Study on the Historical Trends of PCDD/Fs and Coplanar PCBs in Tokyo Bay, Japan

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Abstract

A dated sediment core collected from Tokyo Bay was used to assess the historical inputs of PCDD/Fs and coplanar PCBs from multiple sources. The results clearly showed that the inputs increased drastically from the late 1950s and peaked during the period 1967-1972. From 1972 to 1981, the inputs decreased continuously and then leveled off. PCDD/Fs contributed more than 90 % of the total TEQ throughout the sediment core. Using principal component analysis, two herbicides used in the past, PCP and CNP, and combustion processes were identified to be the major dioxin sources in Tokyo Bay. For coplanar PCBs, PCB products and combustion processes were estimated to be the major sources. Furthermore, multiple regression analysis was performed for dioxin source apportioning and it was found that herbicides (PCP and CNP) have contributed mainly to the total PCDD/F concentration and TEQ since the late 1950s. These findings are of significance for the establishment of comprehensive dioxin and PCB control measures in Japan.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), and biphenyls (PCBs) constitute a group of persistent, bioaccumulative, and toxic contaminants in the environment.

Several PCDD/Fs and coplanar PCBs have been shown to cause toxic responses similar to those caused by 2,3,7,8-TCDD, the most potent congener within these groups of compounds. These toxic responses include dermal toxicity, immunotoxicity, carcinogenicity, and adverse effects on reproduction, development, and endocrine functions (Van den Berg et al. 1998). To conduct a comprehensive dioxin risk assessment for humans and the ecosystem, the toxic equivalent (TEQ) approach has been developed and used worldwide. In Japan, a tolerable daily intake (TDI) of 4 pgTEQ/kg/day for the sum of PCDD/Fs and coplanar PCBs was newly revised in June 1999 to control the exposure to these compounds. For this purpose, a full understanding of the key sources of PCDD/Fs and coplanar PCBs and the relative contributions of these sources is required.

So far, many sources have been identified for PCDD/Fs and the known sources can generally be divided into three groups: industrial processes, thermal processes and secondary sources (Hutzinger and Fiedler 1993). The contribution of dioxins from different sources is a topic of intense discussion. In Europe, incineration is thought to be the key source and it is reported that dioxin uptake has decreased following the strong regulatory control of such processes. Likewise, incineration has been deemed by many to contribute a main portion of PCDD/Fs to the environment and dioxin control measures in Japan have been focused only on incineration up to now. However, our group recently reported some new findings. Masunaga et al. (1998) indicated that a significant portion of dioxins in Japanese surface sediments originated from agrochemicals, especially pentachlorophenol (PCP) and chloronitrofen (CNP) which were widely used as paddy field herbicides in the past. Further, Masunaga and Nakanishi (1999) investigated the dioxin impurities in old Japanese agrochemicals and proposed that annual emissions of dioxins from agrochemicals were far greater than those from combustion sources during the 1960s and 1970s.

The time-course of dioxins and PCBs in the environment provides an important clue as to the sources of these compounds. The objective of our research is to reconstruct the historical trends of PCDD/Fs and coplanar PCBs in an aquatic environment, to provide useful information for the establishment of an effective environmental policy in Japan. As the first step, we have conducted a time trend analysis of PCDD/Fs and coplanar PCBs in Lake Shinji, Japan, and the results revealed that PCP, CNP and incineration were the major sources of dioxin pollution in the basin. For coplanar PCBs, PCB products and incineration were estimated to be the major sources (Masunaga et al. 1999, Yao et al. 1999). Considering the regional characteristics, in the present study, we further investigated PCDD/Fs and coplanar PCBs in a dated sediment core taken from Tokyo Bay. The results will be reported and discussed in this paper.

