

Polychlorinated Naphthalenes and Polychlorinated Biphenyls in Fishes from Michigan Waters Including the Great Lakes

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Polychlorinated naphthalene (PCN) and polychlorinated biphenyl (PCB) congeners were measured in whole body and fillet of fishes collected from Michigan waters, including the Great Lakes, during 1996–1997. PCNs were found in all the fishes analyzed including those from Siskiwit Lake, a remote lake located near the southern shoreline of Isle Royale National Park in Lake Superior. Concentrations of total PCNs in fishes ranged from 19 to 31 400 pg/g, wet wt, and varied depending on sampling location and species. Fishes from the Detroit River contained the greatest concentrations of both PCNs and PCBs. Concentrations of total PCNs in fishes from Michigan waters were significantly correlated with the concentrations of PCBs. As with total PCN concentrations, the profiles of PCN isomer/congener distribution in fishes varied among sampling locations and species. Fishes from the Detroit River contained PCN profile similar to that of Halowax 1014, whereas those from Siskiwit Lake and Lake Superior contained greater proportions of congeners which have great bioaccumulative potential. Estimated concentrations of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin equivalents (TEQs) of PCNs ranged from 0.007 to 11 pg/g, wet wt. PCN congeners 66/67 and 69 accounted for greater than 80% of the TEQs contributed by PCNs. TEQs contributed by PCBs, estimated based on H4IIE bioassay-derived TEFs, were in the range of 0.06–11 pg/g, wet wt, which were similar to those contributed by PCNs. When international TEFs (I-TEFs) for coplanar PCBs were applied, estimated PCB-TEQs ranged from 0.46 to 79 pg/g, wet wt, which were 5–10 times greater than those that were estimated from H4IIE TEFs. PCB congener 126 contributed greater than 50% of the TEQs contributed by PCBs in all the fishes. Overall, when similarly derived TEFs were used, PCNs contributed 2–57% of the sum of TEQs of PCNs and PCBs.

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Introduction

Polychlorinated naphthalenes (PCNs) are a group of 75 compounds consisting of two fused aromatic six membered rings substituted with one to eight chlorine atoms. PCNs were first synthesized in the middle of the 19th century (1) and subsequently were found to possess good electrical insulation properties, excellent weather resistance, and low flammability. This led to the production since the beginning of 20th century as technical PCN formulations for use as capacitor dielectrics, cutting oils, engine oil additives, electroplating stop-off compounds, die casting, ship insulation, wood, paper, and fabric preservatives, and wire insulation (2). Although the production of technical PCN formulations in the U.S. was ceased in 1980, PCNs are still found in electrical equipment (3, 4). Other sources of PCNs include municipal waste incineration (5), co-contaminants in commercial polychlorinated biphenyl (PCB) formulations (6), and certain industrial processes including the chlor-alkali process (7).

Similar to PCBs, PCNs are persistent and lipophilic compounds that tend to bioaccumulate. PCNs are widespread in the biosphere on a global scale (8, 9). Chlorinated naphthalene (CN) congeners have been found in a wide variety of environmental matrices including Arctic and urban air (10, 11), wildlife (8, 9, 12, 13), and human tissues (14–16) including breast milk (17). Consumption of contaminated fish is considered to be an important route of exposure of humans to PCNs. High concentrations of penta- and hexachloronaphthalenes in human blood plasma have been correlated with fish consumption (18).

Compared to PCBs, distribution of PCNs in the environment is less described. Particularly, prior to this study, no concentrations of PCNs in fishes from the Great Lakes have been reported. In this study, concentrations of individual PCN congeners were measured in fishes from inland Michigan waters and the Great Lakes. PCNs were also measured in lake trout from Siskiwit Lake, which is located near the south shore of Isle Royale National Park in Lake Superior. Siskiwit Lake is a remote ombrotrophic lake with no inflow from Lake Superior (19). Therefore, the source of PCNs in fish from this lake would be only from atmospheric deposition.

Several of the PCN congeners elicit toxic effects similar to those of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) through the Ah-receptor mediated mechanism (20). These include induction of aryl hydrocarbon hydroxylase and ethoxyresorufin-*O*-deethylase, chloracne, and liver damage (4, 21). Toxic equivalency factors (TEFs; relative potency of a congener to that of TCDD) have been reported for several chlorinated naphthalene congeners (20). 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 estimated TEQs contributed by PCNs were compared with those estimated for PCBs to evaluate the relative importance of these two classes of contaminants. In addition to PCNs, we report the results of a comprehensive analysis of PCB congeners including mono-, di-, and non-ortho-congeners for fishes originating from Michigan waters.

