DIOXINs, FURANs AND DIOXIN-LIKE PCBs IN LIVERS OF BIRDS FROM JAPAN

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Introduction

Toxic effects of organochlorines on wildlife on the top of food chain are a major concern during past few decades[(1)]. Especially there is growing evidence that PCDDs, PCDFs and PCBs are harmful to wildlife, especially on predatory birds[(2)]. Avians that occupy trophic positions at the top of food chains in aquatic environment have frequently been used as bio-indicators for toxic organochlorine compounds. There are so many reports that demonstrated concentrations of PCDD/DFs and PCBs in eggs and muscle tissue of avians in various parts of the world[(3)]. Only very few documents have reported exposures of dioxin-like PCBs and PCDD/DFs in colonial -fish eating water birds in Japan[(4,5,6)]. Nevertheless, there is not much work on PCDD/DFs and PCBs in livers of range of bird species. In this study we determined PCDD/DF and dioxin-like PCBs in livers Japanese birds with four ecologically different habitat.

Materials and Methods

Sample collection: Most of bird liver (excluding rock pigeon muscle) samples were obtained from Gyotoku wild-birds Observatory located in Chiba, Tokyo, Japan, which is a re-habilitation center/captivity for some physically injured birds in wild. Silky chicken liver was obtained from Nihon University. A few bird samples were collected in and around Haneda Airport, Atsugi-city, Tanuma-cho and Tochigi areas. All the birds collected in these locations were dissected to separate liver tissues for chemical analysis. Further birds were grouped into granivores (silky chicken, common pheasant and rock pigeon), piscivorous (gray heron, spot-billed duck, whimbrel, short-tailed shearwater, cattle egret and great egret), omnivores (large-billed crow, black-headed gull and sea gull) and predators (black-eared kite, ural owl, northern goshawk, common kestrel and mountain hawk eagle) according to the feeding habit and ecology for discussions.

Sample analysis: Prior to analysis, the samples were freeze-dried. Moisture content determined and extracted with Soxhlet apparatus for 10-15 h in dichloromethane. Details of the analytical procedures have been reported previously[(6,7)]. Identification and quantification of 2,3,7,8-substituted congeners of PCDD/DFs and dioxin-like PCBs were performed by a high-resolution gas chromatography (HRGC) (Hewlett Packard 6890 Series) coupled with a high-resolution mass spectrometer (HRMS) (Micromass Autospec- Ultima).

Results and Discussion

The concentrations of 2378-chlorine substituted PCDD/DFs ranged from 80-840 pg/g fat wt. in granivores, 33-17500 pg/g fat wt. in piscivores, 2300-8200 pg/g fat wt. in omnivores and 480-490000 pg/g fat wt. in predators (Table 1). Concentrations of dioxin-like PCBs were 100- to 250 times elevated than of PCDD/DFs in same individuals. Concentrations of 12-dioxin-like PCBs measured were 31-83 ng/g fat wt. in granivors, 58-12000 ng/g fat wt. in piscivores, 1800-67000 ng/g fat wt. in omnivores and 30-55000 ng/g fat wt. in predators (Table 1). The observed results suggested feeding habit might have influenced the variation in concentrations between species. Besides, differences in metabolic and elimination capacity in between species also might have played a role.

Table 1. PCDD/DFs (pg/g fat weight)* and dioxin-like PCBs (ng/g fat weight)* concentrations in the livers of birds from Japan.

Group	PCDDs[a]	PCDFs[a]	Non-*ortho* PCBs[b]	Mono-*ortho* PCBs[b]
	240	**170**	**1.2**	**49**
Granivores	(55-510)	(25-330)	(0.3-2.6)	(31-80)
	3300	**1400**	**69**	**2300**
Piscivorous	(15-15000)	(18-2500)	(2.3-380)	(56-12000)
	2300	**3000**	**620**	**29000**
Omnivores	(1400-4000)	(860-4200)	(3.9-1200)	(1800-66000)
	28000	**46000**	**1200**	**7700**
Predators	(180-180000)	(300-310000)	(1.4-8400)	(29-47000)

The figures in parentheses indicates range and bold figures are means.*values rounded.
[a] and [b], respectively 2378-chlorine substituted PCDD/DFs and IUPAC Nos. of 81, 77, 126, 169, 105, 114, 118, 123, 156, 157, 167, 189

The congener specific patterns are slightly different between species (Table 2). On the whole, 12378-PeCDD and 123678-HxCDD and 23478-PeCDF, 123678-HxCDF are the prevalent congeners in most of birds analyzed. In addition, 12346789-HpCDD, OCDD, 123478-HxCDD and 234678-HxCDF, 12378-PeCDF, 123478-HxCDF, 123789-HxCDF and 2378-TCDF also accumulated in some birds (Table 2). Similarly, IUPAC Nos. of 77 and 126 were most prevalent among non-*ortho* PCBs in many species. Although, some species accumulated greater levels of IUPAC 169 and very few species accumulated IUPAC 81. The mono-*ortho* PCB 118 and 105 were mostly observed in many birds apart from 156, 189 and 114 (Table 2). However, mono-*ortho* PCBs were several orders of magnitude higher than non-*ortho* PCBs in all birds.