2. Materials and Methods

Sampling and Sediment Dating. Tokyo Bay is a typical closed inner bay located southeast of Tokyo Metropolitan City. Its surface area is 980 km² and the catchment area is 7,600 km² in which

25.6 million people reside. Tokyo Bay is considered to be one of the water systems most impacted by anthropogenic activities in Japan. For example, many industrial plants are located along the shoreline. Municipal solid waste incinerators in the area burn more than 6 million ton/yr. Furthermore, herbicides have been used in paddy fields and other types of agricultural fields, which comprise approximately 20 % of the catchment area (Sakurai et al. in press). In this study, a sediment core sample was collected from Tokyo Bay in September 1993 at the position of 35°33' N latitude and 139°55' E longitude. The core was sliced into 1-cm-interval disks on-site and the disks were dried by the freeze-drying method. The average sedimentation rate was estimated to be 0.27 g/cm^2/yr and 0.26 g/cm^2/yr by the ^{210}Pb method and the ^{137}Cs method, respectively (Sanada et al. 1999). For PCDD/F and coplanar PCB analysis, the disks were subsampled to make up 13 samples with the depths of 0-3, 3-6, 6-9, 9-15, 15-20, 20-25, 25-30, 30-35, 35-40, 40-45, 45-50 and 55-58 cm, respectively. The ages of these samples were determined by the ^{210}Pb method.

Aanlytical Methods. After the addition of twenty ^{13}C-labeled PCDD/F and coplanar PCB internal standards, each sample (5~10 g) was Soxhlet-extracted with toluene for 20 h. Then they were treated with alkaline hydrolysis, sulfuric acid oxidation, and sulfur removal. Sample cleanup included chromatography on silica gel, aluminum and activated carbon columns. The final PCDD/F and coplanar PCB fractions were further concentrated to 25 μL and spiked with two ^{13}C-labeled recovery standards for high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) analysis. The tetra- to octa-chlorinated PCDD/Fs and four coplanar PCBs (IUPAC Nos. 81, 77, 126, and 169) were congener-specifically analyzed with DB-5 and DB-17 columns.

Data Analysis. In this study, STATISTICA software was used for statistical analysis. Source identification was performed using principal component analysis (PCA). PCA is a multivariate technique that can be used to reduce the dimensionality of complex data. It has been applied to PCDD/F and PCB data by several researchers (Czuczwa and Hites 1986, Kjeller and Rappe 1995, Macdonald et al. 1998, Bonn 1998, Bright et al. 1999). For our PCDD/F and coplanar PCB congener-specific data set, each congener or congener cluster was constituted as a variable, while each disk was treated as a case. Principal components (PCs) were obtained by varimax rotation and then they were identified by comparing their characteristic congeners with those of known sources. Furthermore, multiple regression analysis was carried out for dioxin source apportioning. The congener-specific data of PCDD/F concentrations in PCP, CNP (Masunaga and Nakanishi 1999), and atmospheric deposition obtained in the Kanto area (Ogura et al. 1999) were used to estimate the historical contributions of different sources to dioxin pollution in Tokyo Bay.

3. Results and Discussion

Nearly all the tetra- to octa-chlorinated PCDD/Fs were detected from the samples examined. The results are summarized in Table 1. According to the obtained data, the historical trends of

Table 1. Concentrations and TEQs of PCDD/Fs and Co-PCBs in the sediment core (pg/g dry wt)

