

Mass Balance and Bioaccumulation of Major Dioxins in Sendai Bay^{*1}

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Abstract: “Dioxins” is the general term for polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and coplanar polychlorinated biphenyls (Co-PCBs). Because dioxins are stable chemical compounds, dioxins released into the environment have remained for long periods. The dioxins carried from the terrestrial to the marine environment may affect marine organisms, and it is possible that fishery resources are diminished through the toxicity of dioxins. The aim of this study is to clarify the behavior of dioxins that are emitted from Miyagi Prefecture and enter Sendai Bay via rivers.

First, Chapter 2 describes the properties of dioxins in Sendai Bay, and discusses the bioaccumulation of dioxins through the marine food web and the bioaccumulation of dioxins with respect to the body length of flatfish. The order of concentration of PCDD/Fs was Pacific oyster > Japanese anchovy \approx marbled sole > Japanese flounder; the concentration in Japanese flounder, which is a higher-trophic-level consumer in the marine food web, was lower than that in shellfish (Pacific oyster) and Japanese anchovy, which are lower-trophic-level consumers. The order of concentration of Co-PCBs was Pacific oyster < Japanese anchovy \approx marbled sole < Japanese flounder; the concentrations in the higher-trophic-level consumers were higher than the concentrations in the lower-trophic-level consumers. Different PCDD/F congeners tended to bioaccumulate in different organisms. On the other hand, all species of Co-PCB congener tended to bioaccumulate in all organisms.

The relationship between the concentrations of these dioxins and the body length of Japanese flounder was examined. The total PCDD and total PCDF concentrations did not correlate with body length (both $r^2 < 0.1$, both $p > 0.05$), whereas the total non-*ortho* PCB and total mono-*ortho* PCB (Co-PCBs) concentrations were significantly correlated ($r^2 = 0.8$, $p < 0.05$ and $r^2 = 0.63$, $p < 0.05$, respectively). The bioaccumulation properties of PCDD/Fs in Japanese flounder differed from those of Co-PCBs. Toxicity equivalency quotient (TEQ) values derived from the Co-PCBs made up 46.3–63.7% of the total TEQ value for all the dioxins. These results show that from the standpoint of risk management, non-*ortho* Co-PCBs are the most important of the dioxins in Japanese flounder.

In Chapter 3, the vertical distribution of dioxins in a sediment core was investigated to elucidate historical trends of dioxins discharged into Sendai Bay. In the off Naruse sample, the dioxin concentration was 410 pg/g dw in sediments deposited in the mid-1930s and 3870 pg/g dw in those deposited in the mid-1980s. Dioxin fluxes increased from the mid-1930s and then reached a maximum in the mid-1980s. While sedimentation rates of total dioxins in the off Ishinomaki sample 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 gradually decreased from the mid-1980s to the early 2000s.

Chapter 4 describes the terrestrial sources of dioxins and their concentrations in rivers

leading to Sendai Bay. The major dioxin congeners in the river water were 1, 3, 6, 8-TeCDD, 1, 3, 7, 9-TeCDD, and OCDD. Chemical mass balance model results suggested that chloronitrophen (CNP) and pentachlorophenol (PCP), which are impurities in chlorinated pesticides used in paddy fields, accounted for >90% of PCDD/F contributions, and exhaust gases for <10%. PCA results suggested that PCB products were the major sources of Co-PCBs, although total Co-PCB concentrations were lower than total PCDD/F concentrations.

Concentrations of 1, 3, 6, 8- and 1, 3, 7, 9-TeCDD and suspended solids in river water increased with increasing flow rates. During periods of high flow, dioxin concentrations may have increased because of resuspension of bottom sediments that had adsorbed dioxins. In major rivers, the relative magnitudes of the annual average of daily fluxes of 1, 3, 6, 8- and 1, 3, 7, 9-TeCDD were: Kyu-Kitakami River > Naruse River > Abukuma River > Natori River. The flux from the Kyu-Kitakami River to Sendai Bay accounted for 49% to 84% of the total flux from the four rivers. The annual fluxes of major dioxin congeners tended to depend on both the size of the land area covered by paddy fields in the river catchments and the discharge rates of the rivers.

Finally, Chapter 5 presents estimates of the flux of major dioxin congeners from Miyagi Prefecture to Sendai Bay. Large quantities of dioxins from CNP and PCP sources were introduced into the terrestrial environment (30.7 t). As the rivers and drainage ditches acted as transport bottlenecks, their inflow from the terrestrial environment to Sendai Bay was limited (241 kg). The bulk of dioxins from CNP and PCP sources remained in the terrestrial environment. Almost all dioxins entering Sendai Bay (7.7 kg/y) either flowed out of the bay or settled to the bay bottom. The amount that bioaccumulated in marine organisms (3.2 g/y) was much less than the amount inflowing from the terrestrial environment to the bay (0.04 %). The major dioxin congeners from impurities in CNP and PCP have much lower toxicities and bioaccumulation rates in marine organisms than low-chlorine 2, 3, 7, 8-substituted PCDD/Fs such as 2, 3, 7, 8-TeCDD, which has an extremely high TEF. Therefore, although the influx of dioxins of CNP and PCP origin to Sendai Bay will continue in the future, their bioaccumulation in marine organisms in Sendai Bay will not be a serious problem for fisheries resources.

Keywords: dioxin flux, marine food web, aquatic organisms, chlorinated pesticides, Miyagi Prefecture

Contents	HRGC/HRMS analysis
Chapter 1. General Introduction	2.1.1.3. Calculations of toxic equivalents (TEQ)
Chapter 2. Properties of dioxins in Sendai Bay	2.1.2. Results
2.1. Major dioxin sources and bioaccumulation of dioxins in aquatic organisms through the food web	2.1.2.1. Dioxin compositions and concentrations
2.1.1. Materials and Methods	2.1.2.2. Comparison of TEQ values
2.1.1.1. Sampling	2.1.3. Discussion
2.1.1.2. Analysis of PCDDs, PCDFs, and Co-PCBs (dioxins)	2.1.3.1. Major sources of dioxins in Sendai Bay
Preparation of analytical samples	2.1.3.2. Bioaccumulation of dioxins through the food web in Sendai Bay
Clean-up column chromatography	Bioaccumulation of dioxins in phytoplankton and seaweed
	Bioaccumulation of PCDD/Fs in fish
	Bioaccumulation of PCDD/Fs in

- higher-trophic-level invertebrates
- Bioaccumulation of Co-PCBs in organisms
- 2.1.3.3. Comparison of TEQ values
- 2.2. Bioaccumulation of dioxins with respect to body length of flatfish
- 2.2.1. Materials and Methods
- 2.2.1.1. Data analysis
- 2.2.1.2. Multiple range test of dioxin concentrations
- 2.2.1.3. Linear regression analysis of the relationship between dioxin concentration and body length
- 2.2.2. Results
- 2.2.2.1. Relationship between total dioxin concentration and body length
- 2.2.2.2. Relationship between PCDD/F congener concentrations and body length
- 2.2.2.3. TEQ values
- 2.2.3. Discussion
- 2.2.3.1. Bioaccumulation of PCDDs and the relationship between concentration and body length
- 2.2.3.2. Bioaccumulation of PCDFs and the relationship between concentration and body length
- 2.2.3.3. Bioaccumulation of Co-PCBs and the relationship between concentration and body length
- 2.2.3.4. TEQ values in Japanese flounder
- Chapter 3. Historical trend of dioxins in sediment cores from Sendai Bay
- 3.1. Materials and Methods
- 3.1.1. Sampling
- 3.1.2. Analysis of density, ignition loss, and water content of sediment core samples
- 3.1.3. Analysis of ^{210}Pb and ^{137}Cs concentrations
- 3.1.4. Analysis of dioxins and TEQs
- 3.2. Results
- 3.2.1. Sediment accumulation histories as determined from ^{210}Pb and ^{137}Cs activities
- 3.2.2. Composition and historical trends of dioxins in sediment cores
- 3.2.3. History of dioxin sources
- 3.2.4. TEQ values
- 3.3. Discussion
- 3.3.1. Sedimentation rate in Sendai Bay compared with other areas of Japan
- 3.3.2. History of dioxin sources in Sendai Bay
- 3.3.3. Dioxin concentrations in sediments in Sendai Bay compared with those in other areas of Japan
- 3.3.4. Relationship between maximum dioxin concentrations in the sediments and the time of maximum use of CNP, PCP, and PCB products
- 3.3.5. TEQ values
- Chapter 4. Discharge of dioxins from terrestrial to marine environments
- 4.1. Dioxin concentrations and estimated sources in four major rivers of Miyagi Prefecture
- 4.1.1. Materials and Methods
- 4.1.1.1. Sampling of river water
- 4.1.1.2. Measurement of dry weight of total suspended solids
- 4.1.1.3. Analysis of dioxins
- 4.1.1.4. Principal components analysis (PCA) and chemical mass balance (CMB) analysis
- 4.1.2. Results
- 4.1.2.1. Dioxin congeners and TEQs in river water
- 4.1.2.2. Characterization of dioxin concentrations by PCA and CMB
- 4.1.2.3. Variations in dioxin concentrations with river flow rate and suspended solids content
- 4.1.3. Discussion
- 4.1.3.1. Dioxin congeners and TEQs in river water
- 4.1.3.2. Characterization of dioxin concentrations by PCA and CMB
- 4.1.3.3. Variations in dioxin concentrations with river flow rate
- 4.1.3.4. Changes in total dioxin concentrations with suspended solid loads
- 4.2. Estimated dioxin discharges into Sendai Bay from terrestrial sources in Miyagi Prefecture
- 4.2.1. Materials and Methods
- 4.2.2. Results
- 4.2.2.1. Daily flow rate
- 4.2.2.2. Relationship between daily fluxes of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD and river

flow rate	
4.2.2.3. Estimation of annual fluxes of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD and OCDD and TEQs into Sendai Bay	
4.2.3. Discussion	
4.2.3.1. Calculation of daily 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD fluxes in relation to river flow rate	
4.2.3.2. Estimation of annual fluxes of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD, and OCDD into Sendai Bay, including TEQ fluxes	
Chapter 5. Mass balance of major dioxin congeners from impurities in pesticides used in Miyagi Prefecture	
5.1. Materials and Methods	
5.1.1. Total amounts of major pesticide dioxins in the terrestrial environment of Miyagi Prefecture from 1963 to 2002	
5.1.2. Total emissions from major rivers to Sendai Bay from 1963 to 2002	
5.1.3. Annual flux of the major pesticide dioxins in Sendai Bay	
5.1.4. Bioaccumulation of the major pesticide dioxins in commercially valuable fish, shellfish, and seaweeds	
5.1.5. Discharge from Sendai Bay to offshore waters	
5.2. Results	
5.2.1. Dioxin flux in the terrestrial environment	
5.2.2. Dioxin flux in the marine environment	
5.3. Discussion	
5.3.1. Dioxin flux in the terrestrial environment	
5.3.2. Dioxin flux in the marine environment	
Chapter 6. General discussion and summary	
6.1. Properties of dioxins in Sendai Bay	
6.2. Properties of bioaccumulation of dioxins to marine organisms	
6.3. Historical trend of dioxins in sediment cores from Sendai Bay	
6.4. Discharge of dioxins from terrestrial to marine environments	
6.5. Mass balance of major dioxin congeners from impurities in pesticides used in Miyagi Prefecture	
Acknowledgements	
References	

Chapter 1. General Introduction

“Dioxins” is the general term for polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and coplanar polychlorinated biphenyls (Co-PCBs) (Fig. 1). Dioxins have 75 PCDD congeners, 135 PCDF congeners, and 12 Co-PCB congeners. Dioxins are highly thermally stable (to >700 °C), highly lipophilic ($\log [P_{ow}] < 6$), and water-insoluble (< 690 ng/L) compounds (Sarna, *et al.* 1984, Woodburn *et al.* 1984, Miller and Waslk 1985, Morita 1991, Devillers *et al.* 1996). Because dioxins are stable chemical compounds, dioxins released into the environment have remained for long periods (Hashimoto *et al.* 1990).

Previously, 2, 3, 7, 8-tetra chlorinated dibenzo-*p*-dioxin (2, 3, 7, 8-TeCDD), as an impurity in herbicides, was emitted into the environment by the spraying of the herbicide “Agent Orange” in the Vietnam War (Booker 2001), by the spraying of waste oil on roads in Times Beach, Missouri, USA, in the early 1970s (U.S. Environmental Protection Agency 1983), and through a blast incident at a chemical plant in Seveso, Italy, in 1976 (Mocarelli *et al.* 1990). These events had worldwide consequences because dioxins have severe toxic effects in humans.

In a laboratory experiment to determine acute toxicity, the 50% lethal dose (34d LD50) of 2, 3, 7, 8-TeCDD for guinea pigs was 0.6 µg/kg (Schwetz *et al.* 1973). Although acute toxicity varies with species, the toxicity of 2, 3, 7, 8-TeCDD is higher than that of sarin or potassium cyanide, and 2, 3, 7, 8-TeCDD is thought to be the most toxic poison among artificial chemicals (Ministry of Environment, Japan 2000a). The toxicity of dioxins is also known to vary with the type of congener. Toxicity equivalency factors (TEFs) for highly toxic dioxin congeners have been established by the World Health Organization (WHO; Van den Berg *et al.* 1998). At present, the TEF of the most toxic congener, 2, 3, 7, 8-TeCDD, is set at 1 as a standard, that for octachlorodibenzo-*p*-dioxin (OCDD) is set at 0.001, and the TEF for 2, 3', 4, 4', 5, 5'-hexachlorobiphenyl (2, 3', 4, 4', 5, 5'-HCB) is set at 0.00001. The TEFs of 29 dioxin congeners have been defined based on the intensity of their toxicities. The

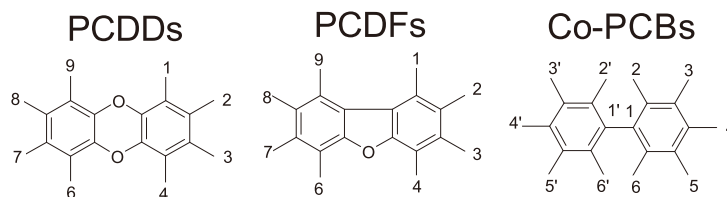


Fig. 1. The skeletal formulas and substituent numbering scheme for dioxins. In polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), chlorine atoms are attached to this structure at any of 8 places on the molecule (positions 1-4 and 6-9; Wikipedia 2008). In coplanar polychlorinated biphenyls (Co-PCBs), chlorine atoms are attached to this structure at any of 10 places on the molecule (positions 2-6 and 2'-6'). PCDDs, PCDFs, and Co-PCBs are released into the terrestrial environment as impurities in chlorinated pesticides (Masunaga *et al.* 2001a, Seike *et al.* 2003), in industrial wastewater discharged from pulp mills (Rappe *et al.* 1989, Koistinen *et al.* 1993) and dye manufacturing plants (Kakimoto *et al.* 2006), in fly ash and exhaust gases from incinerators (Sakai *et al.* 1993), and as residues from the manufacture of electrical insulating oil (Kannan *et al.* 1987).

toxic equivalent (TEQ) of a mixture of dioxin compounds is calculated by multiplying the actual mass of each dioxin compound in grams by its corresponding TEF (e.g., 10 g 0.1 TEF = 1 g TEQ) and then summing the results (U.S.E.P.A. 2009).

The chronic toxicity of some dioxin congeners results in carcinogenic or endocrine-disrupting effects (Mocarelli *et al.* 1996). These congeners have large reproductive and immunological impacts on organisms. They also show high bioaccumulation rates and resistance to biodegradation in living organisms. The half-life of TeCDDs in humans is 8.7 y (Booker 2001). Therefore, once in the atmospheric and terrestrial environments, dioxins are eventually transferred to the aquatic environment, where they bioaccumulate in all organisms. In humans, the dominant uptake route is through food (Birmingham *et al.* 1989). To protect humans from risk from dioxins, tolerable daily intake (TDI) values for dioxins have been established by the WHO, or by individual countries throughout the world. In Japan, the TDI was established at 10 pg-TEQ per kg of weight per day (TEQ/kg/d) in 1996, 5 pg-TEQ/kg/d in 1997, and 4 pg-TEQ/kg/d from 1999 to the present (Ministry of Environment, Japan 1999). The regulations concerning TDIs have been strengthened year after year. To comply with these

reductions in the TDI, it is necessary to decrease the emission of dioxins. To make this decrease in emission possible, the sources of dioxins have been investigated.

The distributions of the dioxin congeners vary with the source. To determine the relative importance of these various dioxin sources over time, the vertical distribution of concentrations of major dioxin congeners in sediment cores has been investigated (Czuczwa and Hites 1984, Czuczwa *et al.* 1985, Juttner *et al.* 1997, Vartiainen *et al.* 1997, Sakai *et al.* 1999, Masunaga *et al.* 2001b, Yao *et al.* 2002, Kubota *et al.* 2002). In Japan, the major sources of dioxins are thought to be impurities in chlorinated pesticides such as pentachlorophenol (PCP) and chloronitrophen (CNP), and combustion from incinerators (Masunaga *et al.* 2001b). The major sources of dioxins are thought to vary over time.

In 1999, dioxins from incinerator combustion were regulated by the law concerning special measures against Dioxins (the law number 105; Ministry of Internal Affairs and Communications, Japan 1999). As a result, the quantity of dioxins emitted from industrial activity, such as incineration, was gradually reduced from 7680-8135 g-TEQ/y in 1997 to 341-363 g-TEQ/y in 2004, an 8-y decrease of over

95% (Ministry of Environment, Japan 2005). Dioxins from electrical insulating oil, particularly Co-PCBs, were regulated by the law concerning such things as the evaluation of chemical substances and regulation of their manufacture (Chemical Substances Control Law, the law number 117) in 1973 (Ministry of the Environment, Japan 2007, Ministry of Internal Affairs and Communications 2010) and a 2001 special law concerning adequate disposal of PCBs, the law number 65 (Ministry of Internal Affairs and Communications, Japan 2005). During the period from 2001 to 2016, all waste PCBs in safe storage at various sites throughout Japan must be broken down into harmless products by a thermal treatment plant at the Japan Environmental Safety Corporation (Japan Environmental Safety Corporation 2004). However, dioxins from large quantities of chlorinated pesticides are thought to remain in rice paddies (Kobayashi *et al.* 2004a), even though permission to use these agrochemicals was cancelled in 1996 for CNPs and over the period from 1975–1989 for PCPs (Agricultural Chemicals Inspection Station 2007). For a complete assessment of the environmental impacts of residual dioxins from CNP and PCP products, it is important to understand their behavior in terrestrial and aquatic environments near an area of grain production.

Dietary intake of dioxins by the Japanese population has been investigated by the Ministry of Health, Labour and Welfare (2007). Dioxin intake decreased from 8.18 pg-TEQ/kg/d in 1977 to 1.04 pg-TEQ/kg/d in 2006. However, in 1999, when countermeasures against dioxins were enacted into law, the dioxin intake was 2.72 pg-TEQ/kg/d. Despite the 95% decrease in industrial dioxin emissions during the 8 years from 1997 to 2004, the decrease in dietary dioxin intake during the 8 years from 1999 to 2006 was only about 60%; from 2.72 to 1.04 pg-TEQ/kg/d. The dioxin intake was reduced, but not far enough. For the Japanese, fish and shellfish are thought to be major components of dioxin intake (Takayama *et al.* 1991, Toyoda *et al.* 1999, Tsutsumi *et al.* 2001). Thus, to further decrease dioxin intake, it is necessary to investigate the bioaccumulation properties of dioxin congeners in marine organisms.

Chemicals emitted from the terrestrial

environment are carried to the marine environment both by rivers and via the atmosphere (Takada 1997). Some chemicals, such as dichloro-diphenyl-trichloroethane (DDT) or triphenyltin compounds (TPTs), are known to bioaccumulate in marine organisms through the marine food web (Woodwell *et al.* 1967, Ikeda *et al.* 2002). Dioxins are toxic compounds that accumulate in aquatic organisms (Satomi 1992). Therefore, dioxins carried from the terrestrial to the marine environment may affect marine organisms, and it is possible that fishery resources are diminished through the toxicity of dioxins.

Sendai Bay, located in the Tohoku region of Japan, is an area of fishing and aquaculture. Miyagi Prefecture near Sendai Bay is a granary area of Japan. The aim of this study is to clarify the behavior of dioxins that are emitted from Miyagi Prefecture and enter Sendai Bay via rivers. First, Chapter 2 describes the properties of dioxins in Sendai Bay, and discusses the bioaccumulation of dioxins through the marine food web and the bioaccumulation of dioxins with respect to the body length of flatfish. Chapter 3 describes historical trends of dioxins in sediments. Chapter 4 describes the terrestrial sources of dioxins and their concentrations in rivers leading to Sendai Bay. Finally, Chapter 5 presents estimates of the flux of major dioxin congeners from Miyagi Prefecture to Sendai Bay.

Chapter 2. Properties of dioxins in Sendai Bay

To decrease the risk of dioxin exposure for the Japanese people, the findings from several studies of dioxins have been compiled by the government of Japan (Prime Minister of Japan and His Cabinet 2007). The dioxin concentrations in fishes, which are main dietary uptake route of dioxins for Japanese (Takayama *et al.* 1991, Toyoda *et al.* 1999, Tsutsumi *et al.* 2001), were frequently monitored to compare the dioxin levels in the several species of fish collected from several areas (Fisheries Agency, Japan 2003). For example, high TEQ values of 4.5–16 pg-TEQ/g-wet-weight were detected in samples of Japanese conger (*Conger myriaster*) and sea bass (*Cynoscion nobilis*) collected from Tokyo Bay, which

is adjacent to urban areas. The supply of dioxins to Tokyo Bay is through transport by river inflows (Iimura *et al.* 2002). The dioxin concentrations in sediments in marine environments were also monitored to trace the sources of dioxin emissions (Ministry of the Environment, Japan 1996–2005). The major dioxin sources in Tokyo Bay are multiple incinerators and impurities in chlorinated pesticides (Yamashita *et al.* 2000); in Lake Shinji, in western Japan, the major dioxin source is impurities in chlorinated pesticides (Masunaga *et al.* 2001b). The dioxin sources are not always the same at different locations.

There is not much data available concerning dioxin levels in the Tohoku region of Japan, which thrives on agriculture and aquaculture. This study was undertaken to determine levels of dioxin pollution in the Tohoku region of Japan.

2.1. Major dioxin sources and bioaccumulation of dioxins in aquatic organisms through the food web

Sendai Bay is a fishing ground for marbled sole; *Pseudopleuronectes yokohamae* and Japanese flounder; *Paralichthys olivaceus* and an aquaculture ground for the Pacific oyster; *Crassostrea gigas*. The data in this section includes the concentrations of dioxin congeners in the phytoplankton, seaweed, zooplankton, mysids, shrimp, sand worms, the Pacific oyster, sand lance; *Ammodytes personatus*, Japanese anchovy; *Engraulis japonica*, and the 2 flatfish species as well as in seawater and sediment samples from Sendai Bay as determined by high-resolution gas chromatography/high-resolution mass spectroscopy (HRGC/HRMS).

Phytoplankton and seaweed are primary producers and the lowest-trophic-level organisms in coastal waters. Small zooplankton, which mostly consume phytoplankton, are regarded as primary consumers and low-trophic-level invertebrates. Mysids consume both phytoplankton and small zooplankton (Yamada *et al.*, 1995), and shrimp prey mainly on zooplankton (Ikematsu, 1963). Both of these crustaceans are considered to be secondary consumers and higher-trophic-level invertebrates. Sand worms are benthic sediment feeders and omnivores (Fauchald and Jumars, 1979). The Pacific

oyster, a suspension feeder whose main food is plankton, is a lower-trophic-level consumer in the marine food web (Tamura 1960). The sand lance, which feeds mainly on planktonic and epibenthic zooplankton, including mysids (Kobayashi *et al.*, 1995; Yamada, 1997b) and the Japanese anchovy, whose main prey organisms are zooplankton (Mitani 1988), can be classified as secondary consumers. Japanese flounder, which feed on small fishes such as Japanese anchovy and Japanese sand lance (Yamada *et al.* 1998), and marbled sole, which feed on benthos such as polychaetes (Omori 1974), are higher-trophic-level consumers. Measuring the PCDD, PCDF, and Co-PCB concentrations in samples of these organisms helps to investigate the major sources of these chemicals as well as the relationships between several trophic levels in the marine food web along with the concentrations of these chemicals.

2.1.1. Materials and Methods

2.1.1.1. Sampling

The following types and numbers of samples were collected from November 1999 to August 2001 in Sendai Bay (Fig. 2): land soil ($n=1$), surface seawater ($n=4$), sea bottom sediments ($n=3$), seaweed (*Eisenia bicyclis*, $n=1$; *Porphyra yezoensis*, $n=1$), phytoplankton ($n=1$), Pacific oyster (*Crassostrea gigas*, $n=3$), zooplankton ($n=2$), mysids (*Acanthomysis mitsukurii*, $n=1$), other shrimp (*Trachypena* sp., $n=1$; *Crangon* sp., $n=2$), sand lance (*Ammodytes personatus*, $n=2$), Japanese anchovy (*Engraulis japonica*, $n=6$), Japanese flounder (*Paralichthys olivaceus*, $n=11$), sand worm (Cirratulidae, Nereidae, and Eunicidae mixed, $n=2$), and marbled sole (*Pseudopleuronectes yokohamae*, $n=12$). The land soil sample was collected from a point approximately 50 m from the coast of Sendai Bay and approximately 500 m from the nearest incinerator. The surface seawater samples, which were collected using a water-sampling bucket, were transferred to two 10-L glass bottles and stored in a refrigerator. Phytoplankton were collected by pumping surface seawater and filtering it through a plankton net (mesh size, 20 μm) on board of a fishing boat. Zooplankton were collected by level tows with a ring net ($\phi = 130$ cm; mesh size, 0.33 mm). Mysids

were caught from the bay bottom at 10 m depth with a beam trawl (mesh size, 3 mm). Shrimp and sand lance were collected with a bottom trawl net. Sand worms were handpicked from the intertidal zone of Matsushima Bay. Pacific oysters were obtained from a nearby aquaculture ground. Fish samples were collected with a bottom trawl net. The body lengths (total length) of the flatfish were measured, several small fish were combined together as a sample, and their average body length was calculated. Sediment samples were collected with an Ekman-Berge bottom sampler, or by scooping. Sediment, soil, and biological samples of approximately 100 g wet-weight were used for dioxin analyses. Since the weight of each organism was much less than 100 g, samples collected from the same station at the same sampling time were mixed, and the combined samples were used for the analysis. Biological, sediment, and soil samples were kept frozen until analysis.

To identify species, a given quantity of phytoplankton, zooplankton, mysid, shrimp and sand worm samples were fixed in neutral formalin and identified under a light microscope. The predominant algal class in the phytoplankton sample was Bacillariophyceae. Diatom cells constituted

approximately 95% of all algal cells. In particular, *Skeletonema costatum* constituted approximately 68%. In the zooplankton sample, zoea of *Brachyura* accounted for more than 97% of the total number of individuals. In the mysid sample, *Acanthomysis mitsukurii* constituted approximately 53% of the total number of individuals.

Seawater samples were filtered through a Millipore HA filter (ϕ : 47 mm; pore size: 0.45 μ m), dried, and then weighed to determine the dry weight (dw) of total suspended matter (mainly phytoplankton; Uematsu *et al.* 1978). The dw of suspended matter (mainly phytoplankton) in a 1-L seawater sample was estimated to be approximately 1 g, on the assumption that 1 g dry weight of suspended matter (phytoplankton) was equal to 10 g wet weight (Motoda 1994, Tanaka 2006).

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

Concentrations of PCDDs and PCDFs with from 4 to 8 chlorines, and Co-PCBs were determined by the methods reported by the Ministry of the Environment (Ministry of the Environment: 1998a, 1998b, 2000b). Briefly, the methods are as follows.

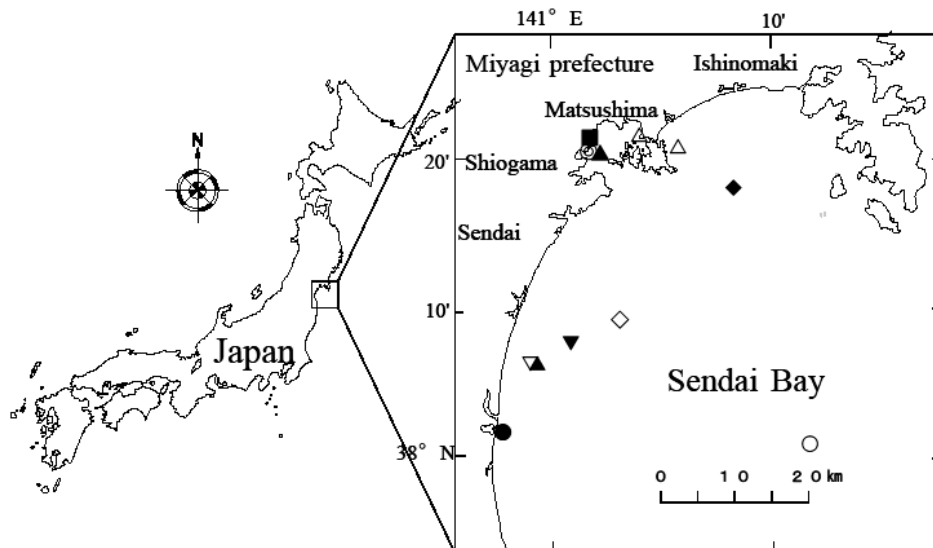


Fig. 2. Sampling sites in Sendai Bay. ■: Soil; ●: sediment and sand worms; ▲: seawater and sediment; △: Pacific oyster; ◆: seawater; ◇: Japanese anchovy, marbled sole, and Japanese flounder; ▼: phytoplankton, shrimp, and zooplankton; ▽: mysids and zooplankton; ○: sand lance and shrimp; ●: seaweed.

Preparation of analytical samples

The frozen sediment and soil samples were thawed and then air-dried overnight. Each air-dried sample was weighed, spiked with a ^{13}C -labeled internal standard and copper, and then Soxhlet-extracted for 18 h in toluene. The extract was concentrated by rotary evaporation at low pressure, redissolved in hexane, concentrated for clean-up, and then treated with sulfuric acid and concentrated again prior to HRGC/HRMS analysis.

The frozen, whole-body biological samples were homogenized, weighed, spiked with a ^{13}C -labeled internal standard, and saponified with potassium hydroxide and methanol for 8–12 h, and then extracted 3 times with hexane in a separating funnel using a shaker for 10 min. The hexane extracts were treated with sulfuric acid and concentrated again prior to HRGC/HRMS analysis.

Twenty liters of the refrigerated seawater samples were filtered through glass-fiber filters (ϕ : 95 mm; pore size: 0.8 μm) (Kiryama glass Co., Tokyo, Japan). The filtrate was extracted into dichloromethane, and the residue was Soxhlet-extracted in toluene for more than 16 h. Each extract was spiked with a ^{13}C -labeled internal standard and then treated with sulfuric acid and concentrated again prior to HRGC/HRMS analysis.

Clean-up column chromatography

Each sample extract was purified by silica-gel, alumina, and activated-carbon column chromatography. The final eluate from the column chromatograph was concentrated and subjected to congener-specific analysis by HRGC/HRMS on an AutoSpec Ultima spectrometer (Micromass Ltd.).

HRGC/HRMS analysis

Tetra- to hexachlorodibenzo-*p*-dioxin and -dibenzofuran congeners were analyzed on an SP-2331 column (ϕ 0.32 mm \times 60 m) (Sigma-Aldrich). Hepta- to octachlorodibenzo-*p*-dioxin and -dibenzofuran congeners and tetrachlorobiphenyls were analyzed on a DB-17 column (ϕ 0.32 mm \times 60 m) (J&W Scientific). Non-*ortho* and mono-*ortho* penta- to heptachlorinated biphenyls were analyzed on DB-17 (J&W Scientific) and DB-5MS (ϕ 0.25 mm \times 60 m) (J&W Scientific) columns, respectively. The temperature program for the analysis using the SP-2331 column was: 150 °C for 1 min, 15 °C/min to 200

°C, hold for 5 min, 2 °C/min to 250 °C, and then hold for 30 min. The temperature program for the DB-17 column was: 150 °C for 1 min, 15 °C/min to 270 °C, and then hold for 20 min. The temperature program for the DB-5MS column was: 150 °C for 1 min, 15 °C/min to 200 °C, hold for 5 min, 2 °C/min to 270 °C, and then hold for 5 min. The temperatures of the injector and ion source were both 260 °C. Mass spectrometry was performed in electron impact (EI) mode. The voltage and current of the electron-impact ionization energy were 30 eV and 500 μA , 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 sediment and soil samples were 1, 1, 2, 2, and 5 $\mu\text{g/g}$ dry weight (dw), respectively. The detection limits in seawater were 0.05, 0.05, 0.1, 0.1, and 0.2 $\mu\text{g/L}$, respectively. The detection limits in the biological samples were 0.05, 0.05, 0.1, 0.1, and 0.2 $\mu\text{g/g}$ wet weight (ww). The detection limits for Co-PCBs in the sediment and soil, seawater, and biological samples were 1 $\mu\text{g/g}$ dw, 0.1 $\mu\text{g/L}$, and 0.1 $\mu\text{g/g}$ ww, respectively.

2.1.1.3. Calculations of toxic equivalents (TEQ)

The average TEQ of each biological sample was calculated by using toxic equivalency factors (TEFs) for humans/mammals provided by the World Health Organization (Van den Berg *et al.* 1998).

2.1.2. Results

2.1.2.1. Dioxin compositions and concentrations

Of the environmental dioxin samples, the relative amounts of dioxins in soil increased in the following order: Co-PCBs < PCDFs < PCDDs (Fig. 3). The soil sample was the only one in which PCDF concentrations were higher than Co-PCB concentrations. Concentrations in sediment and seawater samples, as well as in seaweed, phytoplankton, and Pacific oyster of the biological samples, increased in the following order: PCDFs < Co-PCBs < PCDDs. The relative proportions of these components in seaweed, phytoplankton, and Pacific oyster were similar to those in the sediment and seawater samples. The concentrations of dioxins in

the other biological samples increased in the following order: PCDFs < PCDDs < Co-PCBs. Co-PCB concentrations were higher than PCDD/F concentrations.

