Temporal Trends of PCDDs/DFs and Dioxin-Like PCBs in Preserved Fish Samples from 1953 to 1999

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Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/DFs) are not manufactured on deliberate purpose; however, these toxic compounds are chemical impurities, unintentional by-products of industrial processes involving chlorine, or burning of organic matter in the presence of chlorine[1]. On the other hand, dioxin-like polychlorinated biphenyls (non-*ortho*- and mono-*ortho*-substituted CBs) enter into the environment from two potential sources; firstly as a commerical PCB formulations and secondly by combustion processes[2]. These hydrophobic chemicals are highly persistent in the environment especially with a strong affinity for sediments and a high potential for accumulating in biological tissues. Recently, many studies have reported that these hydrophobic chemicals have been found in all variety of environmental media.

Many investigations into the temporal trends of these toxic compounds have been carried out to date. The majority of historical temporal trend studies have been performed using mainly sediment cores and stored human tissues. However, information on temporal trends for wildlife is very scarce. In the case of time trend studies on residual PCDDs/DFs in wildlife, Herbert *et al.*[3] have reported that levels of PCDDs/DFs in pooled herring gull eggs collected in the Great Lakes and the St. Lawrence River declined in most colonies between 1981 and 1984, with no clear trends after 1984.

In this study, we examined temporal changes in levels of PCDDs/DFs and dioxin-like PCBs in goby collected in Tokyo Bay and Tateyama Bay from 1953 to 1999. The objectives of this study were to quantify the contamination levels of PCDDs/DFs and dioxin-like PCBs in fish samples from the past and to investigate the accumulation profiles of these compounds.

Materials and Methods

Sample Collection

Table 1 lists the details of fish samples used in the present study collected from Tokyo Bay and Tateyama Bay from 1953-1999. Formalin-preserved samples were obtained from Tokyo University, Agricultural and Life Sciences School, excluding the fish sample from 1999 which is collected by hook. Almost all analyzed fish samples were collected from Tokyo Bay, excluding the sample code # G75S9 which is only sample collected at Tateyama Bay in 1975.

Determination of PCDDs/DFs and dioxin-like PCBs

Approximately 50 g from the pooled fish samples was homogenized, freeze-dried and extracted using a Soxhlet apparatus with dichloromethane. Fractionation was carried out with an

activated silica-gel and an alumina column. In the charcoal- impregnated silica-gel mixture column fractionation step, adsorbed PCDDs/DFs and dioxin-like PCBs were eluted into two fractions. The first fraction, eluted with 25% dichloromethane in hexane, consisted of mono-*ortho*-substituted CBs. The second fraction, eluted with toluene, comprised PCDDs/DFs and non-*ortho*-substituted CBs. Identification and quantification of PCDD/DF homologues and non-*ortho*- and mono-*ortho*- substituted CBs was performed by HRGC-HRMS. The separation of PCDDs/DFs was achieved using a HP 6890 instrument equipped with DB-5 and DB-17 columns with splitless and solvent cut mode. Gas chromatographic separation of non-*ortho* and mono-*ortho*-substituted CBs was carried out on a DB-5 capillary column.

Table 1. Details of fish samples from Tokyo Bay and Tateyama Bay, 1953-1999.

Sample code	Common name	Sampling area	Sampling Year	Analyzed part	Weight (g)	Length (cm)	Fat content (%)
G53S2	Goby [4]	Tokyo Bay	1953	Whole	15.6±5.1	12.3±1.1	5.6
G57S3	Goby [4]	Tokyo Bay	1957	Whole	17.6±6.7	13.1±2.1	10.8
G63S4	Goby [4]	Tokyo Bay	1963	Whole	10.6±5.5	10.6±2.8	6.9
G66S5	Goby [3]	Tokyo Bay	1966	Whole	35.9±3.9	15.9±0.9	12.5
G67S6	Goby [7]	Tokyo Bay	1967	Whole	10.4±1.9	11.2±0.6	7.0
G70S7	Goby [5]	Tokyo Bay	1970	Whole	9.5±2.5	11.2±1.1	9.0
G75S9	Goby [7]	Tateyama Bay	1975	Whole	9.2±3.6	10.1±1.3	8.5
G85S10	Goby [1]	Tokyo Bay	1985	Whole	41.4	16.0	12.1
G99S11	Goby [6]	Tokyo Bay	1999	Whole	11.4±0.9	10.9±0.5	8.6

Figures in brackets [ ] indicate the number of samples pooled.

Result and Discussion

Residue levels of PCDDs/DFs and dioxin-like PCBs in fish samples

Concentrations of individual congeners and the isomers of PCDDs/DFs in the fish samples collected in Tokyo Bay and Tateyama Bay from 1953 to 1999 are listed in Table 2. PCDDs/DFs were detected in all fish samples from 1953 to 1999. The concentrations expressed on a wet weight basis of total PCDDs/DFs varied between pooled goby samples from a low concentration of 3.9 pg/g in 1999 to a high concentration of 109 pg/g in 1970. The total PCDD/DF concentrations in goby from 1953 to 1967 did not differ significantly. On the other hand, the total PCDD/DF concentrations in goby samples from the 1970's were higher than those in fish samples from the other ages.

