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Mass Balance of Dioxins Derived from Pesticides in Sendai Bay, Japan

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Abstract

We calculated the mass balance of major congeners of dioxins derived from chloronitrophen (CNP) and pentachlorophenol (PCP) found in Sendai Bay, in order to characterize the present status of marine pollution caused by dioxins and enable the establishment of appropriate countermeasures against dioxin contamination. According to published statistics, about 58 000 t of CNP and about 22 000 t of PCP were shipped to Miyagi Prefecture over a 40-year period, and based on the these amounts of CNP and PCP, we estimated that 30.7 t of 1,3,6,8-tetrachlorinated dibenzo-*p*-dioxin (1,3,6,8-TeCDD), 1,3,7,9-TeCDD, and octa-chlorodibenzo-*p*-dioxin (OCDD) were introduced into the terrestrial environment as impurities contained in both pesticides. Mass balance analysis results show that most of these dioxins remained in the terrestrial environment and were not transported by runoff into Sendai Bay. Moreover, degradation mainly reduced the amount of dioxins in the terrestrial environment, instead of runoff or volatilization. Although large amounts of CNP and PCP were shipped to Miyagi Prefecture, only 0.8% of the total quantity of 1,3,6,8-TeCDD, 1,3,7,9-TeCDD, and OCDD contained in pesticides that were applied to paddy fields reached Sendai Bay via the discharge of major rivers. Moreover, most dioxins transported to the bay either flowed offshore or settled at the bottom of the bay. And there was very little bioaccumulation in marine organisms, particularly commercially valuable species.

Discipline: Fisheries
Additional key words: bioaccumulation, box model, CNP, dioxin fluxes, PCP

Introduction

Dioxins, polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like coplanar polychlorinated biphenyls (Co-PCBs) are highly hydrophobic and persistent organic pollutants. The sources of these chemicals include fly ash and exhaust gas from incinerators, industrial wastewater from pulp mills, and impurities in chlorinated pesticides. Once released into the environment, these pollutants enter aquatic environments via the hydrologic cycle.

In Miyagi Prefecture — the so-called granary of Japan that borders Sendai Bay — large amounts of chloronitrophen (CNP) and pentachlorophenol (PCP) were used in the past[8]. As Sendai Bay (located off the Pacific coast of northern Honshu) is the site of both wild fishery and aquaculture activities, there are growing concerns over the possible pollution of the bay's waters by dioxins derived from pesticides, and the uptake of such dioxins by marine organisms. Catch data on fish, shellfish, and seaweed in Sendai Bay have been published[5], and previous studies investigated the sources of dioxins in Sendai Bay, bioaccumulation thereof by flatfish, yearly changes in dioxin concentrations, and the rate of dioxin inflow into Sendai Bay from the terrestrial environment via runoff and river discharge[17-23]. The results of these studies have shown that impurities contained in PCP and CNP (i.e. pesticides used in rice cultivation) are the main sources of dioxin pollution in Sendai Bay[22].

The two main dioxin congeners occurring as impurities in CNP are 1,3,6,8-tetra-chlorodibenzo-*p*-dioxin (1,3,6,8-TeCDD) and 1,3,7,9-TeCDD; the main congener that occurs as an impurity in PCP is octa-chlorodibenzo-*p*-dioxin (OCDD)[13,25]. It has been shown that CNP and PCP applied to paddy fields account for more than 90% of PCDDs and PCDFs found in river water in Miyagi Prefecture, while incinerator exhaust gases account for

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less than 10%[22]. The predominant dioxin congeners detected in river water, seawater, and the sediments of Sendai Bay are 1,3,6,8-TeCDD, 1,3,7,9-TeCDD, and OCDD, whereas the concentration of 2,3,7,8-TeCDD, the most hazardous compound among PCDDs, is below the detection limit in most river water, seawater, and sediment samples[18,19,21,22].

To clarify the present status of marine pollution caused by dioxins so that appropriate countermeasures against dioxin contamination can be established, it is useful to determine the mass balance of these three predominant dioxin congeners (hereinafter, pesticidal PCDDs). We therefore calculated the mass balance of dioxins in Sendai Bay and Miyagi Prefecture by using available data on pesticidal PCDDs (Fig. 1, Table 1), and took into account the residual quantities in the terrestrial environment, inflow into Sendai Bay via the discharge of major rivers, concentrations in seawater, bioaccumulation in organisms, sedimentation, and outflow from Sendai Bay to offshore waters. Moreover, by calculating the mass balance of dioxins, we summarized the findings from various studies conducted on dioxin pollution in Sendai Bay.