Core depth (cm)		55-58	50-55	45-50	40-45	35-40	30-35	25-30	20-25	15-20	9-15	6-9	3-6	0-3
Age range (year)		1935-1938	1938-1945	1945-1951	1951-1956	1956-1962	1962-1967	1967-1972	1972-1977	1977-1981	1981-1986	1986-1989	1989-1991	1991-1993
Average age (year)		1937	1942	1948	1954	1959	1965	1970	1975	1979	1984	1988	1990	1992
TCDD	1368	4.4	7.5	7.2	8.4	16	68	2300	6200	2700	2200	2800	1900	1800
	1379	3.0	4.1	3.8	4.1	7.1	28	780	2100	990	820	1000	730	670
	1369	0.46	0.60	0.41	0.45	0.84	1.5	24	57	25	23	25	19	17
	1247/1248/1378/1468	1.0	1.7	2.0	1.6	2.5	4.5	17	39	23	20	24	19	17
	1248/1249/1268/1478	1.1	1.0	1.1	0.77	1.2	2.0	5.2	12	7.1	7.6	10	7.0	5.4
	1279	0.62	0.72	0.56	0.60	0.63	1.1	3.0	5.4	3.6	3.0	3.9	3.6	2.9
	1234/1236/1269	0.44	0.27	0.44	0.22	0.54	1.3	3.2	7.5	4.6	5.1	5.9	3.6	3.6
	1237/1238	0.70	0.83	0.83	0.73	1.2	2.4	25	61	48	47	65	47	43
	2378	0.23	0.23	0.23	0.23	0.44	0.90	1.9	2.0	1.7	1.8	1.8	1.8	1.5
	1239	0.20	0.20	0.20	0.20	0.25	0.49	1.2	2.4	1.8	1.7	2.5	2.1	1.4
	1278	0.28	0.34	0.32	0.27	0.40	0.70	1.2	1.4	1.0	1.4	1.5	1.0	1.2
	1267	0.06	ND	0.09	ND	0.15	0.16	ND	ND	ND	0.28	0.43	ND	0.24
	1269	0.20	0.17	0.26	0.09	0.29	0.36	0.43	0.50	0.42	0.47	0.65	0.23	0.44
TCDDs		13	19	17	18	31	110	3200	8500	3800	3100	3900	2800	2500
TCDF	1368	0.32	0.68	0.21	0.01	0.38	2.7	5.8	0.68	5.9	6.6	0.90	0.83	1.6
	1468	0.30	0.43	0.49	0.76	1.4	4.1	5.9	4.1	4.5	4.5	4.5	4.5	4.4
	2468	0.61	1.0	1.0	1.5	2.3	7.3	100	220	100	89	110	83	74
	1247/1347/1378/1348/1246	2.9	3.4	3.8	4.9	7.6	19	27	21	21	23	25	24	21
	1367/1348/1379/1248	2.1	2.4	2.7	3.5	6.6	14	25	22	19	23	27	23	21
	1269/1457/1478	1.6	2.0	2.4	3.2	5.7	15	25	19	17	19	22	19	19
	1369/1237/2368	1.3	1.7	1.9	2.2	3.0	10	19	15	14	15	17	16	14
	2457/1238/1236/1469/1678/1234	2.0	2.4	2.7	3.5	6.7	15	25	24	26	28	31	30	29
	1278	3.2	3.4	3.3	4.0	5.5	9.5	13	8.9	8.5	8.8	10	9.0	8.0
	1267/1349	2.3	1.1	2.4	1.5	3.1	5.2	8.5	7.0	5.9	7.5	7.5	8.1	7.2
	2348/2378/2347/2348/1249/1279	8.3	8.6	8.9	7.9	12	23	35	25	25	27	31	29	27
	2367	0.70	0.95	1.2	1.3	2.9	7.4	12	8.9	8.8	9.2	10	9.4	8.8
	3467/1269	0.67	0.76	0.91	0.97	1.9	4.8	7.2	5.2	7.0	8.0	9.2	8.4	8.0
	1239	0.10	0.09	0.07	0.11	0.18	0.42	1.2	0.57	0.76	0.77	1.0	0.76	0.91
	1269	0.33	0.30	0.92	0.28	0.96	0.68	0.93	1.1	0.72	0.72	0.77	0.56	0.67
TCDFs		25	27	31	36	59	140	310	380	270	270	300	270	240
PeCDD	12469/12479	5.2	5.9	5.6	6.2	7.8	19	96	170	100	99	100	93	90
	12459	1.1	1.3	1.1	1.2	1.7	3.8	8.6	5.6	5.4	6.9	5.3	5.8	5.1
	12368	2.5	3.2	3.1	3.4	4.7	12	280	790	360	340	370	300	270
	12478	0.94	1.0	1.0	1.3	1.8	3.9	7.3	10	6.3	6.9	6.5	7.4	5.6
	12379	2.4	2.9	2.4	2.5	3.3	6.6	98	250	130	120	120	100	92
	12369	0.22	0.65	0.22	0.49	0.63	1.6	5.5	2.7	5.3	1.6	3.2	1.9	1.9