On the whole, OCDD in goby from 1953 to 1999 was detected in the highest concentration among the analyzed PCDD/DF congeners. In fish samples collected from Tokyo Bay, although the OCDD concentration from 1970 was lower than that from the 1950's or 1960's. Nevertheless, the temporal trend for PCDD/DF congener profiles in goby was not significant. In contrast, we found that the PCDD/DF congener profiles of goby collected from Tateyama Bay in 1975 differed considerably from that of goby sampled from Tokyo Bay. In particular, the contribution of TeCDF to the total PCDD/DF concentrations in goby collected from Tateyama Bay was markedly lower than that in Tokyo Bay goby from 1953 to 1970.

The concentrations of dioxin-like PCBs, such as non-*ortho*-and mono-*ortho*-substituted CBs in goby samples from 1953-1999, are presented in Table 3. Residues of dioxin-like PCBs in goby were detected from 1953 and the level gradually increased until 1970, however, the concentration of these compounds in goby from 1975 declined rapidly. In Japan, the production of commercial

Table 2. Concentrations of PCDDs/DFs (pg/g on a wet wt. basis) in fish samples.

Sample Code / Isomers	G53S2	G57S3	G63S4	G66S5	G67S6	G70S7	G75S9	G85S10	G99S1
2,3,7,8-TeCDD	0.12	0.16	0.17	0.35	0.49	4.97	0.18	0.06	0.05
Other TeCDD	0.68	0.55	1.27	2.35	0.78	10.14	11.93	0.66	0.41
1,2,3,7,8-PeCDD	0.44	0.35	0.52	0.98	0.54	1.83	0.49	0.19	0.14
Other PeCDD	1.13	0.29	0.61	0.24	0.07	1.24	1.02	0.12	0.06
1,2,3,4,7,8-HxCDD	0.13	0.11	0.30	0.59	0.34	0.73	0.26	0.21	0.05
1,2,3,6,7,8-HxCDD	0.52	1.12	0.92	2.18	0.97	2.10	0.71	0.71	0.13
1,2,3,7,8,9-HxCDD	0.56	0.09	0.16	0.23	0.18	0.31	0.28	0.11	0.02
Other HxCDD	3.36	0.22	0.63	0.22	0.12	0.35	0.46	0.03	0.03
1,2,3,4,6,7,8-HpCDD	2.07	1.12	1.46	2.24	1.37	1.95	2.66	1.78	0.16
Other HpCDD	2.07	0.47	0.72	0.59	0.44	0.44	0.87	0.10	0.04
OCDD	8.81	8.03	9.17	10.07	5.25	6.66	23.39	1.71	0.38
PCDDs	19.91	12.5	15.92	20.03	10.56	30.7	42.24	5.68	1.48
2,3,7,8-TeCDF	4.68	3.40	3.75	8.76	40.79	31.2	0.51	0.14	0.34
Other TeCDF	2.32	1.04	2.59	0.87	1.50	24.31	1.19	0.44	0.18
1,2,3,7,8-PeCDF	0.44	0.44	0.53	0.99	0.68	2.09	0.12	0.52	0.14
2,3,4,7,8-PeCDF	0.76	1.40	1.27	2.23	1.56	6.02	0.34	0.11	0.36
Other PeCDF	0.91	1.07	3.07	2.71	0.85	7.05	0.71	0.78	0.43
1,2,3,4,7,8-HxCDF	0.27	1.07	0.52	1.52	0.56	1.26	0.31	0.51	0.17
1,2,3,6,7,8-HxCDF	0.10	0.15	0.30	0.46	0.19	0.82	0.15	0.45	0.10
2,3,4,6,7,8-HxCDF	0.09	0.15	0.29	0.30	0.16	0.94	0.21	0.24	0.16
1,2,3,7,8,9-HxCDF	0.01	ND	ND	ND	0.01	0.03	0.01	ND	0.01
Other HxCDF	0.65	2.32	2.4	5.16	0.96	3.31	0.90	2.40	0.41
1,2,3,4,6,7,8-HpCDF	0.28	1.02	0.53	0.70	0.23	0.53	0.45	0.40	0.06
1,2,3,4,7,8,9-HpCDF	0.03	0.06	0.06	0.10	0.03	0.10	0.07	0.02	0.02
Other HpCDF	0.23	1.3	0.41	1.20	0.26	0.53	0.52	0.54	0.05
OCDF	0.50	1.95	0.35	0.68	0.14	0.32	0.41	0.14	0.03
PCDFs	11.26	15.37	16.07	25.69	47.92	78.51	5.88	6.69	2.45
PCDDs/DFs WHO-TEQ	1.63	1.86	2.00	3.93	6.18	13.68	1.12	0.59	0.48
PCDDs/DFs I-TEQ	1.42	1.69	1.74	3.45	5.92	12.77	0.89	0.50	0.41