Methods of data analysis

1. Total amounts of pesticidal PCDDs in the terrestrial environment of Miyagi Prefecture from 1963 to 2002

CNP was used in Miyagi Prefecture from 1966 to 1994, and PCP was used there from 1963 to 1985 (Fig. 2). The annual shipments of CNP and PCP to Miyagi Prefecture have been separately calculated by using data obtained from literature[5,18]. The concentrations of 1,3,6,8-TeCDD and 1,3,7,9-TeCDD in CNP, and the OCDD concentration in PCP varied according to when these pesticides were manufactured[13,25]. For this study, we used published the concentrations[13] and calculated the quantities of 1,3,6,8-TeCDD and 1,3,7,9-TeCDD released annually into the terrestrial environment, by multiplying the annual shipment amounts of CNP by the concentrations of 1,3,6,8-TeCDD and 1,3,7,9-TeCDD in CNP (Table 1, step 1). Similarly, we calculated the quantity of OCDD that entered the terrestrial environment annually by multiplying the annual shipment amounts of PCP by the OCDD concentration in PCP (Table 1, step 2). We then summed the amounts of these three pesticidal PCDDs (Table 1, step 3; Fig. 2). The quantities of dioxin com-

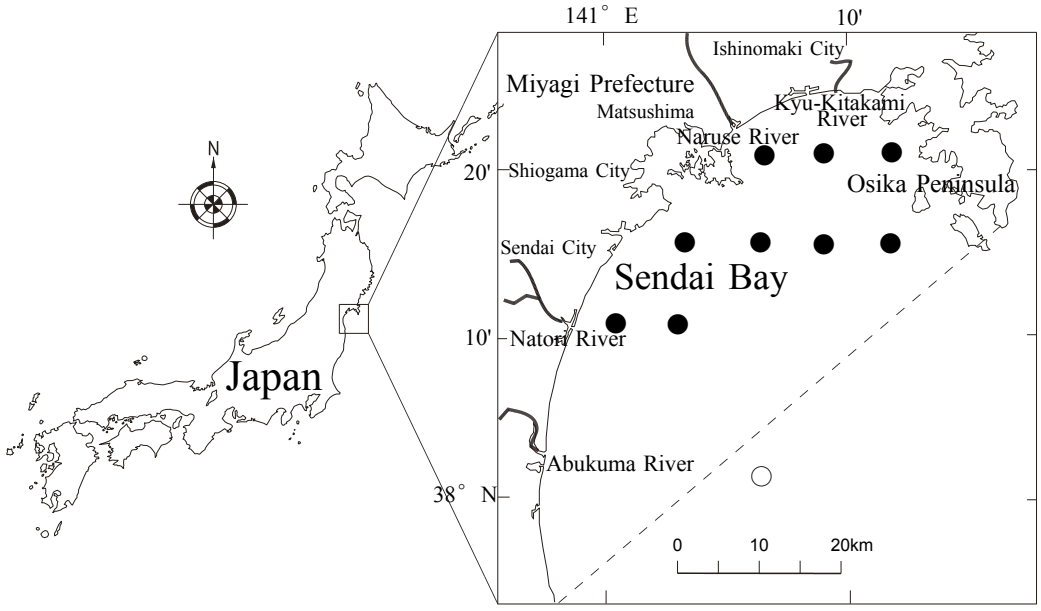

Fig. 1. Study area

We defined Sendai Bay as the area northwest of the dotted line extending from the tip of Oshika Peninsula to Sohma port in Fukushima Prefecture. The major rivers inflowing into Sendai Bay are the Kyu-Kitakami, Naruse, Natori, and Abukuma. The Kyu-Kitakami and Abukuma rivers originate in the prefectures of Iwate and Fukushima, respectively, and then flow through Miyagi Prefecture before entering the bay. We calculated the sea area of Sendai Bay to be 2747 km^2. The symbols ● and ○ denote sampling sites inside and outside of the bay, respectively. Salinities were determined at stations in the bay (●) during oceanographic surveys undertaken by the Miyagi Prefectural Fisheries Technology Institute. In the box model used in this study, we used the vertical salinity profiles measured at each sampling site during these oceanographic surveys to estimate outflow from Sendai Bay to offshore waters.

pounds in the terrestrial environment gradually decrease as a result of degradation, runoff, and volatilization[2,14,27]. It has been estimated that the quantities of pesticidal PCDDs remaining in the terrestrial environment decrease at an annual rate of 2 % through these processes (Table 1, step 4; Fig. 2)[14]. Table 1 summarizes the calculation steps.

2. Total quantities of pesticidal PCDDs entering Sendai Bay in the discharge of major rivers from 1963 to 2002

The Kyu-Kitakami, Naruse, Natori and Abukuma are the major rivers whose discharge flows into Sendai Bay. We determined the average amount of pesticidal PCDDs discharged annually into Sendai Bay by these major rivers during 1999-2002 from published data (7.7 kg/year; Table 2, steps 1-3)[23]. We also examined historical changes in the dioxin concentrations in river waters by taking into account the vertical concentration changes in a sediment core collected in Sendai Bay. Dioxin concentrations in the sediment core gradually increased from the mid-1930s to the mid-1980s, and then decreased slightly from the mid-1980s to the early 2000s[18,21]. Given the higher total concentration of 1,3,6,8-TeCDD and 1,3,7,9-TeCDD in sediments during 1986-1992 (630 pg/g dw) than during 1993-2002 (480 pg/g dw)[21], we assumed that the inflow of 1,3,6,8-TeCDD and 1,3,7,9-TeCDD from the major rivers into Sendai Bay during 1986-1992 was 1.3 times that during 1993-2002 (i.e., 630/480; Table 2, step 5). We similarly calculated the ratios for all pesticidal PCDDs in all periods during the 40 years from 1963 to 2002 (Table 2, steps 4-17) for use in correcting the annual quantities entering Sendai Bay via the major rivers (Fig.3). We then calculated the total inflows during the four decades by integrating the annual inflows (Table 2, steps 18-20; Fig. 3). Table 2 describes all calculation steps in detail.

