Polychlorinated Naphthalenes, -Biphenyls, -Dibenzo-*p*-dioxins, and -Dibenzofurans in Double-Crested Cormorants and Herring Gulls from Michigan Waters of the Great Lakes

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Concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), naphthalenes (PCNs), and biphenyls (PCBs) were measured in eggs of double-crested cormorants and herring gulls collected from Michigan waters of the Great Lakes. Concentrations of PCNs in eggs of double-crested cormorants and herring gulls were in the ranges of 380–2400 and 83–1300 pg/g, wet wt, respectively. Concentrations of 2,3,7,8-substituted PCDDs and PCDFs were 10–200 times less than those of PCNs in eggs whereas those of total PCBs (380–7900 ng/g, wet wt) were 3–4 orders of magnitude greater. While the profile of PCB isomers and congeners between double-crested cormorants and herring gulls was similar, the PCN isomer profile differed markedly between these two species. PCN congeners 66/67 (1,2,3,4,6,7/1,2,3,5,6,7) accounted for greater than 90% of the total PCN concentrations in herring gulls, whereas their contribution to total PCN concentrations in double-crested cormorants ranged from 18 to 40% (mean, 31%). The ratios of concentrations of PCDDs to PCDFs were greater in herring gulls than in double-crested cormorants collected from the same locations, suggesting the ability of the former to metabolize PCDF congeners relatively rapidly. 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) equivalents (TEQs) contributed by PCNs in double-crested cormorant and herring gull eggs were 2–3% of the sum TEQs of PCBs, PCDDs, PCDFs, and PCNs. PCB congener 126 (3,3′,4,4′,5-PeCB) accounted for 57–72% of the total TEQs in double-crested cormorant and herring gull eggs.

Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), naphthalenes (PCNs), and biphenyls (PCBs) are ubiquitous environmental contaminants. Several studies have reported the occurrence of PCDDs, PCDFs, and PCBs in fish-eating water birds, particularly double-crested cormorants (*Phalacrocorax auritus*) and herring gulls (*Larus argentatus*) from the Great Lakes (*1*–*7*). Compared to the reports of PCBs and dioxins, studies on PCNs in eggs of fish-eating birds are limited. Particularly, prior to this study, concentrations of PCNs in eggs of birds from the Great Lakes have not been reported. In this study, concentrations of individual PCN congeners were measured in double-crested cormorants and herring gulls from Michigan waters of the Great Lakes.

Similar to PCBs and dioxins, PCNs are persistent, bioaccumulative, and toxic contaminants. Exposure of chicken and eider duck embryos to technical PCNs or selected PCN congeners caused embryolethality and ethoxyresorufin-*O*-deethylase (EROD) induction (*8*). Several of the PCN congeners elicit toxic effects similar to those of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) through the Ah-receptor (AhR) mediated mechanism (*9, 10*). These include induction of aryl hydrocarbon hydroxylase and EROD, chloracne, and liver damage (*11, 12*). Toxic equivalency factors (TEFs; potency of a congener relative to that of TCDD) have been reported for several chlorinated naphthalene congeners (*9, 10*). In this study, TCDD equivalents (TEQs) were estimated by an additive model by multiplying concentrations of individual PCN congeners by their corresponding TEFs and summing the products. The TEQs calculated for PCNs were compared with those estimated for PCBs, PCDDs, and PCDFs to evaluate the relative importance of these contaminants in eggs of birds. In addition to PCNs, results of analysis of PCB congeners including mono-, di- and non-ortho congeners, 2,3,7,8-substituted PCDD, and PCDF congeners are reported in eggs of double-crested cormorants and herring gulls originating from Michigan waters.

Materials and Methods

Eggs of double-crested cormorants and herring gulls were collected from Little Charity (Saginaw Bay) and Scarecrow Islands (Thunder Bay) in Lake Huron and Taquamenon Island (Whitefish Bay) in Lake Superior during May 1998 (Figure 1). The eggs were collected for the purpose of conducting an egg-injection study to elucidate the mechanism of action of dioxins. Eggs were selected from incomplete clutches to ensure that they were freshly laid. Therefore, sampling locations were chosen to avoid highly contaminated locations. The eggs were placed individually in clean I-chem jars and kept frozen at −20 °C until analysis. Randomly selected eggs from each colony were analyzed for PCNs, PCBs, PCDDs, and PCDFs. The whole egg contents were homogenized and extracted for analysis. For cormorants, each sample was comprised of an entire egg (30–52 g); whereas for herring gulls an aliquot of 35 g of the homogenate from each egg was used for extraction.

