CONCENTRATIONS OF PCDDs, PCDFs AND DIOXIN-LIKE PCBs; THEIR BIOMAGNIFICATION FACTOR IN COMMON CORMORANTS (*Phalacrocorax carbo*), FROM JAPAN

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Introduction

There are enormous work have put forward PCDD/Fs concentrations, toxicity, effect, population status as for cormorant as concern in USA, Canada and European nations[1,2]. However, there is no work relate with PCDD/Fs and dioxin-like PCBs in common cormorant collected from Japan excluding common cormorants of Lake Biwa, Shinobazu pond and Odaiba, Japan[3] in which they reported only dioxin-like PCBs but not PCDDs and PCDFs. According to their pioneer work, elevated concentrations of PCBs have been observed. Therefore, in present study, common cormorant collected from Tokyo Bay, Japan was used to determine concentrations of PCDD/Fs, in liver and egg and their diet samples of 3 different fish species. Since, diet samples included in this study provided biomagnification potential of cormorants. Eventually, toxic equivalency factor was also determined in liver and egg of cormorants using WHO- bird's TEF values[4]. This is the first study of this kind to be undertaken in cormorant of Japan for PCDD/Fs.

Materials and Methods

Sample collection

Stranded common cormorants were collected from 1997-1999 at Sinobazu Pond (n=10), captive dead cormorant was obtained from Sayama Lake (n=1). Four dead cormorants were provided by Gyotoku Birds Observatory and only one bird were shot for survey of diet in Sagami River, was dissected and liver was stored at –30°C until analysis. In case of egg samples (n=9), it was collected by our team during 1998 in 6th Odaiba Island, Tokyo Bay, with a permission of Environmental Agency, Government of Japan. Three species of fish [viz., Sea bass (n=1, *Lateolablax japonicus*), Gizzard shad (n=3, *Konosirus punctatus*) and Conger eel (n=1, *Conger myriaster*)] were collected in Tokyo Bay in 1998.

Determination of PCDD/Fs and dioxin-like PCBs

Three different species of fish pool were homogenized, freeze-dried and used for analysis. Homogenized cormorant whole liver tissue and egg samples were freeze-dried, moisture content measured then sample was extracted by Soxhlet apparatus with dichloromethane. After fat content determination, sulfuric acid was treated and purified for fractionation. Silica gel and alumina was used for fractionation, in that, silica gel removed most of other pesticides like DDT (if any) and its metabolies. Alumina column removed most of mono-*ortho* and di-*ortho* substituted PCBs. Further, in a charcoal-impregnated silica-gel mixture column fractionation step was subjected, adsorbed

PCDD/Fs and dioxin-like PCBs in two fractions. The first fraction, eluted with 25% dichloromethane in hexane, consisted of mono-*ortho* substituted PCBs. The second fraction, eluted with toluene, comprised PCDD/Fs homologues and non-*ortho* substituted PCBs. Quantification and identification techniques adopted for non-*ortho* and mono-*ortho* substituted PCBs followed by HRGC-HRMS. The separation of PCDD/Fs was achieved using a HP 6890 machine equipped with DB-5 and DB-17 columns with splitless and solvent cut mode. Gas chromatographic separation of non-*ortho* and mono-*ortho* substituted PCBs was performed in DB-5 capillary column.

Results and Discussion

Residual concentrations

A mean (n=16) of total PCDD/Fs found in cormorant liver was 33000 pg/g fat, in that PCDDs contributes 16000, remaining 17000 was shared by PCDFs (Table 1). Since, concentration level showed wide difference in each sample despite, isomer-specific profiles were similar with each other (Fig.1). Especially, 2,3,7,8-substituted PCDD/Fs comprised approximately 97% of the total concentration. Particularly, 1,2,3,7,8-PeCDD, 1,2,3,6,7,8-HxCDD, 2,3,4,7,8-PeCDF and OCDD recorded higher levels among all isomers studied. Besides, as for as an age of concern, chicks (n=1) contained 10000pg/g fat followed by juvenile (n=9) 31000 and adult (n=6) 41000.

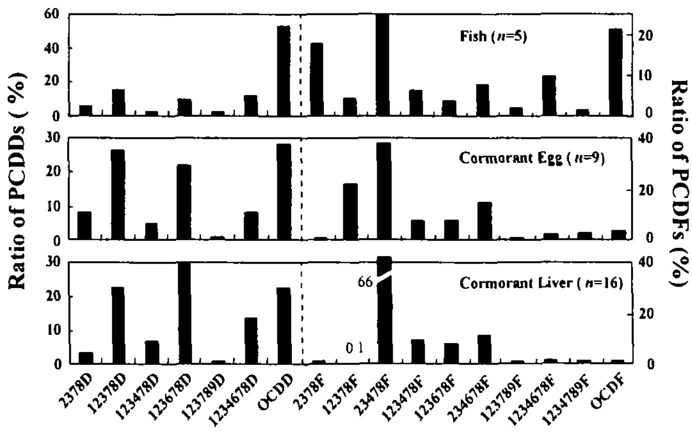

Fig.1. Composition of 2,3,7,8-substituted PCDD/Fs in the liver and egg of common cormorants and fish collected from Tokyo bay, Japan.