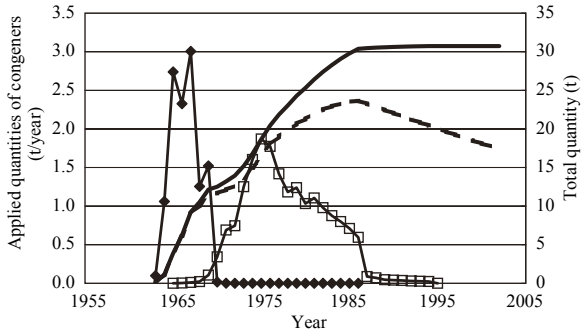

Fig. 2. Yearly changes in the quantities of pesticidal PCDDs in pesticides applied in Miyagi Prefecture

□: denotes the quantities of 1,3,6,8-TeCDD and 1,3,7,9-TeCDD introduced into the prefecture each year, as calculated by multiplying the amount of CNP shipped annually[5] by the sum of 1,3,6,8-TeCDD and 1,3,7,9-TeCDD concentrations in CNP in each year[13]. ◆: denotes the quantities of OCDD introduced, similarly calculated from the annual shipment of PCP[5] and its OCDD concentration in each year[13]. The solid lines show the cumulative values calculated under the assumption of 2 % annual loss (see text).

According to Taniguchi[29], up to 10% of all river water flowing into the bay can be considered derived from groundwater. It is generally recognized that dioxin is insoluble in water but easily adsorbed into suspended solids[1]. As a result, the concentrations of dioxins dissolved in water are much lower than those adsorbed into suspended materials[12]. We thus considered the inflow of dioxins dissolved in groundwater to be inconsequential, and ignored the contribution of dioxins in groundwater in this study.

3. Sedimentation of pesticidal PCDDs in Sendai Bay

We estimated the total quantity of pesticidal PCDDs precipitating and settling at the bottom of the bay by cal-

Table 1. Stepwise calculations of the quantities of pesticidal PCDDs in Miyagi Prefecture

Flux factor	Calculation	Value	Units	Refs.	Step no.
Total quantity of 1,3,6,8-TeCDD, and 1,3,7,9-TeCDD derived from CNP from 1966 to 1994		18.7	t	6, 18, 21	(1)
Total quantity of OCDD derived from PCP from 1963 to 1985		12.0	t	6, 18, 21	(2)
Sum total of pesticidal PCDDs	(1) + (2) = 18.7 +12.0	30.7	t		(3)
Annual loss		2	%	14	
Residual quantity in 2002 estimated by assuming a 2% annual loss		17.4	t		(4)

Table 2. Stepwise calculations for the inflow of pesticidal PCDDs into Sendai Bay

Flux factor	Calculation	Value	Units	Ref.	Step no.
Average annual inflow of 1,3,6,8-TeCDD and 1,3,7,9-TeCDD from four major rivers during 1999-2002		4.7	kg/y	23	(1)
Average annual inflow of OCDD from four major rivers during 1999-2002		3.0	kg/y	23	(2)
Average annual inflow of major pesticidal PCDDs from four major rivers during 1999-2002	(1) + (2) = 4.7 + 3.0	7.7	kg/y	23	(3)
Ratio of 1,3,6,8-TeCDD and 1,3,7,9-TeCDD concentrations by period (as calculated based on the historical trend in bottom sediments) to the concentration in 1993-2002					
(1993-2002)		1.0		18, 21	(4)
(1986-1992)		1.3		18, 21	(5)
(1982-1985)		0.86		18, 21	(6)
(1976-1981)		0.72		18, 21	(7)
(1971-1975)		0.57		18, 21	(8)
(1967-1970)		0.54		18, 21	(9)
(1966)		0.44		18, 21	(10)
Ratio of OCDD concentration by period (as calculated from the historical trend in bottom sediments) to the concentration in 1993-2002					
(1993-2002)		1.0		18, 21	(11)
(1986-1992)		1.0		18, 21	(12)
(1982-1985)		0.63		18, 21	(13)
(1976-1981)		0.66		18, 21	(14)
(1971-1975)		0.40		18, 21	(15)
(1967-1970)		0.65		18, 21	(16)
(1963-1966)		0.46		18, 21	(17)
Total inflow of 1,3,6,8-TeCDD and 1,3,7,9-TeCDD from four major rivers from 1966 to 2002	*1	151	kg/40y		(18)
Total inflow of OCDD from four major rivers from 1963 to 2002	*2	89	kg/40y		(19)
Total inflow of three pesticidal PCDDs from four major rivers from 1963 to 2002	(18) + (19) = 151 + 89	241	kg/40y		(20)

