ENANTIOMER RATIOS OF TOXAPHENE IN ABIOTIC AND BIOLOGICAL SAMPLES FROM LAKE SUPERIOR

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Introduction

Chiral pollutants such as chlordane, α-HCH and atropisomer PCBs can be an important tool for determining sources, pathways and fate of these compounds in the environment [1-3]. There is a need to understand pathways of toxaphene in Lake Superior because of persistently high levels in lake water and fish [4,5]. Fugacity ratios of toxaphene in Lake Superior in August 1996 were > 1, implying volatilization of toxaphene from water to air [6]. Significant isomer and enantioselective biodegradation in the lake may therefore be influencing the toxaphene composition in the air above the lake. Such observations have recently been made for α-HCH and chlordanes in Lake Superior [7].

Enantioselective accumulation of toxaphene has already been established for several fish species such as hake [8] and herring [9,10] and enantiomer ratios (ERs) of toxaphene in fish and cod oil were in general also non-racemic [11]. Furthermore, the ER of a heptachloro- bornane in sediments was also non-racemic [12].

The aim of this study was to determine if enantiomer selective degradation of toxaphene congeners was occurring in Lake Superior and if it was a significant pathway for removal of toxaphene from the lake. Lake trout, the top predator in the pelagic food web of Lake Superior, and its prey rainbow smelt and lake herring were chosen as an indicators of enantioselective degradation. We anticipated that species at higher trophic levels in the food web would generally have higher degradative capacities as demonstrated by changes in ER [13]. In addition, sediments, air and lake water were also congener specific and enantioselective analyses were also conducted to assess pathways and sources of toxaphene for biota and for abiotic compartments in Lake Superior.

Experimental

Samples: Air and water from Lake Superior was collected in Aug. 1996 (L. Jantunen and T. Bidleman, AES Toronto) and by W. Strachan and D. Burniston (NWRI). Sediments were collected at Jackfish Bay in 1998 from the C.C.G.S. Limnos by C. Teixeira and B. Moore of NWRI. Lake Trout and forage fish (rainbow smelt and lake herring) from western Lake Superior were obtained by C. Bronte (US FWS, Ashland WI) in May 1998.

Methods: Isomer-selective analysis was performed as described in ref [14]. Enantioselective analysis was done by low resolution ECNIMS using HP6890 GC connected to a HP5973 MSD [14]. Installation of a Gerstel DCS2 heart-cut valve in combination with a Gerstel liquid nitrogen cold trap into the GC oven allowed use of multidimensional GC (MDGC). The following temperature program was used for all separations: 90°C for 1 min then 10°C/min to 200°C for 0

min, 2°C/min to 240°C for 25 min, 20°C/min to 120°C for 1 min, 10°C/min to 200°C for 25 min and finally 4°/min to 240°C for 20 min. The corresponding temperature program for the cold trap was 150°C for 19 min then 20°C/s to 60°C for 44 min and finally 20°C/s to 240°C for 64 min. Helium was used as carrier gas and the column head pressure and heart-cut valve pressure was set to 172.4 KPa and 73.9 KPa, respectively. Isomer 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) [15-17]. The isomer separation on the pre-column was continuously monitored with an ECD. The ECD was kept at 240°C and nitrogen was used as a makeup gas at a flow of 60 ml/min. The splitless injector had a temperature of 220°C.

Results and Discussion

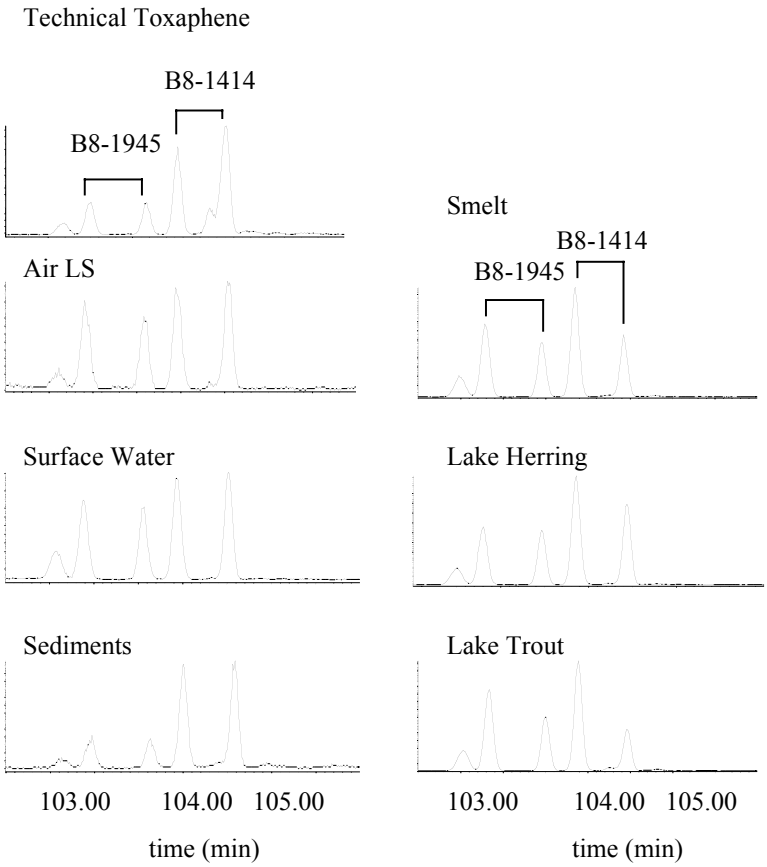
Enantiomer ratios of B7-515, B8-1412, B8-1945 and B8-806/9 were racemic in air and water of Lake Superior (Table 1; Fig. 1). B8-1414 had ERs of 1.13-1.20 in air above Lake Superior and ERs of 1.18-1.21 in the surface water, which supports volatilization of toxaphene from lake water into air in August [7]. The proportions of B8-1414 and/or B8-1945 as well as B8-806/9 were depleted in air and water from Lake Superior in comparison with technical toxaphene [18]. The sediment sample was close to racemic for all compounds except B8-806/9. Microbial degradation of toxaphene in anaerobic sediments has been shown to