The predominant PCDD congeners were OCDD in soil, 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD and OCDD in sediment, seawater and phytoplankton, and 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD in invertebrates (Figs. 4 and 5). In all samples, concentrations of 2, 3, 7, 8-substituted PCDDs except OCDD, were much lower than those of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD and OCDD, and 2, 3, 7, 8-TeCDD, with few chlorine substitutions, was frequently below the detection limit. Of the Co-PCBs, concentrations of mono-*ortho* PCBs (PCB #104, #114, #118, #123, #156, #157, #167, and #189) were higher than those of non-*ortho* PCBs (PCB #77, #81, #126, and #169). Mono-*ortho* PCBs accounted for over 80% of the Co-PCBs. PCB #118 was the predominant congener of the mono-*ortho* PCBs, and PCB #77 was the predominant congener of non-*ortho* PCBs, whereas PCB #169 was lowest in concentration of all Co-PCBs. However, in the environmental samples, the ratio of PCB #118 to total mono-*ortho* PCBs and the ratio of PCB #77 to total non-*ortho* PCBs in soil tended to be slightly

lower than these ratios in sediment and seawater.

Co-PCB concentrations in food webs increased in the following order: seaweed < phytoplankton < Pacific oyster, phytoplankton < zooplankton < mysids and other shrimp < sand lance and Japanese anchovy < Japanese flounder, sand worm < marbled sole (Fig. 3). Co-PCB concentrations in the higher-trophic-level consumers tended to be higher than those in the lower-trophic-level consumers.

The trends of PCDD/F concentrations in food webs were more complex: seaweed < phytoplankton < Pacific oyster, zooplankton < mysids and other shrimp, mysid and other shrimp > sand lance and Japanese anchovy > Japanese flounder, sand worm > marbled sole. PCDD/F concentrations in the higher-trophic-level invertebrates tended to be higher than those in the lower-trophic-level invertebrates, whereas PCDD/F concentrations in the higher-trophic-level fishes tended to be lower than those in the lower-trophic-level fishes.

2.1.2.2. Comparison of TEQ values

In a comparison of TEQ values among all samples, PCDD TEQs were higher than PCDF and Co-PCB TEQs in environmental, plant, and invertebrate

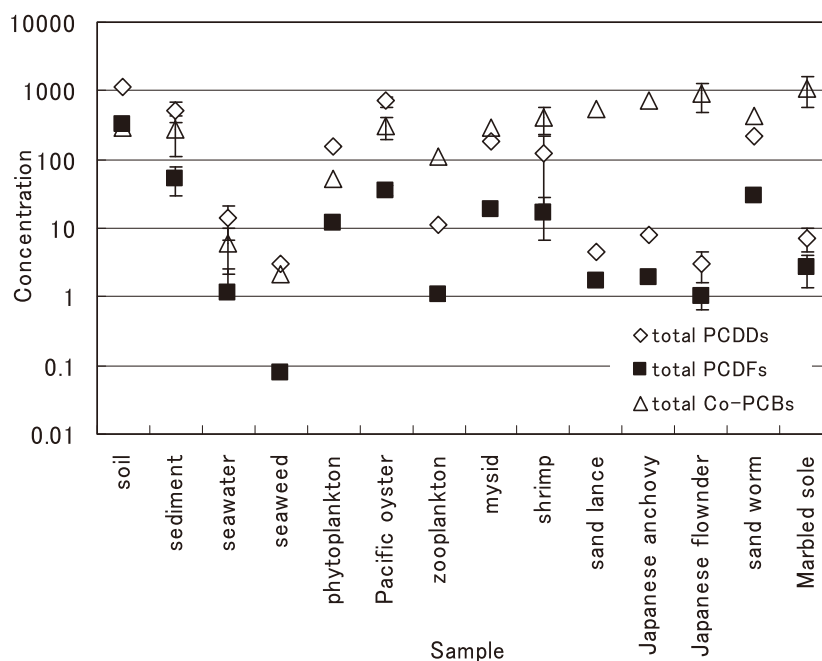


Fig. 3. Total PCDD, total PCDF, and total Co-PCB concentrations in soil (pg/g dry weight), sediment (pg/g d.w.), seawater (pg/L), and biological samples (pg/g wet weight).

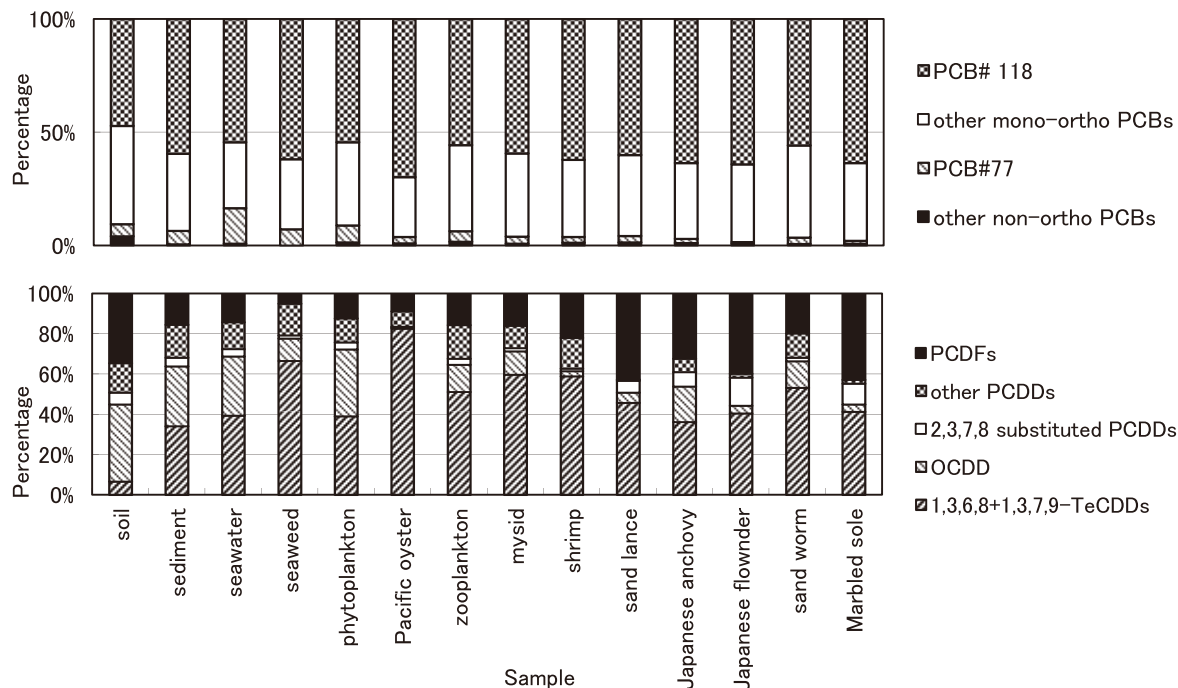


Fig. 4. Relative amounts of PCDDs, PCDFs, and Co-PCBs in soil, sediment, seawater, and biological samples. “Other” mono-*ortho* PCBs are PCB #104, #114, #123, #156, #157, #167, and #189. “Other” non-*ortho* PCBs are #81, #126, and #169. 2, 3, 7, 8-substituted PCDDs include 2, 3, 7, 8-TeCDD, 1, 2, 3, 7, 8-PeCDD, 1, 2, 3, 4, 7, 8-HxCDD, 1, 2, 3, 7, 8, 9-HxCDD, and 1, 2, 3, 4, 6, 7, 8-HpCDD, and exclude OCDD.

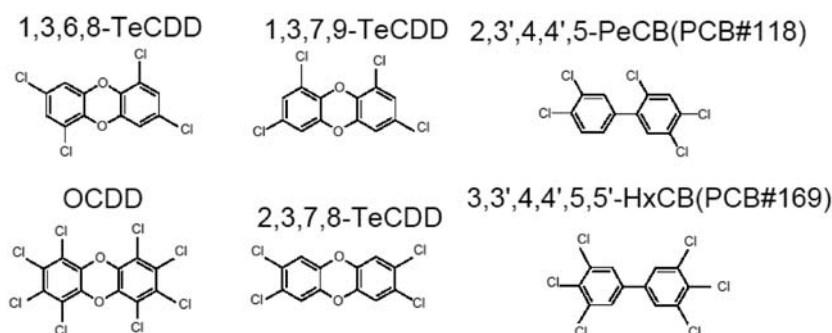


Fig. 5. Structures of typical dioxin congeners. 1, 3, 6, 8- and 1, 3, 7, 9-TeCDD — which are non-2, 3, 7, 8-substituted PCDD/Fs with no chlorine substitution at the 1, 4 and/or 6, 9 positions — are known to show high bioaccumulation and high elimination in fish. OCDD is in the group of 1, 4- or 6, 9-substituted PCDD/F congeners, which are known to show low bioaccumulation in fish. 2, 3, 7, 8-TeCDD is one of the PCDD/Fs without chlorine substitutions at the 1, 4 and/or 6, 9 positions, known to show high bioaccumulation and low elimination in fish (they are easily adsorbed into fatty tissue, thereby delaying their elimination; Sijm *et al.* 1993, Yamada 1997a). Compared to the bioaccumulation properties of PCDD/F congeners, bioaccumulations of Co-PCB congeners are all relatively similar, with bioaccumulations higher than those of PCDD/Fs (Niimi 1996). 1, 3, 6, 8- and 1, 3, 7, 9-TeCDD congeners are thought to be impurities of the pesticide 1, 3, 5-trichloro-2-(4-nitrophenoxy)benzene (CNP), and the OCDD congener is thought to be an impurity of the pesticide pentachlorophenol (PCP; Masunaga *et al.* 2001a, Seike *et al.* 2003). OCDD has also been detected in fly ash and exhaust gases from incinerators (Sakai *et al.* 1993). PCB #118 was the predominant congener of the mono-*ortho* PCBs in samples. PCB #169 is thought to originate from incinerator emissions rather than from the manufacture of such items as electrical insulating oil (Masunaga 2000).

samples (Table 1). In fish samples, Co-PCB TEQs were higher than PCDD and PCDF TEQs. Dioxin TEQs in the Pacific oyster, Japanese flounder, and marbled sole, which comprise the major fishery in Sendai Bay, ranged from 0.87 to 1.6 pg-TEQ/g ww.

2.1.3. Discussion

2.1.3.1. Major sources of dioxins in Sendai Bay

1, 3, 6, 8- + 1, 3, 7, 9-TeCDD were the predominant PCDD congeners in seawater and sediment collected from Sendai Bay (Fig. 4). Almost all other studies report that the predominant PCDD congener in oceanic sediment is OCDD; TeCDDs are not major PCDD congeners (Rappe *et al.* 1987, Evers *et al.* 1993, Gotz *et al.* 1993, Wenning *et al.* 1993, Brochu *et al.* 1995, Sook-Hyeon *et al.* 1995, Masunaga *et al.* 1997, Sakurai *et al.* 2000, Wenning *et al.* 2000, Wu *et al.* 2001). The profiles of PCDD/F congeners in Sendai Bay, in which TeCDDs were the major PCDD congeners, are more similar to the profile of paddy field soil (Masunaga *et al.* 1997) than to that of sediment (Rappe *et al.* 1987, Evers *et al.* 1993, Gotz *et al.* 1993, Wenning *et al.* 1993, Brochu *et al.* 1995, Sook-Hyeon *et al.* 1995, Masunaga *et al.* 1997, Sakurai *et al.* 2000, Wenning *et al.* 2000, Wu *et al.* 2001). In many samples from Sendai Bay, the sum of the concentrations of the 1,3,6,8- and 1,3,7,9-TeCDD congeners, which are thought to be impurities of the pesticide CNP (Masunaga *et al.* 2001a, Seike *et al.* 2003), was highest among the PCDD/F congeners (Figs. 4 and 5). This reflects the fact that shipments of CNP products to Miyagi Prefecture, the so-called granary of Japan, were higher than to any other prefecture in Japan in 1971, 1975, 1976, 1979, 1981, 1982, and from 1984 to 1989, and that in 1975 more than 4000 t of CNP products were shipped to Miyagi Prefecture, the highest shipment between 1965 and 1995 (Japan Plant Protection Association 1963–1995).

The composition of PCDD congeners in soil, which was influenced by atmospheric deposition, differed from those in seawater and sediment (Fig. 4). OCDDs were the major PCDD congeners, whereas the ratio of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD to total PCDDs in soil was much lower than those in seawater and sediment, suggesting that the PCDD concentrations in Sendai Bay are influenced more by

pesticide impurities than by atmospheric deposition.

The total PCDF concentration in soil, which was influenced by atmospheric deposition, was slightly higher than the total Co-PCB concentration, and the ratio of the PCDF to the Co-PCB concentrations was higher than that in seawater and sediment (Fig. 3). Thus, it is possible that the major source of PCDFs in Miyagi Prefecture is atmospheric deposition. On the other hand, total PCDF concentrations in sediment and seawater samples were lower than total Co-PCB concentrations, and were approximately 1 order of magnitude lower than total PCDD concentrations. Accordingly, PCDFs were not major contributors to dioxin concentrations in Sendai Bay.

The profiles of non-*ortho* PCBs (PCB #77, #81, #126, and #169) in the seawater and sediment samples, of which more than 80% was PCB #77 (Fig. 4), were similar to those of non-*ortho* PCBs released during the manufacture of items such as electrical insulating oil (Kannan *et al.* 1987). In contrast, in the soil sample, PCB #77 comprised only approximately 60% of the total non-*ortho* PCBs (Fig. 4); the profile of non-*ortho* PCBs was similar to that resulting from fly ash and atmospheric deposition rather than that from the manufacture of items such as electrical insulating oil (Kurokawa *et al.* 1994). The concentration of PCB #118 accounted for a larger proportion of the mono-*ortho* Co-PCB concentrations in sediment and seawater than in soil (Fig. 4). PCB #118 is thought to originate from the manufacture of items such as electrical insulating oil rather than from incinerator emissions (Takasuga *et al.* 1995, Anezaki *et al.* 2007). The low percentages of PCB #77 and high #118 suggest that the dioxin concentrations in seawater and sediment in Sendai Bay were influenced more by the manufacture of items such as electrical insulating oil than by atmospheric deposition of incinerator emissions.

2.1.3.2. Bioaccumulation of dioxins through the food web in Sendai Bay

Bioaccumulation of dioxins in phytoplankton and seaweed

The composition of PCDD/F congeners in phytoplankton was similar to that in sediment rather than to that in the other organisms analyzed in this study (Fig. 4). This difference may indicate that

adsorption of dioxin particles onto the surface of phytoplankton plays an important role in the concentration of dioxins in phytoplankton. Even though both phytoplankton and seaweeds are autotrophic, dioxin concentrations were much higher in phytoplankton than in seaweed (Fig. 3). Even with the same “efficiency”, there would be more adsorption on an equal phytoplankton biomass because of the greater surface area.

Bioaccumulation of PCDD/Fs in fish

The bioaccumulation of PCDD/Fs in fish is known to vary by kind of congener. It is possible to classify these congeners into three groups based on their bioaccumulation properties in fishes (Fig. 5). For example, 2, 3, 7, 8-TeCDD is a member of the 2, 3, 7, 8-substituted PCDD/Fs with no chlorine substitution at the 1,4 and/or 6,9 positions, which are known to show high bioaccumulation and low elimination; they are easily adsorbed into fatty tissue, thereby delaying their elimination (Sijm *et al.* 1993, Yamada 1997a). 1, 3, 6, 8- and 1, 3, 7, 9-TeCDD, which are non-2, 3, 7, 8-substituted PCDD/Fs with no chlorine substitution at the 1, 4 and/or 6, 9 positions, are known to show high bioaccumulation and high elimination (Sijm *et al.* 1993, Yamada 1997a). OCDD belongs to the group of 1, 4- or 6, 9-substituted PCDD/F congeners, which are known to show low bioaccumulation (Sijm *et al.* 1993, Yamada 1997a). The major PCDD/F congeners in seawater and sediment samples from Sendai Bay were 1, 3, 6, 8-TeCDD and OCDD (Fig. 4). The concentrations of 2, 3, 7,8-substituted PCDD/Fs, such as 2, 3, 7, 8-TeCDD, were below the detection limit or were much lower than those of 1, 3, 6, 8-TeCDD and OCDD. PCDD/F congeners in Sendai Bay which were the type showing high elimination and low bioaccumulation in fishes. Therefore, PCDD/F concentrations in the higher-trophic-level fishes tended to be lower than those in the lower-trophic-level fishes.

Bioaccumulation of PCDD/Fs in higher-trophic-level invertebrates

The bioaccumulation patterns of PCDD/Fs in invertebrates differ from those in fishes (Sasaki, 2000). The concentration of 1, 3, 6, 8-TeCDD was higher in the snail *Indoplanorbis exustus* than in the fish *Oryzias latipes* (Allinson *et al.*, 1994).

Furthermore, the concentrations of PCDD/Fs with few chlorines, such as 1, 3, 6, 8-TeCDD, in invertebrates tended to be higher than those of highly chlorine-substituted PCDD/Fs, such as OCDD (Hashimoto *et al.*, 1998, 1999; Sakurai *et al.*, 2000; Sasaki, 2000). The bioaccumulation in invertebrates may be influenced more by the number of chlorine substituents in PCDD/F homologs (that is, differences between PCDD/Fs with fewer or more chlorine atoms), rather than by difference in structure (such as non-2, 3, 7, 8-substituted PCDD/Fs compared to 2, 3, 7, 8-substituted PCDD/Fs). The major PCDD/F congeners in sediment samples from Sendai Bay were 1, 3, 6, 8-TeCDD and OCDD (Fig. 4). Almost all PCDD/F congeners in Sendai Bay were the type showing higher bioaccumulation in invertebrates than in fish. Therefore, the PCDD/F concentrations in the higher-trophic-level invertebrates were higher than in the lower-trophic-level organisms (e.g., phytoplankton < Pacific oyster, zooplankton < mysids and shrimp).

Bioaccumulation of Co-PCBs in organisms

The bioaccumulation patterns of Co-PCBs are known to vary from those of PCDD/Fs. Compared to PCDD/F congeners, bioaccumulation patterns of Co-PCB congeners are all relatively similar (Niimi 1996). Furthermore, bioaccumulations of Co-PCBs are higher than those of PCDD/Fs (Niimi 1996). As all Co-PCB congeners are thought to bioaccumulate in organisms throughout the food web, it was no surprise that Co-PCB concentrations were higher in higher-trophic-level organisms than in lower-trophic-level organisms.

2.1.3.3. Comparison of TEQ values

The TEQ values of total dioxins in Pacific oyster, Japanese flounder, and marbled sole, which are major fishery resources in Sendai Bay, ranged from 0.87 to 1.6 pg-TEQ/g ww (Table 1). These TEQs were calculated based on whole-body samples in this study. In other studies, the TEQs of fish and shellfish averaged 0.932 pg-TEQ/g ww (Fisheries Agency, Japan 2000a), 0.816 pg-TEQ/g (Fisheries Agency, Japan 2000b), and 1.468 pg-TEQ/g ww (Ministry of Health, Labour and Welfare 1999). The levels in our study agree with these previously published TEQs of fish and shellfish.

2.2. Bioaccumulation of dioxins with respect to body length of flatfish

The bioaccumulation of chemicals is known to vary with the body size of aquatic organisms (Schimmel *et al.* 1977, Yamada *et al.* 1995), but few field studies have examined the relationship between the body length of fish and the concentration of dioxins. For the purpose of determining the bioaccumulation properties of each dioxin congener in higher-trophic-level fish with respect to body length, I measured the concentrations of dioxin congeners in Japanese flounder (*Paralichthys olivaceus*) of various body lengths collected from Sendai Bay, Japan, and investigated the relationship between body length and dioxin concentration. In one study, Japanese flounder—whose main prey organisms are Japanese anchovy and sand lance—was found to be a higher-trophic-level organism (Ochiai 1966). Another study reported that the total length of Japanese flounder was significantly correlated with body weight (Kitagawa *et al.* 1994). The maturation age was estimated from maturation size to be three years (Sato 1975).

2.2.1. Materials and Methods

2.2.1.1. Data analysis

The data analyses presented in the following sections were performed on the data already presented in Chapter 2.1.

2.2.1.2. Multiple range test of dioxin concentrations

The values for dioxin concentrations below detection limits were set to 0 pg/g ww. Multiple range tests were conducted to compare the mean difference of TEQ values among PCDDs, PCDFs, non-*ortho* PCBs, and mono-*ortho* PCBs. After a one-way analysis of variance was conducted to examine whether the variances were equal or unequal, multiple range tests for unequal variances (Tamhane's test) were conducted. The data from these tests were analyzed with the SPSS 11.0J for a Windows base system (SPSS Inc., Chicago, USA).

2.2.1.3. Linear regression analysis of the relationship between dioxin concentration and body length

The coefficients of determination (r^2) and the probability values (P) for the relationship between the dioxin concentrations and flounder body lengths were calculated by simple linear regression: concentration of dioxin congener (pg/g ww) = $ax + b$, where x is the body length (cm), a the slope, and b the intercept. When the linear relationship was not significant ($P > 0.05$), polynomial regressions were conducted using $y = a_1x^2 + a_2x + b$, where y is the concentration of the dioxin congener (pg/g ww), x the body length (cm), a_1 and a_2 the slope, and b the intercept. Polynomial regression provided when the relationship between x and y was nonlinear. The polynomial regressions were also conducted using the SPSS 11.0J system.

Table 1. TEQ of each sample

	PCDDs	PCDFs	Co-PCBs	Total Dioxins
soil	5.8	5.7	0.97	12
sediment	1.5 ± 1.3	0.73 ± 0.62	0.14 ± 0.12	2.4 ± 1.6
seawater	0.0063 ± 0.003	0.003 ± 0.0038	0.0059 ± 0.011	0.015 ± 0.015
seaweed	0.0006	0	0.0003	0.0008
phytoplankton	0.24	0.14	0.045	0.43
Pacific oyster	0.47 ± 0.19	0.22 ± 0.095	0.19 ± 0.046	0.87 ± 0.32
zooplankton	0.054	0.041	0.14	0.23
mysid	0.25	0.23	0.18	0.66
shrimp	0.46 ± 0.19	0.34 ± 0.11	0.39 ± 0.04	1.2 ± 0.33
sand lance	0.23	0.26	0.63	1.1
Japanese anchovy	0.29	0.31	0.67	1.3
Japanese flounder	0.3 ± 0.084	0.19 ± 0.064	0.65 ± 0.25	1.1 ± 0.38
sand worm	0.54	0.36	0.49	1.4
Marbled sole	0.62 ± 0.35	0.33 ± 0.2	0.67 ± 0.2	1.6 ± 0.72

Units: seawater-pgTEQ/L; sediment, soil-pgTEQ/g dw; biological sample-pgTEQ/g ww.

2.2.2. Results

2.2.2.1. Relationship between total dioxin concentration and body length

The total PCDD and total PCDF concentrations were not significantly correlated with body length ($r^2 = 0.03$ and 0.007 , respectively; $P > 0.05$ for both) (Fig. 6). In contrast, the total non-*ortho* PCB and total mono-*ortho* PCB concentrations were significantly correlated with body length ($r^2 = 0.80$ and 0.63 , respectively; $P < 0.01$ for both), and the slopes of the linear regressions were positive (0.81 and 39.2, respectively). The relationships between concentration and body length varied with the type of dioxin.

2.2.2.2. Relationship between PCDD/F congener concentrations and body length

Among the PCDD congeners, the concentration of 1, 3, 6, 8-TeCDD was the highest, and was not significantly correlated with body length ($r^2 < 0.1$, $P > 0.05$; Fig. 7). In contrast, 2, 3, 7, 8-TeCDD and OCDD concentrations were significantly correlated with body length ($r^2 = 0.55$ and 0.72 , respectively; $P < 0.01$ for both), and the slopes of the linear regressions were positive (0.0035) and negative (-0.017), respectively. The concentration of 1, 2, 3, 6, 7, 8-HxCDD was significantly correlated with body length by polynomial regression ($r^2 = 0.53$, $P < 0.01$).

Of the PCDF congeners, concentrations of 2, 3, 7, 8-TeCDF and 2, 3, 4, 7, 8-PeCDF were significantly correlated with body length ($r^2 = 0.56$ for both, $P < 0.01$ for both; Fig. 8), and the slopes of the linear regressions were positive (0.011 and 0.0098, respectively).

The concentrations of 2, 3, 4, 6, 7, 8-HxCDF, and the concentrations of 1, 2, 3, 4, 7, 8- and 1, 2, 3, 4, 7, 9-HxCDF combined were significantly correlated with body length ($r^2 = 0.41$ and 0.40 , respectively; $P < 0.05$ for both), and the slopes of the linear regressions were negative (-0.0072 and -0.004, respectively).

The concentrations of all Co-PCB congeners were significantly correlated with body length ($r^2 > 0.55$, $P < 0.01$ for all; Fig. 9) and increased with increasing body length. The slopes of all linear regressions

were positive, ranging from 0.024 to 25.7.

2.2.2.3. TEQ values

The TEQ values for PCDDs, PCDFs, non-*ortho* PCBs, and mono-*ortho* PCBs were 0.18–0.43, 0.084–0.29, 0.28–0.82, and 0.064–0.24 pg-TEQ/g ww, respectively, decreasing in the order non-*ortho* PCBs > PCDDs > PCDFs = mono-*ortho* PCBs (Fig. 6). The mean differences of TEQ values for non-*ortho* PCB and PCDDs were significant at the 0.05 level. Despite the fact that the concentrations of non-*ortho* PCBs were lower than those of mono-*ortho* PCBs, the TEQ values for non-*ortho* PCBs were higher than those of mono-*ortho* PCBs. TEQ values for the Co-PCBs ranged from 0.337 to 1.06 pg TEQ/g ww and accounted for 46.3%–63.7% of the total TEQ value for all the dioxins.

Although the TEQ values for total PCDDs and total PCDFs were not significantly correlated with body length ($r^2 = 0.34$ and 0.35 , respectively; $P > 0.05$ for both) (Fig. 6), all of the linear regressions had positive slopes. The TEQ values for total non-*ortho* PCBs and total mono-*ortho* PCBs were significantly correlated with body length ($r^2 = 0.82$ and 0.64 , respectively; $P < 0.01$ for both), and the non-*ortho* PCBs had the highest linear regression slope of all the dioxins ($a = 0.021$).

2.2.3. Discussion

2.2.3.1. Bioaccumulation of PCDDs and the relationship between concentration and body length

Although the bioaccumulation rate for 1, 3, 6, 8-TeCDD is high, the elimination rate is also high (Sijm *et al.* 1993, Yamada 1997a). This might explain why 1, 3, 6, 8-TeCDD concentrations were not significantly correlated with body length (Fig. 7). And because 1, 3, 6, 8-TeCDD was the major PCDD congener in Miyagi Prefecture, total PCDD concentrations also showed no significant correlation with body length (Fig. 6).

The congener 2, 3, 7, 8-TeCDD shows high bioaccumulation rates and low elimination rates (Sijm *et al.* 1993, Yamada 1997a). Researchers believe that 2, 3, 7, 8-TeCDD bioaccumulates in fish more than 1, 3, 6, 8-TeCDD and OCDD (Allinson *et al.* 1993,

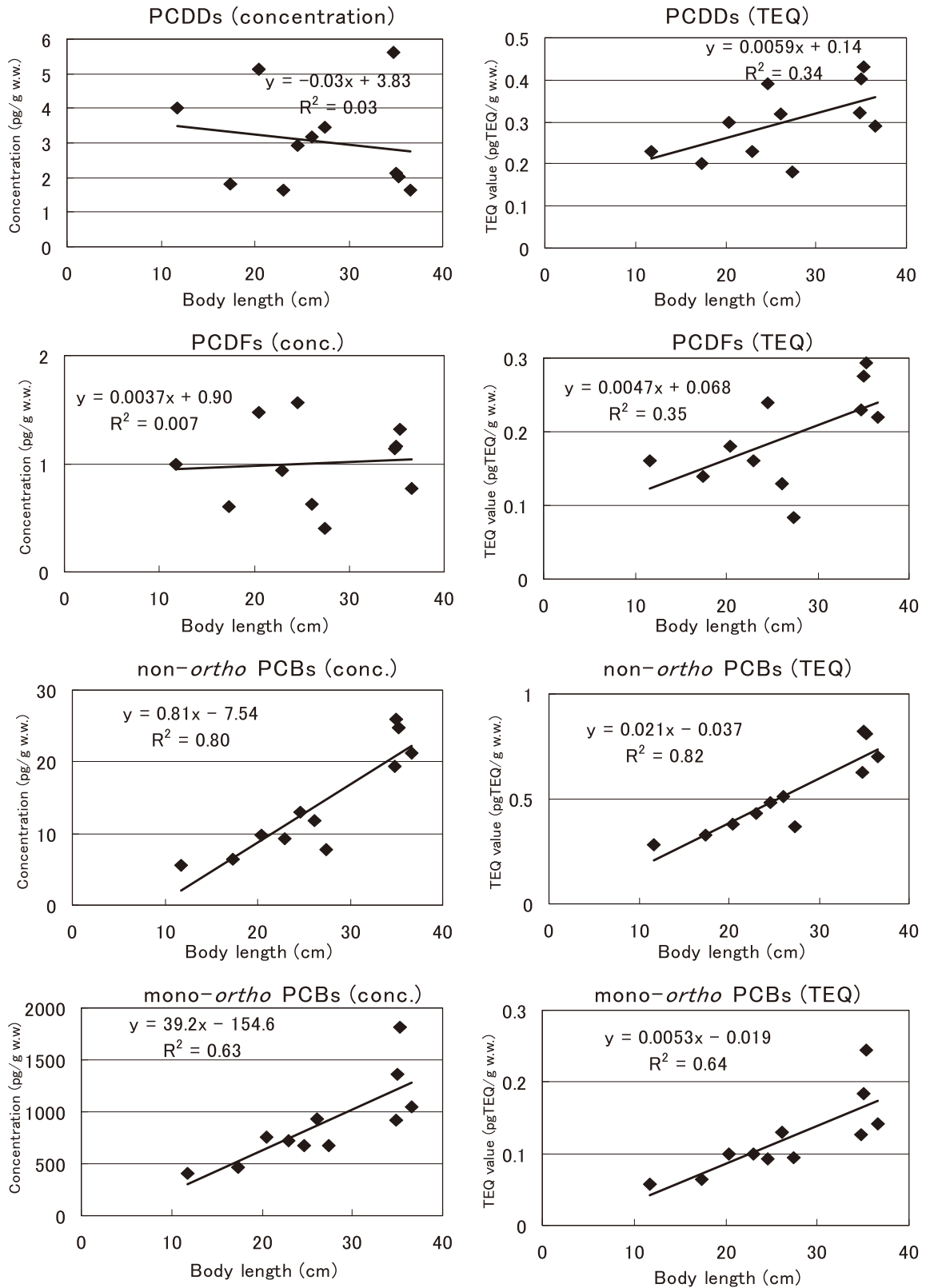


Fig. 6. Relationships between body length and concentration, and body length and TEQ value, for total PCDDs, total PCDFs, and total Co-PCBs.

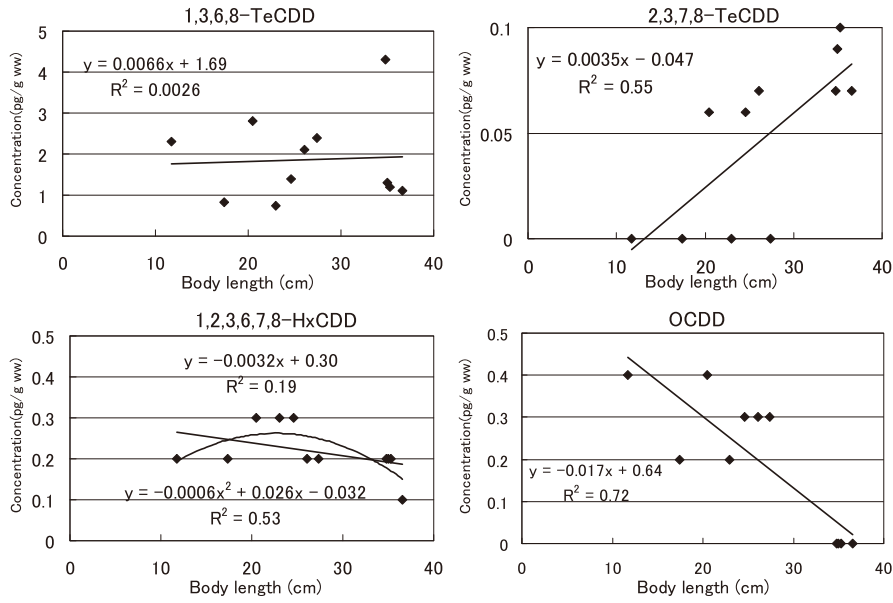


Fig. 7. Relationship between body length and concentration for major PCDD congeners.