*1: (1) × [(4) × 10y + (5) × 7y + (6) × 4y + (7) × 6y + (8) × 5y + (9) × 4y + (10.) × 1y]
= 4.7×[1.000 × 10 + 1.313 × 7 + 0.863 × 4 + 0.718 × 6 + 0.566 × 5 + 0.544 × 4 + 0.442 × 1]
*2: (2) × [(11) × 10y + (12) × 7y + (13) × 4y + (14) × 6y + (15) × 5y + (16) × 4y + (17) × 4y]
= 3.0×[1.000 × 10 + 1.017 × 7 + 0.629 × 4 + 0.656 × 6 + 0.398 × 5 + 0.647 × 4 + 0.462 × 4]

culating the area of Sendai Bay (2747 km^2; Fig. 1; Table 3, step 1) and multiplying it by the annual sedimentation rate as determined from the concentrations of ^{210}Pb and ^{137}Cs in the sediment core (0.213 g dw/cm^2 y; Table 3, step 2), and the concentration of pesticidal PCDDs in the surface layer of bottom sediments (747.6 pg/g dw; Table 3, step 4). We estimated the total quantities of pesticidal PCDDs in seawater by multiplying the seawater volume (4578×10^{10} L; Table 4, step 3) by the dioxin concentrations in the seawater of Sendai Bay (11 pg/L; Table 4, step 4). We then calculated the volume of seawater from the area and maximum depth of Sendai Bay by using the

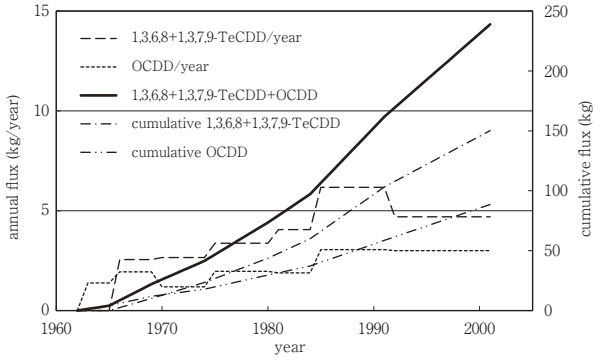

Fig. 3. Inflow of pesticidal PCDDs into Sendai Bay from major rivers

The annual inflow of pesticidal PCDDs was calculated from the average inflow from 1999 to 2002 (7.7 kg/y; Table 2, step 3) as corrected by considering historical changes in their concentrations in sediments (Table 2, steps 4–17). The total inflow during the four decades was calculated by summing the annual inflows.

equation for the volume of a pyramid ([area × depth]/3 = [2747 km^2 × 50 m]/3).

4. Bioaccumulation of pesticidal PCDDs in commercially valuable fish, shellfish, and seaweed

Pacific oyster (*Crassostrea gigas*) and several kinds of seaweed (*Porphyra yezoensis, Laminaria japonica*, and *Undaria pinnatifida*) are aquacultured in Sendai Bay, and the total biomass of aquacultured organisms is harvested. We estimated the total quantities of pesticidal PCDDs in Pacific oysters and these three kinds of seaweed by multiplying the dioxin concentration in each species by the total weight of annual production (3177 t × 650.4 pg/g wet weight and 23 247 t × 2.4 pg/g ww; Table 5, steps 1-5 and 16-18). We also estimated the total quantities of pesticidal PCDDs in the wild catch of fish and crustaceans by multiplying the concentration in each species by the annual catch of each species, and by the ratio (w/w) of the total biomass of each species in the bay

Table 3. Stepwise calculations for the sedimentation of the three pesticidal PCDDs in Sendai Bay

Flux factor	Calculation	Value	Units	Ref.	Step no.
Area of Sendai Bay		2747	km^2		(1)
Average sedimentation rate		0.213	g dw/ (cm^2 y)		(2)
Average annual quantity of sedimentation in Sendai Bay	(1) × (2) = 1874 × 0.213	585.0	×10^{10}g dw/y		(3)
Average concentration of the three pesticidal PCDDs in the surface layer of bottom sediments (deposited from the 1990s to 2002) in Sendai Bay		747.6	pg/g dw	17	(4)
Average annual quantity of three pesticidal PCDDs deposited in bottom sediments	(3)×(4)×1000^{-5} (kg/pg) = 399.1×747.6×1000^{-5} (kg/pg)	4.4	kg/y		(5)

Table 4. Stepwise calculations for total quantity of the pesticidal PCDDs in seawater of Sendai Bay

Flux factor	Calculation	Value	Units	Ref.	Step no.
Area of Sendai Bay		2747	km^2		(1)
Maximum depth of Sendai Bay		50	m		(2)
Total seawater quantity in Sendai Bay (the volume of a pyramid = Area × Maximum depth /3)	*1	4578	×10^{10} L		(3)
Average concentration of the pesticidal PCDDs in seawater collected from 1999 to 2002		11	pg/L	17	(4)
Average total quantity of pesticidal PCDDs in seawater under steady-state conditions	*2	0.50	kg (/3123 × 10^{10}L)		(5)

*1: (25) × (30) / 3×1000^2 (m^2/km^2) ×100^3 (cm^3/m^3) ×10^{-3} (L/cm^3) = 2747×50/3×1000^2 (m^2/km^2) ×100^3 (cm^3/m^3) ×10^{-3} (L/cm^3)
*2: (3) × (4) ×1000^{-5} (g/pg) = 4578 × 11 × 1000^{-5} (g/pg)

to the total catch biomass (e.g., 15 221 t × 6.4 pg/g ww × 4.2, etc.; Table 5, steps 6-15 and 19-38). We calculated the total quantity of pesticidal PCDDs bioaccumulated in commercially valuable fish, shellfish, and seaweed (produced by aquaculture or caught in the wild) by summing the values for each species (2.1 g/y + 406 mg/y + 72 mg/y + 56 mg/y + 49 mg/y + 40 mg/y + 0.726 mg/y + 492 mg/y; Table 5b, step 39). Table 5 describes the calculation steps in detail.

