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Dioxin concentrations in marbled sole collected from Sendai Bay, Japan

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Abstract : The concentrations of dioxins [polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), non-*ortho* polychlorinated biphenyls (non-*ortho* PCBs), and mono-*ortho* polychlorinated biphenyls (mono-*ortho* PCBs)] in marbled sole (*Pseudopleuronectes yokohamae*) collected from Sendai Bay, Japan, were measured using high-resolution gas chromatography-mass spectrometry. The relationship between the concentrations of these compounds (dioxins) and the body length of marbled sole was examined. Among the PCDD/F congeners, 1,3,6,8- and 1,3,7,9-TeCDD, and OCDD occur as impurities in chlorinated pesticides, and some 2,3,7,8- substituted congeners tend to bioaccumulate in marbled sole. Co-PCB congener concentrations were higher than those of PCDD/F congeners, and PCB #118 and PCB #105 concentrations were higher than those of other Co-PCB congeners. Several dioxin congeners were significantly correlated with marbled sole body length, and polynomial regressions tended to have better fits than linear regressions. Although dioxin concentrations in marbled sole increased with increasing total length in fish with short to medium total lengths, they decreased with increasing total length in medium to long fish. Further, the TEQ values of Co-PCBs accounted for more than 50% of sum of TEQ values for all dioxins. The investigation of Co-PCB concentrations is important from the point of view of risk assessment.

Keywords : *dioxin congeners, monitoring, bioaccumulation, marbled sole, Sendai Bay, total length*

Introduction

Several congeners of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and coplanar polychlorinated biphenyls (Co-PCBs) are highly toxic to organisms (MOCARELLI *et al.,* 1996). For Asians, fish and shellfish are thought to be the major route of intake of PCDDs, PCDFs, and Co-PCBs (dioxins) (TAKAYAMA *et al.,* 1991, TOYODA *et al.,* 1999, TSUTSUMI *et al., 2001*). To assess risk from dioxins, marine organisms have been monitored (LING *et al.,* 1995, IIMURA *et al.,* 2002, NAITO *et al.,* 2003, GURUGE and TANABE, 2004).

We investigated dioxin concentrations in Sendai Bay, northeastern Japan. Dioxin congeners that occur as impurities in agricultural chemicals (YAMAGISHI *et al.,* 1981, MASUNAGA *et al.,* 2001) are predominant in seawater and sediment there (OKUMURA *et al.,* 2003, 2004a). Accumulation through the marine food web in fish of the predominant PCDD/F congeners has been lower than that in invertebrates (OKUMURA *et al.,* 2003, 2004b), and the predominant PCDD/F congeners have accumulated less than Co-PCB congeners in Japanese flounder (*Paralichthys olivaceus*) in relation to total length (OKUMURA *et al.,* 2004c).

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Sendai Bay is a fishery for both marbled sole (*Pseudopleuronectes yokohamae*) and Japanese flounder. The total amount of marbled sole landed in Miyagi Prefecture from Sendai Bay in 2001 was about 4640 t. Marbled sole is one of the important fish resources of fisheries in Sendai Bay. Although marbled sole is in the same order as Japanese flounder, the diet of marbled sole (invertebrates such as the sand worm) is different from that of Japanese flounder (small fishes such as Japanese anchovy and sand lance ; OCHIAI, 1966, OMORI, 1974, YAMADA *et al.,* 1998). Therefore, it is necessary to investigate the influence of diet on dioxin concentrations in different fish species.

In this study, the concentrations of PCDD, PCDF, and Co-PCB congeners in marbled sole from Sendai Bay were determined by high-resolution gas chromatography/high-resolution mass spectroscopy (HRGC/HRMS). First, we examined the composition and concentration of dioxins in marbled sole, and then we compared the relationship between total length of marbled sole and dioxin concentrations with that in Japanese flounder in order to investigate the influence of diet on the concentrations of dioxins in fish.

2. Materials and methods

The procedures for sampling, chemical analysis of dioxins, statistical manipulation of data, and calculation of TEQ are described in our previous report (OKUMURA *et al.,* 2004c). In this study, data on the marbled sole (n = 4, body length ; 26.6, 28.2, 28.5, and 32.8 cm) previously described (OKUMURA *et al.,* 2003) were used in the analysis of dioxin concentration and body size.

2.1. Sampling

Marbled sole were collected in Sendai Bay, Japan, in November 2000 with a bottom trawl net (n = 8, the body lengths are shown in the Appendix). After the total lengths of the fish were measured, the fish were frozen at −20℃ until chemical analysis.

2.2. Analysis of PCDDs, PCDFs, and Co-PCBs (Dioxins)

The concentrations of PCDDs and PCDFs bearing from 4 to 8 chlorines and the concentrations of Co-PCB congeners in whole-body samples (including head and fins) were determined. Briefly, the methods are as follows.

2.2.1. Preparation of analytical samples

The frozen whole-body samples were homogenized, weighed (100 g), spiked with a ^{13}C-labeled internal standard (40 pg, TeCDD/Fs-HxCCDD/Fs analysis ; 200 pg, OCDD/F analysis ; 400 pg, non-*ortho* PCBs analysis ; 1000 pg, mono-*ortho* PCBs analysis), saponified with 300 mL of potassium hydroxide (2 mol/L) and 150 mL of methanol for 8–12 h, and then extracted 3 times with hexane. The hexane extracts were washed with sulfuric acid until no color was visible in the sulfuric acid layer, and the extracts were then concentrated again prior to HRGC/HRMS analysis.

2.2.2. Clean-up column chromatography

The extract of each sample was then poured through a column of silica gel (2 g, baked at 130 ℃ for 3 h) and eluted with 200 mL of hexane. The eluate was poured through a column of alumina (15 g, basic), rinsed with 150 mL of hexane, and eluted with 200 mL of dichlorome thane : hexane (2 : 98, mono-*ortho* PCBs analysis ; or 60 : 40, PCDD/Fs and non-*ortho* PCBs analysis). The eluate of PCDD/Fs and non-*ortho* PCBs was poured through an activated-carbon column (0.5 g, drying column), rinsed with 100 mL of dichloromethane : hexane (5 : 95), and eluted with 250 mL of toluene. The final eluate purified by column chromatography was concentrated and subjected to congener-specific analysis by HRGC/HRMS on an AutoSpec Ultima spectrometer (Micromass Ltd., UK).