Table 1. Enantiomer Ratios selected hepta and octachloro- toxaphene congeners in air, surface water, sediments, lake trout and forage fish in Lake Superior. Parlar numbers for each congener are shown in parentheses.

	B7-515 (P32)	**B8-1413 (P26)**	**B8-1412 -**	**B8-1414 (P40)**	**B8-1945 (P41)**	**B8-806/9 (P42a/42b)**
Parlar 22	0.96±0.04	n.r.[1]	n.i.s.[2]	0.99±0.01	0.92±0.01	1.0± 0.02
Tech.Tox.	1.03	n.r.	0.98	1.06	0.87	0.98
Air	0.95	n.r.	0.99	1.13	0.89	1.01
	1.02		Int[3]	1.20	0.98	n.a.[4]
Water	0.99	n.r.	1.01	1.18	0.97	0.93
	0.97		0.98	1.18	0.99	0.95
	0.99		0.99	1.19	0.98	1.02
	1.03		0.97	1.21	0.99	1.03
	1.00		1.00	1.21	0.98	0.95
Sediments	n.d.	n.r.	1.04	1.05	1.01	0.92
Lake Trout	0.53	n.r.	1.42	2.66	1.57	0.78
	0.53		1.47	n.a.	n.a.	0.87
Lake Herring	0.69	n.r.	1.05	1.43	1.15	0.87
Smelt	n.a.	n.r.	0.97	1.96	1.44	0.92

[1]n.r.= not resolved; [2]n.i.s.=not in standard;[3]Interference; [4]na=not analysed

Figure 1. Chiral column separation of the octachlorobornanes B8-1945 and B8-1414 in technical toxaphene, air, surface water, sediments, lake trout, rainbow smelt and lake herring, from western Lake Superior. The compounds were monitored with ECNI-MS at m/z 379.



dechlorinate selected chlorobornanes including B7-515 and B8-806/809 [19]. Sediment microorganisms may not have the ability to degrade all chlorobornanes enantioselectively since the ER of B7-1001 in sediments from toxaphene treated lakes was non racemic [12].

Lake trout, rainbow smelt and lake herring were found to metabolize several of the hepta- and octachlorobornanes enantioselectively (Table 1). Smelt and lake herring had lower ERs for most congeners than lake trout. This is consistent with observations that species at higher trophic levels do have greater capabilities for enantioselective biodegradation [8,13]. Smelt and lake herring showed significant differences in ERs for B8-1414 and B8-1945 consistent with structural differences (B8-1945 has an unsubstituted 6 position; B8-1414 has the stable 2,-endo-3-exo,5-endo,6-exo-substitution) indicating species differences in the capacity to metabolize these congeners even at lower trophic levels.

MDGC-ECNI-MS is a powerful tool for determining enantiomer ratios of toxaphene in environmental samples. The numerous co-elutions, especially with abiotic samples makes MDGC mandatory. The complexity of the analysis can be demonstrated for B8-1945 which had a non

racemic ER in technical toxaphene but was racemic in all water and sediment samples and in one of the air samples. The nonracemic ER in the technical mixture is likely due to a co-elution on the chiral column. The degradation of this coeluting toxaphene congener gives a racemic ER in the abiotic samples. Lack of chiral column that separates toxaphenes into enantiomers complicates quality assurance. The two chiral columns used in the study were very efficient in separating toxaphene congeners although the exact composition of the stationary phase is unknown [16,17].

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