POLYCHLORINATED NAPHTHALENES IN SEDIMENT, FISHES AND FISH-EATING WATERBIRDS FROM MICHIGAN WATERS OF THE GREAT LAKES

Kurunthachalam Kannan[1], Takashi Imagawa[2], Nobuyoshi Yamashita[2], Akira Miyazaki[2] and John P. Giesy[1]

[1]National Food Safety and Toxicology Center, Michigan State University, East Lansing, MI, USA
[2]National Institute for Resources and Environment, 16-3 Onogawa, Tsukuba 305-8569, Japan

Introduction

Polychlorinated naphthalenes (PCNs), similar to polychlorinated -dibenzo-*p*-dioxins (PCDDs), -dibenzofurans (PCDFs), and -biphenyls (PCBs), are ubiquitous, persistent, bioaccumulative and toxic environmental contaminants [1-5]. While studies have reported the occurrence of PCDDs, PCDFs and PCBs in fish, fish-eating water birds and sediment from the Great Lakes, information pertaining to the occurrence and dioxin-like activities of PCNs are limited. In this study, we report the concentrations of PCNs in fishes, fish-eating water birds such as double-crested cormorants (*Phalacrocorax auritus*) and herring gulls (*Larus argentatus*) and sediment collected from selected locations of Michigan coastal waters of the Great Lakes. Samples were collected from both point and non-point source areas of contamination to evaluate the extent of spatial contamination by these compounds. In addition, concentrations of aryl hydrocarbon receptor (AhR) active congeners of PCDDs, PCDFs and PCBs were measured in selected samples to estimate 2,3,7,8-tetrachlorodibenzo-*p*-dioxin equivalents (TEQs). Contributions of PCNs to TEQs were compared with those estimated for PCBs, PCDDs and PCDFs to elucidate relative significance of each group of compounds to exert dioxin-like toxicity.

Materials and Methods

Fishes from the Great Lakes (Lakes Superior, Michigan and Huron) and inland Michigan lakes and rivers were collected with electro-shocking gear or gill nets or trawls or trap nets during April-September of 1996 and 1997 (for details see Table 1 and Figure 1). Fishes were analyzed as 'skin on' or 'skin-off' fillets or as whole fish. Eggs of double-crested cormorants and herring gulls were collected from Little Charity Island and Scare Crow Island in Lake Huron and Taquamenon Island in Lake Superior. Surface sediments were collected from the Detroit and Rouge Rivers in Michigan and off of Muskegon in Lake Michigan using a Ponar grab sampler. Sampling locations of sediment, fish and birds are shown in Figure 1.

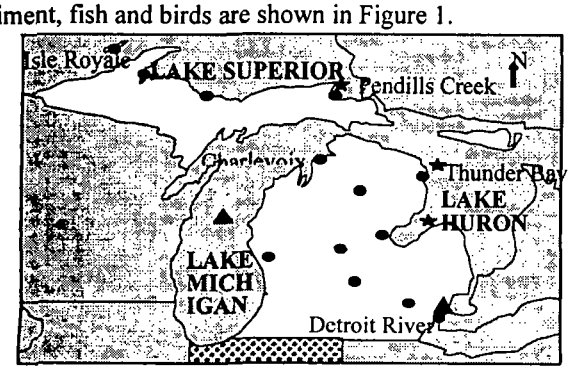

FIGURE 1. Map of Michigan showing sampling locations of sediment (triangle), fish (circle) and birds (star).

Chloronaphthalene (CN), chlorobiphenyl (CB) and 2,3,7,8-substituted PCDD and PCDF congeners were analyzed following the method described elsewhere [4] with some modifications. 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). Target compounds were determined by selected ion monitoring (SIM) at the two most intensive ions of the molecular ion cluster. Quality control criteria for positive identification of target compounds include signal to noise ratio of over three, isotope ratios of the two ions monitored for each compound within 15% of the theoretical chlorine values and the retention time. Recoveries of ^{13}C-labelled internal standards, which elute in the second fraction containing PCNs and non-*ortho* coplanar PCBs, were 77-95%. Recoveries of PCB, PCN, PCDD and PCDF congeners through the analytical procedure were between 90 and 95%. The detection limits of individual PCN and PCB congener varied, but were generally 0.2 pg/g, on a wet weight basis.