2.2.3. HRGC/HRMS analysis

Tetra- to hexachlorodibenzo-*p*-dioxin and -dibenzofuran congeners were analyzed on an SP-2331 column (ϕ0.32 mm × 60m) (Sigma-Aldrich). Hepta- to octachlorodibenzo-*p*-dioxin and -dibenzofuran congeners and tetrachlorobiphenyls were analyzed on a DB-17 column (ϕ0.32 mm × 60m) (J&W Scientific). Non-*ortho* and mono-*ortho* penta- to heptachlorinated biphenyls were analyzed on

DB-17 (J&W Scientific) and HT8 (ϕ0.22 mm $\times$50m) (SGE) columns, respectively. The temperature program for the analysis using the SP-2331 column was 150℃ for 1 min, 15℃/min to 200℃, hold for 5 min, 2℃/min to 250℃, and then hold for 30 min. The temperature program for the DB-17 column was 150℃ for 1 min, 15℃/min to 270℃, and then hold for 20 min. The temperature program for the HT8 column was 160℃ for 1 min, 15℃/min to 220℃, hold for 5 min, 2℃/min to 270℃, and then hold for 5 min. The temperatures of the injector and ion source were both 260℃. Mass spectrometry was performed in electron impact (EI) mode. The voltage and current of the electron-impact ionization energy were 30 eV and 500μA, respectively. The mass spectrometer was operated at a resolution of 10,000. The detection limits for the tetra-, penta-, hexa-, hepta-, and octachlorinated PCDD/F congeners in the samples were 0.05, 0.05, 0.1, 0.1, and 0.2 pg/g wet weight (ww). The detection limits of Co-PCBs in the samples were 0.1 pg/g ww, respectively.

2.3. Data analysis

2.3.1. Box plot and t tests

Values below the detection limits were set at 0 pg/g ww. Box plots of dioxin profiles of marbled sole were created with SPSS 11.5J for a Windows-based system (SPSS Inc., Chicago, IL, USA). *T* tests (SPSS 11.5J) were used to compare total length between marbled sole and Japanese flounder samples.

2.3.2. Calculation of the relationship between dioxin concentration and total length by linear regression

The coefficients of determination (r^2) and the *p* values (p) for the relationship between the dioxin concentrations and marbled sole total lengths were calculated by simple linear regression : concentration of dioxin congener (pg/g ww) $= ax + b$, where x is the total length (cm), a the slope, and b the intercept. Polynomial regressions were also conducted : $y = a_1x^2 + a_2x + b$, where y is the concentration of the dioxin congener (pg/g ww), x the total length (cm), a the slope, and b the intercept. Because polynomial regression provided a better fit than linear regression, when the relationship between x and y was nonlinear. The linear and polynomial regressions were conducted with Excel XP (Microsoft).

2.4. Calculation of toxic equivalency quotient (TEQ) values

The values below detection limits were set to zero. The average TEQ of each biological sample was calculated by using the toxic equivalency factors (TEF) for humans/mammals provided by the World Health Organization (VAN DEN BERG *et al.,* 1998).

3. Results and Discussion

3.1. Total lengths and fat concentration of marbled sole and Japanese flounder

The total length of marbled sole ranged from 15.2 to 32.8 cm (Appendix, OKUMURA *et al.,* 2003), and that of Japanese flounder from 11.7 to 36.6 cm (OKUMURA *et al.,* 2004c), but the difference was not significant (t test ; $p > 0.05$). The marbled sole total lengths used in this study were therefore similar to those of Japanese flounder reported previously.

Fat concentrations of four marbled sole (29.0 ± 2.66 ; average length ± S.D.) and four Japanese flounder (35.4 ± 0.81), which were caught in 1999 (OKUMURA *et al.,* 2003, 2004c), were determined. The average fat concentration of marbled sole (3.7% ± 0.22 ; average ± S.D.) was about 1.5 times that of Japanese flounder (2.5% ± 0.41), but both values were similar to the average fat concentration of sea bass, and they are lower than that of conger eel by one order of magnitude (IIMURA *et al.,* 2002).

3.2. Dioxin concentrations in marbled sole and Japanese flounder

In marbled sole, average dioxin concentrations were 7.2 pg/g ww for PCDDs, 2.7 pg/g ww for PCDFs, 23.2 pg/g ww for non-*ortho* PCBs, and 1070.1 pg/g ww for mono-*ortho* PCBs (Fig. 1 and Appendix). On the other hand, in Japanese flounder, they were 3.1 pg/g ww for PCDDs, 1.0 pg/g ww for PCDFs, 14.1 pg/g ww for non-*ortho* PCBs, and 887.2 pg/g ww for mono-*ortho* PCBs. Total PCDDs, PCDFs, non-*ortho* PCBs, and mono-*ortho* PCBs were higher in marbled sole than in Japanese flounder, and the difference was significant