	12457/12469	1.3	1.4	1.4	1.4	2.0	3.1	5.5	7.5	7.5	6.4	7.2	5.5	5.1
	12347	0.62	0.60	0.66	0.69	0.90	2.1	5.3	8.0	7.3	10	6.8	6.6	6.8
	12346	0.25	0.33	0.22	0.25	0.40	0.75	1.4	1.7	1.4	1.9	1.8	1.7	1.5
	12378	0.79	1.0	0.90	1.0	1.5	3.3	8.8	6.1	5.9	6.7	6.3	6.1	5.3
	12367	0.27	0.39	0.29	0.30	0.50	0.93	2.1	2.6	2.4	2.2	2.5	2.0	2.3
	12389	0.52	0.95	0.54	0.75	0.79	1.4	2.3	3.7	3.6	2.1	3.6	2.2	2.4
PeCDDs		16	20	17	20	26	59	500	1300	650	600	630	630	480
PeCDF	13468/12468	1.4	1.9	2.4	4.5	9.5	40	46	44	44	55	76	100	97
	13678	0.34	0.48	0.47	0.63	0.89	1.9	3.9	4.5	5.2	4.8	5.1	5.5	4.5
	12369/12479/13467/13478/12467	4.7	5.5	5.2	8.5	13	33	53	42	45	46	56	53	47
	13479/14578	0.41	0.62	0.63	0.96	1.7	3.9	6.0	5.8	6.8	7.5	9.4	8.8	7.5
	12479	0.06	0.10	0.10	0.09	0.17	0.31	0.49	0.57	0.95	0.98	0.90	0.74	0.65
	15469	0.10	0.15	0.15	0.27	0.37	0.85	1.5	1.1	1.5	1.5	1.7	1.4	1.3
	23468/12469/12347/12348	1.2	1.5	1.7	2.5	4.3	11	29	45	35	35	40	36	34
	12348	0.64	0.78	0.69	1.1	1.6	3.1	4.4	3.1	3.7	3.6	4.2	3.9	3.4
	12378	3.2	3.5	3.5	4.1	5.1	7.5	11	8.7	8.7	8.9	9.7	9.2	8.3
	12367	0.36	0.55	0.51	0.79	1.1	2.5	4.2	3.9	4.8	6.1	5.2	5.2	4.7
	12678/12379	1.3	1.5	1.5	1.7	2.4	4.7	7.1	5.3	7.4	8.2	9.0	8.9	7.9
	23478/12469/12679/12369	1.5	1.9	1.9	2.5	3.6	6.7	12	9.3	12	11	13	13	12
	23467	1.2	1.5	1.6	2.0	3.2	7.2	13	13	13	19	20	24	27
	12349	0.06	0.10	0.09	0.13	0.17	0.44	0.68	0.55	1.3	1.1	1.3	1.5	1.2
	12369	0.18	0.24	0.21	0.29	0.29	0.42	0.74	0.52	0.69	0.68	0.66	0.77	0.59
PeCDFs		17	20	22	30	47	120	210	190	200	210	260	290	240
HxCDD	124679/124689	16	17	16	17	28	90	110	90	80	83	92	77	70
	123468	5.8	7.0	6.1	6.8	8.4	18	36	62	49	53	66	68	50
	123679/123689	7.2	8.8	8.6	13	26	91	140	130	99	110	110	96	85
	123469	0.33	0.64	0.36	0.63	1.4	5.2	7.5	6.2	4.5	6.4	6.3	5.6	5.1
	123478	0.73	1.0	0.96	1.3	2.5	6.7	16	9.7	9.5	9.9	11	9.0	6.4
	123678	1.4	1.8	1.8	3.9	9.0	42	70	42	35	36	34	31	29
	123467/123789	2.7	3.5	2.9	3.9	5.4	20	30	23	21	23	22	20	19
HxCDDs		34	40	37	45	82	270	410	360	270	340	340	300	270
HxCDF	123468	1.5	1.9	2.9	5.2	13	50	72	51	44	45	55	53	49
	134678/124678	6.0	7.1	10	17	44	190	290	170	160	170	220	230	210
	134679	0.21	0.27	0.42	0.41	0.49	1.9	3.0	3.0	3.0	3.5	4.7	6.0	4.3
	124678	0.31	0.55	0.55	0.67	1.6	4.4	6.7	6.1	7.3	8.5	9.4	11	9.1
	124689	0.94	2.2	3.4	15	49	290	440	230	170	190	200	190	170
	123467/123478	6.0	6.8	8.1	11	16	37	60	42	45	46	51	53	49
	123678	1.8	2.3	2.7	3.5	5.1	12	20	16	19	17	20	21	19
	123479	0.20	0.23	0.24	0.34	0.38	1.1	1.9	1.5	1.3	2.3	2.7	2.4	2.1
	123469/123679	0.31	0.58	0.55	1.2	2.3	4.2	2.6	4.8	6.0	8.3	9.0	8.4	8.1
	123589	0.32	0.46	0.44	0.60	1.7	5.8	12	6.7	6.9	6.5	7.0	7.1	6.4
	234678	1.2	1.7	1.9	2.5	4.1	10	21	21	29	29	31	39	34
	123789	0.25	0.69	0.42	0.67	0.49	1.0	1.8	1.3	1.6	1.4	1.9	1.9	1.6
