Dynamics of PCDDs and PCDFs in Coastal Sea Water around Tokyo Bay in Japan

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Introduction

In spite of world attention about PCDDs and related chemicals in the environment, little information of their residue in sea water is available because of very low concentrations. Tokyo Bay is one of the most contaminated semi-closed estuaries in Japan. It has suffered large amounts of pollutants including PCDDs caused by human activities in the metropolitan area. Due to the fact that Tokyo Bay produces many marine products consumed by humans, PCDDs exposure through these is important issue for Japan. Despite this, no information about PCDDs/DFs movements in sea water around Tokyo Bay has been reported up to the present. In this report, we present the results of isomer specific analysis of PCDDs/DFs and PCBs in different layers of sea water in Tokyo Bay. We performed ultra-trace measurement of these chemicals in sea water using *in-situ* filtration/extraction water sampler (Kiel *in-situ* pump; KISP and INFILTREX II) and from the data, reconstructed a three dimensional distribution. We also tried to make a schematic representation of PCDDs/DFs movement in sea water which would enable us to understand the dynamics of these chemicals in the marine environment. As preliminary results were reported previously at Dioxin '97 (1), our goal in this report is to describe the movements of these chemicals in sea water.

Material and Methods

Table 1 shows a list of coastal sea water samples collected from six locations around Tokyo Bay in Japan. Each location is represented in Fig.1 and 2. We applied KISP at station A, B, D, E and F for *in-situ* water filtration/extraction. Chemicals absorbed on to XAD-2 resin and particulate matter collected on the filter were applied to laboratory analysis and quantification was performed by HRGC (HP5890II) - HRMS (VG AutoSpec-Ultima system). More details of sampling and analytical methods were described in previous report (1). Additional descriptions are as follows. The extraction efficiency of target chemicals on to XAD-2 resin was tested using dual column connected in series. It was confirmed that no leaks of target compounds were observed in the seconds column under the sampling condition (1L/min, 9hrs). Another *in-situ* filtration/extraction system for INFILTREX II was applied at station C. In station C, one of samplers was set to a 10m depth for collection of surface sea water. Two of the samplers were set to the same depth (30m). One of the latter was programmed to collect sea water continuously. The other one was programmed to collect sea water only during ebb periods for a 10days. This sampling system enabled us to compare PCBs/PCDDs/PCDFs concentrations in sea water between ebb and flood tides.

Results and Discussion

Concentration of total (dissolved and particulate fraction of) PCBs/PCDDs/PCDFs in sea water around Tokyo Bay are shown in Table 2. Three dimensional distributions of PCDDs and PCDFs appear in Figure 1 and 2 respectively. The most interesting result is that the bottom layer of Stn. D and the middle layer of Stn. E contained larger amount of chemicals than the surface layer of each location. It is clear that the surface sea water does not represent water pollutions in these areas.

We calculated transportation rates of these chemicals from the inside of the Bay to the outside by exchange of sea water through tidal process using a "ebb-flood comparison test". Fig. 3 shows differences of PCDDs/DFs concentrations in sea water between ebb and flood at Stn. C over a 10day period. We assume that the x-axis value (ebb-flood) represents a transportation rate of these chemicals from inside of the Bay. Estimated values are 20fg/L/day for PCDDs and 6fg/L/day for PCDFs, respectively. One more interesting point of this result is the "ebb-flood" value difference between dissolved and particulate fractions. Dissolved fractions have the greater part of total transportation in this figure. On the other hand, the partition ratio between particulate and dissolved fraction in Fig. 1 and 2 shows that more than half of PCDDs/DFs were found in particulate fraction in principle. Considering the hydrophobic nature of PCDDs/DFs, "apparently dissolved fraction" measured in this study seems to be constituted of dissolved organic matter (*e.g.* colloid) which absorbs these chemicals. Hence, it may be concluded that only small part of PCDDs/DFs are presented in dissolved organic matter in sea water but it is more important in transportation process of these chemicals by sea water than large particles.

The total amounts of PCBs, PCDDs and PCDFs in the whole sea water in Tokyo Bay were estimated on the basis of the concentrations given in Table 2 using international TEF value, compared to Baltic Sea result (2) (Table 3). In the estimations we assumed that the five samples (station A, B and C) of this study were representative for the concentrations in the sea water in Tokyo Bay. The total amounts of PCBs and PCDDs/DFs was then estimated to be approximately 410g to 13,000g and 17g to 96g (equivalent to 96mg to 560mg of TEQs), respectively.