PCBs by two firms (Kanegafuchi and Mitsubishi-Monsanto) began in 1954, but were banned from domestic purpose since 1973[4]. Although, the domestic production of PCBs began from 1954, environmental contamination had been evidenced by the presence of dioxin-like PCBs in fish samples even before 1954, indicating the possibility of environmental contamination due to the limited use of imported PCBs by local industries prior to 1954 and another plausible explanation is that by emission of combustion processes. Presence of this residue from the early 1950s revealed that environmental contamination of PCBs started soon after these compounds were put to use in Japan. On the other hand, we found that the residue level of dioxin-like PCBs declined in goby collected from Tateyama Bay. This seems to be due to the geographic difference rather than temporal fluctuation. Despite, the wide difference between dioxin-like PCB levels in 1970 and 1975 suggests that the contamination situations within each region were different during the 1970s.

Temporal trend of Toxic Equivalents in fish samples from Tokyo Bay

In fish samples from Tokyo Bay, the total toxic equivalents(ΣPCDDs/DFs-TEQ +Σdioxin-like

Table 3. Concentrations of non-*ortho*-(pg/g on a wet wt. basis) and mono-*ortho*-substituted CBs (ng/g) in fish samples.

Sample Cod / Isomers	G53S2	G57S3	G63S4	G66S5	G67S6	G70S7	G75S9	G85S10	G99S11
# 81	0.58	6.75	54.36	373.5	140.6	409.8	4.29	12.15	4.93
# 77	24.4	197.3	810.4	1452	1265	3144	71.45	274.8	77.60
# 126	ND	9.87	48.86	187.3	85.60	158.5	7.6	25.63	8.38
# 169	ND	0.49	2.02	9.42	3.90	6.18	0.75	6.74	1.85
non-*ortho* CBs (pg/g)	24.98	214.5	915.6	2022	1495	3719	84.09	319.32	92.77
# 123	0.1	0.19	0.73	2.41	1.25	1.84	0.19	0.55	0.07
# 118	0.96	4.99	20.18	62.31	40.52	46.52	4.38	11.07	2.59
# 114	0.01	0.15	0.71	2.33	1.02	1.99	0.15	0.23	0.04
# 105	0.3	1.92	8.2	28.85	14.41	23.94	1.62	4.02	0.72
# 167	0.01	0.07	0.33	2.46	1.25	0.71	0.08	0.31	0.06
# 156	0.08	0.48	2.12	5.61	2.80	3.71	0.98	1.20	0.15
# 157	0.02	0.09	0.41	1.24	0.59	0.74	0.13	0.25	0.04
# 189	0.002	0.01	0.03	0.19	0.11	0.07	0.03	0.13	0.01
mono-*ortho* CBs (ng/g)	1.48	7.91	32.73	105.4	61.94	79.52	7.55	17.77	3.68
PCBs WHO-TEQ (pg/g	0.19	2.09	9.54	33.0	16.59	26.73	2.02	5.08	1.32
PCBs Alborg-TEQ (pg/g	0.24	2.18	9.86	33.6	17.2	27.86	2.07	5.32	1.36

PCBs-TEQ) levels ranged from 1.8 pg TEQ/g (on a wet weight basis) in 1999 to 40.4 pg TEQ/g in 1970. The total TEQ level in Tateyama Bay goby was 3.14 pg TEQ/g in 1975. Since, we could not get samples in the year of 1975 from Tokyo Bay. It is therefore, very difficult to estimate the accurate regulation of PCDDs/DFs and dioxin-like PCBs in between the locations.

The contribution of dioxin-like PCBs-TEQ to the total TEQ in Tokyo Bay goby samples from 1953 was lower than that of PCDDs/DFs-TEQ. However, after the period of commercial PCB production in Japan, the dioxin-like PCBs-TEQ proportion increased slightly in 1957 and then the contributions of dioxin-like PCBs-TEQ still remain greater than those of PCDDs/DFs-TEQ even to date. As compared with the increasing trend of dioxin-like PCBs-TEQ, the temporal change of PCDDs/DFs-TEQ concentration was relatively sluggish, from 1953 to 1970. In contrast, it was found that the declining tendency of PCDDs/DFs and dioxin-like PCBs-TEQ concentrations in goby samples from 1985 and 1999 very rapidly. During the period from the early 1970s to 1985, the temporal trends of PCDDs/DFs and dioxin-like PCBs-TEQ concentration in goby from Tokyo Bay were not measurable due to unavailability of the samples. Nevertheless, this decline tendency in 1985 and 1999 indicated the contamination due to lowering rate of these harmful substances, when compared with samples collected in 1970s.

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