DETERMINATION OF DIOXINS, FURANS AND CO-PLANAR PCBs IN AQUATIC ORGANISMS FROM LAKE KASUMIGAURA (KUL), JAPAN

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Introduction

Polychlorinated dibenzo- para- dioxins (PCDDs), -dibenzofurans (PCDFs) and -biphenyls (PCBs) present as trace impurities in some manufactured chemicals and industrial wastes. The chemical and environmental stability of PCDD/DFs and their tendency to accumulate in fat have resulted in their detection within many ecosystems[1-4]. In general, wherever high levels of PCDD/DFs and PCBs have been detected, the source has been a hazardous waste dump, an industrial discharge, or an application of PCDD-contaminated herbicide[4-6]. In order to prevent adverse effects on human health caused by PCDDs, PCDFs and PCBs found in environment, a new law was established recently in Japan. However, emissions of dioxins into the environment will be decreased by enforcement of the new law. The remediation of soil, sediment and former disposal sites, in which dioxins accumulated, is essential to immediately lower exposure levels. But the implementation of the remediations which are more expensive, must be decided on based on a more precise risk assessment from site to site.

KasumigaUra Lake (KUL) is the second largest in Japan which located in mouth of the Tone River and about 70 km northeast of Tokyo, with the maximum depth about 7 m. The organochlorine compounds in catchments area of KUL were deposited slowly in the paddy field soil, lake water and are suspected to remain still in the lake sediment through the years[7]. Consequently, the determination of organohalogen compounds in KUL organisms is necessary in order to understand their dynamics and any existing effects. In this study, we measured co-planar PCBs and 2,3,7,8-chlorine substituted PCDDs and PCDFs in aquatic wildlife of KUL from 1978 to 2001. Eventually, the toxic equivalency quantity (TEQs) of PCDDs/DFs and dioxin-like PCBs were calculated based on WHO-TEFs to evaluate the risk of the organisms analyzed in this study.

Materials and Methods

Sampling: The samples were collected by trawling during 1970s to 2001. The gill net (*Geta-ami* in Japanese) which was used for collected the samples that found suitable to collect the most of the biota employed in this study. For plankton collection, the smaller mesh sized net has been adopted for trawling for the period of 30 minutes/netting time with a boat speed of 40 km/h. The samples collected in this study includes {plankton-1 *Cyclops vicinus (CV, Ken-mijinko in Japanese)*,

plankton-2 *Neomysis intermedia (NI, Isaza-ami in Japanese)*}, shrimp *Microbrachium nipponense (MN, Tenaga-ebi in Japanese)*, small fish *Tridentiger obscurus (TO, Cicibu in Japanese)* and large fish *Hemibarbus barbus (HB, Nigoi in Japanese), Micropterus salmoides (MS, Ookuchi-bass in Japanese), Mugil chepallus Linn*aeus *(MCL, Bora in Japanese*). The sampling done at 3 stations proposed by National Institute of Environmental Studies, Kasumigaura Water Research Station (KWRS) at Ibaraki Prefecture, Tsukuba, Japan[8]. Most of the old samples were then kept under formalin solution at room temperature in KWRS. They were freeze dried before chemical analysis (Table 1).

Chemical Analysis: Basically the formalin was decanted and the sample weight was recorded. After weigh the samples, it was placed in a chemically clean jars and freeze-dried. The freeze-dried sample weight was measured to calculate moisture content and then powdered in Mortar and Pestle. The known amount of powdered samples was extracted in a Soxhlet apparatus for 16-h using dichloromethane and then further analysis procedures has been described earlier[8-10].

Table 1. Sum concentrations of 2,3,7,8-PCDDs, PCDFs, dioxin-like PCBs and TEQ (pg/g fat weight) in aquatic organisms from Lake Kasumigaura, Japan.

