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Exposure of Remote Maritime Populations to Coplanar PCBs

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Two remote maritime populations were evaluated for their biological exposure to organochlorines in 1989-1990. Because of their high intake of seafood, these two populations have high biological levels. One hundred nine breast milk samples from Inuit women from Arctic Québec were analyzed to determine levels of polychlorodibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and coplanar polychlorinated biphenyls (PCBs) including non-*ortho*, mono-*ortho*, and di-*ortho* congeners. Total 2,3,7,8-tetrachlorodibenzo-*p*-dioxin equivalents (TEqs) for PCBs were 3.5 times higher in Inuit milk samples than in 96 Caucasian milk samples. Among the 185 fishermen from the Lower North Shore of the Gulf of the St. Lawrence River, we evaluated 10 highly exposed fishermen for their coplanar PCB blood levels. Total TEqs were 900 ng/kg for highly exposed individuals with 36 ng/kg for controls. In these two nonoccupationally exposed populations, coplanar PCBs make a larger contribution to the TEq than PCDDs and PCDFs. However, the mono-*ortho* penta CB No. 118 is the major contributor for the total toxicity.

Introduction

Fish consumption is a major contributor of organochlorinated compound (OCs) intake of humans. To mimimize human exposure, regulations on fish contamination in Canada have been set at 2mg/kg for polychlorinated biphenyls (PCBs) and 20 ng/kg for (2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). Of all foods for the general Canadian population, fish contains the highest levels of PCBs (*1*), and one of the highest for polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (*2*). Because the daily intake of fish products in Canada by the general population is only moderate, i.e, about 12 g (*3*), the percentage daily intake of these contaminants from fish is not high. However, various groups and communities consume large quantities of fish (e.g., sportsfishermen, commercial fishermen, and native peoples), and these individuals are potentially highly exposed to these contaminants.

In the Province of Québec, two remote populations are of special concern. About 6500 Inuit people of Arctic Québec are scattered in 14 communities along the 1500 km of seashore. Arctic Québec is located between 55° and 63° north latitude (Fig. 1). The main source of proteins and lipids for these people arises from fish (Arctic char, cod) and sea mammal consumption (seal, beluga, walrus). The second population is 2000 km north east from Montréal on the north shore of the Gulf of the St. Lawrence River. Fishing is the main activity of these 6500 people (14 settlements) of Caucasian origin. These two populations are linked to the southern part of Canada only by plane. Because dietary habits of these populations are based principally on seafood, we decided to evaluate their biological exposure for different contaminants including organochlorines.

Organochlorines are part of a group of halogenated aromatic hydrocarbons (HAHs) and consist of chlorinated pesticides, PCBs, and by-products of industrial processes such as furans and dioxins. PCBs, PCDDs and polychlorinated dibenzofurans (PCDFs) are probably the most toxic organochlorine compounds. Recent developments in experimental toxicology gave convincing evidence that these toxic halogenated aromatic hydrocarbons have common toxic properties due to a common receptor-mediated mechanism of action (*4*). Toxic equivalent factors (TEFs) were developed for PCDDs and PCDFs and more recently for PCBs (*5*). Compared with 2,3,7,8-TCDD toxicity, specific PCB congeners have TEF values ranging from 0.1 for non-*ortho* coplanar 3,3,,4,4',5,-penta CB (IUPAC no. 126) to 0.00002 for di-*ortho* coplanar PCBs, which are the predominant congeners found in humans. In human tissues and fluids of nonoccupationally exposed populations, recent work shows that coplanar PCBs are present at higher levels than dioxins and furans and, based on the TEF concept, they account for the majority of possible toxic effects (*6–8*).

