PCDDs, PCDFs and PCBs in Avian Species from Nakdong River Estuary in Korea

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Introduction

Avian species that occupying positions near top of food chains in aquatic environment have frequently been used as bioindicator for toxic organochlorine compounds such as polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) 1). These compounds are environmental concern because of their toxicity, persistence, and bioaccumulation potential 2). The Nakdong River Estuary, a key area for resident and migratory birds in Korea, is also an area of concern due to high contamination by various effluents from two-large industrial area 3). In this area, a number of visiting species has been declined for a decade. Habitat destruction, water contamination and related food depletion have been pointed as the main causes of the decrease. However, the research on toxic chemicals has been scarcely investigated. The objectives of this study were to determine the PCDD/DFs and PCBs level in avian species collected from the Nakdong River estuary and to investigate the contribution of PCDF sources, mainly for combustion process and impurities of PCBs. Additionally, toxic potencies of PCDD/DFs were assessed on the resident and migratory species.

Material and Methods

During 1992 to 1994, a total of 11 species of resident (1 species, n=10) and migratory birds (10 species, n=34) were collected from the Nakdong River estuary, Korea. All the samples were stored at -20℃ until analysis, and subcutaneous fat was used for chemical analysis. The fat tissues were analyzed according to the method of Nakamura et al [4]. Briefly, the samples were homogenized with Na_2SO_4, and extracted with 300ml dichloromehthane by a Soxhlet apparatus. After determination of lipid weight, the extracted fat was transferred to hexane and spiked with ^{13}C-labeled PCDDs and PCDFs. The solvent was treated with sulfuric acid and further cleanup was made on a silica, alumina, active carbon column mixed with silica gel and silica cartridge (Sep-Pak, Waters Corp.). PCBs were determined by a GC-ECD (HP 5890Ⅱ) and analysis for PCDD/DFs by gas chromatography/ mass spectrometry (GC/MS) were performed with a HP5890Ⅱ-JEOL SX102A with selected ion monitoring (SIM) mode.

Results and Discussion

Analysis Results

The levels of 2,3,7,8-substituted PCDD/DFs and estimated TEQs by using I-TEF and WHO-TEF in birds from the Nakdong River estuary are given in Table 1. The concentrations of PCDD/DFs in black-tailed gull (BTG), which are resident species in the Nakdong River estuary were significantly higher than those of migratory gulls such as black-headed gull, herring gull, common gull, and other two species of terns ($p < 0.01$). Therefore, BTG is thought to be the suitable resident bird to indicate the PCDD/DFs contamination of the Nakdong River estuary. Two large industrial complexes located in this area could be the potential sources for PCDD/DFs and PCBs contamination. There were no significant differences in PCDD/DF levels between the resident gulls and the 4 species of migratory snipes. The elevated PCDD/DFs levels observed in snipes may have resulted from the intake of contaminated foods since they have arrived in this estuary. The PCB levels in residents (BTG) were ranged 6700 to 27000 ng/g (fat weight). Although the PCBs concentrations of the herring gulls were the highest among the migratory species, the mean concentration in the herring gull was significantly lower than the resident (BTG, $p<0.05$). According to the PCBs contamination investigated for other environmental and biological samples in the relevant area during 1993 to 1994 [3], occurrence of this compounds in resident birds shows that PCBs are easily accumulated in the birds as reported previously[2].

Congener Profiles

There have been reported on selective congener profiles of PCDD/DFs in wildlife. Particularly, 2,3,7,8- substitutes are readily accumulated in biotic samples including birds [1]. In this study, 4-6 chlorinated PCDD/DFs congeners were persistent and OCDD, OCDF and non-2,3,7,8-substituted congeners were in small quantity or not detected most of the species analyzed. Moreover, relatively low level of OCDD in PCDDs was different from those earlier reported in Korean adipose samples [5]. Besides, using the two abundant congeners, 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF, found in the bird's fat, the specific bioaccumulation of dioxins was compared among the species. From the results of relative congeneric ratio, 6 species including BTG were shown similar accumulative pattern. In two species of terns, 2,3,7,8-TCDF ratio was relatively higher, while great knot (n=1) indicated higher 1,2,3,4,7,8-HxCDD. In the others, such as black-headed gull and bar-tailed godwit, other 2378-substitutes were predominant.

These fluctuations of congener ratios could be due to the 'biotransformation' dependent on their different food habits and metabolic capacity for PCDD/DFs.