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 during Apr-Sep 1996 and 1997.

Waterbody	Location	Species	Sample type[a]	Weight (g)	Fat (%)	Total PCBs (ng/g)	Total PCNs (pg/g)
Pine River	Below Alma Dam	Largemouth bass	F	960	0.67	140	110
Pine River	Below Alma Dam	Carp	Fs	2395	1.52	240	430
Detroit River	Grassy Island	Walleye	W	860	12.3	4500	31400
Grand River	Moores River Impoundment	Largemouth bass	F	600	0.77	170	250
Topico Wetland	Bay County	Northern pike	Fs	1650	0.57	31	19
Maceday Lake	Oakland County	Northern pike	Fs	1880	0.59	140	110
Lake Huron	Thunder Bay	Lake whitefish	F	1660	9.01	150	1100
Lake Huron	Thunder Bay	Lake trout	F	1370	13.8	1000	980
Lake Michigan	Charlevoix	Lake trout	F	1870	20.7	1000	1200
Lake Superior	Keweenaw Bay	Lake whitefish	F	730	8.02	160	240
Lake Superior	Keweenaw Bay	Lake trout	W	2000	16.8	430	370
Lake Superior	Marquette	Lake trout	W	1300	14.6	250	340
Lake Superior	Pendills Creek	Coho salmon	F	1230	1.1	380	240
Muskegon River	Newaygo	Redhorse sucker	F	1040	0.6	77	160
Siskiwit Lake	Isle Royale	Lake trout	F	850	3.61	87	140
Siskiwit Lake	Isle Royale	Lake trout	F	1250	0.78	73	95
Siskiwit Lake	Isle Royale	Lake trout	F	2100	1.42	40	41
Siskiwit Lake	Isle Royale	Lake trout	W	1300	2.44	460	250
N. Au Sable R.	Lovells	Brown trout	F	250	4.93	14	35
N. Au Sable R.	Lovells	Brown trout	F	450	3.43	11	44
Detroit River	Grassy Island	Carp	W	1520	5	740	1310
Detroit River	Grassy Island	Carp	W	1820	19.8	5600	26400

[a]F=Fillet; Fs=Skin-on-fillet; W=Whole body

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. Concentrations of total PCBs in fish were 100 to 1000-fold greater than that of total PCNs. PCB concentrations in fishes varied from 11 to 5,600 ng/g, wet wt (Table 1). Concentrations of PCBs walleye and carp (whole body) were 4500 and 3200 ng/g, respectively.

Penta-CNs were the predominant homologs in all fishes except for whole lake trout from Siskiwit Lake, which had greater proportions of hexa-CNs (64% of total PCN concentrations).

TABLE 2. Concentrations of PCN homologs in sediments (ng/g, dry wt) collected from Detroit and Rouge Rivers.

Location	Tri-CN	Tetra-CN	Penta-CN	Hexa-CN	Hepta-CN	OCN	Total PCNs
N. Peche Island	0.002	0.0252	0.0097	0.0241	0.0173	<0.001	0.08
S. Peche Island	0.28	0.58	0.76	1	0.64	0.59	3.85
Scott middle ground	1.84	4.01	6.56	5.49	1.274	1.2875	20.46
Belle Isle South	0.02	0.051	0.056	0.028	0.027	<0.001	0.18
GLS Shoal - B	9.11	43	73	47	12	2.6	186.71
Penn Dixie-A	1.89	3.65	6.94	7.89	2.07	1.07	23.51
CG-B	7.15	13.15	35	44	6.58	1.011	106.89
Powerline - Inner	0.78	5.61	26.31	33.09	3.75	0.72	70.26
Ont-Powerline	0.57	1.75	3.2	3.07	0.86	0.49	9.94
Upper Rouge B	1.37	2.6	6.07	6.08	1.81	0.247	18.18

TABLE 3. 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 in May 1998.

