LEVELS OF NON-ORTHO AND MONO-ORTHO PCBs IN FISH AND MARINE MAMMALS FROM THE CANADIAN ARCTIC

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The presence of polychlorinated biphenyls (PCBs) in the Canadian Arctic has been known since the early 1970's. Atmospheric transport has been recognized as the main mechanism by which these industrial chemicals are occurring in the Arctic marine food chain. Recent studies have documented the levels of individual PCB congeners and other organochlorine contaminants (toxaphene, chlordanes, DDT-related compounds) in marine mammals and fish from the Canadian Arctic (for review see Muir et al. (1)). Very little work has been done on the presence of the non-ortho substituted PCBs in the Arctic marine food chain. Three of the non-ortho substituted congeners 3,3',4,4'-tetra (PCB 77), 3,3',4,4',5-penta (PCB 126), and 3,3',4,4',5,5'-hexa (PCB 169), are stereoisomers of 2,3,7,8-TCDD and show similar toxic effects and binding to Ah receptors (2,3). The presence of these PCB congeners in the Arctic ecosystem is a human health concern because marine mammals and fish tissues form a significant portion of the traditional diet of the Inuit of the Canadian Arctic and Greenland (1,4). Elevated levels of PCBs, including the non-ortho congeners, have been found in human milk samples from Northern Quebec (4).

Objectives of this study were to (*1*) determine the presence of non-ortho PCBs in the Arctic marine food chain (to complement earlier work in this area on organochlorine pesticides), (*2*) to observe any biomagnification occurring through the food chain, and (*3*) to contribute to assessments of human dietary exposure.

METHODS

Samples (arctic char (*Salvelinus alpinus*) whole fish; ringed seal (*Phoca hispida*), narwhal (*Monodon monoceros*), and beluga (*Delphinapterus leucas*) blubber) were collected from various locations in the Canadian Arctic by personnel of Dept. of Fisheries and Oceans, Central and Arctic Region, and by the Government of the NWT, and stored at -40°C (Table 1). Whole fish were ground and a 25 g subsample taken for Soxhlet extraction. Blubber samples (2 g subsamples) were extracted using a ball mill technique. ^{13}C-PCBs 77, 126, and 169 internal standards were added at the initial extraction. Percent lipid content was determined gravimetrically on an aliquot of the extracted sample. Lipid clean-up was performed on an automated 1002B GPC system (ABC Laboratories, Columbia, MO). A portion (for non-ortho PCBs) was further cleaned-up on a silica gel column. Non-ortho PCBs were separated from other organochlorines on a 1:10 AX21 carbon/glass fibre column (2), using a FMS (Watertown, MA) automated pumping system. Sample extracts were concentrated to a final volume of 20μl and t-nonachlor added as a volume corrector. Analysis was completed on a HP 5971A MSD (SIM) and HP 5890 GC. Confirmatory and quantitative ions used were the M^+ and $(M+2)^+$: m/z 290, 292 PCB 77; 324, 326 PCB 126; and 360, 362 PCB 169. The recovery standards were quantitated using m/z 304 ^{13}C-77, 338 ^{13}C-126, and 372 ^{13}C-169. The remaining sample was separated on Florisil and analysed for ortho substituted PCBs on a Varian 6000 GC with a ^{63}Ni ECD (5,6). Pooled samples of arctic char, beluga and narwhal were analyzed for polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDFs) (7,8).

RESULTS AND DISCUSSION

All samples contained low ng/kg levels of non-ortho substituted PCBs (based on tissue wet weight). Concentrations of non-ortho PCBs in Arctic char were the lowest of the species analysed. PCB 77 was the dominant congener while PCB 169 was rarely detected (Table 1). In char, PCB 77 constituted a higher percentage of ΣPCB (0.02-0.05% females, 0.04-0.07% males) than is found in Aroclor mixtures (0.025%). In seals PCB 77, 126 and 169 occurred in proportions greater than those found in Aroclor 1254 (9). In beluga and narwhal PCB 77 was present at a lower percentage of ΣPCBs and PCB 169 was enriched in relation to Aroclor 1254. Levels of ΣPCBs found in ringed seals and belugas have been shown to be significantly correlated with the age and sex of the animal (5,6,10). In male narwhals log concentrations of PCB 126 and 105 were significantly correlated ($p < 0.05$) with log length. PCB 118 levels were not significantly correlated with length. Although levels of non-ortho PCBs were higher in male than in female narwhal, results were not significantly different (t-test $p < 0.05$) because of the wide range of values observed. Marine mammal blubber contained higher proportions of penta, hexa and hepta ortho substituted PCBs than fish, with biomagnification occurring up the food chain (10). Total non-ortho PCBs made up a higher proportion of ΣPCB in char than in marine mammals (0.03-0.08% females, 0.06-0.10% males). Asplund et al. (11) found similar results in their study of Baltic seals and fish. These results suggest that non-ortho PCBs do not biomagnify to the same extent as the ortho-substituted PCBs, in the marine food chain.

