

HISTORICAL PROFILES OF TOXAPHENE CONGENERS IN DATED SEDIMENT CORES COLLECTED NEAR TWO PULP MILLS

Derek Muir¹, Heidi Karlsson¹, Mohan Kohli¹, Xiaowa Wang¹, Sean Backus¹, Lyle Lockhart², and Paul Wilkinson²

¹Environment Canada, National Water Research Institute, 867 Lakeshore Road, Burlington ON L7R 4A6,

²Freshwater Institute, Department of Fisheries and Oceans, Winnipeg, MB R3T 2N6, Canada

Introduction:

The possibility that toxaphene, or toxaphene related chlorinated pinenes/camphenes, could be emitted as a byproduct of chlorine bleaching of pulp has been discussed in several studies published over the past 15 years [1-3]. Recent studies by Rappe et al. [4,5] and Shanks et al. [6] have concluded that pulp mills in the mid-west USA, some of which had previously used elemental chlorine for pulp bleaching currently, are not sources of toxaphene-like compounds. Shanks et al. [6] analysed surficial sediments collected near 6 pulp mills, as well as at 5 sites that were thought to have previous toxaphene contamination from agricultural use, and at 2 background sites in Wisconsin and Minnesota. They found low (all <10 ng/g dw) levels of toxaphene both upstream and downstream of pulp mills. Slightly higher levels were found in rivers from areas of previous toxaphene use and both sites had higher levels than "background" riverine sites. Rappe et al. [4,5] analysed sample splits from the same study and reached similar conclusions although they obtained quite different concentrations (about 0.01 of those reported by Shanks et al [6]). [The discrepancy could be explained if Rappe et al used individual congeners rather than technical toxaphene to quantify the small number of peaks observed]. Rappe et al. [5] also detected the persistent dechlorination products of toxaphene "hex-sed" (B6-923) and "hepsed" (B7-1001), upstream and downstream of one of the mills. Rappe et al [7] also found that chlorobornanes in Baltic Sea sediments did not show a trend with distance from former chlorine bleaching mills. Taken together these recent studies clearly show that recent sediments near bleached pulp and paper mills have no toxaphene signal. However, because the sediment cores were comprised of material of unknown date of deposition, the question of past emissions was not addressed very well. Shanks et al.[6] left open the possibility of past emissions. These studies also showed that fine grained sediments with higher organic carbon content had generally higher toxaphene levels. These sediments may eventually be deposited in lake depositional areas. Sediments from the Great Lakes [8] and in many remote lakes in Canada [9] have been shown to preserve a record of toxaphene deposition with varying degrees of dechlorination.

Our goal in this study was to analyse toxaphene in dated sediment cores showing uniform sedimentation rates collected from depositional areas of lakes downstream of pulp mills that formerly used elemental chlorine for bleaching. Here we report results of analysis of two such cores collected near pulp mills in northwestern Ontario.

Materials and Methods

Samples: Sediment cores were collected in May 1998 in Jackfish Bay, an inlet on the north shore of Lake Superior, in a depositional area about 1.5 km (48°48'N, 86°59'W) from the outfall of Blackbird Creek which receives the effluent of the pulp mill at Terrace Bay, ON. For comparison a core was collected, at site 80 in the central Lake Superior basin in May 1998. Cores were collected from the vessel CCS Limnos using a oceanographic box corer which was carefully subsampled with 10 cm dia acrylic tubes. These cores were extruded at 0.5 cm and 1 cm intervals. Slices were subsampled for ^{210}Pb and ^{137}Cs dating and the remaining sample was stored at 4°C and analysed for toxaphene and PCBs. Another core from the same box core was analysed for $\delta^{13}\text{C}$ and total organic carbon (TOC). A sediment core was also collected in Clay Lake (50°03' N, 93°33'W), the first major depositional area downstream of the pulp mill at Dryden ON, in June 1995 using a KB corer (10 cm dia). The core was sliced in 1 cm intervals. The slices were freeze dried and subsamples dated with ^{210}Pb [12]. Dry samples were stored in glass jars at 4°C until subsequently analysed for toxaphene in 1998.

Analysis: Sediments were extracted using previously described methods [10]. In brief, wet sediment was centrifuged to remove excess water, mixed with Celite and then extracted with dichloromethane using a Dionex Accelerated Solvent Extractor. Freeze dried sediments were extracted with the same procedure. Prior to extraction each sample was spiked with ^{13}C chlordane. Sulfur was removed with elemental Hg and samples were chromatographed on activated silica columns to separate most chlorobornanes from PCBs [10].

GC analysis of chlorbornane (CHB) congeners: Analysis of hexa- to decachloro- toxaphene congeners in sediment extracts was conducted by low resolution ECNIMS using a HP6890 GC/HP5973 MSD as described previously [9]. Separation was performed with a HP5 column (30m x 0.25 mm id; film thickness, 0.25 μm) using a temperature program optimized earlier by Glassmeyer et al. [11] and splitless injection. Total toxaphene was quantified using a technical toxaphene standard and twenty four toxaphene congeners were quantified using standards from Dr. Ehrenstorfer (Augsburg Germany) or Promochem (Wesel, Germany).

