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Accumulation of Polychlorinated Dibenzo-*p*-Dioxins, Dibenzofurans, and Dioxin-like PCBs in Black-Tailed Gulls and Eggs

J.-W. Choi,[1,2] M. Matsuda,[2] M. Kawano,[2] N. Iseki,[3] S. Masunaga,[3] T. Wakimoto[2]

[1] National Institute of Environmental Studies, Onogawa 16-2, Tsukuba, Ibaraki 305-0053, Japan
[2] Department of Environment Conservation, Ehime University, Tarumi 3-5-7, Matsuyama 790-8566, Japan
[3] Institute of Environment Science and Technology, Yokohama National University, Tokiwadai 79-7, Hodogaya-ku, Yokohama 240-8501, Japan

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Environmental contamination with polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like compounds such as non-*ortho* PCBs is ubiquitous (Bernes 1998). These planar-structured aromatic halogenated hydrocarbons are spread globally by atmospheric transport and are present in detectable levels even in Arctic regions (Harner et al. 1998). These chemicals have high octanol-water coefficients and accumulate in fish, birds and mammals including humans through the marine and terrestrial food chains. Ah-receptor mediated toxic symptoms, and disruption of endocrine functions are typical toxic effects of these chemicals.

There have been a number of PCDD/F congeners found in various sources, such as stack gas in municipal waste incinerators (MWI), effluents from paper mills, and commercial chemicals like chlorophenols and PCBs. Information on the specific accumulation of these planar-structured compounds in biological samples is useful for investing the source and metabolic properties of the contaminants. Selected numbers of PCDD/F congeners have been found in birds, mammals and humans and specific accumulation of planar PCBs in the biosphere has been reported (Kannan et al. 2000). In Japan, PCDD/Fs and planar PCBs have been identified in air, water, sediments, fish and birds. However, there are few studies of the levels and specific accumulation of PCDD/F congeners in wildlife. The objectives of the present study were to determine the concentrations and specific accumulation of PCDD/Fs and non-*ortho* PCBs in black-tailed gulls and eggs from Rishiri Island, Japan. Correlations among congeners were used to determine the selective accumulation of individual PCDD/F and non-*ortho* PCB congeners in black-tailed gull eggs.

Correspondence to: J.-W. Choi, National Institute of Environmental Studies

MATERIALS AND METHODS

Black-tailed gull (n=10) and eggs (n=10) were obtained from the Rishiri Island near Hokkaido, Japan during June 1998. Egg samples were collected and measured; weight, length, fat contents etc. Samples in polyethylene bags were frozen at –20℃ until analysis. Analytical procedures were followed according to previous paper (Choi et al. 1999) with small modifications. Eggs were freeze-dried prior to extraction. Subcutaneous fat of adult birds and yolk of eggs were homogenized with sodium sulfate and extracted with dichloromethane in a Soxhlet apparatus. The extractable lipid was transferred to hexane and each sample was spiked with 1.0 ng of 15 ^{13}C-labeled PCDDs, PCDFs and 4 ^{13}C-labeled non-*ortho* PCBs purchased from Cambridge Isotope Laboratories. Samples were treated with sulfuric acid and further clean-up procedure was made using silicagel, alumina, silica-mixed carbon column and silica-packed solid cartridge.

Analysis of PCDD/Fs and non-*ortho* PCBs performed on a HRGC-HRMS (HP5890 II - JEOL SX102A) with selected ion monitoring (SIM) using EI mode. PCDD/Fs and non-*ortho* PCB congeners were identified with ion ratios inside the correct tolerance range (±30%) and with retention times of standards. Gas chromatograph equipped with capillary columns CP-Sil (50m×0.25mm i.d., 0.20 μm for TeCDD/Fs to HxCDD/Fs) and DB-5 (30m×0.25mm i.d., 0.25 μm for HpCDD/Fs, OCDD/F and non-*ortho* PCBs) for mass spectrometric detector, respectively, were used. We used the following temperature program for CP-Sil: injector at 270℃, detector at 270℃, initial oven temperature at 100℃, hold for 1 min, heating to 180℃ at 20℃/min, then to 240℃ at 4℃/min, with final 26.5-min hold. For the DB-5, the final temperature and holding time was 270℃ and 2 min, respectively. Helium was used as the carrier gas. Detection limit (DL) for for non-*ortho* PCBs was 0.1-0.8 pg/g, fat weight. DL for PCDD/Fs were 0.2 to 2.0 pg/g, according to congeners. Recoveries of $^{13}C_{12}$-PCDD/Fs and non-*ortho* PCBs were typically 57-114%.