Materials and Methods

Fishes from the Great Lakes (Lakes Superior, Michigan, and Huron) and inland Michigan lakes and rivers were collected during April–September of 1996 and 1997. Details of fish species and sampling locations are shown in Table 1 and

TABLE 1. Details of Fish Samples and Concentrations of Total PCBs (ng/g, Wet Wt) and PCNs (pg/g, Wet Wt) from the Great Lakes and Inland Michigan Waters

sample i.d.	waterbody	location	species	collection date	sample type ^a	total length (cm)	weight (g)	fat (%)	total PCBs (ng/g)	total PCNs (pg/g)
F98-072	Pine River	below Alma Dam	Largemouth bass	29-Jul-97	F	35.8	960	0.67	140	110
F98-085	Pine River	below Alma Dam	Carp	29-Jul-97	Fs	58.2	2395	1.52	240	430
F97-003	Detroit River	Grassy Island	Walleye	12-Jul-96	W	45	860	12.3	4500	31 400
F97-010	Grand River	Moore's River Impoundment	Largemouth bass	7-May-96	F	33	600	0.77	170	250
F97-027	Topico Wetland	Bay County	Northern pike	21-May-96	Fs	62	1650	0.57	31	19
F97-077	Maceday Lake	Oakland County	Northern pike	24-Apr-96	Fs	68	1880	0.59	140	110
F97-082	Lake Huron	Thunder Bay	Lake whitefish	26-Jun-96	F	53.5	1660	9.01	150	1100
F97-091	Lake Huron	Thunder Bay	Lake trout	26-Jun-96	F	52.2	1370	13.8	1000	980
F97-102	Lake Michigan	Charlevoix	Lake trout	27-Aug-96	F	54.9	1870	20.7	1000	1200
F97-142	Lake Superior	Keweenaw Bay	Lake whitefish	23-May-96	F	45.2	730	8.02	160	240
F97-159	Lake Superior	Keweenaw Bay	Lake trout	23-May-96	W	64.3	2000	16.8	430	370
F97-165	Lake Superior	Marquette	Lake trout	10-Jun-96	W	52.3	1300	14.6	250	340
F97-253	Lake Superior	Pendills Creek	Coho salmon	15-Sep-96	F	52.5	1230	1.1	380	240
F97-271	Muskegon River	Newaygo	Redhorse sucker	29-May-96	F	43.5	1040	0.6	77	160
F97-297	Siskiwit Lake	Isle Royale	Lake trout	9-Aug-96	F	48.5	850	3.61	87	140
F97-302	Siskiwit Lake	Isle Royale	Lake trout	9-Aug-96	F	57.4	1250	0.78	73	95
F97-307	Siskiwit Lake	Isle Royale	Lake trout	9-Aug-96	F	64.9	2100	1.42	40	41
F97-311	Siskiwit Lake	Isle Royale	Lake trout	9-Aug-96	W	57	1300	2.44	460	250
F96-502	N.Branch Au Sable River	Lovells	Brown trout	10-Sep-96	F	28	250	4.93	14	35
F96-507	N.Branch Au Sable River	Lovells	Brown trout	10-Sep-96	F	34.5	450	3.43	11	44
F96-511	Detroit River	Grassy Island	Carp	12-Jul-96	W	48	1520	5	740	1310
F96-514	Detroit River	Grassy Island	Carp	12-Jul-96	W	47.5	1820	19.8	5600	26400

^a F = fillet; Fs = skin-on-fillet; W = whole body

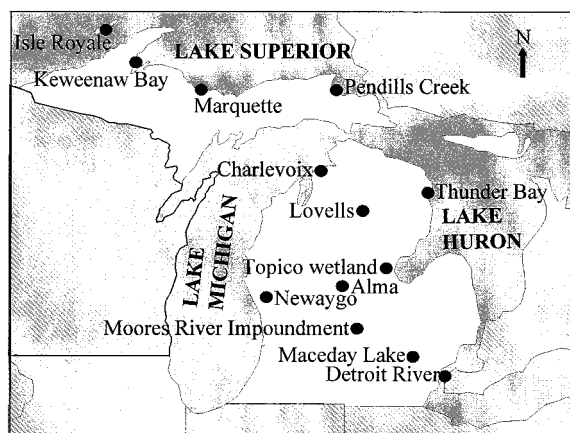


FIGURE 1. Map of Michigan and its surroundings showing sampling locations.

Figure 1. All Great Lakes fishes, except salmon, were captured in trap nets, trawls, or gill nets. Salmon were captured in the fall as they migrate upstream to spawn. Fishes from inland rivers and lakes were collected by electroshocking. Total lengths and weights of the fishes were measured, and samples were wrapped in aluminum foil, placed in polyethylene bags, and frozen. Homogenized samples of "skin on" or "skin-off" fillets or whole fish were analyzed.