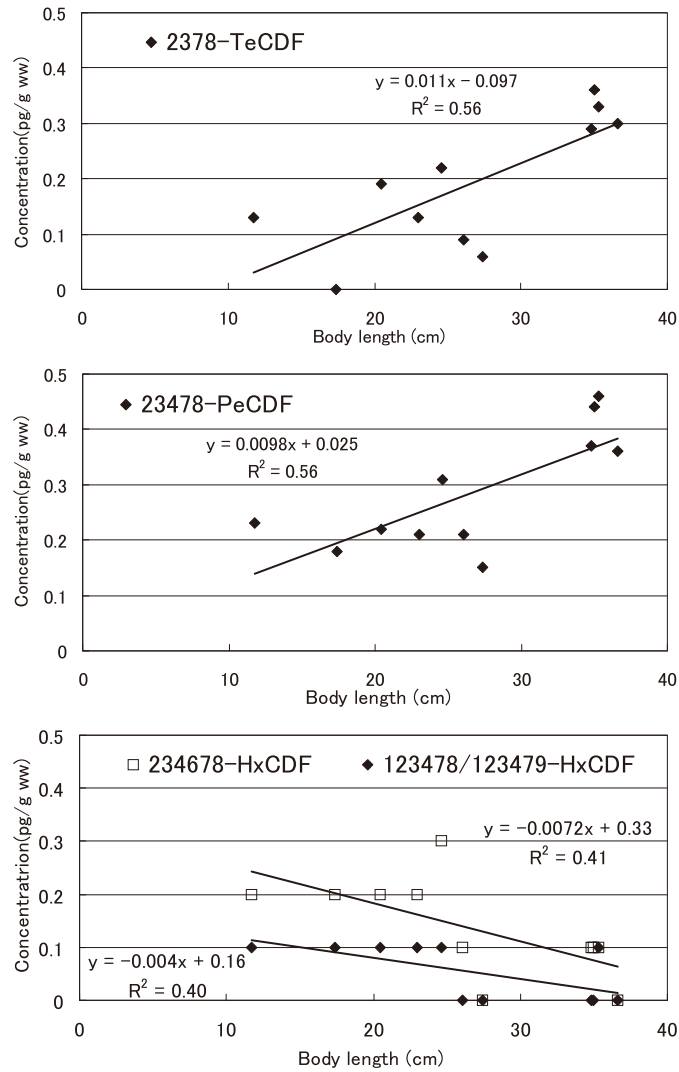


Fig. 8. Relationship between body length and concentration for major PCDF congeners.

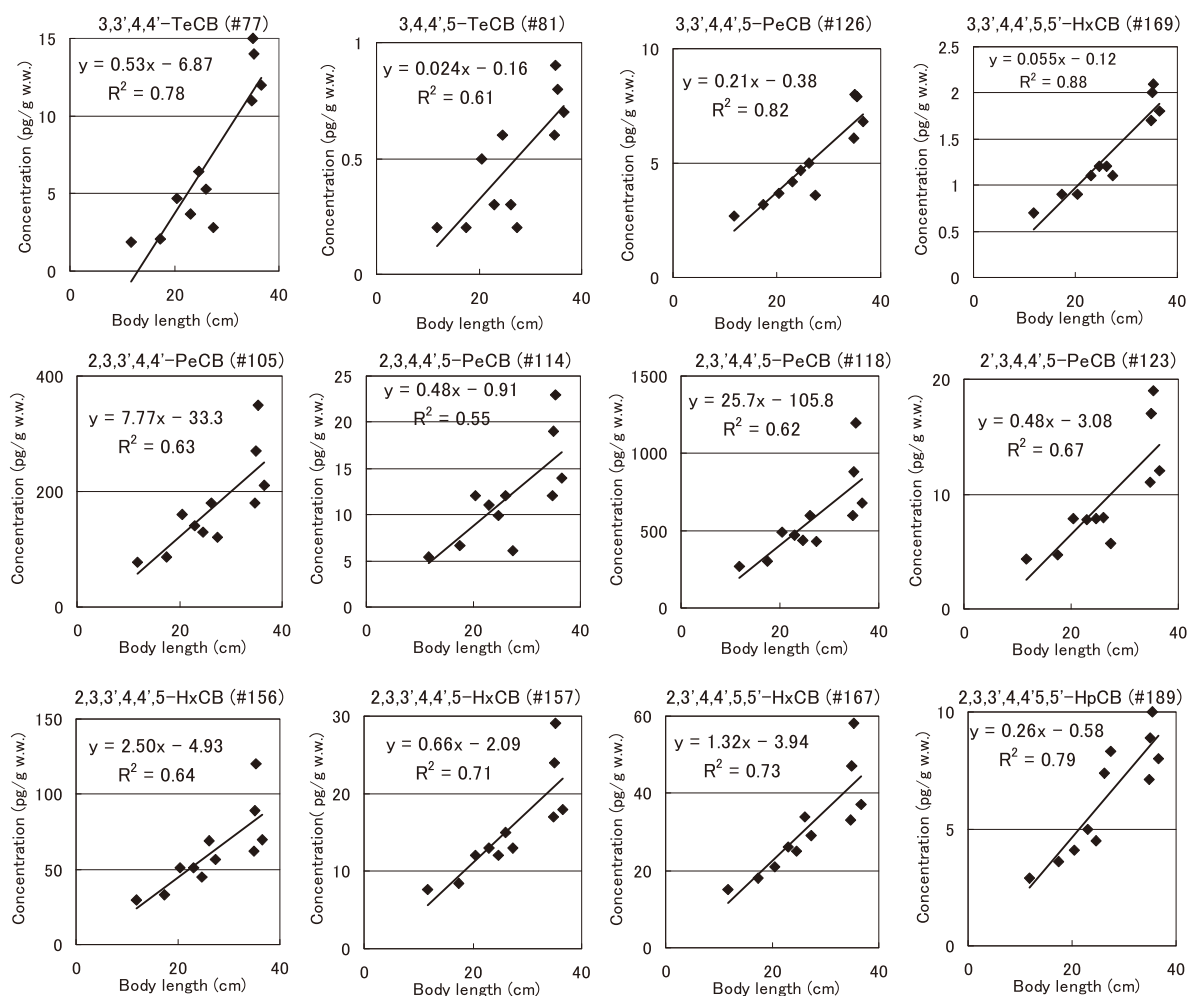


Fig. 9. Relationship between body length and concentration for individual Co-PCB.

Kim *et al.* 1996, Niimi 1996, Yamada 1997a). This may explain why the concentration of 2, 3, 7, 8-TeCDD was significantly correlated with body length, and why the slope of the linear regression was positive (Fig. 7).

OCDD, which belongs to the group of 1, 4- or 6, 9-substituted PCDD/F congeners, does not pass easily through the cell membrane, and consequently does not bioaccumulate in aquatic organisms as do the lower chlorinated 2, 3, 7, 8-substituted PCDD/Fs (Sijm *et al.* 1993, Yamada 1997a). 1, 2, 3, 6, 7, 8-HxCDD is a large and highly chlorinated 2, 3, 7, 8-substituted PCDD/F. It may be that 1, 2, 3, 6, 7, 8-HxCDD, like OCDD, also does not pass easily through the cell membrane.

The accumulation of chemicals can vary at each growth stage of fish; the bioconcentration of the herbicide toxaphene in larvae and juveniles of

killifish (*Fundulus heteroclitus*) is higher than that in adults, and the bioconcentration factor decreases as the fish grow (Schimmel *et al.* 1977). This may be related to the fact that growth rates decrease as the fish grow; for example, 21% growth per day (based on ww) for 30-mm fish compared with 1.5% per day for 280-mm fish in Japanese flounder (Yamashita *et al.* 2001).

The bioaccumulation of 1, 2, 3, 6, 7, 8-HxCDD and OCDD may also be higher in larvae and juveniles than in adult fish. The bioaccumulation of 1, 2, 3, 6, 7, 8-HxCDD and OCDD decreases with increasing size. As a result, the concentrations of 1, 2, 3, 6, 7, 8-HxCDD and OCDD were negatively correlated with body length.

The difference in the regression yielding the best fit—polynomial for 1, 2, 3, 6, 7, 8-HxCDD and linear for OCDD—may be related to the concentrations in

seawater, or may reflect the difference in congener structures. OCDD concentrations were higher than 1, 2, 3, 6, 7, 8-HxCDD in seawater. OCDD may show higher bioaccumulation in larvae and juveniles than 1, 2, 3, 6, 7, 8-HxCDD.

2.2.3.2. Bioaccumulation of PCDFs and the relationship between concentration and body length

There is no consistent pattern to the slopes of the linear regressions for the relationships between the concentrations of PCDF congeners and flatfish body length (Fig. 8). There was no predominant PCDF congener. The total PCDF concentration was not significantly correlated with body length (Fig. 6).

The slopes of the linear regressions for 2, 3, 7, 8-TeCDF and 2, 3, 4, 7, 8-PeCDF concentrations vs. body length were positive (Fig. 8), which suggests that these congeners bioaccumulate in Japanese flounder as fish grow. This result is similar to that obtained for 2, 3, 7, 8-TeCDD. In contrast, the slopes of the linear regressions for 2, 3, 4, 6, 7, 8-HxCDF, and for 1, 2, 3, 4, 7, 8- and 1, 2, 3, 4, 7, 9-HxCDF combined, were negative. It is likely that these three congeners did not bioaccumulate as fish grew. This result is similar to that obtained for OCDD.

2.2.3.3. Bioaccumulation of Co-PCBs and the relationship between concentration and body length

The concentrations of all of the Co-PCB congeners were significantly correlated with body length (Fig. 9) and increased with increasing body length. The slopes of all linear regressions were positive. Therefore, the total Co-PCB concentration was also significantly correlated with body length and increased with increasing body length.

The uptake rate and concentration of PCBs in fish are known to be higher than those of PCDD/Fs (Opperhuizen and Sijm 1990, Niimi 1996). The concentration of total Co-PCBs in Japanese flounder was also higher than total PCDD/Fs concentrations despite the fact that the total Co-PCB concentrations in seawater and sediment were lower than the total PCDD/F concentrations (Chapter 2.1). In addition, the dietary absorption efficiencies of Co-PCB

congeners are known to be similar (Niimi 1996). In this study, the slopes of the linear regressions for the relationship between Co-PCB concentration and body length (that is, the bioaccumulation properties of Co-PCBs) were also similar (Fig. 9). All of the Co-PCB congeners showed high bioaccumulation, so it is possible that the Co-PCB congeners in Japanese flounder bioaccumulated during a long exposure. This long exposure may explain why the concentrations were significantly correlated with body length, and why the slopes of the linear regression were positive (Fig. 9).

2.2.3.4. TEQ values in Japanese flounder

The TEQ values from Co-PCBs made up 46.3%–63.7% of the total TEQ values for all dioxins in Japanese flounder (Table 1, Fig. 6). Despite the fact that the concentration of non-*ortho* PCBs in Japanese flounder was lower than that of mono-*ortho* PCBs, the TEQ values for non-*ortho* PCBs were higher than those for mono-*ortho* PCBs (Fig. 6). The TEQ values for non-*ortho* PCBs showed a greater increase with increasing body length than did the values for PCDDs, PCDFs, and mono-*ortho* PCBs. For risk assessment, these results indicate that non-*ortho* PCBs are the most important dioxins in Japanese flounder in Sendai Bay.

Chapter 3. Historical trend of dioxins in sediment cores from Sendai Bay

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 solids then sink to the sea bottom and accumulate in the bottom sediments. Therefore, sediments have been monitored to investigate pollution by heavy metals (Matsumoto and Yokota 1978), polycyclic aromatic hydrocarbons (Handa and Ohta 1983) and other chemicals (Yamashita *et al.* 2000), from the perspective of risk assessment. In addition, 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).

In this chapter, the density, ignition loss, water content, and ^{210}Pb and ^{137}Cs concentrations in a sediment core collected in Sendai Bay were determined, and the sedimentation rate of the suspended solids was calculated. The vertical change in concentrations of dioxin congeners in sediment core samples also were determined by HRGC/HRMS. The amounts of dioxin congeners released annually from PCP, CNP (Japan Plant Protection Association 1963–1995), and PCB products (Tatsukawa 1972) were obtained from published data. Comparing these data allowed us to investigate changes in dioxin fluxes from the terrestrial areas of Miyagi Prefecture to Sendai Bay over time.

3.1. Materials and Methods

3.1.1. Sampling

Sediment cores approximately 80 cm long were collected with sediment core samplers (ϕ 20 cm \times 100 cm) from two sampling sites in Sendai Bay: off Naruse (lat $38^{\circ}20'N$, long $141^{\circ}13'E$) and off Ishinomaki (lat $38^{\circ}21'N$, long $141^{\circ}23'E$) on 19 September 2002 (Fig. 10). Two sediment cores that were less disturbed by organisms and showed uniform deposition were selected for the analysis from the total of five sediment cores collected. In the laboratory, the cores were sliced into 2-cm-long

segments. Samples were refrigerated or frozen until use.

3.1.2. Analysis of density, ignition loss, and water content of sediment core samples

Density, ignition loss, and water content of the sediments were determined according to methods described by the Japan Industrial Standard (Japan Industrial Standard Committee 1999a, 1999b, 2000). Briefly, 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. Distilled water was added until the pycnometer was full and the pycnometer was weighed. The density of the sediment was calculated.

To measure water content, refrigerated samples were weighed 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 again, and the original water content of each sample was calculated from the weight difference.

To measure ignition loss, refrigerated samples were placed in a crucible and dried overnight in a dryer at 110°C . The dried samples were weighed, and then the samples were combusted at 800°C in an electric furnace for 6 h and reweighed. Ignition

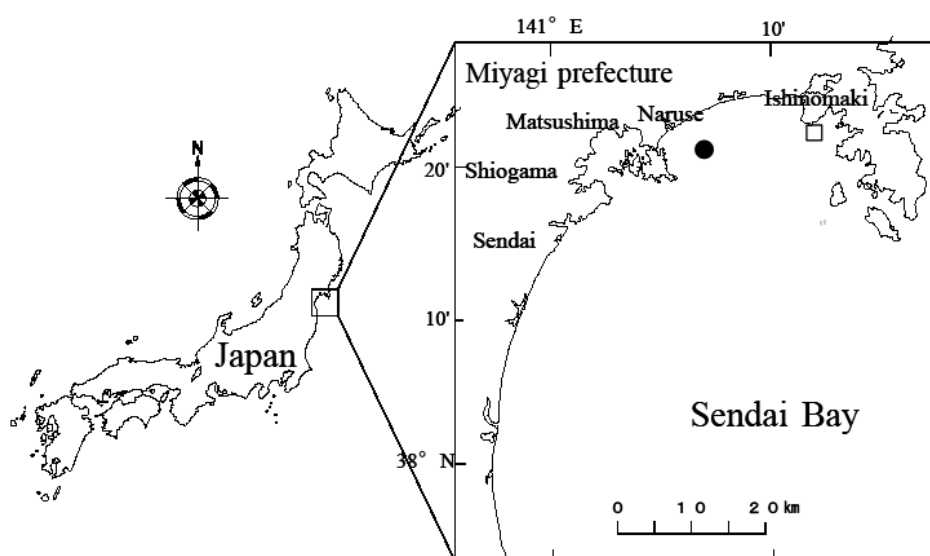


Fig. 10. Location of the sampling sites in Sendai Bay. ●: Sampling site off Naruse; □: sampling site off Ishinomaki.

loss in the sediment sample was calculated as the weight difference.

3.1.3. Analysis of ^{210}Pb and ^{137}Cs concentrations

^{210}Pb and ^{137}Cs 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 combusted in an electric furnace.

Lead from the combusted 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 d, and then the β -emitter (^{210}Bi , 1.1 MeV) in lead sulfate was measured for 24 h with a low-background gas-flow counter (β -spectrometry; OXFORD, Lb4100-W). ^{210}Pb concentrations were corrected by using the count of the β -emitter standard (712 Bq, Japan Radioisotope Association) for ^{210}Pb .

In addition to ^{210}Pb derived from ^{222}Rn in air, ^{210}Pb is also found in sediment (supported ^{210}Pb). Supported (background) ^{210}Pb is a decay product of the ^{226}Ra found in water and sediment not including ^{210}Pb in the suspended sediments that settles from the sea surface to the sea floor. Accordingly, excess ^{210}Pb ($^{210}\text{Pb}_{\text{ex}}$) was calculated as [total ^{210}Pb] - [supported ^{210}Pb]. Here, background ^{210}Pb concentrations (supported ^{210}Pb) were calculated by averaging the ^{210}Pb concentrations in sediments from core depths of 68–70, 58–60, and 48–50 cm.

The cumulative sedimentation rate by weight was calculated as:

$$\text{Sr} = (0.693/22.2)/|S| \quad (3.1)$$

where S is the slope of the line describing the relationship between $\log(^{210}\text{Pb}_{\text{ex}})$ and cumulative weight (-0.0993; Fig. 11), 0.693 is the disintegration coefficient of ^{210}Pb , and 22.2 y is the half-life of ^{210}Pb .

^{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 .

3.1.4. Analysis of dioxins and TEQs

The procedures for chemical analysis of dioxins and calculation of TEQs are described in Chapter 2.1.

3.2. Results

3.2.1. Sediment accumulation histories as determined from ^{210}Pb and ^{137}Cs activities

$^{210}\text{Pb}_{\text{ex}}$ values from 1 and 3 cm depth in the core collected off Naruse (hereafter, Naruse sample) were lower than those in layers below 5 cm (Fig. 11). This surface layer was interpreted as being mixed. Except for in the surface layer, $^{210}\text{Pb}_{\text{ex}}$ values decreased with depth and were significantly correlated with cumulative weight ($r^2=0.90$, $P < 0.01$). The sedimentation rate was calculated from the relationship between cumulative weight and $^{210}\text{Pb}_{\text{ex}}$ (Eq. 3.1) as $0.314 \text{ g cm}^{-2} \text{ y}^{-1}$. In the core collected off Ishinomaki (hereafter, Ishinomaki sample), $^{210}\text{Pb}_{\text{ex}}$ values decreased over the depth interval from 2 to 16 cm and were significantly correlated with cumulative weight ($r^2=0.91$, $P < 0.01$; Fig. 12). Therefore, the layer from 2 to 16 cm depth was interpreted as not mixed. The sedimentation rate in this layer was calculated from the relationship between cumulative weight and $^{210}\text{Pb}_{\text{ex}}$ as $0.112 \text{ g cm}^{-2} \text{ y}^{-1}$.

^{137}Cs activity was detected above 22–24 cm depth in the Naruse sample (Fig. 13), and above 10–12 cm depth in the Ishinomaki sample (Fig. 14). These earliest records of ^{137}Cs activity in these cores are attributed to the detonation of atomic bombs (Hiroshima and Nagasaki in 1945) and to early nuclear testing (e.g., at Bikini atoll in 1954), and so the time of deposition for these sediments was placed from the mid-1940s to the early 1950s. Two peaks in ^{137}Cs activity were observed in the Naruse sample at 6–8 and 14–16 cm depth, the activity was higher than 10 Bq/kg (Fig. 13). Two peaks in ^{137}Cs activity were also observed in the Ishinomaki sample, at 2–4 cm depth and at 6–8 cm depth, with activities above 10 Bq/kg from 2 to 8 cm depth (Fig. 14). The peaks in ^{137}Cs activity at 14–18 cm depth in the Naruse sample and 6–8 cm depth in the Ishinomaki sample were attributed to atmospheric nuclear testing carried out during the 1960s and

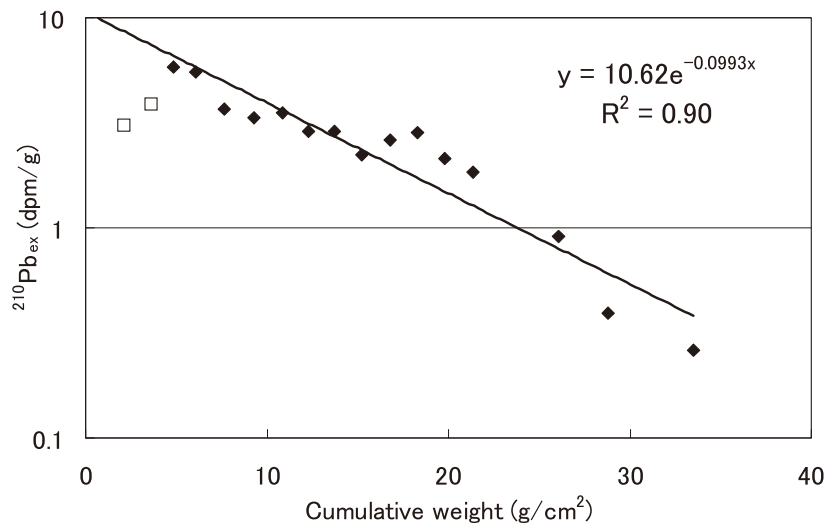


Fig. 11. Relationship between cumulative weight and $^{210}\text{Pb}_{\text{ex}}$ in the sediment core collected off Naruse in Sendai Bay. $^{210}\text{Pb}_{\text{ex}}$ was calculated as the ^{210}Pb activity per gram in each 2-cm sediment sample less the average ^{210}Pb activity (0.42 ± 0.009 dpm/g) in sediments at depths of 48–50, 58–60, and 68–70 cm (used as the background or supported activity). \blacklozenge , Data points used in the calculation; \square , data points for samples from 2–4 and 4–6 cm depth not used in the calculation.

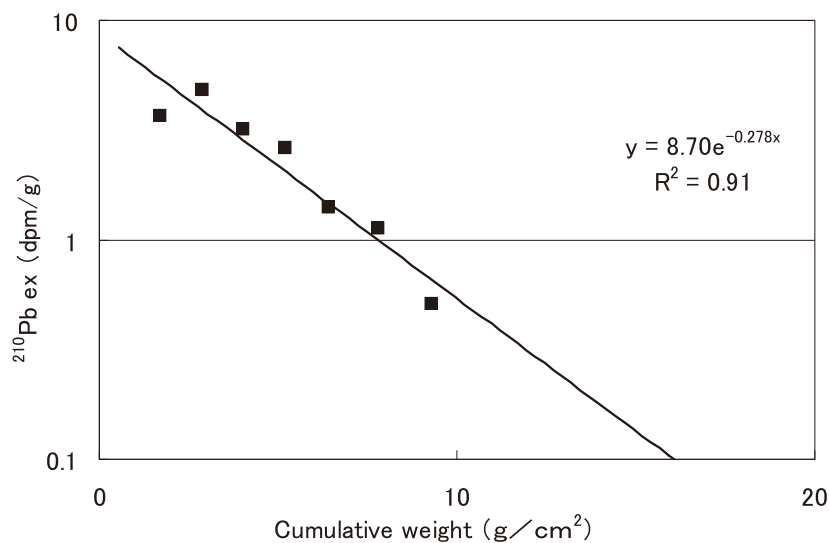


Fig. 12. Relationship between cumulative weight and $^{210}\text{Pb}_{\text{ex}}$ in the sediment core collected off Ishinomaki in Sendai Bay. $^{210}\text{Pb}_{\text{ex}}$ was calculated as the ^{210}Pb activity per gram in each 2-cm sediment sample less the average ^{210}Pb activity (0.63 ± 0.017 dpm/g) in 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).

thus dated those sediments to approximately that time period (Figs. 13 and 14). The peaks at 6–8 cm depth in the Naruse sample and 2–4 cm depth in the Ishinomaki sample were thought to mark the accident at the Chernobyl nuclear power plant in 1986, so the deposition period for these sediments was set to the mid-1980s (Figs. 13 and 14).

These tentative dates were verified by using the sedimentation rates determined from ^{210}Pb activities. Assuming that the sediments at 6–8 cm depth in the Naruse sample were deposited in 1987, then the time elapsed since deposition can be estimated from the cumulative sediment weight (4.83 g cm^{-2} ; Fig. 11) and the ^{210}Pb -based sedimentation rate calculated for this site ($0.314 \text{ g cm}^{-2} \text{ y}^{-1}$) as 15.4 y ($4.83/0.314$). Likewise, the time elapsed since deposition of the sediments at 22–24 cm depth is calculated from the cumulative weight (16.81 g cm^{-2} ; Fig. 11) as 53.5 y ($16.81/0.314$), or 38 years earlier ($53.5 - 15.4$) than the sediments at 6–8 cm depth (1987 - 38 = 1949).

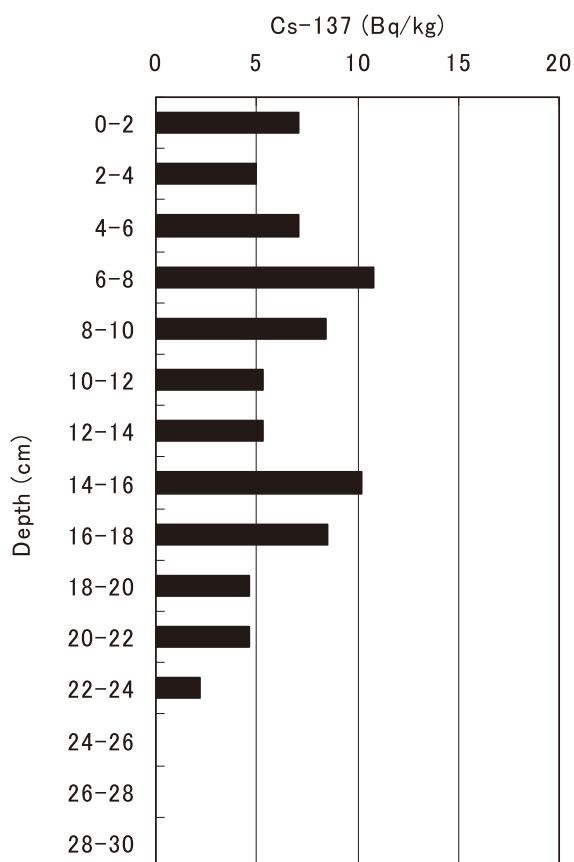


Fig. 13. Vertical distribution of ^{137}Cs activity in the sediment core collected off Naruse in Sendai Bay.

Assuming that the sediments at 2–4 cm depth in the Ishinomaki sample were deposited in 1987, then the time since deposition can be similarly calculated from the cumulative weight (1.69 g cm^{-2} ; Fig. 12) and the ^{210}Pb -based sedimentation rate for this site ($0.112 \text{ g cm}^{-2} \text{ y}^{-1}$) as 15.1 y ($1.69/0.112$). The time since deposition of the sediments at 10–12 cm depth can be likewise calculated from the cumulative weight (6.41 g cm^{-2} ; Fig. 12) as 57.2 y ($6.41/0.112$), or 42 years earlier ($57.2 - 15.1$) than 1987, or 1945. Thus, the periods of deposition determined from the ^{137}Cs activity peaks agree with those calculated by using the sedimentation rates determined from ^{210}Pb activities.

3.2.2. Composition and historical trends of dioxins in sediment cores

In sediments from 0 to 30 cm depth (deposited from the mid-1930s to 2002) in the Naruse sample and from 0 to 4 cm depth (deposited from the early 1980s to 2002) in the Ishinomaki sample, total PCDDs accounted for over 80% of the total dioxin concentrations (Figs. 15 and 16; Table 2). The dominant PCDD congeners were 1, 3, 6, 8-TeCDD, 1, 3, 7, 9-TeCDD, and OCDD, which together accounted for 79%–84% of the total PCDD concentrations; PCDFs accounted for 3%–7% of the

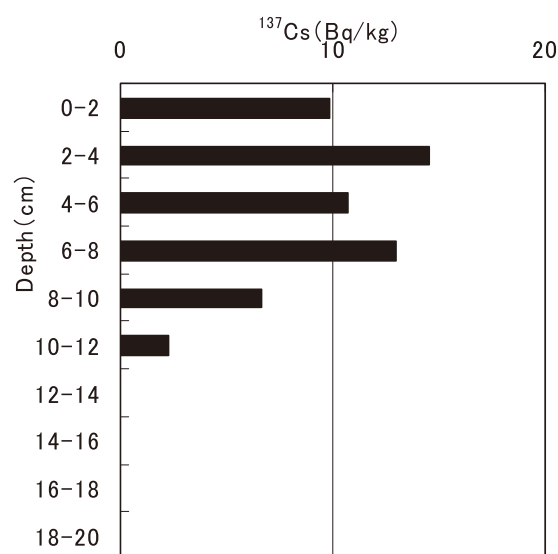


Fig. 14. Vertical distribution of ^{137}Cs activity in the sediment core collected off Ishinomaki in Sendai Bay.

total PCDD + PCDF concentrations (Fig. 15, Table 2). Although Co-PCBs accounted for less than 10% of dioxins, PCB #118, the most abundant Co-PCB congener, accounted for 52%–62% of the total Co-PCB concentration (Fig. 16, Table 2). PCB #105, the next most abundant Co-PCB congener, accounted for

19%–23% of the total Co-PCB concentration. PCB #81 and PCB #169 concentrations were below the detection limit.

In the Naruse sample, dioxin concentrations in sediments deposited in the mid-1930s and in the mid-1980s were 413 and 3870 pg/g dw, respectively

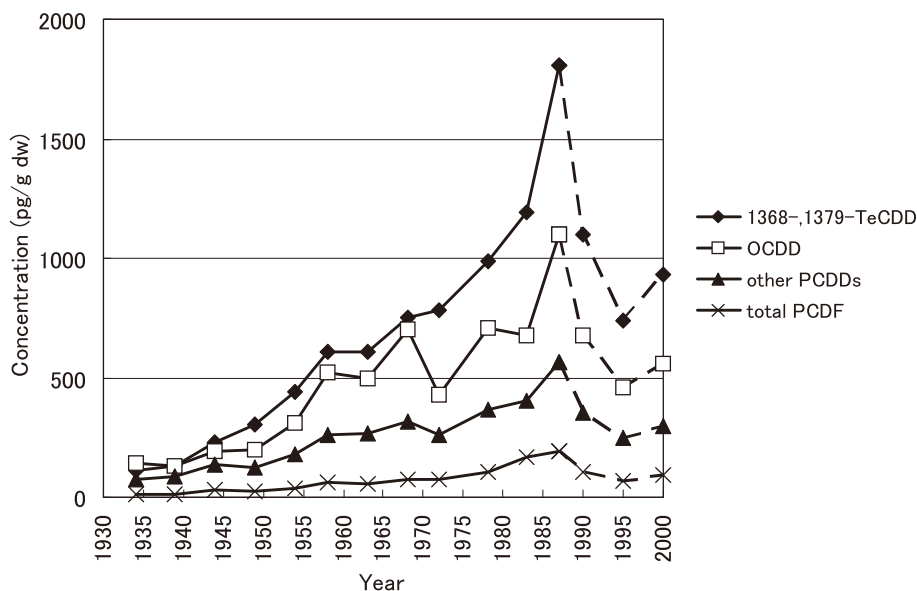


Fig. 15. Changes in PCDD/F concentrations with time in the sediment core collected off Naruse in Sendai Bay. The sediment core depth (cm) corresponding to each sediment deposition year is shown in Table 3.

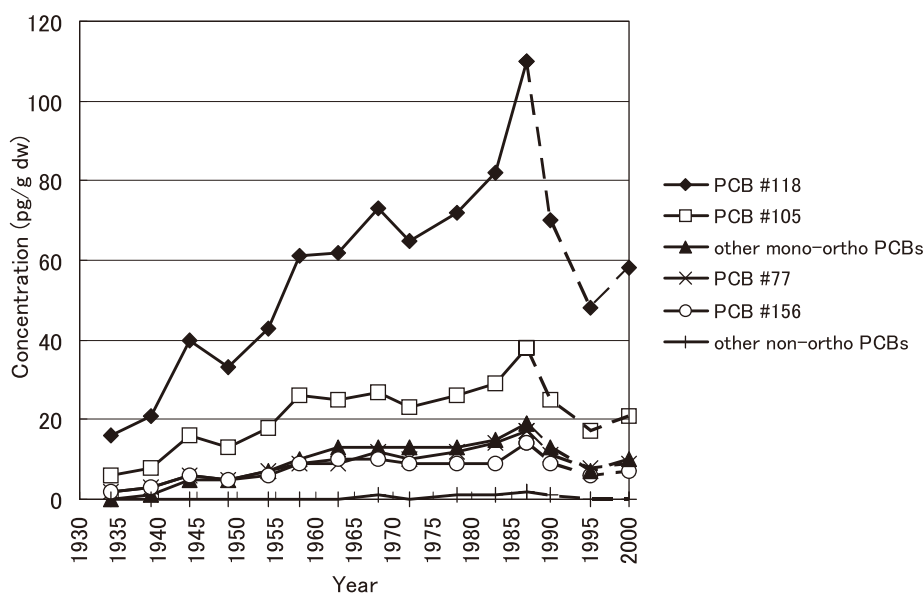


Fig. 16. Changes in Co-PCB concentrations with time in the sediment core collected off Naruse in Sendai Bay. The sediment core depth (cm) corresponding to each sediment deposition year is shown in Table 3.

(Figs. 15 and 16). Dioxin concentrations increased from the mid-1930s and reached a maximum in the mid-1980s. 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD concentrations also increased from the mid-1930s and reached a maximum in the mid-1980s. The concentration in sediments deposited in the mid-1980s (1800 pg/g dw) was more than 10 times that in sediments deposited in the mid-1930s (110 pg/g dw). OCDD showed a similar trend: the concentration in sediments deposited in the mid-1980s (1100 pg/g dw) was about 8 times that in sediments deposited in the mid-1930s (140 pg/g dw). The total concentrations of other PCDD (80–570 pg/g dw), PCDF (10–190 pg/g dw), and Co-PCB (30–200 pg/g dw) congeners, although lower than those of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD or OCDD, showed similar trends.

Although Naruse sample from the surface layer (<5 cm depth) was interpreted as being mixed (Fig. 11), dioxin concentrations in sediments tended to decrease from the late 1980s to the present (Figs. 15 and 16). In the Ishinomaki sample, dioxin concentrations in sediments also decreased from 1847 pg/g dw in sediments deposited in the mid-1980s, to 1564 pg/g dw in sediments deposited in the 2000s (Table 2). Concentrations of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD, OCDD, and other PCDDs, PCDFs, and Co-PCBs showed similar trends, decreasing from the late 1980s to the present.

3.2.3. History of dioxin sources

The history of shipments of CNP and PCP products to Miyagi Prefecture and the amounts of PCBs used in Japan are shown in Figures 17 and 18. 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. In 1970, the amount of PCBs used in Japan reached a maximum of 11,100 t.

3.2.4. TEQ values

TEQ values of dioxins in the sediment core from Sendai Bay (Naruse sample) ranged from 1.05 to 5.95 pg-TEQ/g (Table 3). TEQ values of dioxins increased after the late 1930s, reaching a maximum in the mid-1980s. TEQ values of dioxins then decreased from the late 1980s to the present (Tables 2 and 3).

