TOXAPHENE BIOACCUMULATION IN LAKE SUPERIOR: INSIGHTS FROM CONGENER AND ENANTIOMER ANALYSIS

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Introduction

Toxaphene levels remain persistently high in both lake water and fish from Lake Superior [1,2,3]. A temporal trend study using lake trout samples from 1977, 1982, 1984, 1988 and 1992 found no significant decline in total toxaphene levels [3]. By contrast toxaphene levels appeared to have declined (based on 2 sample points) between the mid-1980's and early 1990's in Lakes Michigan, Huron and Ontario [2]. Toxaphene levels in lake trout from Lake Superior are the highest in the Great Lakes and amongst the highest found in any *Salvelinus* species in North American lakes [4]. Thus Lake Superior is a unique place to study the bioaccumulation of toxaphene where relatively high levels are found even in lower food web organisms [2]. Previous detailed studies of toxaphene in lake water, sediments, and food web samples have been conducted only with total toxaphene and homolog groups [2, 5] with the exception of recent work by Whittle et al. [6] who determined chlorobornane congeners in lake trout by GC-ECD. They found no decline in major chlorobornanes e.g. P50 (B9-1679) and P62 (B9-1025) in lake trout from 1980 to 1998.

In previous work we determined enantiomers ratios (ERs) of selected toxaphene congeners in Lake Superior using multidimensional GC with detection by electron capture negative ion mass spectrometry (ECNIMS) [7]. Lake trout, rainbow smelt and lake herring were found to metabolize several of the hepta- and octachlorobornanes enantioselectively whereas almost all congeners were racemic in air, water and sediments. The enantioselective accumulation of toxaphene has also been established for several marine fish species such as hake [8] and herring [9].

The aim of this study was to examine pathways and sources of toxaphene in Lake Superior using toxaphene congener profiles and the enantiomeric fractions (EFs) from lake water, sediments, food web organisms and top predators in Lake Superior. We anticipated that the congener patterns would help identify contributions from benthic and pelagic food webs while the congener EFs would identify the extent of biotransformation at each tropic level. We also hypothesized that there would be seasonal differences in patterns and EFs due to varying growth rates and dietary shifts.

Experimental

Samples: Surficial sediments were collected in 1997 from the CCS Limnos and a core from the central lake basin (Site 80) was obtained in 1998. Lake water and phytoplankton (~1 to <100 um)

were obtained in May 1998 from 17 sampling stations using the Limnos. In addition we examined lake water samples collected from many of the same sites in summer 1997. On the Limnos the <100 um size fraction was obtained by continuous centrifugation of about 1500 L of 100 um filtered lake water. Phytoplankton were also obtained from the US EPA R\V Lake Guardian from a site near the Apostle Islands in western Lake Superior in May and July 1998 by pumping lake water (100 um filtered) through a vibrating 10 um net ("Phyto vibe"). Dissolved phase toxaphene was extracted using XAD-2 columns (80L; GF/F filtered). Zooplankton and mysis were collected by vertical hauls of 100 um nets in May and July 1998. Amphipods (*Diporeia hoyi*) were collected in western Lake Superior using a ship deployed Ponar grab. Lake trout (*Salvelinus namaycush*) (length range – 550-750 mm) and forage fish (slimy sculpin (*Cottus congatus*), rainbow smelt (*Osmerus mordax*) and lake herring (*Coregonus artedii*)) were obtained from western Lake Superior) in mid-May, mid-June and October 1998.