Chemical Analysis. Chloronaphthalene (CN) and chlorobiphenyl (CB) congeners in fishes were analyzed following the method described elsewhere (7, 22) 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 fat 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 a series of layers of silica 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. The first fraction, which was eluted with 150 mL of hexane contained the major PCB congeners which interfere with the analysis of PCNs. The second fraction, which was eluted with 200 mL of toluene contained non-ortho-substituted PCB congeners, IUPAC numbers 77, 126, and 169, and PCNs.

Identification and quantification of individual CB and CN 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 10⁻⁴ mass units. 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 and non-ortho-coplanar PCBs were separated by DB-1701. 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. CN and CB 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 (23). For PCNs, a mixture of Halowaxes 1001, 1014, and 1051 containing all the tri- through octachloronaphthalenes was used as a standard. Recoveries of ^{13}C -labeled internal standards, which elute in the second fraction containing PCNs and non-orthocoplanar PCBs, were 77–95%. Reported concentrations were not corrected from the recoveries of internal standard. Recoveries of PCB and PCN congeners through the analytical procedure were 90 and 95%, respectively. Procedural blanks were passed through the whole analytical procedure to check for interferences and laboratory contamination. The detection limits of individual PCN and PCB congener varied depending on the sample mass, response factor, and interferences. Generally, the detection limit for individual congeners was 0.2 pg/g, on a wet weight basis. PCN and PCB congeners are represented by their IUPAC numbers throughout this manuscript.

Results and Discussion

Polychlorinated naphthalenes were found in all the fishes analyzed including those from Siskiwit Lake (Table 1). Concentrations of PCNs in fishes ranged from 19 to 31 400 pg/g, wet wt, depending on sampling location and species. Samples of walleye and carp from the Detroit River contained the greatest PCN concentrations, 31 400 and 26 400 pg/g, wet wt, respectively, whereas the lowest concentration (19 pg/g, wet wt) was observed in a northern pike fillet from a wetland in Michigan. PCN concentrations were correlated with lipid content of fish tissues ($p < 0.05$). Whole fish contained greater PCN concentrations than did fillets. For example, on a wet weight basis, whole lake trout from Siskiwit Lake contained 2–6-fold greater PCN concentrations than those in corresponding fillets. The concentrations of PCNs in fishes from the Detroit River were greater than those reported for several species of fishes from the Baltic Sea (8, 24).

Concentrations of total PCBs in fish were 100–1000-fold greater than that of total PCNs. PCB concentrations in fishes varied from 11 to 5600 ng/g, wet wt (Table 1). Concentrations of PCBs in walleye and carp (whole body) were 4500 and 3200 ng/g, respectively, which exceeded the tolerance limit recommended by the U.S. Food and Drug Administration (FDA) of 2000 ng/g, wet wt, for human consumption (25). A few studies have reported the occurrence of PCBs in fishes from Lake Superior including Siskiwit Lake (19, 26, 27). Concentrations of total PCBs in whole lake trout collected during the mid 1970s in Siskiwit Lake were 34 $\mu\text{g/g}$, lipid wt (26). The concentration of total PCBs observed in this study was 2-fold less than those reported for lake trout collected in 1975. Concentrations of selected PCB congeners have been reported in lake trout collected from Siskiwit Lake in 1983 (19). Concentrations of PCB congeners 101, 118, 137, 138, 180, and 187 measured in this study were 2–8-fold greater than those reported for lake trout collected in 1983.

Whole body concentrations of PCBs in lake trout from Lake Superior and Siskiwit Lake appeared to be similar. Nevertheless, lipid-normalized concentrations of PCBs in lake trout from Lake Superior were 9-fold less than those from Siskiwit Lake. This was unexpected because the atmosphere is thought to be the primary source of PCBs to Lake Superior and Siskiwit Lake. Since Siskiwit Lake is further away from point sources compared to Lake Superior, fishes from this remote lake are expected to contain similar or lesser concentrations to those in Lake Superior. Similarly, greater

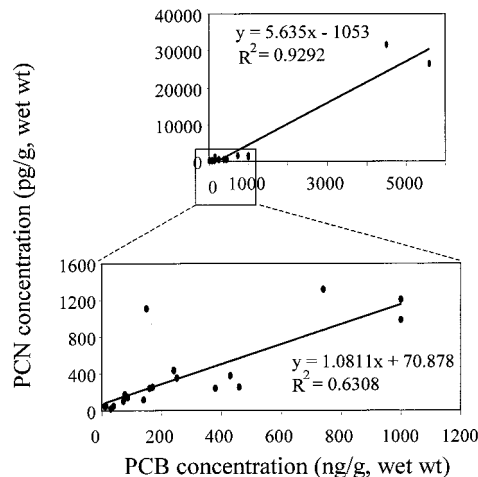


FIGURE 2. Relationship between PCB and PCN concentrations in fishes from Michigan waters.

concentrations of total PCBs in lake trout from Siskiwit Lake than those in Lake Superior have been reported earlier (26). A probable explanation for this difference is that lake trout from Siskiwit Lake grow two to three times slower than those from Lake Superior, i.e., Siskiwit Lake trout are two or three times older than Lake Superior fish of a same size. Earlier studies have suggested that the differences in depths and particle removal rates may contribute to the differences in the aqueous concentrations of PCBs in Siskiwit Lake and Lake Superior (19).

