

Sedimentation rate of dioxins from the mid-1980s to 2002 in a sediment core collected off Ishinomaki in Sendai Bay, Japan

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Abstract : The vertical distribution of dioxins in a sediment core was investigated to elucidate historical trends of dioxins (polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans and coplanar polychlorinated biphenyls) discharged into Sendai Bay, Japan, from the mid-1980s to 2002. Polychlorinated dibenzo-*p*-dioxins (PCDDs) accounted for approximately 85% of total dioxins. The predominant dioxin congeners in the sediment, 1,3,6,8-tetrachlorodibenzo-*p*-dioxin (1,3,6,8-TeCDD), 1,3,7,9-TeCDD, and octachlorodibenzo-*p*-dioxin (OCDD), accounted for 79% of total PCDDs. The source of dioxins deposited off Ishinomaki in Sendai Bay from the early 1980s to 2002 was mainly impurities in pesticides (chloronitrophen and pentachlorophenol). Sedimentation rates of total dioxins were 161.2 pg g⁻¹ year⁻¹ during 1992–2002 and 172.6 pg g⁻¹ year⁻¹ during 1981–1992. Thus, the rate during 1992–2002 was slightly lower than that during 1981–1992, and the dioxin sedimentation rate decreased slightly upward in the core. Furthermore, the sedimentation rate of suspended solids off Ishinomaki, 0.112 g cm⁻² year⁻¹, tended to be lower than those measured in other Japanese ports. The average water content and ignition loss to 60 cm depth were 49.46 ± 3.9% and 6.5 ± 0.6% (average ± SD), respectively. These data suggest that inorganic suspended solids from rivers contributed more to sedimentation in Sendai Bay than in other Japanese ports.

Keywords : PCDD/Fs, Co-PCBs, sediment core, historical trend, Sendai Bay

1. Introduction

Chemicals emitted from the terrestrial environment are carried to the marine environment both by rivers and via the atmosphere (TAKADA 1997). Chemicals reaching the sea are dissolved in seawater or adsorbed onto suspended solids. Those adsorbed onto suspended solids then sink to the sea bottom and accumulate in the bottom sediments. Therefore, sediments are monitored to investigate pollution by heavy metals (MATSUMOTO and YOKOTA 1978) and polycyclic aromatic hydrocarbons

(HANDA and OHTA 1983) and to evaluate historical trends in dioxin concentrations (SAKAI *et al.* 1999, KANNAN *et al.* 2000, MASUNAGA *et al.* 2001b, YAO *et al.* 2002) and other chemicals (YAMASHITA *et al.* 2000) and pollution sources, from the point of view of risk assessment. Further, sedimentation rates of suspended solids are calculated so that chemical fluxes in the marine environment can be estimated (MATSUMOTO 1983, TANIMOTO and HOSHIKA 1994, KANAI *et al.* 1997).

Marine sediments in Sendai Bay have been studied to monitor pollution by dioxins (OKUMURA *et al.* 2003) and to evaluate historical trends in dioxin concentrations (OKUMURA *et al.* 2004). However, the surface layers of the sediment core used for the study was mixed, preventing the accurate determination of the historical trend of dioxins in Sendai Bay from the mid-1980s to 2002. Therefore, to complement the estimate of the historical trend of

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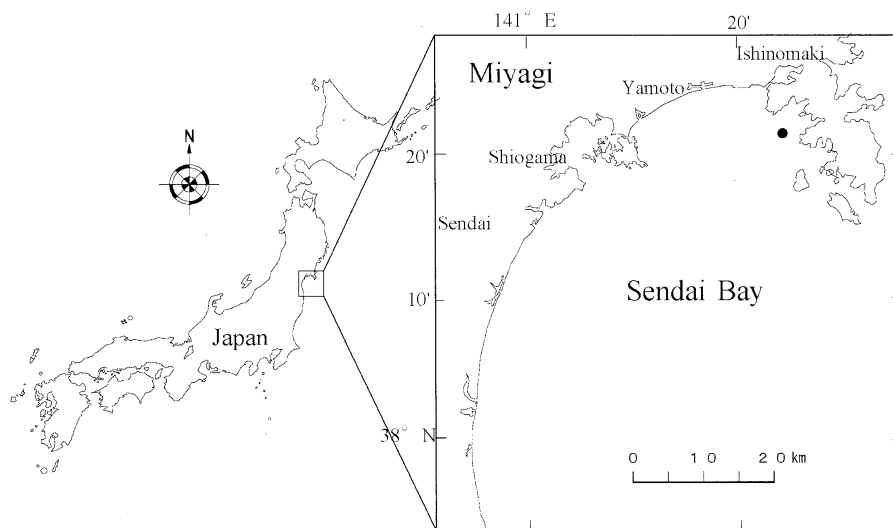


Fig. 1. Location of the sampling site off Ishinomaki in Sendai Bay.

dioxins in Sendai Bay obtained previously, we investigated dioxin concentrations from the mid-1980s to 2002 in another sediment core from Sendai Bay. Moreover, because sedimentation rates of suspended solids are known to vary in different parts of the bay (MINISTRY OF LAND, INFRASTRUCTURE AND TRANSPORT, GOVERNMENT OF JAPAN 2001), we also investigated the sedimentation rate in another part of Sendai Bay.

