

Toxaphene Congener Patterns in Lake Sediment

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1. Introduction

Toxaphene is a complex mixture consisting of between two and three hundred penta- to undecachlorobornanes (CHBs) and camphene/diene isomers^{1,2}. Introduced in the USA in 1945 by Hercules Co. as a new insecticide to control a variety of insect pests, two-thirds of toxaphene production was used for insect control on cotton. It was also used on vegetables, small grains, soya beans and for control of external insects on livestock^{3,4}. In Canada and the USA, toxaphene was also used extensively in fish eradication programs. This practice, however, was discontinued when it was found that toxaphene was extremely persistent and that lakes could not be successfully restocked for years after treatment⁵⁻⁷. Prior to its ban in 1982 by the US Environmental Protection Agency⁸, toxaphene was the most extensively used pesticide in the USA and many other parts of the world. Global production has been estimated to be 1.33 megatons⁹, with production in the USA (1946-1982) accounting for about 0.45 megatons^{8,9}. Although no longer manufactured in the USA, toxaphene and similar products are still being used in Central and South America, Africa, Eastern Europe, the Indian sub-continent and in regions of the former USSR⁸⁻¹⁰.

In a recent paper by Miskimmin *et. al.*¹¹, the distribution of toxaphene in profundal sediment cores from two treated lakes located in Alberta, Canada was examined and the chromatographic patterns between recent and older sediments compared. Peanut Lake (50°01' N, 114°21' W; mesotrophic) was treated with 7.5 µg L⁻¹ of toxaphene in September 1961 and Chatwin Lake (54°15' N, 110°15' W; eutrophic) was treated at 18.4 µg L⁻¹ in October 1962. Gas chromatography, with electron capture detection (GC-ECD), showed that the maximum total toxaphene concentration in the sediment from both treated lakes occurred at depths representing the years of treatment (500 ng/g in Peanut Lake and 1602 ng/g in Chatwin Lake) and that their chromatographic profiles were very similar to that of technical toxaphene. In more recent slices, however, the number of CHB peaks was greatly reduced with the two most prominent peaks corresponding to 2-*exo*,3-*endo*,6-*exo*, 8, 9, 10-hexachlorobornane (Hx-Sed) and 2-*exo*,3-*endo*,5-*exo*,6-*endo*,8,9,10-heptachlorobornane (Hp-Sed)¹². Surface sediments of an untreated basin of Peanut Lake was also analysed for toxaphene and was found to contain levels < 0.1 ng/g, suggesting that external sources of toxaphene to the treated lakes are negligible and that the observed chromatographic pattern in the surface sediment is the sole result of the introduction of the toxaphene during treatment. The predominant levels of Hx- and Hp-Sed suggest that some of the original toxaphene mixture has been dechlorinated and is redistributed through the sediment by porewater diffusion¹¹. That these two CHB congeners correspond to the end metabolites is not surprising. Their lack of geminal

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dichloro substitutions and, like T2 and T12, two CHB's known for their persistence in marine mammals¹³, the staggered positioning of the ring chlorines make them less vulnerable to anaerobic reductive dechlorination. Sediment cores from three Yukon lakes (Laberge (61°11'N, 135°12'W), Kusawa (60°20'N, 136°22'W) and Fox (61°14'N, 135°28'W)) and surface sediment from Great Slave Lake (61°47'N, 113°43'W) in the Northwest Territories and Lake Nipigon in Ontario, just north of Lake Superior (49°50'N, 88°31'W) were analysed for toxaphene and their chromatographic profiles compared to those of the two treated Alberta lakes. Calculated surface and maximum fluxes for total toxaphene are also reported.

2. Experimental

Sediment Extraction and Dating. Sediment cores, collected using a KB corer (10 or 16 cm diameter), were sliced at 1-cm increments and kept at 0°C to -10°C both before and after they were freeze-dried. Extractions were performed as described by Muir *et. al.*¹⁴. For toxaphene analysis using high resolution mass spectrometry, Florisil fractions 1 and 2 were combined. Excess ²¹⁰Pb profiles were log-linear and were used to calculate the median age of each core slice. Focusing factors were calculated using latitude-specific atmospheric fluxes of ²¹⁰Pb and sedimentation rates (g/m²yr) using a simple linear model (assumes constant ²¹⁰Pb flux and constant dry-mass sedimentation rate)¹⁵.