RESULTS AND DISCUSSION

2,3,7,8-substituted PCDD/Fs and non-*ortho* PCBs were detected in all the black-tailed gulls and eggs analyzed. The concentrations of these compounds in adult birds and eggs are presented in Table 1. There were no significant differences in the mean concentrations of PCDD/Fs in black-tailed gulls and eggs, but adult birds had higher concentrations of non-*ortho* PCBs than eggs ($p<0.01$). The geometric mean concentrations of PCDD/Fs were similar to those found in Korean black-tailed gull's eggs (Choi et al., 1999). However, the concentrations of non-*ortho* PCBs were significantly higher than in Korean black-tailed gull's eggs ($p<0.01$). Congener profiles of PCDD/Fs were characterized by a larger proportion of PeCDD/F and HxCDD/F congeners, compared to for HpCDD/Fs and OCDD/F. The proportion of penta and hexachlorinaged congeners were 74.2% and 77.5% in PCDDs and PCDFs in black-tailed gull and eggs, respectively. 12378-PeCDD and 23478-PeCDF were the most dominant congeners of PCDDs and PCDFs in both gulls and eggs (Table 1).

For the non-*ortho* PCB congeners, PCB 126 had the highest concentration, which ranged from 1,985 to 7,990 ng/g fat weight in gull fat tissue and 1,190 to 4,147 ng/g lw in eggs, followed by PCB 77, PCB 169 and PCB81 in adult gulls, but the order of concentrations of PCB 77 and PCB 169 was reversed in eggs. The mean ratio of PCB 77 : PCB 126 was 2.4 : 1 in eggs and 1.03 : 1 in adult gulls. We assumed that the more soluble congener, PCB 77 which accumulated in female fat may have transferred to eggs faster than PCB 169.

From studies of the bioaccumulation of PCDD/Fs and coplanar PCBs in waterfowls, it is known that selective PCDD/F and non-*ortho* PCB congeners such as 2378-TCDD, 12378-PeCDD, 23478-PeCDF, 123678-HeCDD/F, PCB 77 and PCB 126 are more persistent in the livers and lipids of birds and eggs (Jarman et al. 1993). Biomagnification factors (BMFs) of PCDD/Fs in herring gulls were obtained by Braune and Norstrom (1989) who showed that BMFs of 2378-TCDD, 12378-PeCDD in PCDDs and 23478-PeCDF in PCDFs were higher than for other 2378-substituted congeners. In the present study, The concentrations of these congeners were apparently higher than the others. Using the concentrations of each planar-structured congener, the specific accumulation of PCDD/F and non-*ortho* PCBs, especially of compounds and congeners in bla ck-tailed gulls were compared (Fig. 1). The concentration correlation coefficients

Table 1. The mean concentrations (pg/g, fat weight) of 2,3,7,8-substituted PCDD/Fs and non-ortho PCBs, and TEQs (pg/g, fat weight) in black-tailed gulls and eggs from Rishiri Island, Japan

	eggs (n=10)		gulls (n=10)	
Congeners	Mean	Range	Mean	Range
2378-TeCDD	3.8	2.2-7.6	5.8	1.8-11.6
12378-PeCDD	10.5	3.6-19.9	11.5	3.6-21.6
123478-HxCDD	1.1	nd-6.1	1.7	0.3-4.1
123678-HxCDD	8.9	nd-35.8	10.4	2.9-25.2
123789-HxCDD	1.0	nd-7.6	1.2	0.4-3.8
1234678-HpCDD	2.3	0.8-7.6	2.1	0.7-7.3
OCDD	0.8	nd-8.2	1.4	nd-3.2
2378-TeCDF	0.5	nd-1.1	2.3	0.7-5.1
12378-PeCDF	nd	nd	1.1	0.5-2.7
23478-PeCDF	8.7	3.8-12.5	11.0	3.8-19.1
123478-HxCDF	3.5	2.0-6.5	5.0	1.9-11.4
123678-HxCDF	5.0	2.4-7.9	7.7	2.7-19.3
123789-HxCDF	nd	nd	1.2	nd-4.2
234678-HxCDF	0.9	nd-2.3	2.1	0.4-9.1
1234678-HpCDF	1.9	1.1-3.3	1.4	0.4-4.4
1234789-HpCDF	2.3	1.3-3.6	1.8	0.6-5.0
OCDF	1.6	nd-3.8	1.2	0.4-2.3
Σ PCDDs	28.4	9.8-84.5	34.2	11.1-76.0
Σ PCDFs	24.5	13.1-35.7	34.6	14.0-68.5
Σ PCDD/Fs	52.9	22.9-120.2	68.7	25.1-144.5
PCB 77	1463	781-2775	1671	549-3237
PCB 81	282	146-429	515	193-854
PCB 126	2553	1190-4147	5138	1985-7990
PCB 169	608	315-952	1736	675-2558
Σ non-*ortho* PCBs	4905	2455-7434	9060	3402-13501
Σ TEQs	382	194-584	683	263-1050