In this study, density, ignition loss, water content, and ^{210}Pb and ^{137}Cs concentrations in a sediment core collected off Ishinomaki in Sendai Bay were determined, and the sedimentation rate of the suspended solids was calculated. The properties of sediment in Sendai Bay were then compared with data from other parts of Japan. Finally, dioxin concentrations in sediment deposited from the mid-1980s to 2002 were analyzed by high-resolution gas chromatography/high-resolution mass spectroscopy (HRGC/HRMS) in order to clarify trends in the sedimentation rate of dioxins during that period.

2. Materials and Methods

2.1. Sampling

A sediment core approximately 80 cm long was collected with a sediment core sampler (ϕ 20cm \times 100cm) from a sampling site in

Sendai Bay (lat $38^{\circ}21' \text{N}$, long $141^{\circ}23' \text{E}$) on September 19, 2002 (Fig. 1). To protect contamination during sample transfer, the sediment core sampler was tightly sealed and then transferred from the sampling site to the laboratory. In the laboratory, the core was sliced into 2-cm segments, depending on depth. After the outer surface of the sediment, the part which had been in contact with the core sampler, was removed, samples were refrigerated or frozen in glass bottles that had been washed with *n*-Hexane until use.

2.2. Analysis of density, ignition loss, and water content

Density (JAPAN INDUSTRIAL STANDARD 1999a), ignition loss (JAPAN INDUSTRIAL STANDARD 1999b), and water content (JAPAN INDUSTRIAL STANDARD 2000) of the sediments were determined according to methods described by the Japan Industrial Standard. The methods are as follows.

To measure density, refrigerated samples were air-dried overnight, and then the air-dried samples were ground with a mortar and pestle. The sediment powder was transferred to a pycnometer, and distilled water to approximately two-thirds of the total pycnometer volume was added. The pycnometer was warmed in a vessel containing hot water, bubbles in the

pycnometer were removed, and then the pycnometer was removed from the hot water and left at room temperature. Distilled water was added until the pycnometer was full. Then the pycnometer was weighed on an analytical balance (m_b g), and the temperature of its contents was recorded (T °C). The sample was then removed from the pycnometer and dried overnight at 110 °C in a dryer. Dried samples were cooled in a desiccator at room temperature and then weighed on an analytical balance (m_s g). The density of the sediment was calculated as follows:

$$\rho_s = m_s / [m_s + (m_a - m_b)] \times \rho_w(T) \quad (1)$$

where ρ_s is the sediment density (g/cm³), m_a is the weight of the pycnometer containing a full volume of distilled water without the sediment (g), and $\rho_w(T)$ is the density of distilled water at T °C (g/cm³).

To measure water content, refrigerated samples were weighed on an analytical balance (m_c g) and then dried overnight in a dryer at 110 °C. After the dried samples had cooled in a desiccator to room temperature, they were weighed on an analytical balance (m_d g). The water content in a sediment sample (w %) was calculated as follows:

$$w = [(m_c - m_d) / m_d] \times 100 \quad (2)$$

To measure ignition loss, refrigerated samples were placed in a crucible and dried overnight in a dryer at 110 °C. Dried samples were cooled in a desiccator to room temperature and weighed on an analytical balance (m_e g). Then, the samples were heated at 800 °C in an electric furnace for 6 h, cooled in a desiccator to room temperature, and weighed on an analytical balance (m_f g). Ignition loss in the sediment sample (L_i %) was calculated as follows:

$$L_i = [(m_e - m_f) / m_e] \times 100 \quad (3)$$

Humid density (H_d g/cm³) was calculated as follows:

$$H_d = 1 / [w/100 + (1-w)/100/\rho_s] \quad (4)$$

Interstitial water (I_r %) was calculated as follows:

$$I_r = w / 100 \times H_d \quad (5)$$

Cumulative weight (C_w g/cm²) was calculated as follows:

$$C_w = (100 - I_r) / 100 \times \rho_s \times d_p \quad (6)$$

where d_p is depth of the sample (cm)

2.3. Analysis of ²¹⁰Pb and ¹³⁷Cs concentrations

²¹⁰Pb and ¹³⁷Cs activities in samples were determined by the methods of MATSUMOTO (1986). Briefly, refrigerated samples were weighed on an analytical balance, air-dried overnight, and ground with a mortar and pestle. The sediment powder was transferred to a crucible and then ignited in an electric furnace.

Lead from the ignited sediment samples was dissolved in nitric acid in an Erlenmeyer flask. The lead solutions were filtered, and lead sulfate was extracted from the filtered lead solution by electrodeposition. The extracted lead sulfate was allowed to stand for 40 days, and then the β -emitter (²¹⁰Bi, 1.1 MeV) in lead sulfate was measured for 24 h with a low-background gas-flow counter (β -spectrometry; OXFORD, Lb4100-W). ²¹⁰Pb concentrations were corrected by using the count of the β -emitter standard (712 Bq, Japan Radioisotope Association) for ²¹⁰Pb.