Chemical Analysis. Chloronaphthalene (CN), chlorobiphenyl (CB), and 2,3,7,8-substituted congeners of PCDDs and PCDFs were analyzed in eggs following the method described elsewhere (*13*) with some modifications. Samples were homogenized with sodium sulfate and Soxhlet extracted with methylene chloride and hexane (3:1, 400 mL) for 16 h. The extract was rotary evaporated at 40 °C, and an aliquot was used for the determination of lipid content by gravimetry. The remaining extract was spiked with [¹³C]TCDD, [¹³C]TCDF, [¹³C]OCDD, and [¹³C]OCDF as internal standards and interferences removed by fractionation with multilayer silica gel column. The multilayer silica gel column was prepared by packing a glass column (20 mm i.d.) with layers of silica

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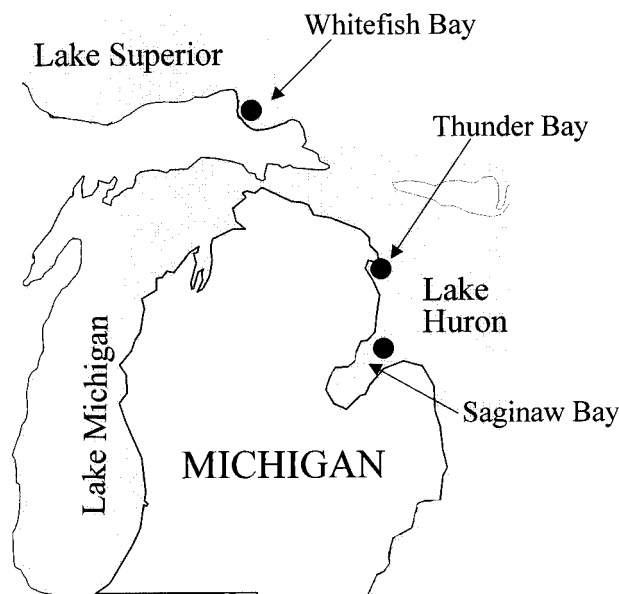§ U.S. Fish and Wildlife Service.

FIGURE 1. Map of Michigan showing sampling locations.

gel (Kiesel gel, mesh size 230−400, Merck, Darmstadt, Germany) in the following order: 2 g of silica, 6 g of 40% acidic silica, 2 g of silica, 5 g of 10% AgNO₃ silica, 2 g of silica, and a thin layer of sodium sulfate at the top. The column was cleaned with 150 mL of hexane prior to the transfer of sample extracts. Samples were then eluted with 200 mL of hexane and rotary evaporated to 5 mL. A portion of the aliquot was taken for the analysis of PCB congeners other than non-ortho coplanar PCBs. The remaining samples were passed through a glass column (10 mm i.d.) packed with 1 g of silica gel-impregnated carbon (Wako Pure Chemical Industries, Tokyo, Japan) for the separation of ortho-substituted PCBs from PCNs and PCDDs/DFs. The first fraction, which was eluted with 150 mL of hexane, contained major PCB congeners that interfere with the analysis of PCNs and PCDDs/DFs. The second fraction, which was eluted with 200 mL of toluene, contained non-ortho-substituted PCB congeners (77, 126, and 169), PCNs, PCDDs, and PCDFs.

Identification and quantification of individual congeners was accomplished with a Hewlett-Packard 6890 series high-resolution gas chromatograph (HRGC) coupled to a JEOL JMS-700 high-resolution mass spectrometer (HRMS). The mass resolution of the spectrometer was greater than 10000 MU. Separation of PCB congeners was achieved by a fused silica capillary column coated with DB-1 (30 m × 0.25 mm i.d.) at 0.25 μm film thickness (J&W Scientific, Folsom, CA) whereas PCN congeners, hepta- and octa-chlorodibenzo-p-dioxins and furans, and non-ortho coplanar PCBs were separated by DB-1701. Tetra- through, hexachlorodibenzo-p-dioxins and -furans were separated by a capillary column coated with SP-2331. The column oven temperature was programmed from 80 to 160 °C at a rate of 40 °C/min and then to 170 °C at 10 °C/min, to 250 °C at 4 °C/min, and then to 296 °C at 8 °C/min with a final hold time of 10 min. Injector and transfer line temperatures were held at 260 and 250 °C, respectively. Helium was used as the carrier gas. The mass spectrometer was operated at an electron impact (EI) energy of 70 eV. PCN, PCB, and PCDD/DF congeners were determined by selected ion monitoring (SIM) at the two most intensive ions of the molecular ion cluster. An equivalent mixture of Kanechlors 300, 400, 500, and 600 with known chlorobiphenyl composition and content was used as a standard for the quantification of PCBs. For PCNs, a mixture of Halowaxes 1001, 1014, and 1051 containing all the tri-through octachloronaphthalenes was used as a standard. For those congeners that were absent in Halowaxes, response

factors derived from their corresponding homologue groups were used for calculation. PCDD and PCDF congeners were quantified by comparing individually resolved peak areas to the corresponding peak areas of the standards. Recoveries of ¹³C-labeled PCDDs/DFs, which elute in the second fraction containing PCNs and non-ortho coplanar PCBs, were 77−95%. Reported concentrations were not corrected from the recoveries of internal standard. Recoveries of PCB, PCN, PCDD, and PCDF congeners through the analytical procedure were between 90 and 100%. Procedural blanks were analyzed through the whole analytical procedure to check for interference and laboratory contamination. The detection limits of individual PCN and PCB congeners varied depending on the sample mass, response factor, and interference. Generally, detection limit for individual congeners was 0.2−1 pg/g on a wet weight basis. Quality control criteria for positive identification of target compounds include signal-to-noise ratio over 3, isotope ratios of the two monitored ions for each compound within 15% of the theoretical chlorine values, and compound eluting at the same GC retention time as the standards. PCN and PCB congeners are represented by their IUPAC numbers throughout this paper. Concentrations among colonies and locations were compared using analysis of variance (ANOVA) or Mann−Whitney U test or Student's t test ($\alpha = 0.05$).

