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Polychlorinated Dibenzo-*p*-Dioxins, Dibenzofurans, and Dioxin-Like Polychlorinated Biphenyls in Livers of Birds from Japan

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Abstract. Concentrations of 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and non- and mono-*ortho*-chlorine-substituted polychlorinated biphenyls (dioxin-like PCBs) were measured in livers of 17 species of birds collected from Japan. Birds were grouped according to their feeding habits as granivores, piscivores, omnivores, and predators for discussions. Livers of granivores contained relatively low concentrations of PCDD/DFs (80–660 pg/g) followed in increasing order by omnivores (2,300–8,000 pg/g), piscivores (61–12,000 pg/g) and predators (480–490,000 pg/g on a fat weight basis). Especially, one species of predatory bird (mountain hawk eagle) contained elevated concentrations of PCDDs, PCDFs, and dioxin-like PCBs, and the measured concentration is one of the highest reported to date. Homolog and congener patterns of PCDDs and PCDFs varied among species; hence, the results suggested that feeding habits, specific elimination, and metabolism influence contamination pattern. Concentrations of dioxin-like PCBs were in the order of granivores (32–83 ng/g) $<$ predators [excluding mountain hawk eagle] (32–2,500 ng/g) $<$ piscivore (61–12,000 ng/g) $<$ omnivores (1,800–67,000 ng/g on a fat weight basis). Mountain hawk eagle contained the highest concentration of dioxin-like PCBs (55,000 ng/g fat weight). 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) toxic equivalents (TEQs) ranged from 53–450,000 pg/g fat weight. 23478-PeCDF, 2378-TCDD/TCDF, and PCB congeners IUPAC 126 and 77 were major contributors to TEQs in birds. To our knowledge, this is the first study of PCDD/DFs and dioxin-like PCBs in livers of several species of Japanese birds.

Polychlorinated diaromatic hydrocarbons (PCDHs), including polychlorinated biphenyls (PCBs), are a group of synthetic chemicals that were first synthesized in the early 1880s. Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs), unlike PCBs, have not been purposely manufactured, but rather are present as impurities associated with chlorophenols (for example, pentachlorophenol), in herbicides, such as 2,4,5-trichlorophenoxyaceticacid and chloronitrophen applied to paddy fields in Japan (Masunaga 1999; Masunaga and Nakanishi 1999). PCBs had been used in various industrial materials, such as transformers, capacitors, and noncarbon copying paper; PCDD/DFs are formed by photochemical and thermal reactions during and after municipal solid waste incinerator and industrial waste incinerator. A significant portion of dioxins accumulated in aquatic sediment in Japan was indicated to have originated from agrochemicals. In addition, the amount of waste incinerated in Japan is very high compared with other countries. Therefore, it is necessary to elucidate the significance of various sources of PCDDs/DFs on wildlife exposures.

Since the late 1940s and early 1950s, there were a series of avian population collapses. For example, populations of bald eagles (*Haliaeetus leucocephalus*) and other fish-eating waterbirds such as double-crested cormorants (*Phalacrocorax auritus*) declined in the Great Lakes, United States, Canada, and other parts of the world in the 1960s and 1970s (Kubiak *et al.* 1989; Walker 1990; Tillitt *et al.* 1991, 1992; Giesy *et al.* 1994; Van den Berg *et al.* 1994, 1995; Sanderson *et al.* 1994a, 1994b; Barron *et al.* 1995; Elliott *et al.* 1996a, 1996b, 1996c; Elliot and Norstrom 1998). The declines were associated with reproductive failure, characterized by severe eggshell thinning and poor hatchability and chick survival that was unrelated to habitat alteration or microbial pathogens. Most of these reproductive effects were correlated with exposure to contaminants like DDT and dioxin-like compounds. These adverse effects have, in turn, been suggested as attributed to declines in avian populations. High correlation has been observed with deformity/anatomical malformations and egg concentrations of PCDDs, PCDFs, and dioxin-like PCBs (for review see Kubiak *et al.* 1989; Yamashita *et al.* 1993; Sanderson *et al.* 1994a, 1994b; Elliott *et al.* 1996b, 1996c).

A few studies have reported the occurrence of dioxin-like PCBs and PCDD/DFs in birds in Japan (Guruge and Tanabe 1997; Guruge *et al.* 2000; Iseki *et al.* 2000). These studies have suggested elevated exposures to PCDD/DFs in fish-eating birds in the mid- and late 1990s. However, efforts have been taken to

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reduce emission of dioxin in Japan in the late 1990s. As an example, increase of temperature and reduction of carbon sources and substitution of oxygen reduced PCDD/DF emissions. There is no study to document dioxin levels in bird species of Japan despite several sources of exposures. Considering these, in the present study, we determined congener-specific accumulation of PCDDs, PCDFs, and dioxin-like PCBs in 17 species of birds belonging to four groups based on their feeding habit. Toxic equivalencies (TEQs) contributed by PCDDs, PCDFs, and dioxin-like PCBs were estimated using toxic equivalency factors (TEFs) for birds (Van den Berg *et al.* 1998). The estimated TEQs were compared with those of the threshold values reported in a few earlier studies.

Materials and Methods

Sample Collection

Most bird liver (excluding rock pigeon muscle) samples were obtained from Gyotoku wild birds observatory located in Chiba, Tokyo, which is a rehabilitation center/captivity for some birds physically injured in the wild. The birds that died in captivity due to severe wounds were dissected, and liver tissues were stored. Silky chicken liver was obtained from Nihon University, Japan. A few bird samples were collected in and around Haneda Airport (birds were shot due to disturbances during take-off and landing of air flights), Atsugi-city, Tanuma-cho, and Tochigi areas. All the dissected bird livers were stored in chemically clean polythene covers and transported to laboratory and kept at $-30°C$ until analyzed. The biometry of samples analyzed and a few ecological notes of the species are shown in Table 1.

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 (Nakamura *et al.* 1994; Iseki *et al.* 2000; Senthilkumar *et al.* 2001a). Briefly, after extraction, samples were concentrated using a Kuderna-Danish concentrator to 10 ml and the solvent transferred to *n*-hexane. The fat content was determined gravimetrically from an aliquot of the extract. Seventeen ^{13}C-labeled tetra-, penta-, hexa-, hepta-, and octa-CDD and CDF congeners substituted at 2,3,7,8-positions, and dioxin-like PCBs (IUPAC nos. 81, 77, 126, 169, 105, 114, 118, 123, 156, 157, 167, 189), were spiked into hexane extracts prior to sulfuric acid treatment. The hexane layer was rinsed two times with hexane-washed water, and dried by passing through anhydrous sodium sulfate in a glass funnel. The solution was concentrated to 2 ml and sequentially subjected to silica gel, alumina and silica gel impregnated activated carbon column chromatography. Extracts were passed through a silica gel–packed glass column (Wakogel, silica gel 60; 2 g) and eluted with 130 ml of hexane, which contained PCDD/DFs and dioxin-like PCBs. The hexane extract was further concentrated and passed through alumina column (Merck-Alumina oxide, activity grade 1) and eluted with 30 ml of 2% dichloromethane as a first fraction, which contained several *ortho*-substituted PCBs. The second fraction eluted with 50% of 30 ml dichloromethane in hexane contained PCDD/DFs and some dioxin-like PCBs, which was purged under a gentle stream of nitrogen nearly to dryness and passed through a silica gel–impregnated activated carbon column (0.5 g) to further separate mono-*ortho* dioxin-like PCBs from non-*ortho* dioxin-like PCBs and PCDD/DFs. The first fraction eluted with 25% dichloromethane in hexane contained mono-*ortho* PCBs. The second fraction eluted with 250-ml toluene contained non-*ortho* PCBs and PCDD/DFs, which was concentrated and analyzed by high-resolution gas chromatograph interfaced with a high-resolution mass spectrometer.

