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Bioaccumulation of Toxaphene Congeners in Freshwater and Marine Food Webs

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Introduction

Despite bans on production and use, toxaphene continues to be a major organochlorine (OC) contaminant present at concentrations similar to or higher than PCBs in freshwater[1] and marine biota[2]. Concentrations of toxaphene in Lake Superior lake trout did not decline significantly between 1982 and 1992[3]. In the marine environment there was no significant decline in toxaphene levels in narwhal or beluga whale blubber from the Canadian arctic over a similar time period[4]. The presence of elevated toxaphene has resulted in dietary consumption advisories on lake trout in Lake Superior and in Lake Laberge in Canada's Yukon Territory as well as on marine mammal fats in the Canadian arctic[5,6].

A complex pattern of toxaphene congeners and homolog groups is observed in environmental samples. There are major differences in congener patterns between abiotic and biological samples and between species[7,8]. The analysis of total toxaphene gives little insight into this complexity. A comparison of congener patterns is useful for understanding sources and transport/bioaccumulation pathways of toxaphene, and also may give insight into the lack of declining concentrations in top predators. Glassmeyer et al.[3] found that the congener (and homolog) pattern in Great Lakes lake trout differed over time and between lakes indicating a shift to less chlorinated congeners. For example, the nonachlorobornane Parlar # 50 (or T12) predominated in samples from 1982 but the octachlorobornane (#26 or T2) was the predominant congener in trout from all lakes in samples collected in 1992.

Stable nitrogen isotope ratios ($\delta^{15}N$) have proven useful for elucidating food web relationships and trophic levels of freshwater organisms[9,10]. $\delta^{15}N$ increases an average of 3 to 5 parts/thousand (‰) from prey to predator[9] because of the enrichment of ^{15}N relative to ^{14}N, and thus can be used as a continuous variable for quantifying trophic position. Recently, several groups have shown that biomagnification of persistent organochlorines (OCs) including toxaphene and PCBsis strongly correlated to $\delta^{15}N$[11,12]. This raises the possibility that $\delta^{15}N$ could be used to predict levels of bioaccumulating contaminants, such as highly chlorinated bornanes, in fish.

The objectives of this study were to examine the patterns and food web bioaccumulation of specific toxaphene congeners in arctic freshwater and marine food webs using $\delta^{15}N$, where possible, as an indicator of trophic position.. We chose the Lake Laberge food web, in which we have previously reported high levels of total toxaphene[11] and the Arctic Ocean marine food web where toxaphene is also a major OC contaminant[13].

Methods

Samples: Piscivorous and forage fishes and invertebrates were obtained from Lake Laberge in the Yukon[11]. Sediment cores were collected using a 15 cm dia corer and extruded on site. Large volume water samples were collected from each lake and particles (<0.2 um) removed by continuous flow centrifugation. In the marine environment, zooplankton and arctic cod were collected by F. McLauglin and R. Macdonald (Institute of Ocean Sciences, Sidney BC) during the Transpolar cruise. Seawater was collected during the Transpolar and Bering/Chukchi Sea cruises by L. Jantunen and T. Bidleman. Greenland halibut were obtained by D. Chiperzak (Fisheries and Oceans Canada, Winnipeg) from the southern Beaufort Sea. Ringed seal blubber was obtained at Eureka (Southwest Ellesmere Is.) by S. Innes (FOC Winnipeg) and beluga whale blubber at Hendrickson Is., in the Mackenzie River delta, by D. Metner (FOC Winnipeg).

Analytical: Skinless dorsal muscle from individual fish, as well as pooled whole invertebrates were analysed for $\delta^{15}N$. Samples were first dried (60 °C) and homogenized. Nitrogen isotopes were determined by combustion of approximately 15 mg of dried tissue using a dual inlet isotope ratio mass spectrometer. Skin+muscle from fishes, liver from burbot, marine mammal blubber, pooled whole invertebrates, sediment and water, were extracted and analysed for toxaphene and selected congeners using published procedures[14,15]. Biological samples were homogenized with dry ice. The homogenate (1-10 g) was mixed with (precleaned) Na_2SO_4 and Soxhlet extracted with hexane:DCM (1:1). Percent lipid was determined gravimetrically on 1/10 of the extract. Lipids were removed by gel permeation chromatography. Freeze-dried sediment was Soxhlet extracted with DCM. Water was extracted with DCM using a Goulden extractor. PCBs were separated from p,p'-DDT, HCH, and most chlordane and toxaphene components by chromatography of the extract on Florisil.