In addition to ²¹⁰Pb derived from ²²²Rn in air, ²¹⁰Pb is also found in sediment (supported ²¹⁰Pb). Supported (background) ²¹⁰Pb is a decay product of the ²²⁶Ra found in water and sediment not including ²¹⁰Pb in the suspended sediments that settled from the sea surface to the sea floor. Accordingly, excess ²¹⁰Pb (²¹⁰Pb ex) was calculated as total ²¹⁰Pb - supported ²¹⁰Pb. Here, background ²¹⁰Pb concentrations (supported ²¹⁰Pb) were calculated by averaging the ²¹⁰Pb concentrations in sediments from depths of 16–30, 34–36, 38–40, 44–46, 48–50, 62–64, and 76–78 cm.

The sedimentation rate of cumulative weight S_r was calculated as follows:

$$S_r = (0.693/22.2) / |S| \quad (7)$$

where S is the slope of the line describing the relationship between \log ²¹⁰Pb ex and cumulative weight (Fig. 2; -0.278). 0.693 is a disintegration coefficient of ²¹⁰Pb. 22.2 (year) is a half-life of ²¹⁰Pb.

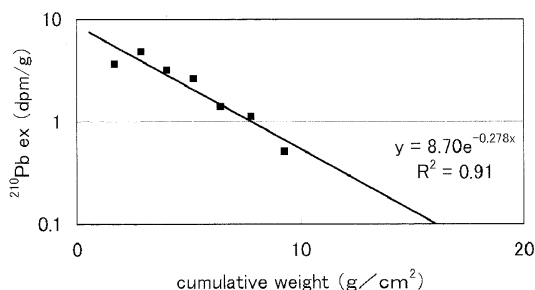


Fig. 2. Relationship between cumulative weight and ^{210}Pb ex in the sediment core collected off Ishinomaki in Sendai Bay. ^{210}Pb ex was calculated as the ^{210}Pb activity concentration of each 2-cm sediment sample less the average ^{210}Pb activity (0.63 ± 0.017 dpm/g) of sediments at depths of 16–30, 34–36, 38–40, 44–46, 48–50, 62–64, and 76–78 cm (used as the background or supported activity).

^{137}Cs (662 keV) in air-dried sediments was also measured with a low-background gas-flow counter (γ -spectrometry; EG & G ORTEC, GMX-25190) and corrected by the count of the γ -emitter standard (mixture of ^{109}Cd , ^{57}Co , ^{139}Ce , ^{51}Cr , ^{85}Sr , ^{137}Cs , ^{54}Mn , ^{88}Y , ^{60}Co , Japan Radioisotope Association) for ^{137}Cs .

2.4. Analysis of PCDDs, PCDFs, and Co-PCBs (dioxins)

Concentrations of polychlorinated dibenzop-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) with 4–8 chlorine substitutions and those of coplanar polychlorinated biphenyls (Co-PCB) congeners in the sliced surface sediment samples were determined by the method of the Environmental Agency (MINISTRY OF THE ENVIRONMENT 2000), as in the previous study (OKUMURA *et al.* 2004).

The detection limits for the tetra-, penta-, hexa-, hepta-, and octachlorinated PCDD/F congeners in the samples were 1, 1, 2, 2, and 5 $\mu\text{g/g}$ dry weight (dw), respectively. The detection limits of Co-PCBs in the samples were 1 $\mu\text{g/g}$ dw. We observed that the concentrations of the congeners were lower than the detection limits in the blank test.

3. Results and Discussion

3.1. History of the sediment core determined from ^{210}Pb and ^{137}Cs activities

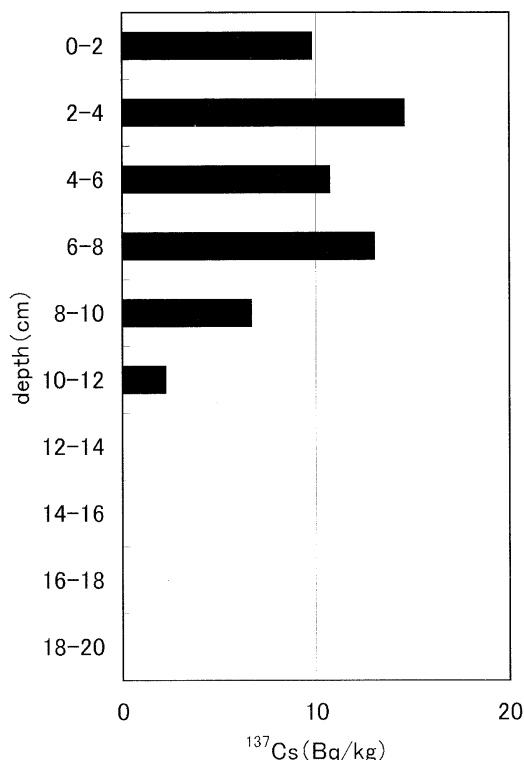


Fig. 2. Vertical distribution of ^{137}Cs activity in the sediment core.