Results and Discussion

Concentrations. Polychlorinated naphthalenes were found in all the egg samples analyzed (Table 1). Total PCN concentrations in eggs varied from 83 to 2400 pg/g on a wet wt basis. Eggs of cormorants contained slightly higher concentrations (380−2400 pg/g, wet wt) than those of herring gulls (83−1300 pg/g, wet wt), although the difference was not statistically significant between the two species ($p > 0.05$). This is despite the fact that herring gull eggs had relatively greater lipid content than those of cormorants. Although the concentrations of PCNs in eggs collected from Whitefish Bay in Lake Superior were expected to be less than those from other locations (due to their remoteness), no significant difference in total PCN concentrations was observed among the three sampling locations ($p > 0.05$). PCN concentrations in eggs varied by 5-fold within colonies except for the colony of herring gulls from Lake Superior, which varied up to 15-fold. The only study that reported the occurrence of PCNs in the eggs of birds was for guillemot and white-tailed sea eagles collected during the 1970s and 1980s from the Baltic Sea (14). Concentrations of PCNs in guillemot and white-tailed sea eagle eggs were in the ranges of 10 000−32 000 and 6 800−14 000 pg/g, wet wt, respectively (14), which were approximately 10−20-fold greater than those reported for herring gulls and cormorant eggs analyzed in our study. However, as mentioned earlier, eggs collected in this study were from locations far from local sources of discharge. Total PCN concentrations of up to 22 000 pg/g, wet wt, were found in double-crested cormorant eggs collected from Gull Island in the northern Green Bay of Lake Michigan (Kannan, unpublished data). Concentrations of PCNs in liver and muscle tissues of white-tailed sea eagles from Poland were up to 100 000 and 22 000 pg/g, wet wt, respectively (15), which were greater than those measured in the eggs of cormorants and herring gulls.

Concentrations of seven PCDD and nine PCDF congeners in eggs of cormorants and herring gulls from the three sampling locations are given in Table 2. Concentrations of PCDDs and PCDFs were 10−90 and 17−200 times, respectively, less than those of PCNs. In general, when the concentrations of all PCDD/DF congeners from the three locations were compared, no significant difference was observed for sum of 2,3,7,8-substituted PCDD and PCDF concentrations between cormorants and herring gulls ($p >$

TABLE 1. Concentrations (pg/g, wet wt) of Total PCBs, PCNs, 2,3,7,8-Substituted PCDDs, and PCDFs in Eggs of Double-Crested Cormorants and Herring Gulls from the Great Lakes[a]

species	sampling location	date of collection	n	lipid (%)	total PCBs	total PCNs	2,3,7,8-PCDDs	2,3,7,8-PCDFs
double-crested cormorant	Little Charity Is., Lake Huron	May 5, 1998	3	4–5.2 (4.6)	1 250 000–2 370 000 (1 650 000)	620–2400 (1 200)	25–97 (62)	28–76 (48)
herring gull	Little Charity Is., Lake Huron	May 5, 1998	2	8.1–9.6 (8.9)	1 000 000–3 010 000 (2 000 000)	430–720 (575)	20–55 (37)	3.4–12 (7.7)
double-crested cormorant	Scarecrow Is., Lake Huron	May 11, 1998	3	5.6–6.5 (6)	1 220 000–1 680 000 (1 420 000)	520–1 900 (1100)	7.4–26 (16)	22–57 (37)
herring gull	Scarecrow Is., Lake Huron	May 11, 1998	2	9.8–10.6 (10.2)	3 600 000–3 950 000 (3 770 000)	390–470 (430)	12–27 (20)	8.7–26 (17)
double-crested cormorant	Taquamenon Is. Lake Superior	May 12, 1998	3	5.3–6.6 (5.8)	1 130 000–2 960 000 (1 790 000)	380–2 000 (1100)	18–37 (26)	20–37 (27)
herring gull	Taquamenon Is., Lake Superior	May 12, 1998	2	10.7–11.9 (11.3)	380 000–7 930 000 (4 150 000)	83–1300 (690)	64[b]	35[b]

[a] Values in parentheses indicate mean. [b] Only one sample was analyzed.

TABLE 2. Concentrations (pg/g, wet wt) of 2,3,7,8-Substituted PCDDs and PCDFs in Double-Crested Cormorants and Herring Gulls from the Great Lakes in May 1998[a]