	123489	0.70	1.1	0.71	1.1	1.2	2.5	5.1	3.5	5.3	4.5	4.5	5.7	5.1
HxCDFs		20	26	33	60	140	610	930	560	490	530	610	620	570
HpCDD	1234679	55	64	65	100	280	1300	1700	1100	750	950	980	900	740
	1234678	21	27	35	110	340	1800	2700	1500	1100	1100	1100	1000	940
HpCDDs		75	82	100	210	620	3100	4400	2600	1900	2000	2000	1800	1700
HpCDF	1234678	11	17	28	65	140	510	740	420	350	330	370	310	310
	1234679	0.69	1.6	1.9	2.0	3.6	11	24	11	14	19	21	27	24
	1234689	4.0	9.2	19	72	250	1400	2000	1100	620	800	830	740	660
	1234789	0.88	1.6	2.3	3.3	7.8	32	55	29	26	28	29	28	29
HpCDFs		17	29	51	130	400	1900	2800	1600	1000	1200	1300	1100	1000
OCDD		390	440	550	1500	5000	24000	30000	17000	12000	13000	14000	11000	11000
OCDF		24	43	96	180	520	2300	2900	1700	1200	1300	1300	1200	1100
TCDD	2,3,7,8	0.23	0.23	0.23	0.23	0.44	0.90	1.9	2.0	1.7	1.8	1.8	1.8	1.5
PeCDD	1,2,3,7,8	0.79	1.0	0.90	1.0	1.5	3.3	8.8	6.1	5.9	6.7	6.3	6.1	5.3
HxCDD	1,2,3,4,7,8	0.76	0.93	1.0	1.3	2.5	6.9	14	9.1	9.0	9.2	10	8.8	8.3
	1,2,3,6,7,8	1.7	2.1	2.1	4.1	9.8	43	73	45	38	37	36	33	31
	1,2,3,7,8,9	2.7	3.0	3.0	3.7	5.9	18	28	20	18	17	18	15	15
HpCDD	1,2,3,4,6,7,8	21	27	36	110	340	1800	2700	1500	1100	1100	1100	1000	940
OCDD		390	440	550	1500	5000	24000	30000	17000	12000	13000	14000	11000	11000
TCDF	2,3,7,8-F	4.5	4.6	4.7	5.4	7.4	12	17	11	10	9.0	10	9.5	9.7
PeCDF	1,2,3,7,8-F	3.2	3.5	3.5	4.1	5.1	7.5	11	8.7	8.7	8.8	9.7	9.2	8.3
	2,3,4,7,8-F	1.6	1.7	1.8	2.3	3.2	6.0	9.7	8.3	9.5	9.5	11	11	9.9
HxCDF	1,2,3,4,7,8-F	6.3	6.9	6.9	9.5	13	33	53	32	30	30	32	30	29
	1,2,3,6,7,8-F	1.8	2.3	2.7	3.5	5.1	12	20	15	19	17	20	21	19
	2,3,4,6,7,8-F	1.2	1.7	1.9	2.5	4.1	10	21	21	28	29	31	39	34
	1,2,3,7,8,9-F	0.33	0.40	0.61	0.66	0.59	1.4	1.9	1.7	2.2	1.8	2.4	2.7	2.1
HpCDF	1,2,3,4,6,7,8-F	11	17	28	65	140	510	740	420	360	330	370	330	310
	1,2,3,4,7,8,9-F	0.9	1.6	2.3	3.3	7.8	32	55	29	26	26	29	28	28
OCDF		24	43	96	180	520	2300	2900	1700	1200	1300	1300	1200	1100
Total PCDDs		520	600	750	1900	5800	29000	38000	30000	19000	19000	20000	17000	16000
Total PCDFs		100	150	220	440	1200	5100	7000	4400	3100	3500	3600	3500	3200
Total PCDD/Fs		620	740	970	2200	7000	33000	45000	34000	22000	22000	24000	20000	19000
WHO-TEQ (PCDD/Fs)		4.2	4.9	5.2	7.4	14	47	76	49	46	44	45	45	41
PCB 81		0.30	0.60	0.83	1.9	5.5	26	47	25	22	19	20	18	17
PCB 77		9.7	27	58	150	430	1100	2100	1100	940	730	790	740	690
PCB 126		0.75	1.0	2.0	3.9	9.4	29	49	30	26	22	24	24	22
PCB 169		0.26	0.40	0.46	0.60	1.1	2.6	4.8	4.0	3.0	3.7	4.1	4.3	4.1
Total Co-PCBs		11	29	61	160	440	1200	2200	1200	990	770	830	790	730
WHO-TEQ (Co-PCBs)		0.08	0.11	0.21	0.41	0.99	3.0	5.1	3.2	2.7	2.3	2.5	2.5	2.3
Total WHO-TEQ (PCDD/Fs + Co-PCBs)		4.2	5.0	5.4	7.8	15	51	81	52	48	46	48	47	43