Lipid-normalized concentrations of PCNs in lake trout from Siskiwit Lake were 8-fold greater than those from Lake Superior. As mentioned above, differences in the age of the fish may have contributed to the differences in concentrations. Interestingly, the presence of PCNs in lake trout from Siskiwit Lake confirms that PCNs are also subjected to atmospheric transport to remote areas, in much the same manner as has been observed for PCBs.

Concentrations of total PCNs in Michigan fishes were significantly correlated with those of total PCBs (Figure 2). This suggests an association between the sources of these two classes of compounds in fishes. Similarly, air samples collected from Chicago exhibited a positive relationship between the concentrations of PCBs and PCNs (10). PCN congeners occur in technical PCB preparations such as Aroclors (6). Concentrations of total PCNs in Aroclors varied from 3.5 to 170 $\mu\text{g/g}$. Thus, the PCBs:PCNs ratios in Aroclors range from 1:0.000035 to 1:0.00017. The ratios of PCBs to PCNs in fishes varied from 1:0.0006 to 1:0.007, which were 4–40-fold greater than those of the maximum observed in technical PCB mixtures. In addition, profiles of PCN congeners in fishes varied widely (discussed below). These results suggest that, in addition to technical PCB preparations, several other sources such as Halowaxes and municipal waste incineration may have contributed to the concentrations of PCNs observed in fishes. Differences in the accumulation/metabolism of PCB and PCN congeners can contribute to the shift in the ratios discussed above, but no information is available on this regard.

Congener Profile. The composition of CN congeners in fishes varied among sampling locations, species, and tissue analyzed. Principal component analysis (PCA) of congener concentrations suggested that the data points could be grouped according to sampling locations (data not shown). A carp and a walleye from the Detroit River qualified statistically as outliers, using the Dixon test and PCA. Despite the high mobility of carp and walleye, great concentrations of both PCBs and PCNs in these fishes may suggest the presence of point sources of contamination and exposure in

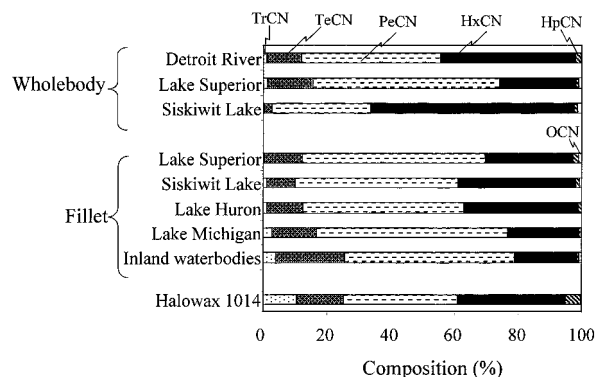


FIGURE 3. Composition (percent) of PCN homologues in fishes from Michigan waters and in Halowax 1014.

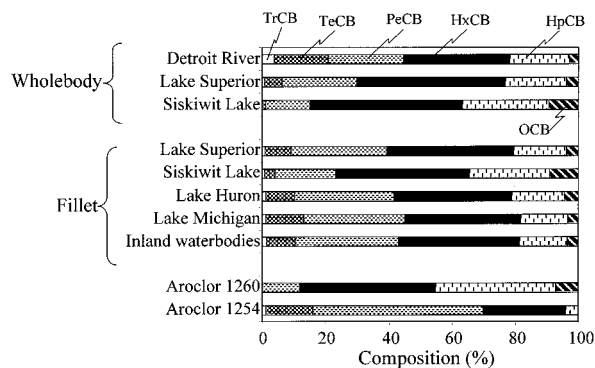


FIGURE 4. Composition (percent) of PCB homologues in fishes from Michigan waters and in Aroclors 1254 and 1260.

the Detroit River. An earlier study has reported the concentrations of PCNs and PCBs, in the order of a few $\mu\text{g/g}$, in sediments from the Detroit River (28). To describe homologue patterns of PCBs and PCNs, samples were grouped according to the locations of origin. For ease of discussion, all the inland fishes were grouped into one category. Whole fish and fillets were examined separately due to the differences in accumulation patterns of PCBs and PCNs and based on the implications for human and wildlife exposure scenarios.