	double-crested cormorants			herring gulls		
	Little Charity Is.	Scarecrow Is.	Taquamenon Is.	Little Charity Is.	Scarecrow Is.	Taquamenon Is.
lipid (%)	4.6 (4–5.2)	6 (5.6–6.5)	5.8 (5.3–6.6)	8.9 (8.1–9.6)	10.2 (9.8–10.6)	11.3 (10.7–11.9)
			PCDDs			
2378	6.9 (1.4–12)	2.4 (0.8–3.7)	4.4 (2.2–6.3)	14.9 (8.7–21.2)	9.6 (3–16.2)	26
12378	12.7 (1–21)	1.9 (0.6–3.6)	3.9 (2–7.6)	8.6 (2.6–14.6)	3.7 (<0.1–3.7)	0.2
123478	2.6 (1.5–3.9)	0.3 (<0.1–0.4)	0.53 (0.2–0.9)	6.1 (1.4–10.8)	<0.1 (<0.1)	35
123678	18.2 (16–20)	1.6 (0.2–3.3)	4.1 (2.4–7.4)	<0.1 (<0.1)	3.6 (2.9–4.2)	<0.1
123789	3.5 (0.93–6.2)	0.5 (0.4–0.7)	1.5 (<0.1–1.7)	<0.1 (<0.1)	0.9 (<0.1–0.9)	<0.1
1234678	4.0 (0.81–6.9)	0.74 (0.11–1.1)	2.2 (1.1–3.9)	1.2 (0.95–1.5)	0.82 (0.71–0.93)	1.5
12346789	20 (17–24)	8.9 (5.3–14)	9.6 (7.9–12)	6.3 (5.6–7)	3.4 (2.3–4.5)	1.3
total PCDDs	62 (25–94)	16 (7.4–26)	26 (18–37)	37 (12–55)	20 (12–27)	64
			PCDFs			
2378	2.0 (1.6–2.3)	2.9 (1.5–5.2)	1.3 (1.2–1.4)	3.3 (2.7–4)	1.3 (1.1–1.4)	6
12348/12378	7.2 (4–13.3)	5.7 (3–11)	1.1 (0.2–2)	0.4 (<0.1–0.4)	13 (6–20)	14
23478	17 (11–29)	12 (6.2–18)	7.1 (5.3–10)	<0.1 (<0.1)	1.5 (1.4–1.6)	2.5
123478/123479	18 (8.8–29)	13 (8.9–15)	17 (12–24)	4.2 (<0.1–4.2)	2.6 (<0.1–2.6)	6.8
234678	2 (1.6–2.7)	1.9 (0.8–2.8)	0.73 (0.3–1.3)	<0.1 (<0.1)	<0.1 (<0.1)	int
123789	<0.1 (<0.1)	<0.1 (<0.1)	<0.1 (<0.1)	<0.1 (<0.1)	<0.1 (<0.1)	1.3
1234678	0.43 (0.27–0.7)	0.53 (0.36–0.62)	0.63 (<0.1–0.63)	0.95 (<0.1–0.95)	0.45 (<0.1–0.45)	<0.1
1234789	0.24 (0.24)	0.18 (0.1–0.31)	0.1 (<0.1–0.1)	1.6 (0.31–2.8)	<0.1 (<0.1)	0.36
12346789	0.22 (0.12–0.31)	<0.1 (<0.1)	<0.1 (<0.1)	<0.1 (<0.1)	<0.1 (<0.1)	<0.1
total PCDFs	48 (28–76)	37 (22–57)	27 (20–37)	7.7 (3.4–12)	17 (8.7–26)	30
PCDD/PCDF ratio	1.3	0.43	0.94	4.8	1.1	2.1

[a] 123678 was not quantified due to an unknown interference. Values in parentheses indicate the range. int, interference.

0.05) (Table 1). Concentrations of 2,3,7,8-substituted congeners of PCDDs in cormorants from Saginaw Bay were significantly greater than those from Thunder Bay and Whitefish Bay ($p < 0.05$). No significant difference was observed for PCDD concentrations in herring gulls from the three locations (Table 2). However, the concentrations of certain congeners varied significantly among locations and between the two species (Table 2). For example, concentrations of 2,3,7,8-TCDD was significantly greater in herring gulls than those in cormorants. Other congeners such as 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8,9-OCDD, 2,3,4,7,8-PeCDF, and 1,2,3,4,7,8-HxCDF were significantly greater in cormorant eggs than in herring gull eggs. While OCDD was the most abundant congener in cormorants, TCDD predominated in the eggs of herring gulls. Occurrence of greater concentrations of TCDD than those of OCDD has been reported in the eggs of herring gulls from the Great Lakes (1). The variation in the composition of PCDD and PCDF congeners between cormorants and herring gulls could be due differences in their ability to selectively metabolize certain congeners. The ratios of concentrations of PCDDs to PCDFs for herring gulls were greater than those for cormorants suggesting the potential

of herring gulls to transform PCDF congeners. The concentration ratios of PCDDs to PCDFs for the samples collected on Little Charity Island were greater than those from Scarecrow and Taquamenon Islands (Table 2). This suggests greater exposure to PCDDs than PCDFs for birds nesting on Little Charity Island. Despite this, the similarity in overall magnitude of PCDD/DF concentrations among the three colonies would seem to indicate that inputs to these areas are generic in both composition and magnitude. This suggests an atmospheric source. Atmospheric deposition has been identified as an important route of entry of PCDDs/DFs into the Great Lakes (16).