Mass Spectrometry. GC-ECNIMS was performed on a Kratos Concept high resolution mass spectrometer (EBE geometry) controlled using a Mach 3X data system. Selected ion ECNIMS was performed at a spectrometer resolution of M/ΔM ~12000. Methane was used as the moderating gas and PFK as the mass calibrant. Optimum sensitivity was obtained at a gas pressure of ~2 x 10⁻⁴ torr as measured by the source ion gauge. The electron energy was adjusted for maximum sensitivity (~180 eV), the accelerating voltage was 5.3 kV and the ion source temperature was 120°C. The following characteristic ions were monitored from the (M-Cl)⁻ isotopic cluster of the hexa- to nonachlorobornane homologue groups; Cl₆ 308.9352, 310.9323; Cl₇ 342.8962, 344.8933; Cl₈ 376.8573, 378.8543; Cl₉ 410.8183, 412.8154. Four groups were set up to monitor the different homologue groups. The hexa and heptachlorinated components were monitored in the first group, the hexa-, hepta- and octachlorinated components in the second, the hepta-, octa- and nonachlorinated components in the third and the nonachlorinated components along with the m/z 409.7747⁻ and 411.7718 ions from the (M-4Cl)⁻ isotopic cluster of ¹³C₈-Mirex in the fourth group. The quantitation ions, underlined above, in the chlorine homologue classes are summed for a total toxaphene area, which is quantitated against the area of a toxaphene standard calculated in the same manner. ¹³C₈-Mirex was monitored to correct for any changes in source performance.

Gas Chromatography. GC separations were performed on a Hewlett Packard model 5890 Series II gas chromatograph using a 60m x 0.25mm i.d. DB-5ms fused silica column (Chromatographic Specialities) which was connected directly to the ion source of the mass spectrometer. He was used as the carrier gas. Samples were run using splitless injection (2 min.) with the injector at 260°C. The initial column temperature was 80°C; at 2 minutes the oven was ramped at 20°Cmin⁻¹ to 200°C, then at 2°Cmin⁻¹ to 230°C then at 10°Cmin⁻¹ to a final temperature of 300°C and held for 8 minutes. Electronic pressure programming was used increase the pressure during the injection cycle and then to maintain a constant flow of 1 ml min⁻¹ during the remainder of the run. All injections were made by a CTC A200SE autosampler under data system control.

3. Results and discussion

The GC-ECNIMS selected ion chromatograms of toxaphene in the surface sediment of the three Yukon lakes are shown in Figure 1. Toxaphene concentrations in the Yukon sediment core slices (covering the past three decades) were highest in Fox Lake, comparable to levels found in other Arctic cores¹⁴ and considerably lower (1000 fold) than the levels observed in Chatwin and Peanut Lake. Little or no Hx- and Hp-Sed is present in Kusawa sediment, however, a pattern consistent with atmospheric deposition is observed, highlighted by a significant presence of T12 (2-*exo*,3-*endo*,5-*exo*,6-*endo*,8,8,9,10,10-nonachlorobornane)¹³. Hx- and Hp-Sed are more significant in Laberge sediment, but are still present at level similar to that which can be associated with atmospheric deposition. As observed in the sediment of the two treated Alberta lakes, Hx- and Hp-Sed correspond to the two most predominant peaks in the Fox lake chromatogram and are responsible for 60-70% of the total observed ion intensity. The relatively low toxaphene concentrations in these three lakes would seem to suggest that the source of toxaphene is atmospheric rather than from elevated inputs of toxaphene from a point source. However, if elevated levels of these two CHB's is a signature by which lakes exposed to an *in situ* source of toxaphene can be identified, it would imply that Fox lake may have in the past, been contaminated by a direct source. The lower levels would be more consistent with a small spill(s) than with direct application as a piscicide. The smaller contributions of Hx- and Hp-Sed to the total toxaphene concentration in Laberge sediment, might be due to the much larger relative size of Laberge compared to Fox and the resulting dilution effect.

Figure 2(a-f) show how the chlorination profile of CHB's change as a function of time since deposition in the three Yukon lakes. For lake Laberge (2a), the percentage of hexa- and heptachlorobornanes increase with the time since deposition, possibly at the expense of the octa- and nonachlorobornanes, which show a decreasing trend with time. Figure 2b, shows that the increasing trend of the hexa- and heptachlorobornanes is, at least partially, due to an increase in Hx- and Hp-Sed concentrations, respectively, while the decreasing nonachlorobornane contributions may be in part, the result of a declining T12 concentration. Similar trends are observed in Fox lake sediment (2e,f). Besides a slight increase in the contributions from octachlorobornanes, due in part to a small increase in T12 concentrations (2c,d), no significant trends are observed with time in Kusawa lake sediment.