3.3. Discussion

3.3.1. Sedimentation rate in Sendai Bay compared with other areas of Japan

The sedimentation rates off Ishinomaki and Naruse in Sendai Bay were $0.112 \text{ g cm}^{-2} \text{ y}^{-1}$ and $0.314 \text{ g cm}^{-2} \text{ y}^{-1}$, respectively. The sedimentation rate off Ishinomaki was approximately one-third that off Naruse. Thus, the sedimentation rate in Sendai Bay varies with location. Various sedimentation rates have been reported for different parts of Japan by other studies (all values are expressed as $\text{g cm}^{-2} \text{ y}^{-1}$; average \pm S.D.): 0.116 ± 0.063 ($n=5$), Funka 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 $0.24 \text{ g cm}^{-2} \text{ y}^{-1}$.

The sedimentation rate off Naruse was between those reported for Tokyo Bay and Nagoya Port, and higher than this average. The sedimentation rate off Ishinomaki was lower than this average and similar to that reported for Funka Bay.

3.3.2. History of dioxin sources in Sendai Bay

The composition of the dioxin congeners in sediments of Sendai Bay did not notably change during the period from the mid-1930s to the 2000s (Figs. 15 and 16, Table 2). This result suggests that the composition of dioxin congeners in the major sources discharged into Sendai Bay from Miyagi Prefecture has been similar since the 1930s.

1, 3, 6, 8-TeCDD and 1, 3, 7, 9-TeCDD were derived from impurities in CNP, and OCDD from impurities in PCP, from the 1960s to the 2000s (Masunaga *et al.* 2001a, Seike *et al.* 2003). Pesticides such as CNP and PCP were shipped mainly to agricultural areas rather than to urban areas. In particular, shipments of CNP products to Miyagi Prefecture, the so-called granary of Japan, were the largest in Japan in 1971, 1975, 1976, 1979, 1981, and

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

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

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

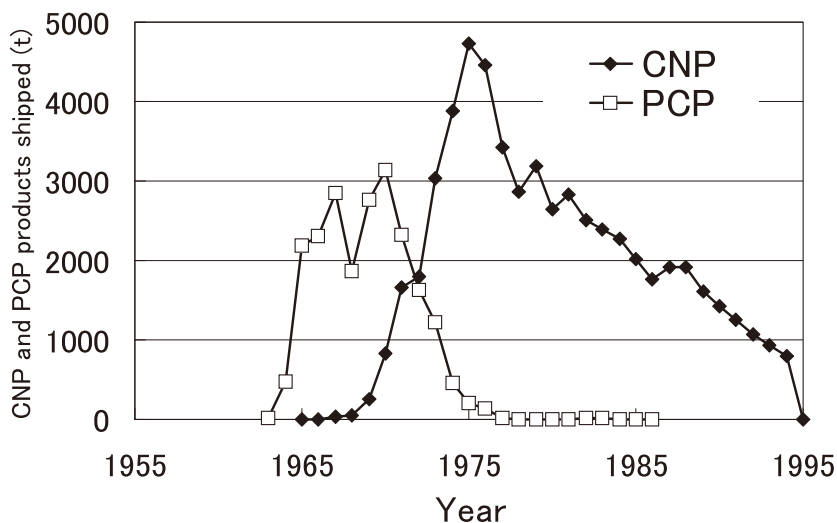


Fig. 17. Amounts of CNP and PCP products (t) shipped to Miyagi Prefecture 1963-1995, calculated from data in the Agrochemical Handbook (Japan Plant Protection Association 1963-1995). Because the Agrochemical Handbook was first published in 1963, information on shipments of PCP products to Miyagi Prefecture before that date is not available.

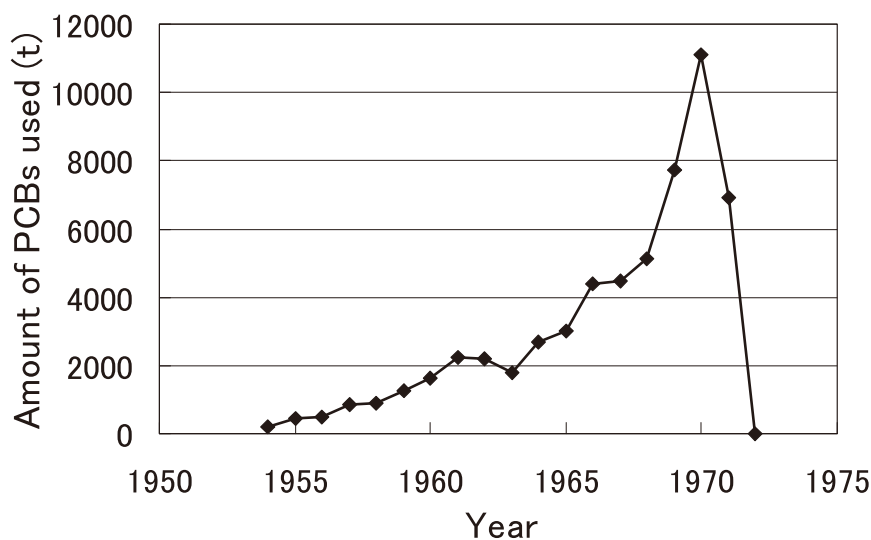


Fig. 18. Quantities of PCBs (t) used in Japan, based on data published by Tatsukawa (1972)

Table 3. TEQ concentrations according to depth in the sediment core from off Naruse.

depth (cm)	28-30	26-28	24-26	22-24	20-22	18-20	16-18	14-16	12-14	10-12	8-10	6-8	4-6	2-4	0-2
age (year)	1934	1939	1944	1949	1954	1958	1963	1968	1972	1978	1983	1987	1990	1995	2000
TEQ of PCDDs	0.73	0.75	0.98	1.07	1.36	1.80	1.80	2.04	1.80	2.40	2.94	3.82	2.39	1.70	2.07
TEQ of PCDFs	0.28	0.37	0.54	0.49	0.62	0.81	0.70	0.86	0.99	1.25	2.00	1.93	1.29	0.84	1.04
TEQ of Co-PCBs	0.04	0.05	0.07	0.06	0.07	0.10	0.10	0.15	0.10	0.13	0.15	0.20	0.13	0.09	0.10
TEQ of dioxins	1.05	1.17	1.59	1.62	2.06	2.71	2.60	3.05	2.90	3.78	5.09	5.95	3.81	2.64	3.20

1982 and from 1984 to 1989 (Japan Plant Protection Association 1971, 1975, 1976, 1979, 1981, 1982, 1984–1989). Although the total amount of CNP products used in Japan was less than the total of PCP products (Yao *et al.* 2002), the total shipments of CNP products to Miyagi Prefecture was greater than that of PCP products (Fig. 17). Thus, TeCDDs have been the predominant homologues in Sendai Bay since the 1960s. Although other studies of dioxin concentrations in sediments have found PCDD concentrations to be higher than PCDF or Co-PCB concentrations, most studies have reported OCDD, rather than TeCDDs, to be the predominant dioxin congener in Japan (Sakai *et al.* 1999, Kubota *et al.* 2002, Yao *et al.* 2002, Masunaga *et al.* 2001b). The sediment cores collected in Sendai Bay were characterized by the dominance of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD, with a concentration higher than that of OCDD for a long period. Therefore, the composition of PCDDs in the sediments of Sendai Bay differed from the compositions in other parts of Japan, such as the offshore region of the Yodo River, the Uwa Sea, Tokyo Bay, and Lake Shinji (Sakai *et al.* 1999, Kubota *et al.* 2002, Yao *et al.* 2002, Masunaga *et al.* 2001b).

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 of this PCB product (Fig. 16, Table 2). PCB #169, which is derived from combustion (Yao *et al.* 2002), was below the detection limit in sediments from Sendai Bay. From these facts, the major source of Co-PCBs in Sendai Bay since the mid-1950s is inferred to be PCB products; combustion was much less important.

Because there are no suitable data concerning the shipment of chlorinated pesticides, accurately determining the sources of dioxins for the 1930s to the 1960s is difficult. However, there are several reports concerning possible sources of dioxins before the 1960s. Coal combustion has been a major energy source since the 19th century (Czuczwa and Hites

1984). An average of 35 million tons of coal was produced each year in Japan from 1930 to 1937 (Yao *et al.* 2002). In the 1940s, the production of chlorinated organic compounds, which are used in a variety of products, including building supplies, herbicides, and packaging, increased substantially (Czuczwa and Hites 1984). Also, chlorinated organic compounds such as DDT were registered and used as agricultural chemicals in Japan during the 1940s (Agricultural Chemicals Inspection Station 2003). Therefore, from the 1930s to the 1960s, major dioxin sources in Miyagi Prefecture may have been coal or agricultural chemicals.

3.3.3. Dioxin concentrations in sediments in Sendai Bay compared with those in other areas of Japan

Dioxin concentrations increased in the cores from the mid-1930s and reached a maximum in the mid-1980s (Figs. 15 and 16). Dioxin concentrations in the sediments then decreased from the late 1980s to the present (Table 2).

For comparison, the maximum PCDD/F concentrations in sediments in the offshore region of the Yodo River were deposited in the early 1990s (Sakai *et al.* 1999). In Tokyo Bay, the maximum concentrations of OCDD, TeCDDs, and most Co-PCBs deposited in sediments were reported from the late 1960s to late 1970s (Yao *et al.* 2002). In Lake Shinji, the maximum concentration of OCDD, which was the predominant congener among PCDD/Fs in sediments, was reported in the early 1970s, and that of total non-*ortho* PCBs in the late 1960s (Masunaga *et al.* 2001b). In southern Lake Biwa, the maximum concentration of PCDD/Fs in sediments was deposited in the early 1970s (Sakai *et al.* 1999). Although the period of maximum use of CNP and PCP products did not vary much in different parts of Japan (Figs. 17 and 18; Yao *et al.* 2002), maximum dioxin concentrations in sediments were observed later in Miyagi Prefecture than in other parts of Japan.

3.3.4. Relationship between maximum dioxin concentrations in the sediments and the time of maximum use of CNP, PCP, and PCB products

The time of deposition of maximum concentrations of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD, OCDD, and Co-PCBs (all in mid-1980s' sediments) (Figs. 15–18, Table 2) did not correspond to the peak period for shipments of CNP (1975) or PCP (1970) products or to the period of maximum PCB use (1970). In other areas of Japan, the maximum concentration of major dioxin congeners in sediments in Lake Shinji (Masunaga *et al.* 2001b), in Tokyo Bay at 35° 33' N and 139° 55' E (Yao *et al.* 2002), and in Lake Biwa-South (Sakai *et al.* 1999), occurred before 1980. Although the timing of the peak period of CNP and PCP shipments to each prefecture differed slightly, the maximum concentrations of TeCDDs, 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. In contrast, the maximum concentrations of major dioxin congeners in sediments in Tokyo Bay at 35° 35' N and 139° 55' E (Yamashita *et al.* 2000), in Lake Biwa-North, and in the Yodo River offshore region (Sakai *et al.* 1999) occurred after 1980, as in Sendai Bay.

The lack of correspondence between maximum concentrations of major dioxin congeners in the sediments in Sendai Bay and the time of maximum use of CNP, PCP, and PCB products may be due to a smaller outflow of dioxins from land to bay, in comparison with total amount of CNP products used in Miyagi Prefecture. The use of CNP and PCP products was extremely high in Miyagi Prefecture compared with that in other Japanese prefectures (Japan Plant Protection Association 1971, 1975, 1976, 1979, 1981, 1982, 1984–1989); shipments of CNP products to Miyagi Prefecture accounted for approximately 8% of total production in Japan. The total PCDD/Fs derived from CNP were estimated to be approximately 190 t (Masunaga *et al.* 2001a), and 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD constituted approximately 88% of all dioxins. Therefore, the sum of 1, 3, 6, 8-TeCDD and 1, 3, 7, 9-TeCDD from CNP products used in Miyagi Prefecture is approximately 13 t (190 t · 0.08 · 0.88). On the other hand, the sedimentation rate in Sendai Bay was estimated at

0.314 g cm⁻² y⁻¹, the area of Sendai Bay is approximately 1600 km², and the concentration of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD in sediments from 1963 to 2000 ranged from 750 to 1810 pg/g dw. Thus, the total input of 1, 3, 6, 8-TeCDD and 1, 3, 7, 9-TeCDD to Sendai Bay between 1965 and 2000 was roughly estimated as 0.2 t (0.314 g cm⁻² y⁻¹ × 1,600 km² × 35 y × 750~1810 pg/g dw). Because the sum of 1, 3, 6, 8-TeCDD and 1, 3, 7, 9-TeCDD from CNP products used in Miyagi Prefecture (13 t) was much higher than the total input of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD to Sendai Bay from 1965 to 2000 (0.2 t), the river flow may function as a bottleneck that restricts the amount of these compounds that can reach the bay.

The delay between the time of maximum use of CNP, PCP, and PCB products and the occurrence of the maximum concentrations of major dioxin congeners in the sediments in Sendai Bay may be related to the distance from the dioxin sources on land to the sampling site in the bay. Major dioxin congeners (1, 3, 6, 8- + 1, 3, 7, 9-TeCDD) in the bay sediments are thought to have been carried by rivers. The Kitakami River, the largest river flowing into Sendai Bay and the fifth longest among all Japanese large rivers (A-class rivers), is 249 km long (River Bureau 2003). Some dioxin emission sources, such as the paddy fields along the river's upper reaches, may be far from Sendai Bay, so that the movement of dioxins from terrestrial areas to Sendai Bay requires a long time.

3.3.5. TEQ values

TEQ values of dioxins in sediment cores ranged from 4.4 to 83 pg-TEQ/g in Tokyo Bay (Yao *et al.* 2002) and from 0.014 to 17 pg-TEQ/g in the Uwa Sea (Kubota *et al.* 2002). TEQ values of PCDD/Fs in sediments in the Yodo River offshore region ranged from approximately 6 to 26 pg-TEQ/g (Sakai 1999). Even though for a period of several years, more CNP products were shipped to Miyagi Prefecture than to any other part of Japan (Japan Plant Protection Association 1963–1995), TEQ values of dioxins in the sediment core from Sendai Bay, ranging from 1.05 to 5.95 pg-TEQ/g (Tables 2 and 3), are lower than those reported from other areas. Because in other parts of Japan, the total amount of

PCP products used is larger than the total of CNP products (Yao *et al.* 2002), a TEF (0.0001) has been established for OCDD, which is the predominant dioxin congener in PCP products and in fly ash and exhaust emitted from incinerators, whereas no TEF (0) has been established for 1, 3, 6, 8-TeCDD or 1, 3, 7, 9-TeCDD, the predominant dioxin congeners in CNP products.

Chapter 4. Discharge of dioxins from terrestrial to marine environments

Dioxins released into the terrestrial environment can reach the marine environment, where they accumulate in marine organisms such as fish and invertebrates, and then accumulate in humans who eat seafood (Mato *et al.* 2007). As part of assessing risk from such chemicals, it is important to investigate their flux from land to sea via rivers, and their contribution to pollution of the marine environment. Numerous risk-assessment investigations have estimated the flux of these pollutants from the land to the sea via rivers (Isoaari *et al.* 2002, Verta *et al.* 2003, Kobayashi *et al.* 2004b). These studies have shown that the types of major dioxin congeners that are present vary in different regions, depending on the dioxin source. Because the point sources of dioxins and their concentrations and profiles vary in different regions, it is necessary to estimate dioxin fluxes independently for specific regions.

4.1. Dioxin concentrations and estimated sources in four major rivers of Miyagi Prefecture

1, 3, 6, 8- and 1, 3, 7, 9-TeCDD are major impurities in CNP. Further, OCDD is an impurity in PCP (Masunaga *et al.* 2001a, Seike *et al.* 2003). Because these congeners are the predominant dioxin homologues detected in paddy soils in Akita Prefecture, also in northern Honshu (Kobayashi *et al.* 2004a, Kiguchi *et al.* 2007), and in the sediments of Sendai Bay off Miyagi Prefecture (Chapters 2 and 3), it is reasonable to suppose that chlorinated pesticides from paddy fields in Miyagi Prefecture are major sources of the dioxins in Sendai Bay. To test this hypothesis, I used HRGC/HRMS to determine the concentrations and compositions of dioxin congeners

in water samples from four major rivers flowing into Sendai Bay. I investigated the major sources of PCDD/F and Co-PCB congeners in river water samples by using principal components analysis (PCA) and a chemical mass balance (CMB) analysis. I also determined the dry weights of total suspended solids (SS) in river water samples, and using previously collected data (Japan River Association 2002–2004, and unpublished data from the Ministry of Land, Infrastructure and Transport, Japan) on the flow rates of the rivers, I investigated the relationship between SS and dioxin concentrations in the river water.

4.1.1. Materials and Methods

4.1.1.1. Sampling of river water

River water sampling sites are shown in Fig. 19. Samples were collected between July 2000 and February 2003 at the mouths of the Kyu-Kitakami, Naruse, Natori, and Abukuma rivers, where the rivers flow into Sendai Bay. Each surface river water sample was collected in a water-sampling bucket and transferred to two 10-L glass bottles and a 5-L bottle. The water samples were stored at 5 °C in a refrigerator until analysis for dioxins and SS. Published river discharge data were obtained from the Japan River Association (2002–2004) and the Ministry of Land, Infrastructure and Transport, Japan.

4.1.1.2. Measurement of dry weight of total suspended solids

The dry weight of suspended solids was determined by the method described by Uematsu *et al.* (1978), with a small modification. First, each filter (Millipore HA filter; pore size: 0.45 μm) was dried in an oven at 60 °C for 3 d, cooled in a desiccator at room temperature, and then weighed with an analytical balance (filter mass = ma , g). After filtering 500–1000 mL of the river water sample from the 5-L bottle through the filter, the filter was dried again at 60 °C for 3 d and weighed (filter mass = mb , g) after cooling at room temperature. The dry weight of suspended solids (DW, g/L) was calculated as:

$$DW = (mb - ma)/v \quad (4.1)$$

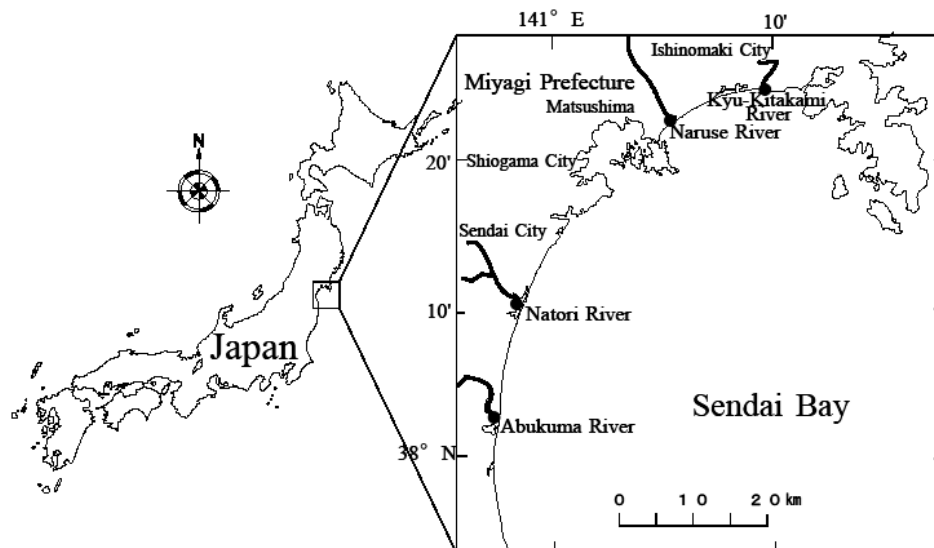


Fig. 19. Sampling sites (●) for surface river water at the mouths of the Kyu-Kitakami, Naruse, Natori, and Abukuma rivers.

where v is the volume (L) of sample water filtered.

The dry weights of SS were measured seven or eight times for each sampling location during the study.

4.1.1.3. Analysis of dioxins

The procedures for chemical analysis of dioxins are described in Chapter 2.1.

4.1.1.4. Principal components analysis (PCA) and chemical mass balance (CMB) analysis

To clarify the major sources of dioxin in the river water samples, I carried out a principal components analysis (PCA) with SPSS (11.5J) software. Because the sources of PCDD/Fs were thought to differ from those of Co-PCBs, I performed PCA with varimax rotation twice, with two data sets. First, I obtained typical profiles of PCDD/F congeners in probable major sources of PCDD/Fs in Japan from a previously published study (Kashiwagi *et al.* 2006); I obtained four profiles of PCDD/F congener impurities in each of the agricultural chemicals CNP and PCP, and one profile of PCDD/F congeners in incinerator exhaust gases (Fig. 20). Each typical profile comprised 27 PCDD/F congener groups (1,3,6,8-TeCDD, 1, 3, 7, 9-TeCDD, 2, 3, 7, 8-TeCDD, other TeCDDs, 1, 2, 3, 7, 8-PeCDD, other PeCDDs, 1, 2, 3, 4, 7, 8-HxCDD, other HxCDDs, 1,

2, 3, 6, 7, 8-HxCDD, 1, 2, 3, 7, 8, 9-HxCDD, 1, 2, 3, 4, 6, 7, 8-HpCDD, other HpCDDs, OCDD, 2, 3, 7, 8-TeCDF, other TeCDFs, 1, 2, 3, 7, 8-PeCDF, 2, 3, 4, 7, 8-PeCDF, other PeCDFs, 1, 2, 3, 4, 7, 8-HxCDF, 1, 2, 3, 6, 7, 8-HxCDF, 1, 2, 3, 7, 8, 9-HxCDF, 2, 3, 4, 6, 7, 8-HxCDF, other HxCDFs, 1, 2, 3, 4, 6, 7, 8-HpCDF, 1, 2, 3, 4, 7, 8, 9-HpCDF, other HpCDFs, and OCDF). The 104 PCDD/F congeners in the river water samples (41 TeCDD/F, 35 PeCDD/F, 20 HxCDD/F, 6 HpCDD/F, and 2 OCDD/F congeners; Table 4) were classified into the same 27 groups. Concentrations of PCDD/F congeners present in quantities lower than the detection limit were defined as zero. I analyzed all profiles, those of the 16 river water samples and 9 from previously published data (Kashiwagi *et al.* 2006), by PCA.

Second, I obtained profiles of PCB products from the likely Co-PCB sources, four for Kanechlor (KC300, KC400, KC500, KC600) and two for exhaust gases, from previously published data (Kashiwagi *et al.* 2006). Concentrations of Co-PCB congeners present in quantities lower than the detection limit were defined as zero. I analyzed all profiles, 16 for the river water samples and 6 from the previously published data (Kashiwagi *et al.* 2006), by PCA.

I conducted CMB analyses of PCDD/Fs using the same data set as used in the PCA, with CMB8J.xls

(Microsoft Excel add-in software; Hayakari and Hanaishi 2001) to clarify the relative contributions of dioxin sources to river water samples. This software is based on the free CMB8 software from the U.S. Environmental Protection Agency (Coulter 2004). Data resulting in low coefficients of determination ($r^2 < 0.8$) were reanalyzed after deletion of several congeners with low concentrations from the data set.

4.1.2. Results

4.1.2.1. Dioxin congeners and TEQs in river water

In Miyagi Prefecture, four major rivers, the Kyu-Kitakami, Naruse, Natori, and Abukuma rivers, flow into Sendai Bay; the upper reaches of the Kyu-Kitakami and Abukuma rivers also flow through the adjacent Iwate and Fukushima prefectures, respectively (Fig. 19).

The dioxin concentrations in samples from the four rivers are shown in Table 4a-c. PCDDs were present in higher concentrations in river water than were Co-PCBs or PCDFs. In all samples, total PCDDs accounted for more than 50% of total dioxins, and in several samples, they accounted for more than 90% of total dioxins (Table 4a). Total TeCDDs and OCDD accounted for more than 80% of total PCDDs. Because TeCDD concentrations were higher than OCDD concentrations, TeCDDs were the dominant PCDD homologues in river water. 1, 3, 6, 8- and 1, 3, 7, 9-TeCDD concentrations were markedly high among all TeCDD congeners, and 1, 3, 6, 8- and 1, 3, 7, 9-TeCDD together accounted for more than 90% of all TeCDDs (Table 4a).

Co-PCBs accounted for 0.7% to 9.8% of all dioxins detected in the Kyu-Kitakami River, 2.8% to 4.5% of those in the Naruse River, 11.3% to 40.9% of those in the Natori River, and 5.7% to 19.2% of those in the Abukuma River (Table 4c).

TEQs of samples collected on 11 July 2002 ranged from 1.16 to 7.49 pg-TEQ/L. TEQs of samples other than those collected on 11 July 2002 ranged from 0.0079 to 1.24 pg-TEQ/L (Table 4c).

4.1.2.2. Characterization of dioxin concentrations by PCA and CMB

In the PCA of PCDD/Fs, including the data from published literature, components 1 and 2 accounted

for 47.9% and 43.0%, respectively, of the total variance (Fig. 20). Thus, the percentage of variance accounted for by these two components was almost equal, and cumulatively they accounted for 90.8% of the total variance. Most PCDD/F congeners in the river water samples were therefore explained by these two components.

The typical CNP profiles plotted near the value of 1 on component 1 (x axis), while PCP and exhaust gas profiles plotted near value 0 on component 1. Thus, I interpreted component 1 as representing CNP. Most typical PCP profiles plotted near value 1 on component 2 (y axis), whereas CNP and exhaust gas profiles, and one PCP profile, plotted near 0 on component 2. Thus, I interpreted component 2 as representing PCP. The sample profiles plotted between values of 0 and 1 on both axes, and thus reflected both CNP and PCP.

In the PCA of Co-PCBs, components 1 and 2 accounted for 85.4% and 8.3% of the total variance, respectively (Fig. 21), and cumulatively accounted for 93.7% of the variance. Components 1 and 2 were strongly influenced by KC400 and KC500. Most samples plotted with KC400, and near KC500. I thus inferred that the sources of Co-PCBs in river water samples were PCB products, and that the importance of exhaust gases was low.

The CMB results indicate that the contribution of CNP as a major source of PCDD/Fs in the water samples ranged from 39% to 77%, and that of PCP from 20% to 58% (Table 4c). In every case, the sum of the CNP and PCP contribution accounted for more than 90% of total PCDD/Fs. Therefore, the CMB results suggest that the major sources of PCDD/Fs were CNP and PCP. Because the contribution from incinerator exhaust gases ranged from 0% to 5.8%, I inferred that their contribution to PCDD/Fs in the water samples was extremely low. In addition, the results of CMB analysis indicate that almost all Co-PCBs in river water samples were from PCB products (data not shown). This is consistent with the results of PCA of Co-PCBs.

4.1.2.3. Variations in dioxin concentrations with river flow rate and suspended solids content

The dioxin concentrations in the four rivers were determined on several sampling dates between 24

Table 4a. River flow rates, PCDD, PCDF, and Co-PCB concentrations in river water samples (pg/L), and sources of PCDD/Fs calculated by CMB.

River name Date	Kyu-Kitakami River			Naruse River			Natori River			Abukuma River			
	3 Oct. 2001	31 Jan. 2002	11 Jul. 2002	3 Oct. 2001	31 Jan. 2002	11 Jul. 2002	2 Oct. 2001	30 Jan. 2002	11 Jul. 2002	2 Oct. 2001	30 Jan. 2002	11 Jul. 2002	28 Feb. 2003
River flow rate (m ³ /s)	186.9	178.4	1222	124.5	13.5	62	28.4	33.7	742.1	5.6	209.3	5966	65.9
1368-TeCDD	46 (41%)	290 (25%)	1900 (36%)	76 (37%)	62 (47%)	57 (45%)	33 (29%)	14 (23%)	160 (21%)	36 (18%)	38 (24%)	79 (26%)	1700 (38%)
1379-TeCDD	15 (13%)	140 (12%)	770 (15%)	5.7 (13%)	78 (14%)	20 (16%)	12 (11%)	6.0 (9.8%)	7.2 (6.1%)	12 (7.5%)	30 (10%)	720 (16%)	1.6 (7.5%)
1378-TeCDD	N.D.	0.5	3.2	N.D.	0.1	N.D.	N.D.	N.D.	0.3	N.D.	0.4	0.9	2.7
1369/1247/1248-TeCDD	0.5	3.5	24	0.2	0.7	0.7	0.4	0.2	1.3	N.D.	0.4	0.9	2.6
1268-TeCDD	N.D.	0.3	1.5	N.D.	N.D.	N.D.	N.D.	N.D.	0.1	N.D.	N.D.	1.4	N.D.
1478-TeCDD	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.1	N.D.
2378-TeCDD	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.2	N.D.
1237-TeCDD	N.D.	0.7	4.9	N.D.	0.1	0.1	N.D.	N.D.	0.3	N.D.	0.1	0.2	4.3
1234/1246/1249/1238-TeCDD	0.4	2.5	18	0.4	0.5	0.5	0.5	0.2	1.0	0.1	0.5	0.9	16
1236/1279-TeCDD	N.D.	0.6	3.0	N.D.	0.1	N.D.	N.D.	N.D.	0.3	N.D.	N.D.	0.1	2.6
1469/1278-TeCDD	N.D.	N.D.	0.5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1239-TeCDD	N.D.	N.D.	0.5	N.D.	N.D.	N.D.	N.D.	N.D.	0.8	N.D.	N.D.	N.D.	0.4
1269-TeCDD	N.D.	N.D.	0.1	N.D.	N.D.	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	0.2
1289-TeCDD	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	N.D.
total TeCDD	62 (55%)	438 (38%)	2726 (52%)	22 (52%)	82 (62%)	78 (61%)	46 (41%)	20 (33%)	234 (30%)	4.9 (25%)	51 (32%)	111 (37%)	2475 (55%)
12468/12479-PeCDD	0.8	7.9	49	0.5	1.2	1.0	0.8	0.4	3.3	0.2	1.0	2.3	0.2
12368-PeCDD	3.7	42	250	1.7	4.7	5.1	4.3	1.7	12	0.5	4.1	11	200
12478-PeCDD	N.D.	0.1	0.8	N.D.	N.D.	N.D.	N.D.	N.D.	0.3	N.D.	N.D.	N.D.	1.4
12379-PeCDD	1.1	14	88	0.6	1.6	1.6	1.3	0.6	4.2	0.2	1.3	3.8	68
12469/12347-PeCDD	N.D.	0.5	3.1	N.D.	N.D.	N.D.	N.D.	N.D.	0.9	N.D.	N.D.	0.2	3.5
12378-PeCDD	N.D.	0.4	2.0	N.D.	N.D.	N.D.	N.D.	N.D.	0.3	N.D.	N.D.	0.1	2.2
12369-PeCDD	N.D.	N.D.	0.6	N.D.	N.D.	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	1.1
12467-PeCDD	N.D.	N.D.	0.3	N.D.	N.D.	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	0.4
12489-PeCDD	N.D.	N.D.	0.3	N.D.	N.D.	N.D.	N.D.	N.D.	0.3	N.D.	N.D.	N.D.	0.5
12346-PeCDD	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.3
12367-PeCDD	N.D.	N.D.	0.3	N.D.	N.D.	N.D.	N.D.	N.D.	0.1	N.D.	N.D.	N.D.	0.4
12389-PeCDD	N.D.	0.1	0.8	N.D.	N.D.	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	0.9
total PeCDD	5.6 (5.0%)	65 (5.7%)	395 (7.5%)	2.8 (6.5%)	7.5 (5.7%)	7.7 (6.0%)	6.4 (5.7%)	2.7 (4.4%)	22 (2.8%)	0.9 (4.5%)	6.4 (4.0%)	17 (5.8%)	316 (7.1%)
123468/124679/124689-HxCDD	0.4	4.7	24	0.3	0.8	0.5	0.6	0.6	7.4	0.3	1.3	1.6	25
123679/123689-HxCDD	0.3	4.0	20	0.2	0.6	0.4	0.4	0.3	3.8	N.D.	0.8	1.2	18
123478-HxCDD	N.D.	0.4	1.9	N.D.	N.D.	N.D.	N.D.	N.D.	0.4	N.D.	N.D.	N.D.	2.2
123678-HxCDD	N.D.	1.3	5.3	N.D.	N.D.	N.D.	N.D.	N.D.	0.9	N.D.	N.D.	0.4	5.5
123469-HxCDD	N.D.	N.D.	0.4	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.6
123789-HxCDD	N.D.	1.1	4.4	N.D.	N.D.	N.D.	N.D.	N.D.	0.3	N.D.	N.D.	0.2	4.1
123467-HxCDD	N.D.	N.D.	0.8	N.D.	N.D.	N.D.	N.D.	N.D.	0.9	N.D.	N.D.	N.D.	1.1
total HxCDD	0.7 (0.6%)	11.5 (1.0%)	56.8 (1.1%)	0.5 (1.2%)	7.4 (1.1%)	0.9 (0.7%)	1.0 (0.9%)	0.9 (1.5%)	14 (1.8%)	0.3 (1.5%)	2.1 (1.3%)	3.4 (1.1%)	56.5 (1.3%)
1234679-HpCDD	2.0	22	100	0.8	3.7	2.0	2.7	1.6	21	0.5	5.6	7.2	57
1234678-HpCDD	1.7	23	93	0.6	2.6	1.7	2.2	1.5	18	0.3	4.2	6.6	66
total HpCDD	3.7 (3.3%)	45 (3.9%)	193 (3.7%)	1.4 (3.3%)	6.3 (4.8%)	3.7 (2.9%)	4.9 (4.4%)	3.1 (5.0%)	39 (5.0%)	0.8 (4.0%)	9.8 (6.2%)	14 (4.6%)	123 (2.7%)
OCDD	29 (26%)	520 (46%)	1500 (29%)	71 (26%)	28 (20%)	26 (20%)	36 (32%)	23 (37%)	280 (36%)	4.6 (23%)	65 (41%)	120 (40%)	690 (15%)
total PCDDs	101 (89%)	1080 (95%)	4871 (93%)	38 (88%)	123 (93%)	117 (91%)	94 (84%)	50 (82%)	588 (76%)	12 (58%)	134 (84%)	266 (89%)	3660 (82%)
1368-TeCDF	N.D.	N.D.	0.6	N.D.	N.D.	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	1.2
1378/1379-TeCDF	N.D.	N.D.	0.4	N.D.	N.D.	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	1.1
1347-TeCDF	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	N.D.	N.D.	0.1	N.D.	N.D.	N.D.	0.5
1468-TeCDF	N.D.	0.3	2.1	N.D.	N.D.	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	2.4
1247/1367-TeCDF	N.D.	N.D.	0.6	N.D.	N.D.	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	1.5
1348-TeCDF	N.D.	N.D.	0.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.5
1346/1248-TeCDF	N.D.	0.1	1.1	N.D.	N.D.	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	2.3
1246/1268-TeCDF	N.D.	0.1	1.1	N.D.	N.D.	N.D.	N.D.	N.D.	0.3	N.D.	N.D.	N.D.	2.0
1478/1369/1237-TeCDF	N.D.	N.D.	0.6	N.D.	N.D.	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	1.4
1678/1234-TeCDF	N.D.	N.D.	0.6	N.D.	N.D.	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	1.2
2468/1238/1467/1236-TeCDF	2.2	13	90	0.7	2	2.5	1.6	0.7	4.8	0.2	1.7	3.5	80

Table 4b.