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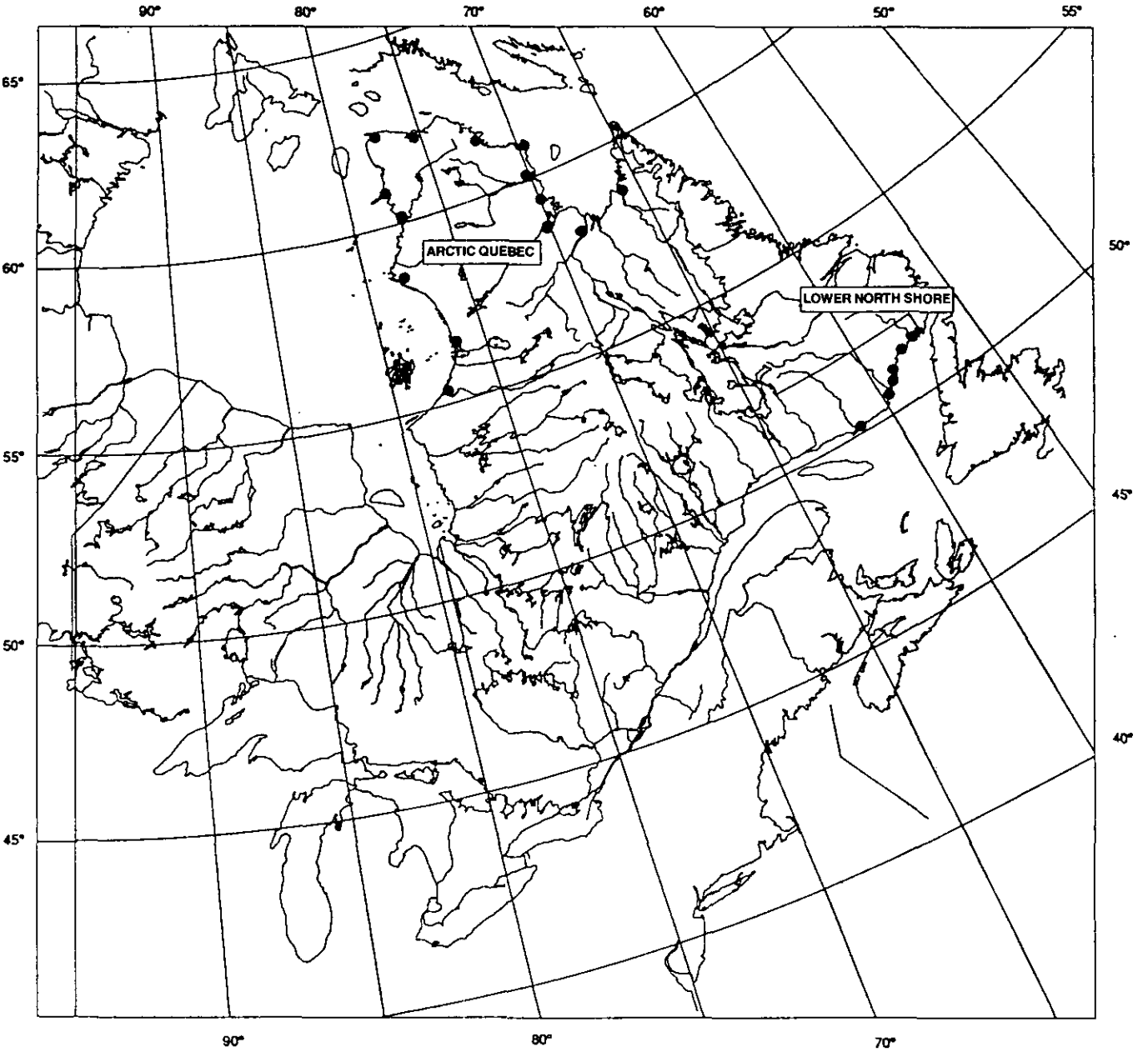

FIGURE 1. Geographical locations of the two populations studied.

This paper presents data on coplanar PCB levels in the breast milk of the Inuit population of Arctic Québec and in the blood of fishermen of the Gulf of the St. Lawrence River in comparison with nonexposed populations. We also discuss the relative importance of these compounds with PCDD and PCDF levels.

Populations and Methods

Populations and Sampling

Inuit Study. Between July 1989 and July 1990, 224 live births occurred among the Inuit studied in Arctic Québec. One hundred nineteen babies were breast fed and 109 of these Inuit women provided us with a 60-mL milk sample collected within the first 3 days after delivery. Chlorinated pesticides and seven PCB congeners were quantitated in these 109 milk samples. Forty randomly selected individual subsamples were used for coplanar PCB and PCDD–PCDF determination analyses, 35 other subsamples were used for complementary measurement of the 118 and 170 (IUPAC nos.) congeners.