Quantification and Identification

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 (Hewlett Packard 6890 Series) coupled with high-resolution mass spectrometry (Micromass Autospec-Ultima). The mass spectrometer was operated in an electron impact mode and in the selected ion monitoring mode at a resolution $R > 10{,}000$ (10% valley). Separation was achieved using a DB-5 (J&W Scientific; 0.25 mm ID $\times$ 60 m length) and a DB-17 column (J&W Scientific; 0.25 mm ID $\times$ 60 m length). The DB-5 and DB-17 column oven temperature was programmed from an initial temperature of 160°C to a final temperature of 310°C (total run time 60 min) and from an initial temperature of 160°C to a final temperature of 280°C (total running time 70 min), respectively. Before injection, ^{13}C-labeled 1,2,3,4-TeCDD and 1,2,3,7,8,9-HxCDD were added for instrumental recovery estimation. Mean and (range) recoveries of spiked internal standard through the whole analytical procedures were 65% (52–95%). The concentrations are given in pg/g fat weight for PCDD/DFs and ng/g fat weight for PCBs unless otherwise specified.

Results

PCDD/DF and Dioxin-like PCB Concentrations

Most of the earlier studies of dioxins and furans in birds have involved egg, carcass, breast muscle or adipose fat as a matrix for monitoring. In this study, 2,3,7,8-substituted PCDDs, PCDFs, and dioxin-like PCBs were analyzed in livers. Only in rock pigeon breast muscle was analyzed due to the small sample size. Analysis of liver tissues has several advantages including its role in physiological functions in birds. In addition, liver is a most sentinel matrix to determine toxic chemicals due to its role in the metabolism of xenobiotics.

Granivores. Concentrations of PCDDs and PCDFs in granivorous birds (silky chicken, common pheasant, and rock pigeon) are shown in Table 2. Among granivores, the muscle tissue of rock pigeon contained the highest concentration of PCDD/DFs (660 pg/g) despite the absence of 6 of the 17 PCDD/DF congeners. Common pheasant contained higher concentrations of PCDD/DFs (480 pg/g) than silky chicken (80 pg/g). PCDD concentrations were greater than PCDFs in silky chicken (68.8%) and rock pigeon (77.2%). However, PCDFs predominated in common pheasant (68.8%) (Figure 1a). Octachlorinated dibenzo-*p*-dioxin (OCDD) was the most prevalent congener in rock, pigeon followed by 23478-PeCDF, 12378-PeCDD, 123678-HxCDD. In common pheasant liver, 23478-PeCDF, 2378-TCDF, and 12378-PeCDD/PCDF were the predominant congeners. In silky chicken, only OCDD was found at elevated concentrations (Table 2, Figure 2).

Dioxin-like PCBs such as non- and mono-*ortho* PCBs were abundant in all the birds analyzed. Common pheasant liver accumulated higher concentrations (83 ng/g) followed in de-

Table 1. Details and few ecological notes of the bird samples analyzed in this study

Bird Name (Scientific Name)	Japanese Local Name	Sample ID Collection Date	PC[a]*	BW[a] (g)	SL[a] (mm)	Age	Sex	Status[b]
Granivore species								
Silky chicken (*Gallus gallus*)	Ukokkei	SC 01.04.98	1	1,615	NM[a]	Adult	M	SA
Common pheasant (*Phasianus colchicus*)	Kiji	CP 24.03.97	2	840	68.2	Adult	M	DC
Rock pigeon (*Columba livia*)	Dobato	RP 22.09.97	2	179	32.4	Adult	UI[a]	DC
Aquatic species								
Gray heron (*Ardea cinerea*)	Aosagi	GH(A) 17.10.97	2	368	495	Adult	M	DC
Gray heron (*Ardea cinerea*)	Aosagi	GH(J) 28.07.98	2	422	NM	Juvenile	M	DC
Spot-billed duck (*Anas poecilorhyncha*)	Karugamo	SBD(1) 30.06.97	2	709	477	Adult	M	DC
Spot-billed duck (*Anas poecilorhyncha*)	Karugamo	SBD(2) 15.06.98	2	722	500	Adult	F	DC
Whimbrel (*Numenius phaeopus*)	Tyuushakusigi	WB 06.02.98	3	431	415	Adult	M	SH
Short-tailed shearwater (*Puffinus tenuirostris*)	H-M[c]	STS 14.05.98	2	438	380	Adult	M	DC
Cattle egret (*Bubulcus ibis*)	Amasagi	CE 17.05.99	4	199	480	Adult	F	DC
Great egret (*Ardea alba*)	NA[d]	GE 22.09.99	5	1,000	910	Adult	UI	D
Omnivore species								
Large-billed crow (*Corvus macrorhynchos*)	Hasibuto-garasu	LBC 05.01.98	2	790	NM	Adult	M	DC
Black-headed gull (*Larus ridibundus common*)	Yurikamome	BHG 29.06.98	2	196	401	Adult	M	DC
Seagull (*Larus crassirostris*)	Umineko	SG 22.07.98	2	453	490	Adult	M	DC
Predator species								
Black-eared kite (*Milvus migrans*)	Tobi	BEK(1) 02.02.98	2	1,040	NM	Adult	M	SH
Black-eared kite (*Milvus migrans*)	Tobi	BEK(2) 01.07.99	3	860	NM	Adult	UI	SH
Black-eared kite (*Milvus migrans*)	Tobi	BEK(3) 12.09.99	3	966	605	Adult	M	SH
Ural owl (*Strix uralensis*)	Hukurou	UO 27.01.96	2	580	NM	Adult	F	DC
Northern goshawk (*Accipiter gentilis*)	Ootaka	NGS 29.09.99	4	1,009	550	Juvenile	F	DC
Common kestrel (*Falco tinnunculus*)	Tyougennbou	CK 07.07.99	2	NM	NM	Adult	UI	DC
Mountain hawk eagle (*Spizaetus nipalensis*)	Kumataka	MH 29.09.99	6	1,240	720	Adult	M	D

[a] PC, UI, NM, BW, SL, M and F denotes place of collection, unidentified, not measured, body weight, standard length, male and female, respectively.
[b] D, SA, DC, and SH, respectively, died, sacrificed, died in captivity, and shooting.
[c] Hasiboso-mizunagidori.
[d] Not available.
* 1 = Nihon University, 2 = Gyotoku Wild Birds Observatory, 3 = Haneda Airport, 4 = Tokyo-Bay Birds Park, 5 = Atsugi-city, Kanagawa Prefecture, 6 = Tanuma-cho, Tochigi Prefecture.

creasing order by rock pigeon muscle (35 ng/g) and silky chicken liver (32 ng/g) (Table 2). Among non-*ortho* dioxin-like PCBs, IUPAC 77 was the prevalent congener in silky chicken and rock pigeon. Concentrations of IUPAC 126 were slightly higher in common pheasant than IUPAC 77 (Figure 3a). Mono-*ortho* PCBs congeners 105 and 118 were abundant in common pheasant and silky chicken. IUPAC 189 was the most abundant congener in rock pigeon (Figure 3b). In all the three species of this group, non-*ortho* dioxin-like PCBs contributed 0.8–3.1% of the total dioxin-like PCB concentrations (Table 2).