River name	Kyu-Kitakami River				Naruse River				Natori River				Abukuma River			
	3. Oct. 2001	31th Ja. 2002	11th Jul. 2002	28th Feb. 2003	24th Jul. 2000	3th Oct. 2001	31th Ja. 2002	11th Jul. 2002	2th Oct. 2001	30th Ja. 2002	11th Jul. 2002	28th Feb. 2003	2th Oct. 2001	30th Ja. 2002	11th Jul. 2002	28th Feb. 2003
1349-TeCDF	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.1	N.D.
1278-TeCDF	N.D.	0.5	N.D.	N.D.	N.D.	N.D.	0.6	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	1.5	N.D.
1267/1279-TeCDF	N.D.	N.D.	0.3	N.D.	N.D.	N.D.	0.4	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	0.8	N.D.
1469-TeCDF	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.4	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.1	N.D.
1249/2368-TeCDF	N.D.	0.1	1.1	N.D.	N.D.	N.D.	1.4	N.D.	N.D.	N.D.	0.3	N.D.	N.D.	1.7	N.D.	N.D.
2467-TeCDF	N.D.	0.3	2.1	N.D.	N.D.	0.1	2.4	N.D.	N.D.	N.D.	0.3	N.D.	N.D.	2.4	N.D.	N.D.
2347-TeCDF	N.D.	N.D.	0.4	N.D.	N.D.	N.D.	0.5	N.D.	N.D.	N.D.	0.1	N.D.	N.D.	1.0	N.D.	N.D.
1269-TeCDF	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.1	N.D.	N.D.
2378-TeCDF	N.D.	0.4	N.D.	N.D.	N.D.	N.D.	0.5	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	1.3	N.D.	N.D.
2348-TeCDF	N.D.	N.D.	0.6	N.D.	N.D.	N.D.	0.8	N.D.	N.D.	N.D.	0.1	N.D.	N.D.	1.0	N.D.	N.D.
2346-TeCDF	N.D.	N.D.	0.8	N.D.	N.D.	N.D.	1.0	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	1.1	N.D.	N.D.
2367-TeCDF	N.D.	N.D.	0.5	N.D.	N.D.	N.D.	0.7	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	1.1	N.D.	N.D.
3467-TeCDF	N.D.	N.D.	0.7	N.D.	N.D.	N.D.	0.8	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	1.0	N.D.	N.D.
1289-TeCDF	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.1	N.D.	N.D.
total TeCDF	2.2 (1.9%)	13.8 (1.2%)	105 (2.0%)	0.7 (1.6%)	2.1 (1.6%)	2.5 (2.0%)	6.1 (1.5%)	118 (2.2%)	1.6 (1.4%)	0.7 (1.1%)	8.6 (1.1%)	0.2 (1.0%)	1.7 (1.1%)	3.7 (1.2%)	107 (2.4%)	0.2 (0.9%)
13468-PeCDF	N.D.	0.7	N.D.	N.D.	N.D.	N.D.	0.8	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	1.1	N.D.
12468-PeCDF	0.2	1.8	9.8	N.D.	0.2	0.7	12	0.2	0.2	0.1	0.8	N.D.	0.3	0.5	9.6	N.D.
13678-PeCDF	N.D.	N.D.	0.3	N.D.	N.D.	N.D.	0.5	N.D.	N.D.	N.D.	0.1	N.D.	N.D.	N.D.	0.9	N.D.
13479-PeCDF	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.2	N.D.
12368/13478-PeCDF	N.D.	0.2	1.4	N.D.	N.D.	0.1	1.7	N.D.	N.D.	N.D.	0.4	N.D.	0.1	0.1	2.4	N.D.
12478-PeCDF	N.D.	0.2	1.2	N.D.	N.D.	N.D.	1.2	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	0.1	2.3	N.D.
12479/13467-PeCDF	N.D.	N.D.	0.7	N.D.	N.D.	N.D.	0.9	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	1.3	N.D.
12467-PeCDF	N.D.	N.D.	0.5	N.D.	N.D.	N.D.	0.7	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	1.4	N.D.	N.D.
14678/12347-PeCDF	N.D.	0.1	0.8	N.D.	N.D.	N.D.	0.9	N.D.	N.D.	N.D.	0.3	N.D.	N.D.	N.D.	1.9	N.D.
13469-PeCDF	N.D.	0.2	N.D.	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.2	N.D.	N.D.
12348/12378-PeCDF	N.D.	0.1	0.8	N.D.	N.D.	N.D.	1.1	N.D.	N.D.	N.D.	0.3	N.D.	N.D.	0.1	2.7	N.D.
12346-PeCDF	N.D.	N.D.	0.4	N.D.	N.D.	N.D.	0.5	N.D.	N.D.	N.D.	0.1	N.D.	N.D.	0.8	N.D.	N.D.
12379-PeCDF	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.1	N.D.	N.D.
12367-PeCDF	N.D.	N.D.	0.4	N.D.	N.D.	N.D.	0.5	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	0.7	N.D.	N.D.
12469/12678-PeCDF	N.D.	0.1	0.8	N.D.	N.D.	N.D.	1.0	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	1.7	N.D.	N.D.
12679-PeCDF	N.D.	0.1	N.D.	N.D.	N.D.	N.D.	0.1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.2	N.D.	N.D.
12368-PeCDF	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.1	N.D.	N.D.
23468-PeCDF	0.3	2.8	17	0.1	0.4	1.2	22	0.3	0.3	0.1	1.0	N.D.	0.3	0.7	15	N.D.
12349-PeCDF	N.D.	N.D.	0.1	N.D.	N.D.	N.D.	0.1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.1	N.D.	N.D.
12489-PeCDF	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.4	N.D.	N.D.
23478-PeCDF	N.D.	0.1	0.8	N.D.	N.D.	N.D.	1.0	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	2.0	N.D.	N.D.
12389-PeCDF	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.1	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.1	N.D.	N.D.
23467-PeCDF	N.D.	0.2	1.6	N.D.	N.D.	N.D.	1.9	N.D.	N.D.	N.D.	0.5	N.D.	N.D.	2.5	N.D.	N.D.
total PeCDF	0.5 (0.4%)	5.6 (0.5%)	37.8 (0.7%)	0.1 (0.2%)	0.6 (0.5%)	0.6 (0.5%)	2.1 (0.5%)	47.4 (0.9%)	0.5 (0.4%)	0.2 (0.3%)	4.9 (0.6%)	0 (0%)	0.7 (0.4%)	1.6 (0.5%)	47.7 (1.1%)	0 (0%)
123468-HxCDF	1.4	5.9	N.D.	N.D.	0.2	0.6	6.3	N.D.	N.D.	N.D.	0.7	N.D.	0.2	0.5	6.5	N.D.
134678/134679-HxCDF	0.2	1.6	N.D.	N.D.	N.D.	N.D.	2.0	N.D.	N.D.	N.D.	0.5	N.D.	N.D.	N.D.	3.1	N.D.
124678-HxCDF	N.D.	2.2	9.2	N.D.	0.3	0.8	8.7	0.2	0.2	N.D.	1.4	N.D.	0.4	0.8	10	N.D.
124679-HxCDF	N.D.	N.D.	0.6	N.D.	N.D.	N.D.	0.6	N.D.	N.D.	N.D.	0.7	N.D.	N.D.	0.8	N.D.	N.D.
123478/123479-HxCDF	N.D.	0.7	2.8	N.D.	N.D.	0.2	2.5	N.D.	N.D.	N.D.	0.4	N.D.	N.D.	0.3	5.4	N.D.
123678-HxCDF	N.D.	0.4	1.9	N.D.	N.D.	N.D.	1.9	N.D.	N.D.	N.D.	0.4	N.D.	N.D.	2.8	N.D.	N.D.
124689-HxCDF	N.D.	1.9	8.0	N.D.	N.D.	0.6	7.9	N.D.	N.D.	N.D.	1.0	N.D.	0.3	9.9	N.D.	N.D.
123467-HxCDF	N.D.	0.3	1.5	N.D.	N.D.	N.D.	1.9	N.D.	N.D.	N.D.	0.5	N.D.	N.D.	3.2	N.D.	N.D.
123679-HxCDF	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.3	N.D.	N.D.
123469/123689-HxCDF	N.D.	0.3	1.5	N.D.	N.D.	N.D.	1.4	N.D.	N.D.	N.D.	0.2	N.D.	N.D.	1.9	N.D.	N.D.
123789-HxCDF	N.D.	N.D.	0.4	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.3	N.D.	N.D.
123489-HxCDF	N.D.	N.D.	0.4	N.D.	N.D.	N.D.	0.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.6	N.D.	N.D.
234678-HxCDF	N.D.	0.6	3.0	N.D.	N.D.	N.D.	3.6	N.D.	N.D.	N.D.	0.5	N.D.	N.D.	3.7	N.D.	N.D.
total HxCDF	0 (0%)	8.0 (0.7%)	36.4 (0.7%)	0 (0%)	0.5 (0.4%)	0 (0%)	2.4 (0.6%)	37.3 (0.7%)	0.2 (0.2%)	0 (0%)	5.9 (0.8%)	0 (0%)	0.9 (0.6%)	2.4 (0.8%)	48.5 (1.1%)	0 (0%)
1234678-HpCDF	0.4	4.6	19	N.D.	0.6	1.6	19	N.D.	0.6	0.4	3.4	N.D.	0.9	1.8	26	N.D.
1234679-HpCDF	N.D.	0.2	1.5	N.D.	N.D.	N.D.	1.8	N.D.	N.D.	N.D.	0.4	N.D.	0.1	N.D.	2.5	N.D.
1234689-HpCDF	0.6	8.1	32	N.D.	0.7	0.6	28	0.9	0.5	0.5	4.7	N.D.	1.3	2.8	0.4	N.D.
1234789-HpCDF	N.D.	0.8	3.7	N.D.	N.D.	N.D.	3.2	N.D.	N.D.	N.D.	0.6	N.D.	0.2	0.3	4.3	N.D.

July 2000 and 28 February 2003; water flow in the rivers varied among the sampling dates (Table 4a-c). The flow rates were low on 24 July 2000 and 28 February 2003. In contrast, a typhoon struck Miyagi Prefecture in the early morning of 11 July 2002 (Japan Meteorological Agency 2002). Rainfall associated with the typhoon began on 10 July 2002, and more than 100 mm of precipitation was observed on both 10 and 11 July at several observation points in Miyagi Prefecture. As a result, the river flow rates increased greatly on those days. On 11 July

2002, after the typhoon had passed, concentrations were markedly higher: 5240 pg/L in the Kyu-Kitakami River, 5401 pg/L in the Naruse River, 777 pg/L in the Natori River, and 4473 pg/L in the Abukuma River (Table 4c, **bold**). When flow rates were low (on 24 July 2000 and on 28 Feb. 2003), dioxin concentrations in all four rivers were below 200 pg/L, and they were particularly low, about 20 pg/L, in the Natori and Abukuma Rivers (Table 4c, *italic*). The dioxin concentrations measured at high flow rates were thus 30 to 200 times those at low

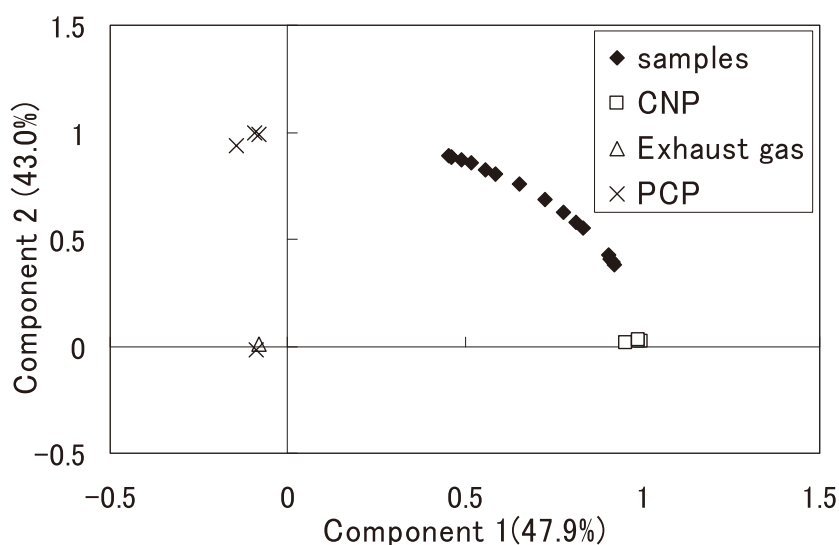


Fig. 20. PCA plot of PCDD/Fs in river water samples and in potential sources (from Kashiwagi et al. 2006).

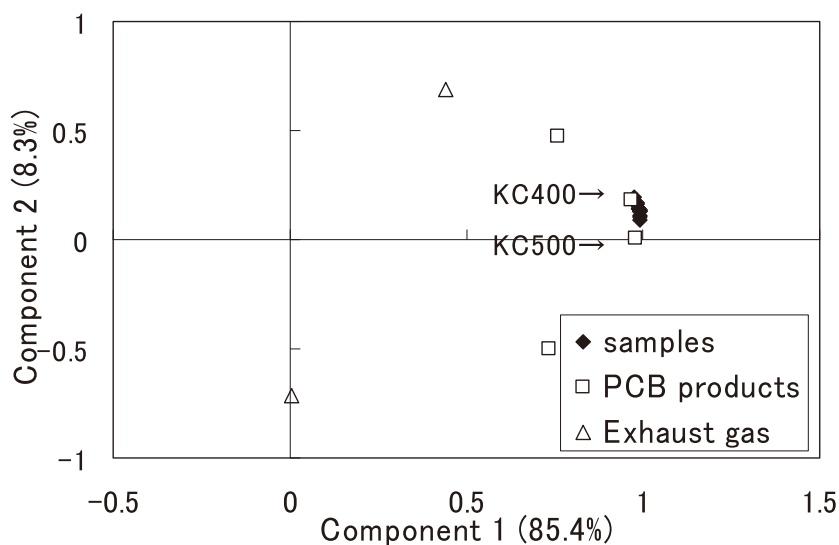


Fig. 21. PCA plot of Co-PCBs in river water samples and in potential sources (from Kashiwagi et al. 2006).

flow rates.

Total dioxin concentrations increased with increasing river flow rates (Fig. 22). For each river, the total dioxin concentration (x ; $\mu\text{g/L}$) was significantly and positively correlated with the daily discharge (y ; m^3/s) (Kyu-Kitakami, $\log y = 1.77 \times \log x - 1.68$, $r^2 = 0.7$; Naruse, $\log y = 0.80 \times \log x + 1.11$, $r^2 = 0.92$; Natori, $\log y = 0.74 \times \log x + 0.79$, $r^2 = 0.96$; and Abukuma, $\log y = 1.11 \times \log x - 0.46$, $r^2 = 0.93$; $P < 0.05$ for all).

Similarly, for each river, the logarithm of the SS concentration (mg/L) was positively correlated with the logarithm of flow rates (m^3/s ; $r^2 = 0.87$ for Kyu-Kitakami, 0.92 for Naruse, 0.84 for Natori, and 0.87 for Abukuma; $P < 0.05$ for all) (Fig. 23).

4.1.3. Discussion

4.1.3.1. Dioxin congeners and TEQs in river water

In river water, 1, 3, 6, 8-TeCDD, 1, 3, 7, 9-TeCDD and OCDD were the dominant dioxin homologues (Table 4). Several dioxin congeners are known to be associated with particular dioxin emission sources (Hashimoto 2004, Verta *et al.* 2007). For example, 2, 3, 7, 8-TeCDF has been detected in pulp mill bleaching wastes (Rappe *et al.* 1989); OCDF from a plant producing vinyl chloride monomers (Isosaari *et al.* 2000); 1, 3, 6, 8-TeCDF, 1, 3, 6, 7, 8-PeCDF, and 1, 2, 3, 4, 7, 9-HxCDF in wastes from a dye manufacturing plant (Kakimoto *et al.* 2006); and 1, 2, 7, 8-TeCDD, 2, 3, 7, 8-TeCDF, 1, 2, 3, 7, 8-PeCDD,

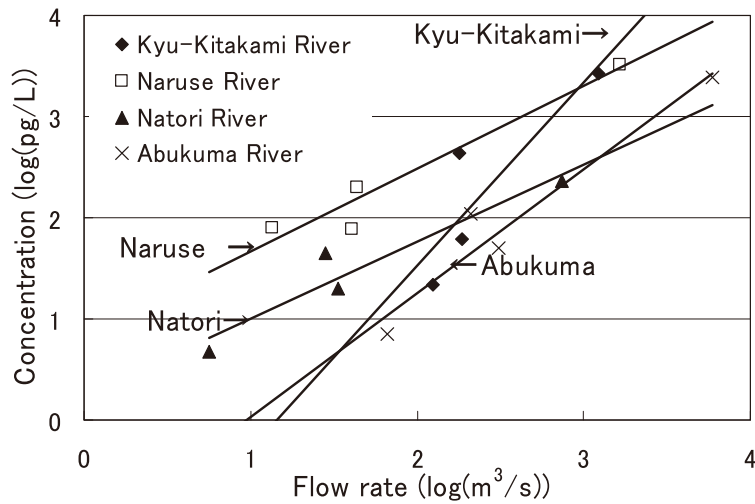


Fig. 22. Relationships between river flow rates and total dioxin concentrations in four large rivers in Miyagi Prefecture.

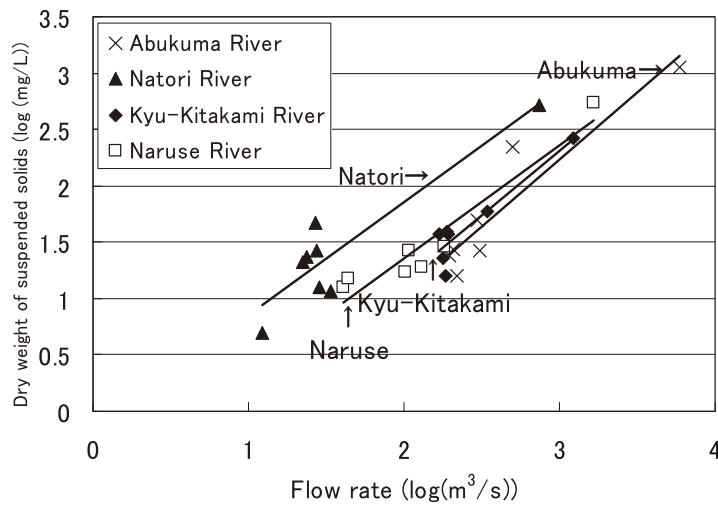


Fig. 23. Relationships between river flow rates and suspended solids concentrations in four large rivers in Miyagi Prefecture.

1, 2, 3, 4, 7, 8-HxCDF, and 1, 2, 3, 4, 6, 7, 8-HpCDF in industrial wastewaters from acetylene, caprolactam, pigment, and potassium sulfate factories (Hashimoto 2004). Similarly, TeCDF is a byproduct of the production of trichlorobenzenes (Schrann *et al.* 1995); 1, 2, 3, 4, 6, 7, 8-HpCDF has been detected in chlorophenols (Verta *et al.* 1999, 2003, Isosaari *et al.* 2002); OCDD in general air samples (Lohmann and Jones 1998) and in PCP (Masunaga *et al.* 2001a, Seike *et al.* 2003); 1, 3, 6, 8-TeCDD and 1, 3, 7, 9-TeCDD in CNP (Masunaga *et al.* 2001a, Seike *et al.* 2003); and 1, 3, 6, 8- and 1, 3, 7, 9-TeCDD, and OCDD are known to be major dioxin congeners in paddy soils in Japan (Seike *et al.* 2003, Kobayashi *et al.* 2004a, Uegaki *et al.* 2006). Moreover, compositions of dioxin congener assemblages in river waters were similar to those in paddy soil, in sediments of rivers draining agricultural areas in Japan (Kobayashi *et al.* 2004a, Kiguchi *et al.* 2007), and in sediments in Sendai Bay (Chapters 2 and 3, this study). I considered paddy fields to be the major source of dioxins in river water, in seawater, and in sediment samples from Sendai Bay.

Impurities in chlorinated pesticides were less abundant and the ratio of Co-PCBs to total dioxins was higher in the Natori River than in the other rivers (Table 4). These differences may be because the Natori River, which flows to Sendai Bay through the city of Sendai, has fewer paddy fields and more PCB products in its catchment than the other rivers.

Except for the TEQs of the samples collected on 11 July 2002, the TEQs found in this study ranged from 0.01 to 1.2. TEQs of river water samples collected in Hokuriku District and near Tokyo Bay ranged from 0.11 to 1.6 pg-TEQ/L (Kakimoto *et al.* 2006) and from about 0.1 to 0.8 pg-TEQ/L (Takada 1997), respectively. Therefore, the TEQs in this study were similar to those reported in studies conducted in other parts of Japan.

4.1.3.2. Characterization of dioxin concentrations by PCA and CMB

The PCA and CMB results indicate that the major dioxins sources in the river water samples were CNP and PCP (Fig. 20 and Table 4c). Impurities in the chlorinated pesticides CNP and PCP, and

incinerator exhaust gases, have been identified as major sources of dioxins in river water in Japan (Kobayashi *et al.* 2003, Kiguchi *et al.* 2007), but the sources are considered to differ according to the character of the river basin, whether urban or agricultural (Kiguchi *et al.* 2007). Major dioxin sources in river water samples collected in the Tokyo Metropolitan Area and in Kanagawa Prefecture, which are largely urbanized, were reported to be exhaust gases (Kobayashi *et al.* 2003), whereas major dioxin sources in river water samples collected in Akita Prefecture were reported to be CNP and PCP (Kobayashi *et al.* 2004a). Thus, in this study, the results of river water samples collected in Miyagi Prefecture were similar to those for agricultural rather than urban areas.

4.1.3.3. Variations in dioxin concentrations with river flow rate

The dioxin concentrations measured at high flow rates on 11 July 2002 were 30 to 200 times those at low flow rates (Table 4; Fig. 22). These results suggest that large amounts of dioxins were discharged into Sendai Bay during the flood event.

In general, paddy fields are flooded with water from rivers in spring and summer during rice plowing, planting, and growing. Dioxin concentrations in rivers during these seasons are reported to be higher than those in autumn (Kakimoto *et al.* 2006). In Miyagi Prefecture, July is the rice-growing season, and the paddy fields are flooded with river water. The high dioxin concentrations on 11 July 2002 is attributable to the fact that the region was struck by a typhoon when the paddy fields were flooded with river water. Thus, dioxins in the paddy field soils could be easily transferred into the rivers.

4.1.3.4. Changes in total dioxin concentrations with suspended solid loads

Total dioxin concentrations increased with increasing river flow rates (Fig. 22). These results are consistent with those of a previous report, in which the TEQ of dioxins was linearly related to river water discharge near Tokyo Bay (Kobayashi *et al.* 2004b). Similarly, for each river sampled in this study, the logarithm of the SS concentration (mg/L)

was positively correlated with the logarithm of daily discharge (Fig. 23). These results are also consistent with previously reported results (Takada 1997).

Dioxin congeners are water-insoluble, and they are easily adsorbed onto suspended solids (Brochu *et al.* 1995). A previous study found that TEQs of suspended-phase dioxins in river water were higher than those of dissolved-phase dioxins (Kobayashi *et al.* 2004b), and TEQ values of dioxins in river water also increased with the concentration of SS (Kobayashi *et al.* 2004b, Kakimoto *et al.* 2006). Thus, the results of this study suggest that dioxins remaining in paddy soils and/or riverbed sediments were discharged in large quantities to Sendai Bay during flooding.

4.2. Estimated dioxin discharges into Sendai Bay from terrestrial sources in Miyagi Prefecture

As part of a program to estimate dioxin flux into Sendai Bay over the last several decades, I estimated the annual flux of major dioxin congeners discharged from the terrestrial environment into Sendai Bay by four major rivers.

4.2.1. Materials and Methods

The daily 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD flux u (g/d) from each river was calculated as:

$$u = w \times x \quad (4.2)$$

where w is the concentration of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD calculated from the relationship between water flow rate (m^3/s) and 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD concentration (pg/L) in each river (Table 5) and x is the daily flow rate (m^3/d). I used the data presented in Chapter 4.1 to determine the linear equations describing the relationships between flow rates and concentrations, and then compiled Table 6. I obtained the daily flow rates for each river from 1999–2002 from published data (Japan River Association 2001–2004). To determine daily 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD concentrations for each river, I used one of the two equations shown in Table 5. The correlation coefficients for the equations based on non-transformed data were higher than those using log-transformed data. When flow rates were high, the daily dioxin fluxes were calculated using non-transformed data. When the flow rate was near zero, the daily dioxin fluxes calculated from the non-

transformed data plotted near the intercept, and a negative intercept implies a negative daily flux. However, daily fluxes calculated from the log-transformed values are always positive. Therefore I used the following approach to determine which equation to use: when the discharge was less than a node between the non-transformed equation and the log-transformed equation, I used the logarithmic equation. Otherwise, I used the real number equation.

The annual 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD flux y (g/y) from each river to Sendai Bay was then calculated as follows:

$$y = \Sigma u \quad (4.3)$$

where Σu is the sum of the daily 1,3,6,8- + 1,3,7,9-TeCDD flux discharges from each river to the bay over 1 year (g/y).

The annual average daily 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD flux z (g/d) for each river was calculated as follows:

$$z = \Sigma u / 365 \quad (4.4)$$

The same approach was used to calculate annual average daily fluxes of OCDD and TEQs.

TEQs were calculated by using toxic equivalency factors (TEFs) provided by the World Health Organization (Van den Berg *et al.* 1998), instead of the I-TEQ calculated by using the international toxic equivalency factors (I-TEFs) given by Kurtz *et al.* (1990).

4.2.2. Results

4.2.2.1. Daily flow rate

Figure 24 shows published daily river flow rates for the Kyu-Kitakami, Naruse, Natori, and Abukuma rivers for 1999–2002 (Japan River Association 2001–2004). The summed average daily flow rate of the four rivers was $526 \text{ m}^3/\text{s}$ in 1999, $510 \text{ m}^3/\text{s}$ in 2000, $357 \text{ m}^3/\text{s}$ in 2001, and $401 \text{ m}^3/\text{s}$ in 2002, and their relative magnitudes were: $1999 > 2000 > 2002 > 2001$. The individual average daily flow rates of the Kyu-Kitakami, Naruse, Natori, and Abukuma rivers ranged from 165 to $296 \text{ m}^3/\text{s}$, 38 to $65 \text{ m}^3/\text{s}$, and 12 to $21 \text{ m}^3/\text{s}$, 139 to $182 \text{ m}^3/\text{s}$, respectively, and their relative magnitudes were: Kyu-Kitakami $>$ Abukuma

Table 5. Linear relationships between dioxin concentrations and river discharge.

dioxin type	river name	linear equation	r ²	N	prediction limit	
1,3,6,8-, and 1,3,7,9-TeCDD	Kyu-Kitakami	log y = 1.81x log X - 2.09	0.76	4	log y = 1.81 x log X - 2.09 ± (0.31 x (1+1/4+(log X-2.48) ² /0.85)) ^{1/2} x 0.82	
		y = 2.36 X - 215	0.98	4	y = 2.36 X - 215 ± (40343 x (1+1/4+(x-508) ² /1148205)) ^{1/2} x 0.82	
	Naruse	log y = 0.82 x l og X + 0.85	0.94	4	log y = 0.82 x l og X + 0.85 ± (0.054 x (1+1/4+(log X-2.16) ² /2.55)) ^{1/2} x 0.82	
		y = 1.94 X + 56.1	0.99	4	y = 1.94 X + 56.1 ± (3519 x (1+1/4+(x-584) ² /2639577)) ^{1/2} x 0.82	
	Natori	log y = 0.76 x l og X - 0.25	0.92	4	log y = 0.76 x l og X - 0.25 ± (0.063 x (1+1/4+(log X-1.72) ² /3.46)) ^{1/2} x 0.82	
		y = 0.288 X + 16.6	0.98	4	y = 0.288 X + 16.6 ± (314 x (1+1/4+(x-260) ² /522436)) ^{1/2} x 0.82	
	Abukuma	log y = 1.22 x l og X - 1.19	0.94	4	log y = 1.22 x l og X - 1.19 ± (0.11 x (1+1/4+(log X-2.64) ² /3.1)) ^{1/2} x 0.82	
		y = 0.409 X - 23.8	0.99	4	y = 0.409 X - 23.8 ± (2469 x (1+1/4+(x-2081) ² /33990748)) ^{1/2} x 0.82	
	OCDD	Kyu-Kitakami	log y = 1.76 x l og X - 2.15	0.7	4	log y = 1.76 x l og X - 2.15 ± (0.61 x (1+1/4+(log X-2.48) ² /0.85)) ^{1/2} x 0.82
			y = 1.25 X - 18.6	0.9	4	y = 1.25 X - 18.6 ± (75084 x (1+1/4+(x-508) ² /1148205)) ^{1/2} x 0.82
		Naruse	log y = 0.77 x l og X + 0.53	0.93	4	log y = 0.77 x l og X + 0.53 ± (0.11 x (1+1/4+(log X-2.16) ² /2.55)) ^{1/2} x 0.82
			y = 0.575 X + 41.7	0.99	4	y = 0.575 X + 41.7 ± (3025 x (1+1/4+(x-584) ² /2639577)) ^{1/2} x 0.82
Natori		log y = 0.81 x l og X + 0.17	0.96	4	log y = 0.81 x l og X + 0.17 ± (0.03 x (1+1/4+(log X-1.72) ² /3.46)) ^{1/2} x 0.82	
		y = 0.36 X + 13.0	0.99	4	y = 0.36 X + 13.0 ± (138 x (1+1/4+(x-260) ² /522436)) ^{1/2} x 0.82	
Abukuma		log y = 0.89 x l og X - 0.43	0.93	4	log y = 0.89 x l og X - 0.43 ± (0.15 x (1+1/4+(log X-2.64) ² /3.1)) ^{1/2} x 0.82	
		y = 0.109 X + 42.8	0.98	4	y = 0.109 X + 42.8 ± (2452 x (1+1/4+(x-2081) ² /33990748)) ^{1/2} x 0.82	
TEQs		Kyu-Kitakami	log y = 2.24 x l og X - 6.06	0.63	4	log y = 2.24 x l og X - 6.06 ± (0.9 x (1+1/4+(log X-2.48) ² /0.85)) ^{1/2} x 0.82
			y = 0.0053 X - 0.451	0.97	4	y = 0.0053 X - 0.451 ± (0.4001 x (1+1/4+(x-508) ² /1148205)) ^{1/2} x 0.82
		Naruse	log y = 1.11 x l og X - 2.8	0.84	4	log y = 1.11 x l og X - 2.8 ± (0.28 x (1+1/4+(log X-2.16) ² /2.55)) ^{1/2} x 0.82
			y = 0.0038 X - 0.0001	0.99	4	y = 0.0038 X - 0.0001 ± (0.0187 x (1+1/4+(x-584) ² /2639577)) ^{1/2} x 0.82
	Natori	log y = 1.05 x l og X - 3.03	0.97	4	log y = 1.05 x l og X - 3.03 ± (0.042 x (1+1/4+(log X-1.72) ² /3.46)) ^{1/2} x 0.82	
		y = 0.0016 X - 0.0156	0.99	4	y = 0.0016 X - 0.0156 ± (0.0003 x (1+1/4+(x-260) ² /522436)) ^{1/2} x 0.82	
	Abukuma	log y = 1.43 x l og X - 4.46	0.88	4	log y = 1.43 x l og X - 4.46 ± (0.3 x (1+1/4+(log X-2.64) ² /3.1)) ^{1/2} x 0.82	
		y = 0.0013 X - 0.116	0.99	4	y = 0.0013 X - 0.116 ± (0.0379 x (1+1/4+(x-2081) ² /33990748)) ^{1/2} x 0.82	

X is daily flow rate. y is dioxin concentration. Linear relationships were determined from data collected between July 2000 and February 2003 from near the river mouths (Chapter 4.1)

> Naruse > Natori. The average daily flow rate of the Kyu-Kitakami was highest in 2000, and those of the Abukuma, Naruse, and Natori, as well as the summed daily flow rate of the four rivers, were highest in 1999. The maximum average flow rates of each of the four rivers were all observed in 2002: 1900 m³/s for the Kyu-Kitakami, 1700 m³/s for the Naruse, 740 m³/s for the Natori, and 5700 m³/s for the Abukuma. A typhoon that struck Miyagi Prefecture on 11 July 2002 (Japan Meteorological Agency 2002) greatly increased the discharge at that time.