Fifteen-fold lower mean concentration (2200pg/g fat) was observed in egg (n=9) comparatively with juvenile and much more lower than adult does. 1,2,3,7,8-PeCDD, 1,2,3,6,7,8-HxCDD, OCDD and 2,3,4,7,8-PeCDF are the major congeners found in egg.

Among three different fish samples analyzed, Gizzard shad and Conger eel showed lower and slightly higher mean PCDD/Fs concentrations of 240 and 210 pg/g fat, respectively. Whereas, highest values obtained from Sea bass with a mean concentration of 710 pg/g. Although, all 3 species combined mean concentration (390pg/g fat) calculated was shown. 1,2,3,7,8-PeCDD, OCDD, 2,3,4,7,8-PeCDF and OCDF are predominant accumulators in fish. It is not known that whole body homogenates used for analysis may have an impact on higher OCDD and OCDF levels in fish.

Bio-magnification features

When results were subjected into bio-magnification factor, highest bio-magnification potential observed in liver then in egg (Fig.3). This feature is similar to concentration levels of egg and liver. 2,3,4,7,8-PeCDF, 1,2,3,6,7,8-HxCDD and 1,2,3,6,7,8-HxCDF seems to bio-magnify with greater amount than the other isomers. In contrast, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF and OCDF were less bio-magnification factor in common cormorant liver and egg. Furthermore, OCDD and OCDF bio-magnification seems to be not significant in either sample analyzed. The peculiar bio-magnification trend was noticed in case of 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-

Table 1. Concentration (pg/g fat) of PCDD/Fs in fish, cormorant egg and liver their biomagnification factor and Toxic equivalency (pgTEQ/g fat) in common cormorant collected from Tokyo Bay, Japan.

	Concentration			BMF[a]		WHO-TEF[(4)]	TEQ[b]	
		Cormorant					Cormorant	
Congeners	Fish	Egg	Liver	Egg/Fish	Liver/Fish	*(birds)*	Egg	Liver
n	*5*	*9*	*16*				*9*	*16*
2,3,7,8-D	9.5 (2.4-23)	94 (53-160)	530 (43-1800)	9.9 (2.3-68)	56 (1.8-760)	*1*	94 (53-160)	530 (43-1800)
1,2,3,7,8-D	26 (2.9-68)	290 (160-460)	3700 (340-19000)	11 (2.4-155)	140 (5.0-6400)	*1*	290 (160-460)	3700 (340-19000)
1,2,3,4,7,8-D	5.4 (2.0-12)	56 (24-94)	1100 (91-7400)	10 (2.0-48)	200 (7.7-3800)	*0.05*	2.8 (1.2-4.7)	55 (4.6-370)
1,2,3,6,7,8-D	16 (6.9-34)	250 (120-370)	4900 (340-33000)	15 (3.5-54)	300 (10-4700)	*0.01*	2.5 (1.2-3.7)	49 (3.4-330)
1,2,3,7,8,9-D	1.5 (0.63-3.3)	9.3 (3.6-16)	63 (6.1-420)	6.2 (1.1-25)	42 (2.0-710)	*0.1*	0.93 (0.36-1.6)	6.3 (0.61-42)
1,2,3,4,6,7,8-D	20 (6.6-40)	92 (70-200)	2300 (200-17000)	4.6 (1.7-30)	110 (4.9-2500)	*0.001*	0.092 (0.070-0.20)	2.3 (0.20-17)
OCDD	88 (33-140)	310 (200-720)	3700 (170-18000)	3.5 (1.5-22)	42 (1.3-550)	-		
2,3,7,8-F	23 (11-38)	11 (0.36-35)	40 (2.9-160)	0.47 (0.0093-3.2)	1.7 (0.075-15)	*1*	11 (0.36-35)	40 (2.9-160)
1,2,3,7,8-F	5.6 (2.5-9.9)	5.6 (n.d.-13)	8.7 (n.d.-36)	1.0 (n.c.-5.0)	1.6 (n.c.-15)	*0.1*	0.56 (n.c.-1.3)	0.87 (n.c.-3.6)
2,3,4,7,8-F	32 (11-69)	500 (270-830)	10000 (1000-47000)	16 (4.0-73)	310 (14-4200)	*1*	500 (270-830)	10000 (1000-47000)
1,2,3,4,7,8-F	8.0 (3.1-18)	99 (50-150)	1500 (140-8900)	12 (2.8-47)	190 (8.2-2800)	*0.1*	9.9 (5.0-15)	150 (14-890)
1,2,3,6,7,8-F	4.8 (1.9-10)	100 (52-150)	1300 (110-7500)	21 (5.0-78)	270 (11-4000)	*0.1*	10 (5.2-15)	130 (11-750)
2,3,4,6,7,8-F	10 (5.3-19)	15 (4.0-47)	1800 (170-7800)	1.5 (0.21-2.5)	180 (9.0-1500)	*0.1*	1.5 (0.4-4.7)	180 (17-780)
1,2,3,7,8,9-F	2.6 (0.61-5.9)	11 (n.d.-34)	36 (4.9-110)	4.2 (n.c.-56)	14 (0.74-180)	*0.1*	1.1 (n.c.-3.4)	3.6 (0.49-11)
1,2,3,4,6,7,8-F	13 (5.1-28)	36 (20-53)	310 (45-1300)	2.8 (0.74-10)	25 (1.6-260)	*0.01*	0.36 (0.20-0.53)	3.1 (0.45-13)
1,2,3,4,7,8,9-F	2.2 (0.78-4.5)	36 (19-84)	170 (17-780)	16 (4.2-110)	77 (3.7-1000)	*0.01*	0.36 (0.19-0.84)	1.7 (0.17-7.8)
OCDF	28 (10-45)	51 (21-99)	170 (24-580)	1.8 (0.47-10)	6.2 (0.53-57)	*0.0001*	0.0051 (0.0021-0.0099)	0.017 (0.0024-0.058)
2,3,7,8-PCDDs*	79	792	12593	57	848		390	4343
2,3,7,8-PCDFs*	128	864	15335	77	1075		534	10509
PCDD/Fs*	207	1655	27928	8.0	135		925	14852
Fat (%)	7.0	6.1	4.0					