5. Advection from Sendai Bay to offshore

We estimated the advection of pesticidal PCDDs from Sendai Bay into offshore areas by multiplying the outflow of seawater from the bay by the average con-

Table 5. Stepwise calculations of the pesticidal PCDDs bioaccumulated in commercially valuable organisms

Flux factor	Calculation	Value	Units	Ref.	Step no.
Bioaccumulation in Pacific oyster					
Average yearly production of Pacific oyster, 1984-2004		31765	t	30	(1)
(total wt – shell wt)/total wt		0.1		30	(2)
Average weight of soft tissue (total weight – shell weight)	(1) × (2) = 31765 ×0.1	3177	t		(3)
Average concentration of the three pesticidal PCDDs in soft tissue of Pacific oyster		650.4	pg/g ww	17	(4)
Average annual quantity of the three pesticidal PCDDs in Pacific oyster	*1	2.1	g/y		(5)
Bioaccumulation in anchovy					
Average yearly catch of anchovy, 2003-2005		15221	t	30	(6)
Concentration of three pesticidal PCDDs in anchovy		6.4	pg/g ww	17	(7)
Average total quantity of the three pesticidal PCDDs in the anchovy catch	*2	97	mg/y		(8)
Average ratio of total biomass to catch biomass (w/w) of anchovy		4.2		4	(9)
Average annual quantity of the three pesticidal PCDDs in anchovy biomass	(8) × (9) = 97 × 4.2	406	mg/y		(10)
Bioaccumulation in sand lance					
Average yearly catch of sand lance, 1989-2004		5012	t	30	(11)
Average concentration of the three pesticidal PCDDs in sand lance		4.0	pg/g ww	17	(12)
Average total quantity of major dioxins in the sand lance catch	*3	20	mg/y		(13)
Average ratio of total biomass to catch biomass (w/w) of sand lance		3.6		3, 11	(14)
Average annual quantity of the three pesticidal PCDDs in sand lance biomass	(13) × (14) = 20 × 3.6	72	mg/y		(15)
Bioaccumulation in seaweeds					
Average yearly production of seaweeds, 1984-2004		23247	t/y	30	(16)
Average concentration of the three pesticidal PCDDs in seaweeds		2.4	pg/g ww	17	(17)
Average annual quantity of the three pesticidal PCDDs in seaweeds	*4	56	mg/y		(18)
Bioaccumulation in marbled sole					
Average yearly catch of marbled sole, 1998-2004		4105	t	30	(19)
Average concentration of the three pesticidal PCDDs in marbled sole		5.62	pg/g ww	17	(20)
Average total quantity of the three pesticidal PCDDs in the marbled sole catch	*5	23	mg/y		(21)
Average ratio of total biomass to catch biomass (w/w) of marbled sole		2.1		4	(22)
Average annual quantity of the three pesticidal PCDDs in marbled sole biomass	(21) × (22) = 23 × 2.1	49	mg/y		(23)

centration of pesticidal PCDDs in the seawater (11 pg/L; Table 4, step 4). Following Unoki[31], we used a box model to estimate the outflow of seawater (Fig. 4). In the box model, the volumetric flows of seawater are calculated from the total discharge of the major rivers (i.e., Kyu-Kitakami, Naruse, Natori, Abukuma) flowing into the Sendai Bay and the average salinity in each box of the model (Appendix). The flow rate of each river during 1999-2002 was obtained from published data[6], and salinity data (at the stations shown in Fig. 1) were obtained from surveys conducted by the Miyagi Prefecture Fisheries Technology Institute, which kindly permitted us to use the data for this study.

The outflow of seawater (Q′, m^3/s) from inshore to

Table 5. – continued –

Bioaccumulation in crustaceans (shrimp and crab)					
Average yearly catch of crustaceans, 1993-2004		312	t	30	(24)
Average concentration of the three pesticidal PCDDs in shrimp		95.7	pg/g ww		(25)
Average total quantity of the three pesticidal PCDDs in the crustacean catch	*6	30	mg/y		(26)
Average ratio of total biomass to catch biomass (w/w) of shrimp		1.3		24	(27)
Average annual quantity of the three pestcidal PCDDs in crustacean biomass	(26) × (27) = 30 × 1.3	40	mg/y		(28)
Bioaccumulation in Japanese flounder					
Average yearly catch of Japanese flounder, 1998-2004		154	t	30	(29)
Average concentration of the three pesticidal PCDDs in Japanese flounder		2.2	pg/g ww	20	(30)
Average total quantity of the Japanese flounder catch from Sendai Bay	*7	345	µg/y		(31)
Average ratio of total biomass to catch biomass (w/w) of Japanese flounder		2.1		4	(32)
Average annual quantity of three pestcidal PCDDs in Japanese flounder	(31) × (32) = 345 × 2.1	726	µg/y		(33)
Bioaccumulation in other fishes					
Average yearly catch of other fishes, 1998-2004		33188	t	30	(34)
Average concentration of the three pesticidal PCDDs in anchovy, marbled sole, sand lance, and Japanese flounder		4.6	pg/g ww	17, 20	(35)
Average total quantity of the three pesticidal PCDDs in the catch of "other fishes"	*8	152	mg/y		(36)
Average ratio of total biomass to catch biomass (w/w) of anchovy, marbled sole, sand lance, and flounder		3.2		3, 4, 11	(37)
Average annual quantity of the three pesticidal PCDDs in the biomass of other fishes	(36) × (37) = 152 × 3.2	492	mg/y		(38)
Total bioaccumulation of major dioxins in commercially valuable fishes, shellfish, and seaweeds					
Average annual quantity in fishes, shellfish, and seaweeds	*9	3.2	g/y		(39)