Values for PCDD/PCDFs in arctic char (from Somerset Island, Spence Bay and Pond Inlet) ranged from <1 to 1 ng/kg for 2,3,7,8-TCDF, <1 to 2 ng/kg for 2,3,7,8-TCDD, and 3 to 9 ng/kg for other non-2,3,7,8-substituted TCDD isomers. No higher chlorinated congeners were detected. In narwhal 2,3,7,8-TCDD and TCDF concentrations were <1 ng/kg, and non-2,3,7,8-substituted TCDD isomers were present at 10 ng/kg. TCDD equivalent concentrations (TEC) for this study were calculated using the values of Safe (3) for the non-ortho PCBs and TCDD/TCDFs, and the values of Smith et al. (12) for the mono-ortho PCBs (Fig. 1). PCDD/PCDF values for ringed seals (W. Davis Strait) were taken from Norstrom et al. (13). In Arctic char PCDD/PCDFs accounted for greater than 40% of the TECs, PCB 126 made up 12 to 20%, PCB 105 was 10 to 15%, and PCB 77 contributed 5 to 8%. In ringed seals the proportions change to 35% as PCDD/PCDFs, 20% as PCB 126, and 25% as PCB 105. In narwhal and beluga PCDD/PCDFs did not contribute significantly to TEC (<5%) while PCB 169 contributes a greater proportion than in seals and char (10% of TEC). The mono-ortho PCB 156 was only significant in the narwhal and beluga samples. These contributions to total TEC mirror the biomagnification behaviour of the ortho substituted PCBs; no clear pattern exists for the non-ortho substituted PCBs.

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Table 1. Concentrations of Non-ortho and Mono-ortho substituted PCBs in Arctic samples

Species	N	% Lipid	Sex	PCB congeners (mean ± SD) ng/kg (wet weight) 77	126	169	105	156	118
Blubber									
Narwhal	18	85.2	M	203±204	187±100	50±24	57000±25000	6000±4000	183000±63000
			F	128±70	93±68	42±30	31000±24000	30000±62000	96000±93000
Beluga	6	83.8	M	105±106	201±127	97±29	25000±22000	22000±11000	150000±32000
Ringed Seal	8	84.8	M	49±27	94±3	8±11	7900±170	1450±160	38000±230
			F	123±3	95±63	21±30	9600±1800	1780±60	46000±12800
Char whole fish									
Ungava Bay	5	7.8	M	25±18	13±7	<1	410±230	110±150	4200±2000
Davis Str.	8	11.0	-	63±36	10±5	1±1	<10	130±150	2900±1550
Somerset Island	10	6.5	M	13±6	3±1	2±1	325±180	43±31	2030±1200
			F	6±5	1±1	<1	260±100	70±45	2400±1300
Pond Inlet	10	11.5	M	6±6	1±1	<1	170±40	10±2	1830±680
			F	6±3	2±1	2±1	165±30	<10	1600±640
Spence Bay	9	13.0	M	10±7	3±3	1±2	215±100	18±35	2200±650
			F	4±5	1±1	<1	240±105	26±36	2600±1525

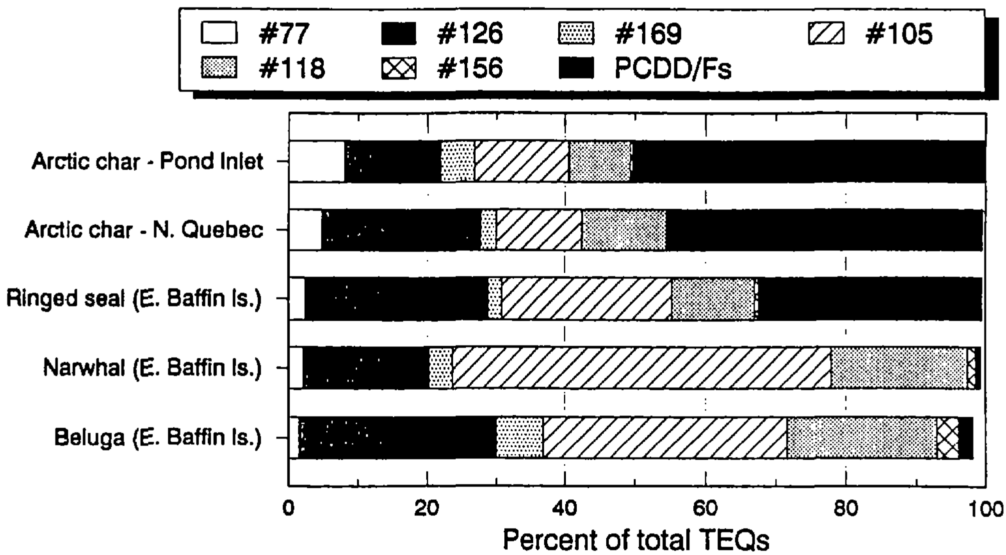

Fig. 1. Proportion of TECs as non-ortho and mono-ortho PCBs and PCDD/Fs