Toxaphene profiles for the surface slices of core#1 and 3, taken from the central and southeastern parts of lake Nipigon, respectively, and from core#19 of Great Slave lake near the mouth of the Slave river (the major river entering the lake) are shown in Figure 3. Although the profiles of both Nipigon cores are virtually identical, Hx- and Hp-Sed in the surface sediment of core#3 are approximately three times more prevalent than that observed for core#1. Calculated total toxaphene concentration and surface flux are also proportionally higher. The southeastern part of lake Nipigon is and has been in the past, used heavily for recreational purposes. Although no record of its use is available, the predominant levels of Hx- and Hp-Sed might once again suggest the usage of toxaphene, possibly as a lampricide, sometime in the past. With the exception of the most intense peak in the chromatogram, which corresponds to a structurally unknown heptachlorobornane, the toxaphene profile of the Great Slave lake surface sediment is very similar to that which is observed in the Nipigon sediment. Work towards attaining complete core profiles for these three cores is ongoing. Surface and maximum fluxes for total toxaphene (ng/m²yr) for the Yukon lakes, lake Nipigon and Great Slave lake are presented in Table 1.

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4. References

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Table 1. Surface and maximum fluxes of total toxaphene (ng/m²yr) in sediment cores from lakes in the Yukon Territories, Northwest Territories and Ontario.

Lake	Core#	Surface flux	Date	Maximum flux	Date
Laberge, Yukon	3	169	1991	340	1973
Fox, Yukon	1	458	1992	260	1983
Kusawa, Yukon	1	37	1991	140	1974
Lindemann, Yukon	1	31	1992	-	-
Great Slave, N.W.T	19	550	1994	-	-
Nipigon, Ont. (central)	1	188	1992	-	-
Nipigon, Ont. (Southeast)	3	625	1992	-	-

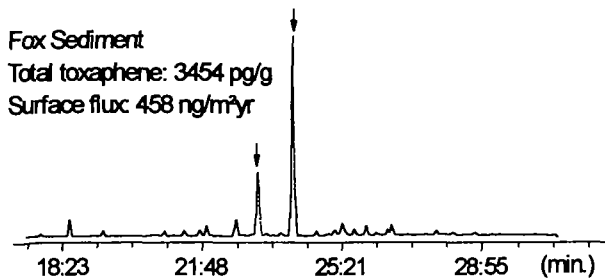
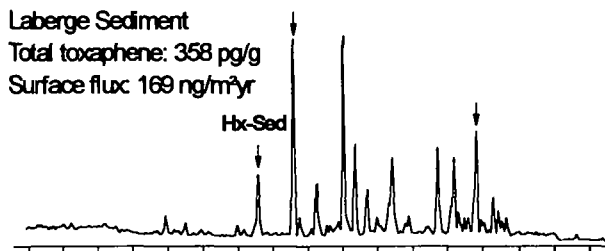
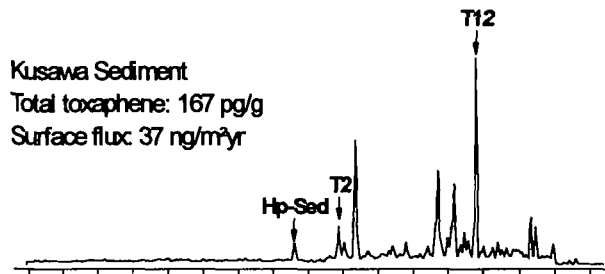


Figure 1. GC-ECNIMS selected ion chromatograms (sum of hexa- to nonachlorobornanes) of surface sediment from three Yukon lakes.

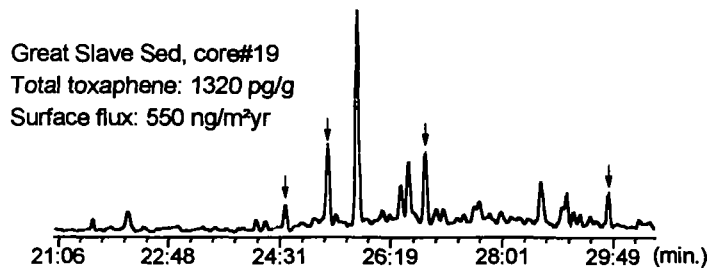
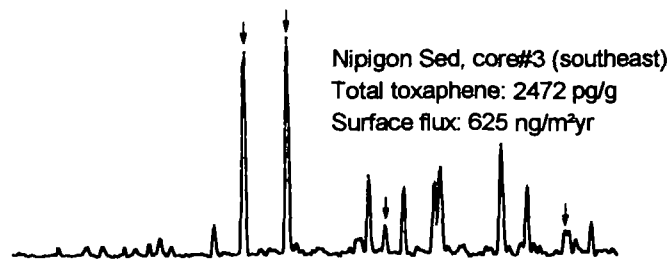
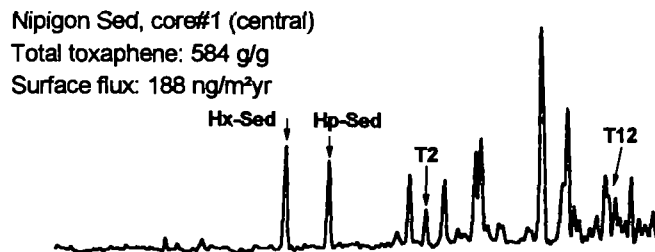


Figure 3. GC-ECNIMS selected ion chromatograms (sum of hexa- to nonachlorobornanes) of Nipigon and Great Slave Lake surface sediment.