Organism	Collection Date (D/M/Y)	Fat %	PCDDs	PCDFs	Non-ortho PCBs	Mono-ortho PCBs	TEQ
Plankton[a]	14.02.1980	1.05	7300	400	9200	NA	34
Plankton[b]	07.07.1993	0.93	2100	170	3500	NA	25
Prawn[c]	17.10.1978	3.04	480	85	8600	NA	46
"	13.10.1983	1.98	200	76	2200	NA	28
"	20.09.1984	0.95	140	29	1600	NA	11
"	22.09.1986	0.81	410	100	6100	NA	46
"	20.08.1987	0.70	450	73	5600	NA	21
"	07.07.1993	1.44	720	110	4400	NA	45
"	02.08.2000	1.64	860	220	3900	NA	68
Small fish[d]	19.09.1978	1.25	580	82	7500	NA	28
"	14.09.1979	1.40	630	150	7700	NA	30
"	05.08.1982	0.63	240	67	8800	NA	21
"	18.08.1983	0.81	1100	160	2800	NA	40
"	07.09.1984	0.77	340	140	2000	NA	66
"	22.09.1986	0.93	380	98	3500	NA	31
"	20.08.1987	1.11	130	59	1600	NA	14
Bass[e]	27.09.2000	1.82	120	120	3900	82000	79
"	12.10.2001	2.43	57	59	3200	71000	38
Carp[f]	06.04.2001	2.63	45	50	1600	34000	32
"	10.04.2001	2.90	44	76	2800	69000	38
Mullet[g]	06.04.2001	8.97	18	36	1300	22000	14

[a,b,c,d,e,f,g] respectively *Cyclops vicinus, Neomysis intermedia, Macrobrachium nipponense, Tridentiger obscurus, Micropterus salmoides, Hamibarbus barbus and Mugil chepallus Linnaeus*
NA=not analyzed; The values rounded

Identification and Quantification: Identification and quantification of PCDD/DFs and co-planar PCBs were performed using a HRGC (Hewlett Packard 6890 Series) coupled with a HRMS (Micromass Autospec- Ultima). The detailed HRGC-HRMS conditions were described elsewhere[9-10]. Prior to injection in HRGC-HRMS, ^{13}C-labelled 1,2,3,4-TeCDD and 1,2,3,7,8,9-HxCDD were added as injection recovery standards. Mean (range) recoveries of spiked internal standards through the whole analytical procedure were 78% (52-89%). 2,3,7,8-PCDD/DFs, dioxin-like PCBs and TEQ concentrations are presented as pg/g on a fat weight basis unless otherwise specified. Concentrations of co-planar PCBs refer to the sum of 4 non-ortho substituted PCB congeners in most of the samples and only few fish species mono-ortho PCBs are also included.

Results and Discussion

PCDD/DFs: Mean concentrations of sum 2,3,7,8-chlorine substituted PCDD/ and PCDFs were noticed in the following order *MCL* < *HB* < *MS* < *MN* < *TO* < *NI* < *CV* with respectively, 54 < 110 < 180 < 570 < 1400 < 2300 < 7700 pg/g fat weight. PCDDs were greater until 1987 samples (69-98% to the total 2,3,7,8-PCDD/DFs) while PCDFs were increased in 2000 and 2001 samples (51-67% to the total 2,3,7,8-PCDD/DFs) as shown in Table 1. Particularly, OCDD contributed 7 to 93% to the total 2,3,7,8-PCDD/DFs. Next to OCDDs, 1,2,3,4,6,7,8-HpCDD, 1,2,3,6,7,8-HxCDD and 1,2,3,7,8,-PeCDD was prevalent congeners. While 2,3,7,8-TCDF, OCDF, 1,2,3,4,7,8-HxCDF was prevalent congeners among PCDFs. The domination of OCDD in all samples indicated this congener has greater accumulation potential with similar to the sediment and soil[4,6]. The greater abundance of OCDD likely reflecting the domination of dioxin originated from PCP consumption as well as incineration source[5].

The KUL can be considered representative of the Japanese water system for PCDD/DF pollution for the following reasons. Mainly, the lake is located about 70-km northeast of the Tokyo metropolitan just west of Kashima evolved from this industrial area. Thus PCDD/DF from various thermal process including municipal solid waste incineration and industrial activities may impact the lake area through atmospheric transport. Waste incineration and steel production have been considered as the major sources of PCDD/DFs in organisms. About 33,00,000 t/yr of municipal solid waste is incinerated in Tokyo metropolitan also considered as a sources. Besides, Japan's largest steel works is located in Kashima industrial area near KUL. In addition, there are 1000 hectares of paddy fields around the lake (>20% drainage area), and application of herbicides may additionally contribute to the PCDD/DF burden in this area[7]. Occurrence of TCDF is of major concern in all organisms analyzed in this study. The herbicide CNP had been applied in large amounts in this area for weed control in paddy fields. This herbicide was reported to contain 1,3,6,8- and 1,3,7,9-TCDDs and 2,4,6,8-TCDF as the main components of its PCDD/DF impurities[5]. Formation of 2,3,7,8-congener from CNP has been discussed earlier[5,7]. Earlier studies also demonstrated noticeable concentrations of TCDD and TCDF arises from the sources such as kraft pulp mill, wood-treating facilities, and combustion related atmospheric deposition[4,9-10].