Fig. 1. Historical trends of PCDD/F concentration in the sediment core from Tokyo Bay
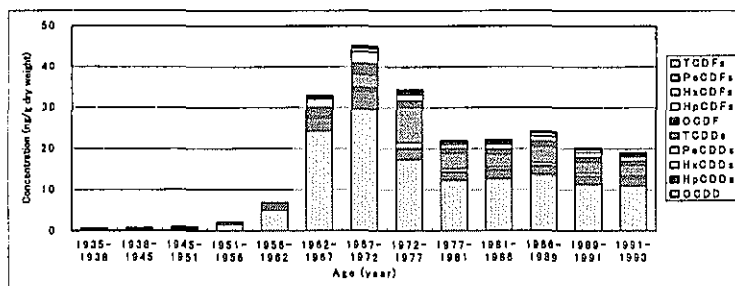
PCDD/F concentration in the Tokyo Bay sediment core were reconstructed (see Figure 1). The total dioxin concentration increased during the period 1935-1972, in which a drastic increase occurred from the late 1950s and peaked around 1970. During 1972-1981, the total dioxin concentration decreased continuously and then leveled off. A distinct homolog profile, dominated by OCDD, was observed throughout the sediment core. On the other hand, some trends in the profile and pattern were also found from the bottom to the top of the core. OCDD, HpCDDs, OCDF, HpCDFs, HxCDFs, and HxCDDs showed similar trends. They increased dramatically during 1956-1972, decreased rapidly during 1972-1981, and subsequently leveled off. In contrast to the highly chlorinated dioxins, TCDDs, PeCDDs and TCDFs, especially 1,3,6,8-TCDD and 1,3,7,9-TCDD, increased during 1962-1977, decreased rapidly during 1977-1981, and subsequently leveled off. Moreover, PeCDFs showed a different trend from those of other homologs mentioned above, increasing slowly to date. These characteristics indicate the existence of different dioxin sources in the Tokyo Bay area. To identify these sources, PCA was performed using a correlation matrix calculated from the PCDD/F data set and three PCs with proportions of approximately 35, 33, and 28 % were extracted. PC-1 includes OCDD, HpCDDs, OCDF, and most HpCDFs as its characteristic congeners. Considering the fact that these compounds are known impurities of PCP and their trends described above agree with the situation of PCP use in Japan, PC-1 was judged to be the dioxin impurities of PCP. In the case of PC-2, most PeCDFs, particularly 1,2,3,4,9-PeCDF and 2,3,4,6,7-PeCDF, are the characteristic congeners. According to the homolog pattern of a typical combustion process reported by Hutzinger and Fiedler (1993) in which PeCDFs and HxCDFs are the main components, we assumed that PC-2 corresponds to combustion processes, in which incineration is considered to be the main factor. The characteristic congeners of PC-3 include some TCDD, PeCDD, and TCDF congeners, especially