Table 2. Specific congener accumulation and toxic equivalency by PCDD/DFs and dioxin-like PCBs in Japanese birds.

	High accumulants[a]				High TEQ[b]			
Birds	PCDDs[c]	PCDFs[c]	NO[d]	MO[e]	PCDDs[c]	PCDFs[c]	NO[d]	MO[e]
Granivores								
Silky chicken	12378, 1234678	23478, 234678	77, 126	189, 118	12378, 2378	23478, 2378	77, 126	189, 118
Common pheasant	12378, OCDD	2378, 123478	126, 77	105, 118	12378, 2378	23478, 2378	126, 77	105, 118
Rock pigeon	12378, OCDD	23478, 123478	77, 169	118, 156	12378, 2378	23478, 123478	77, 126	156, 157
Piscivorous								
Gray heron	1234678, 123678	12378, 123478	77, 126	105, 118	2378, 12378	23478, 123478	77, 126	105, 156
Spot-billed duck	12378, OCDD	2378, 23478	77, 126	105, 118	2378, 12378	23478, 2378	126, 77	105, 156
Whimbrel	1234678, OCDD	23478, 234678	126, 169	118, 105	2378, 12378	23478, 234678	81, 77	105, 118
STS	1234678, OCDD	23478, 123789	126, 77	114, 118	2378, 12378	23478, 2378	126, 77	114, 105
Cattle egret	12378, 123678	23478, 234678	126, 169	118, 105	2378, 12378	23478, 123678	126, 81	105, 156
Great egret	12378, 123678	23478, 234678	126, 169	118, 167	2378, 12378	23478, 123678	126, 81	105, 156
Omnivores								
Large-billed crow	1234789, OCDD	23478, 1234678	77, 126	118, 156	12378, 2378	23478, 123478	169, 126	105, 118
Black-headed gull	12378, 123678	123678, 234678	126, 77	118, 105	12378, 2378	23478, 234678	126, 77	105, 118
Sea gull	12378, 123678	23478, 123478	126, 169	118, 105	12378, 2378	23478, 123478	126, 77	105, 118
Pradators								
Black-eared kite	OCDD, 12378	23478, 234678	126, 77	118, 105	12378, 2378	23478, 123478	126, 81	105, 156
Ural owl	12378, 123678	23478, 123678	77, 126	118, 105	12378, 2378	23478, 123678	77, 126	105, 156
Northern goshawk	123678, 12378	12378, 123678	81, 126	118, 156	12378, 2378	23478, 2378	126, 77	105, 156
Common kestrel	123478, 123678	23478, 123478	126, 169	118, 156	12378, 2378	23478, 2378	126, 81	118, 156
Mountain hawk eagle	123678, 12378	123478, 123678	169, 126	118, 156	12378, 123478	23478, 123478	126, 81	156, 118

[a, b, c, d] and [e], respectively highly accumulated congeners, highly contributed to toxic equivalency, 2378-chlorine substituted PCDD/DFs, Non-*ortho* PCBs of 81, 77, 126, and 169 and Mono-*ortho* PCBs of 105, 114, 118, 123, 156, 157, 167, 189

The toxic equivalents (WHO-[bird] TEFs) were high in mountain hawk eagle, sea gull and black-headed gull (Fig.1). In all three species, dioxin-like PCBs greatly contributed to the toxicity than those of PCDD/DFs. Toxicity contribution by PCDD/DFs was found higher in northern goshawk, ural owl, great egret, spot-billed duck, common pheasant and rock pigeon. In most of bird species 12378-PeCDD, 2378-TCDD and 123478-HxCDD and 23478-PeCDF, 2378-TCDF, 123478-HxCDF and 123678-HxCDF greatly contributed to toxicity despite greater accumulation by other congeners like 1234678-HpCDD, 123678-HxCDD, OCDD and 123789- and 12378-PeCDF, 123678-HxCDF and 1234678-HpCDF (Table 2). Therefore, the former congeners are considered to have an great impact on avians. Among dioxin-like PCBs the toxicity can be rated in the following order: 126>77>81>169>105>118>156>114>189>157 in most bird species (Table 2).