*1: (3) × (4) × 1000^2 (g/t) × 1000^{-4} (g/pg) = 3177 × 650.4 × 1000^2 (g/t) × 1000^{-4} (g/pg)
*2: (6) × (7) × 1000^2 (g/t)/1000^3 (mg/pg) = 15221 × 6.4 × 1000^2 (g/t)/1000^3 (mg/pg)
*3: (11) × (12) × 1000^2 (g/t) × 1000^{-3} (mg/pg) = 5012 × 4.0 × 1000^2 (g/t) × 1000^{-3} (mg/pg)
*4: (16) × (17) × 1000^2 (g/t)/1000^{-3} (mg/pg) = 23247 × 2.4 × 1000^2 (g/t)/1000^{-3} (mg/pg)
*5: (19) × (20) × 1000^2 (g/t) × 1000^{-3} (mg/pg) = 4105 × 5.62 × 1000^2 (g/t) × 1000^{-3} (mg/pg)
*6: (24) × (25) × 1000^2 (g/t) × 1000^{-3} (mg/pg) = 312 × 95.7 × 1000^2 (g/t) × 1000^{-3} (mg/pg)
*7: (29) × (30) × 1000^2 (g/t) × 1000^{-2} (µg/pg) = 154 × 2.2 × 1000^2 (g/t) × 1000^{-2} (µg/pg)
*8: (34) × (35) × 1000^2 (g/t) × 1000^{-3} (mg/pg) = 33188 × 4.6 × 1000^2 (g/t) × 1000^{-3} (mg/pg)
*9: (5) + (10) + (15) + (18) + (23) + (28) + (33) + (38) = 2.1 + 0.406 + 0.072 + 0.056 + 0.049 + 0.04 + 0.000726 + 0.492

offshore waters in the upper water layer of Sendai Bay was calculated as follows:

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

Where, R denotes the sum of flow rates (m^3/s) of the four major rivers, S1 the salinity (psu) in the upper layer of inshore waters, and S4 the salinity (psu) in the lower layer of offshore waters (Fig. 4).

Results and Discussion

1. Total amounts of pesticidal PCDDs in the terrestrial environment

The total quantity of 1,3,6,8-TeCDD and 1,3,7,9-TeCDD derived from CNP during the 29 years from 1966 to 1994 was estimated to be 18.7 t, and the total quantity of OCDD derived from PCP during the 23 years from 1963 to 1985 was estimated to be 12 t (Table 1, steps 1 and 2; Fig. 2). Thus, approximately 30.7 t of pesticidal PCDDs were introduced into Miyagi Prefecture from CNP and PCP during the period when these pesticides were applied to paddy fields (Table 1, step 3; Fig. 2). By assuming an annual loss of 2%, (Table 1, step 4) as determined by Masunaga et al.[14], an estimated quantity of 17.4 t remained in the terrestrial environment as of 2002 (Table 1, step 4; Fig. 2). Therefore, the quantity eliminated from the terrestrial environment was 13.3 t (30.7 t – 17.4 t). The estimated quantity of pesticidal PCDDs discharged into Sendai Bay by the major rivers during the 40 years from 1963 to 2002 was 241 kg (Table 2, step 20; Fig. 3). Should the total amount of CNP and PCP shipped to Miyagi Prefecture be applied to the fields, then 56.7% of the pesticidal PCDDs introduced into the terrestrial environment would remain in the soil as residual dioxins in 2002 (Fig. 5). The quantity of pesticidal PCDDs discharged into Sendai Bay by the major rivers accounts for only 0.8% of the total amount applied to the paddy fields in Miyagi Prefecture. The upper reaches of the Kyu-Kitakami and Abukuma rivers flow through Iwate Prefecture and Fukushima Prefecture, respectively. Therefore, in this mass balance model, the inflows of pesticidal PCDDs contained in river discharge into Sendai Bay include inflow from both the prefectures of Fukushima and Iwate, whereas the total quantities of pesticidal PCDDs in the terrestrial environment (30.7 t) were calculated by using only the shipment data of CNP and PCP products to Miyagi Prefecture. If we include the amounts of pesticidal PCDDs used in Iwate and Fukushima in the total quantities, the total amount of terrestrial pesticidal PCDDs would exceed 30.7 t. Although pesticidal PCDDs from the prefectures of Iwate and Fukushima were contained in the inflow from all rivers into Sendai Bay, the inflow did not vary much over 40 years. Thus, there would only be a small difference in the result obtained for pesticidal PCDDs in river discharge, regardless of whether pesticidal PCDDs used in Iwate and Fukushima were added, due to the very small total inflow to Sendai Bay during the period (241 kg; Table 2, step 20) .