Concentrations of total PCBs in cormorants were 3 orders of magnitude greater than those of PCNs. Total PCB concentrations in herring gull eggs were up to 4 orders of magnitude greater than those of PCNs (Table 1). Concentrations of total PCBs in herring gulls (380–7900 ng/g, wet wt) were significantly greater than those in cormorants (1100–3000 ng/g, wet wt). Concentrations of PCBs in cormorant and herring gull eggs varied greatly within locations, although the difference in PCB concentrations among locations was not statistically significant. The measured concentrations of
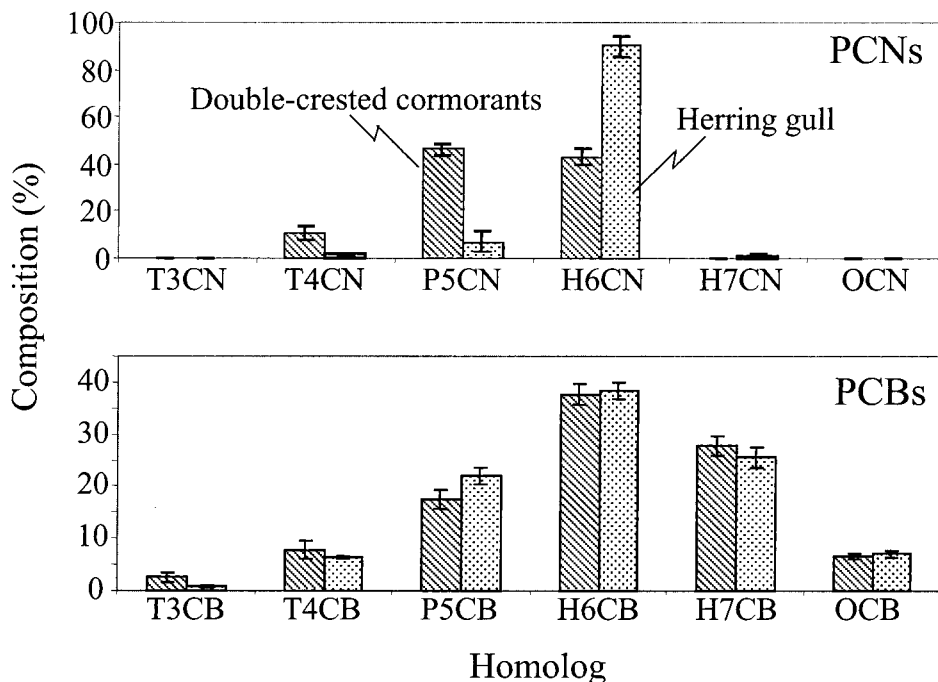
FIGURE 2. Composition (%) of PCN and PCB homologues in eggs of double-crested cormorants and herring gulls from three colonies in the Great Lakes. Error bars indicate standard deviation of the mean.

PCBs in cormorant eggs were less than those reported for eggs collected in 1988 and 1989 (100−15 000 ng/g, wet wt) from various locations in the Great Lakes (5). Average concentration of PCBs in the eggs of cormorants from Thunder Bay, Lake Huron, during 1987−1991 was 12 000 ng/g, wet wt (17), which is 8-fold greater than those observed in this study. These results suggest a decline in the concentrations of PCBs in the eggs of double-crested cormorants in recent years.

A wide variety of sources of PCNs can be suggested for their occurrence in eggs. PCN congeners (PCN Nos. 19, 25, 26, 29, 31, 44, and 70) that were absent in Halowaxes (technical PCN preparations) (18) either were not found or were present only in small concentrations in eggs. While this suggests that technical PCN preparations have been the major sources of PCNs to birds, abundance of congeners 52/60 in cormorants suggests the sources originating from municipal solid waste incineration (19), although congeners 52/60 may possess great bioaccumulation potential. Similarly, technical PCBs such as Aroclors contain total PCN concentrations of up to 67 μg/g (20). However, the ratios of total PCNs to total PCB concentrations in bird eggs were greater than those observed in Aroclors, suggesting the existence of sources other than Aroclors. A similar observation has been made for fishes from the Great Lakes (13).

Congener Profiles. Penta- and hexachloronaphthalenes accounted for 89% of the total PCN concentrations in eggs of double-crested cormorants (Figure 2). The profiles of PCN congeners in herring gull eggs were considerably different from that observed for cormorants. Hexachloronaphthalenes alone accounted for greater than 90% of the total PCN concentrations in herring gull eggs. Particularly, HxCN congeners 1,2,3,4,6,7 (PCN 66) and 1,2,3,5,6,7 (PCN 67) accounted for over 90% of the total PCN concentrations in herring gull eggs (Figure 3). PCN congeners 66 and 67 are highly bioaccumulative and contribute to a significant proportion of the total PCN concentrations in higher trophic level organisms in the food chain (11, 13, 21). PCN congeners 66 and 67 collectively accounted for over 60% of the total PCN concentrations in guillemot eggs from the Baltic Sea (14). In white-tailed sea eagle eggs collected from the Baltic

Sea, PeCNs 1,2,3,5,7/1,2,4,6,7 (PCN 52/60) were the most abundant congeners (14). Pentachloronaphthalenes accounted for 70% of the total PCN concentrations in liver and muscle of white-tailed sea eagles from Poland (15). These results indicate that the accumulation profiles of PCN congeners in birds vary widely depending on species. A remarkable difference in profiles of PCNs in herring gulls and double-crested cormorants collected from the same locations in the Great Lakes suggests that the two species differ in their ability to metabolize PCN congeners. The profiles of PCN congeners in herring gulls or cormorants were similar among colonies/locations. The predominant congeners in cormorant eggs include PCNs 66, 67, 52/60, 61 (1,2,4,6,8-), and 42 (1,3,5,7-), which collectively accounted for 70% of the total PCN concentrations (Figure 3); whereas, in herring gull eggs, congeners 66/67 accounted for greater than 90% of the total PCN concentrations.