Piscivores. Among piscivores, short-tailed shearwater contained the lowest concentrations of 33 pg/g PCDD/DFs followed by spot-billed duck (n = 2; mean 1,800; range 1,100–2,500 pg/g), whimbrel (2,200 pg/g), cattle egret (2,700 pg/g), great egret (4,900 pg/g), and gray heron (n = 2; mean 11,000; range 5,500–16,000 pg/g) (Table 2). Relatively high concentrations of PCDDs than PCDFs were found in gray heron, spot-billed duck, and cattle egret (Figure 1b). On the other hand, one individual spot-billed duck, whimbrel, short-tailed shearwater, and great egret had slightly higher PCDF concentrations than PCDDs. Accumulation profile of congeners in gray heron was 1234678-HpCDD > 123678-HxCDD > 12378-PeCDD > 12378-PeCDF. Spot-billed duck accumulated 23478-PeCDF > OCDD > 2378-TCDD > 12378-PeCDD at high levels (Table 2 and Figure 2). Whimbrel contained 123789-HxCDF, 1234678-HpCDF, 23478-PeCDF, and OCDD at great concentrations. Short-tailed shearwater contained OCDD > 23478-PeCDF > 12378-PeCDD > 1234678-HpCDD. Both the egret species showed uniform congener profiles of 23478-PeCDF > 12378-PeCDD > 123678-HxCDD. Notably, 123478-,123678-, and 123789-chlorinated HxCDFs accumulated at low levels in these species.

Six species of piscivorous birds analyzed in this study accumulated greater concentrations of dioxin-like PCBs than the granivores (range: 61–12,000 ng/g) (Table 2). Great egret accumulated higher levels than the other species. Similar to that observed for PCDD/DFs, short-tailed shearwater accumulated the lowest concentrations of dioxin-like PCBs. Elevated concentrations of non-*ortho* PCBs were found in gray heron (mean 210, range 38–380 ng/g). IUPAC 77 was the most abundant in gray heron, one individual spot-billed duck, and whimbrel followed in order by 126 > 81 > 169. IUPAC 126 was predominant in one individual spot-billed duck, short-tailed shearwater, cattle egret, and great egret (Figure 3a). Mono-*ortho* PCBs were 3–280 times higher than those of non-*ortho* PCBs. Among mono-*ortho* PCBs, congeners 105, 118, and 156 were the most predominant (Figure 3b).

Table 2. Concentrations of PCDDs, PCDFs (pg/g fat weight), and dioxin-like PCBs (ng/g fat wt.) in the liver of granivore and piscivorous bird species collected from Japan

	Granivores			Piscivores							
Homologs	SC	CP	RP	GH(A)	GH(J)[b]	SBD(1)	SBD(2)	WB	STS	CE	GE
Fat (%)	8.7	2.9	1.0	5.0	3.3	2.3	3.0	8.4	4.7	9.5	4.2
PCDDs[a]											
2378-TCDD	1.2	21	13	91	91	110	44	8.9	1.3	120	240
12378-PeCDD	3.5	45	46	860	1,400	400	290	30	1.8	750	1,200
123478-HxCDD	0.9	7.6	19	310	610	110	160	27	0.9	94	220
123678-HxCDD	2.7	15	37	1,100	1,200	170	260	42	2.9	310	570
123789-HxCDD	0.1	0.9	1.8	29	46	7.3	9.1	3.6	0.3	7.1	8.3
1234678-HpCDD	5.0	14	33	790	2,100	61	210	150	1.8	63	69
OcCDD	41	57	360	1,200	9,400	220	610	220	6.0	150	86
PCDFs[a]											
2378-TCDF	1.5	99	< 0.1	10	8.4	560	240	7.1	1.7	6.4	6.9
12378-PeCDF	3.5	45	< 0.1	19	18	560	120	8.3	0.4	< 0.1	< 0.1
23478-PeCDF	5.0	110	94	420	400	720	410	230	8.0	840	1800
123478-HxCDF	2.4	14	17	91	220	190	100	120	2.8	80	150
123678-HxCDF	2.7	17	< 0.1	160	130	200	62	170	1.0	84	150
234678-HxCDF	4.8	21	< 0.1	210	96	200	69	850	0.9	100	200
123789-HxCDF	< 0.1	1.8	< 0.1	5.4	7.4	15	3.7	2.6	0.9	4.7	7.5
1234678-HpCDF	3.1	11	17	71	150	40	26	250	0.9	24	54
1234789-HpCDF	0.5	2.6	< 0.1	17	43	9.2	9.0	48	0.3	17	33
OcCDF	1.4	5.7	18	57	41	23	12	49	0.6	11	72
PCDDs	55	160	510	4,400	15,000	1,100	1,600	480	15	1,500	2,400
PCDFs	25	330	150	1,100	1,100	2,500	1,100	1,700	18	1,200	2,500
Sum of PCDDs/DFs	80	480	660	5,500	16,000	3,600	2,700	2,200	33	2,700	4,900
PCDD/DF-TEQ (pg/g)	13	290	160	1,500	2,000	1,900	1,000	400	18	1,800	3,500
Non-*ortho* PCBs[a]											
344'5-TCB (81)	0.01	0.2	0.02	52	4.3	2.8	2.6	0.3	0.4	0.3	5.5
33'44'-TCB (77)	0.5	1.0	0.2	220	22	21	2.6	1.6	0.8	3.0	4.9
33'44'5-PCB (126)	0.1	1.1	0.03	99	10	1.7	9.2	0.4	3.7	25	24
33'44'55'-HxCB (169)	0.04	0.3	0.1	3.6	1.7	0.5	1.1	0.1	0.5	11	9.1
Mono-*ortho* PCBs[a]											
233'44'-PCB (105)	0.3	16	1.4	460	25	290	170	85	4.5	610	2,200
2344'5-PCB (114)	< 0.1	0.3	1.6	11	0.05	14	4.1	3.3	19	77	160
23'44'5-PCB (118)	1.1	58	16	47	72	560	290	230	28	2,000	4,100
2'344'5-PCB (123)	0.0	0.3	0.2	0.3	0.1	3.9	1.6	3.0	< 0.1	12	160
233'44'5-HxCB (156)	0.1	2.0	11	72	8.5	73	43	21	2.0	470	1,800
233'44'5'-HxCB (157)	< 0.01	1.9	2.4	19	2.3	17	11	5.0	0.5	110	450
23'44'55'-HxCB (167)	< 0.01	< 0.01	1.5	31	4.8	30	22	11	1.5	290	3,000
233'44'55'-HpCB (189)	29	2.1	1.0	6.6	1.7	4.8	4.6	0.8	0.1	66	88
Non-*ortho* PCBs	0.7	2.6	0.3	380	38	26	16	2.3	5.4	39	44
Mono-*ortho* PCBs	31	80	35	650	110	990	550	360	56	3,600	12,000
Sum of dioxin-like PCBs	32	83	35	1,000	150	1,000	570	360	61	3,600	12,000
PCBs-TEQ (ng/g)	0.04	0.2	0.02	26	2.5	1.5	1.3	0.2	0.5	2.8	3.2
Total TEQ (pg/g)[c]	53	480	180	28,000	4,500	3,400	2,300	600	520	4,600	6,700

[a] Figures rounded.
[b] Juvenile.
[c] Total of PCDD/DFs and dioxin-like PCBs on pg/g fat weight.
SC, CP, RP, GH, SPD, WB, STS, CE, and GE, respectively: silky chicken, common pheasant, rock pigeon, gray heron, spot-billed duck, whimbrel, short-tailed shearwater, cattle egret, and great egret.

Omnivores. Concentrations of PCDD/DFs ranged from 2,300 to 8,000 pg/g fat weight in three species of omnivores analyzed. Large-billed crow contained the lowest concentration, and seagulls contained the highest PCDD/DF concentrations (Table 3). Concentrations of PCDDs were greater than PCDFs in large-billed crow, while black-headed gulls contained greater concentrations of PCDFs than PCDDs (Figure 1c). Notably, PCDDs and PCDFs accumulated at similar levels in seagull. Major PCDD/DF congeners in large-billed crow were OCDD, 1234678-HpCDD, 23478-PeCDF, and 1234678-HpCDF and in black-headed gulls were 123789-HxCDF, 123678-HxCDF, 12378-PeCDD, and 23478-PeCDF. Seagulls contained 23478-PeCDF, 123678-HxCDD, 12378-PeCDD, and 123478-HxCDF as abundant congeners.

