flounder	Dab	Stingray	Littleneckc clam	Hardshell clam	Mactridae	
2,3,7,8-TeCDD	1.39± 0.18	0.93 ± 0.03	0.8	1.47	0.64	ND	ND	ND	ND
Other TeCDD	19.8± 18.3	5.9 ± 5.97	15.5	46.3	26.4	122.6	380.2	90.5	1190
1,2,3,7,8-PeCDD	2.23 ± 0.48	2.44 ± 0.04	0.82	1.5	10.9	1.58	1.45	1.06	2.75
Other PeCDD	0.66± 0.08	1.08 ± 0.61	0.69	1.06	2.44	18.5	29	13.7	172.4
1,2,3,4,7,8-HxCDD	0.28± 0.03	0.54 ± 0.02	0.08	0.07	0.78	2.09	0.77	0.79	1.9
1,2,3,6,7,8-HxCDD	1.84 ± 0.12	1.66 ± 0.26	1.18	1.87	2.12	4.17	2.75	1.84	5.55
1,2,3,7,8,9-HxCDD	0.14± 0.04	0.32 ± 0.12	0.12	0.25	1.43	2.09	0.95	0.69	2.8
Other HxCDD	0.11 ± 0.06	0.79 ± 0.26	0.43	0.57	0.81	12.8	12.9	8.07	134.4
1,2,3,4,6,7,8-HpCDD	0.94± 0.16	3.18 ± 1.22	2.26	1.91	5.46	14.6	17.7	9.4	47
Other HpCDD	0.12 ± 0.01	1.35 ± 0.95	0.39	0.27	0.55	14.1	22.6	8.38	202.6
OCDD	1.76± 0.71	16.9 ± 17.4	3.34	3.15	8.84	70.8	127.3	62.6	468.8
Total PCDDs	29.3 ± 19.4	35.1 ± 26.9	25.6	58.5	50.5	263.2	595.6	197	2228
2,3,7,8-TeCDF	8.77 ± 2.52	3.88 ± 2.86	7.89	13.4	6.39	2.72	5.23	3.45	5.86
Other TeCDF	5.46 ± 0.66	6.79 ± 5.58	4.64	19	12.3	53.1	82.3	48.7	220.1
1,2,3,7,8-PeCDF	1.62 ± 0.33	1.63 ± 0.11	1.08	1.84	1.72	ND	0.63	ND	2.78
2,3,4,7,8-PeCDF	4.46 ± 0.25	5.43 ± 0.54	1.65	4.72	3.92	1.59	0.68	1.26	4.14
Other PeCDF	7.15 ± 2.49	8.31 ± 4.7	9	21.9	15.3	17.5	51.6	28.6	110.7
1,2,3,4,7,8-HxCDF	1.02 ± 0.01	0.94 ± 0.06	0.54	1.17	1.73	3.29	0.87	1.41	2.99
1,2,3,6,7,8-HxCDF	0.57 ± 0.07	0.73 ± 0.12	0.65	0.99	1.22	1.37	0.73	0.85	1.99
2,3,4,6,7,8-HxCDF	1.03 ± 0.16	1.93 ± 0.08	1.67	1.91	2.98	ND	0.9	1.57	4.03
1,2,3,7,8,9-HxCDF	ND	ND	0.07	ND	0.18	1.35	ND	0.29	ND
Other HxCDF	8.71 ± 2.58	7.79 ± 2.24	7.23	18.6	7.51	25.6	33.8	20.5	63.9
1,2,3,4,6,7,8-HpCDF	1.2 ± 0.02	1.56 ± 0.36	0.95	1.59	1.58	7.02	5.72	4.52	17.4
1,2,3,4,7,8,9-HpCDF	0.19 ± 0.03	0.32 ± 0.1	0.09	0.28	0.43	3.09	0.95	0.63	1.66
Other HpCDF	4.19 ± 0.44	2.73 ± 0.77	0.92	4.48	1.38	7.9	7.77	6.49	21.6
OCDF	0.68 ± 0.09	2.00 ± 1.43	0.28	0.62	0.75	9.9	12.7	6.78	22.3
Total PCDFs	45.1 ± 9.47	44.0 ± 17.8	36.7	90.5	57.4	134.5	203.9	125.1	479.4
∑ PCDDs/DFs-TEQ	7.33±0.14	7.23 ± 0.12	3.76	7.43	5.54	4.41	3.42	2.99	8.62