Penta-CN congeners were the predominant homologues in all fishes except for whole lake trout from Siskiwit Lake, which had greater proportions of hexa-CN congeners (64% of total PCN concentrations) (Figure 3). The distribution of PCN homologues in fishes from the Detroit River was similar to that observed in corresponding sediment (28) and Halowax 1014, except for a lesser proportion of tri-CN congeners. Flounder collected from the Gdynia seaport in Poland contained PCN profiles similar to those in Halowax 1014 (24). A similar pattern was observed in fish from the Detroit River. Despite the geographical proximity to Lake Superior, lake trout from Siskiwit Lake contained a greater proportion of hexa-CN congeners (64%) than Lake Superior lake trout (24%). This observation suggests the possibility of a difference in the metabolic features or weathering/aging of lower chlorinated PCN congeners derived from the past inputs to Siskiwit Lake.

Among PCBs, hexa-CBs were the dominant congeners in fishes accounting for 34 to 48% of the total PCBs (Figure 4). Lake trout from Siskiwit Lake contained greater proportions of higher chlorinated homologues than that of fishes from other locations. This result was similar to those observed for PCNs.

Relative concentrations of individual PCN congeners in whole fish samples varied among sampling locations (Figure 5). Compared to those for whole fish samples, profiles of relative concentrations of PCN congeners in fillets were similar (Figure 7, Supporting Information). Hexa-CN con-

geners 71/72 (1,2,4,5,6,8-/1,2,4,5,7,8-) and 69 (1,2,3,5,7,8-) and penta-CN congeners 61 (1,2,4,6,8-) and 52/60 (1,2,3,5,7-/1,2,4,6,7-) were most abundant in whole carp from the Detroit River, accounting for 15, 13, 11, and 9% of the total PCN concentrations, respectively. This profile of hexa-CN is similar to that in Halowax 1014. Penta-CN congeners 52/60 accounted for 32% of the total PCN concentrations in whole lake trout from Lake Superior (Figure 5), whereas in lake trout from Siskiwit Lake 34 and 20% of the total PCN concentrations were contributed by hexa-CN congeners 66/67 (1,2,3,4,6,7-/1,2,3,5,6,7-) and 52/60, respectively. Earlier studies have reported the abundance of congeners 52/60 in fishes collected from the Baltic Sea (8, 12). Penta-CN congeners 52/60 are relatively less abundant in Halowax 1014 but have been reported to be formed during incineration of municipal solid waste (5). The abundance of congeners 52/60 in fishes from several locations suggests their relatively great bioaccumulation potential and sources originating from waste incineration. In fillets, congeners 52/60, 61, and 66/67 were the most abundant accounting for 15–28, 7–11, and 9–22% of the total PCN concentrations, respectively. In general, our results suggest that the profile of PCNs vary depending upon the sources of PCNs and fish species and that the congeners 52/60, 61, 66/67, 69, and 71/72 accounted for $58 \pm 10\%$ of the total PCN concentrations in fishes from Michigan waters.

Among PCB congeners, hexa-CB congener 153 (2,2,4,4',5,5'-) was the most abundant, followed by 138 (2,2',3,4,4',5'-) in both whole fish and fillets (Figure 6). These two congeners collectively accounted for $25 \pm 5\%$ of the total PCB concentrations in fishes. Fishes from the Detroit River contained several tri-, tetra-, and penta-CB congeners, which were relatively less abundant in fishes from other sampling locations. This suggests the exposure of fishes to recent sources of PCBs in the Detroit River ecosystem. In contrast, fishes from Siskiwit Lake contained a predominant proportion of higher chlorinated congeners than in fish from other locations studied (Figure 6). The relative abundance of individual PCB congeners in fillets was similar among the lakes (Figure 8, Supporting Information).

Toxic Potential. All PCN congeners are planar and several of them exhibit Ah-receptor mediated cytochrome P450 induction, analogous to TCDD (21). Toxic equivalency factors (TEFs), which are fractional potencies of individual congeners relative to TCDD, have been reported for several PCN congeners based on in vitro bioassays using H4IIE rat hepatoma cells (20). 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 (20). This permitted the estimation of TEQs for PCBs and PCNs by summing the product of concentrations and their corresponding TEFs. However, it should be noted that TEFs for all PCN congeners are not available due to the lack of sufficient quantities of pure, well-characterized individual congeners.