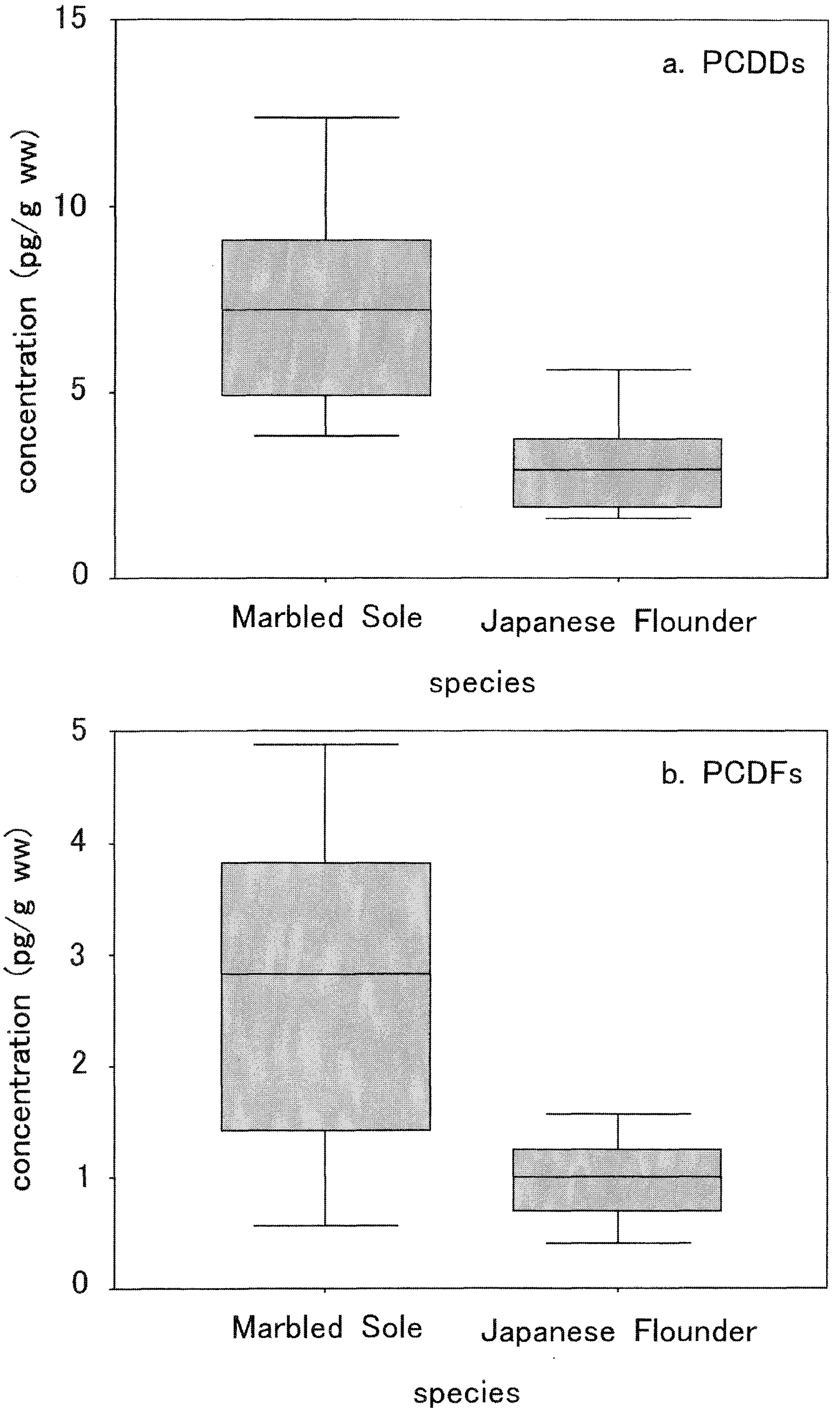

Fig. 1a, 1b. Box plots of total PCDDs, PCDFs in marbled sole (n = 12) and Japanese flounder (n = 11). The horizontal line in each box plot indicates the median, the box extends from the 25th to the 75th percentiles, and the whiskers extend to the 10th and 90th percentiles. The data for Japanese flounder and four data points for marbled sole are from OKUMURA *et al.*, (2003, 2004c).

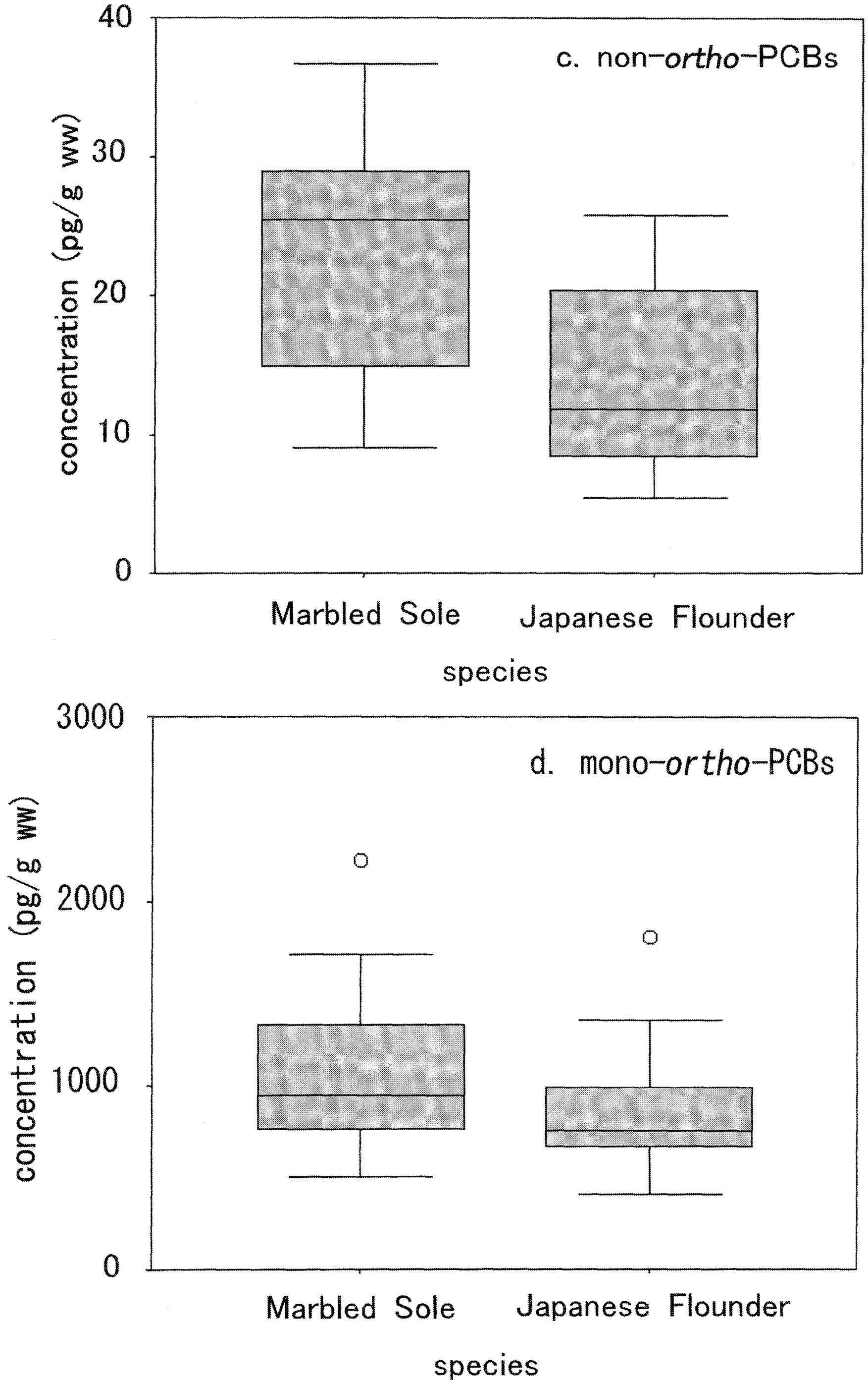

Fig. 1c, 1d. Box plots of total non-*ortho* PCBs, and mono-*ortho* PCBs in marbled sole ($n = 12$) and Japanese flounder ($n = 11$). The horizontal line in each box plot indicates the median, the box extends from the 25th to the 75th percentiles, and the whiskers extend to the 10th and 90th percentiles ; the symbol ○ indicates outliers. The data for Japanese flounder and four data points for marbled sole are from OKUMURA *et al.,* (2003, 2004c).