4.2.2.2. Relationship between daily fluxes of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD and river flow rate

Daily fluxes of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD in the four rivers for each of the years 1999–2002 are shown in Fig. 25. The annual average daily fluxes of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD were calculated from equations (4.3) and (4.4). For the Kyu-Kitakami, Naruse, Natori, and Abukuma rivers the fluxes ranged from 3.0 to 14 g/d, 0.7 to 2.9 g/d, 0.021 to 0.11 g/d, and 1.0 to 4.4 g/d, respectively. The relative magnitudes of the annual average daily fluxes of the four rivers were: Kyu-Kitakami > Abukuma > Naruse > Natori. The annual average

daily flux of these congeners from the Kyu-Kitakami River into Sendai Bay accounted for 49% to 84% of the total flux from the four rivers, whereas that from the Natori River accounted for 0.13% to 0.83%. The Kyu-Kitakami River was thus the major source of 1,3,6,8- and 1,3,7,9-TeCDD discharged into Sendai Bay.

The daily fluxes of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD increased with increasing river flow rates (Figs. 24 and 25). Periods during which flow rate was higher than the average daily flow rate accounted for 18% to 36% of the year; the fluxes of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD during these periods accounted for 49% to 97% of the total annual fluxes. The highest daily fluxes of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD from the four rivers were observed in 2002. For the Kyu-Kitakami, Naruse, Natori, and Abukuma rivers they were approximately 690, 480, 15, and 1100 g/d, respectively. These values were more than 10 times the average daily flux for each river.

4.2.2.3. Estimation of annual fluxes of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD and OCDD and TEQs into Sendai Bay

The annual fluxes of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD and OCDD ranged from 2100 to 8500 g/y for the

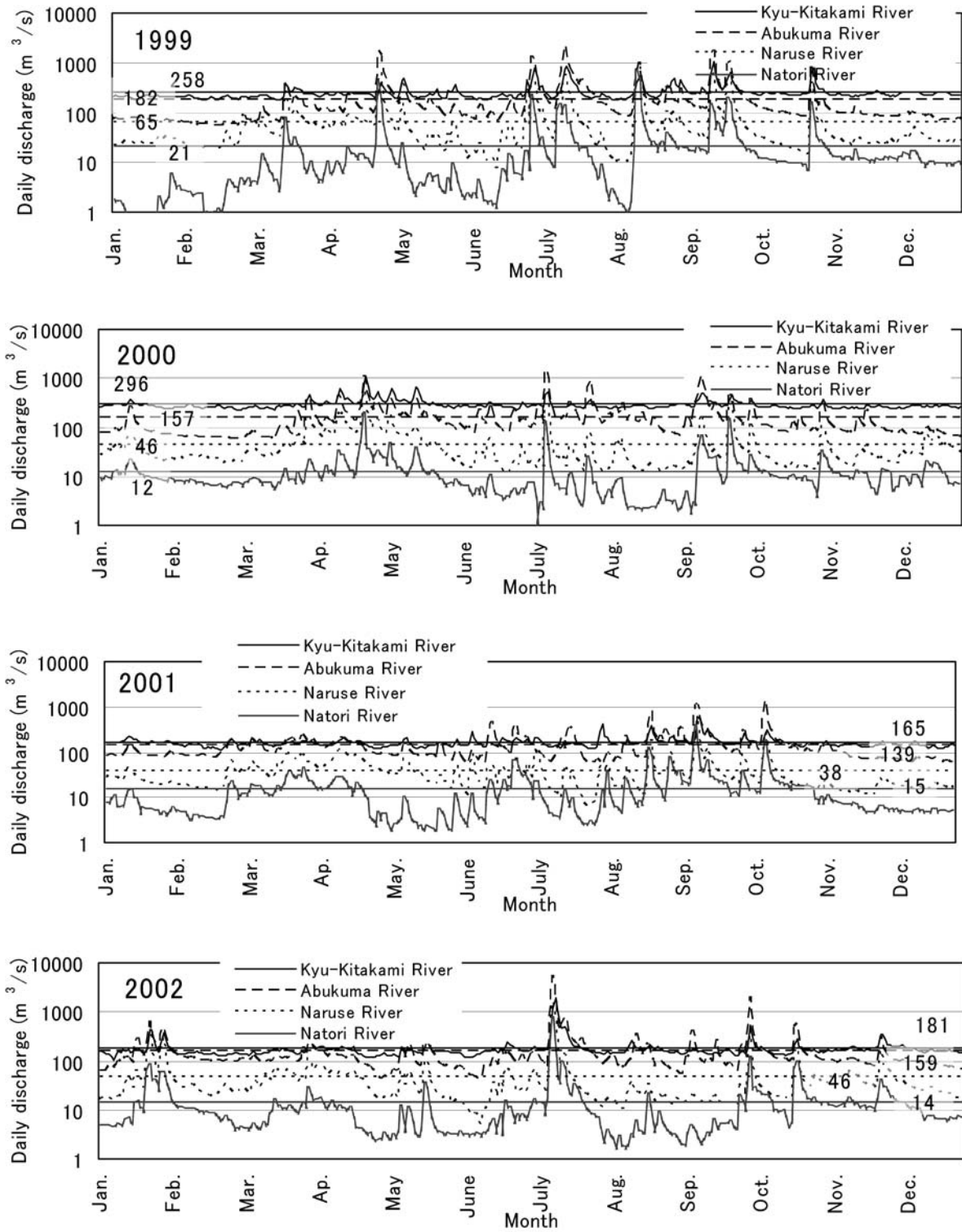


Fig. 24. Daily discharge from 1999 to 2002 of the Kyu-Kitakami, Abukuma, Naruse, and Natori rivers in Miyagi Prefecture, Japan (Japan Meteorological Agency 2002). Annual average daily discharges for each river are also shown with straight lines.

Kyu-Kitakami River, 360 to 1400 g/y for the Naruse River, 15 to 87 g/y for the Natori River, and 580 to 2200 g/y for the Abukuma River, and their relative

magnitudes were Kyu-Kitakami > Abukuma > Naruse > Natori (Table 6). The areas under paddy field in the vicinity of the Kyu-Kitakami, Naruse,

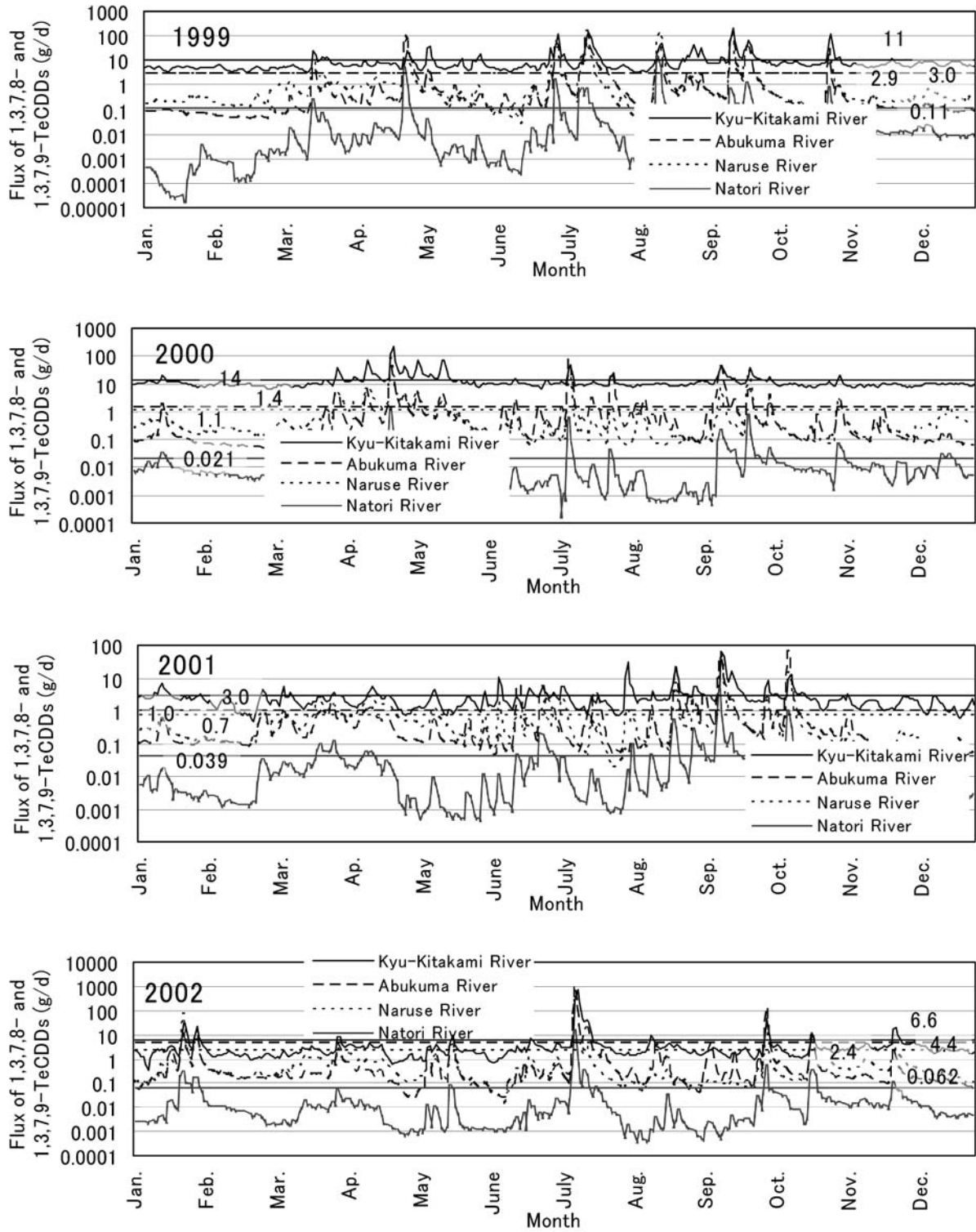


Fig. 25. Daily fluxes from 1999 to 2002 of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD to Sendai Bay from the Kyu-Kitakami, Abukuma, Naruse, and Natori rivers. Annual average daily fluxes of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD for each river are also shown with straight lines.

Natori, and Abukuma rivers in Miyagi Prefecture from 1999 to 2002 were approximately 147,742, 42,762, 9510, and 70,260 ha, respectively (Ministry of

Agriculture, Forestry and Fisheries 2010). For these four rivers, the annual river water discharge ranged from 1900 to 3400 km³/y, 440 to 750 km³/y, 140 to

240 km³/y, and 1600 to 2100 km³/y, respectively. The annual fluxes of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD and OCDD were highest in the Kyu-Kitakami River, where both the area of paddy fields and the water discharge were greatest. In contrast, the annual fluxes of these contaminants were lowest in the Natori River, where both the area of paddy fields and the water discharge were smallest.

1, 3, 6, 8- + 1, 3, 7, 9-TeCDD and OCDD and TEQ concentrations were highest in the Kyu-Kitakami River in 2000, and highest in the Naruse and Natori rivers in 1999. In years when flow rates were high, dioxin concentrations also tended to be high (Fig. 24, Table 6). In the Abukuma River, major dioxin and TEQ concentrations were highest in 2002, despite the flow rates being lower than in 1999.

Interannual variations in the summed fluxes of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD for the four rivers ranged from 1700 to 6200 g/y and those of OCDD ranged from 1400 to 4000 g/y. Interannual variations in the summed TEQ fluxes of the four rivers ranged from 4.04 to 14.5 g WHO-TEQ/y. The greatest interannual variability in TEQ flux over the period 1999–2002 was observed in the Natori River, where the flux ranged from 0.02 to 0.17 g WHO-TEQ/y. The least interannual variability in TEQ flux was observed in the Kyu-Kitakami River, where it ranged from 2.6 to 11.5 g WHO-TEQ/y. Thus, the annual fluxes of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD and OCDD, and of the TEQs, varied by factors ranging from approximately 3 to 10 in individual rivers during the 4 years covered by this study.

4.2.3. Discussion

4.2.3.1. Calculation of daily 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD fluxes in relation to river flow rate

The daily fluxes of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD increased with increasing river flow rate (Figs. 24 and 25). Days of high water flow contributed greatly to the annual fluxes of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD from these rivers into Sendai Bay. During periods of flooding and high flow rate, high concentrations of dioxin were observed in river samples (Stachel *et al.* 2004) and in a modeling study (Kobayashi *et al.* 2004b). My calculations of dioxin fluxes were consistent with those in these previous reports.

There is a good correlation between dioxin concentration and the concentration of suspended solids (Kakimoto *et al.* 2006, this study [Chapter 4.1]). Particulate-phase dioxins are known to be in higher concentrations than dissolved dioxins, and discharge occurs mainly in the particulate phase (Kobayashi *et al.* 2004b). High concentrations of chemicals at times of high flow rate are thought to be the result of resuspension of river sediments (Takada *et al.* 1992). I believe that particulate dioxins resuspended from sediments during periods of high flow rate are the main contributor to dioxin fluxes into Sendai Bay.

4.2.3.2. Estimation of annual fluxes of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD, and OCDD into Sendai Bay, including TEQ fluxes

The annual fluxes of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD and OCDD were highest in the Kyu-Kitakami River, where both the area of paddy fields and the flow rate were greatest (Fig. 24, Table 6). In contrast, the annual fluxes of these contaminants were lowest in the Natori River, where both the area of paddy fields and the flow rate were smallest. These results suggest that the annual fluxes of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD and OCDD are dependent on the land area under paddy fields in the river catchments and, by extrapolation, the amount of chlorinated pesticides (CNP and PCP) used in the rice-growing areas.

The summed annual fluxes (in TEQs) for the four rivers during 1999–2002 ranged from 4.04 to 14.5 g TEQ/y (Table 6). In previously published reports, the total flux from six rivers into Tokyo Bay was 12.6 g TEQ/y (Kobayashi *et al.* 2004b); from the Kymijoki River into the Gulf of Finland the value was 44 g I-TEQ in 2001 (Verta *et al.* 2003). Thus, the TEQs of the fluxes into Sendai Bay and Tokyo Bay were similar, although the major sources of the dioxins and the flow rates for these two regions were different. The TEQ values for the fluxes into Sendai Bay (calculated as WHO-TEQ) were lower than for those into the Gulf of Finland (calculated as I-TEQ), although I-TEQ values are sometimes slightly lower than WHO-TEQ values (You *et al.* 2004, Nakatani 2006).

1, 3, 6, 8- + 1, 3, 7, 9-TeCDD and OCDD and TEQ concentrations were highest in the Kyu-Kitakami

Table 6. Calculated annual flux of dioxins (g/y) from the Kyu-Kitakami, Abukuma, Naruse, and Natori rivers to Sendai Bay.

species	year	Kyu-Kitakami River	Naruse River	Natori River	Abukuma River	total
1,3,6,8- and 1,3,7,9-TeCDD	1999	4000 (2500, 5500)	1100 (950, 1200)	40 (33, 49)	1100 (930, 1300)	6200 (4400, 8000)
	2000	5000 (3300, 6700)	410 (240, 500)	7.6 (5.0, 12)	520 (370, 660)	5900 (4000, 8000)
	2001	1100 (350, 2100)	260 (210, 330)	14 (10, 20)	370 (260, 490)	1700 (820, 2900)
	2002	2400 (1500, 2500)	860 (790, 950)	23 (19, 28)	1600 (1500, 1700)	4900 (3800, 6200)
OCDD	1999	2900 (900, 4700)	360 (270, 460)	46 (42, 52)	480 (320, 700)	3800 (1500, 5900)
	2000	3500 (1100, 5900)	150 (100, 220)	7.7 (6.0, 10)	280 (160, 460)	4000 (1400, 6600)
	2001	1100 (130, 1700)	100 (61, 160)	15 (13, 19)	210 (120, 360)	1400 (320, 2200)
	2002	1800 (700, 2600)	280 (230, 360)	26 (23, 29)	570 (440, 750)	2700 (1400, 3700)
TEQs	1999	9.2 (4.4, 13.1)	1.8 (1.6, 2.1)	0.17 (0.16, 0.18)	3.3 (2.7, 3.9)	14.5 (8.8, 19.3)
	2000	11.5 (6.0, 17.0)	0.66 (0.50, 0.83)	0.017 (0.014, 0.02)	1.5 (0.96, 1.9)	13.7 (7.5, 19.8)
	2001	2.6 (0.47, 3.8)	0.39 (0.26, 0.53)	0.043 (0.038, 0.048)	1.0 (0.65, 1.4)	4.0 (1.4, 5.8)
	2002	5.6 (3.0, 7.2)	1.5 (1.4, 1.7)	0.092 (0.087, 0.096)	4.9 (4.4, 5.4)	12.1 (8.9, 14.3)

(,): lower and upper of prediction limit

River in 2000, and highest in the Naruse and Natori rivers in 1999. In years when flow rates were high, dioxin concentrations also tended to be high (Fig. 24, Table 6). In the Abukuma River, major dioxin and TEQ concentrations were highest in 2002, despite the flow rates being lower than in 1999. In 2002, the highest flow rate of the study period was observed in the Abukuma River as a result of a typhoon (Japan Meteorological Agency 2002). This suggests that typhoon-related high flow rates caused the high major dioxin and TEQ fluxes.

The annual fluxes of 1, 3, 6, 8- + 1, 3, 7, 9-TeCDD and OCDD, and the TEQs, varied by factors from approximately 3 to 10 in individual rivers during the 4 years covered by this study (Table 6). This study shows that dioxin fluxes vary considerably from year to year; therefore, it is essential that investigations of

riverine fluxes of dioxins to the sea are carried out over a span of several years.

Chapter 5. Mass balance of major dioxin congeners from impurities in pesticides used in Miyagi Prefecture

Because marine pollution is generally observed near urban areas rather than near agricultural areas, investigations of marine pollution have been conducted mainly in urban areas. Moreover, bays near urban areas are affected by sludge, by anoxic water at the bay bottom, and by red tides caused by eutrophication, all of which produce severe environments for marine organisms and render such bays unsuitable for fisheries.

Sendai Bay is an important area for coastal

fisheries, including aquaculture. In Miyagi Prefecture, face to Sendai Bay, large amounts of the chlorinated pesticides CNP and PCP were used in the past (Kato *et al.* 2005). By using the published shipment data for CNP and PCP for Miyagi Prefecture (Japan Plant Protection Association 1963–1995), it is possible to calculate the total quantity of the major dioxin congeners that were introduced as impurities in these chlorinated pesticides. Moreover, in a series of investigations in Sendai Bay and Miyagi Prefecture, past dioxin concentrations in seawater, sediment, marine organisms, and river water were determined (Chapters 2–4). In this chapter, the mass balance of dioxins from CNP and PCP sources are calculated, taking into account residual quantities in the terrestrial environment, emissions from major rivers to Sendai Bay, accumulation in seawater, bioaccumulation in organisms, settling to the sea bottom, and discharges from Sendai Bay to offshore waters. Although there have been attempts to estimate the mass balance of PCBs (Tanabe and Tatsukawa 1981, Yanagi and Hashimoto 2000), studies on the mass balance of dioxins are limited.

5.1. Materials and Methods

1, 3, 6, 8- and 1, 3, 7, 9-TeCDD were the major dioxin congeners occurring as impurities in CNP products, and OCDD was the major dioxin congener occurring in PCP products (Masunaga *et al.* 2001a, Seike *et al.* 2003). In this study, 1, 3, 6, 8- and 1, 3, 7, 9-TeCDD and OCDD were used as tracers, and a mass balance was calculated for the sum of the concentrations of these three congeners in Sendai Bay and the surrounding Miyagi Prefecture (Fig. 26, Table 7). These three congeners are collectively referred to as “the major pesticide dioxins” in this chapter. For these calculations, the seaward boundary was set as shown in Fig. 26 and the size and shape of the bay were defined, and then the seawater volume of the bay was calculated.

5.1.1. Total amounts of major pesticide dioxins in the terrestrial environment of Miyagi Prefecture from 1963 to 2002

CNP and PCP products were shipped to Miyagi Prefecture from 1966 to 1994, and from 1963 to 1985, respectively. The annual shipments of CNP and PCP

products into Miyagi Prefecture were separately calculated using data from the literature (Japan Plant Protection Association, 1963, 1964, ...1995; Chapter 4.1, this work). The concentrations of 1, 3, 6, 8- and 1, 3, 7, 9-TeCDD in CNP products and OCDD concentrations in PCP products varied according to the date of manufacture (Masunaga *et al.* 2001a, Seike *et al.* 2003). The concentrations used for this study were from published values (Masunaga *et al.* 2001a). The quantities of 1, 3, 6, 8- and 1, 3, 7, 9-TeCDD released annually to the environment were calculated by multiplying the annual amounts of CNP products shipped by the concentrations of 1, 3, 6, 8- and 1, 3, 7, 9-TeCDD in CNP products each year. Similarly, the annual quantities of OCDD were calculated by multiplying the annual shipments of PCP products by the OCDD concentration in those products each year (Table 7a, steps 1–3).

Dioxin compounds in the environment gradually disappeared as a result of degradation, runoff, and volatilization (Claudia and Matsumura 1978, Sinkkonen and Paasivirta 2000, Masunaga *et al.* 2001b). The residual quantities of the major pesticide dioxins in the terrestrial environment were calculated by assuming a 2% annual loss through these processes (Masunaga *et al.* 2001b; Table 7a, step 4).

5.1.2. Total emissions from major rivers to Sendai Bay from 1963 to 2002

The annual flux data for the major pesticide dioxins from the major rivers of Miyagi Prefecture to Sendai Bay were obtained as shown in Chapter 4.2 (Table 7a, steps 5–7). Historically, dioxin concentrations in sediment samples from Sendai Bay gradually increased from the mid-1930s to the mid-1980s, and then decreased slightly from the mid-1980s to the early 2000s (Chapter 3). The estimated annual fluxes were corrected taking into account this historical trend of concentrations in sediments (Table 7a, steps 8–21). The total fluxes for four decades were calculated by integrating the annual fluxes (Table 7a; steps 22–24).

Generally, groundwater inflow to the bay was thought to range from several percent to 10% of river water inflow (Taniguchi 2005). Dioxin congeners were water-insoluble and easily adsorbed

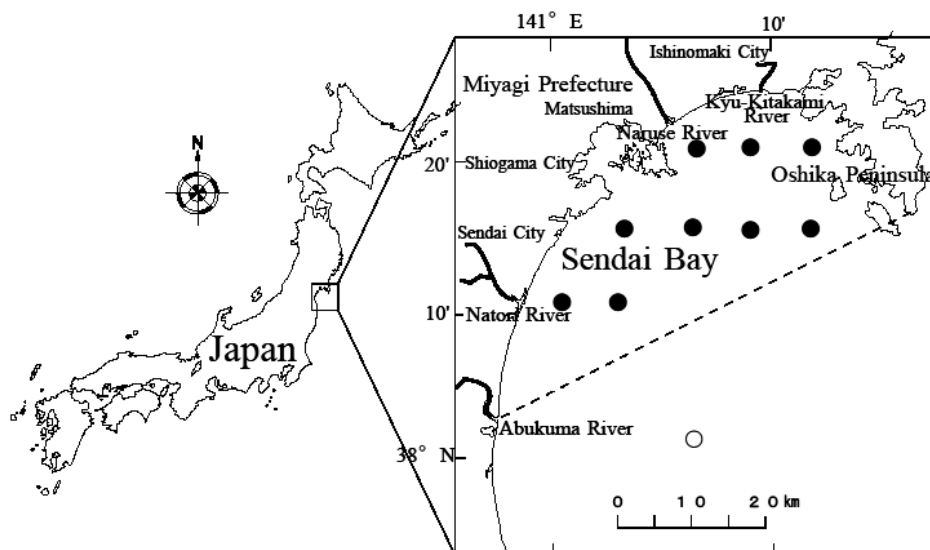


Fig. 26. Study area. Sendai Bay was defined as the area north of the dotted line extending from the tip of Oshika Peninsula to the mouth of the Abukuma River. From this, the area of Sendai Bay was calculated as 1874 km². The symbols ● and ○ indicate the sampling sites within and outside of the bay, respectively, sampled as part of the oceanographic survey by Miyagi Prefecture Fisheries Technology Institute. In the box model used for this study, the vertical salinity data measured at each sampling site during the oceanographic survey were used to estimate discharge from Sendai Bay to offshore waters.

onto suspended solids (Brochu *et al.* 1995). As the concentrations of dissolved-phase dioxins were lower than those of suspended-phase dioxins (Kobayashi *et al.* 2004b), the inflow of dissolved-phase dioxins from groundwater to the bay was thought to be limited. In this study, dioxin fluxes from groundwater to the bay were ignored as being inconsequential.

5.1.3. Annual flux of the major pesticide dioxins in Sendai Bay

The total sedimentation of major pesticide dioxins to the bay bottom was determined by multiplying the area of Sendai Bay by the sedimentation rate and the concentration of major dioxins in surface sediments (Table 7a, steps 25–29). The total quantities of the major pesticide dioxins in seawater were determined by multiplying the seawater volume by the dioxin concentrations in seawater in Sendai Bay (Table 7b, steps 30–33). The volume of seawater was calculated from the area and maximum depth of Sendai Bay using the equation for the volume of a pyramid ($[\text{area} \times \text{depth}]/3$).

5.1.4. Bioaccumulation of the major pesticide dioxins in commercially valuable fish, shellfish, and seaweeds

The Pacific oyster and the seaweeds *Porphyra yezoensis*, *Laminaria japonica*, and *Undaria pinnatifida* are raised in aquaculture operations in Sendai Bay, and almost all of the biomass of these organisms is harvested. The total quantities of the major pesticide dioxins in Pacific oysters and these seaweeds were calculated by multiplying the dioxin concentrations in each species by the total weight of the yearly harvest (Table 7b, steps 34–38 and 49–51). The total quantities in fish and crustaceans were calculated by multiplying the concentrations in each species by the annual harvest of that species, and by the ratio (w/w) of the total biomass of that species in the bay to the amount harvested (Table 7b-c, steps 39–48 and 52–71). The total bioaccumulations in fish, shellfish, and seaweeds of the commercial fisheries were calculated by adding together the values for each species (Table 7c, step 72).

5.1.5. Discharge from Sendai Bay to offshore waters

Discharge from Sendai Bay to waters further offshore was calculated by multiplying the outflow of seawater from the bay by the average concentrations of the major pesticide dioxins (Table 7a, step 32). The outflow of seawater was estimated by using the box model described by Unoki (1998). A schematic of the box model and parameters is shown in Figure 27. In the box model, the volumetric flows of seawater were calculated from the sum of the flow rates of the major rivers discharging into Sendai Bay (Kyu-Kitakami, Naruse, Natori, and Abukuma rivers) and the average salinity concentrations in each box of the model (Table 8). The flow rates for each river for 1999–2002 were obtained from published data (Japan River Association 2001, 2002, 2003, 2004); the salinity data for the stations shown in Figure 26 are unpublished (Miyagi Prefecture Fisheries Technology Institute).

The outflow of seawater (Q' , m^3/s) from inshore to offshore in the upper layer of Sendai Bay was calculated as:

$$Q' = R \times S_4 / (S_4 - S_1), \quad (5.1)$$

where R is the sum of the flow rates (m^3/s) of the four major rivers, S_1 is the salinity (PSU) of the upper layer inshore, and S_4 is the salinity (PSU) of the lower layer offshore (Fig. 27).

5.2. Results

5.2.1. Dioxin flux in the terrestrial environment

The estimated total quantity of 1, 3, 6, 8- and 1, 3, 7, 9-TeCDD from CNP sources from 1966 to 1994 was 18.7 t, and that of OCDD from PCP sources from 1963 to 1985 was 12 t (Table 7a, steps 1 and 2; Fig. 28). Thus, the total amount of the major pesticide dioxins from CNP and PCP sources introduced into Miyagi Prefecture over the period when these pesticides were used was 30.7 t (Table 7a, step 3; Fig. 28). If the annual loss is 2% (Masunaga *et al.* 2001b; Table 7a), then the residual quantity in the terrestrial environment in 2002 was 17.4 t. Therefore, the quantity lost from the terrestrial environment was calculated as 13.3 t (30.7 t – 17.4 t). The discharge from major rivers into Sendai Bay from 1963 to 2002 was estimated to be

241 kg (Table 7a, step 24; Fig. 29).

If the total quantity of the major pesticide dioxins from CNP and PCP products shipped to Miyagi Prefecture is set to 100%, then as of 2002, 56.7% remained as residual dioxin in the terrestrial environment, and discharge from major rivers into Sendai Bay accounts for only 0.8% (Fig. 30).

5.2.2. Dioxin flux in the marine environment

The annual fluxes of major pesticide dioxins in the marine environment around 2002 were calculated as 3.0 kg/y settling to the bottom and 0.34 kg remaining in the seawater for steady-state (Table 7a, steps 29, and 33; Fig. 30). The total bioaccumulation in commercially valuable fish, shellfish, and seaweed in Sendai Bay is thus 3.2 g/y (Table 7c step 72; Fig. 30). The average discharge from Sendai Bay to offshore (outside of the bay) from 1999 to 2002 was calculated as 6.17 kg/y (Figs. 30 and 31). If the inputs to the bay from major rivers (7.7 kg/y) are set as 100%, then the amount discharged from the bay to offshore waters accounts for 80.1%, 39.0% settles to the sea bottom, 4.4% remains in seawater in the bay, and 0.04% is bioaccumulated in marine organisms in the bay (Fig. 30).

Thus, the estimated total flux in the marine environment (6.17 kg/y + 3.0 kg/y + 3.2 g/y = 9.17 kg/y) is overestimated by 1.47 kg/y (19%) in comparison with estimated inflows from major rivers to the bay (7.7 kg/y).

5.3. Discussion

5.3.1. Dioxin flux in the terrestrial environment

High dioxin levels have been detected in Japan, mainly in paddy fields (Kobayashi *et al.* 2004b, Kadota *et al.* 2007, Kiguchi *et al.* 2007). Although released dioxins as constituent of pesticide have been gradually removed from the field as results of decomposition, runoff and volatilization, the large part of the pesticide dioxins from CNP and PCP products shipped to Miyagi Prefecture was thought to remain as residual dioxins in the terrestrial environment (17.4 t; Table 7a, steps 3 and 4; Fig. 30). The estimates of dioxin flux show that only 0.8% (241 kg; Table 7a, step 24) of the residual dioxins in the terrestrial environment were transported to

Table 7a. Stepwise calculations for the quantities and fluxes of the major pesticide dioxins in Sendai Bay.