Fig. 2. Historical contributions of different sources to the PCDD/F concentration and TEQ in Tokyo Bay

(A)

(B)
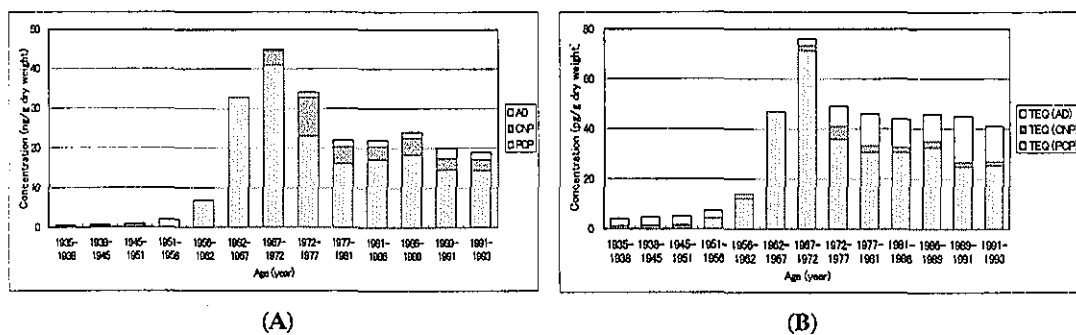
1,3,6,8-TCDD, 1,3,7,9-TCDD, 1,2,3,6,8-PeCDD, 1,2,3,7,9-PeCDD, and 2,4,6,8-TCDF. Since these compounds are reported to be the major impurities of CNP and their trends mentioned above are in agreement with the situation of CNP use in Japan, PC-3 was identified to be the dioxin impurities of CNP.

After source identification, we performed multiple regression analysis for source apportioning. The congener-specific concentrations of HpCDDs, OCDF, and HpCDFs in PCP (Masunaga and Nakanishi 1999) were modified using the typical homolog pattern of PCP reported by Hutzinger and Fiedler (1993) and used in this analysis. Based on the obtained apportionment of each source, the historical contributions of PCP, CNP, and atmospheric deposition to PCDD/F concentration and TEQ in Tokyo Bay were estimated and the results are shown in Figures 2-A and 2-B, respectively. It can be seen that PCP has been the greatest contributor to both PCDD/F concentration and TEQ in Tokyo Bay. The contribution of PCP peaked around 1970, decreased during 1972-1981, and then leveled off. CNP has played a minor role in dioxin concentration since 1967. The contribution of CNP reached its maximum around 1975, decreased during 1977-1986, and subsequently leveled off. On the other hand, incineration is a secondary contributor to PCDD/F TEQ but its proportion has generally increased to date.

Fig. 3. Historical trends of coplanar PCB concentration in the sediment core
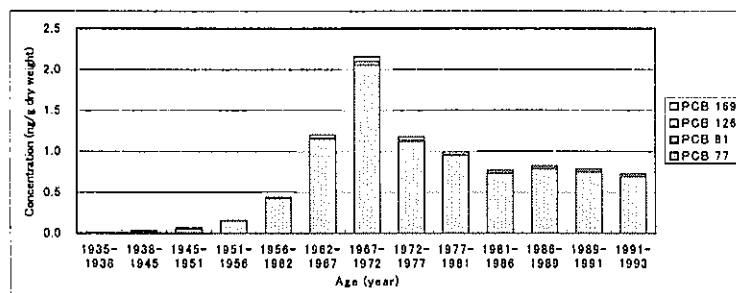
For coplanar PCBs, the four target congeners were found to be ubiquitous in all the core layers examined (see Table 1). Figure 3 shows the historical trends of coplanar PCB concentration in the sediment core. The total coplanar PCB concentration increased drastically form 1951 to 1972. Subsequently, a decrease occurred during 1972-1986 and then the concentration leveled off. PCB 77 was the dominant congener, contributing more than 88 % of the total coplanar PCB concentration throughout the core. The total coplanar PCB TEQ was dominated by PCB 126 due to its largest TEF within the coplanar PCB group.