^{210}Pb ex values decreased from 2 to 16 cm depth and were significantly correlated with cumulative weight ($r^2 = 0.91$, $p < 0.05$; Fig. 2). We therefore interpreted the layer from 2 to 16 cm depth as not mixed. The sedimentation rate in the layer was calculated from the relationship between cumulative weight and ^{210}Pb ex as $0.112 \text{ g cm}^{-2} \text{ year}^{-1}$ (Eq. 7).

^{137}Cs activity was detected at 10–12 cm depth and above (Fig. 3). Two peaks were observed, at 2–4 and at 6–8 cm depth, and from 2 to 8 cm depth, the activity was higher than 10 Bq/g. We attributed the first ^{137}Cs activity, at 10–12 cm depth, to the detonation of atomic bombs at Hiroshima and Nagasaki in 1945 and to early nuclear testing (e.g., at Bikini Atoll in 1954); thus, we considered the sediments at 10–12 cm depth to have been deposited from the mid-1940s to the early-1950s. We attributed the peak in ^{137}Cs activity at 6–8 cm depth to atmospheric nuclear testing carried out during the 1960s and thus dated those sediments to

Table 1 Properties of the sediment core (0–60cm depth) from off Ishinomaki.

depth	average age	mean date	period of age	time of deposition	sediment density	water content	ignition loss	humid density	interstitial water	cumulative
(cm)	(year)	(date)	(years)	(date range)	(g/cm ³)	(%)	(%)	(g/cm ³)	(%)	(g/cm ²)
					equation1	equation2	equation3	equation4	equation5	equation6
0–2	4.9	1997	9.7	2002–1992	2.54	59	7.2	1.33	78.51	0.55
2–4	15.1	1986	10.7	1992–1981	2.54	56	7.5	1.36	76.38	1.69
4–6	25.5	1976	10.2	1981–1971	2.50	57.5	7.8	1.34	77.18	2.86
6–8	35.8	1966	10.4	1971–1961	2.51	56.9	7.7	1.35	76.83	4.01
8–10	46.2	1955	10.5	1961–1950	2.60	56.7	7.4	1.36	77.28	5.19
10–12	57.1	1944	11.3	1950–1939	2.53	54.2	7.1	1.38	74.95	6.41
12–14	69.2	1932	13.0	1939–1926	2.54	49.5	6.9	1.44	71.33	7.77
14–16	82.5	1919	13.6	1926–1912	2.53	47.7	6.7	1.46	69.77	9.26
16–18	95.9	1906	13.1	1912–1899	2.60	49.4	6.7	1.45	71.76	10.76
18–20	109.0	1893	13.1	1899–1886	2.52	49.1	6.6	1.44	70.88	12.23
20–22					2.54	48	6.6	1.46	70.07	13.73
22–24					2.57	47	6.2	1.48	69.52	15.27
24–26					2.57	48.5	6.4	1.46	70.78	16.81
26–28					2.53	47.1	6.2	1.47	69.28	18.34
28–30					2.59	47.5	6.2	1.48	70.08	19.89
30–32					2.50	43.6	5.8	1.51	65.90	21.52
32–34					2.58	45.5	5.8	1.50	68.28	23.19
34–36					2.56	47.1	6	1.48	69.52	24.78
36–38					2.64	47.6	6	1.48	70.56	26.34
38–40					2.59	49.9	6.8	1.44	72.06	27.84
40–42					2.55	47.2	6.3	1.47	69.54	29.34
42–44					2.50	47.2	6	1.46	69.11	30.89
44–46					2.57	48.3	6.3	1.46	70.60	32.42
46–48					2.58	48.6	6.2	1.46	70.93	33.93
48–50					2.50	46.3	6.1	1.48	68.32	35.47
50–52					2.54	46.7	6.1	1.48	68.97	37.05
52–54					2.50	48.2	6.1	1.45	69.94	38.59
54–56					2.52	48.3	6.5	1.45	70.15	40.09
56–58					2.52	47.7	6.5	1.46	69.71	41.61
58–60					2.58	47.5	6.3	1.47	69.98	43.15

approximately that time. We related the peak at 2–4 cm depth to the accident at the Chernobyl nuclear power plant in 1986, so we interpreted those sediments to have been deposited in the 1980s.

Assuming that the sediment at 2–4 cm depth was deposited in 1987 [cumulative weight 1.69 g cm⁻²; Fig. 2; sedimentation period from the surface, 15.1 years (1.69/0.112)], then the time of deposition of the sediment at 10–12 cm depth can be calculated as 1945 [cumulative weight 6.41 g cm⁻²; Fig. 2; sedimentation period from the surface, 57.2 years (6.41/0.112); 1987 – (57.2 – 15.1) = 1945] by using the sedimentation rate obtained from the ²¹⁰Pb activities. Thus, the periods of deposition determined from the ¹³⁷Cs activity peaks agree with those calculated by using the sedimentation rate determined from

²¹⁰Pb activities.