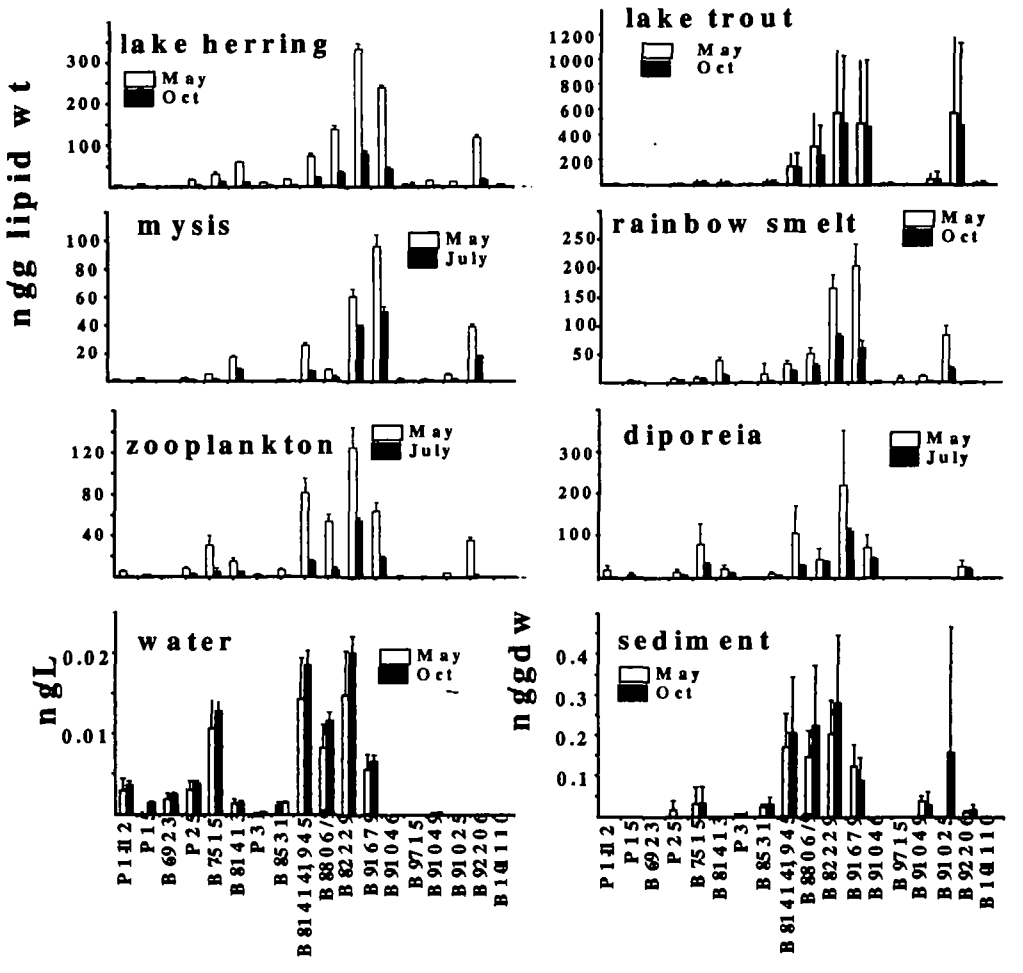
Methods: Analytical methods for toxaphene followed established procedures [10]. All lake trout and forage fish were analysed as whole fish. Fish homogenates were Soxhlet extracted with hexane:dichloromethane (DCM)(1:1), cleaned up gel-permeation and silica gel chromatography. Toxaphene congeners were quantified by low resolution ECNIMS using HP6890 GC/HP5973 MSD using a 22 congener standard mixture plus congeners B6-923 and B7-1001. Enantioselective analysis was done by GC-ECNIMS on a HP6890 with a Gerstel DCS2 heart-cut valve in combination with a Gerstel liquid nitrogen cold trap in the GC oven that allowed use of multidimensional GC [7]. Congener separation was performed on HP-5 (30 m x 0.25 mm i.d. x 0.25 μm film thickness) prior to heart-cut onto the chiral columns BGB-172 (30 m x 0.25 mm i.d. x 0.18 μm film thickness) or BGB-TBDM (30 m x 0.25 mm i.d. x 0.15 μm film thickness).

Quality Assurance: Blanks and certified reference materials (NIST 1588 cod liver and DFO Lake trout) were analysed with each sample batch of about 10 samples. The laboratory also participated in the QUASIMEME interlab comparison on toxaphene in 1999 [11].

Results and Discussion

About 22 congeners (including co-eluters B8-1414/1945 and B6-806/809) were routinely quantified in all samples (Table 1). Two other congeners (B7-499 (P21) and B8-786 (P51)) were detected but had unusually high response factors ECNIMS and are not reported. Distinct congener patterns were observed in water and sediment (Figure 1). Greater amounts of hexa- and heptachloro- bornanes were found in water. Indeed there were many additional heptachloro- congeners in water that were not quantified due to lack of standards. There were no significant seasonal differences in levels or proportions of congeners in water, sediment or lake trout (Figure 1). However, concentrations of most heptachloro- and octachloro- congeners in zooplankton, mysis and diporeia were much higher in May than in July samples. Similarly in lake herring and smelt, higher levels were found in samples from May than in October. These differences may be due to the effect of much higher growth rates of all the smaller organisms during the summer months, which could result in growth dilution of congeners.

EFs for selected toxaphene congeners in lake trout and biomagnification factors (BMF; lipid wt conc'n in predator/lipid wt conc'n in prey) for lake herring to lake trout are shown in Table 1. Octa- and nonachlorobornanes with both 2,3,5,6-endo-/exo- substitution Figure 1. Concentration profiles of toxaphene congeners in Lake Superior water, sediment and food web samples. Open bars are mean concentrations (+/-SD) for samples from May and solid bars are from either July or October.



(B8-1414.1945,-2229, B9-1679) and with geminal-Cl substitution at the 2- position (B8-806/809, B9-1046, B9-1049, B9-1025) are observed to biomagnify (BMF >1) between lake herring and lake trout. As well, many of the same congeners had non-racemic EFs in lake trout. Smelt and lake herring had lower EFs for most congeners than lake trout while most congeners were racemic in lake water and sediment. This is consistent with observations that species at higher trophic levels do have greater capabilities for enantioselective biodegradation [8,9].

Table 1. Enantiomeric fractions (EF) in lake trout, biomagnification factors (BMF) from Lake Superior herring to lake trout, and important structural features of toxaphene congeners

Congener #	EF	BMFs	Important Structural features
P25	-[1]	0.71	
B7-515	0.50	0.99	Geminal Cl at C2
B8-1413	0.50	0.38	2,3,5,6-Endo/Exo substitution
P31	-	0.62	
B8-531	-	1.28	
B8-1414/1945	0.65	2.07	2,3,5,6-Endo/Exo substitution
B8-806/809	0.43	2.53	Geminal Cl at C2
B8-2229	0.45	2.06	2,3,5,6-Endo/Exo substitution
B9-1679	0.48	2.71	2,3,5,6-Endo/Exo substitution
B9-1046	-	1.89	Geminal Cl at C2
B9-715	0.55	0.09	Geminal Cl at C2
B9-1049	-	3.10	Geminal Cl at C2
B9-1025	0.60	5.74	Geminal Cl at C2 &C5
B9-2206	-	2.32	
B10-1110	-	-[2]	Geminal Cl at C2

[1]EF not determined; [2]BMF(herring to trout) not determined where congener was non-detect

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