Fig. 4. Component scores of the two principal components for coplanar PCBs
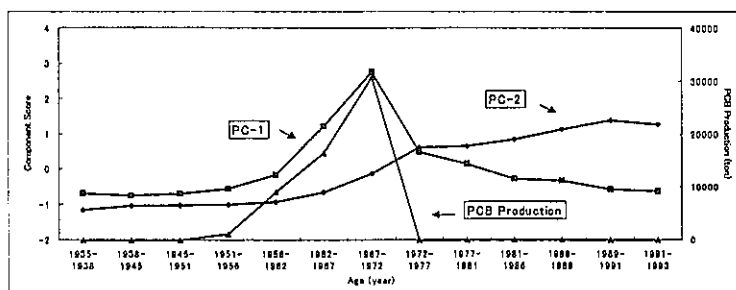
To obtain information about the sources of coplanar PCBs in Tokyo Bay, PCA was performed and two PCs with proportions of approximately 94 and 5 % were extracted. Their characteristic congeners were PCB 77, 81, 126 and PCB 169, respectively. The time trends of component scores of PC-1 and PC-2 are shown in Figure 4. PC-1 increased drastically during 1951-1972, decreased quickly during 1972-1977, and subsequently leveled off. This agrees well with the situation of PCB production and use in Japan (Chemical Society of Japan 1980). On the other hand, PC-2 has increased slowly to date, being consistent with the temporal influence of combustion processes described above. Based on these comparisons, we estimated that PCB products and combustion processes were the major sources of coplanar PCB pollution in Tokyo Bay.

Fig. 5. Historical trends of total PCDD/F and coplanar PCB TEQ in the sediment core
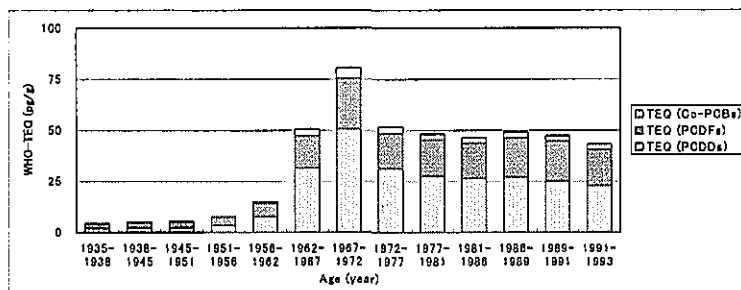
Figure 5 shows the historical trends of total PCDD/F and coplanar PCB TEQ in the sediment core. It can be seen clearly that the total TEQ has remained at the same level since the late 1970s. PCDD/Fs contributed more than 90 % of the total TEQ throughout the core.

4. Conclusion

In this study we elucidated the historical trends of PCDD/Fs and coplanar PCBs in Tokyo Bay. Both PCDD/Fs and coplanar PCBs were detected during the period 1935-1938 (total PCDD/Fs 620 pg/g, total coplanar PCBs 11 pg/g). This provides information about PCDD/F and coplanar PCB "background levels" before World War II in Tokyo Bay. PCDD/F and coplanar PCBs levels were found to increase drastically during the period 1956-1972 (total PCDD/Fs 7,000 – 45,000 pg/g, total coplanar PCBs 440 – 2,200 pg/g). Principal component analysis and detailed comparison of the homolog profiles and isomeric patterns indicate that PCP, CNP and combustion processes are the major sources of PCDD/Fs in Tokyo Bay. PCB products and combustion processes were estimated to be the major sources of coplanar PCBs. Furthermore, multiple regression analysis reveals that herbicides (PCP and CNP) have contributed mainly to the total PCDD/F concentration and TEQ since the late 1950s; PCP has been the greatest contributor to dioxin burdens. The inputs originating from PCP and CNP did not significantly decrease even after the decline of their use. This suggests that dioxins remaining in agricultural land will continue to run off and pollute the aquatic environment in Japan for a long time. These results are consistent with those observed in the Lake Shinji basin and further demonstrate the significant impact of herbicides. These findings are of

significance for the establishment of comprehensive dioxin and PCB control measures in Japan.

5. Acknowledgements

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