Despite the difference in profiles of PCN congeners between herring gulls and double-crested cormorants, the composition of individual PCB isomers to total PCB concentrations was similar (Figure 2). This further indicates that the species-specific difference in the profiles of PCNs was not source-related but due to metabolism. Hexachlorobiphenyls accounted for 38% of the total PCB concentrations in both cormorant and herring gull eggs, which was followed by hepta- (26−28%) and pentachlorobiphenyls (18−22%). PCB congeners 153 (2,2′,4,4′,5,5′ 17−19%), 138 (2,2′,3,4,4′,5′ 12−13%), 180 (2,2′,3,4,4′,5,5′ 9−10%), 118 (2,3′,4,4′,5 6−7%), and 99 (2,2′,4,4′,5 5−6%) collectively accounted for 51−54% of the total PCB concentrations in herring gull or cormorant eggs (Figure 4).

Toxic Potential. All PCN congeners are planar, and several of them exhibit AhR-mediated cytochrome P450 induction analogous to TCDD (9, 10). Toxic equivalency factors (TEFs) or relative potencies have been reported for several PCN congeners based on in vitro bioassays using H4IIE rat hepatoma cells (9, 10). Hexa-CN congeners 63, 66/67, and 69 were the most potent among the congeners examined so far. Each of these congeners has been assigned a TEF value of 0.002 (Table 3). This permitted the estimation of TEQs for PCNs by summing the product of concentrations and their
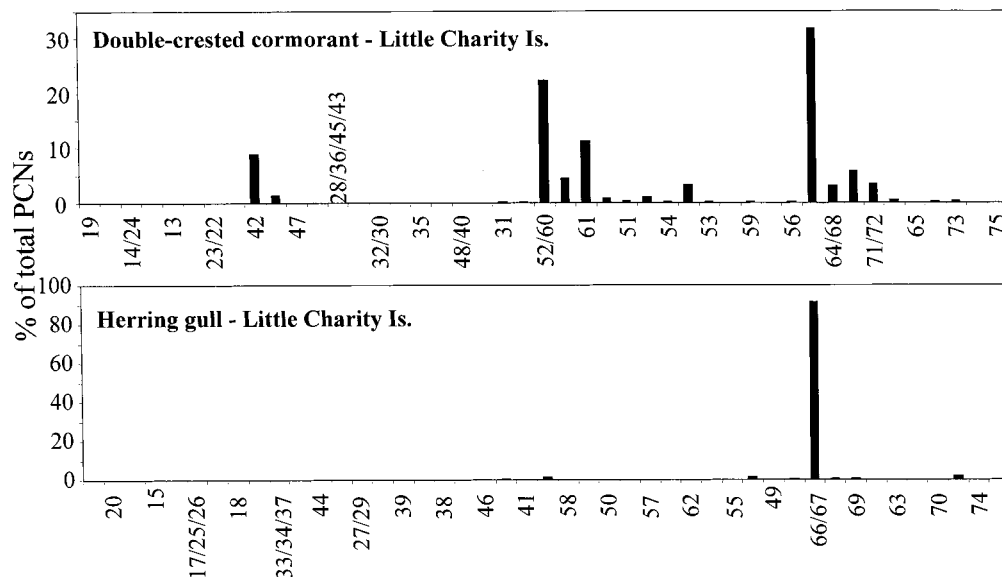
FIGURE 3. Composition (%) of PCN isomers and congeners to total PCN concentrations in eggs of double-crested cormorants and herring gulls from three colonies in the Great Lakes.
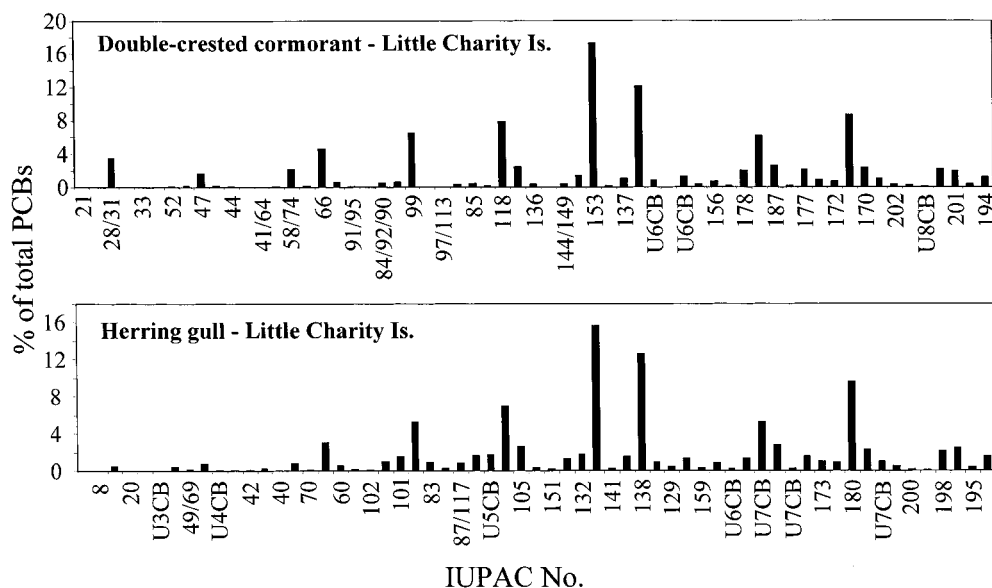

FIGURE 4. Composition (%) of PCB isomers and congeners to total PCB concentrations in eggs of double-crested cormorants and herring gulls from three colonies in the Great Lakes. "U" refers to unidentified chlorobiphenyl congeners.

corresponding TEFs. However, it should be noted that TEFs (or relative potencies) for all PCN congeners are not available due to the lack of sufficient quantities of pure, well-characterized individual congeners. For comparison of TEQs contributed by PCNs, PCBs, PCDDs, and PCDFs, it is appropriate to use TEFs derived using similar bioassays. Since the only TEFs available for PCNs were derived from in vitro H4IIE bioassays (9, 10), H4IIE bioassay derived TEFs were used for PCBs, PCDDs, and PCDFs to estimate their corresponding TEQs (22).