($p < 0.05$) for PCDDs, PCDFs, and non-*ortho* PCBs (Fig. 1a–1c). Marbled sole is known to prey mainly on invertebrates such as sand worms, whereas Japanese flounder is known to prey mainly on small fishes such as Japanese anchovy and sand lance (OCHIAI, 1966, OMORI, 1974, YAMADA *et al.*, 1998). Average dioxin concentrations in sand worm (1540 pg/g ww ; OKUMURA *et al.*, 2004b) are higher than those in Japanese anchovy (730 pg/g ww ; OKUMURA *et al.*, 2003) and sand lance (560 pg/g ww ; OKUMURA *et al.*, 2004b). Thus, dioxin concentrations are higher in the diet of marbled sole than in that of Japanese flounder. We expected that dioxin concentrations would be higher in marbled sole than in Japanese flounder.

Irrespective of total length, dioxin concentrations in marbled sole decreased in the order total mono-*ortho* PCBs > total non-*ortho* PCBs > total PCDDs > total PCDFs. This result is consistent with that for Japanese flounder (OKUMURA *et al.*, 2004c). We inferred thought that bioaccumulation properties were similar in marbled sole and Japanese flounder as same order.

3.3. Dioxin congeners in marbled sole

The PCDD congener with the highest concentration in marbled sole was 1,3,6,8-TeCDD (4.95 pg/g ww), and concentrations decreased in the order 1,2,3,7,8-PeCDD (0.47 pg/g ww) > OCDD (0.45 pg/g ww) > 1,2,3,6,7,8-HeCDD (0.39 pg/g ww) > 1,2,3,4,6,7,8-HxCDD (0.24 pg/g ww) > 1,3,7,9-TeCDD (0.22 pg/g ww ; Fig. 2a). Among these PCDD congeners, 1,3,6, 8-and 1,3,7,9-TeCDD occur as impurities in the chlorinated pesticide chlornitrophen (CNP ; YAMAGISHI *et al.*, 1981, MASUNAGA *et al.*, 2001), and OCDD occurs as an impurity in the chlorinated pesticide pentachlorophenol (PCP ; MASUNAGA *et al.*, 2001). These three congeners are the predominant PCDD congeners in sediment and seawater in Sendai Bay (OKUMURA *et al.*, 2003, 2004a). Therefore, we expected that the concentration of these three congeners would also be high in marbled sole. In contrast, 1,2,3,7,8-PeCDD, 1,2,3,6,7,8-HeCDD, and 1,2,3,4, 6,7,8-HxCDD are less abundant PCDD congeners in sediment and seawater in Sendai Bay ; the concentrations of these three congeners are much lower than those of 1,3,6,8- and 1,3,7,9-TeCDD and OCDD, or they are below the detection limit (OKUMURA *et al.*, 2003, 2004a). However, bioaccumulation of 2,3,7,8-substituted PCDD congeners (such as 1,2,3,7,8-PeCDD) in fishes is thought to be higher than that of non–2,3,7,8-substituted PCDD congeners (such as 1,3,6,8-TeCDD ; SIJM *et al.*, 1993), thus explaining the high concentrations of 1,2,3,7,8-PeCDD, 1,2,3,6,7,8-HeCDD, and 1,2, 3,4,6,7,8-HxCDD among PCDD congeners in marbled sole.

Although the concentrations of all PCDF congeners were lower than that of 1,3,6,8-TeCDD, the concentrations of 2,3,7,8-TeCDF (0.68 pg/g ww) and 2,3,4,7,8-PeCDF (0.44 pg/g ww) were higher than those of 1,3,7,9-TeCDD, 1,2,3,7,8-PeCDD, 1,2,3,6,7,8-HeCDD, or 1,2,3,4, 6,7,8-HxCDD in marbled sole (Fig. 2b). Concentrations of 2,3,7,8-TeCDF and 2,3,4,7,8-PeCDF are low in sediment and seawater of Sendai Bay, usually below the detection limit (OKUMURA *et al.*, 2003, 2004a), but the PCDF congeners 2,3,7,8-TeCDF and 2,3,4,7,8-PeCDF, as well as 1,2,3,7,8-PeCDD, 1,2,3,6,7,8-HeCDD, and 1,2,3,4,6,7,8-HxCDD, are 2,3,7,8-substituted PCDD/F congeners. The bioaccumulation of 2,3,7,8-substituted PCDF congeners such as 2,3,7,8-TeCDF in fishes is also thought to be higher than that of non–2,3, 7,8-substituted PCDF congeners (SIJM *et al.*, 1993). As a result, the concentrations of 2,3,7,8-TeCDF and 2,3,4,7,8-PeCDF were comparatively high in marbled sole.

The concentration of PCB #118 (average, 695.8 pg/g ww) was highest among dioxin congeners in marbled sole, and the next most abundant PCB congener was PCB #105 (200.0 pg/g ww) (Fig. 2c). In agreement with this result, these Co-PCB congeners were previously found to be predominant in biological samples (IIMURA *et al.*, 2002, KUMAR *et al.*, 2001, NAITO *et al.*, 2003, WAN *et al.*, 2005). They were also predominant in commercial PCB products such as Kanechlor (TAKASUGA *et al.*, 1995) and in environmental samples such as river sediment (HATTORI *et al.*, 2004), exhaust gas of incinerator (SAKAI *et al.*, 1996), air and deposition at Yokohama (KIM *et al.*, 2004), and seawater and marine sediment (IIMURA *et al.*, 2002). The

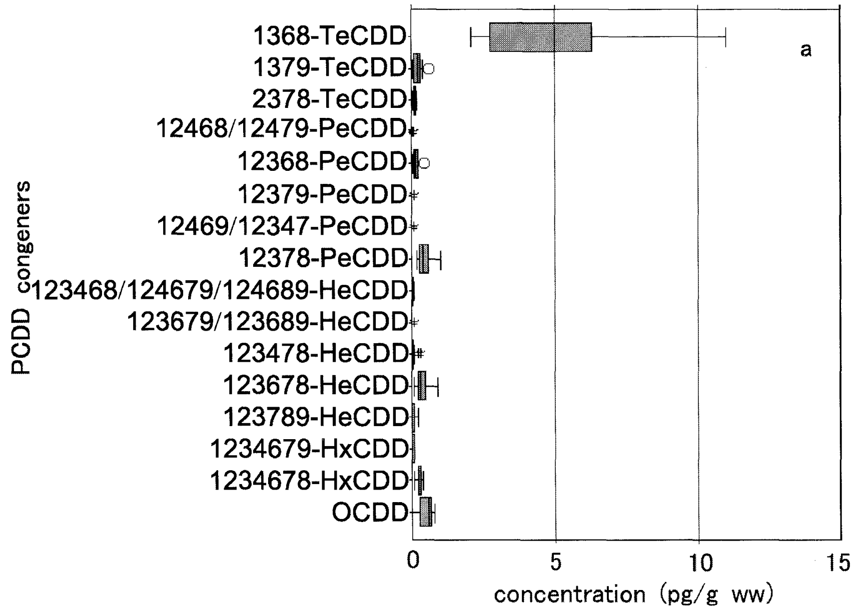

Fig. 2a. Box plots of PCDD congeners in marbled sole. Four data points for marbled sole are from OKUMURA *et al.*, (2003).