Concentrations of dioxin-like PCBs in the three species of omnivores are shown in Table 3. Highest concentrations of

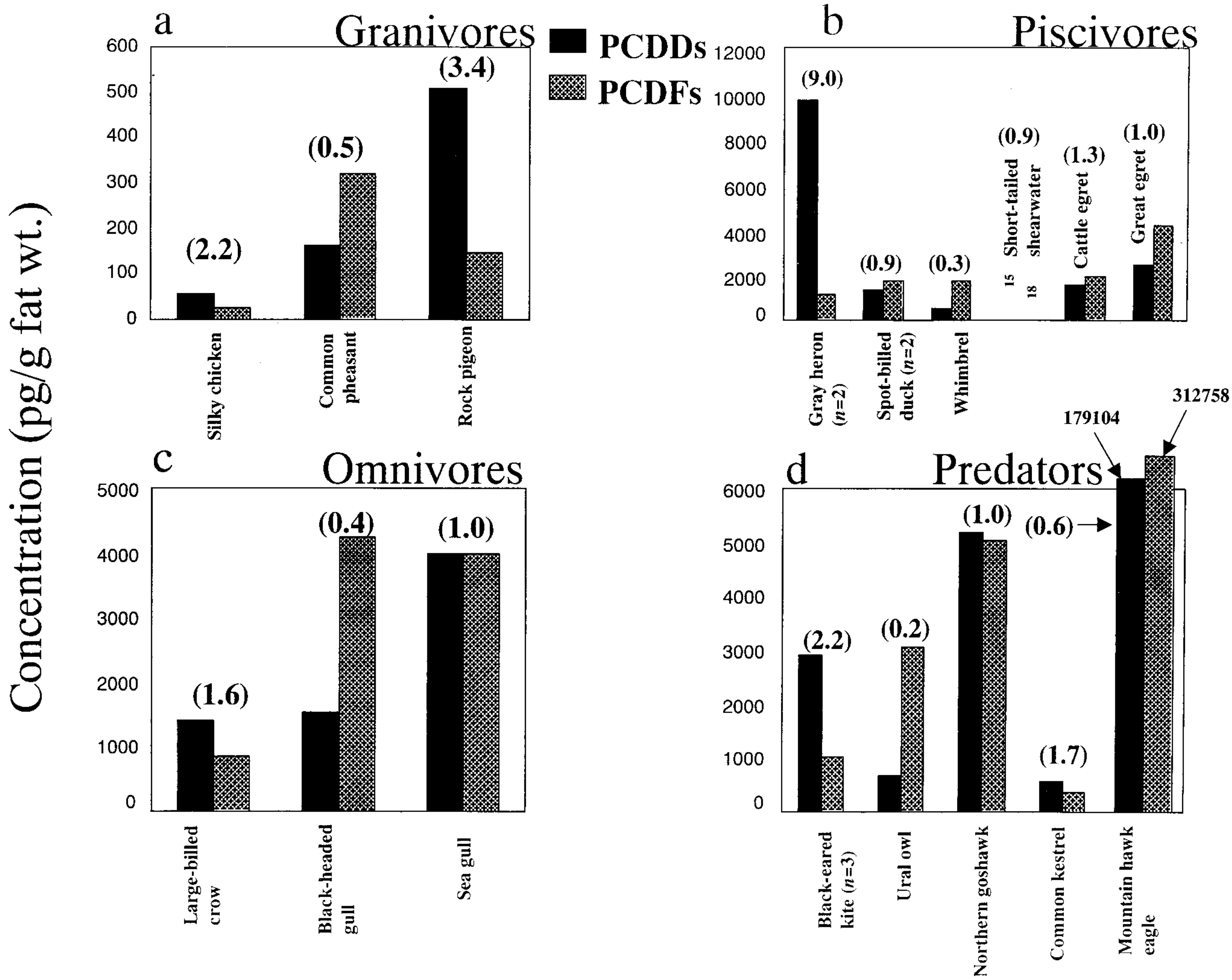

Fig. 1. Concentrations of PCDD and PCDF and ratio (the values in the parentheses indicates ratio [PCDDs to PCDFs]) in liver of birds from Japan

dioxin-like PCBs were observed in sea gull (67,000 ng/g). Similar to PCDD/DFs, black-headed gull accumulated approximately 3.5 times lower concentrations of dioxin-like PCBs (19,000 ng/g) than sea gulls (67,000 ng/g). In omnivores, concentrations of mono-*ortho* PCBs were 50–500 times higher than those of non-*ortho* PCBs. The non-*ortho* PCB pattern in large-billed crow was 169 > 126 > 77 > 81 (Figure 3c). In black-headed gull, the profile was 126 > 77 > 169 > 81, and in seagull it was 126 > 169 > 77 > 81. IUPAC 118 was the most prevalent mono-*ortho* congener, followed by 105 and 156 (Figure 3d) in this group of birds.

Predators. Five species of predators analyzed in this study (Table 3) showed elevated concentrations of dioxins and furans. Particularly, mountain hawk eagle contained the highest concentration of 490,000 pg/g, fat weight, followed by northern goshawk (10,000 pg/g). Common kestrel contained the lowest concentrations of PCDD/DFs (940 pg/g) followed by ural owl (3,600 pg/g) and black-eared kites (range 480–8,700 pg/g) Concentrations of PCDDs were greater than PCDFs in one individual black-eared kite, northern goshawk, and common kestrel. On the other hand, PCDF concentrations were greater than PCDDs in two individual black-eared kite, ural owl, and mountain hawk eagle (Figure 1d). In black-eared kites, OCDD and 23478-PeCDF were the predominant congeners followed by 12378-PeCDD, 123678-HxCDD. In ural owl, 23478-PeCDF, 123678-HxCDF, 123678-HxCDD, and 12378-PeCDD were the abundant congeners. Northern goshawk accumulated 23478-PeCDF, 123678-HxCDD, 12378-PeCDD, and 1234678-HpCDD at great concentrations. Mountain hawk, which had the highest concentration of PCDD/DFs contained the following congeners in livers; 23478-PeCDF > 123678-HxCDD > 123478-HxCDF > 123789-HxCDF. In addition, 12378-PeCDD/123678-HxCDF > 123478-HxCDD > 1234678-HpCDD > OCDD were also found in mountain hawk (Table 3 and Figure 2).

Similar to that observed for PCDD/DFs, concentrations of dioxin-like PCBs (55,000 ng/g) were also high in mountain hawk eagle (Table 3). Concentrations of dioxin-like PCBs in other predatory species were similar to or less than those found in piscivorous and omnivorous birds. Non-*ortho* PCBs were 3–1,600 times lower than those of mono-*ortho* PCBs. IUPAC