Contribution of Sources

Most of the species investigated in this study, PCDF levels were higher than PCDDs. A number of PCDD/DF sources, such as combustion process, chemical impurities including PCBs, PCP, CNP, 2,4-D. have been reported 6, 7). In addition, a study on cetaceans in our laboratory, PCBs contribution to PCDFs occurrence was found to be important 8). Considering the correlations among compounds, it could be possible to estimate the sources of dioxins approximately. From the results of correlations between PCDDs-PCDFs and PCBs-PCDFs, combustion process was seemed likely important to PCDF levels in the resident and migratory birds ($r=0.95$, 0.92, 0.81, $p<0.001$, respectively). Furthermore, significant correlations between PCBs and PCDFs in the residents and migratory snipes indicate that PCB impurities were likely to be partly responsible for those elevation of PCDFs ($r=0.67$, 0.69, $p<0.05$, respectively).

Toxic Risk Assessment

Under different specific metabolism and accumulation of PCDD/DFs in birds, fishes, and human, the use of species specific TEFs in wildlife for appropriate risk assessment is important 9). WHO-TEF for birds proposed on last year 10) was also calculated to TEQs and compared to I-TEQs. In conclusion, there were no critical levels of PCDD/DFs were observed to generate acute toxicity in wild birds analyzed in this study. However, it is important to monitor the toxic chemicals using birds in Nakdong River estuary environment, because the high contamination in birds indicates the concern to human health as well as to aquatic food chains.

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Table 1. Concentrations of 2378-substituted PCDD/DFs (pg/g, fat), TEQs in Birds fat collected from the Nakdong River estuary.