3.2. Sedimentation rate, water content, and ignition loss in Sendai Bay in comparison with those in other areas of Japan

The sedimentation rates off Ishinomaki and off Yamoto in Sendai Bay were 0.112 g cm⁻² year⁻¹ (this study) and 0.314 g cm⁻² year⁻¹ (OKUMURA *et al.* 2004), respectively. The sedimentation rate off Ishinomaki was approximately one-third that off Yamoto. Thus, the sedimentation rate in Sendai Bay varies by location. Various sedimentation rates have been reported for different parts of Japan by other studies (all values are expressed as g cm⁻² year⁻¹): 0.116 ± 0.063 (*n*=5; average ± S.D.), Funaka Bay near Hokkaido; 0.26 ± 0.12 (*n*=3), Sakai-Izumi Port; 0.22 ± 0.17 (*n*=3),

Yokohama Port; 0.335 ($n=1$), Nagoya Port; 0.341 ($n=1$), Nagasaki Port; and 0.552 ($n=2$), Osaka Port (MINISTRY OF LAND, INFRASTRUCTURE AND TRANSPORT, GOVERNMENT OF JAPAN 2001); 0.2 ± 0.091 ($n=6$), Harima-Nada (HOSHIKA *et al.* 1983); and 0.27 ± 0.11 ($n=7$), Tokyo Bay, (FOUNDATION FOR PROMOTING PERSONAL MOBILITY AND ECOLOGICAL TRANSPORTATION 2001). Excluding values from Sendai Bay, the average sedimentation rate is $0.24 \text{ g cm}^{-2} \text{ year}^{-1}$. The sedimentation rate off Ishinomaki was lower than this average and similar to that reported for Funka Bay.

The average water content of sediment from the surface to 60 cm depth off Ishinomaki in Sendai Bay was $49.46 \pm 3.9\%$ (average \pm S.D., Table 1). The value off Yamoto in Sendai Bay is $47.01 \pm 4.6\%$ (OKUMURA *et al.* 2004). The average reported water content (%) of sediments from Nagoya, Osaka, Nagasaki, Yokohama, and Sakai-Izumi ports is 50.1 ± 6.7 , 58.6 ± 7.9 , 58.8 ± 6.8 , 59.5 ± 10.2 , and 63.1 ± 5.0 , respectively (MINISTRY OF LAND, INFRASTRUCTURE AND TRANSPORT, GOVERNMENT OF JAPAN 2001). The average water content of sediments from Sendai Bay (off Ishinomaki and Yamoto), less than 50%, is therefore lower than those of sediments from other Japanese ports.

The average ignition loss from the surface to 60 cm depth off Ishinomaki in Sendai Bay was $6.5 \pm 0.6\%$ (average \pm S.D., Table 1). That off Yamoto in Sendai Bay is $5.8 \pm 0.9\%$ (OKUMURA *et al.* 2004). The average reported ignition loss (%) of sediments from Nagoya, Osaka, Sakai-Izumi, Yokohama, and Nagasaki ports is 6.8 ± 2.1 , 8.4 ± 1.5 , 8.3 ± 0.8 , 9.6 ± 3.5 , and 16.0 ± 3.3 , respectively (MINISTRY OF LAND, INFRASTRUCTURE AND TRANSPORT, GOVERNMENT OF JAPAN 2001). The average ignition loss, like the average water content, is lower in Sendai Bay than in other Japanese port sediments.

Water content and ignition loss are considered indicators of organic matter content. Because sediments in Sendai Bay had lower water content and ignition loss than those reported for sediments from other Japanese ports, the ratio of inorganic matter to organic matter in Sendai Bay sediments is inferred to be higher

than that in sediments of other Japanese ports. We infer that inorganic suspended solids from rivers dominantly contributed to sedimentation in Sendai Bay.

3.3. Composition of dioxins in the sediment core

The average of total PCDDs in sediments at 0–4 cm depth (deposited from the early 1980s to 2002) accounted for 85% of the total dioxin concentration (Table 2). The dominant PCDD congeners were tetrachlorodibenzo-*p*-dioxin (1, 3, 6, 8-TeCDD), 1, 3, 7, 9-TeCDD, and octachlorodibenzo-*p*-dioxin (OCDD), which together accounted for 79% of the total PCDD concentration. PCDFs accounted for 5% of the total PCDD + PCDF concentration. Although Co-PCBs accounted for 10% of dioxins, PCB # 118, the most abundant Co-PCB congener, accounted for 54% of the total Co-PCB concentration. PCB # 105, the next most abundant Co-PCB congener, accounted for 19% of the total Co-PCB concentration. PCB # 81 and PCB # 169 concentrations were below the detection limit.