The concentrations of coplanar-PCBs in the aquatic organisms collected from Lake Shinji and Tokyo bay are listed in Tables 4 and 5, respectively. The total coplanar-PCB concentrations varied according to the trophic level for organisms from Lake Shinji, from a mean low value of 56.2 pg/g (on a dry weight basis) in shijimi clams to a mean high value of 283 pg/g in sea bass. On the other hand, the total coplanar-PCB levels in the biological samples from Tokyo bay ranged

Table 4. Concentrations (pg/g dry wt. basis) of coplanar-PCBs in biological samples collected from Lake Shinji.

Species	Waterfowl	Fish				Bivalve
Isomer	Tufted duck	Sea bass	Gizzard shad	Large-eyed herring	Goby	Shijimi clam
3,4,4`,5-TCB	8.87 ± 5.68	9.58 ± 8.94	8.59 ± 4.96	5.22	10.9	2.35 ± 0.52
3,3`,4,4`-TCB	200.9 ± 50.5	222.5 ± 189.1	169.3 ± 71.5	103.4	195.5	45.9 ± 12
3,3`,4,4`,5-PeCB	30.4 ± 10.9	45.2 ± 37.2	37.9 ± 31.9	24.5	45.8	7.42 ± 5.51
3,3`,4,4`5,5`-HxCDB	4.68 ± 3.0	5.63 ± 4.73	7.1 ± 6.28	7.01	3.51	0.57 ± 0.5
Total Non-*ortho* CBs	244.8 ± 64.1	282.9 ± 239.9	223 ± 115.5	140	255.6	56.2 ± 17.4
∑ Non-*ortho* CBsTEQ	3.11 ± 1.09	4.59 ± 3.78	3.89 ± 3.36	2.52	4.63	0.75 ± 0.55

Table 5. Concentrations (pg/g dry wt. basis) of coplanar-PCBs in biological samples collected from Tokyo bay.

Species	Fish					Bivalve			Polychaete
Isomer	Sea bass	Gizzard shad	Stone flounder	Dab	Stingray	Littleneck clam	hard-shell clam	Mactridae	
3,4,4`,5-TCB	54.0 ± 9.38	25.9 ± 4.57	35.6	101.9	16.5	ND	9.92	11.2	ND
3,3`,4,4`-TCB	1187± 259.9	756 ± 249	739.5	1784	254.1	191.2	180.4	236.8	465.9
3,3`,4,4`,5-PeCB	157.1 ± 35.5	99.4 ± 1.88	47.3	153.3	48.2	ND	11.4	9.7	31.9
3,3`,4,4`5,5`-HxCDB	33.3± 9.07	25.4 ± 0.32	9.42	27.8	15.3	6.1	3.28	1.35	6.74
Total Non-*ortho* CBs	1431± 313	907 ± 243	831.8	2067	334	197.3	205.1	259.1	504.5
∑ Non-*ortho* CBs TEQ	16.2 ± 3.67	10.3 ± 0.16	4.9	15.8	5.0	0.08	1.2	1.01	3.31

from 205.1 pg/g in hard-shell clam to 2067 pg/g in dab. On the whole, the contamination levels of these persistent contaminants in aquatic organisms from Tokyo bay were higher than those from Lake Shinji food chain. The values of PCDDs/DFs and coplanar-PCBs TEQ, based on WHO-TEFs for human (van den Berg *et al.*, 1998), for each sample are shown in Tables 2-5. The total TEQ concentrations ranged from 11.8 pg TEQ/g for gizzard shad to 1.91 pg TEQ/g for shijimi clam collected from Lake Shinji and from 23.5 pg TEQ/g for sea bass to 4.0 pg TEQ/g for mactridae collected from Tokyo bay.