Parameter	Calculation	Value	Unit	Ref. Step no.
<i>Quantity in the regional environment of Miyagi Prefecture</i>				
Total quantity of 1,3,6,8-, and 1,3,7,9-TeCDD in CNP sources from 1966 to 1994		18.7	t	a, b (1)
Total quantity of OCDD in PCP sources from 1963 to 1985		12.0	t	a, b (2)
Sum of three dioxin congeners from CNP and PCP sources	(1)+(2)	30.7	t	(3)
Annual loss		2	%	c
Residual quantity in 2002 assuming a 2% annual loss		17.4	t	(4)
<i>Emission from major rivers to Sendai Bay</i>				
Average annual flux of 1,3,6,8- and 1,3,7,9-TeCDD from four major rivers during 1999-2002		4.7	kg/y	e (5)
Average annual flux of OCDD from four major rivers during 1999-2002		3.0	kg/y	e (6)
Average annual flux of major pesticide dioxins from four major rivers during 1999-2002	(5)+(6)	7.7	kg/y	e (7)
Concentration of 1,3,6,8- and 1,3,7,9-TeCDD relative to 1993-2002 concentrations calculated from historical trend in sediments				
(1993-2002)		1.000		b (8)
(1986-1992)		1.313		b (9)
(1982-1985)		0.863		b (10)
(1976-1981)		0.718		b (11)
(1971-1975)		0.566		b (12)
(1967-1970)		0.544		b (13)
(1966)		0.442		b (14)
Concentration of OCDD relative to 1993-2002 concentrations calculated from historical trend in sediments				
(1993-2002)		1.000		b (15)
(1986-1992)		1.017		b (16)
(1982-1985)		0.629		b (17)
(1976-1981)		0.656		b (18)
(1971-1975)		0.398		b (19)
(1967-1970)		0.647		b (20)
(1963-1966)		0.462		b (21)
Total flux of 1,3,6,8- and 1,3,7,9-TeCDD from four major rivers from 1966 to 2002	(5) × [(8) × 10y + (9) × 7y + (10) × 4y + (11) × 6y + (12) × 5y + (13) × 4y + (14) × 1y]	151	kg	(22)
Total flux of OCDD from four major rivers from 1963 to 2002	(6) × [(15) × 10y + (16) × 7y + (17) × 4y + (18) × 6y + (19) × 5y + (20) × 4y + (21) × 4y]	89	kg	(23)
Total flux of all major pesticide dioxins from four major rivers from 1963 to 2002	(22)+(23)	241	kg/40y	(24)
<i>Dioxins settled to the bottom of Sendai Bay</i>				
Area of Sendai Bay		1874	km ²	(25)
Average sedimentation rate		0.213	g dw/cm ² /y	b (26)
Average annual sediment accumulation (25) × (26) × (100cm × 1000m) ²		399.1	× 10 ¹⁰ g dw/y	(27)
Average concentration of major pesticide dioxins in surface sediment which deposited from 1990s to 2002 in inshore		747.6	pg/g dw	b, f (28)
Average annual quantity of major pesticide dioxins settling to the bay bottom	(27) × (28) × 1000 ⁻⁵ (kg/pg)	3.0	kg/y	(29)

Table 7b. (continued)

<i>Total dioxin quantity in seawater</i>				
Maximum depth of Sendai Bay	50	m		(30)
Total seawater quantity in Sendai Bay	$(25) \times (30) / 3 \times 1000^2 (\text{m}^2/\text{km}^2) \times 100^3 (\text{cm}^3/\text{m}^3) \times 10^{-3} (\text{L}/\text{cm}^3)$	3123	$\times 10^{10} \text{L}$	(31)
Average concentration of major dioxins in seawater collected from 1999 to 2002	11	pg/L	f	(32)
Average total quantity of major dioxins in seawater for steady-state	$(31) \times (32) \times 1000^{-5} (\text{g}/\text{pg})$	0.34	kg	(33)
<i>Bioaccumulation in Pacific oyster</i>				
Average yearly harvest of Pacific oyster, 1984–2004	31765	t	g	(34)
(total wt – shell wt)/total wt	0.1		g	(35)
Average annual soft tissue harvest (total weight – shell weight)	$(34) \times (35)$	3177	t	(36)
Average concentration of major dioxins in Pacific oyster tissue	650.4	pg/g ww	f	(37)
Average annual quantity of major dioxins in Pacific oyster	$(36) \times (37) \times 1000^2 (\text{g}/\text{t}) \times 1000^{-4} (\text{g}/\text{pg})$	2.1	g/y	(38)
<i>Bioaccumulation in anchovy</i>				
Average yearly harvest of anchovy, 2003–2005	15221	t	g	(39)
Concentration of major dioxins in anchovy	6.4	pg/g ww	f	(40)
Average total quantity of major dioxins in the anchovy catch	$(39) \times (40) \times 1000^2 (\text{g}/\text{t}) / 1000^3 (\text{mg}/\text{pg})$	97	mg/y	(41)
Average ratio of total biomass to catch (w/w) of anchovy	4.2		h	(42)
Average annual quantity of major dioxins in anchovy biomass	$(41) \times (42)$	406	mg/y	(43)
<i>Bioaccumulation in sand lance</i>				
Average yearly harvest of sand lance, 1989–2004	5012	t	g	(44)
Average concentration of major dioxins in sand lance	4.0	pg/g ww	f	(45)
Average total quantity of major dioxins in sand lance catch	$(44) \times (45) \times 1000^2 (\text{g}/\text{t}) \times 1000^{-3} (\text{mg}/\text{pg})$	20	mg/y	(46)
Average ratio of total biomass to catch (w/w) of sand lance	3.6		i, j	(47)
Average annual quantity of dioxins in sand lance biomass	$(46) \times (47)$	72	mg/y	(48)
<i>Bioaccumulation in seaweeds</i>				
Average yearly harvest of seaweeds, 1984–2004	23247	t/y	g	(49)
Average concentration of major dioxins in seaweeds	2.4	pg/g ww	f	(50)
Average annual quantity of major dioxins in seaweeds	$(49) \times (50) \times 1000^2 (\text{g}/\text{t}) / 1000^{-3} (\text{mg}/\text{pg})$	56	mg/y	(51)
<i>Bioaccumulation in marbled sole</i>				
Average yearly harvest of marbled sole, 1998–2004	4105	t	g	(52)
Average concentration of major dioxins in marbled sole	5.62	pg/g ww	f	(53)
Average total quantity of major dioxins in the marbled sole catch	$(52) \times (53) \times 1000^2 (\text{g}/\text{t}) \times 1000^{-3} (\text{mg}/\text{pg})$	23	mg/y	(54)
Average ratio of total biomass to catch (w/w) of marbled sole	2.1		h	(55)
Average annual quantity of major dioxins in marbled sole biomass	$(54) \times (55)$	49	mg/y	(56)

Table 7c. (continued)

<i>Bioaccumulation in crustaceans (shrimp and crab)</i>				
Average yearly harvest of crustaceans, 1993–2004	312	t	g	(57)
Average concentration of major dioxins in shrimp	95.7	pg/g ww		(58)
Average total quantity of major dioxins in of crustaceans catch	$(57) \times (58) \times 1000^2(\text{g/t}) \times 1000^{-3}(\text{mg/pg})$	30	mg/y	(59)
Average ratio of total biomass to catch (w/w) of shrimp	1.3		k	(60)
Average annual quantity in crustacean biomass	$(59) \times (60)$	40	mg/y	(61)
<i>Bioaccumulation in Japanese flounder</i>				
Average yearly harvest of Japanese flounder, 1998–2004	154	t	g	(62)
Average concentration of major dioxins in Japanese flounder	2.2	pg/g ww	l	(63)
Average total quantity in Japanese flounder catch from Sendai Bay	$(62) \times (63) \times 1000^2(\text{g/t}) \times 1000^{-2}(\mu\text{g/pg})$	345	$\mu\text{g/y}$	(64)
Average ratio of total biomass to catch (w/w) of Japanese flounder	2.1		h	(65)
Average annual quantity of major dioxins in Japanese flounder	$(64) \times (65)$	726	$\mu\text{g/y}$	(66)
<i>Bioaccumulation in other fishes</i>				
Average yearly harvest of other fishes, 1998–2004	33188	t	g	(67)
Average of major dioxin concentrations in anchovy, marbled sole, sand lance and Japanese flounder	4.6	pg/g ww	f, l	(68)
Average total quantity of major dioxins in catch of "other fishes"	$(67) \times (68) \times 1000^2(\text{g/t}) \times 1000^{-3}(\text{mg/pg})$	152	mg/y	(69)
Average of the ratio of total biomass to catch (w/w) for anchovy, marbled sole, sand lance, and flounder	3.2		h, i, j	(70)
Average annual quantity of major dioxins in biomass of other fishes	$(69) \times (70)$	492	mg/y	(71)
<i>Total bioaccumulation of major dioxins in commercially valuable fishes, shellfish, and seaweeds</i>				
Average annual quantity in fishes, shellfish, and seaweeds	$(38)+(43)+(48)+(51)+(56)+(61)+(66)+(71)$	3.2	g/y	(72)

References: a, Japan Plant Protection Association (1963–1995); b, Chapter 3 (this work); c, Masunaga et al. (2001b); d, Kadota et al. (2007); e, Chapter 4 (this work); f, Chapter 1 (this work); g, Tohoku Regional Agricultural Office (1987–2006); h, Fisheries Agency and Fisheries Research Agency of Japan (2001–2006); i, Ebe et al. (1991); j, Kobayashi et al. (1995); k, Sakaji (2002); l, Chapter 2 (this work)

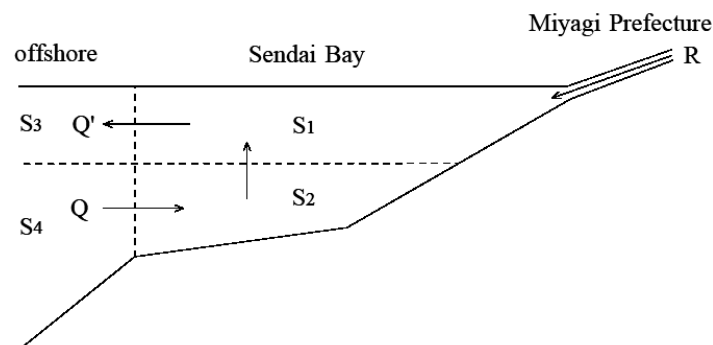


Fig. 27. Schematic of the box model used to estimate transport offshore from Sendai Bay. S_1 is the average of salinities from the surface and 5 m and 10 m depths at the nine sampling sites within the bay (Fig. 26, symbol ●). S_4 is the average salinity below 20 depth at an offshore sampling site (Fig. 26, symbol ○).

Table 8. Values for the parameters R (river inflow) and S_1 and S_4 (salinities) used in the box model, and the calculated flow offshore (Q').

	1999				2000			
	R (m ³ /s)	S_1 (PSU)	S_4 (PSU)	Q' (m ³ /s)	R (m ³ /s)	S_1 (PSU)	S_4 (PSU)	Q' (m ³ /s)
Jan	307.6	33.65	34.10	23053	425.9	33.57	34.27	20825
Feb	290.8	33.37	34.06	14396	356.1	33.63	33.89	46582
Mar	456.0	33.45	33.77	47877	447.7	33.58	33.87	52183
Apr	647.8	32.69	33.72	21112	823.0	33.04	33.64	46133
May	443.7	32.49	33.80	11467	626.8	30.84	33.32	8426
Jun	438.2	32.30	33.67	10762	436.7	31.64	33.48	7968
Jul	915.9	32.20	33.63	21593	645.3	31.21	33.58	9113
Aug	646.2	31.98	33.93	11268	436.5	32.02	33.57	9447
Sep	908.8	31.98	33.65	18227	671.3	32.96	33.79	27383
Oct	497.9	32.47	33.51	16050	425.1	32.75	33.43	20805
Nov	396.9	32.43	33.70	10520	433.3	32.90	33.55	22359
Dec	366.2	33.12	33.87	16482	392.3	32.94	33.81	15150

	2001				2002			
	R (m ³ /s)	S_1 (PSU)	S_4 (PSU)	Q' (m ³ /s)	R (m ³ /s)	S_1 (PSU)	S_4 (PSU)	Q' (m ³ /s)
Jan	297.5	32.96	33.98	9839	461.7	34.07	34.58	31100
Feb	274.4	33.42	34.02	15373	287.9	33.43	33.90	20680
Mar	388.7	32.92	33.69	16966	340.5	33.31	33.69	29808
Apr	376.0	32.25	33.15	13922	335.3	32.33	33.51	9480
May	277.7	32.30	33.29	9372	316.7	32.48	33.42	11286
Jun	381.6	32.27	33.36	11753	279.3	31.86	33.75	4988
Jul	310.8	31.75	33.52	5903	977.3	31.73	33.45	18984
Aug	425.1	32.89	33.53	22242	313.4	30.18	33.59	3093
Sep	581.2	32.01	33.76	11233	299.9	32.07	33.42	7460
Oct	469.7	32.63	33.49	18402	503.4	32.52	33.77	13525
Nov	264.8	32.75	33.42	13180	365.9	33.12	33.62	25003
Dec	234.1	33.13	33.91	10179	295.2	32.92	33.73	12198

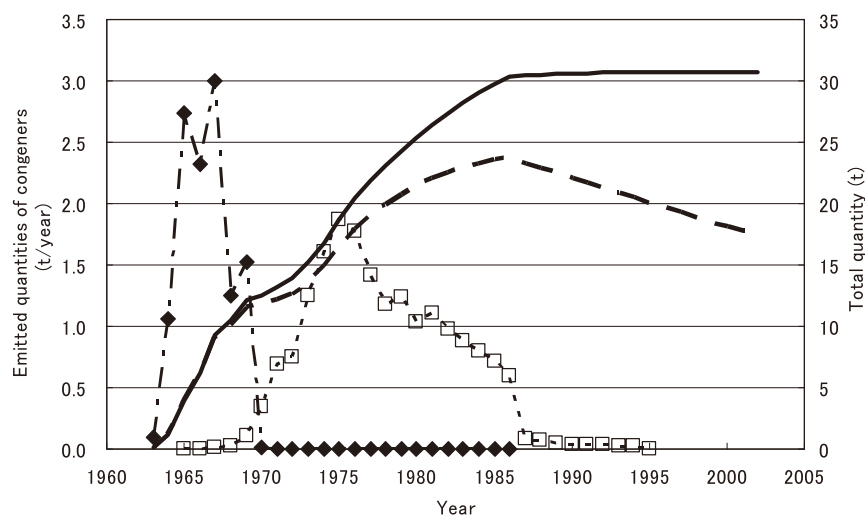


Fig. 28. Trends in the quantities of the major pesticide dioxins in Miyagi Prefecture. □, annual quantities of 1, 3, 6, 8- and 1, 3, 7, 9-TeCDD introduced into the prefecture, calculated by multiplying the amounts of CNP products shipped annually (Japan Plant Protection Association 1963–1995) by the cumulative 1, 3, 6, 8- and 1, 3, 7, 9-TeCDD concentrations in CNP products each year (Masunaga et al., 2001a). ◆, annual quantities of OCDD introduced, similarly calculated from the annual shipments of PCP products (Japan Plant Protection Association 1963–1995) and the OCDD concentration in those products each year (Masunaga et al., 2001a). The solid line represents the cumulative quantity, and the dashed line is the cumulative quantity allowing for a 2% annual loss.

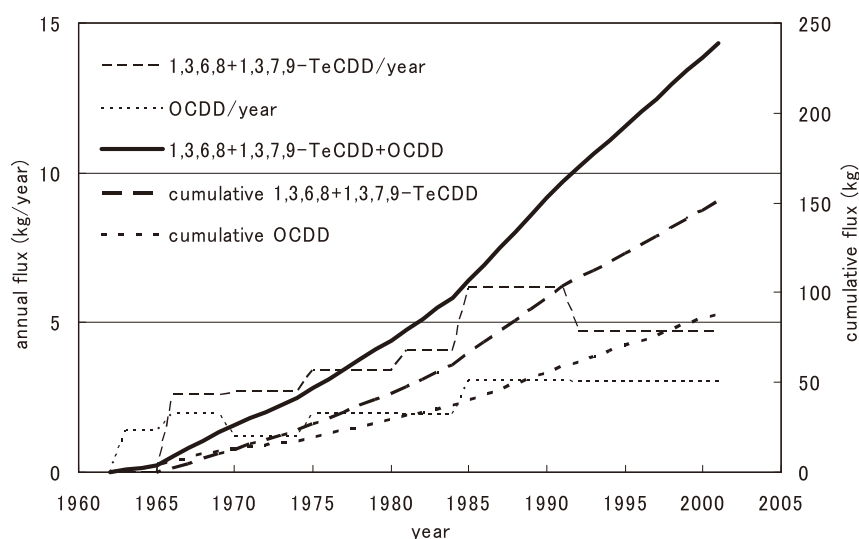


Fig. 29. Dioxin emissions from major rivers into Sendai Bay. The annual fluxes of the major pesticide dioxins were calculated from the average flux for 1999–2002 (7.7 kg/year; Table 7a, step 7) corrected in accordance with the historical trends of their concentrations in sediments (Table 7a, steps 8–21). The total flux over four decades was calculated by summing the annual fluxes.

Sendai Bay (Fig. 30). However, this transport is much higher than the values ranging from 0.0021% to 0.0031% which were published from the Ministry of the Environment Japan (Sampling sites have not been made public; the Ministry of the Environment of Japan 2002), so the dioxin emissions to Sendai Bay estimated in this study should not be considered low.

Concerning the estimated loss of dioxins (13.3 t), volatilization, which occurs during the spraying of the agricultural chemicals, is unlikely to be a major factor. The amount lost through emissions to Sendai Bay (241 kg) is slight in comparison with the total loss of 13.3 t. Therefore, the major loss of dioxins is thought to be through degradation, although the half-lives of dioxins were known to vary depending on the environment, from a few hundred days to hundreds of years (Claudia and Matsumura 1978, Kjeller and Rappe 1995, Masunaga *et al.* 2001b).

5.3.2. Dioxin flux in the marine environment

The annual average flow of dioxins from the major rivers to Sendai Bay from 1999 to 2002 was calculated as 7.7 kg/y (Table 7a, step 7; Fig. 30). The total bioaccumulation in commercially valuable

fish, shellfish, and seaweed over the same period averaged 3.2 g/y. If the input from major rivers to the bay is set at 100%, then the bioaccumulation in these organisms accounts for only 0.04 % of the total (Fig. 30). This bioaccumulation was calculated only using fishery data (Tohoku Regional Agricultural Office 1987, 1988, ...2006) and non-fishery-targeted marine organisms were not considered. So the calculated bioaccumulation is thought to be an underestimate in comparison with the actual bioaccumulation. However, this indicates that very limited amount of pesticide origin dioxins move back from Sendai Bay to terrestrial areas as seafood for human. Even the calculation of dioxin bioaccumulation in marine organisms is underestimated, it appears to be much lower than the inputs from major rivers to the bay (7.7 kg/y), discharge from the bay to offshore waters (6.17 kg/y), and settling to the bay bottom (3.0 kg/y). In addition, 1, 3, 6, 8- and 1, 3, 7, 9-TeCDD and OCDD were thought to bioaccumulate at lower rates than the other 2, 3, 7, 8-substituted PCDDs and PCBs (Sijm *et al.* 1993, Yamada 1997). This may be one of causes of very low bioaccumulation of pesticide origin dioxins in fishery products.

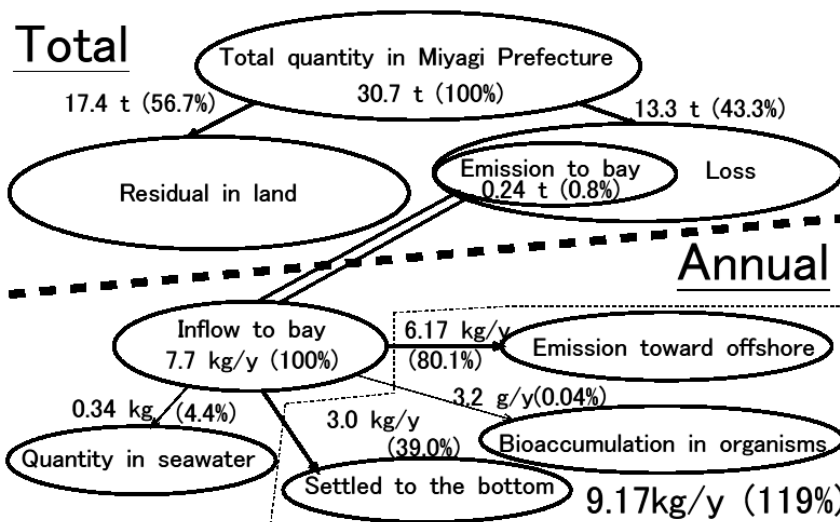


Fig. 30. Schematic diagram showing the total quantities and fluxes of the major pesticide dioxins in the terrestrial environment around Sendai Bay in 2002, and the estimated annual values for Sendai Bay.

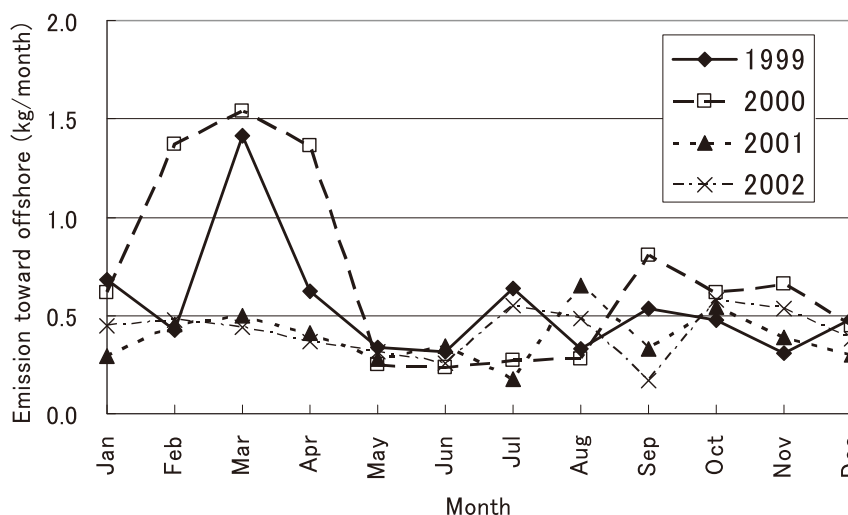


Fig. 31. The monthly discharge of major pesticide dioxins from Sendai Bay to waters offshore (outside of the bay) from 1999 to 2002 as calculated by a box model.

The estimated total flux in the marine environment ($6.17 \text{ kg/y} + 3.0 \text{ kg/y} + 3.2 \text{ g/y} = 9.17 \text{ kg/y}$) was larger than estimated inflows from the major rivers to the bay (7.7 kg/y). The seawater and sediment samples used to estimate these flux were collected mainly near the coast. Therefore, it is possible that the values of dioxin concentrations in seawater and sediments used in the flux calculations were higher than the average values of the whole study area (Fig. 26), and the values of dioxin discharge from the bay to offshore waters and

settling to the bay bottom may be overestimates. The estimated discharge of dioxins from the bay to offshore waters (6.17 kg/y) and settling to the bay bottom (3.0 kg/y) accounted for 64.9% and 31.6% of total flux in the marine environment (9.17 kg/y), respectively (Fig. 30); their sum accounted for 96.5% of the total flux. It appears that most of the dioxins carried by major rivers to the bay were discharged to offshore or settled to the bay bottom. It has been reported that 87.7% of PCBs were emitted to offshore waters from the Seto Inland Sea (Tanabe

and Tatsukawa 1981) and that 99.7% of PCBs in Tokyo Bay were likewise discharged into waters farther offshore (Yanagi and Hashimoto 2000). In contrast, 99% of the inflow of dioxins to Tokyo Bay was reported to settle on the bay bottom, whereas only 1% left the bay for offshore (Masunaga *et al.* 2006). Although the discharge of chemicals from inshore to waters farther offshore varies with the kind of chemical, the location, topography and the method of calculation, the value calculated for dioxin emissions from Sendai Bay to offshore waters falls in the middle of the range of other reported values.

Chapter 6. General discussion and summary

6.1. Properties of dioxins in Sendai Bay

The types of dioxin congeners are known to vary with the sources of emission (Czuczwa and Hites 1984, Kannan *et al.* 1987, Rappe *et al.* 1989, Sakai *et al.* 1993, Schrann *et al.* 1995, Takasuga *et al.* 1995, Lohmann and Jones 1998, Verta *et al.* 1999, 2003, 2007, Isosaari *et al.* 2000, 2002, Masunaga *et al.* 2001a, Yao *et al.* 2002, Seike *et al.* 2003, Hashimoto 2004, Kakimoto *et al.* 2006). In Sendai Bay, 1, 3, 6, 8- and 1, 3, 7, 9-TeCDD which are the impurities in CNP and OCDD in PCP (Masunaga *et al.* 2001a, Seike *et al.* 2003), were the predominant congeners in seawater and sediment (Chapter 2.1). The chlorinated herbicides used in paddy fields were inferred to be the major dioxin sources.

6.2. Properties of bioaccumulation of dioxins to marine organisms

The bioaccumulation of dioxins in aquatic organisms is known to vary with the kinds of dioxin congeners (Sijm *et al.* 1993, Yamada 1997a). 1,3,6,8- and 1,3,7,9-TeCDD, and OCDD, which are predominant congeners in Sendai Bay and belong to PCDD, were of the type showing low bioaccumulation in fishes. PCDD/F concentrations in the higher-trophic-level fishes tended to be lower than those in the lower-trophic-level fishes (Chapter 2.1). In contrast, PCDD/F concentrations in the higher-trophic-level invertebrates tended to be higher than those in the lower-trophic-level invertebrates. The bioaccumulation properties of dioxins in

invertebrates are different from those in fishes, as the bioaccumulation in invertebrates may be influenced more by the number of chlorine substituents in PCDD/F homologues than by differences in structure (such as 2,3,7,8-substituted PCDD/Fs vs. non 2,3,7,8-substituted PCDD/Fs).

Co-PCBs are known to show higher bioaccumulation than PCDD/Fs (Niimi 1996), and organisms at higher trophic levels in Sendai Bay had higher Co-PCB concentrations (Chapter 2.1). Co-PCB concentrations in environmental samples were lower than concentrations of PCDD/Fs from CNP and PCP sources; however, monitoring of Co-PCBs in Sendai Bay is probably more important than monitoring of PCDD/Fs because of their high toxicity (TEQs) and high bioaccumulation nature.

The bioaccumulation of chemicals is known to vary with the body size of aquatic organisms (Schimmel *et al.* 1977, Yamada *et al.* 1995). In Japanese flounder, the total PCDD/F concentrations were not correlated with body length, whereas the total non-*ortho* PCB and total mono-*ortho* PCB concentrations were significantly correlated with total body length (Chapter 2.2). The bioaccumulation properties of PCDD/Fs in Japanese flounder differed from those of Co-PCBs. Although the concentrations of non-*ortho* PCBs were lower than those of mono-*ortho* PCBs, the toxic equivalent (TEQ) value for non-*ortho* PCBs was higher than that for mono-*ortho* PCBs. The TEQ value for non-*ortho* PCBs increased more with increasing body length than did the values for PCDDs, PCDFs, and mono-*ortho* PCBs. These results show that from the standpoint of risk management, non-*ortho* Co-PCBs are the most important dioxins in Japanese flounder.

6.3. Historical trend of dioxins in sediment cores from Sendai Bay

Historical trends in dioxin levels have been investigated using sediment cores from throughout the world (Czuczwa and Hites 1984, Sakai *et al.* 1999, Masunaga *et al.* 2001b, Kubota *et al.* 2002, Yao *et al.* 2002). In Sendai Bay, 1, 3, 6, 8-TeCDD + 1, 3, 7, 9-TeCDD, OCDD, and Co-PCB concentrations in sediment increased from the mid-1930s and then reached a maximum in the mid-1980s (Chapter 3). Data from these cores support the conclusion that

over long periods of time, the major sources of dioxins in Sendai Bay were CNP and PCP. The times of peak shipments of CNP (1975) and PCP (1970) in Miyagi Prefecture (Japan Plant Protection Association 1963–1995), and of Co-PCBs in Japan (1970; Tatsukawa 1972) did not coincide with the peaks in concentration of 1, 3, 6, 8- and 1, 3, 7, 9-TeCDD, OCDD, or Co-PCBs in the sediment cores, which lagged by more than 10 years. The lack of correspondence between maximum concentrations in the sediments and the time of maximum use of CNP, PCP, and PCB products may be due to a lower outflow of dioxins from land to the bay in comparison with the total amount of these products used in Miyagi Prefecture.

6.4. Discharge of dioxins from terrestrial to marine environments

Dioxin congeners from CNP and PCP sources were detected in paddy soil and river water (Kobayashi *et al.* 2004a, Kadota *et al.* 2007, Kiguchi *et al.* 2007). It was clear from statistical analyses by PCA and CMB that CNP and PCP were major sources of dioxins in rivers in Miyagi Prefecture (Chapter 4). Dioxin congeners are transported from paddy fields adsorbed on suspended solids into rivers (Kobayashi *et al.* 2004b, Kadota *et al.* 2007). Concentrations of 1, 3, 6, 8- and 1, 3, 7, 9-TeCDD and suspended solids in river water increased with increasing flow rates. During periods of high flow, dioxin concentrations may have increased because of resuspension of bottom sediments that had adsorbed dioxins. Dioxin fluxes from rivers to the bay also increased with increasing river flow.

6.5. Mass balance of major dioxin congeners from impurities in pesticides used in Miyagi Prefecture

Several reports address the mass balance of dioxins in marine environments (Tanabe and Tatsukawa 1981, Yanagi and Hashimoto 2000, Masunaga *et al.* 2006). In the present study, the mass balance was analyzed for Sendai Bay, which is an important area for fisheries and aquaculture (Chapter 5). Large quantities of dioxins from CNP and PCP sources were introduced into the terrestrial environment. As the rivers and drainage ditches

acted as transport bottlenecks, their inflow from the terrestrial environment to Sendai Bay was limited. The bulk of dioxins from CNP and PCP sources remained in the terrestrial environment.

Almost all dioxins entering Sendai Bay either flowed out of the bay or settled to the bay bottom. The amount that bioaccumulated in marine organisms was much less than the amount inflowing from the terrestrial environment to the bay. The major dioxin congeners from impurities in CNP and PCP have much lower toxicities and bioaccumulation rates in marine organisms than low-chlorine 2, 3, 7, 8-substituted PCDD/Fs such as 2, 3, 7, 8-TeCDD, which has an extremely high TEF. Therefore, although the influx of dioxins of CNP and PCP origin to Sendai Bay will continue in the future, their bioaccumulation in marine organisms in Sendai Bay will not be a serious problem for fisheries resources.

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References

- Agricultural Chemicals Inspection Station, 2007: Report regarding permission of agrochemicals. <http://www.acis.famic.go.jp/toroku/sikkouseibun.htm> (in Japanese).
- Allinson G., Ueoka M. and Morita M., 1993: Effect of dietary 1, 3, 6, 8- tetrachlorodibenzo-*p*-dioxin on the Japanese freshwater fish *Oryzias latipes* (Medaka) and aquatic snail *Indoplanorbis exustus* (Indohiramakigai). *Chemosphere*, **28**, 1369-1383.
- Anezaki K., Yamaguchi K., Natsume S., Iwate R. and Hashimoto S., 2007: Estimation of PCB sources using statistical methods. *Japan Soc. Anal. Chem.*, **56**, 639-648 (in Japanese).
- Birmingham B., Gilman A., Gant D., Salmineb J., Boddington M., Thorpe B., While I., Toft P. and Armstrong V., 1989: PCDD/PCDF multimedia exposure analysis for the Canadian population: Detailed exposure estimation, *Chemosphere*, **19**, 637-642.
- Booker S. M., 2001: Dioxin in Vietnam: fighting a legacy of war. *Environ. Health Perspective*, **109**, A116-A117.
- Brochu C., Moore S. and Pelletier E., 1995: Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in sediments and biota of the Saguenay Fjord and the St Lawrence Estuary. *Mar. Poll. Bull.*, **30**, 515-523.
- Broman D., Naf C., Rolff C., Zebuhr Y., Fry B. and Hobbie J., 1992: Using ratios of stable nitrogen isotopes to estimate bioaccumulation and flux of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in two food chains from the Northern Baltic. *Environ. Toxicol. Chem.*, **11**, 331-345.
- Claudia T. W. and Matsumura F., 1978: Fate of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin in a model aquatic environment. *Arch. Environ. Contam. Toxicol.*, **7**, 349-357.
- Coulter C.T., 2004: EPA-CMB8.2 Users Manual, EPA-452/R-04-011 (<http://www.epa.gov/scram001/models/receptor/EPA-CMB82Manual.pdf>).
- Czuczwa J.M. and Hites R.A., 1984: Environmental fate of combustion-generated polychlorinated dioxins and furans. *Environ. Sci. Technol.*, **18**, 444-450.
- Czuczwa J.M., Niessen F. and Hites R.A., 1985: Historical record of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in Swiss Lake sediments. *Chemosphere*, **14**, 1175-1179.
- Devillers J., Bintein S. and Domine D., 1996: Comparison of BCF models based on log P. *Chemosphere*, **33**, 1047-1065.
- Ebe K., Tachibana K., Hirakawa H. and Ishida T., 1991: Trend in stock of sand lance in the coastal of Fukushima. *Bull. Fukushima Pref. Fish. Exp. Stn.*, **7**, 141-146 (in Japanese).
- Evers E.H.G., Klamer H.J.C. Laane R.W.P.M. and Govers A.J., 1993: Polychlorinated dibenzo-*p*-dioxin and dibenzofurans residues in estuarine and coastal north sea sediments: sources and distribution. *Environ. Toxicol. Chem.*, **12**, 1583-1598.
- Fauchald K. and Jumars P.A., 1979: The diet of worms: A study of polychaete feeding guilds. *Oceanogr. Mar. Biol. Ann. Rev.*, **17**, 193-284.
- Fisheries Agency, Japan, 2000a: Daiokishinruino-Gyokairuikarano-Sesyuryo nitsuite, Press release. <http://www.jfa.maff.go.jp/rerys/12.02.04.1.html> (in Japanese).
- Fisheries Agency, Japan, 2000b: Heisei 11nendo-Gyokairuityuno-Daiokishinrui no-Jittai tyosa kekka nitsuite, Press release. <http://www.jfa.maff.go.jp/rerys/12.10.25.1.html> (in Japanese).
- Fisheries Agency and Fisheries Research Agency of Japan, 2001-2006: Marine Fisheries stock assessment and evolution for Japanese waters. <http://abchan.job.affrc.go.jp/> (in Japanese).
- Fisheries Agency Japan, 2003: A report on dioxins in fish and shellfish from 1999 to 2002. http://www.jfa.maff.go.jp/release/20030627press_11.htm (in Japanese).
- Fisk A.T., Hobson K.A. and Norstrom R.J., 2001: Influence of chemical and biological factors on trophic transfer of persistent organic pollutants in the Northwater Polynya marine food web. *Environ. Sci. Technol.*, **35**, 732-738.
- Foundation for Promoting Personal Mobility and Ecological Transportation 2001: The investigation of dioxins in ports. Tokyo, 93pp, (in Japanese).
- Gotz R., Friesel P., Roch K., Papke O., Ball M., Lis