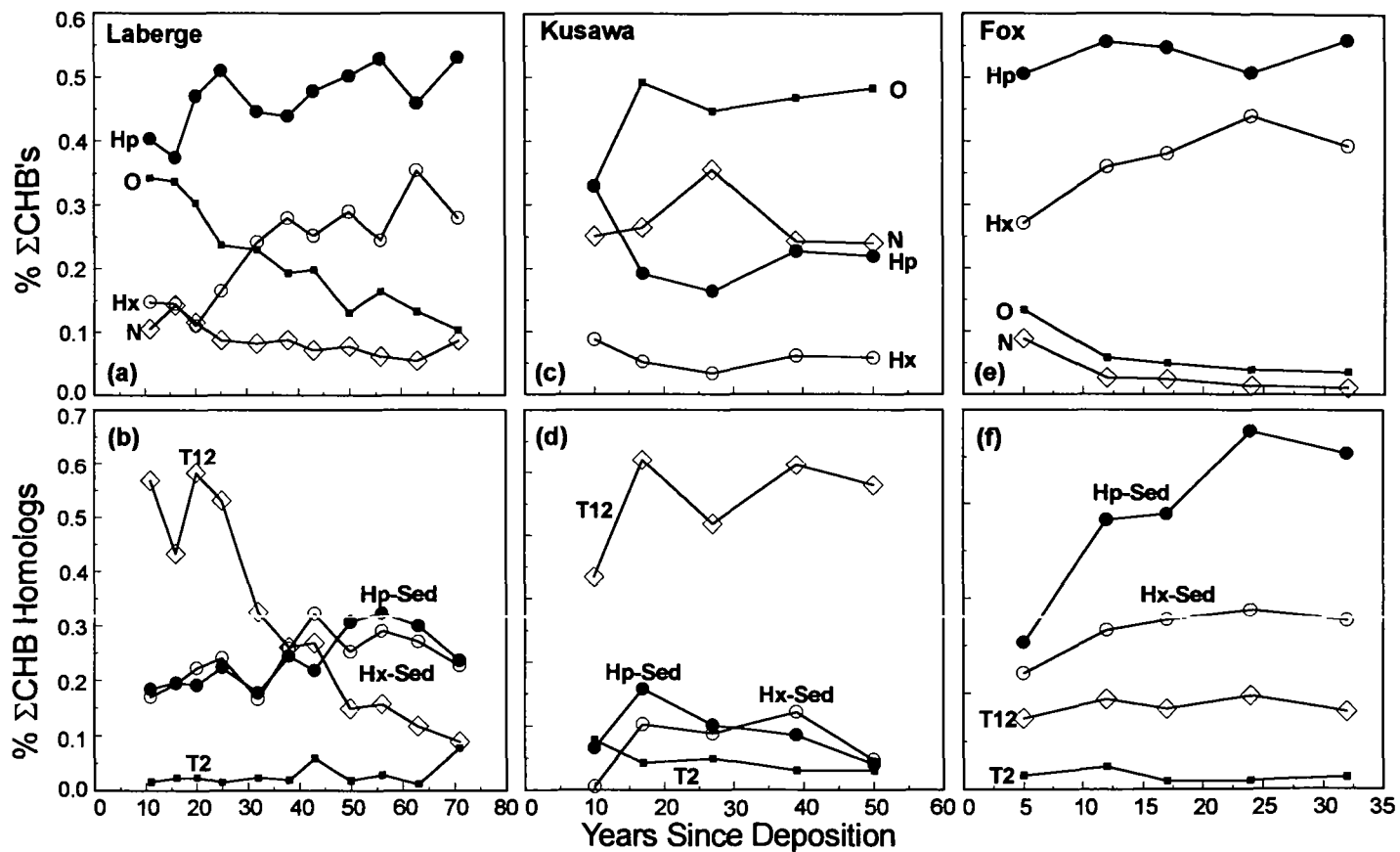


Figure 2. % Σ CHB's (Hx, Hp, O and N) and Σ CHB homologs (Hx-, Hp-Sed, T2 and T12) as a function of time since deposition in the sediment cores of three Yukon lakes (Laberge, Kusawa and Fox).