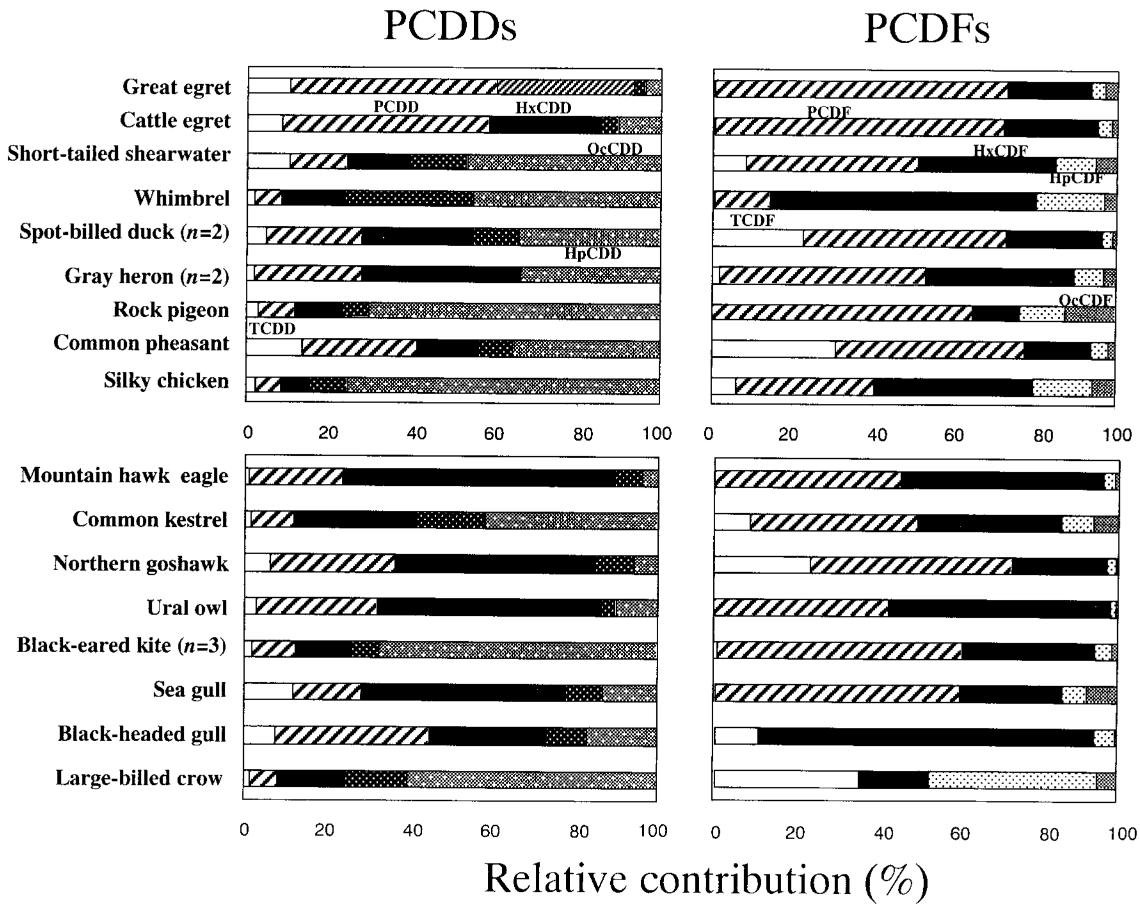

Fig. 2. Mean composition (%) of PCDD and PCDF homologs in liver of birds from Japan

126 predominated in black-eared kite, northern goshawk, and common kestrel while IUPAC 77 predominated in ural owl (Figure 3d). The mountain hawk eagle contained similar concentrations of IUPAC 126 and 169. Furthermore, among mono-*ortho* PCBs, black-eared kite, ural owl, and common kestrel contained 118 > 105 > 157. Northern goshawk showed 105 > 156 > 167 while mountain hawk eagles showed 118 > 156 > 189 > 105 > 157 = 167 profiles (Figure 3d).

TCDD Toxic Equivalents

TEQs are a means of expressing the toxicity of a complex mixture of different PCDD/Fs and PCBs in terms of an equivalent quantity of 2,3,7,8-TCDD, which is considered to be the most potent member of this family of chemicals (Safe 1990; Giesy and Kannan 1998). Each of the 17 2,3,7,8-substituted PCDD/DF congeners and non- and mono-*ortho* PCBs have all been assigned a TEF based on their toxicity relative to 2,3,7,8-TCDD, which is assigned a TEF of 1. TEQ concentrations are obtained by multiplying the concentration of each of the toxic PCDD/Fs and PCBs by its assigned TEF. Although, several TEF schemes have been proposed, the WHO-TEFs for birds developed by Van den Berg *et al.* (1998) is applied for PCBs and PCDD/DFs.

Concentrations of TEQs in birds analyzed in this study are shown in Tables 2 and 3. Among granivores, the mean TEQs of PCDD/DFs in the livers of common pheasant was 290 pgTEQ/g, fat weight, followed by rock pigeon muscle 160 pgTEQ/g and silky chicken liver (13 pgTEQ/g). 23478-PeCDF, 12378-PeCDD, 2378-TCDF, and 2378-TCDD were the major contributors of TEQs in granivores. TEQs of dioxin-like PCBs in granivores were 20–200 pg/g, fat weight. Among piscivores, mean TEQ concentration in gray heron was 17,000 pgTEQ/g, whereas in short-tailed shearwater it was 520 pgTEQ/g. PCDD/DF congeners 12378-PeCDD, 23478-PeCDF, 2378-TCDD, and 2378-TCDF (only in spot-billed duck) primarily contributed to the TEQs. Among dioxin-like PCBs, TEQs ranged from 200–28,000 pg/g fat weight with a gray heron showing the highest and short-tailed shearwater showing the lowest (Table 2). IUPACs 77 and 126 were among the congeners that contributed to TEQs in both granivorous and piscivorous groups.

TEQ concentrations of PCDD/DF in omnivores are given in Table 3. Seagulls showed the highest TEQs (3,700 pgTEQ/g), followed by black-headed gull (1,500 pgTEQ/g) and large-billed crow (360 pgTEQ/g). 23478-PeCDF, 12378-PeCDD, 2378-TCDD, 123678-HxCDF, 123789-HxCDF, and 123478-HxCDF were the major contributors to PCDD/DF-TEQs. Among omnivores, PCB-TEQ was higher (67,000 pgTEQ/g) in