1, 3, 6, 8-TeCDD and 1, 3, 7, 9-TeCDD derive from impurities in chloronitrophen (CNP), and OCDD derives from impurities in pentachlorophenol (PCP), pesticides used from the 1960s to the 1990s (CNP) and to the 1970s (PCP) in Japan (YAMAGISHI *et al.* 1981, MASUNAGA *et al.* 2001a). Shipments of CNP products to Miyagi Prefecture, the so-called granary of Japan, were higher than those to any other prefectures in Japan during this period (JAPAN PLANT PROTECTION ASSOCIATION 1963–1995). It is clear that the major source of the dioxins deposited from the early 1980s to 2002 in Sendai Bay, as reported in this study as well as previously (OKUMURA *et al.* 2003, 2004), was impurities in CNP and PCP. However, the total shipment volume of CNP products was higher than that of PCP products in Miyagi Prefecture (JAPAN PLANT PROTECTION ASSOCIATION 1963–1995). Consistent with that observation, 1,3,6,8-TeCDD + 1,3,7,9-TeCDD concentrations in sediment of Sendai Bay reported previously by OKUMURA *et al.* (2003, 2004) were also higher than OCDD concentrations. However, it is difficult to explain why, in

Table 2. Dioxin concentrations in the sediment core sampled from off Ishinomaki in Sendai Bay.

	0-2cm 1997 (2002-1992)		2-4cm 1987 (1992-1981)		0-2cm 1997 (2002-1992)		2-4cm 1987 (1992-1981)		
	conc.	conc. * /year	conc.	conc. * /year	conc.	conc. * /year	conc.	conc. * /year	
1368-TeCDD	330	34.0	420	39.3	12368/13478-PeCDF	N.D.	-	1	0.1
1379-TeCDD	150	15.5	210	19.6	12478-PeCDF	1	0.1	1	0.1
1378-TeCDD	1	0.1	1	0.1	12479/13467-PeCDF	N.D.	-	N.D.	-
1369/1247/1248-TeCDD	4	0.4	6	0.6	12467-PeCDF	N.D.	-	N.D.	-
1268-TeCDD	1	0.1	2	0.2	14678/12347-PeCDF	N.D.	-	N.D.	-
1237-TeCDD	N.D.	-	1	0.1	13469-PeCDF	N.D.	-	N.D.	-
1234/1246/1249/1238-TeCDD	4	0.4	4	0.4	12348/12378-PeCDF	1	0.1	1	0.1
1236/1279-TeCDD	2	0.2	2	0.2	12346-PeCDF	N.D.	-	N.D.	-
total TeCDDs	492	50.7	646	60.4	12379-PeCDF	N.D.	-	N.D.	-
12468/12479-PeCDD	17	1.8	21	2.0	12367-PeCDF	N.D.	-	N.D.	-
12368-PeCDD	59	6.1	76	7.1	12469/12678-PeCDF	N.D.	-	N.D.	-
12478-PeCDD	N.D.	-	1	0.1	12679-PeCDF	N.D.	-	N.D.	-
12379-PeCDD	23	2.4	27	2.5	12369-PeCDF	N.D.	-	N.D.	-
12469/12347-PeCDD	2	0.2	2	0.2	23468-PeCDF	4	0.4	5	0.5
12378-PeCDD	N.D.	-	1	0.1	12349-PeCDF	N.D.	-	N.D.	-
total PeCDDs	101	10.4	128	12.0	12489-PeCDF	N.D.	-	N.D.	-
123468/124679/124689-HxCDD	25	2.6	29	2.7	23478-PeCDF	N.D.	-	N.D.	-
123679/123689-HxCDD	13	1.3	15	1.4	12389-PeCDF	N.D.	-	N.D.	-