	BTG (n=10)	BNGB (n=1)	GRN (n=1)	SND (n=5)	GRS (n=3)	BTGW (n=3)	BHG (n=5)	HRG (n=7)	CMG (n=4)	CMT (n=2)	LTT (n=3)
2378-TeCDD	ND-219.2	12.8	4 2	31.8 (13 0-159.2)	9.9 (3.4-22.9)	9.8 (2.5-15.8)	25.9 (6.2-86.5)	ND-193.8	20.4 (3.3-60.1)	3.7 (2.9-4.4)	21.5 (16.0-26.3)
12378-PeCDD	ND-294.4	21.6	4.7	40.1 (10.6-200.7)	26.2 (8.7-55.2)	59.1 (6.0-151.9)	ND-17.7	ND-59.0	ND-26.3	7.7 (5.8-9.6)	33.2 (28.7-40.1)
123478-HxCDD	ND-26.9	< 2.2	4.7	ND	4.9 (2.0-9.7)	ND-125.4	ND	ND-4.3	ND-1.9	ND	6.7 (12.2-27.7)
123678-HxCDD	ND-117.3	< 7.2	ND	13.4 (5.0-67.1)	21.1 (6.5-47.2)	118.6 (6.5-332.6)	ND-28.3	ND-317.7	ND-14.5	ND	19.8 (12.2-27.7)
123789-HxCDD	ND-20.9	< 1.4	ND	ND-9.4	ND-7.5	ND-54.1	ND	ND-1.1	ND	ND	ND-4.2
1234678-HpCDD	ND	< 1.0	< 1.8	2.6 (3.1-13.2)	2.9 (1.0-6.0)	ND-258.6	ND-10.2	ND-8.6	ND-5.2	1.4 (0.9-1.8)	5.8 (3.8-8.3)
OCDD	ND-47.7	ND	ND	ND	ND	ND-115.9	ND-25.6	ND	ND-12.5	ND	ND
2378-TeCDF	ND-76	14.7	10.4	18.0 (8.6-39.2)	14.3 (4.2-30.7)	9.8 (7.4-13.0)	11.4 (1.9-33.0)	ND-35.0	ND-17.3	10.6 (6.4-14.8)	46.7 (33.0-55.1)
12378-PeCDF	ND-32.8	6.2	10.8	14.9 (9.5-32.2)	6.7 (2.3-11.6)	9.1 (4.7-12.1)	ND-6.4	ND-24.5	ND-4.6	5.3 (4.2-6.5)	15.1 (13.6-17.2)
23478-PeCDF	85.1 (13.1-292.9)	70.5	24.3	108.3 (26.9-150.9)	51.3 (12.1-122.1)	27.1 (5.7-56.3)	ND-11.7	57.4 (19.1-118.6)	21.3 (3.3-41.3)	11.4 (2.7-20.0)	40.8 (37.3-47.3)
123478-HxCDF	ND-96.1	< 5.3	ND	16.1 (8.1-25.3)	15.7 (4.6-31.5)	16.8 (3.5-33.6)	ND-9.5	ND-79.1	ND-7.0	ND-2.6	20.8 (16.6-24.1)
123678-HxCDF	ND-104.3	< 5.0	ND	8.1 (2.5-21.7)	10.5 (3.3-24.3)	18.3 (1.5-42.3)	ND-7.0	ND-175	ND-10.0	ND-3.5	18.7 (16.2-21.0)
123789-HxCDF	ND-20.6	ND	ND	ND-1.5	ND	ND	ND	ND	ND	ND	ND
234678-HxCDF	ND-29.9	< 2.1	ND	ND-5.2	ND-9.4	ND-21.6	ND-1.6	ND-43.9	ND-1.0	ND	ND
1234678-HpCDF	ND-31.8	< 1.2	< 2.7	3.6 (4.3-8.2)	7.8 (1.5-19.2)	42.5 (2.9-92.9)	ND-5.3	ND-12.1	ND-7.9	2.2 (1.5-2.8)	4.2 (3.2-4.7)
1234789-HpCDF	ND-42.8	< 0.6	ND	ND-1.2	ND-8.1	2.2 (ND-5.4)	ND-1.9	ND-10.4	ND-2.4	ND-1.2	ND
OCDF	ND	< 2.3	ND	ND	ND-54.1	ND	ND-10.6	ND	ND-3.1	ND-2.6	ND
Total PCDDs	167.4 (13.5-657.8)	46.2	15.3	93.2 (28.7-190.2)	67.6 (22.4-148.6)	375.8 (15.0-1054.5)	51.0 (19.0-97.6)	ND-511.5	48.8 (25.4-62.0)	12.7 (10.5-14.9)	89.5 (71.2-109.0)
Total PCDFs	228 (54.6-655.6)	107.9	48.1	170.7 (68.4-254.6)	130.7 (37.0-311.1)	133.0 (27.4-271.7)	33.2 (25.0-40.4)	138.0 (41.3-364.7)	42.1 (12.4-81.3)	34.4 (18.7-50.1)	146.3 (131.9-165.6)
Total PCDD/Fs	395.5 (68.1-1313.4)	154.2	63.4	263.9 (97.1-444.8)	198.3 (68.9-459.7)	508.8 (42.4-1326.1)	84.2 (52.4-131.0)	261.2 (66.9-876.2)	90.9 (37.8-128.9)	47.1 (29.2-65.0)	235.7 (229.7-240.8)
I-TEQs	131.7 (12.9-558.4)	63.0	20.8	112.8 (35.6-200.7)	56.5 (17.4-128.6)	77.8 (10.7-185.9)	35.6 (11.4-90.0)	90.8 (28.3-289.0)	39.9 (13.8-72.0)	14.9 (8.0-21.7)	70.8 (67.0-73.4)
WHO-TEQs	226.7 (23.1-899.1)	121.9	44.9	202.7 (66.9-353.3)	106.3 (34.7-240.6)	116.6 (24.4-258.6)	51.7 (15.8-120.0)	134.5 (56.9-293.0)	61.2 (20.9-90.3)	34.2 (18.2-50.1)	148.4 (139.7-154.0)
WHO/I ratio	1.8 (1.6-2.2)	1.9	2.2	1.8 (1.8-1.9)	1.9 (1.9-2.0)	1.8 (1.4-2.3)	1.5 (1.3-1.9)	1.8 (1.0-2.2)	1.6 (1.2-2.1)	2.3 (2.3, 2.3)	2.1 (1.9-2.3)

BTG: Black-tailed Gull *(Larus crassirostris)*, BNGB: Black-necked Grebe *(Podiceps nigricollis)*, GRN: Great Knot *(Calidris tenuirostris)*, SND: Sanderling *(Crocethia alba)*, GRS: Greenshank *(Tringa nebularia)*, BTGW: Bar-tailed Godwit *(Limosa lapponica)*, BHG: Black-headed Gull *(Larus ridibundus)*, HRG: Herring Gull *(Larus argentatus)*, CMG: Common Gull *(Larus canus)*, CMT: Common Tern *(Sterna hirundo)*, LTT: Little Tern *(Sterna albifrons)*.