Concentrations of PCN congeners that elicit AhR-mediated mechanism of toxic action and their corresponding TEQs are shown in Table 3. Similarly, concentrations of non- and mono-ortho coplanar PCBs in herring gull and cormorant eggs are presented in Table 3. The mean TEQs contributed by PCNs, PCBs, PCDDs, and PCDFs in the eggs of cormorants and herring gulls from Michigan waters were in the ranges of 0.85−1.5, 21−51, 3.2−19, and 0.92−7.8 pg/g, wet wt, respectively (Table 4). The sum TEQs (ΣTEQs) in eggs were in the ranges of 35−55 pg/g in cormorant eggs and 36−70

pg/g, wet wt, in herring gull eggs (Table 4). Contribution of PCNs to TEQs was 2−3% of the total TEQs, which is less than those by PCBs, PCDDs, or PCDFs. In locations such as Little Charity Island, contribution of PCNs to TEQs was similar to those of PCDFs. Among PCNs, hexachloronaphthalene congener 66 accounted for 83% of the PCN-TEQs in cormorant and 98% in herring gull eggs (Figures 5 and 6). PCN congener 66 accounted for 1.8% of the total TEQs in guillemot eggs from the Baltic Sea (23). In contrast, PCNs contributed up to 57% of the TEQs in fishes from the Detroit River (13). Similarly, PCNs contributed to greater TEQs than those of PCBs in tissues of birds collected from a coastal marsh contaminated by the disposal of wastes from a chlor-alkali facility (24, 25). These results suggest that the toxic impact of PCNs may be relatively more localized than those of PCBs, PCDDs, and PCDFs. Since all PCNs are planar, they tend to bind strongly to sediment organic matter; therefore, their availability is limited to sediment-dwelling organisms including benthic fish. Therefore, fish from localized areas

TABLE 3. Concentrations (pg/g, wet wt) of Dioxin-like PCBs and PCNs in Double-Crested Cormorants and Herring Gulls from the Great Lakes in May 1998[a]

	TEF	double-crested cormorants			herring gulls		
		Little Charity Is.	Scarecrow Is.	Taquamenon Is.	Little Charity Is.	Scarecrow Is.	Taquamenon Is.
lipid (%)		4.6 (4−5.2)	6 (5.6−6.5)	5.8 (5.3−6.6)	8.9 (8.1−9.6)	10.2 (9.8−10.6)	11.3 (10.7−11.9)
			Coplanar PCBs				
77	0.000018	580 (280−920)	280 (250−310)	320 (130−510)	260 (160−360)	360 (210−500)	200 (73−340)
126	0.022	1500 (880−2200)	1100 (750−1500)	1300 (660−2400)	1460 (590−2300)	940 (340−1600)	2300 (135−4400)
169	0.00047	220 (140−340)	180 (160−210)	270 (130−450)	370 (150−580)	43 (27−58)	570 (27−1110)
105	0.00000035	40 (31−53)	32 (29−34)	34 (18−60)	52 (23−81)	71 (68−74)	97 (7.1−190)
118	0.000008	130 (110−170)	110 (95−120)	110 (72−190)	140 (59−220)	230 (230)	260 (21−510)
156	0.000055	11 (8.2−16)	9.5 (8.9−10.4)	12 (6.8−20)	16 (8.5−23)	29 (29)	33 (3−62)
			Dioxin-like PCNs				
54	0.00017	2.6 (1.4−3.9)	1.3 (0.7−2.3)	1.3 (0.31−2)	<0.1	<0.1	0.48 (<0.1−0.48)
56	0.000049	1.3 (0.47−2.9)	0.75 (0.46−1.1)	0.51 (0.16−1)	3.3 (0.5−6.1)	0.98 (0.87−1.1)	0.4 (0.13−0.68)
57	0.0000037	12 (6−21)	9.7 (6.7−15)	13 (1.9−23)	<0.1	0.63 (0.87−1.1)	0.94 (<0.1−0.94)
60	1.42E−05	280 (150−520)	290 (130−550)	300 (98−600)	9.5 (7−12)	38 (17−58)	21 (6.3−35)
63	0.002	6.5 (3.6−12)	4.2 (2.9−6.3)	5 (1−8)	0.27 (<0.1−0.27)	0.64 (0.61−0.68)	0.27 (0.24−0.31)
66	0.0024	400 (160−770)	330 (190−500)	310 (120−620)	530 (390−660)	350 (270−420)	630 (60−1190)
68	0.0015	38 (20−70)	31 (19−51)	37 (11−69)	3.3 (2.4−4.2)	5.8 (3.6−8)	3.3 (0.6−6)
69	0.002	72 (30−140)	88 (30−190)	59 (20−110)	2.3 (2−2.6)	7.6 (5.1−10)	4.2 (1.5−7)
70	0.0095	1.1 (0.61−1.6)	0.31 (0.22−0.41)	0.51 (0.51)	0.76 (<0.1−0.76)	0.48 (<0.1−0.48)	0.60 (0.23−0.97)
73	0.001	3.7 (0.92−6.7)	1.7 (1.5−2)	1.6 (1.3−2.2)	12 (3.2−22)	0.72 (<0.1−0.72)	4.5 (0.89−8.2)