To sum up above results, we described a schematic representation of PCDDs/DFs movement in sea water around Tokyo Bay in Fig. 4. PCDDs/DFs discharges to the Tokyo Bay region during the last 35years were estimated at approximately 8559kg (6674gTEQ) by Masunaga (3). The amount of residue of these in surface sediment was also estimated at approximately 748kg (2200gTEQ). The annual transportation rate from inside of Tokyo Bay by sea water was calculated at 430g/year (2.5gTEQ/year) on the basis of mean values of total amounts in sea water in Table 3 and residence time (1.6 month) of fresh water in Tokyo Bay estimated by Unoki (4). During the last 35 years, 8.7% (33% in TEQ) of total PCDDs/DFs discharged to the Tokyo Bay region remains in sediment. Only 0.2% (1% in TEQ) were transported outside of the Bay by sea water (may be by dissolved organic matter). These "apparently dissolved" PCDDs/DFs may be absorbed into newly produced particles outside of the Bay. The rest of the amount seems to correspond to three reasons; accumulation in land (soil and river sediment), degradation and transportation by large particles which resuspended from sediment surface, with no consideration of output into air form sea water which is unlikely to occur. The presence of intermittent outflow of high turbidity bottom water was reported by Yanagi (5, 6) and such a large particle transportation process along the shelf edge may be important in PCDDs/DFs movement in sea water around Tokyo Bay.

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References

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Table 1. Sample list

Sample name	Latitude / Longitude	Depth (m)	Layer (m)	Date	Volume (L)	Sampler
A / S	N 35°34' / E 139°50'	10	2	1995 / 8 / 18	240	KISP
B / S	N 35°31' / E 139°49'	12	2	1995 / 8 / 25	348	KISP
C / S C / B1 C / B2*	N 35°17' / E 139°42'	40	10 30 30	1995 / 5 / 29 - 1995 / 6 / 8	1230 1430 741	INFILTREX II
D / S D / M D / B	N 34°53'-54' / E 139°33'-34'	940-1021	100 400 750	1996 / 4 / 22 - 1996 / 4 / 23	316 702 260	KISP
E / S E / M E / B	N 35°03'-04' / E 139°20'-21'	1450-1452	100 600 1200	1996 / 4 / 22	262 253 328	KISP
F / S F / M F / B	N 34°39'-40' / E 139°34'-35'	1608-1743	100 700 1500	1996 / 4 / 23 - 1996 / 4 / 24	504 240 228	KISP

*: ebb only

Table 2. Concentration of total (particulate and dissolved fraction of) PCDDs, PCDFs and PCBs in sea water around Tokyo Bay.

	A/S	B/S	C/S	C/B1	C/B2	D/S	D/M	D/B	E/S	E/M	E/B	F/S	F/M	F/B
PCDDs (fg/L)														
TetraDDs	871.4	728.0	235.5	376.0	260.4	*< 20	38.1	*67.2	324.0	527.1	153.8	87.3	111.9	75.1
PentaDDs	110.7	104.2	17.7	32.0	18.9	*4.3	6.2	*14.7	10.6	28.5	12.2	30.4	12.4	75.3
HexaDDs	195.8	120.8	17.7	37.5	17.5	*6.7	3.5	*18.0	9.4	24.4	9.5	15.6	13.9	8.0
HeptaDDs	480.9	302.9	40.2	115.2	56.7	*23.9	16.0	*50.5	29.0	67.4	7.9	22.2	11.7	30.1
OctaDD	1,426	1,374	316.9	1,107	578.2	*65.1	143.0	*268.7	96.9	207.2	109.3	104.5	88.0	35.0
∑ DDs	3,084	2,629	628	1,668	932	*100	207	*419	470	855	293	260	238	224
PCDFs (fg/L)														
TetraDFs	412.6	548.8	129.2	195.3	128.4	*5.2	38.4	*< 3.6	19.5	364.1	< 52	97.2	< 16.1	26.8
PentaDFs	684.8	281.8	94.3	204.8	107.7	*10.6	34.0	*91.1	61.4	292.5	61.0	51.6	27.8	22.7
HexaDFs	890.1	333.0	59.4	179.6	82.1	*18.4	31.6	*94.7	45.1	157.1	< 15.6	36.5	36.4	16.7
HeptaDFs	229.5	166.8	38.9	133.9	69.4	*13.1	16.6	*43.8	18.4	50.1	38.2	25.1	28.6	29.4
∑ DFs	2,217	1,330	321.8	714	388	*47	121	*230	144	864	99	210	93	96
PCBs (pg/L)	697	348	23	58	32	21	22	80	16	88	12	16	7.3	2.7

*particulate fraction only

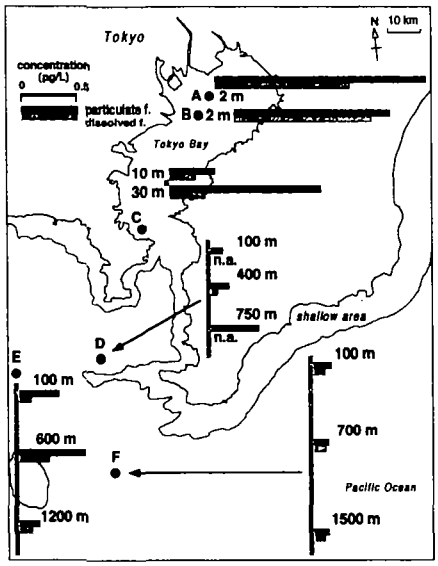

Fig. 1 Three dimensional distribution of PCDDs in sea water around Tokyo Bay.