Fishermen Study. One hundred eighty-five volunteers (fishermen and their spouses) from 7 of the 14 settlements were randomly selected within the local Fishermen Association list. Blood samples were collected in March 1990 for various analytes (organochlorines, heavy metals, biochemistry, biomarkers). For coplanar PCB and PCDD/PCDF determination, only those 10 individuals with the highest total PCB levels were chosen. Because a more complete evaluation is in progress, only preliminary results on coplanar PCBs are presented. Among the three

Table 1. Coplanar PCBs in the breastmilk of Inuit women and Caucasian women, Québec, Canada (lipid basis).

		Arctic (Inuit) Québec				Québec (Caucasian)			
PCB congeners	TEFs	*n*	Mean	95%CI	TEqs	*n*	Mean	95%CI	TEqs
Non-*ortho*-Coplanar PCBs			ng/kg (ppt)		ng/kg (ppt)		ng/kg (ppt)		ng/kg (ppt)
3,3',4,4' CB (77)	0.01	40	24.7	19.6–29.8	0.25	16	8.1	6.7–9.4	0.08
3,3',4,4',5 CB (126)	0.1	40	209.3	165.2–253.4	20.93	16	80.4	64.8–96.2	8.05
3,3'4,4',5,5' CB (169)	0.05	40	220.9	185.2–256.6	11.04	16	32.7	26.8–38.7	1.63
Mono-*ortho*-Coplanar PCB			μg/kg (ppb)		ng/kg (ppt)		μg/kg (ppb)		ng/kg (ppt)
2,3',4,4',5 CB (118)	0.001	35	58.7	39.1–78.3	58.70	16	17.4	14.0–20.9	17.40
Di-*ortho*-Coplanar PCBs			μg/kg (ppb)		ng/kg (ppt)		μg/kg (ppb)		ng/kg (ppt)
2,2',3,4,4',5' CB (138)	0.00002	109	230.6	194.2–266.9	4.61	16	38.9	29.7–48.2	0.78
2,2',4,4',5,5' CB (153)	0.00002	109	394.8	328.2–461.4	7.91	16	37.4	26.7–48.1	0.75
2,2',3,3',4,4',5 CB (170)	0.00002	35	45.9	34.4–57.5	0.92	16	10.3	8.3–12.2	0.21
2,2',3,4,4',5,5' CB (180)	0.00002	109	191.2	154.1–228.3	3.82	16	20.2	15.7–24.7	0.40

Abbreviations: PCB, polychlorinated biphenyl; TEF, toxic equivalency factor; TEq, TCDD equivalent, CI, confidence interval.

non-*ortho* coplanar PCBs only the penta CB (no. 126) and hexa CB (no. 169) have been analyzed.

Laboratory Procedures

2,3,7,8-Chloro-substituted congeners of PCDDs and PCDFs, coplanar PCBs 3,3',4,4'-tetra CB,3,3',4,4',5-penta CB, and 3,3',4,4',5,5'-hexa CB were determined by high-resolution mass spectroscopy (HRMS). Milk samples, 25–40 g, were fortified with nine $^{13}C_{12}$-labeled PCDD and PCDF and three $^{13}C_{12}$-PCB internal quantitation standards. These internal standards represented each of the PCDD and PCDF homologs and the three coplanar PCBs of interest (IUPAC nos. 77, 126, and 169). The milk samples were mixed with an aqueous solution of sodium oxalate, ethyl ether and ethanol, and then extracted with hexane. The hexane extracts were washed and then concentrated to constant weight, and the percent lipid was determined gravimetrically.

The lipid residue was diluted in hexane and was cleaned using a sulfuric acid-silica gel slurry followed by elution through a neutral/acid-silical gel chromatographic column. Subsequent clean-up steps included separation of the PCDDs/PCDFs and coplanar PCBs from interferences using neutral alumina 22 and Carbopack C/Celite columns. The eluent from the Carbopack C/Celite was concentrated to 5 μL. The final extracts were analyzed using a VG 70250s HRMS at a mass resolution of 10,000. Separation was achieved using a 60-m DB-5 column. Two ions characteristic of each PCDD and PCDF homolog, the coplanar PCBs, and the respective internal quantitation standards were monitored for each analysis. Identification of the PCDDs, PCDFs, and coplanar PCBs was based on retention time information and the comparison of the ratios of the characteristic ions with theoretical values.