concentrations of these PCB congeners in sediment and seawater of Sendai Bay are higher than those of PCDD/F congeners (OKUMURA *et al.,* 2003, 2004a). Moreover, absorption efficiencies are similar among PCB congeners (NIIMI, 1996), and Co-PCB congeners are thought to bioaccumulate in fishes more than PCDD/F congeners. Therefore, it was expected that PCB #118 and PCB #105 would be predominant in marbled sole.

3.4. Relationships between total length and the concentration of dioxin congeners

Relationships between total length and dioxin concentrations are shown in Table 1 and Fig. 3. The concentrations of one PCDD congener (OCDD), five PCDF congeners (2,3,7,8-, 2, 3,6,7-TeCDF, 1,3,4,6,8-, 1,2,3,6,7-, and 2,3,4,6,7-PeCDF), and one non-*ortho* PCB (PCB #77) showed a significant linear correlation with total length (r^2 = 0.36–0.54, $p < 0.05$). The slopes of the regression lines were positive (0.006–0.71) for the five PCDFs and the non-*ortho* PCB, but negative (–0.029) for OCDD. The relationships of two PCDD congeners (1,2,3,7,8-PeCDD and OCDD), 13 PCDF congeners (1,3,7, 8/1,3,7,9-, 2,3,7,8-, 2,3,6,7-TeCDF, 1,3,4,6,8-, 1,2, 3,6,8/1,3,4,7,8-, 1,2,3,4,8/1,2,3,7,8-, 1,2,3,6,7-, 2, 3,4,7,8- and 2,3,4,6,7-PeCDF, and 1,2,3,4,6,7-HeCDF) and three non-*ortho* PCB congeners (PCB #77, PCB #126, and PCB #169) to total length could be correlated by using polynomial expressions. The correlation coefficients (r^2) ranged from 0.35 to 0.71 and were significant ($p < 0.05$; Table 1 and Fig. 3). Polynomial expressions showed a better fit than linear expressions for most congeners. On the other hand, no mono-*ortho* PCB congeners could be correlated with total length by either linear or polynomial expressions ($r^2 < 0.26$, $p > 0.05$).

Previously, OKUMURA *et al.,* (2004c) reported that linear rather than polynomial regression resulted in more significant correlations between the concentrations of dioxin congeners in Japanese flounder and total length. Moreover, the mean concentration of all Co-PCB congeners in Japanese flounder was also significantly linearly correlated with total length (r^2 = 0.55 and 0.88 ; $p > 0.05$). Thus, the results for marbled sole are not consistent with those for Japanese flounder (OKUMURA *et al.,* 2004c).

It is difficult to explain why a linear relationship to total length was found for fewer

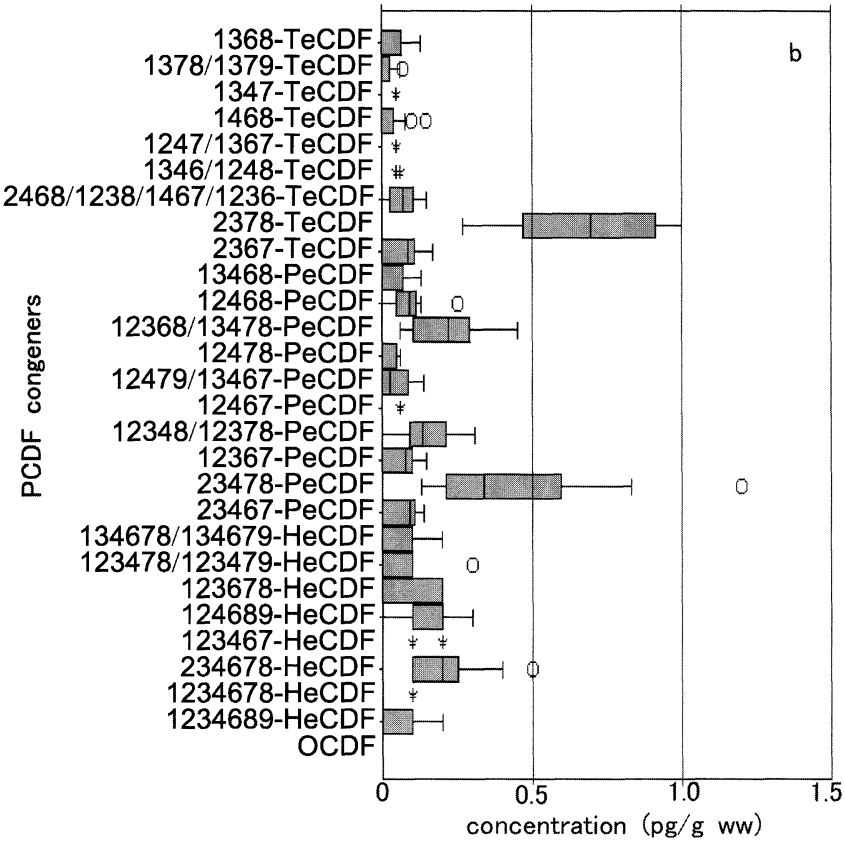

Fig. 2b. Box plots of PCDF congeners in marbled sole. Four data points for marbled sole are from OKUMURA *et al.*, (2003).

congeners in marbled sole. As fish grow, their rate of growth is thought to decrease (YAMASHITA *et al.,* 2001), and the bioconcentration of chemicals by fish is also thought to decrease as they grow (SCHIMMEL *et al.,* 1977). Thus, bioaccumulation of dioxin congeners in marbled sole may decrease as their total length increases. As a result, the slopes of regression lines would tend to be positive when total length is short (small body size), and they would tend to become negative as total length increases. This may explain the better fit of polynomial expressions than linear expressions to this relationship in the case of most congeners. Further, dioxin concentrations are higher in the diet of marbled sole than in that of Japanese flounder (OKUMURA *et al.,* 2003, 2004b). Several dioxin congeners may therefore reach equilibrium faster in marbled sole than in Japanese flounder. The reason why no mono-*ortho* PCB congeners could be correlated by linear or polynomial expressions with total length may be related more to the availability of different types of prey than to the bioaccumulation properties of mono-*ortho* PCB congeners in marbled sole, because dioxin concentrations in sand worm are higher than those in marbled sole (a predator of sand worm), whereas those in sand lance and Japanese anchovy are lower than those in Japanese flounder (OKUMURA *et al.,* 2003, 2004b, 2004c).