between 2378-TCDD and PCDDs, and between 12378-PeCDD and PCDDs were high (Fig. 1-a and c, R^2=0.84, 0.77, $p<0.001$). The correlations between 2378-TCDF and PCDFs (Fig. 1-b, R^2=-0.02, $p>0.1$) were low compared to those between 23478-PeCDF and PCDFs (Fig. 1-d, R^2= 0.42, $p<0.05$). From these correlations, the bioaccumulation of 2378-TCDF, which was reassessed as 1.0 toxic equivalent factor for birds, seemed to be unstable in black-tailed gulls. A low BMF of 0.9 for 2378-TCDF was found previously, and Braune and Norstrom (1989) also reported the BMF of 2378-TCDF in herring gull to be <1.0.

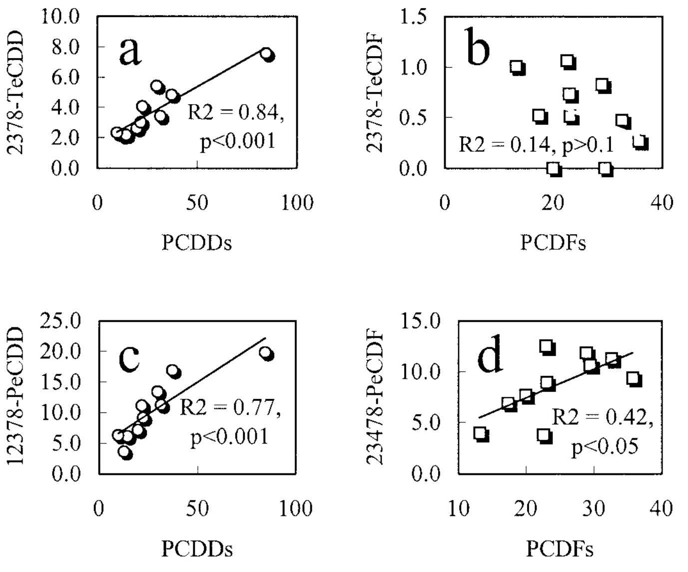

Figure 1. Correlations between selective congeners in black-tailed gull's eggs

The accumulation patterns of PCDD/F and PCB congeners in birds do not directly reflect the patterns of prey or sources in the environment due to differences in physical and metabolic properties, and bioavailability. However, estimations of the correlations among congeners may be useful for estimating the specific accumulation and sources of three groups of planar-structured compounds in our study. We compared the correlations between PCDD, PCDF and non-*ortho* PCB congeners. Specific accumulation of dioxin-like PCBs differs according to the number and substitute location of chlorine (Leonards et al. 1997). Among the most persistent congeners of di-*ortho* PCBs accumulated in mammals, hexa- and heptachlorinated biphenyls such as PCB 138, PCB 153 and PCB 180 have been demonstrated (Mossner and Ballschmiter 1997). However, tetra- or penta chlorinated non-*ortho* PCB congeners such as PCB 77 and PCB 126 persist in birds and human milk (Ankley et al. 1993; Noren et al. 1990).

Non-*ortho* PCB congeners have similar chemical structure and elution patterns to 2,3,7,8-substituted PCDD/Fs since these congeners found in the same fraction of silica-mixed carbon column chromatography (Choi et al. 1999).