For blood plasma analyses, isotope-labeled $^{13}C_{12}$-PCDD, $^{37}Cl_4$-PCDF, and $^{13}C_{12}$-PCBs were added followed by ethanol and ammonium sulfate, and the mixture was extracted with hexane. After weighing the total hexane extracts to constant weight for the sample lipid content, the extract was defatted with H_2SO_4, purified on columns of silicate, Florisil, and carbon, and measured by GC–MS according to Ryan et al. (*9*). The same extract was used to measure both the PCDDs/PCDFs and coplanar PCBs using the isotope dilution MS technique.

All data presented in Tables 1 and 2 are arithmetic means. Comparison data for the Inuit study are taken from a provincial survey (536 women) from which 16 pools of 6 milk samples each (96 milk samples) were constituted and analyzed at the same period by the same laboratory. In the fishermen study we used comparison data from a pool of 10 plasma samples collected in 1988 from Red Cross donors from Ontario. For mono-*ortho* and di-*ortho* coplanar PCB comparison, we used new data from 59 blood samples collected in 1989 among firefighters in Québec.

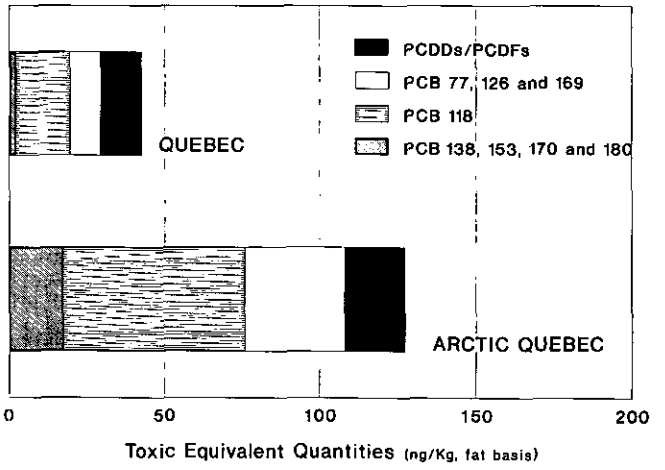

FIGURE 2. Relative toxicity of coplanar polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins, and polychlorinated dibenzofurans in breastmilk samples of Caucasian and Inuit women, Québec, Canada.

Levels of PCBs and PCDDs/PCDFs were detected in all samples except for the 59 control blood samples, where mean values of PCB congeners were calculated only on plasma samples with levels above the detection limit (0.1 μg/L). TEFs used in Table 1 are international values for PCDDs and PCDFs (*4*) and those proposed by Safe for PCBs (*5*).

Results and Discussion

As shown in Table 1, levels of non-*ortho* coplanar PCBs range from 24.7 to 220.9 ng/kg for Inuit women, three times more than comparison levels except for the hexa CB (no.169), which is seven times higher in Inuit samples. These differences are also observed for mono-*ortho* and di-*ortho* coplanar PCBs with ratios ranging from 1/3 (no. 118) to 1/10 (nos. 153 and 180).

The pattern of distribution of the three non-*ortho* coplanar PCBs in Inuit mothers' milk is different from that of Caucasian

Table 2. Coplanar PCBs in plasmas of fishermen from the Gulf of the St. Lawrence River and controls Québec, Canada (lipid basis).