PCBs, OC pesticides and selected toxaphene congeners were quantified by GC-electron capture detection (GC-ECD) using a 60 m x 0.25 mm i.d. DB5 column and H_2 carrier gas. Total toxaphene was determined by high resolution electron capture negative ion MS (ECNIMS) with selected ion monitoring (SIM) for C_6-C_{10} homologs following the method of Swackhamer et al.[16] but using a resolving power of 12,000. For this study we focussed on four chlorobornane congeners: the octachlorobornane T2 (Parlar 26 or the Andrews/Vetter's[17], B8-1413) and the nonachlorobornane T12 (Parlar 50, B9-1679) as well as the heptachlorobornane "HpSed" or B7-1001, and the hexachlorobornane "HxSed" (or B6-923) recently identified by Stern et al.[14]. The congeners were quantified by ECNI-SIM and by GC-ECD using standards supplied by Dr. Ehrenstorfer GmbH, Germany or isolated from sediment (for B6-923 and B7-1001)[14]. Results for total toxaphene and individual congeners analysed by GC-ECNIMS and by GC-ECD were compared by analysing samples by both methods. Good agreement was found between concentrations of total toxaphene, B8-1413 and B9-1679 determined by GC-HRECNIMS and by GC-ECD (r^2 ranging from 0.90 for B8-1413 to 0.95 for B9-1679). B6-923 and B7-1001 could not be determined reliably by GC-ECD due

to low sensitivity and interference from other OCs.

Results and Discussion

All four congeners were detectable in almost all samples from the freshwater and marine environment. B6-923 and B7-1001 were prominent toxaphene congeners in Lake Laberge water (Fig 1). Results are not yet available for B6-923 and B7-1001 for Arctic Ocean water or biota. However, B8-1413 and B9-1679 were detectable at low pg/L levels in seawater[18]. In Lake Laberge, B6-923 was less prominent in zooplankton and in top predators (Table 1). B9-1679 was the major toxaphene congener in all freshwater and marine biota analysed and was generally one of the most prominent individual OCs present. For e.g., concentrations of B9-1679 averaged 65 ng/g ww in lake trout similar to levels of p,p'-DDE (geometric mean 93 ng/g ww) and greater than CB153 (19 ng/g).

Table 1. Mean concentrations of selected CHB congeners and total toxaphene in Lake Laberge and in the Arctic Ocean/Beaufort Sea

Sample (N)	%lipid	B6-923	B7-1001	B8-1413	B9-1679	Toxaph[a]
Lake Laberge (Yukon)						
Water (1), pg/L		9	28	3	10	209
Sediment (1) pg/g dw	3.9 (OC)	9	27	2	22	360
Zooplankton (2) ng/g ww	1.5	0.07	0.12	0.10	0.30	3.8
Least Cisco (7) ng/g ww	5.0	6.0	2.1	1.8	5.8	61
Lake whitefish (30) ng/g ww	2.7	16	67	2.5	6.8	61
Lake trout (12) ng/g ww	8.4	0.3	4.4	17	65	390
Arctic Ocean/Beaufort Sea						
Sea water (pg/L)[b]		-[c]	-	1.2	1.4	35-100
Zooplankton (10) ng/g ww	26	-	-	2.7	4.6	25
Arctic cod (5) ng/g ww	3.2	-	-	1.3	3.6	33
Greenland halibut (10) ng/g ww	15	-	-	15	29	375
Ringed seal fat - Female (10) ng/g ww	91	-	-	32	75	440
- Male (9)	91			34	86	560
Beluga whale fat - Female (5) ng/g ww	88	-	-	304	630	6200
- Male (20)	89			468	840	5900

[a] Toxaphene quantified by GC-MS with the technical standard following Swackhamer et al.[16] or by GC-ECD using a single response factor based on technical toxaphene.
[b] Unpublished results provided by Jantunen and Bidleman[18]
[c] Hexa- and heptachlorobornanes not determined in marine biota