3.5. Toxic equivalency (TEQ) values

The whole-body total TEQ values ranged from 0.68 to 2.9 pg TEQ/g ww for marbled sole (Appendix) and from 0.73 to 1.78 pg TEQ/g ww for Japanese flounder (OKUMURA *et al.,*

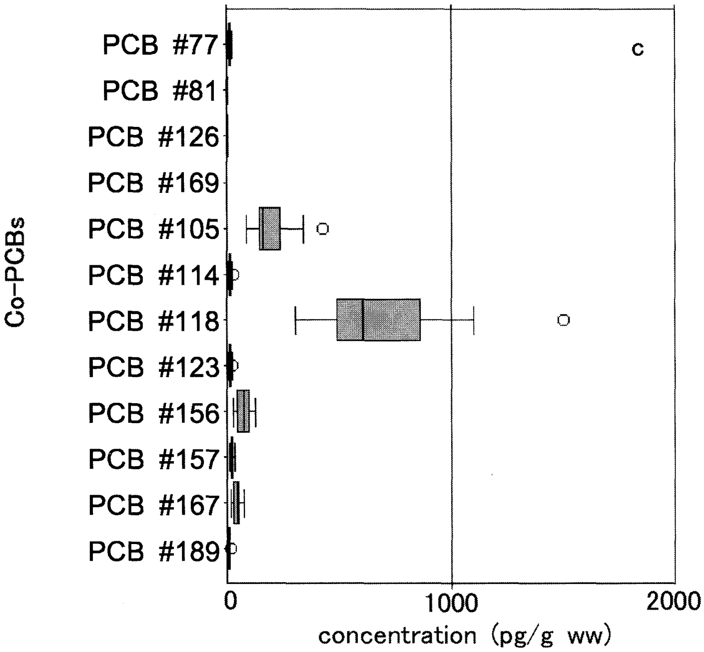

Fig. 2c. Box plots of mono-*ortho* PCB congeners in marbled sole. Four data points for marbled sole are from OKUMURA *et al.* (2003).

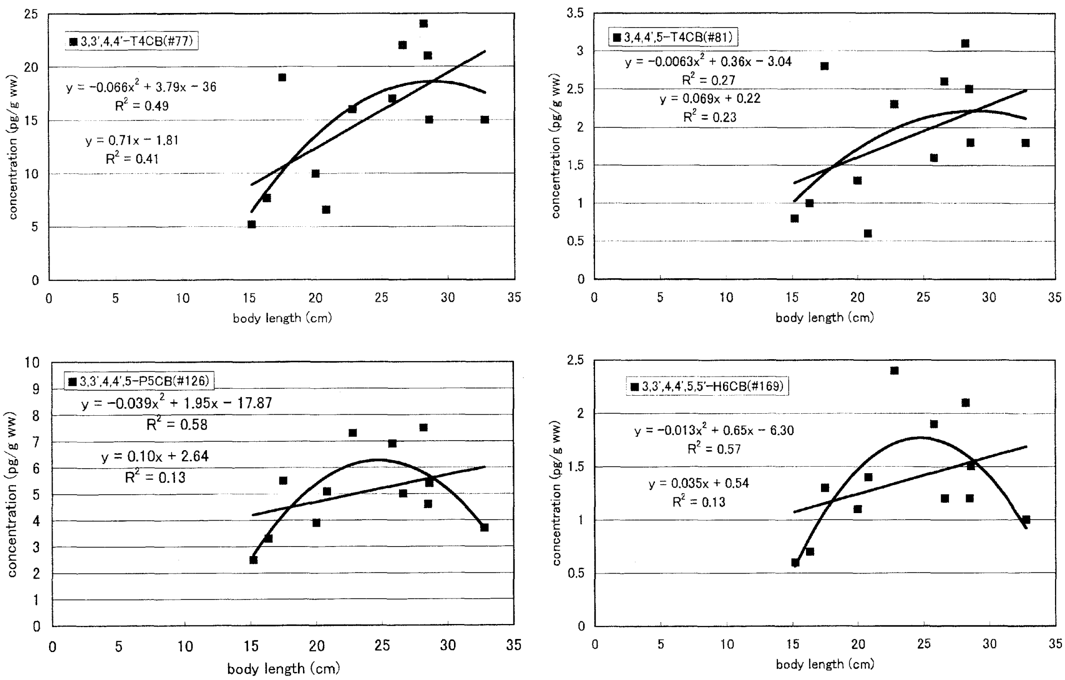

Fig. 3. Relationships between concentrations of non-*ortho* PCBs and body length of marbled sole. Four data points for marbled sole are from OKUMURA *et al.*, (2003).

Table 1. Equation parameters for the relationship between body length of marbled sole and the concentrations of PCDD/Fs and mono-*ortho* PCBs.