123678-HxCDD	3	0.3	3	0.3	23467-PeCDF	1	0.1	1	0.1
123469-HxCDD	N.D.	-	N.D.	-	total PeCDFs	9	0.9	13	1.2
123789-HxCDD	3	0.3	4	0.4	123468-HxCDF	2	0.2	3	0.3
123467-HxCDD	N.D.	-	N.D.	-	134678/134679-HxCDF	N.D.	-	2	0.2
total HxCDDs	44	4.5	51	4.8	124678-HxCDF	4	0.4	5	0.5
1234679-HpCDD	69	7.1	79	7.4	124679-HxCDF	N.D.	-	N.D.	-
1234678-HpCDD	48	4.9	49	4.6	123478/123479-HxCDF	3	0.3	2	0.2
total HpCDDs	117	12.1	128	12.0	123678-HxCDF	N.D.	-	N.D.	-
OCDD	590	60.8	600	56.1	124689-HxCDF	2	0.2	3	0.3
total PCDDs	1344	138.6	1553	145.1	123467-HxCDF	N.D.	-	N.D.	-
1368-TeCDF	N.D.	-	N.D.	-	123679-HxCDF	N.D.	-	N.D.	-
1378/1379-TeCDF	N.D.	-	N.D.	-	123469/123689-HxCDF	N.D.	-	N.D.	-
1347-TeCDF	N.D.	-	N.D.	-	123789-HxCDF	N.D.	-	N.D.	-
1468-TeCDF	N.D.	-	N.D.	-	123489-HxCDF	N.D.	-	N.D.	-
1247/1367-TeCDF	N.D.	-	N.D.	-	234678-HxCDF	N.D.	-	2	0.2
1348-TeCDF	N.D.	-	N.D.	-	total HxCDFs	11	1.1	17	1.6
1346/1248-TeCDF	N.D.	-	N.D.	-	1234678-HpCDF	10	1.0	11	1.0
1246/1268-TeCDF	N.D.	-	N.D.	-	1234679-HpCDF	N.D.	-	N.D.	-
1478/1369/1237-TeCDF	N.D.	-	N.D.	-	1234689-HpCDF	12	1.2	14	1.3
1678/1234-TeCDF	N.D.	-	N.D.	-	1234789-HpCDF	N.D.	-	N.D.	-
2468/1238/1467/1236-TeCDF	11	1.1	15	1.4	TOTAL HpCDF	22	2.3	25	2.3
1349-TeCDF	N.D.	-	N.D.	-	OCDF	19	2.0	20	1.9
1278-TeCDF	N.D.	-	N.D.	-	total PCDFs	72	7.4	90	8.4
1267/1279-TeCDF	N.D.	-	N.D.	-	total PCDD/Fs	1416	146.0	1643	153.6
1469-TeCDF	N.D.	-	N.D.	-	3,3',4,4'-TeCB(#77)	12	1.2	15	1.4
1249/2368-TeCDF	N.D.	-	N.D.	-	3,4,4',5'-TeCB(#81)	N.D.	-	N.D.	-
2467-TeCDF	N.D.	-	N.D.	-	3,3',4,4',5'-PeCB(#126)	1	0.1	1	0.1
1239-TeCDF	N.D.	-	N.D.	-	3,3',4,4',5,5'-HxCB(#169)	N.D.	-	N.D.	-
2347-TeCDF	N.D.	-	N.D.	-	total non-ortho PCBs	13	1.3	16	1.5
1269-TeCDF	N.D.	-	N.D.	-	2,3,3',4,4'-PeCB(#105)	27	2.8	40	3.7
2378-TeCDF	N.D.	-	N.D.	-	2,3,4,4',5'-PeCB(#114)	1	0.1	2	0.2
2348-TeCDF	N.D.	-	N.D.	-	2,3',4,4',5'-PeCB(#118)	81	8.4	110	10.3
2346-TeCDF	N.D.	-	N.D.	-	2,3,4,4',5'-PeCB(#123)	6	0.6	5	0.5
2367-TeCDF	N.D.	-	N.D.	-	2,3,3',4,4',5'-HxCB(#156)	10	1.0	17	1.6
3467-TeCDF	N.D.	-	N.D.	-	2,3,3',4,4',5'-HxCB(#157)	3	0.3	3	0.3
1289-TeCDF	N.D.	-	N.D.	-	2,3,4,4',5,5'-HxCB(#167)	5	0.5	7	0.7
total TeCDFs	11	1.1	15	1.4	2,3,3',4,4',5,5'-HpCB(#189)	2	0.2	4	0.4
13468-PeCDF	N.D.	-	N.D.	-	total mono-ortho PCBs	135	13.9	188	17.6
12468-PeCDF	2	0.2	4	0.4	total Co-PCBs	148	15.3	204	19.1
13678-PeCDF	N.D.	-	N.D.	-	total dioxins	1564	161.2	1847	172.6
13479-PeCDF	N.D.	-	N.D.	-	total TEQ	1.711	0.2	2.94	0.3