Concentrations (wet wt) of B9-1679 and B8-1413 as well as CHB7 (not shown) increased significantly with $\delta^{15}N$ in the Lake Laberge food web (Figure 2). Lipid normalized concentrations also increased with trophic level but there was only a weak correlation between $\delta^{15}N$ and lipid. The increase of toxaphene congeners with trophic level can therefore be explained primarily by food chain transfer rather than by differences in lipid content. The slope of the relationship between organochlorine concentration and $\delta^{15}N$ is an indicator of the biomagnification potential of the

compound. B8-1413 and B9-1679 had "biomagnification slopes" of 0.17 and 0.20, respectively, similar to that of p,p'-DDE (0.19) and CB 153 (0.18) in the same invertebrate-forage fish-lake trout food web. Thus both B8-1413 and B9-1679 have similar biomagnification potential as other highly recalcitrant OCs.

In the marine food web, concentrations of B8-1413 and B9-1679 increased with trophic position within the zooplankton-arctic cod-beluga/ringed seal food web (Table 1, Figure 3). Concentrations were much lower in ringed seal than in beluga although both feed at the same trophic level. Toxaphene/total PCB ratios in Canadian arctic ringed seals are ~0.3, much lower than for beluga in the same region (~1.5). This suggests that seals have greater capability to degrade chlorinated bornanes compared with cetaceans although it may also reflect dietary differences between these species.

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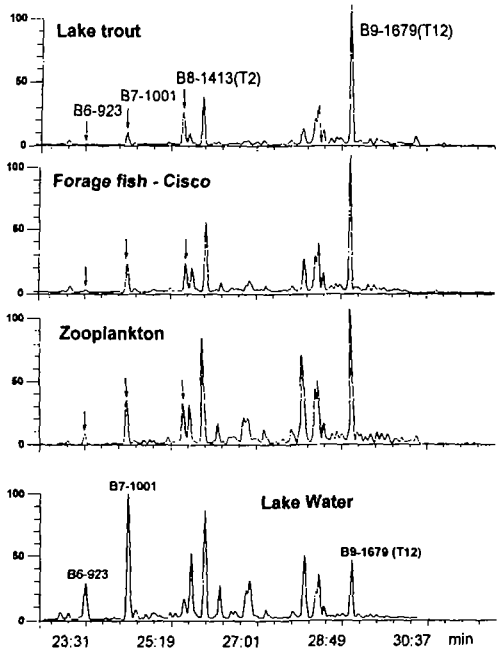

Figure 1. GC-ECNIMS chromatograms for Cl_6 to Cl_9 chlorobornanes in samples from Lake Laberge , Yukon.

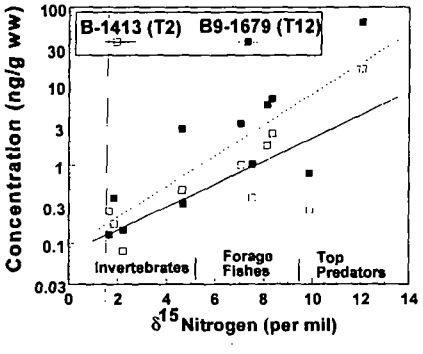

Fig 2. Relationship between the mean concentrations of B8-1413 (T2) and B9-1679 (T12) and the trophic position of biota measured with $\delta^{15}N$, in the Lake Laberge (Yukon) food web

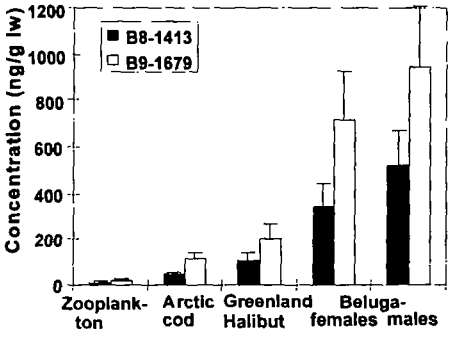

Fig 3. Relationship between the mean concentrations (lipid wt ±SD) of B8-1413 and B9-1679 and trophic position in the Arctic Ocean marine food web