Results and Discussion

The cores from Jackfish Bay, the central Lake Superior basin and from Clay Lake all had relatively uniform mass sedimentation rates based on excess ^{210}Pb calculated using the RSSM model [12]. Slices dated to the early 1960's with ^{210}Pb agreed well with the ^{137}Cs peak for bomb fallout. In the Jackfish Bay core, TOC ranged from 1.5 to 2.5% from the mid-1950's to 1990's. $\delta^{13}\text{C}$ shifted from -24.0‰ in sediments dated to the mid-1950's to -26.5‰ in samples from the late 1980's reflecting inputs of terrestrial plant carbon from the pulp mill which had maximum BOD emissions in the mid to late 1970's (Figure 1).

Toxaphene was detected in all three cores at low or sub ng/g (dry wt) concentrations (Table 1, Figure 1). In the Jackfish Bay and Lake Superior cores the onset of toxaphene occurred in the late 1950's and reached maximum concentrations in slices dated to the mid-1980's. This is 2-5 years later than observed by Swackhamer et al. [4] in 3 of 4 cores from Lake Superior but given the slightly greater temporal resolution of our cores is consistent with recent conclusion that atmospheric sources, and long range transport, resulting from agricultural use of toxaphene explains the historical deposition pattern in this lake [14]. The core from Clay Lake had lower toxaphene levels with only the persistent congeners B6-923 and B7-1001 detectable. The

historical profile shows a slightly earlier onset of deposition to Lake Superior with a maximum deposition beginning in the 1960's and continuing to the early 1980's.

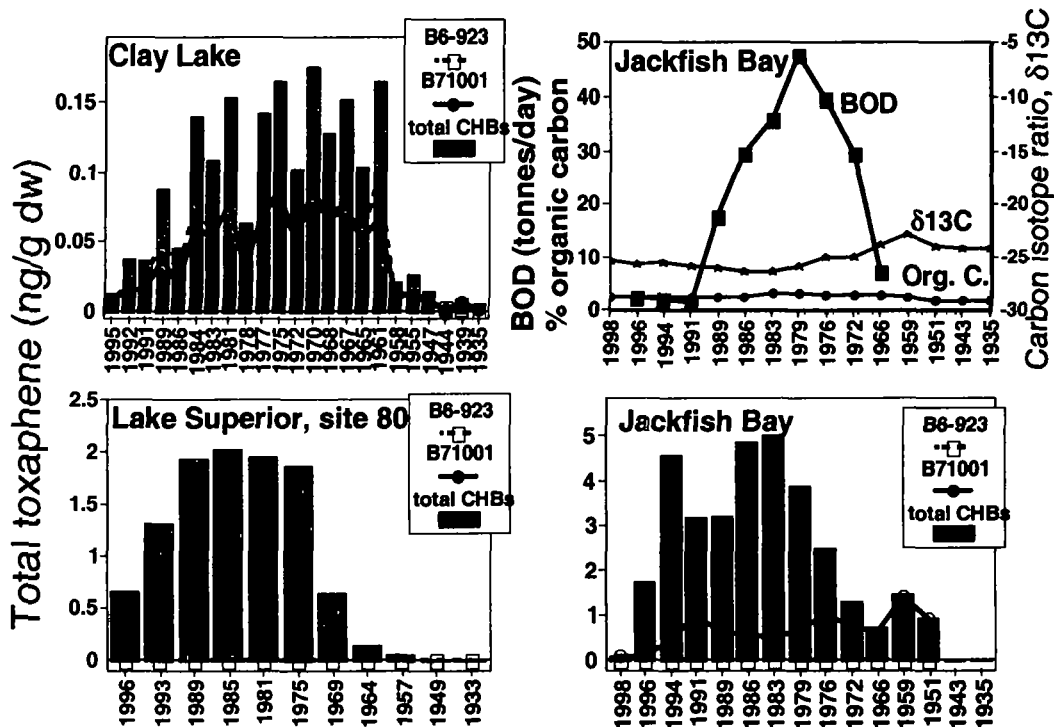


Figure 1. Depth profiles of total toxaphene congeners (ng/g dw) and two "terminal" chlorobornanes, B6-923 and B7-1001, in two dated sediment cores collected downstream of pulps (Jackfish Bay, Clay Lake) and in at background site (Lake Superior, Site 80). The upper right panel shows historical trends of % organic carbon and $\delta^{13}C$ in the core from Jackfish Bay and in BOD at the Terrace Bay mill.