PCB congeners	TEFs	Fishermen *n*	Fishermen Mean ng/kg (ppt)	Fishermen 95%CI	Fishermen TEqs ng/kg (ppt)	Controls *n*	Controls Mean ng/kg (ppt)	Controls 95%CI	Controls TEqs ng/kg (ppt)
Non-*ortho*-Coplanar PCBs									
3,3′,4,4′5 CB (126)	0.1	10	1540	597-2483	154.0	10[a]	48	—	4.8
3,3′,4,4′,5 CB (169)	0.05	10	1010	675-1345	50.5	10	29	—	1.5
Mono-*ortho*-Coplanar PCB			μg/kg (ppb)		ng/kg (ppt)		μg/kg (ppb)		ng/kg (ppt)
2,3′,4,4′,5 CB (118)	0.001	10	568	454-682	568	51[b]	25.4	20.1-30.6	25.4
Di-*ortho*-Coplanar PCBs			μg/kg (ppb)		ng/kg (ppt)		μg/kg (ppb)		ng/kg (ppt)
2,2′,3,4,4′,5′CB (138)	0.00002	10	1677	1522-1833	33.5	58[b]	55.5	44.5-66.5	1.11
2,2′,4,4′,5,5′CB (153)	0.00002	10	2457	2225-2690	49.1	58	72.6	58.2-86.9	1.45
2,2′,3,3′,4,4′,5 CB (170)	0.00002	10	539	443-636	10.8	47	27.7	23.6-31.7	0.55
2,2′,3,4,4′,5,5′CB (180)	0.00002	10	1776	1569-1984	35.5	57	48.2	38.3-58.1	0.96

Abbreviations: PCB, polychlorinated biphenyl; TEF, toxic equivalency factor; TEq, TCDD equivalent, CI, confidence interval.
[a]Ten pooled samples.
[b]Plasmas with detected levels [Carrier et al. (*13*).

women. Congener 169 is the most prominent in Inuit milk, whereas congener 126 predominates in control samples. For PCDDs and PCDFs (data not shown), differences are not so great: 13.3 ng/kg TEqs for Caucasian women and 19.1 ng/kg TEqs for Inuit women.

The relative contributions for toxicity of PCBs and PCDDs/PCDFs are presented in Figure 2. For di-*ortho*, mono-*ortho*, non-*ortho* coplanar PCBs and PCDDs/PCDFs, TEqs are, respectively, 17.3, 58.7, 32.2, and 19.1 ng/kg for Inuit women and 2.1, 17.4, 9.8, and 13.3 for Caucasian women.

Total PCBs represent 70 and 85% of total TEqs for Caucasians and Inuits, respectively. In the fishermen study, levels of coplanar PCBs were 30 times more than those of controls (Table 2). However, coplanar PCBs were determined only on those 10 fishermen with the highest total PCB blood levels. Levels of the sum of the 10 main PCB congeners was 46.4 μg/L of plasma in this highly exposed group compared with 12.3 μg/L in the overall fishing population studied. If we assume that this ratio (1 to 4) also holds true for coplanar PCBs, then we can estimate that plasma levels of non-*ortho* coplanar PCBs are probably near 400 and 250 ng/kg lipids for coplanars 126 and 169 respectively, 8 to 10 times more than in southern populations. For the highly exposed fishermen, TEqs of 204 ng/kg are due to the two non-*ortho* coplanar PCBs measured. The main contributors for total TEqs is the mono-*ortho* coplanar 118 with a TEq of 568 ng/kg (60% of total PCB TEqs).

Conclusion

Inuit people from Arctic Québec and fishermen from the lower north shore of the St. Lawrence River depend on fish consumption for their subsistence. Because of their extremely high daily intake of seafood (300 g for Inuit, 140 g for fishermen) and despite the relatively low concentrations of contaminants in fish from these remote areas (*10*), it appears that not only consumers of highly contaminated fish but also remote maritime communities obtain elevated doses.

In these two maritime populations, as in general populations, the main contributors to total TEqs are PCBs, particularly 2,3′,4,4′,5 penta-CB (no.118), which is responsible for more than 60% of the total toxicity. This finding indicates the necessity for further experimental studies to confirm TEFs for non- and mono-*ortho* coplanar PCBs. In these two regions, epidemiologic studies are now in progress and the recent knowledge of the relative toxicity of coplanar PCBs, PCDDs, and PCDFs will be useful to better characterize biological exposure. However, it is not clear whether all the toxic effects linked to these PCB exposures are mediated by a TCDD-like mechanism. The principal effects reported for OCs in children exposed during their fetal life affect the central nervous system (*11*) and seem not to be mediated by Ah receptors (*12*). This example demonstrates the present limitations of using TEFs in exposure assessment.

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