Figure 2 shows proportions of PCDDs, PCDFs and coplanar-PCBs to the total contamination levels and total TEQ values in aquatic organisms from Lake shinji and Tokyo bay. Average coplanar-PCB proportions (89%) to the total concentrations in fish samples collected from Tokyo bay appeared to be higher than those of bivalves (32%) and polychaete (15%). This inclination is also observed for fishes and bivalves from Lake Shinji. In this study, we found that in the upper end of the food chain (sea bass), the total coplanar-PCB concentrations were one order of magnitude higher than in bivalves. On the contrary, the total concentrations of PCDDs/DFs in fish samples were relatively lower than those in bivalves and polychaetes. The coplanar-PCB proportions to the total TEQ in various organisms from Lake Shinji and Tokyo bay also displayed the same tendency with contamination levels. This result indicated that biomagnification of PCDDs/DFs through with aquatic food chains was poor compared with that of coplanar-PCBs.

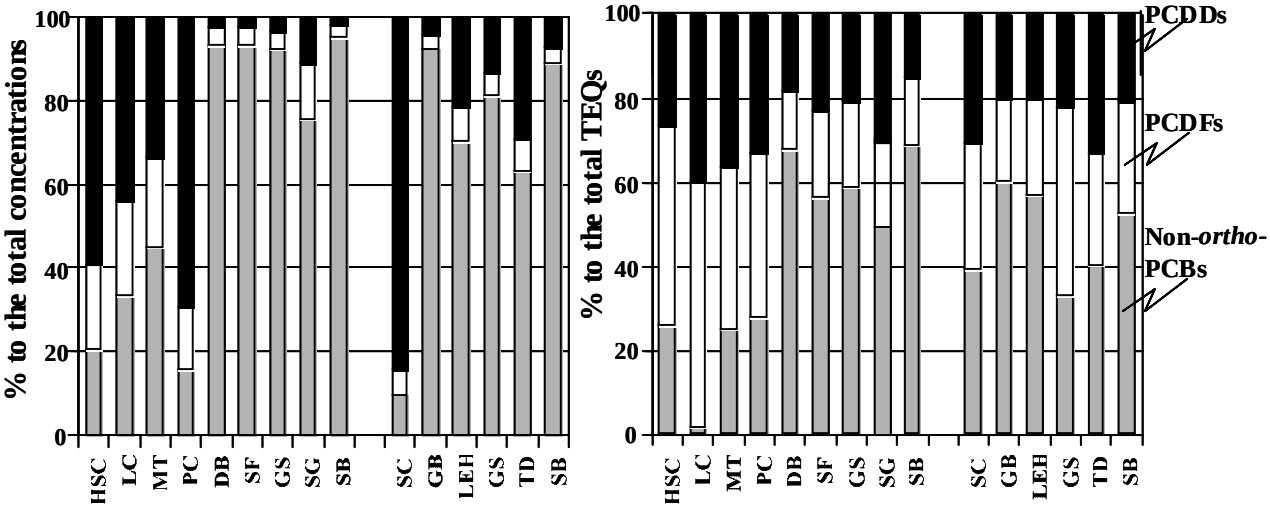

Fig. 2. Composition of individual compounds of PCDDs, PCDFs and Non-*ortho*-PCBs on levels (left side) and 2,3,7,8-TeCDD toxic equivalents (right side) in various biological samples from Lake Shinji and Tokyo bay.
HSC : Hard-shell clam, LC : Littleleck clam, MT : Mactridae, PC : Polychaete, DB : Dab, SF : Stone flounder, GS : Gizzard shad, SG : Stingray, SB : Sea bass, SC : Shijimi clam, GB: Goby, LEH : Large-eyed herring, TD : Tufted duck