	y=ax+b			$y=a_1x^2+a_2x+b$			
	a	b	r^2	a	b	c	r^2
1368−TeCDD	0.19	0.37	0.19	−0.017	0.27	−0.52	0.19
1379−TeCDD	−0.072	0.39	0.07	0.0002	−0.017	0.5	0.07
2378−TeCDD	0.0012	0.07	0.05	−0.0005	0.026	−0.21	0.28
12468/12479−PeCDD	0.001	−0.013	0.05	−0.0002	0.011	−0.12	0.09
12368−PeCDD	0.0006	0.13	0.0009	−0.0007	0.032	−0.22	0.03
12379−PeCDD	0.0014	−0.025	0.08	−0.00003	0.003	−0.04	0.08
12469/12347−PeCDD	0.001	−0.017	0.07	−0.00003	0.0025	−0.034	0.08
12378−PeCDD	0.0067	0.31	0.02	***−0.007***	***0.33***	***−3.3***	***0.47***
123468/124679/124689−HeCDD	0.0021	−0.024	0.07	−0.0006	0.03	−0.35	0.21
123679/123689−HeCDD	−0.0002	0.014	0.002	−0.0004	0.017	−0.17	0.12
123478−HeCDD	0.00006	0.049	0.00001	−0.018	0.085	−0.89	0.24
123678−HeCDD	0.0061	0.24	0.02	−0.0054	0.26	−2.55	0.35
123789−HeCDD	0.0018	0.016	0.02	−0.014	0.066	−0.69	0.23
1234679−HxCDD	−0.0033	0.11	0.14	0.0004	−0.02	0.29	0.18
1234678−HxCDD	0.0037	0.15	0.07	−0.0006	0.03	−0.14	0.11
OCDD	***−0.029***	***1.14***	***0.37***	***−0.0009***	***0.012***	***0.69***	***0.38***
1368−TeCDF	0.0043	−0.067	0.28	0.0002	−0.064	0.051	0.29
1378/1379−TeCDF	0.0028	−0.05	0.32	0.0002	−0.0052	0.038	0.35
1347−TeCDF	0.0004	−0.0059	0.03	−0.0001	0.0061	−0.069	0.08
1468−TeCDF	0.0048	−0.085	0.27	0.0002	−0.0035	0.007	0.28
1247/1367−TeCDF	0.0007	−0.012	0.07	−0.00002	0.0018	−0.024	0.08
1346/1248−TeCDF	0.0012	−0.02	0.1	−0.0002	0.009	−0.11	0.15
2468/1238/1467/1236−TeCDF	0.0022	0.017	0.06	0.0001	−0.0035	0.079	0.06
2378−TeCDF	***0.028***	***0.007***	***0.36***	***−0.0059***	***0.3***	***−3.06***	***0.71***
2367−TeCDF	***0.0082***	***−0.12***	***0.56***	***−0.0003***	***0.02***	***−0.25***	***0.58***
13468−PeCDF	***0.0055***	***−0.099***	***0.4***	***0.0002***	***−0.0025***	***−0.0097***	***0.41***
12468−PeCDF	0.0067	−0.069	0.32	−0.0002	0.16	−0.17	0.33
12368/13478−PeCDF	0.012	−0.059	0.31	***−0.0019***	***0.1***	***−1.06***	***0.49***
12478−PeCDF	−0.001	0.042	0.05	0.00001	−0.0017	0.049	0.05
12479/13467−PeCDF	0.0042	−0.055	0.22	−0.00001	0.0048	−0.062	0.22
12467−PeCDF	0.0005	−0.0071	0.03	−0.0001	0.0073	−0.082	0.08
12348/12378−PeCDF	0.0083	−0.053	0.22	***−0.0022***	***0.11***	***−1.21***	***0.59***
12367−PeCDF	***0.006***	***−0.077***	***0.42***	***−0.0007***	***0.037***	***−0.42***	***0.53***
23478−PeCDF	0.0071	0.27	0.02	***−0.0079***	***0.38***	***−3.83***	***0.44***
23467−PeCDF	***0.0063***	***−0.08***	***0.43***	***−0.0004***	***0.023***	***−0.27***	***0.46***
134678/134679−HeCDF	0.0059	−0.066	0.2	−0.0007	0.037	−0.41	0.25
123478/123479−HeCDF	−0.0005	0.06	0.0009	−0.0014	0.064	−0.66	0.17
123678−HeCDF	0.0014	0.043	0.006	−0.0014	0.066	−0.67	0.15
124689−HeCDF	−0.0022	0.68	0.04	−0.0006	0.028	−0.26	0.12
123467−HeCDF	0.0062	−0.0039	0.19	***−0.0012***	***0.06***	***−0.6***	***0.35***
234678−HeCDF	0.0065	0.063	0.08	−0.0014	0.073	−0.67	0.17
1234678−HxCDF	0.0011	−0.009	0.02	−0.0004	0.021	−0.24	0.12
1234689−HxCDF	−0.004	0.15	0.11	−0.00009	0.00001	0.1	0.12
OCDF	−	−	−	−	−	−	−
2,3,3',4,4'−PeCB (#105)	−4.02	294.83	0.05	−0.44	16.6	66	0.07
2,3,4,4',5−PeCB (#114)	−0.47	25.54	0.17	−0.035	1.19	7.13	0.19
2,3',4,4',5−PeCB (#118)	−18.92	1142.2	0.09	−2.18	83.4	6.66	0.12
2',3,4,4',5−PeCB (#123)	−0.17	18	0.03	−0.051	2.23	−8.65	0.09
2,3,3',4,4',5−HeCB (#156)	−2.04	121.63	0.13	−0.34	14.1	−57.47	0.22
2,3,3',4,4',5'−HeCB (#157)	−0.06	22.24	0.002	−0.12	5.73	−42	0.21
2,3',4,4',5,5'−HeCB (#167)	−0.68	59.66	0.05	−0.23	10.33	−62.43	0.18
2,3,3',4,4',5,5'−HxCB (#189)	−0.07	9.85	0.02	−0.05	2.3	−16.39	0.26

bold and italic ; r^2 is significant

Appendix. PCDD, PCDF, and Co-PCB concentrations and TEQs in marbled sole (*Pseudopleuronectes yokohamae*).