Concentrations of PCN congeners that elicit Ah-receptor mediated mechanism of toxic action and their corresponding TEQs are shown in Table 2. The mean (\pm SD) TEQs contributed by PCNs in fishes from Michigan waters was 1.2 ± 3.2 pg/g, wet wt. Among fish samples analyzed, the greatest contribution of PCNs to TEQs was observed in whole carp and walleye from the Detroit River (11 pg/g wet wt). Concentrations of PCN-TEQs in fish fillets ranged from 0.007 (in largemouth bass from Pine River) to 0.65 pg/g, wet wt (in lake trout from Thunder Bay, Lake Huron). PCN-TEQs in fishes from inland waters and Siskiwit Lake were similar. Overall, PCN congeners 66/67 and 69 accounted for greater than 80% of the TEQs contributed by PCNs. Particularly, congeners 66/67 contributed 55–70% of the PCN-TEQs in fishes except those from Detroit River and inland waters, in

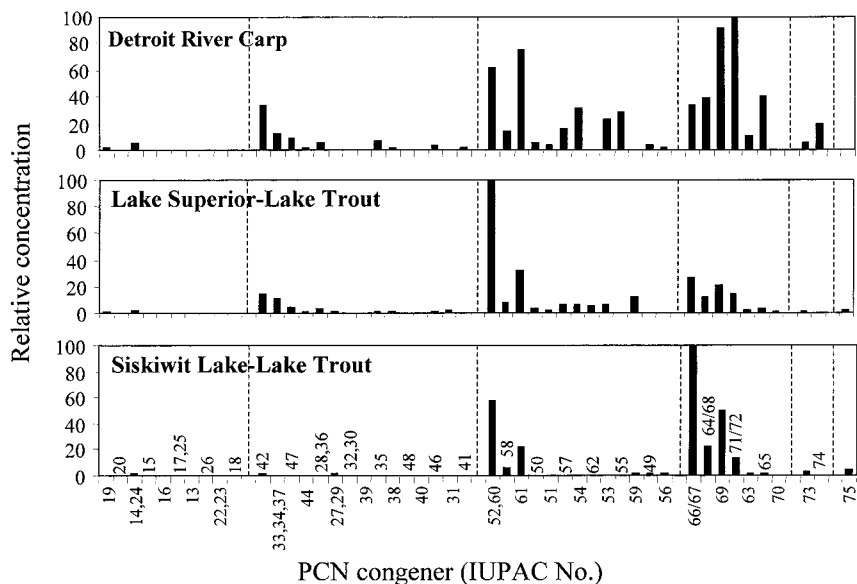


FIGURE 5. Relative concentrations of PCN isomers and congeners in whole body of fishes collected from Detroit River, Lake Superior, and Siskiwit Lake. Concentrations were normalized relative to that of the most abundant congener, which was treated as 100.

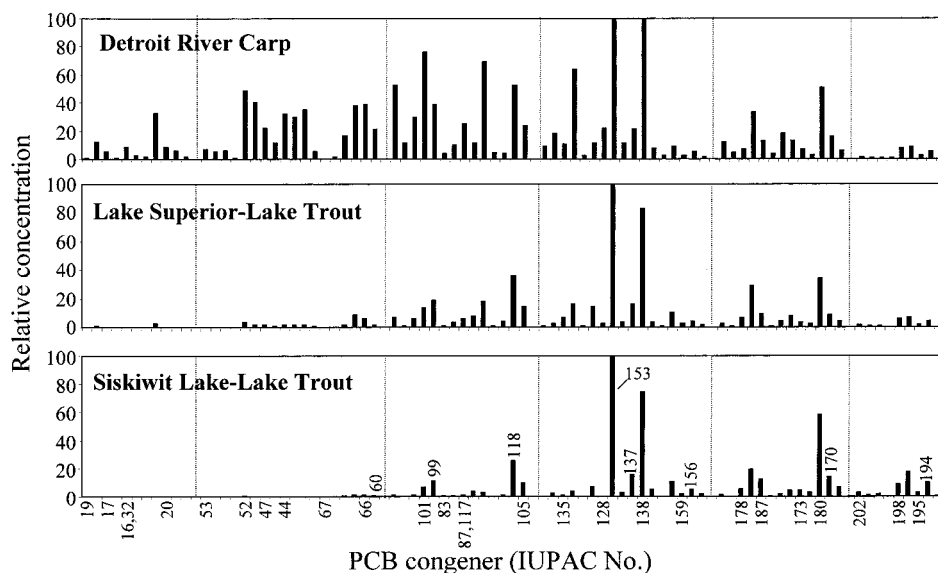


FIGURE 6. Relative concentrations of PCB isomers and congeners in whole body of fishes collected from Detroit River, Lake Superior, and Siskiwit Lake. Concentrations were normalized relative to that of the most abundant congener, which was treated as 100.

which congener 69 accounted for 50–60% of the TEQs contributed by PCNs.

Mono- and non-ortho-PCB congeners were observed in all the fish samples analyzed including those from Siskiwit Lake (Table 3). The distribution of non-ortho-coplanar PCBs was in the order of 77 > 126 > 169, a pattern similar to those present in technical PCB preparations (22). However, the order of concentrations of non-ortho-coplanar PCBs in whole lake trout from Siskiwit Lake was 169 > 126 > 77, which is different from those observed in samples from other locations and in technical preparations. Fillets of lake trout from Siskiwit Lake contained a greater proportion of congener 77 than 126 or 169. The pattern of coplanar PCBs observed in lake trout from Siskiwit Lake reflects long-term accumulation from past inputs rather than recent exposure. This corresponds with the accumulation of greater chlorinated congeners of PCBs and PCNs in lake trout from Siskiwit Lake compared to those from other locations.