*: The average annual dioxin concentrations (conc./year) were calculated by dividing dioxins concentration (conc.) by period of age of each layer in Table 1. The values of conc./year were rounded off to one decimal place.

this study, the 1,3,6,8-TeCDD + 1,3,7,9-TeCDD concentration in the sediment was the same as that of OCDD at 2–4 cm depth, and lower than that of OCDD at 0–2 cm.

Major sources of Co-PCBs are thought to be PCBs in electrical insulating oil (KANNAN *et al.* 1987, TAKASUGA *et al.* 1995) and in fly ash and exhaust gases from incinerators (CZUCZWA and HITES 1984, SAKAI *et al.* 1993). In Kanechlor, a PCB mixture used in Japan, PCB # 118 and PCB # 105 are the major congeners (TAKASUGA *et al.* 1995). Thus, the dominant Co-PCB congeners in sediments from Sendai Bay corresponded to those in this PCB product. PCB # 169, which is derived from combustion (YAO *et al.* 2002), was below the detection limit in sediments from Sendai Bay. From these findings, we infer that the major source of Co-PCBs in Sendai Bay from the early 1980s to 2002 was PCB products and that combustion was much less important.

3.4. Dioxin concentrations from the early 1980s to 2002

Dioxin concentrations in Sendai Bay increased from the mid-1930s and reached a maximum level in the 1987 (OKUMURA *et al.* 2004). However, accurate determination of dioxin concentrations in sediments from the late-1980s could not be measured in that study because the sediments from the late-1980s to 2002 were mixed. In this study, the average concentration in the 1992–2002 layer was 34.0 $\text{pg g}^{-1} \text{year}^{-1}$ for 1,3,6,8-TeCDD, 15.5 $\text{pg g}^{-1} \text{year}^{-1}$ for 1,3,7,9-TeCDD, 60.8 $\text{pg g}^{-1} \text{year}^{-1}$ for OCDD, and 161.2 $\text{pg g}^{-1} \text{year}^{-1}$ for total dioxins (Table 2). The values in the 1981–1992 layer were 39.3 $\text{pg g}^{-1} \text{year}^{-1}$ for 1,3,6,8-TeCDD, 19.6 $\text{pg g}^{-1} \text{year}^{-1}$ for 1,3,7,9-TeCDD, 56.1 $\text{pg g}^{-1} \text{year}^{-1}$ for OCDD, and 172.6 $\text{pg g}^{-1} \text{year}^{-1}$ for total dioxins.

Degradation of dioxins is thought to occur by sunlight or in anaerobic environments by aquatic microorganisms (SINKKONEN and PAASIVIRTA 2000). For example, the half-lives of dioxins in sediments are generally more than 100 years in the Baltic Proper (KJELLER and RAPPE 1995), about 35 years in Lake Shinji, Japan (MASUNAGA *et al.* 2001b), and 600 days in Lake Mendota, USA (CLAUDIA and

MATSUMURA 1978). Although half-lives of dioxins vary with the aquatic environment or the specific congener, it is reasonable to suppose that fewer dioxins have been degraded in the 1992–2002 layer for the shorter residence time in the sediment than in the 1981–1992 layer. Despite the influence of degradation on the dioxin concentrations, the average annual concentration in the 1992–2002 layer was slightly lower than that in the 1981–1992 layer. In general, the dioxin sedimentation rate increased upward from the mid-1930s, reached a maximum in the mid-1980s, and then decreased slightly upward from the (OKUMURA *et al.* 2004) mid-1980s to 2002.

Shipments of CNP and PCP to Miyagi Prefecture were highest in 1975, when 4700 t of CNP products were shipped, and in 1970, when 3100 t of PCP products were shipped (OKUMURA *et al.* 2004). In 1970, the amount of PCBs used in Japan reached a maximum of 11,100 t (TATSUKAWA 1972). Therefore, the maximum concentrations of 1,3,6,8-TeCDD + 1,3,7,9-TeCDD, OCDD, and Co-PCBs in the sediment did not correspond in time to the peak period of shipments of CNP and PCP products or to the period of maximum use of PCBs (Table 1). Comparing our data with data collected elsewhere in Japan, the maximum concentration of TeCDDs, OCDD, and Co-PCBs in Lake Shinji (MASUNAGA *et al.* 2001b) and Tokyo Bay at 35°33' N and 139°55' E (YAO *et al.* 2002), and of total PCDD/Fs in Lake Biwa-South (SAKAI *et al.* 1999), were reported from sediments deposited before the 1980s. Although the timing of the peak period of shipments of CNP and PCP to each prefecture differed slightly, the maximum concentrations of TeCDD, OCDD, and Co-PCBs in these sediments tended to correspond to the peak period of shipments of CNP and PCP products and of PCB use. The time trends of dioxins in Lake Biwa and Tokyo Bay varied with the sampling site. The maximum concentration of OCDD in Tokyo Bay (35°35' N and 139°55' E) was reported from sediments deposited during 1979–1981 (YAMASHITA *et al.* 2000). The maximum concentrations of 1,3,6,8- and 1,3,7,9-TeCDD and total PCBs in Tokyo Bay at 35°35' N and 139°55' E (Yamashita *et al.* 2000) and the

maximum total PCDD/F concentrations in Lake Biwa-North and the Yodo River offshore region (SAKAI *et al.* 1999) were in sediments deposited after the 1980s. The maximum concentrations of dioxins in these sediments therefore did not correspond in time to the peak period of shipments of CNP and PCP products or of PCB use. The dioxin distribution in Sendai Bay most closely resembled the distributions at these latter sites.

Shipments of CNP and PCP to Miyagi Prefecture were higher weight than those to any other prefecture in Japan (OKUMURA *et al.* 2004). The period of maximum concentrations of 1,3,6,8-TeCDD + 1,3,7,9-TeCDD, OCDD, and Co-PCBs in the sediment of Sendai Bay did not correspond to the peak period of shipments of CNP and PCP products and of PCB use, but was later. It is possible that the dioxin sedimentation rate increased upward in the core. However, from this study, it is clear that the dioxin concentration per year in the 1992-2002 layer was slightly lower than that in the 1981-1992 layer. Dioxin concentrations in the sediment of Sendai Bay, as well as those in sediments elsewhere reported previously (SAKAI *et al.* 1999, Yamashita *et al.* 2000), may gradually decrease in the future. Although the degradation rate of dioxins in sediments of paddy fields and rivers in Miyagi Prefecture and in Sendai Bay is not clear, degradation may have an important role in decreasing dioxin concentrations in sediment of Sendai Bay.

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