	2000–1	2000–2	2000–3	2000–4	2000–5	2000–6	2000–7	2000–8
body length (cm)	15.2	16.35	17.5	20	20.8	22.8	25.8	28.6
1368−TeCDD	2.1	4.6	6.3	2.6	2.6	3.4	5.4	5.9
1379−TeCDD	0.26	0.37	0.3	0.2	0.09	0.2	0.27	0.59
2378−TeCDD	0.07	0.06	0.13	0.08	0.08	0.13	0.12	0.1
total TeCDD	2.43	5.03	6.73	2.88	2.77	3.73	5.79	6.59
12468/12479−PeCDD	N.D.	N.D.	N.D.	N.D.	N.D.	0.05	N.D.	0.08
12368−PeCDD	0.12	0.16	0.18	0.08	0.07	0.23	0.22	0.43
12379−PeCDD	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.1
12469/12347−PeCDD	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
12378−PeCDD	0.17	0.17	0.54	0.32	0.51	0.98	1	0.44
total PeCDD	0.29	0.33	0.72	0.4	0.58	1.26	1.22	1.05
123468/124679/124689−HeCDD	N.D.	N.D.	N.D.	N.D.	N.D.	0.1	N.D.	0.1
123679/123689−HeCDD	N.D.	N.D.	N.D.	N.D.	N.D.	0.1	N.D.	N.D.
123478−HeCDD	N.D.	N.D.	N.D.	N.D.	0.2	0.1	0.3	N.D.
123678−HeCDD	0.1	0.2	0.5	0.2	0.4	0.8	0.9	0.4
123789−HeCDD	N.D.	N.D.	0.1	N.D.	N.D.	0.2	0.2	N.D.
total HeCDD	0.1	0.2	0.6	0.2	0.6	1.3	1.4	0.5
1234679−HxCDD	0.1	0.1	N.D.	N.D.	N.D.	0.1	N.D.	0.1
1234678−HxCDD	0.2	0.2	0.3	0.1	0.2	0.3	0.3	0.3
total HxCDD	0.3	0.3	0.3	0.1	0.2	0.4	0.3	0.4
OCDD	0.7	0.8	0.6	0.3	0.4	0.6	0.6	0.7
total PCDDs	3.82	6.66	8.95	3.88	4.55	7.29	9.31	9.24
1368−TeCDF	N.D.	N.D.	0.05	N.D.	N.D.	N.D.	N.D.	N.D.
1378/1379−TeCDF	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1347−TeCDF	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1468−TeCDF	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1247/1367−TeCDF	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1346/1248−TeCDF	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
2468/1238/1467/1236−TeCDF	N.D.	0.09	0.12	0.05	N.D.	0.07	0.05	0.11
2378−TeCDF	0.27	0.3	0.62	0.55	0.41	1	1	0.82
2367−TeCDF	N.D.	N.D.	0.08	N.D.	N.D.	0.09	0.07	0.11
total TeCDF	0.27	0.39	0.87	0.6	0.41	1.16	1.12	1.04
13468−PeCDF	N.D.	N.D.	N.D.	N.D.	N.D	N.D.	N.D.	N.D.
12468−PeCDF	N.D.	0.05	0.12	0.05	N.D	0.07	0.08	0.11
12368/13478−PeCDF	0.06	0.08	0.21	0.13	0.08	0.45	0.25	0.23
12478−PeCDF	N.D.	0.05	0.06	N.D.	N.D	N.D.	0.05	0.05
12479/13467−PeCDF	N.D.	N.D.	0.07	N.D.	N.D	0.08	N.D.	0.05
12467−PeCDF	N.D.	N.D.	N.D.	N.D.	N.D	N.D.	N.D.	N.D.
12348/12378−PeCDF	N.D.	N.D.	0.15	0.08	0.1	0.31	0.28	0.13
12367−PeCDF	N.D.	N.D.	0.06	N.D.	N.D.	0.15	0.09	0.09
23478−PeCDF	0.13	0.13	0.39	0.23	0.76	0.83	1.2	0.32
23467−PeCDF	N.D.	N.D.	0.1	N.D.	N.D.	0.13	0.06	0.09
total PeCDF	0.19	0.31	1.16	0.49	0.94	2.02	2.01	1.07
134678/134679−HeCDF	N.D.	N.D.	0.1	N.D.	N.D.	0.2	0.1	N.D.
123478/123479−HeCDF	N.D.	N.D.	0.1	N.D.	N.D.	0.3	0.1	N.D.
123678−HeCDF	N.D.	N.D.	0.2	N.D.	N.D.	0.2	0.2	N.D.
124689−HeCDF	N.D.	0.1	0.2	0.1	0.1	0.1	0.2	0.1
123467−HeCDF	N.D.	N.D.	0.1	N.D.	N.D.	0.2	N.D.	N.D.
234678−HeCDF	0.1	0.1	0.3	0.1	0.1	0.5	0.2	0.2
total HeCDF	0.1	0.2	1	0.2	0.2	1.5	0.8	0.3
1234678−HxCDF	N.D.	N.D.	N.D.	N.D.	N.D.	0.1	N.D.	N.D.
1234689−HxCDF	N.D.	0.2	0.1	N.D.	N.D.	0.1	0.1	0.1
total HxCDF	0	0.2	0.1	0	0	0.2	0.1	0.1
OCDF	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
total PCDFs	0.56	1.1	3.13	1.29	1.55	4.88	4.03	2.51
3,3',4,4'−TeCB (#77)	5.2	7.7	19	10	6.6	16	17	15
3,4,4',5−TeCB (#81)	0.8	1	2.8	1.3	0.6	2.3	1.6	1.8
3,3',4,4',5−PeCB (#126)	2.5	3.3	5.5	3.9	5.1	7.3	6.9	5.4
3,3',4,4',5,5'−HeCB (#169)	0.6	0.7	1.3	1.1	1.4	2.4	1.9	1.5
total non− *orth* PCBs	9.1	12.7	28.6	16.3	13.7	28	27.4	23.7
2,3,3',4,4'−PeCB (#105)	89	280	430	140	150	200	170	180
2,3,4,4',5−PeCB (#114)	7.4	22	30	12	13	15	14	13
2,3',4,4',5−PeCB (#118)	330	1000	1500	510	570	730	650	660
2',3,4,4',5−PeCB (#123)	6.7	17	26	11	12	15	14	14
2,3,3',4,4',5−HeCB (#156)	36	110	130	66	70	90	77	75
2,3,3',4,4',5'−HeCB (#157)	9.9	24	28	19	20	27	24	24
2,3',4,4',5,5'−HeCB (#167)	23	55	71	34	44	54	48	43
2,3,3',4,4',5,5'−HxCB (#189)	5.4	9.2	9.3	7	7.9	15	9.4	8.7
total mono− *orth* PCBs	507.4	1517.2	2224.3	799	886.9	1146	1006.4	1017.7
total Co−PCBs	516.5	1529.9	2252.9	815.3	900.6	1174	1033.8	1041.4
PCDD/Fs TEQ*	0.06999	0.20917	0.29124	0.11564	0.12593	0.16254	0.14232	0.1427
Co−PCBs TEQ*	0.32659	0.54704	0.85642	0.51777	0.65065	0.91837	0.85318	0.69938
total Dioxins TEQ*	0.68066	0.90412	1.91398	1.1228	1.73869	2.77293	2.88024	1.55095

unit ; pg/g ww, *-pgTEQ/g ww

2004c). Although the maximum TEQ value was higher in marbled sole than in Japanese flounder, the difference in TEQ was not significant. The TEQ ranges for PCDD/Fs and Co-PCBs in marbled sole were 0.07–0.29 and 0.33–0.92 pg TEQ/g ww, respectively. The TEQ values of Co-PCBs accounted for more than 50% of total TEQ for all dioxins. The results for marbled sole were similar to those for Japanese flounder. TEQ values of Co-PCBs were higher than those of PCDD/Fs in 92% of fish samples (223 individuals) (FISHERIES AGENCY 2003). These results indicate that Co-PCBs are the most important dioxins in fishes, and, in particular, non-*ortho* Co-PCBs are the most important dioxins in marbled sole in Sendai Bay.

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