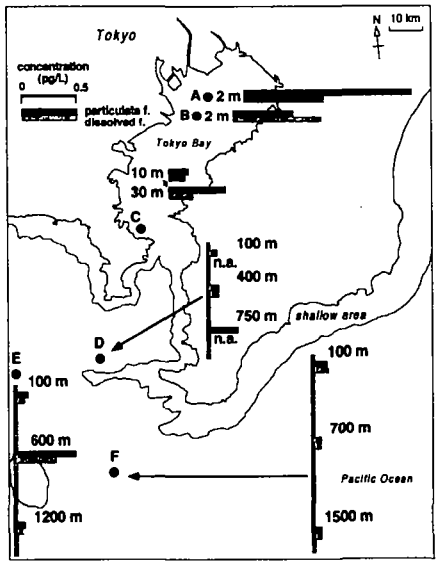

Fig. 2 Three dimensional distribution of PCDFs in sea water around Tokyo Bay.

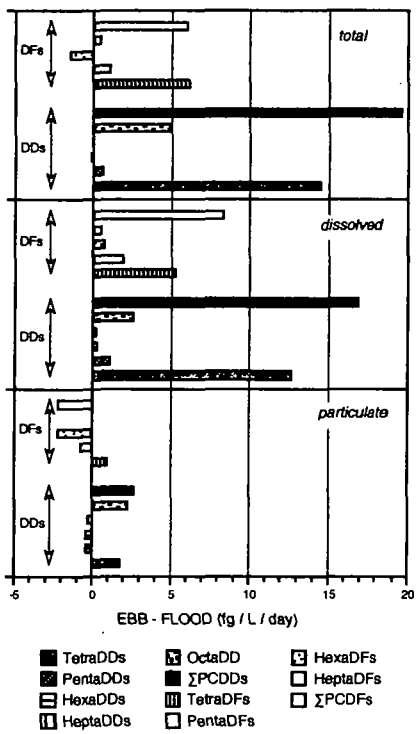

Fig. 3

Differences of PCDDs/DFs concentrations in sea water between ebb and flood in Station C.

Table 3. Total amounts of PCBs, PCDDs/DFs and TEQs in sea water in Tokyo Bay and Baltic Sea.

	Area (km^2)	Volume (km^3)		∑ PCBs (g)	∑ PCDDs/DFs (g)	∑ TEQs (g)
Tokyo Bay	1.2×10^3	18	particulate f.	220 - 1,700	10 - 61	0.065 - 0.34
			dissolved f.	190 - 10,800	6.8 - 35	0.031 - 0.22
Baltic Sea*	3.7×10^5	-	particulate f.	-	1,700	13
			dissolved f.	-	900	7.7

* : reported by Broman *et.al.* (1991)

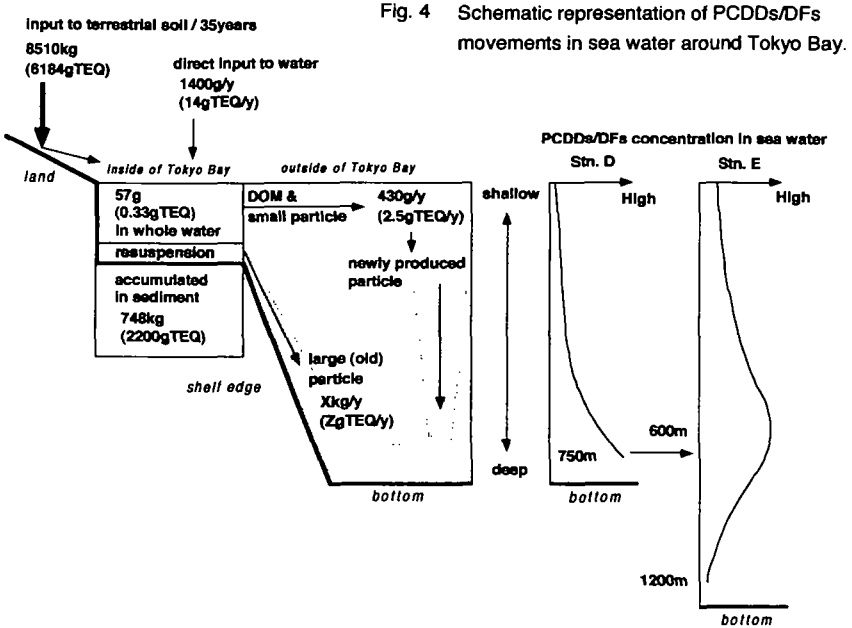

Fig. 4 Schematic representation of PCDDs/DFs movements in sea water around Tokyo Bay.