Greater accumulation of PCDD/DFs in plankton suggested their potential to bioaccumulation and less metabolic capacity. With increasing tropic level, the concentrations decreased which is possibly due to greater metabolic capacity in higher tropic animals as well as habitat of the particular animal in aquatic environment. The small fish (*Cicibu* in Japanese) had higher levels

than prawn these results indicated different metabolic capacity in between tropic animals. The temporal trends of PCDD/DF and TEQ concentrations in prawn and small fish were different (Figure 1). In general, in prawn, PCDD/DF and TEQ were decreased from 1978-1984 and then level increased until 2000. Whereas, in small fish, the contamination pattern were fluctuated.

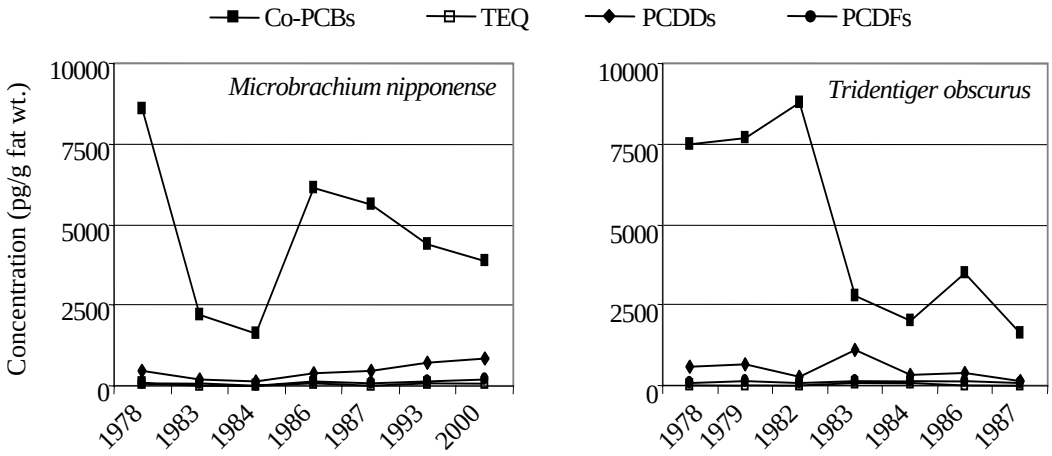

Figure 1. Temporal trends of organohalogens in prawn and small fish.

Dioxin-like PCBs: The average concentrations of non-ortho PCBs were in the same order of PCDD/DF contamination pattern with 1200 < 2200 < 3500 < 3600 < 4600 < 7500 < 9200, respectively for *MCL* < *HB* < *MS* < *MN* < *NI* < *TO* < *CV* (Table 1). The CB-77 is predominant congener followed by CB-126, CB-81 and CB-169. The temporal trend is not well pronounced due to fluctuation of concentration levels. The temporal trends of coplanar PCBs in prawn were decreased from '78-'84 samples and elevated in 1986 samples and decreased in latter samples. In contrast the small fish showed opposite trend with those of prawn. Multitude of contamination variation between animals suggested the different metabolic rates.

Toxic equivalent quantities (TEQs): Toxic equivalency (TEQ) were estimated by applying WHO-TEFs proposed in 1998[1] using fish TEFs. The TEQs based on PCDD/DFs and non-ortho PCBs were in the following order 14 < 25 < 33 < 34 < 35 < 38 < 59 pg/g fat weight respectively, *MCL* < *NI* < *TO* < *CN* < *HB* < *MN* < *MS*. The TEQ contribution by PCDD/DFs were significant (>90-95%). While non-ortho PCBs contributes about <2.3-11%. Whereas, mono-ortho PCBs were less than 1% to the TEQ contribution in 5 large fish species. Consequently, neglect of mono-ortho PCBs TEQ for the plankton, shrimp and small fish do not have any impact in the overall discussions. Overall, TEQ contribution by PCDDs was predominated followed by PCDFs, non-ortho PCBs and mono-ortho PCBs.

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