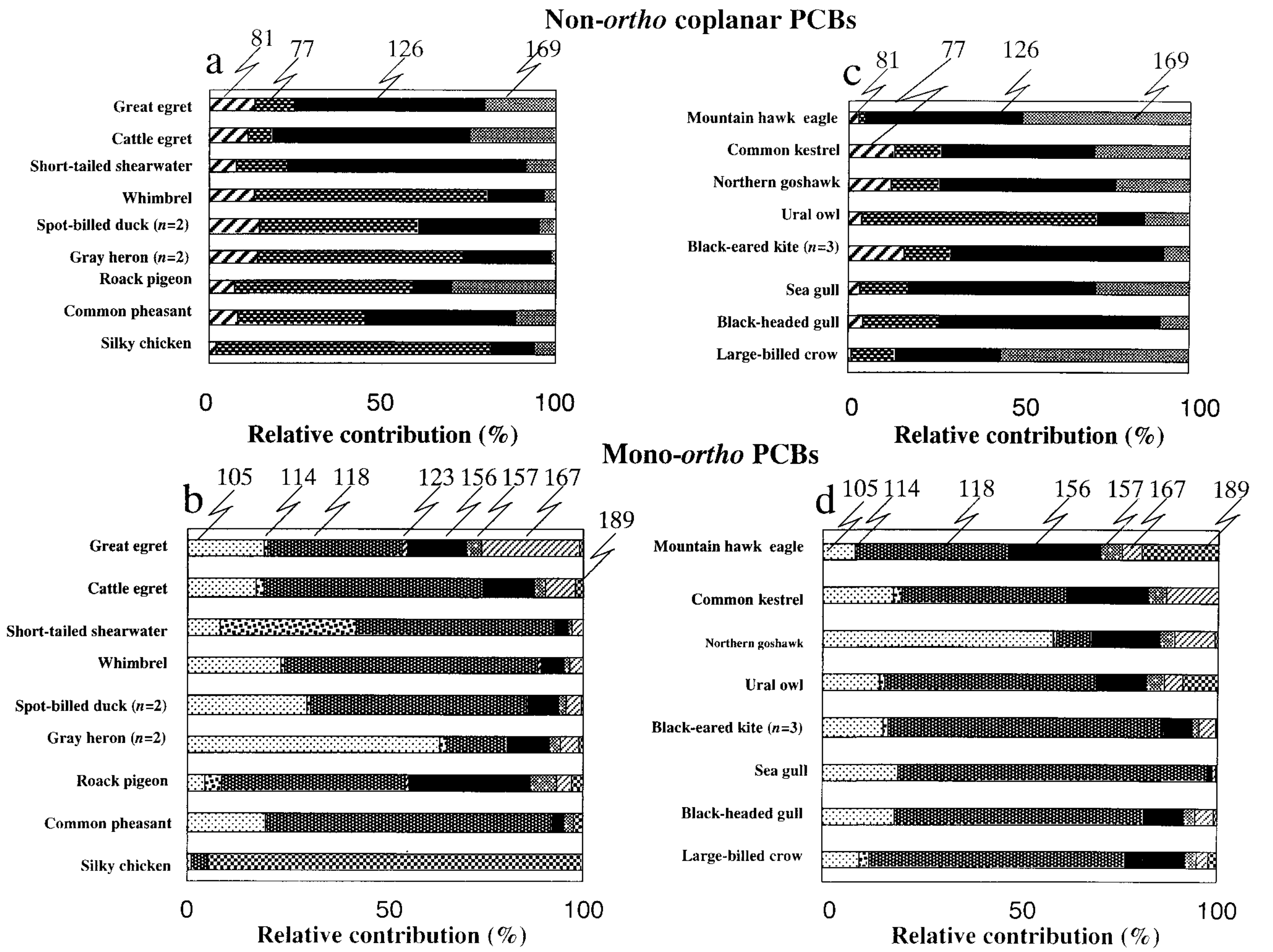

Fig. 3. Mean composition (%) of dioxin-like non- and mono-*ortho* PCB congeners in liver of birds from Japan

seagull (Table 3). Considerably, IUPAC 126 and 105 and 156 greatly contributed to the toxicity.

PCDD/DF-TEQ concentration of mountain hawk eagle was 20,000 pgTEQ/g (Table 3). The major contributors of PCDD/DF-TEQs in predatory birds were 23478-PeCDF > 12378-PeCDD > 2378-TCDD. However, in mountain hawk eagle TEQs were primarily contributed by the following congeners: 23478-PeCDF > 12378-PeCDD > 123478-HxCDF > 123789-HxCDF > 123678-HxCDF. Dioxin-like PCB-TEQs were also the highest in mountain hawk eagle (430,000 pgTEQ/g). Particularly, IUPACs, 126, 81, and 156 greatly contributed to TEQs.

Toxicity Contribution

Overall, PCDFs contributed most to the TEQs in grain-eating species, except silky chicken in which major TEQ contributors were non-*ortho* PCBs (Figure 4). Non-*ortho* PCBs contributed to major portion of TEQ concentrations in gray heron, spot-billed duck, short-tailed shearwater, cattle egret, and great egret. PCDF contributed greater TEQs in whimbrel than the other target analytes. Among omnivores, non-*ortho* PCBs contributed greater TEQs in gull species. PCDF contributed to TEQs in large-billed crow. Except black-eared kite and mountain hawk eagle, all the other predators had greater TEQs from PCDF homologs. Despite considerable accumulation of PCDDs, only rock pigeon, large-billed crow, great egret, and northern goshawk showed considerable TEQ contribution from PCDDs. Predominance of high PCDF toxicity might have considerable impact in Japanese birds that is somewhat different from that observed in the United States and Canadian birds (Elliott *et al.* 1996b, 1996c; Kannan *et al.* 2001). Furthermore, non-*ortho* coplanar PCBs have also contributed to TEQs due to their prevalence in some birds.

Discussion

Contamination Status

Mountain hawk eagle collected at Tanuma-cho, Tochigi Prefecture, contained elevated concentrations of 2,3,7,8-chlorine-substituted PCDDs, PCDFs, and dioxin-like PCBs compared to other predators, omnivores, and granivores. One possible ex-

Table 3. Concentrations of PCDDs, PCDFs (pg/g fat weight), and dioxin-like PCBs (ng/g fat weight) in the liver of omnivore and predator bird species collected from Japan

	Omnivores			Predators						
Homologs	CRW	BHG	SG	BEK(1)	BEK(2)	BEK(3)	UO	NGS	CK	MH
Fat (%)	4.2	4.0	3.3	11.1	4.2	5.0	2.8	5.9	5.1	8.8
PCDDs[a]										
2378-TCDD	18	110	470	48	22	55	20	310	7.0	1,700
12378-PeCDD	96	570	670	310	61	280	190	1,600	61	40,000
123478-HxCDD	110	67	320	79	13	120	45	590	83	35,000
123678-HxCDD	120	350	1,600	580	33	310	300	1,900	90	83,000
123789-HxCDD	3.5	8.0	21	3.9	1.5	8.3	2.1	19	1.4	340
1234678-HpCDD	210	150	370	290	16	170	23	490	96	11,000
OcCDD	850	260	520	6,000	30	190	63	300	250	7,000
PCDFs[a]										
2378-TCDF	2.2	17	13	2.6	4.6	15	3.9	1,200	31	86
12378-PeCDF	96	1.1	< 0.1	310	3.9	< 0.1	190	320	24	< 0.1
23478-PeCDF	210	460	2,400	550	160	800	1,100	2,200	120	140,000
123478-HxCDF	150	140	640	120	44	130	450	470	55	61,000
123678-HxCDF	< 0.1	1,600	230	120	34	110	990	280	29	40,000
234678-HxCDF	< 0.1	1,700	150	170	33	200	240	410	35	56,000
123789-HxCDF	1.2	6.7	1.5	1.8	0.7	0.8	5.8	2.0	3.3	11
1234678-HpCDF	330	160	200	59	14	42	28	96	17	5,700
1234789-HpCDF	25	61	38	10	3.0	7.7	12	28	11	4,200
OcCDF	41	23	300	43	1.3	6.2	10	28	20	2,200
PCDDs	1,400	1,500	4,000	7,300	180	1,100	640	5,200	590	180,000
PCDFs	860	4,200	4,000	1,400	300	1,300	3,000	5,000	350	310,000
Total PCDDs/DFs	2,300	5,700	8,000	8,700	480	2,400	3,600	10,000	940	490,000
PCDD/DF-TEQ (pg/g)	360	1,500	3,700	990	260	1,200	1,500	5,500	230	20,000
Non-*ortho* PCBs[a]										
344'5-TCB (81)	0.03	30	40	0.8	3.7	6.0	0.9	0.2	0.3	240
33'44'-TCB (77)	0.5	150	160	6.9	1.2	3.7	15	0.2	0.4	140
33'44'5-PCB (126)	1.2	430	650	5.3	13	23	3.1	0.7	1.2	3,900
33'44'55'-HxCB (169)	2.1	56	320	3.8	1.8	1.0	2.9	0.3	0.7	4,100
Mono-*ortho* PCBs[a]										
233'44'-PCB (105)	170	3,300	12,000	214	70	150	6.0	1,500	5.3	3,700
2344'5-PCB (114)	46	21	99	12	11	15	0.5	24	0.6	190
23'44'5-PCB (118)	1,200	11,000	52,000	800	210	890	23	220	12	18,000
2'344'5-PCB (123)	9.5	8.8	12	7.3	1.8	1.2	0.2	0.3	< 0.1	15
233'44'5-HxCB (156)	270	1,900	750	97	29	79	5.2	420	6.2	11,000
233'44'5'-HxCB (157)	56	500	180	23	7.0	19	2.0	95	1.3	2,600
23'44'55'-HxCB (167)	57	880	490	47	16	49	1.9	250	3.8	2,300
233'44'55'-HpCB (189)	38	180	260	18	2.5	0.2	3.8	21	< 0.1	9,000
Non-*ortho* PCBs	3.9	670	1,200	17	20	34	22	1.4	2.6	8,400
Mono-*ortho* PCBs	1,800	18,000	66,000	1,200	680	2,300	42	2,500	29	47,000
Sum of dioxin-like PCBs	1,800	19,000	67,000	1,200	700	2,400	64	2,500	32	55,000
PCBs-TEQ (ng/g)	0.2	54	79	1.2	1.8	3.1	1.2	0.3	0.2	430
Total-TEQ (pg/g)[b]	560	56,000	83,000	2,200	2,100	4,300	2,700	5,800	430	450,000