High concentrations of dioxins have mainly been observed in the paddy fields of Japan[7,9,12]. Although dioxins

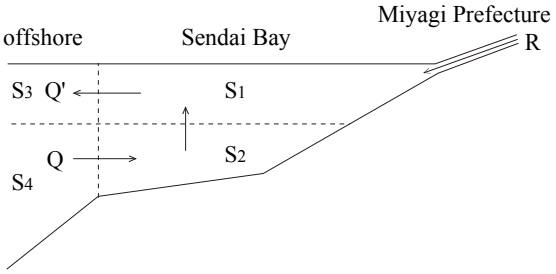

Fig. 4. Schematic of the box model used to estimate the offshore transport of pesticidal PCDDs from Sendai Bay

The amount transported offshore (Q') was calculated by using S_1 [average salinity as measured at the surface and at depths of 5 and 10 m at nine sampling sites inside the bay (Fig. 1, symbol ●)], S_4 [average salinity as measured at depths greater than 20 m at the offshore sampling sites (Fig. 1, symbol ○)], and R [amount of pesticidal PCDDs entering the bay via rivers]. Note that S_2 [average salinity as measured at depths greater than 20 m inside the bay] and S_3 [average salinity as measured at the surface and at depths of 5 and 10 m at the offshore sampling sites] were not used in the calculations.

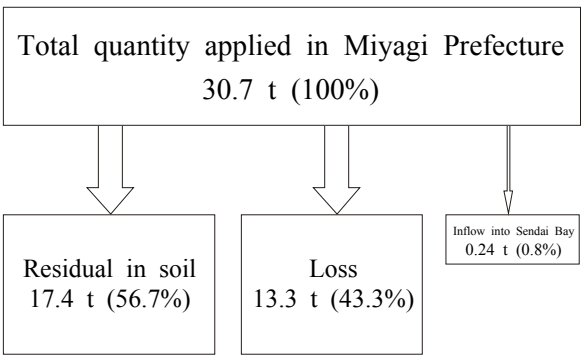

Fig. 5. Schematic diagram showing the quantities and mass balance (estimated 40-year values) of pesticidal PCDDs in the terrestrial environment in 2002

derived from the impurities in pesticides are gradually removed from the fields as a result of decomposition, runoff and volatilization, the largest portion of dioxins from such pesticides as CNP and PCP applied to paddy fields probably remains as residual dioxins in the terrestrial environment (17.4 t; Table 1, steps 3 and 4; Fig. 5). Here, we calculated that the quantity of dioxins entering Sendai Bay from rivers was only 0.8% (241 kg; Table 2, step 20) of the total dioxins applied to the terrestrial environment (Fig. 5). Japan's Ministry of the Environment (MOE) has estimated that 0.0021-0.0031% of dioxins applied to agricultural fields in Japan runs off in surface waters[16]. As our research has revealed that the inflow into Sendai Bay is larger than the amount reported in runoff by MOE, we therefore believe that we have not underestimated the amount of pesticidal PCDDs in river discharge.

Volatilization that occurs during the application of pesticides is unlikely to be a major factor regarding the total amount of dioxins eliminated from the terrestrial environment (13.3 t), and the inflow into Sendai Bay (241 kg) is extremely small compared with the total loss of 13.3 t. Therefore, most dioxins must be lost through degradation, even though the half-lives of dioxins, which are known to vary depending on the environment, range from a few hundred days to hundreds of years[2,10,14].

2. Mass balance of dioxins in Sendai Bay

We calculated the mass balance of pesticidal PCDDs in Sendai Bay in 2002 (Fig. 6). Sedimentation accounts for 4.4 kg/y, with 0.5 kg/y remaining in the water column under steady-state conditions (Table 3, step 5, and Table 4, step 5; Fig. 6). We calculated the total bioaccumulation in commercially valuable fish, shellfish, and seaweed in Sendai Bay to be 3.2 g/y (Table 5, step 39; Fig. 6). We also calculated the average annual outflow from Sendai Bay into offshore waters from 1999 to 2002 to be 6.2 kg/y (Figs. 6 and 7). Should the total inflow from the major rivers (7.7 kg/y) enter the bay, then the outflow from the bay into offshore waters would be equal to 80.1% of the inflow. Similarly, we estimated that sedimentation accounted for 57.1% of the inflow, 6.5% of inflow remaining in seawater, and 0.04% of bioaccumulation in commercially exploited marine organisms in Sendai Bay (Fig. 6).

The sum (11.1 kg/y) of outflow from the bay (6.2 kg/y), sedimentation (4.4 kg/y), the quantity in seawater (0.5kg/y), and bioaccumulation (0.0032 kg/y) exceeded inflow into the bay from the major rivers (7.7 kg/y) by 3.4 kg/y (44%). The seawater and sediment samples used to estimate these fluxes were mainly collected near the coast. Therefore, the values of dioxin concentrations in seawater and sediments used for mass balance calculations could possibly be higher than the average values for the entire study area (Fig. 1). In that case, the calculated values for outflow from the bay into offshore waters and sedimentation could be overestimates.