[a] Concentrations of PCB congeners 105, 118, and 156 are in ng/g,wet wt. Congeners 64 and 67 elicit dioxin like activity, but they coelute with congeners 68 and 66, respectively. Congeners 71 and 72 are active, but their potencies relative to TCDD are uncertain. H4IIE-TEFs for PCNs were from refs *9, 10,* or *12.* H4IIE-TEFs for PCBs were from ref *22.*

TABLE 4. Mean 2,3,7,8-Tetrachlorodibenzo-*p*-Dioxin Equivalents (pg/g, wet wt) of PCBs, PCNs, PCDDs, and PCDFs in Double-Crested Cormorants and Herring Gulls Collected from the Great Lakes in May 1998

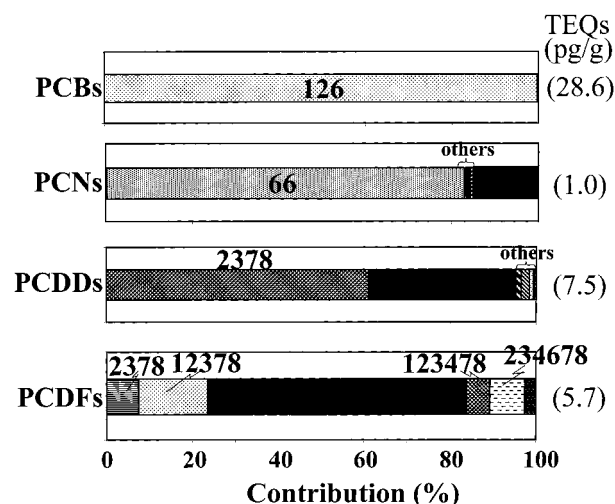|	double crested cormorants			herring gulls		
	Little Charity Is.	Scarecrow Is.	Taquamenon Is.	Little Charity Is.	Scarecrow Is.	Taquamenon Is.
PCBs	33 (60)	25 (71)	28 (73)	32 (60)	21 (58)	51 (73)
PCNs	1.1 (2)	1 (3)	0.89 (2)	1.3 (2)	0.85 (2)	1.5 (2)
PCDDs	13 (24)	3.2 (9)	6.3 (17)	19 (36)	11 (30)	15 (22)
PCDFs	7.8 (14)	6 (17)	3.1 (8)	0.92 (2)	3.4 (10)	2.4 (3)
total	55	35	38	53	36	70

FIGURE 5. Contribution (%) of congeners of PCBs, PCNs, PCDDs, and PCDFs to their corresponding TEQs in eggs of double-crested cormorants from three colonies in the Great Lakes.
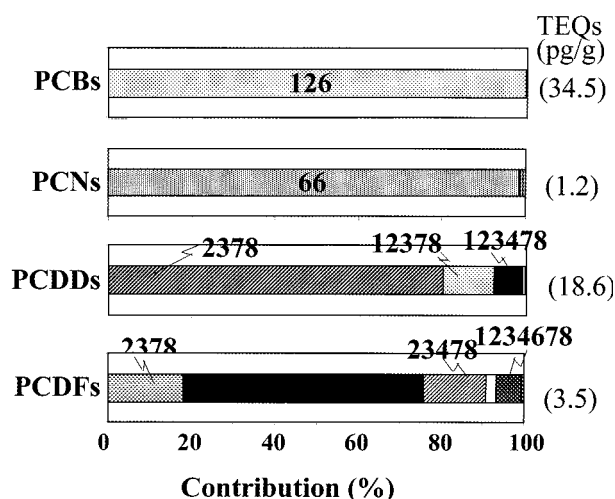

FIGURE 6. Contribution (%) of congeners of PCBs, PCNs, PCDDs, and PCDFs to their corresponding TEQs in eggs of herring gulls from three colonies in the Great Lakes.

of contamination can be exposed to great PCN concentrations resulting in their contribution to TEQs overwhelming those due to PCBs or PCDDs or PCDFs.

PCB 126 accounted for 99% of the PCB TEQs in both cormorant and herring gull eggs (Figures 5 and 6). The contribution of PCDD and PCDF congeners to their corresponding TEQs varied between species (Figures 5 and 6).

2,3,7,8-TCDD alone accounted for 60 and 80% of the PCDD TEQs in cormorants and herring gulls, respectively. Among PCDFs, 1,2,3,7,8-PeCDF was a major contributor to TEQs in herring gulls, while 2,3,4,7,8-PeCDF was the major contributor in cormorants. Overall, PCB 126 was the predominant contributor accounting for 57−72% of the ΣTEQs in herring gulls and cormorant eggs.

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