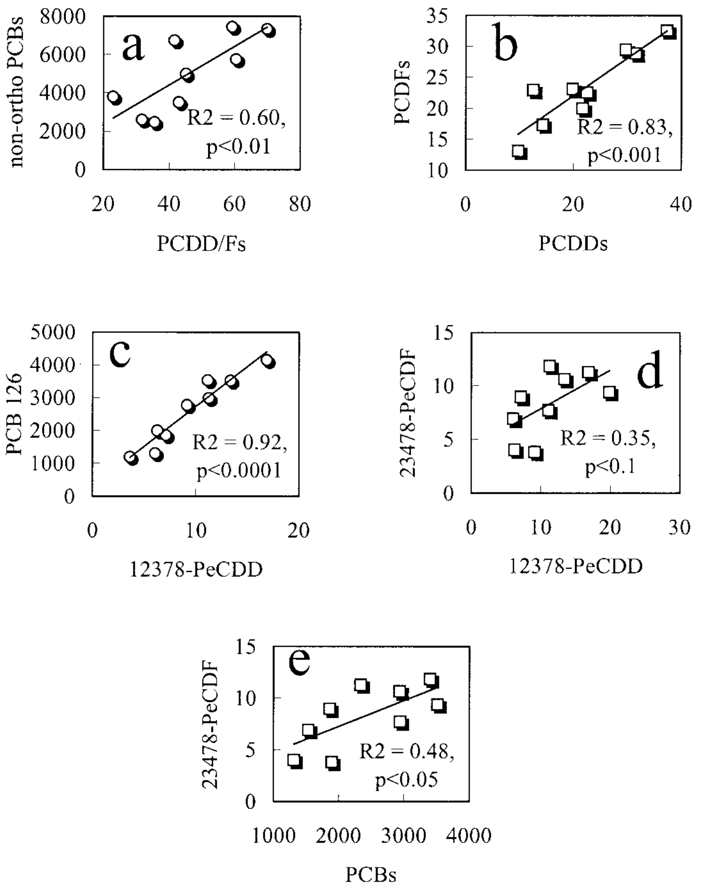

Figure 2. Correlations between selective planar-structured congeners and homo logues in black-tailed gull's eggs

The more persistent planar-structured congeners of PCDD/Fs and non-*ortho* PCBs were expected to have high correlations with each other. Figure 2-a and b, shows good correlations between planar-structured compounds; PCDDs, PCDFs and PCBs. Correlations between PCB126 and 12378-PeCDD, which are highly persistent in mammal and birds, were elevated (R^2=0.92, Fig. 2-c). However, the correlations between persistent 12378-PeCDD and 23478-PeCDF were lower than expected (R^2=0.35, Fig. 2-d). This may indicate that various PCDD/F sources exist in the environment. PCDF congeners in commercial PCBs as well as in fly ash from municipal waste incinerators were reported. For example, good correlations were seen between 23478-PeCDF and PCBs (R^2=0.48, Fig. 2-e).

Estimation of the sources of PCDD/Fs in birds and mammals is more difficult than those of air, sediment or water, since metabolism to non-2378 -substituted congeners occurs in the liver. From these results, further analysis of prey fish or crustaceans is needed for accurate estimation of the sources of PCDD/F in black-tailed gulls.

REFERENCES

Ankley GT, Niemi GJ, Lodge KB, Harris HJ, Beaver DL, Tillit DE, Schwartz TR, Giesy JP, Jones PD, Hagley C (1993) Uptake of planar polychlorinated biphenyls and 2,3,7,8-substituted polychlorinated dibenzofurans and dibenzo-p-dioxins by birds nesting in the lower Fox river and Green bay, Wisconsin, USA. Arch Environ Contam Toxicol 24: 332-344

Bernes C (1998) Persistent Organic Pollutants – A Swedish View of an International Problem. Varnamo, Sweden

Braune BM, Norstrom RJ (1989) Dynamics of organochlorine compounds in herring gulls : III. Tissue distribution and bioaccumulation in lake Ontario gulls. Environ Toxicol Chem 8: 957-968

Choi JW, Nakamura H, Matsuda M, Kawano M, Min BY, Wakimoto T (1999) Development of trace multi-residue analytical method of persistent organic pollutants (POPs) including PCDD/Fs and coplanar PCBs, and its application to biological samples (In Korean). J Korea Soc Environ Anal 2: 181-192

Harner T, Kylin H, Bidleman TF, Halsall C, Strachan WM, Barrie LA, Fellin P (1998) Polychlorinated naphthalenes and coplanar polychlorinated biphenyls in Arctic air. Environ Sci Technol 32:1494-1502

Jarman WM, Burns SA, Chang RR, Stephens RD, Norstrom RJ, Simon M (1993) Determination of PCDDs, PCDFs, and PCBs in California peregrine falcons (Falco peregrinus) and their eggs. Environ Toxicol Chem 12:105-114

Kannan K, Ueda M, Shelby JA, Mendonca MT, Kawano M, Matsuda M, Wakimoto T, Giesy JP (2000) Polychlorinated dibenzo-*p*-dioxins

(PCDDs), dibenzofurans (PCDFs), biphenyls (PCBs) and organochlorine pesticides in yellow-blotched map turtle from the Pascagoula River basin, Mississippi, USA. Arch Environ Contam Toxicol 38: 362-370

Loenards PEG, Zierikzee Y, Brinkman UATh, Cofino WP, van Straalen NM, van Hattum B (1997) The selective dietary accumulation of planar polychlorinated biphenyls in the otter (Lutra lutra). Environ Toxicol Chem 16:1807-1815

Mossner S, Ballschmiter K (1997) Marine mammals as global pollution indicators for organochlorines. Chemosphere 34:1285-1296

Noren K, Lunden A, Sjovall J, Bergman A (1990) Coplanar polychlorinated biphenyls in Swedish human milk. Chemosphere 20:935-941