In Table 1 we report toxaphene concentrations based on total CHB congeners (24 were determined although typically 10-16 were detected) as well as using a technical toxaphene standard following Glassmeyer et al [11]. On average difference toxaphene quantified with the technical standard was 3.5x higher than by summing results for individual congeners reflecting the fact that the ECNIMS method detected peaks for which no standards were available.

The hexa- and heptachloro bornanes, B6-923 and B7-1001 were detected in all cores and were present at higher proportions of total CHBs in the two cores collected downstream of the pulp mills (Figure 1). B6-923 and B7-1001 were the only congeners detected in the Clay Lake core. Rappe et al [5,6] also detected levels of B6-923 and B7-1001 in sediments especially in a deep sample collected downstream of the Port Edwards/Nekoosa. Shanks et al [4] also found higher levels of hexa- and heptachlorobornanes in that sample but were unable to confirm the presence of B6-923 and B7-1001. We have previously shown that the presence of B6-923 and B7-1001 at high proportions of total CHBs indicates the historical use of technical toxaphene [9].

ORGANOHALOGEN COMPOUNDS

TOXAPHENE - POSTERS

Table 1. Maximum and surface concentrations and fluxes of toxaphene in sediment cores

Core/ pulp mill	Sedimentation rate, g/m ² yr	Maximum total CHBs ¹ ng/g dry wt	Maximum toxaphene ng/g dry wt	H6-923 Range (%)	H7-1001 Range (%)
Jackfish Bay (Terrace Bay, ON)	700	4.82	23.5	0.1 - 0.9	5 - 83
Lake Superior, Site 80 (background site)	200	1.94	8.67	0.1 - 0.2	³
Clay Lake (Dryden ON)	1090	0.18	0.61	31 - 68	32 - 69

¹Sum of individual congeners; ²Flux is based on toxaphene quantified with technical standard; ³not determined.

Highest proportions are found in lakes treated with toxaphene and in sediments downstream of areas that had toxaphene use in agriculture or possibly for biting insect control. The most likely explanation for the presence of elevated proportions of B6-923 and B7-1001 at Jackfish Bay and Clay Lake is small scale upstream use of technical toxaphene, possibly for local insect control during the 1950 and '60's, and its slow "leakage" into the watershed from the terrestrial environment. The toxaphene profile in these cores is therefore a mixture of atmospheric deposition and local use. Another possibility is that the toxaphene originates from wood chips, especially tree bark, that may have absorbed toxaphene from the atmosphere and subsequently contributed to organic carbon deposited in these cores as indicated by the $\delta^{13}\text{C}$ signal. The profile of BOD emissions at Terrace Bay (Figure 1), which may be indicative of higher (untreated) carbon flows to Jackfish Bay, does not coincide well with the profiles of total toxaphene nor with these two "terminal" toxaphene products.

References

- [1] Jarnuzi, G., Matsuda, M. Wakimoto, T. *Kanyo Kagaku*, **1992**, 2, 364.
- [2] Larson, R.A., Marley, K.A. *Formation of Toxaphene-like Contaminants during Simulated Paper Pulp Bleaching*. Water Resources Center, U of Illinois, Chicago WRC 205.
- [3] Krinstad, K.P., Lindström, K. *Environ. Sci. Technol.* **1984**, 18, 236A.
- [4] Shanks, K.E., Macdonald, J.G., Hites, R.A. *J. Great Lakes Res.* **1999**, 25, 383.
- [5] Rappe, C., Haglund, P., Andersson, R., Buser, H. *Organohalogen Compds.* **1998**, 35, 291.
- [6] Rappe, C., Haglund, P., Andersson, R., Buser, H. *Organohalogen Compds.* **1998**, 35, 287.
- [7] Rappe, C., Andersson, R., Bonner, M., Cooper, K., Fiedler, H., Lau, C., Howell, F. *Chemosphere* **1997**, 34, 1297.
- [8] Pearson, R.F., Swackhamer, D.L., Eisenreich, S.J., Long, D.T. *Environ. Sci. Technol.* **1997**, 31, 3523.
- [9] Muir, D.C.G., Stern, G., Karlsson, H. *Organohalogen Compds.* **1999**, 41, 565.
- [10] Muir, D.C.G., Omelchenko, A., Grift, N. P., Savoie, D.A., Lockhart, W. L., Wilkinson, P., Brunskill, G. J. *Environ. Sci Technol.* **1996**, 30, 3609.
- [11] Glassmeyer, S.T., Shanks, K.E., Hites, R.A. *Anal. Chem.* **1999**, 71, 1448.
- [12] Robbins, J.A. In: *Biogeochemistry of Lead in the Environment*, J.O. Niragu Ed. Elsevier, Amsterdam. **1978**. p 285.
- [13] Swackhamer, D.L., Pearson, R.F., Schottler, S.P. *Chemosphere* **1998**, 37, 2545.
- [14] Swackhamer, D.L., Schottler, S.P., Pearson, R.F. *Environ. Sci. Technol.* **1999**, 33, 3864.