In the past decade, several different TEF schemes have been developed for coplanar PCBs (29). TEF values derived

for coplanar PCBs varied by severalfold depending upon the type of bioassay systems, end points, and calculation methods of relative potencies (29, 30). For comparison of TEQs contributed by different types of compounds in species collected from a given location, it would be appropriate to use TEFs derived using similar bioassays. Since TEFs for PCNs were derived from *in vitro* H4IIE bioassays (20, 21), we used H4IIE bioassay derived TEFs for PCBs to estimate PCB-TEQs (31). H4IIE bioassay derived TEFs for coplanar PCBs were 10–100-fold less than those proposed as international TEFs (I-TEFs). When H4IIE derived TEFs were used, TEQs contributed by coplanar PCBs in fishes were in the range of 0.06 to 11 pg/g, wet wt (Table 3). This range is similar to those found for PCNs. Non-ortho-coplanar congener 126 accounted for, on average, 88% of the PCB-TEQs, which was followed by congeners 156 (6.8%) and 105 (4%). Overall, when TEFs derived from similar bioassays were used, contributions of PCBs and PCNs to sum TEQs (sum of TEQs of PCBs and PCNs) in fishes were 86% (43–98%) and 14% (2–57%), respectively. Interestingly, contribution of PCNs to sum TEQs

TABLE 2. Mean Concentrations of Dioxin-Like PCN Congeners and Their 2,3,7,8-TCDD Equivalents (pg/g, Wet Wt) in Fishes from Michigan Waters

congener	TEF ^e	wholebody						fillet									
		Detroit River (3) ^a		Lake Superior (2)		Siskiwit Lake (1)		Lake Superior (2)		Siskiwit Lake (3)		Lake Huron (2)		Lake Michigan (1)		inland waterbodies (8)	
		concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs
40	0.00016	ND ^f	ND	ND	ND	ND	ND	ND	ND	0.03	<0.0001	0.91	<0.0001	ND	ND	0.18	<0.0001
54	0.00017	420	0.07	5.8	0.001	ND	ND	2.95	0.0005	0.74	0.0001	10	0.0017	8.1	0.001	2.2	0.0004
63	0.002	330	0.66	3.9	0.008	0.69	0.0014	2.94	0.006	0.54	0.001	20	0.034	8.1	0.016	1.4	0.003
66/67 ^b	0.0023	890	2.1	29	0.066	87	0.2	31	0.071	13	0.029	180	0.41	110	0.25	6	0.014
68 ^c	0.00015	1300	0.19	12	0.002	19	0.002	8.9	0.001	5.5	0.0008	45	0.007	43	0.006	4.2	0.0006
69	0.002	2400	4.7	21	0.042	43	0.09	14	0.028	7.7	0.015	77	0.15	58	0.12	9.3	0.019
70	0.00059	ND	ND	0.69	0.0004	ND	ND	0.43	0.0003	0.29	0.0002	1.8	0.001	0.64	0.0004	ND	ND
71/72 ^d	0.000007	3000	0.02	13	<0.0001	11	<0.0001	7.8	<0.0001	4.9	<0.0001	43	0.0003	47	0.0003	14	0.0001
73	0.001	80	0.08	3.1	0.003	2.2	0.002	2.9	0.003	0.63	0.0006	8.2	0.008	4.8	0.005	0.37	0.0004
total			7.8	0.12		0.29		0.11		0.047		0.63		0.4		0.04	

^a Values in parentheses indicate the number of samples. ^b TEF for 66/67 represents mean TEF of each congener. ^c Congener 68 coelutes with 64, but the TEF value is available only for congener 68. ^d Congener 71 is inactive (ref 21), but a mixture of 71/72 was active (ref 20). ^e TEFs for PCNs are from ref 20 and 21. ^f ND = not detected; <0.0001 indicates that the congeners were detected but at attogram levels.