Our estimates of the bioaccumulation of pesticidal PCDDs are very small. In this research, we calculated bioaccumulation by using only the data obtained from aquacultured species and fishery catches[30], without considering species that are not commercially valuable. For this reason, the calculated bioaccumulation is likely

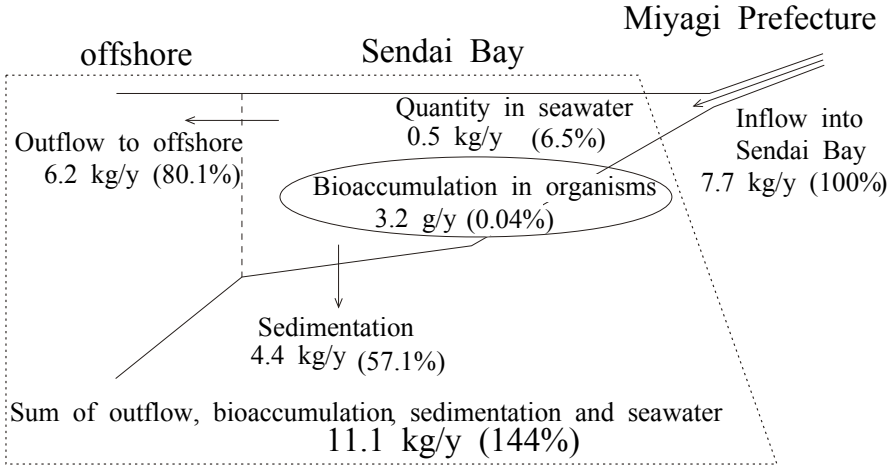

Fig. 6. Schematic diagram showing the quantities and mass balance (estimated annual values) of pesticidal PCDDs in Sendai Bay in 2002

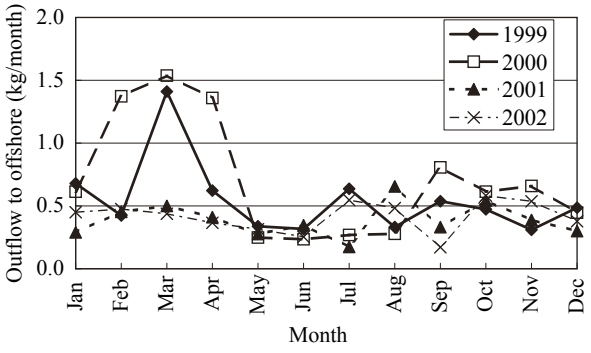

Fig. 7. Monthly outflows of pesticidal PCDDs to offshore waters from Sendai Bay

to underestimate the actual bioaccumulation in marine organisms in Sendai Bay. However, many studies have reported that bioaccumulations of 1,3,6,8-TeCDD, 1,3,7,9-TeCDD, and OCDD were lower than those of 2,3,7,8-TeCDD and PCBs[26,32], which could account for the very low bioaccumulation of pesticidal PCDDs in species covered by this research. The amount of bioaccumulation in edible marine organisms indicates that very little of the total amount of dioxins returns to terrestrial areas from Sendai Bay in seafood intended for human consumption. Even if bioaccumulation in marine organisms is underestimated, it is still likely to be very low compared with the amounts that flow into the bay from major rivers (7.7 kg/y), flow from the bay into offshore waters (6.2 kg/y), and settlement on the sea floor (4.4 kg/y).

The amount of outflow from the bay into offshore waters (6.2 kg/y) and sedimentation (4.4 kg/y) account for 56% and 40%, respectively, of the total of outflow, sedimentation, seawater, and bioaccumulation amounts in Sendai Bay (11.1 kg/y) (Fig. 6). Outflow and sedimentation together account for 96% of the total. Thus, nearly all of the pesticidal PCDDs introduced into Sendai Bay from the major rivers flow out to offshore waters or settle at the bottom of the bay. It has been reported that 87.7% of PCBs entering the Seto Inland Sea are discharged into offshore waters[28], and that 99.7% of PCBs in Tokyo Bay are likewise discharged into offshore waters[33], although another study reported that 99% of dioxins flowing into Tokyo Bay settled at the bottom of the bay, and only 1% flowed out of Tokyo Bay into offshore waters[15]. Estimates of the transfer of chemicals from inshore to offshore waters depend on the chemical properties, location, seabed topography, and method used to calculate mass balance. As Sendai Bay is an open-type bay, the outflow of pesticidal PCDDs from Sendai Bay into offshore waters as calculated in this study is expected to be larger than that from a semi-enclosed bay such as Tokyo Bay.

Conclusions

We analyzed the mass balance of pesticidal PCDDs in Sendai Bay, which is an important fisheries and aquaculture area. Large quantities of pesticidal PCDDs were introduced into the terrestrial environment in the past by the application of CNP and PCP in agricultural fields. Most of the pesticidal PCDDs remained in the terrestrial environment, and only 0.8% of the total quantity applied to paddy fields entered the bay via major rivers.

Almost all dioxins entering Sendai Bay either flowed out of the bay into offshore waters or settled at the bottom of the bay. The bioaccumulation of pesticidal PCDDs in marine organisms was much smaller than the amount flowing into the bay from the terrestrial environment. Moreover, the major congeners of dioxins occurring as impurities in CNP and PCP were not bioaccumulated in marine organisms at concentrations as high as the bioaccumulated concentration of 2,3,7,8-TeCDD, which has extremely high toxicity. Therefore, although pesticidal PCDDs continue to flow into Sendai Bay, the present mass balance results suggest that the amount of bioaccumulation in marine organisms is very small.

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Appendix. Values of the parameters R (river inflow), 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

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