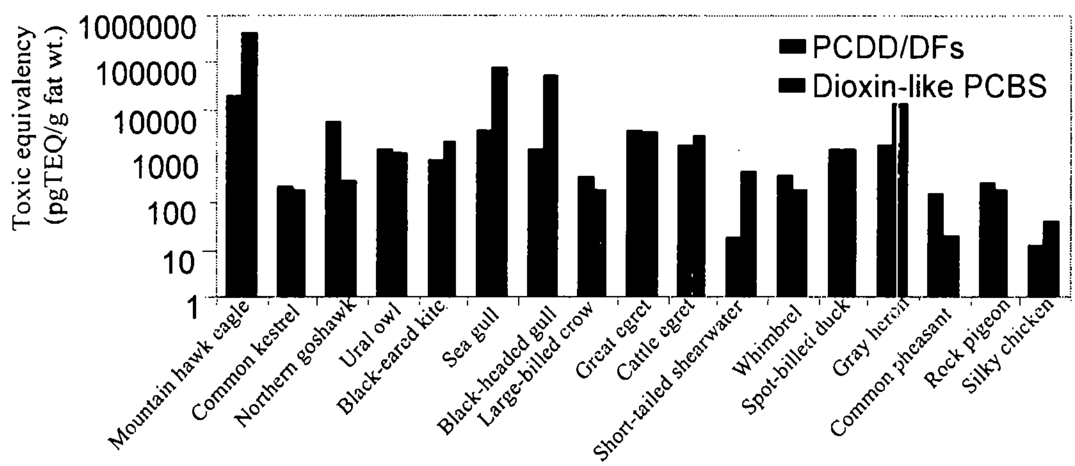

Figure 1. Toxic equivalency in Japanese birds.

The toxic threshold concentrations were available for free ranging birds of the Great Lakes, USA. Similarly, the NOAEL and LOAEL values are also available for eggs of bald eagles from Canada. Besides, more recently LOAEL for the common tern chick liver has been reported. The TEQ levels were compared with those reported in above-mentioned studies. Despite greater concentrations of PCDD/DFs and dioxin-like PCBs in birds in this study, the present TEQ levels in any species of birds were less than the reported threshold values. However, it should be mentioned that the US and the Canadian studies values are based on egg thresholds. Therefore, more suitable studies are needed to compare the toxic threshold levels in livers of adult birds analyzed in this study.

When the concentrations were compared with those of the other countries, PCDD/DFs were elevated in one predatory bird from Japan, followed by the birds in the Baltic Sea, cormorants and other birds in the Great Lakes region (Fig. 2). Among dioxin-like PCBs, White-tailed sea eagles from Poland and cormorants from Japan showed most elevated levels followed by the levels reported in the present study (Fig. 2). The lower most concentrations were observed in birds from Midway Atoll, USA followed by granivore birds of the present study and then Indian birds (Fig. 2).

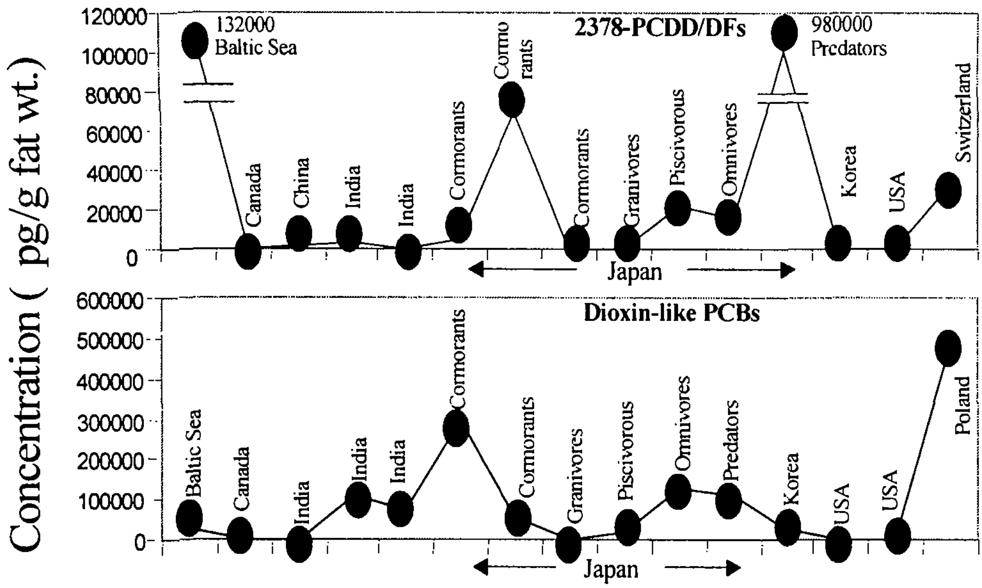

Figure 2. Comparison of PCDD/DF and dioxin-like PCBs concentration in other countries.

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