Values in parentheses denotes range, a=Biomagnification factor, b=Toxic equivalency.
n.d. represents the not detected, n.c. indicates not caluculated

HxCDD in common cormorants comparatively with same species and results suggested from the Netherlands[(5)].

Toxic-equivalent contribution

Toxic equivalent factor calculated using WHO-*bird* TEFs; 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD and 2,3,4,7,8-TCDF contributed major toxic equivalency in both liver and egg (Fig 3). Other than that, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF and 2,3,4,6,7,8-HxCDF contributed slightly moderate toxic equivalency in cormorant liver and egg. When the results were compared with other cormorant studies(5), TEQ in our study showed somewhat lower values. Although, 1,2,3,7,8-PeCDD TEQ alone contributed to 16-fold higher in our study with those of common cormorant from the Netherlands.

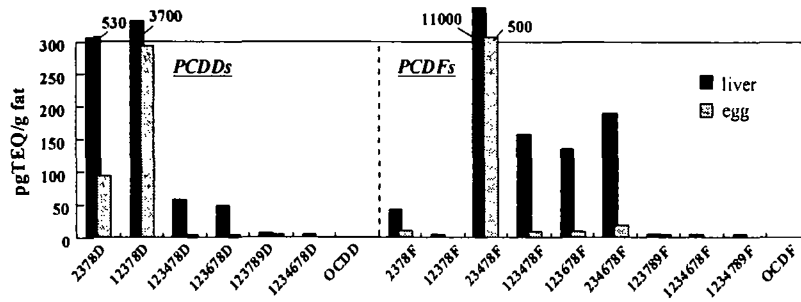

Fig. 3. Comparison of Toxic Equivalent (WHO-Birds TEF) in the liver and egg of common cormorants collected from Tokyo Bay, Japan

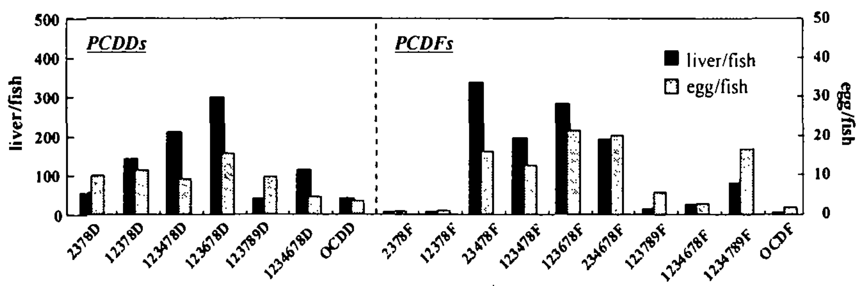

Fig. 2. Biomagnification factor of common cormorant in the liver and egg /fish collected from Tokyo Bay, Japan

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