[a] The values are rounded.
[b] Total TEQs of PCDD/DFs and dioxin-like PCBs on pg/g fat weight.
CRW, BHG, SG, BEK, UO, NGS, CK, and MH, respectively: large-billed crow, black-headed gull, seagull, black-eared kite, ural owl, northern goshawk, common kestrel, and mountain hawk eagle.

planation for great concentrations in this species may be specific feeding habit rather than any specific sources of exposure. Similar to mountain hawk eagles, omnivorous species such as black-headed gull and seagull exhibited the highest concentrations of all the contaminants analyzed. The scavenging nature of gulls near the areas of high industrial activity (Hoyo *et al.* 1996) is an explanation for great concentrations of PCDD/DFs in gulls. Besides, gulls eat fish predominantly compared to crows, which eat domestic waste and garbage. Thus the relative concentrations of PCDDs and PCDFs in birds vary depending on the source of exposure, which varies as a function of a number of factors including species, ecology, age, sex, and feeding habit. Iseki *et al.* (2000) reported high concentrations of PCDD/DFs in cormorants collected in and around Tokyo Bay of Japan.

Granivores accumulated the lowest concentrations of PCDD/DFs and PCBs. A recent study has shown that chicken collected from Belgium contained 3–119 pg/g fat weight PCDD/Fs (Covaci *et al.* 2000) and 11.3–248 pg/g fat weight dioxin-like PCBs. Much lower levels of PCDD/DFs (11 pg/g

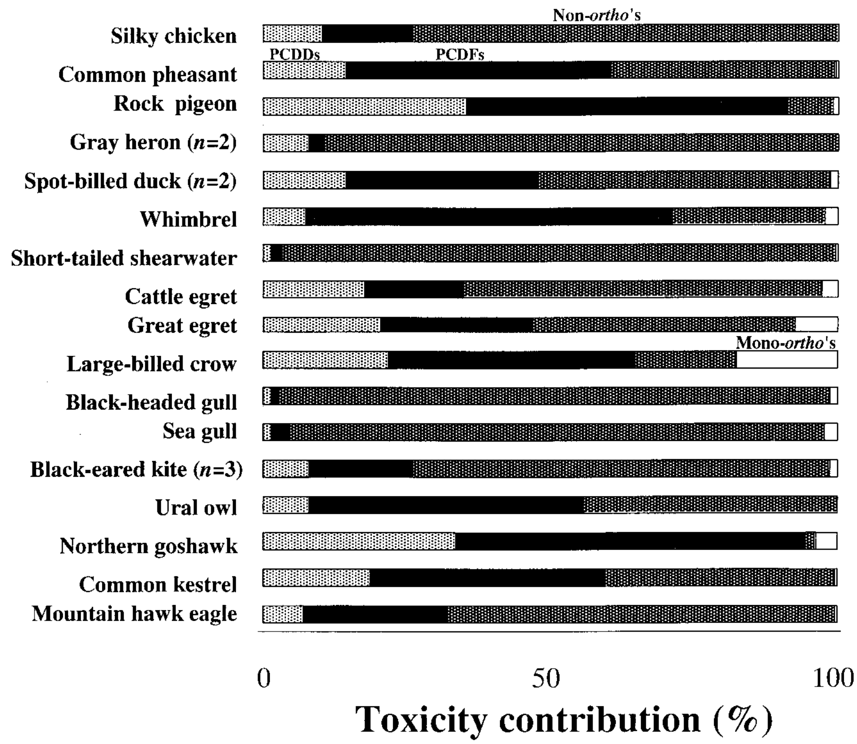

Fig. 4. Composition of relative contributions of TCDD-like toxic equivalents by PCDDs, PCDFs, and non- and mono-*ortho* PCB congeners in birds of Japan

fat) and dioxin-like PCBs (130 pg/g fat) were found in chicken collected from India (Senthilkumar *et al.* 2001a). Relatively low exposures to pesticides and PCBs by granivorous birds has been shown earlier (Tanabe *et al.* 1998; Senthilkumar *et al.* 2001b). Among granivores, slightly higher concentrations in common pheasant may be due to its diet, which comprises worms and insects.

Among piscivores, gray herons accumulated greater levels of dioxins. However, concentrations of dioxin-like PCBs were higher in great egret. This difference may be due to the differences in metabolic capacity and elimination of chemicals between the two species. Furthermore, differences in the sampling locations may have an impact on the observed variation. Species like spot-billed duck and egrets feed on sediment-dwelling organisms and accumulate considerable levels of PCDD/DFs and PCBs than short-tailed shearwater, which feed at oceans. Open ocean species accumulated less concentrations of contaminants than continental or coastal species (Tanabe *et al.* 1998). Lesser-crested tern and white-cheeked tern breed in the Middle East and Asia and migrate to India during winter by different routes (Tanabe *et al.* 1998). Lesser-crested tern, that migrate through open ocean accumulated lesser concentration of contaminants than white-cheeked tern, which accumulated five times higher concentrations due to their inland migratory route. PCDD/DF concentrations in piscivorous and omnivorous birds from Korea varied from 47–510 pg/g fat weight (Choi *et al.* 1998), which is lower than that found in birds analyzed in this study. This is suggestive of elevated contamination by PCDD/DFs in birds in Japan. Nevertheless, black-tailed gull collected from Hokkaido, Japan, contained total PCB concentrations of 1,900–7,100 ng/g fat weight and PCDD/DF concentrations of 32–140 pg/g fat weight (Choi *et al.* 2000).

The difference in lipid content in black-eared kite livers is one of the main reasons for variations in concentrations between and also within species. In addition, feeding rates between juveniles and adults explain the reason for the differences in PCDD/DF and PCB concentrations in adult and juvenile gray herons. Field observations showed that juveniles feed nearly 44 times/day than the adults, which feed nearly 11 times a day (Guruge *et al.* 2000). Both mountain hawk eagle and northern goshawks accumulated greater levels of PCDD/DFs and PCBs than the other predators. The food habit would probably explain greater accumulation in these hawk species. Eventually, ural owls analyzed in this study were females, thus, comparison of the concentrations with those in males of other predatory birds is notwithstanding.

Homolog Profiles

PCDDs were predominant in silky chicken, rock pigeon, gray heron (mean of two individuals), cattle egret, large-billed crow, black-eared kite (mean of three individuals), northern goshawk, and common kestrel. There are two possible explanations that could explain this fact: (1) exposure to greater concentrations of PCDDs than PCDFs, and (2) metabolism/elimination of PCDF congeners. PCDF congeners were prevalent in common pheasant, spot-billed duck (mean of two individuals), whimbrel, short-tailed shearwater, great egret, black-headed gull, ural owl, and mountain hawk eagle. The high concentrations of PCDFs, compared to PCDDs, present in these species would suggest the lack of elimination or metabolic capacity of these homologs.

PCDD and PCDF concentrations and profiles in spot-billed duck, great egret, seagull, and northern goshawk were similar. Greater uniformity in the concentrations in these species may be explained by their exposure from over a wider geographical area that is less influenced by local sources. Greater concentrations of PCDFs relative to PCDDs have been found in sources originated from PCBs (Wakimoto *et al.* 1988; Giesy and Kannan 1998). Ratios of PCDDs to PCDFs was less than 1 in some species of birds (Figure 1a–d). These results again suggested that some species have low metabolic and elimination capacity of these homologs. The PCDD to PCDF ratios greater than 1 suggest that these birds are exposed PCDDs through Pentachlorophenol and chloronitrophen. Greater contamination by OCDD and OCDF could also be explained by incineration sources or sewage sludge–related sources (Loganathan *et al.* 1995).