TABLE 3. Mean Concentrations of Non- and Mono-Ortho-PCB Congeners and Their H4IIE-in Vitro Bioassay TEF Based 2,3,7,8-TCDD Equivalents (pg/g, Wet Wt) in Fishes from Michigan Waters

congener	H4IIE-TEF ^a	wholebody						fillet									
		Detroit River (3) ^b		Lake Superior (2)		Siskiwit Lake (1)		Lake Superior (2)		Siskiwit Lake (3)		Lake Huron (2)		Lake Michigan (1)		inland waterbodies (8)	
		concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs
77	1.8E-05	3980	0.07	290	0.005	60	0.001	475	0.009	46	0.001	1600	0.029	3810	0.07	88	0.002
126	2.2E-02	256	5.60	120	2.7	97	2.1	72	1.58	17	0.37	220	4.76	430	9.46	13	0.283
169	4.7E-04	24	0.01	35	0.02	110	0.05	16	0.007	19	0.009	41	0.019	43	0.02	1.3	0.001
105	8E-06	50 900	0.41	8700	0.07	9400	0.08	8300	0.067	1400	0.011	20 000	0.16	32900	0.26	2500	0.02
118	3.5E-07	119 000	0.05	21 600	0.01	23 900	0.01	17 300	0.007	3200	0.001	41 800	0.017	64 800	0.03	7100	0.003
156	5.5E-05	13 700	0.69	2500	0.13	4800	0.24	1800	0.09	570	0.028	4180	0.209	6300	0.32	880	0.044
total			6.9	2.9		2.5		1.8		0.42		5.2		10		0.352	

^a H4IIE-TEFs for PCBs are from ref 31. ^b Values in parentheses indicate the number of samples.

TABLE 4. Mean Concentrations of Non- and Mono-Ortho-PCB Congeners and Their I-TEF Based 2,3,7,8-TCDD Equivalents (pg/g, Wet Wt) in Fishes from Michigan Waters

congener	I-TEF ^a	wholebody						fillet									
		Detroit River (3) ^b		Lake Superior (2)		Siskiwit Lake (1)		Lake Superior (2)		Siskiwit Lake (3)		Lake Huron (2)		Lake Michigan (1)		inland waterbodies (8)	
		concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs	concn	TEQs
77	0.0001	3980	0.40	290	0.29	60	0.01	475	0.05	46	0.005	1600	0.16	3810	0.38	88	0.009
126	0.1	256	25.6	120	12	97	9.7	72	7.2	17	1.7	220	22	430	43	13	1.3
169	0.01	24	0.24	35	0.35	110	1.1	16	0.16	19	0.19	41	0.41	43	0.43	1.3	0.013
60	0.0001	39 800	3.98	1200	0.12	310	0.03	1400	0.14	150	0.015	4000	0.4	10 800	1.1	570	0.057
105	0.0001	50 900	5.09	8700	0.87	9400	0.94	8300	0.83	1400	0.14	20 000	2	32 900	3.3	2500	0.252
118	0.0001	119 000	11.9	21 600	2.2	23 900	2.4	17 300	1.7	3200	0.32	41 800	4.2	64 800	6.5	7100	0.71
156	0.0005	13 700	6.85	2500	1.3	4800	2.4	1800	0.9	570	0.28	4180	2.1	6300	3.2	880	0.44
total			54	17		17		11		2.6		31		58		2.8	

^a I-TEFs for PCBs are from ref 29. ^b Values in parentheses indicate the number of samples.

in fishes from the Detroit River was similar to or greater than those contributed by coplanar PCBs.

Earlier studies have used I-TEFs to estimate TEQs of coplanar PCBs, which were compared with those estimated for PCNs (8, 11). Moreover, I-TEFs have also been suggested for use in risk assessment (29). When I-TEFs were used to estimate PCB-TEQs, PCB-derived TEQs were increased by 5–10-fold compared to those generated using H4IIE-bioassay derived TEFs. Walleye from the Detroit River contained the greatest PCB-TEQs of 79 pg/g, wet wt (Table 4). TEQs contributed by PCBs in fillets ranged from 0.46 to 58 pg/g, wet wt. PCB congener 126 accounted for 50–83% of the TEQs

contributed by PCBs in fishes from most locations except those from the Pine River and the Detroit River, where its contribution was in the range of 29–42%. Other major contributors to PCB-TEQs are mono-ortho-congeners 118 (7–36%) and 156 (4–21%), which collectively accounted for, on average, 27% of the PCB-TEQs. Overall, when I-TEFs were used to estimate TEQs for PCBs, contribution of PCNs to sum TEQs in fishes from Michigan waters were in the range of 0.2–14% (mean: 2.6%). This is similar to that reported for fishes from the Baltic Sea, in which PCN congener 66/67 accounted for 0.3 to 13% of the total TEQs (8). Relatively greater contributions of PCNs to TEQs (13–14%) were found

near industrialized urban areas such as the Detroit River. Overall, the results of this study suggest that PCNs are widespread contaminants in fishes and that their profile varies depending on the sources of contamination. In some industrialized locations, contributions of PCNs to TEQs are great enough to be of concern.

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Supporting Information Available

Figures of relative concentrations of PCN (Figure 7) and PCB (Figure 8) isomers and congeners in filets of lake trout collected from Lakes Huron and Michigan and Siskiwit Lake. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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