- A., 1993: Polychlorinated-p-dioxins (PCDDs), dibenzofurans (PCDFs), and other chlorinated compounds in the River Elbe: Results on bottom sediments and fresh sediments collected in sedimentation chambers. *Chemosphere*, **27**, 105–111.
- Guruge K. S. and Tanabe S., 2004: Polychlorinated dibenzo-p-dioxins, dibenzofurans and dioxin-like biphenyls in biota from Sri Lankan coast. *Mar. Pollut. Bull.*, **48**, 1004–1008.
- Handa N. and Ohta, K., 1983: Sedimentary record of polycyclic aromatic hydrocarbon pollution in Tokyo Bay. *Geochemical J.*, **16**, 60–67 (in Japanese).
- Hashimoto S., Wakimoto T. and Tatsukawa R., 1990: PCDDs in the sediments accumulated about 8120 years ago from Japanese coastal areas. *Chemosphere*, **20**, 825–835.
- Hashimoto S. and Morita M. 1995: Analysis of PCDDs, PCDFs, planar and other PCBs in seaweed from Japanese coast. *Chemosphere*, **31**, 3887–3897.
- Hashimoto S., Hyeon-Seo C. and Morita M., 1998: Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in shellfishes from south coast of Korea. *Chemosphere*, **37**, 951–959.
- Hashimoto S., Horiguchi T., Shibata Y. and Morita M., 1999: Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in invertebrate animals from a rural beach in Japan. *Chemosphere*, **39**, 2661–2669.
- Hashimoto S., 2004: Basic study on estimation of dioxin sources using statistical methods. *J. Environ. Chem.*, **14**, 263–285 (in Japanese with English abstract).
- Hattori Y., Shimizu T., Kishida M., Kamada A., Takahashi K., Tamura T., Uebori M. and Yamamoto, H., 2004: Distribution and characterization for dioxins in river water and sediment of Osaka Prefecture. *J. Environ. Chem.*, **14**, 575–585 (in Japanese).
- Hayakari S. and Hanaishi R., 2001: Introduction of spreadsheet application macros for environmental data analysis and analytical example (II) –Macro for CMB Analysis-. *J. Jpn. Atoms. Environ.*, **36**, 39–45 (in Japanese).
- Hoshika A., Shiozawa T. and Matsumoto E., 1983: Sedimentation rate and heavy metal pollution in sediments in Harima Nada (Harima Sound), Seto Inland Sea. *J. Oceanogr.*, **39**, 82–87 (in Japanese).
- Iimura F., Sasaki Y., Tsukui T., Yoshioka H., Higashino K., Takeda Y. and Kasai K., 2002: Contamination of dioxins and PCBs in fish in Tokyo Bay. *J. Environ. Chem.*, **12**, 343–352.
- Ikeda K., Minani T., Yamada H. and Koyama J., 2002: bioaccumulation of organotin compounds through the food web developed in the deep water of Japan Sea. *J. Environ. Chem.*, **12**, 105–114 (in Japanese).
- Ikematsu W., 1963: Ecological studies on the fauna of Macrura and Mysidacea in the Ariake Sea. *Bull. Seikai Fish. Res. Lab.*, **30**, 1–124 (in Japanese).
- Isosaari P., Kohonen T., Kiviranta H., Tuomisto H. and Vartiainen T., 2000: Assessment of levels, distribution, and risks of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the vicinity of a vinyl chloride monomer production plant. *Environ. Sci. Technol.*, **34**, 2684–2689.
- Isosaari P., Kankaanpaa H., Mattila J., Kiviranta H., Verta M., Salo S. and Vartiainen T., 2002: Spatial distribution and temporal accumulation of polychlorinated dibenzo-*p*-dioxins, dibenzofurans, and biphenyls in the Gulf of Finland. *Environ. Sci. Technol.*, **36**, 2560–2565.
- Japan Environmental Safety Corporation, 2004: PCB waste treatment program. <http://www.jesconet.co.jp/business/scheme/index.html> (in Japanese).
- Japan Industrial Standard Committee, 1999a: Test method for density of soil particles. JISA1202.
- Japan Industrial Standard Committee, 1999b: Test method for water content of soils. JISA1203.
- Japan Industrial Standard Committee, 2000: Test method for ignition loss of soils. JISA1226.
- Japan Meteorological Agency, 2002: <http://www.jma.go.jp/jma/indexe.html>.
- Japan Plant Protection Association, 1963–1995: The shipments of agricultural chemicals, in Japan Plant Protection Association (ed.), *Agricultural chemicals handbook*, Tokyo, Japan (in Japanese).
- Japan River Association, 2001–2004: Daily Discharge Tables, In: River Bureau. Ministry of Land, Infrastructure and Transport, Japan (Ed.),

- Discharge Tables 2000–2002, Tokyo Japan (in Japanese).
- Juttner I., Henkelmann B., Steinberg C.E.W., Winkler R. and Kettrup, A., 1997: Occurrence of PCDD/F in dated lake sediments of the black forest, Southwestern Germany. *Environ. Sci. Technol.*, **31**, 806–812.
- Kadota Y., Kawano M., Matsuda M. and Wakimoto T., 2007: The outflow properties of PCDD/DFs in ricefield. 1. The relationship between discharged paddy soil particle and PCDD/DFs. *J. Environ. Chem.*, **17**, 185–195 (in Japanese with English abstract).
- Kakimoto H., Oka H., Miyata Y., Yonezawa Y., Niikawa A., Kyudo H., Tang N., Toriba A., Kizu R. and Hayakawa K., 2006: Homologue and isomer distribution of dioxins observed in water samples collected from Kahokugata Lagoon and inflowing rivers, Japan. *Wat. Res.*, **40**, 1929–1940.
- Kanai Y., Inouchi Y., Yamamuro M., and Tokuoka T., 1997: Sedimentation rate and environment in Lake Shinji, Shimane Prefecture. *Geochemistry*, **32**, 71–85 (in Japanese).
- Kannan N., Tanabe S., Wakimoto T. and Tatsukawa R., 1987: A simple method for determining non-ortho PCB substituted PCBs in Kanechlors, Arochlors and environmental samples, *Chemosphere*, **16**, 1631–1634.
- Kannan N., Tanabe S. and Tatsukawa R., 1989: Persistency of highly toxic coplanar PCBs in aquatic ecosystem: uptake and release kinetics of coplanar PCBs in green-lipped mussels (*Perna viridis* Linnaeus). *Environ. Poll.*, **56**, 65–76.
- Kannan K., Villeneuve D. L., Yamashita N., Imagawa T., Hashimoto S., Miyazaki A. and Giesy, J. P., 2000: Vertical profiles of dioxin-like and estrogenic activities associated with a sediment core from Tokyo Bay, Japan. *Environ. Sci. Technol.*, **34**, 3568–3573.
- Kashiwagi N., Yoshizawa T., Ibaraki T., Kato K., Hashimoto A. and Sasaki Y., 2006: Estimation of contribution of unidentified sources to environmental concentration. *Proceedings Inst. Statistical Math.*, **54**, 123–146 (in Japanese with English abstract).
- Kato K., Nakamura T., Hishinuma S., Suzuki S., Saito Y., Hashimoto S. and Kashiwagi N., 2005: Study on estimation of dioxin source II (case of estimation in Miyagi). *Annual report of Miyagi Prefecture Institute of Public Health and Environment*, **23**, 65–67 (in Japanese).
- Kiguchi O., Kobayashi T., Wada Y., Saitoh K. and Ogawa N., 2007: Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in paddy soils and river sediments in Akita, Japan. *Chemosphere*, **67**, 557–573.
- Kim J.G., Suzuki N., Masunaga S., Nakanishi J., 1996: Concentrations and biota-sediment accumulations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in fish and shrimp from Lake Kasumigaura. *J. Environ. Chem.*, **6**, 541–549.
- Kim K. S., Hirai Y., Kato M., Urano K. and Masunaga S., 2004: Detailed PCB congener patterns in incinerator flue gas and commercial PCB formulations (Kanechlor). *Chemosphere*, **55**, 539–553.
- Kitagawa D., Ishito Y., Sakurai Y., Fukunaga T., 1994: Age, growth and maturation of the Japanese Flounder *Paralichthys olivaceus* in coastal waters of the Northern Sanriku District. *Tohoku Natl. Fish. Res. Inst.*, **56**, 69–76 (in Japanese).
- Kjeller L.O. and Rappe C., 1995: Time trends in levels, patterns, and profiles for polychlorinated dibenzo-*p*-dioxins, dibenzofurans, and biphenyls in a sediment core from the Baltic Proper. *Environ. Sci. Technol.*, **29**, 346–355.
- Kobayashi N., Nagashima H., Kodama J., Kikuchi Y., Kobayashi I. and Sato, K., 1995: Study on the ecology and resource of the sandeel, *Ammodytes personatus* Girard, in Sendai Bay (in Japanese). *Bull. Miyagi. Pref. Fish. Res. Dev. Center*, **14**, 37–49.
- Kobayashi N., Masunaga S. and Nakanishi J., 2003: Source identification and behavior of PCDD/Fs and dioxin-like PCBs in Japanese river water. *J. Japan Soc. Wat. Environ.*, **26**, 655–662 (in Japanese with English abstract).
- Kobayashi J., Kajiwara H. and Takahashi Y., 2004a: Behavior and mass balance of PCDD/Fs and herbicides in paddy fields. *J. Environ. Chem.*, **14**, 109–120 (in Japanese with English abstract).

- Kobayashi N., Masunaga S. and Nakanishi J., 2004b: Transportation and sources of dioxin and dioxin-like PCBs in rivers flowing into Tokyo Bay. *J. Jpn. Soc. Wat. Environ.*, **27**, 465-472 (in Japanese with English abstract).
- Koistinen J., Paasivirta J. and Lahtipera M., 1993: Bioaccumulation of dioxins, coplanar PCBs, PCFEs, HxCNs, R-PCNs, R-PCPHs and R-PCBBs in fish from a pulp-mill recipient watercourse. *Chemosphere*, **27**, 149-156.
- Kubota A., Someya M., Watanabe M. and Tanabe S., 2002: Contamination status of PCBs (including coplanar congeners), polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in sediments from Uwa Sea, Japan. *Nippon Suisan Gakkaishi*, **68**, 695-700 (in Japanese).
- Kumar K.S., Kannan K., Paramasivan O.N., Sundaram V.P.S., Nakanishi J., and Masunaga S., 2001: Polychlorinated Dibenzo-*p*-Dioxins, Dibenzofurans, and Polychlorinated Biphenyls in Human Tissues, Meat, Fish, and Wildlife Samples from India. *Environ. Sci. Technol.*, **35**, 3448-3455.
- Kurokawa Y., Matsueda T., Osaki Y., Nakamura M., Takata S. and Fukumachi K. 1994: Concentration and characteristics of non-*ortho* coplanar PCBs in the atmosphere. *J. Environ. Chem.*, **4**, 29-38 (in Japanese).
- Kurtz F., Barnes D.G., Bottimore D.P., Greim H. and Bretthauer E.W., 1990: The international toxicity equivalency factor (I-TEF) method of risk assessment for complex mixtures of dioxins and related compounds. *Chemosphere*, **20**, 751-757.
- Ling Y. C., Soong D.K. and Lee M.K., 1995: PCDD/DFs and coplanar PCBs in sediment and fish samples from the Er-Jen River in Taiwan. *Chemosphere*, **31**, 2863-5872.
- Lohmann R. and Jones K.C., 1998: Dioxins and furans in air and deposition: a review of levels, behavior and processes. *Sci. Total. Environ.*, **219**, 53-81.
- Masunaga S., Sakurai T., Kim J.G., Suzuki N. and Nakanishi J., 1997: Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in sediment, soil, and biological samples from Lake Kasumigaura area. *Bull. Inst. Environ. Sci. Technol., Yokohama Natl. Univ.*, **23**, 1-12 (in Japanese).
- Masunaga S., Sakurai T. and Nakanishi J., 1998: Dioxin mass balances in Tokyo Bay and Kasumigaura Lake basin. *Bull. Inst. Environ. Sci. Technol., Yokohama Natl. Univ.*, **24**, 1-10 (in Japanese with English abstract).
- Masunaga S., 2000: Comprehensive analysis of dioxin and co-PCB behavior in Lake Shinji Basin. Proc. Third International Workshop on Risk Evaluation and Management of Chemicals. *Yokohama, Japan, January 2000*, pp. 80-93.
- Masunaga S., Takasuga T. and Nakanishi J., 2001a: Dioxin and dioxin-like PCB impurities in some Japanese agrochemical formulations. *Chemosphere*, **44**, 873-885.
- Masunaga S., Yao Y., Ogura I., Nakai S., Kanai Y., Yamamuro M. and Nakanishi J., 2001b: Identifying sources and mass balance of dioxin pollution in Lake Shinji Basin, Japan. *Environ. Sci. Technol.*, **35**, 1967-1973.
- Masunaga S., Nakanishi J. and Kameda Y., 2006: Dioxins in Tokyo Bay: Its environmental behavior and ecological risk assessment to birds. <http://bio-eco.eis.ynu.ac.jp/jpn/database/report/masunaga.pdf> (in Japanese with English abstract).
- Mato Y., Suzuki N., Katani N., Kadokami K., Nakano T., Nakayama S., Seki. H., Komoto S., Miyake S. and Morita M., 2007: Human intake of PCDDs, PCDFs, and dioxin like PCBs in Japan, 2001 and 2002. *Chemosphere*, **67**, S247-S255.
- Matsumoto E. and Yokota S., 1978: Accumulation rate and heavy metal pollution in Osaka Bay sediments. *J. Oceanogr.*, **34**, 108-115 (in Japanese).
- Matsumoto E. 1983: The sedimentary environment in Tokyo Bay. *Geochemistry*, **17**, 27-32 (in Japanese).
- Matsumoto E., 1986: The measurement of sedimentation rate in sediments. In "The manual of investigation of the coastal environment" (ed. The Oceanographic Society of Japan), pp. 37-42 (in Japanese).
- Miller M. M. and Waslk S. P., 1985: Relationships between Octanol-Water Partition Coefficient and Aqueous Solubility. *Environ. Sci. Technol.*, **19**,

- 522-529.
- Ministry of Agriculture, Forestry and Fisheries, 2010: Cultivated paddy field acreage in Miyagi Prefecture. http://www.maff.go.jp/j/tokei/kouhyou/sityo_tyouki/kouti/k4.html (in Japanese).
- Ministry of Health, Labour and Welfare, 1999: Heisei 10nendo syokuhintyuno daiokishin osen jittai tyosa kekka nitsuite. http://www1.mhlw.go.jp/topics/dioxin_13/tds.html (in Japanese).
- Ministry of Health, Labour and Welfare, 2007: Heisei 18nendo syokuhintyuno daiokishin osen jittai tyosa kekka nitsuite. <http://www.mhlw.go.jp/topics/bukyoku/iyaku/syoku-anzen/dioxin/sessyu06/index.html> (in Japanese).
- Ministry of Internal Affairs and Communications, Japan, 1999: The law concerning special measures against dioxins. <http://law.e-gov.go.jp/htmldata/H11/H11HO105.html> (in Japanese).
- Ministry of Internal Affairs and Communications, Japan, 2005: Special law concerning adequate disposal of PCB. <http://law.e-gov.go.jp/htmldata/H13/H13HO065.html> (in Japanese).
- Ministry of Internal Affairs and Communications, Japan, 2010: Chemical Substances Control Law. <http://law.e-gov.go.jp/htmldata/S48/S48HO117.html> (in Japanese).
- Ministry of Land, Infrastructure and Transport, Government of Japan, 2001: The investigation of endocrine disrupting chemicals in ports. (ed. Waterfront Vitalization and Environment Research Center), Tokyo, 259pp (in Japanese).
- Ministry of the Environment, Japan, 1996-2005: Chemicals in the Environment. <http://www.env.go.jp/chemi/kurohon/index.html> (in Japanese).
- Ministry of the Environment, 1998a: The manual of the investigation of dioxins in water, Tokyo (in Japanese).
- Ministry of the Environment, 1998b: The manual of the investigation of dioxins in aquatic organisms, Tokyo (in Japanese).
- Ministry of the Environment, Japan, 1999: Tolerable Daily Intake. <http://www.env.go.jp/chemi/dioxin/report/TDI/gaiyo.html> (in Japanese).
- Ministry of the Environment, Japan, 2000a: What are dioxins? <http://www.erc.pref.fukui.jp/news/d00.html> (in Japanese).
- Ministry of the Environment, 2000b: The manual of the investigation of dioxins in sediments, Tokyo (in Japanese).
- Ministry of the Environment, Japan, 2002: Emissions of dioxins from paddy fields and other farm fields. <http://www.env.go.jp/water/dojo/sui-diox/13sui-dio.pdf> (in Japanese).
- Ministry of the Environment, Japan, 2005: Inventory of dioxin emissions. <http://www.env.go.jp/press/press.php?serial=6584> (in Japanese).
- Ministry of the Environment, Japan, 2007: The law concerning the evaluation of chemical substances and regulation of their manufacture, etc. (Chemical Substances Control Law). <http://www.env.go.jp/chemi/kagaku/index.html> (in Japanese).
- Mitani I., 1988: Food habits of Japanese anchovy in the Shirasu fishing ground within Sagami Bay (in Japanese). *Nippon Suisan Gakkaishi*, **54**, 1859-1865.
- Mocarelli P., Patterson D. G. Jr., Marocchi A. and Needham L. L., 1990: Pilot study (Phase II) for determining polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) levels in serum of Seveso, Italy residents collected at the time of exposure: Future plans. *Chemosphere*, **20**, 967-974.
- Mocarelli P., Brambilla P., Gerthoux P.M., Patterson D.G.Jr. and Needham L.L., 1996: Change in sex ratio with exposure to dioxin. *Lancet*, **348**, 409.
- Morita M., 1991: Dioxins, their chemistry and toxic effects. *Jpn. Tappi J.*, **45**, 887-901.
- Motoda S., 1994: An estimation of primary and secondary production of the coral reef areas in Palau, Western Caroline Islands. Rep. Akajima *Mar. Sci. Lab.*, **5**, 5-8.
- Muir D.C.G., Marshall W.K. and Webster G.R.B., 1985: Bioconcentration of PCDDs by fish: effects of molecular structure and water chemistry. *Chemosphere*, **14**, 829-833.
- Muir D.C.G. and Yarechewski A.L., 1988: Dietary accumulation of four chlorinated dioxin congeners by rainbow trout and fathead minnows. *Environ. Toxicol. Chem.*, **7**, 227-236.

- Naito W., Jin J., Kang Y., Yamamuro M., Masunaga S., Nakanishi J., 2003: Dynamics of PCDDs/DFs and coplanar-PCBs in an aquatic food chain of Tokyo Bay. *Chemosphere*, **53**, 347-362.
- Nakatani T., 2006: Dioxins (polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans and coplanar PCBs) in human milk. *Seikatsu Eisei*, **50**, 185-196.
- Niimi A.J., 1996: Evaluation of PCBs and PCDD/Fs retention by aquatic organisms. *Sci. Total Environ.*, **192**, 123-150.
- Ochiai A., 1966: *Paralichthys olivaceus*. in "Gyoryugaku" (eds. Matsubara, K., Ochiai, A.), Kouseisha Kouseikaku, Tokyo, pp. 911-913 (in Japanese).
- Omori M., 1974: On the production ecology of the flatfish, *Limanda yokohamae* - I Feeding habit and distribution. *Bull. Jpn. Sci. Fish.*, **40**, 1115-1126 (in Japanese).
- Opperhuizen A., Sijm D.T.H.M., 1990: Bioaccumulation and biotransformation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in fish. *Environ. Toxicol. Chem.*, **9**, 175-186.
- Owens J.W., Swanson S.M. and Birkholz D.A., 1994: Bioaccumulation of 2, 3, 7, 8-tetrachlorodibenzo-*p*-dioxin, 2, 3, 7, 8-tetrachlorodibenzofuran and extractable organic chlorine at a bleached-kraft mill site in a northern Canadian river system. *Environ. Toxicol. Chem.*, **13**, 343-354.
- Prime Minister of Japan and His Cabinet, 2007: A summary of projects related to dioxins and endocrine disrupters in the environment. <http://www.kantei.go.jp/jp/mille/daiokisin/index.html> (in Japanese).
- Rappe C., Andersson R., Bergqvist P.A., Brohede C., Hansson M., Kjeller L.O., Lindstrom G., Marklund S., Nygren M., Swanson S.E., Tysklind M. and Wiberg K., 1987: Overview on environmental fate of chlorinated dioxins and dibenzofurans. Sources, levels and isomeric pattern in various matrices, *Chemosphere*, **16**, 1603-1618.
- Rappe C., Bergqvist P.A. and Kjeller L.O., 1989: Levels, trends, and patterns of PCDDs and PCDFs in Scandinavian environmental samples. *Chemosphere*, **18**, 651-658.
- Rappe C., Bergqvist P.A., Kjeller L.O. and Swanson S., 1991: Levels and patterns of PCDD and PCDF concentration in fish, crabs, and lobsters from Newark Bay and the New York bight. *Chemosphere*, **22**, 239-266.
- River Bureau, Ministry of Land, Infrastructure and Transport, 2003: The distance of A-class rivers, <http://www.mlit.go.jp/river/jiten/toukei/index.html> (in Japanese).
- Sakai, S., Hiraoka M., Takeda N. and Shiozaki K., 1993: Coplanar PCBs and PCDDs/PCDFs in municipal waste incineration. *Chemosphere*, **27**, 233-240.
- Sakai S., Hiraoka M., Takeda N. and Shiozaki K., 1996: Behavior of coplanar PCBs and PCNs in oxidative conditions of municipal waste incineration. *Chemosphere*, **32**, 79-88.
- Sakai S., Deguchi S., Urano S., Takatsuki H., and Megumi K., 1999: Time trends of PCDDs/Fs in Lake Biwa and Osaka Bay. *J. Environ. Chem.*, **9**, 379-390 (in Japanese).
- Sakaji H., 2002: Fishery biological studies on penaeid shrimps in Tosa Bay, Pacific coast of Japan. *Bull. Fish. Res. Agency*, **6**, 73-127 (in Japanese with English abstract).
- Sakurai T., Kim J.G., Suzuki N., Matsuo T., Li D.Q., Yao Y., Masunaga S. and Nakanishi J., 2000: Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in sediment, soil, fish, shellfish, and crab samples from Tokyo Bay area, Japan. *Chemosphere*, **40**, 627-640.
- Sarna L. P., Hodge P. E. and Webster G. R. B., 1984: Octanol-water partition coefficients of chlorinated dioxins and dibenzofurans by reversed-phase HPLC using several C18 columns. *Chemosphere*, **13**, 975-983.
- Sasaki Y., 2000: Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in organisms. *J. Environ. Chem.*, **10**, 517-532 (in Japanese).
- Sato Y., 1975: Studies on the life history of the bastard halibut, *Paralichthys olivaceus* (Temminck et Schlegel), near Sendai Bay. *Bull. Tohoku Reg. Fish. Res. Lab.*, **35**, 15-30 (in Japanese).
- Satomi Y. 1992: Toxicity of dioxins to aquatic organisms. *Seisan-no-kenkyu (Study of Fishery)*, **11**, 61-76. (in Japanese).

- Schimmel S.C., Patrick J.M. Jr., Forester J., 1977: Uptake and toxicity of toxaphene in several estuaries organisms. *Arch. Environ. Contam. Toxicol.*, **5**, 353-367.
- Schrann K.W., Henkelmann B. and Kettrup A., 1995: PCDD/F sources and levels in river Elbe sediments. *Wat. Res.*, **29**, 2160-2166.
- Schwetz B.A., Norris J.M., Sparschu G.L., Rowe V.K., Gehring P.J., Emerson J.L. and Gerbig C.G., 1973: Toxicology of chlorinated dibenzo-*p*-dioxins. *Environ. Health Perspect.*, **5**, 87-99.
- Seike N., Otani T., Ueji M., Takasuga T. and Tsuzuki N., 2003: Temporal change of polychlorinated dibenzo-*p*-dioxins, dibenzofurans and dioxin like polychlorinated biphenyls source in paddy soils. *J. Environ. Chem.*, **13**, 117-131.
- Hashimoto S., Wakimoto T. and Tatsukawa R., 1990: PCDDs in the sediments accumulated about 8120 years ago from Japanese coastal areas. *Chemosphere*, **20**, 825-835.
- Sijm D.T.H.M., Wever H. and Opperhuizen A., 1993: Congener - specific biotransformation and bioaccumulation of PCDDs and PCDFs from fly ash in fish. *Environ. Toxicol. Chem.*, **12**, 1895-1907.
- Sinkkonen S. and Paasivirta J. 2000: Degradation half-life times of PCDDs, PCDFs and PCBs for environmental fate modeling. *Chemosphere*, **40**, 943-949.
- Sook-Hyeon I.M., Byung-Yoon M.I.N., Matsuda M. and Wakimoto T., 1995: Levels of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in surface sediments at and surface soils around Masan Bay in Korea. *J. Environ. Chem.*, **5**, 625 (in Japanese).
- Stachel B., Gotz R., Herrmann T., Kruger F., Knoth W., Papke O., Rauhut U., Reincke H., Schwartz R., Steeg E. and Uhlig S., 2004: The Elbe flood in August 2002 - occurrence of polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans (PCDD/F) and dioxin-like PCB in suspended particulate matter (SPM), sediment and fish. *Wat. Sci. Technol.*, **50**, 309-316.
- Stapleton H.M., Masterson C., Skubinna J., Ostrom P., Ostrom N.E. and Baker J.E., 2001: Accumulation of atmospheric and sedimentary PCBs and toxaphene in a Lake Michigan food web. *Environ. Sci. Technol.*, **35**, 3287-3293.
- Takada H., Ogura N., and Ishiwatari R. 1992: Seasonal variations and modes of riverine input of organic pollutions to the coastal zone: 1. Flux of detergent-derived pollutants to Tokyo Bay. *Environ. Sci. Technol.*, **26**, 2517-2523.
- Takada H., 1997: Fluxes of land-derived materials to Japanese coastal zones. *Bull. Coastal Oceanogr.*, **34**, 111-117 (in Japanese).
- Takasuga T., Inoue T., and Ohi E., 1995: All congener specific analytical method for polychlorinated biphenyls (PCBs) with various chromatographic clean-up and HRGC/HRMS. *J. Environ. Chem.*, **5**, 647-675 (in Japanese).
- Takayama K., Miyata H., Aozasa O., Mimura M. and Kashimoto T., 1991: Dietary intake of dioxin-related compounds through food in Japan. *Syokueishi*, **32**, 525-532 (in Japanese).
- Tamakawa K., Ohgane Y., Aihara Y., Hiroshima K., Katoh M., Mishima Y. and Seki T., 1984: SEK-PAK katorizi - niyuru - gifenirueteru - kei - josozaino - kanibunsekihou. *Sendaishi eisei sikenjohou*, **14**, 261-266 (in Japanese).
- Tamura T., 1960: Suisangaku-zensyu. in "Senkai-zosyokugaku", Kouseisha-Kouseikaku, Tokyo, Japan, vol. 2, pp. 210-221 (in Japanese).
- Tanabe S. and Tatsukawa R., 1981: Behavior of chlorinated hydrocarbons in coastal zones and estuaries. *Bull. Coastal Oceanogr.*, **19**, 9-19 (in Japanese).
- Tanaka Y., 2006: The measurement of green algae: *Spirogyra*. *Ai-ken letter*, **2**, 2-4.
- Taniguchi M., 2005: Flax material through marine boundary. in "global atmospheric and aquatic chemistry", Tokyo, Japan, 2005, vol. 6, 249-252 (in Japanese).
- Tanimoto T. and Hoshika A., 1994: Settling velocity of suspended particles in Osaka Bay and Etauchi Bay. *Oceanogr. Jpn.*, **3**, 13-20 (in Japanese).
- Tatsukawa R., 1972: PCB pollution. *P.P.M.*, **8**, 43-52 (in Japanese).
- Tohoku Regional Agricultural Office, 1987-2006: Annual report of Agriculture, Forestry and Fisheries in Miyagi Prefecture (in Japanese).
- Toyoda M., Uchibe H., Yanagi T., Kono Y., Hori T. and Iida T. 1999: Dietary daily intake of PCDDs, PCDFs, and coplanar PCBs by total diet study

- in Japan. *Syokueishi*, **40**, 98–110 (in Japanese).
- Trowbridge A.G. and Swackhamer D.L., 2002: Preferential biomagnification of aryl hydrocarbon hydroxylase-inducing polychlorinated biphenyls in the Lake Michigan, USA, lower food web. *Environ. Toxicol. Chem.* **21**, 334–341.
- Tsutsumi T., Yanagi T., Nakamura M., Kono Y., Uchibe H., Iida T., Horii T., Nakagawa R., Tobiishi K., Matsuda R., Sasaki K. and Toyoda M., 2001: Update of daily intake of PCDDs, PCDFs, and dioxin-like PCBs from food in Japan. *Chemosphere*, **45**, 1129–1137.
- Uegaki R., Seike N. and Otani T., 2006: Polychlorinated dibenzo-*p*-dioxins, dibenzofurans, and dioxin-like polychlorinated biphenyls in rice plants: possible contaminated pathways. *Chemosphere*, **65**, 1537–1543.
- Uematsu M., Minagawa M., Arita H. and Tsunogai S., 1978: Determination of dry weight of total suspended matter in seawater (in Japanese). *Bull. Fac. Fish. Hokkaido Univ.*, **29**, 164–172.
- U.S. Environmental Protection Agency, 1983: NPL Site Narrative for Times Beach Site. <http://www.epa.gov/superfund/sites/npl/nar833.htm>.
- U.S. Environmental Protection Agency, 2009: TRI Dioxin and Dioxin-like Compounds Toxic Equivalency (TEQ) Information Rule- Final rule. <http://www.epa.gov/tri/lawsandregs/teq/teqfinalrule.html#Q2>.
- Van den Berg M., Birnbaum L., Bosveld A. T., Brunstrom B., Cook, P., Feeley M., Giesy J. P., Hanberg A., Hasegawa R., Kennedy S. W., Kubiak T., Larsen J. C., van Leeuwen F. X., Liem A. K., Nolt C., Peterson R. E., Poellinger L., Safe S., Schrenk D., Tillitt D., Tysklind M., Younes M., Waern F. and Zacharewski T., 1998: Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environ. Health Perspect.*, **106**, 775–792.
- Vartiainen T., Mannio J., Korhonen M., Kinnunen K. and Strandman T., 1997: Levels of PCDD, PCDF and PCB in dated lake sediments in subarctic Finland. *Chemosphere*, **34**, 1341–1350.
- Verta M., Lehtoranta J., Salo S., Korhonen M. and Kiviranta H., 1999: High concentrations of PCDD's and PCDF's in river Kymijoki sediments, South-Eastern Finland, caused by wood preservative Ky-5. *Organohalogen Compounds*, **43**, 261–264.
- Verta M., Salo S., Malve O. and Kiviranta H., 2003: Continued transport of PCDD/F contaminated sediments from River Kymijoki to Gulf of Finland, the Baltic Sea. *Organohalogen Compounds*, **61**, 405–408.
- Verta M., Salo S., Korhonen M., Assmuth T., Kiviranta H., Koistinen J., Ruokojarvi P, Isosaari P., Bergqvist P.A., Tysklind M., Cato I., Vikelsoe J. and Larsen M.M., 2007: Dioxin concentrations in sediments of the Baltic Sea – A survey of existing data. *Chemosphere*, **67**, 1762–1775.
- Wan Y., Hu J., Yang M., An L., An W., Jin X., Hattori T. and Itoh M., 2005: Characterization of Trophic Transfer for Polychlorinated Dibenzop-dioxins, Dibenzofurans, Non- and Mono-ortho Polychlorinated Biphenyls in the Marine Food Web of Bohai Bay, North China. *Environ. Sci. Technol.*, **39**, 2417–2425.
- Wenning R.J., Harris M.A., Finley B., Paustenbach D.J. and Bedbury H., 1993: Application of Pattern Recognition Techniques to Evaluate Polychlorinated Dibenzop-dioxin and Dibenzofuran Distributions in Surficial Sediments from the Lower Passaic River and Newark Bay. *Ecotoxicol. Environ. Safety*, **25**, 103–125.
- Wenning R., Dodge D., Peck B., Shearer K., Luksemburg W., Sala S.D. and Scazzola R., 2000: Screening-level ecological risk assessment of polychlorinated dibenzop-dioxins and dibenzofurans in sediments and aquatic biota from the Venice Lagoon, Italy. *Chemosphere*, **40**, 1179–1187.
- Wikipedia, 2008: Polychlorinated dibenzodioxins. http://en.wikipedia.org/wiki/Polychlorinated_dibenzodioxins.
- Woodburn K. B., Doucette W. J. and Andren A. W., 1984: Generator column determination of octanol/water partition coefficients for selected polychlorinated biphenyl congeners. *Environ. Sci. Technol.*, **18**, 457–459.
- Woodwell G. M., Wurster C. F. Jr, Peter A.I., 1967: DDT residues in an east coast estuary: A case of biological concentration of a persistent

- insecticide. *Science*, **156**, 821-824.
- Wu W.Z., Schramm K.W. and Kettrup A., 2001: Bioaccumulation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the foodweb of Ya-er Lake area, China. *Water Res.*, **35**, 1141-1148.
- Yamada H., Kawamura T., Takeuchi T. and Yamashita Y., 1995: Effects of dietary condition on the survival, growth and reproduction of *Acanthomysis mitsukuri* (Crustacea, Mysidacea). *Bull. Plankton Soc. Jpn.*, **42**, 43-52.
- Yamada H., Tateishi M., Ikeda K., 1995: The effect of the size of test fish species on bioconcentration characteristics of *a*-hexachlorocyclohexane. *Nippon Suisan Gakkaishi*, **61**, 905-911 (in Japanese).
- Yamada H., 1997a: Bioaccumulation of polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs) in aquatic organisms'. *Bull. Natl. Res. Inst. Fish. Sci.*, **9**, 139-161 (in Japanese).
- Yamada H., 1997b: Hatching and early feeding of Japanese sand eel *Ammodytes personatus* in the Ise Bay. *Nippon Suisan Gakkaishi*, **64**, 440-446 (in Japanese).
- Yamada H., Sato K., Nagahora S., Kumagai A. and Yamashita Y., 1998: Feeding habit of the Japanese flounder *Paralichthys olivaceus* in Pacific coastal water of Tohoku district, Northeastern Japan. *Nippon Suisan Gakkaishi*, **64**, 249-258 (in Japanese).
- Yamagishi T., Miyazaki T., Akiyama K., Morita M., Nakagawa J., Horii S. and Kaneko S., 1981: Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in commercial diphenyl ether herbicides, and in freshwater collected from the application area. *Chemosphere*, **10**, 1137-1144.
- Yamashita N., Kannan K., Imagawa T., Villeneuve D. L., Hashimoto S., Miyazaki A. and Giesy J. P., 2000: Vertical profile of polychlorinated dibenzo-*p*-dioxins, dibenzofurans, naphthalenes, biphenyls, polycyclic aromatic hydrocarbons, and alkylphenols in a sediment core from Tokyo Bay, Japan. *Environ. Sci. Technol.*, **34**, 3560-3567.
- Yamashita Y., Tanaka M., Miller J.M., 2001: Ecophysiology of juvenile flatfish in nursery grounds. *J. Sea Res.*, **45**, 205-218.
- Yanagi T., and Hashimoto T., 2000: Behavior of PCB in Tokyo Bay. *Bull. Coastal Oceanogr.*, **37**, 25-27 (in Japanese with English abstract).
- Yao Y., Masunaga S., Takada H. and Nakanishi J., 2002: Identification of polychlorinated dibenzo-*p*-dioxin, dibenzofurans, and coplanar polychlorinated biphenyl sources in Tokyo Bay, Japan. *Environ. Toxicol. Chem.*, **21**, 991-998.
- You J.C., Kim S.C., Choi K.H., Jeon S.E., Youn S.J. and Joo C.H., 2004: Study of indicator isomer in dioxin analysis. *Organohalogen Compounds*, **66**, 365-368.