Considering the profiles of non-*ortho* PCBs, IUPAC 126 was prevalent in 50% of the bird species analyzed in this study. IUPAC 77 was the second most prevalent non-*ortho* PCB congener found in birds (Figure 3a, c). Similarly, mono-*ortho* PCB congeners 118, 105, and 156 were abundant in all the bird species. Ormerod and Tyler (1992) reported the differences in PCB congener patterns in Eurasian dipper from several regions. Isomer 153 was the most abundant in one region, and congener 118 was prevalent in the another. Falandysz *et al.* (1994) showed that congeners 118, 153, and 180 were the most abundant in the muscle of white-tailed eagles and that there were differences between adults and juveniles of the same species in the distribution of these congeners, suggesting possible differences in capabilities to depurate PCBs at different ages. The differences in isomer profiles of PCBs among bird species have been associated with differences in diet. For example, the accumulation of PCB congeners 138, 153, and 180 was different among herons from several locations in the United Kingdom and the difference was associated with diet of herons rather than metabolism (Boumphrey *et al.* 1993).

Global Comparison

The observed mean PCDD and PCDF concentrations in birds analyzed in this study were higher than those in the tissues of birds such as feral pigeon of Japan (Morita *et al.* 1987), fish-eating birds of The Netherlands (Van den Berg *et al.* 1987), albatross of Midway Atoll, US (Jones *et al.* 1996), white-tailed sea eagles of the Baltic Sea (Koistinen *et al.* 1997), aquatic birds of Switzerland (Zimmermann *et al.* 1997), bald eagles of Canada (Elliott *et al.* 1996b; Elliott and Norstrom 1998), omnivore and migratory birds of Korea (Choi *et al.* 1998), common cormorants of Japan (Iseki *et al.* 2000), predator birds of India (Senthilkumar *et al.* 2001a), and aquatic birds of China (Wu *et al.* 2000) (Table 4).

Table 4. Comparison of PCDDs, PCDFs, and dioxin-like PCBs in bird tissues from other parts of the world

Country or Area	Bird	Tissue	2,3,7,8-PCDD/DFs* (pg/g)	Dioxin-like PCBs (pg/g)	Reference
Baltic Sea	White-tailed eagle	Muscle	265	3,490–30,310	Koistinen *et al.* (1997)
Canada	Bald eagle	Liver	44–6,550	98–7898[c]	Elliott *et al.* (1996b)
Canada	Bald eagle	Plasma	1.08–9.19	10.2–65	Elliott and Norstrom (1998)
China	Piscivorous birds	Liver	1694	NA	Wu *et al.* (2000)
India	Spotted owlet	Liver	2,646 (2,321–3,288)	62,967 (34,083–109,274)[d]	Senthil Kumar *et al.* (2001a)
Japan	Feral pigeon	Liver	4,600	NA	Morita *et al.* (1987)
Japan	Common cormorant	Liver	NA	11,423[c]	Guruge *et al.* (1997)
Japan	Common cormorant	Liver	41,000 (5,800–70,000)	67,000 (6,600–300,000)[a]	Iseki *et al.* (2000)
Japan	Common cormorant	Liver	NA	18,000–58,000[b]	Guruge *et al.* (2000)
Japan	Granivores	Liver	80–660	32–83[a]	Present investigation
Japan	Piscivores	Liver	33–16,000	61–12,000[a]	Present investigation
Japan	Omnivores	Liver	2,300–8,000	1,800–67,000[a]	Present investigation
Japan	Predators	Liver	480–490,000	32–55,000[a]	Present investigation
Korea	Residents/migrants (n = 44)	Fat	47.1–509	6,700–27,000[a]	Choi *et al.* (1998)
Midway Atoll, USA	Laysan albatross	Liver	40.3–57.2[d]	63–89[c]	Jones *et al.* (1996)
Midway Atoll, USA	Albatross	Liver	NA	3,480[a]	Klasson-Wehler *et al.* (1998)
Netherlands	Cormorants	Liver	55–9,741	NA	Van den Berg *et al.* (1987)
Netherlands	Grebe	Liver	89	NA	Van den Berg *et al.* (1987)
Netherlands	Heron	Liver	455–957	NA	Van den Berg *et al.* (1987)
Poland	White-tailed eagle	Muscle	NA	66,000–480,000[c]	Falandysz *et al.* (1994)
Switzerland	Aquatic birds (n = 32)	Muscle	NA	1,493–31,759[a]	Zimmermann *et al.* (1997)
USA	Peregrine falcons	Immature	133	NA	Jarman *et al.* (1993)

[a] ng/g fat weight.
[b] pg/g wet weight.
[c] ng/g wet weight.
[d] pg/g fat weight.
[e] Whole-body homogenates,
NA = not available.
* Sum of 2,3,7,8-PCDD/DFs.

The concentrations of dioxin-like PCBs were also higher in the present study when compared with those reported for birds from India (Senthilkumar *et al.* 2001a), the United States (Jones *et al.* 1996; Klasson-Wehler *et al.* 1998), Japan (Guruge and Tanabe 1997), the Baltic Sea (Koistinen *et al.* 1997), Canada (Elliott *et al.* 1996b; Elliott and Norstrom 1998), China (Wu *et al.* 2000), Korea (Choi *et al.* 1998), and Switzerland (Zimmermann *et al.* 1997) but relatively similar to that found in Poland (Falandysz *et al.* 1994) and Japan (Iseki *et al.* 2000). However the values were lower than the cormorants of Odaiba Island, Japan (Guruge *et al.* 2000) (Table 4).

Toxic Potential

The total TEQs in birds analyzed in this study were greater than those reported in black-headed and black-tailed gulls from Japan (Yamashita *et al.* 1992), double-crested cormorants (0.35–1.3 ng/g wet weight) and Caspian tern (1.0–2.4 ng/g wet weight) from the Great Lakes (Yamashita *et al.* 1993), double-crested cormorants and herring gulls (4.12–26.8 pg/g wet weight) in the Great Lakes (Kannan *et al.* 2001), common cormorants of Japan (Iseki *et al.* 2000), and aquatic birds of Korea (Choi *et al.* 2000).

Toxic threshold for avian species has been reported elsewhere (Giesy *et al.* 1994; Elliott *et al.* 1996c). The lowest observable adverse effect level of 3.5 ppm PCBs has been estimated for egg concentrations in free-ranging birds (Giesy *et al.* 1994). The no-observed-effect-level of 100 pg/g TEQs and low-observed-effect-level of 210 pg/g TEQs on a wet-weight basis are suggested for bald eagle eggs (Elliott *et al.* 1996c). However, both observations were not comparable with the present study because of the different sample matrix. More recently, Bosveld *et al.* (2000) have reported 25 ng TEQ/g in liver on a lipid wt basis as lowest-observed-effect level for induction of CYP1A and 50% reduction of plasma thyroxine levels in common tern chicks. Thus our estimation of TEQs in liver lipid found to be somewhat suitable to compare with the tern study. Based on this comparison, all the birds analyzed in this study contained less than 25 ngTEQ/g fat in the liver.

Conclusions

In general, concentrations, and homolog/congener profiles of PCDD, PCDF, and dioxin-like non- and mono-*ortho* PCBs were different according to the feeding habit and ecology of birds. Birds with in the same group showed considerable variation in accumulation profiles. The grain-eating and some piscivore species accumulated lesser concentrations of PCDD/DFs and PCBs. Some aquatic, omnivore, and predator hawk species showed higher concentrations of organochlorines. The homolog/congener pattern showed that some birds have limited metabolic capacity to PCDFs and dioxin-like PCBs. 23478-PeCDD/PeCDF, 2378-TCDD/TCDF, and IUPACs 126 and 77 were the major contributors of TEQs in birds. Altogether, this is the first attempt to show contamination status of highly toxic PCDD/DFs and PCBs in a range of species of birds in Japan.

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