3.3 *Relationship between PCDDs/DFs, coplanar-PCBs and trophic levels.*

The relationship between nitrogen isotope ratios and contaminant concentrations in biological samples collected from Lake Shinji and Tokyo bay were represented in Figure 3. Broman *et al*. (1992) and Rolff *et al*. (1993) developed an equation relating the regression $\delta^{15}N$ to the contaminant concentration : $A \cdot e^{(B^* \delta 15N)}$, where A is a constant dependent on background concentration, and B is the change in concentration per unit of $\delta^{15}N$ across the food chain. Positive values of B indicate that a substance is biomagnified in the food chain, and negative values indicate biodepuration of the contaminant. 3,3',4,4'-TeCB (IUPAC No. 77) was found to increase exponentially with increasing trophic level (Fig. 3).

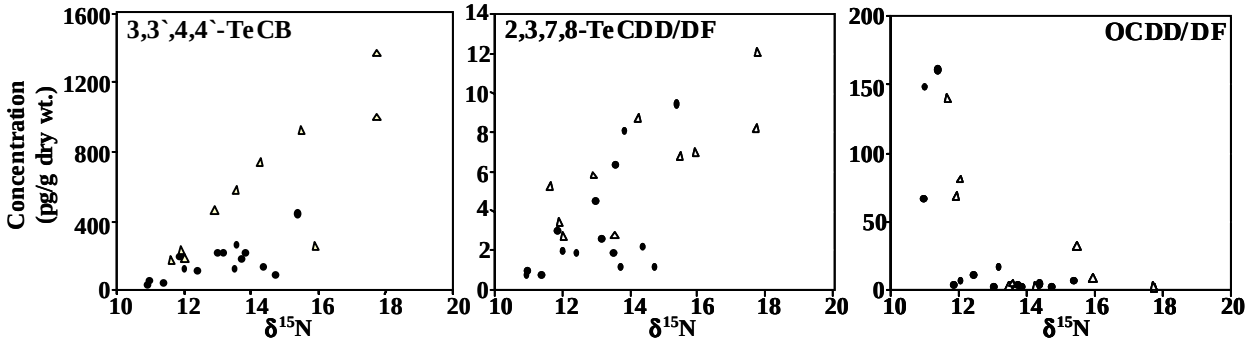

Fig. 3. Relationship between the concentrations of 3,3',4,4'-TeCB (#77), 2,3,7,8-TeCDD/DF, OCDD/DF and the trophic levels of biota measured with $\delta^{15}N$, in aquatic food chains from Lake Shinji (●) and Tokyo bay (△).

Among the four non-*ortho* PCB isomers analyzed, the biomagnification power of 3,3',4,4'-TeCB (IUPAC No. 77) is the highest, with a slope of 0.36 for Lake Shinji and 0.25 for Tokyo bay.

The relationship between the total 2,3,7,8-substituted PCDDs/DFs concentrations and trophic levels was not very clear, however, it was positively correlated with the trophic level for lower-chlorinated congeners and negatively correlated for higher-chlorinated congeners. Although the relationship between the PCDDs/DFs concentrations and trophic level was not significant, the OCDD/DF concentration was found to decrease with increasing trophic level. On the other hand, the concentrations of total 2,3,7,8-TCDD/DF were low at the lower trophic levels, and increased with increasing stable nitrogen isotope ratio. This result indicated a lack of biomagnification of higher-chlorinated PCDDs/DFs in aquatic food chains from Lake Shinji and Tokyo bay. The molecular cross-sectional size of higher-chlorinated PCDDs/DFs is above 0.95 nm. Previous investigations have revealed that PCDDs/DFs with a molecular cross-section >0.95 nm is less efficiently taken up by organisms (Opperhuizen *et al.*, 1985). Based on this point of view, Broman *et al.* (1992) reported the lack of food chain biomagnification of the higher-chlorinated compounds. These results also indicate the low bioaccumulation or biotransfer potential of higher-chlorinated PCDDs/DFs in aquatic organisms from Lake Shinji and Tokyo bay.

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