Species	Sampling location	n	Fat (%)	Total PCBs	Total PCNs	2,3,7,8-PCDDs	2,3,7,8-PCDFs
Double crested cormorant	Little Charity Is., Lake Huron	3	4-5.2 (4.6)	1250,000-2370,000 (1650,000)	620-2430 (1240)	25-97 (62)	28-76 (48)
Herring gull	Little Charity Is., Lake Huron	2	8.1-9.6 (8.9)	1000,000-3010,000 (2000,000)	430-720 (575)	20-55 (37)	3.4-12 (7.7)
Double crested cormorant	Scare Crow Is., Lake Huron	3	5.6-6.5 (6)	1220,000-1680,000 (1420,000)	520-1850 (1050)	7.4-26 (16)	22-57 (37)
Herring gull	Scare Crow Is., Lake Huron	2	9.8-10.6 (10.2)	3600,000-3950,000 (3770,000)	390-470 (430)	12-27 (20)	8.7-26 (17)
Double crested cormorant	Taquamenon Is., Lake Superior	3	5.3-6.6 (5.8)	1130,000-2960,000 (1790,000)	380-1950 (1140)	18-37 (26)	20-37 (27)
Herring gull	Taquamenon Is., Lake Superior	2	10.7-11.9 (11.3)	380,000-7930,000 (4150,000)	83-1290 (690)	64 (64)	35 (35)

Values in parentheses indicate mean.

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, 71/72 accounted for 58±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. These two congeners collectively accounted for 25±5% of the total PCB concentrations in fishes. The mean TEQs contributed by PCNs in fishes from Michigan waters was 1.2±3.2 pg/g, wet wt. The greatest contribution of PCNs to TEQs was observed in whole carp and walleye from the Detroit River (11 pg/g wet wt). Interestingly, contribution of PCNs to sum TEQs in fishes from the Detroit River was similar to or greater than those contributed by PCBs.

Concentrations of PCNs in sediments from Detroit and Rouge Rivers ranged from 0.08 to 190 ng/g, dry wt (Table 2). The lowest concentrations were found in sediments collected in Peche Island in the Detroit River. Penta- and hexa-CNs accounted for a major portion of the total PCNs in sediments. Sediments collected from a non-point source area of contamination in Lake Michigan (off Muskegon) contained PCN concentrations in the range of 0.31-0.78 ng/g, dry wt. Tetra- and penta-CNs were the predominant congeners in this non-point source location. TEQs contributed by PCNs in sediments from the Detroit River were greater than those contributed by PCBs, PCDDs and PCDFs. This suggests the presence of localized sources of PCN contamination in the Detroit River.

Concentrations of PCNs in eggs of double-crested cormorants and herring gulls ranged from 83 to 2430 pg/g, wet wt (Table 3). These concentrations were approximately 1000-fold less than those of PCBs and 10-100 fold greater than those of PCDDs and PCDFs. TEQs of PCNs in eggs ranged from 0.89 to 1.5 pg/g, wet wt, which were 2-3% of the sum of TEQs of PCBs, PCDDs, PCDFs and PCNs.

Since PCNs are planar, they tend to bind strongly to sediment organic matter. Therefore, sediment can act as a sink for PCNs in the environment. Alternatively, sediments can act as a source of PCNs to benthic organisms including fish. Therefore, bottom-feeding fish from localized areas of contamination can accumulate high concentrations of PCNs. In such locations, the relative contribution of PCNs to TEQs may overwhelm those due to PCBs, PCDDs or PCDFs.

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