

Toxaphene in the Great Lakes: Review and Current Status

Derek Muir¹, Deborah Swackhamer², Terry Bidleman³, Liisa Jantunen³

¹National Water Research Institute, Environment Canada

²Environmental Health Sciences and Water Resources Sciences Program, University of Minnesota, Minneapolis

³Centre for Atmospheric Research Experiments, Meteorological Service of Canada,

Introduction

Toxaphene was introduced as an insecticide in 1947 and became one of the most widely used chlorinated pesticides in the United States and in the world during the 1970s. The story of toxaphene in the Great Lakes, like that of most other persistent organochlorines, has only become clear after the ban on the use of this pesticide in the mid-1980s. Although much of the peer-reviewed literature on environmental fate of toxaphene has involved measurements in the Great Lakes, delineating the extent of contamination has proved very challenging because of the difficulties of quantifying this multi-component mixture. The spatial and temporal trends of toxaphene in the Great Lakes are now reasonably well documented. Our objective is to summarize the key findings and conclusions on toxaphene in the context of the Great Lakes; many of these conclusions may be broadly applicable to the global fate of this chemical. This short paper touches on the highlights. More details are available in our recent review¹.

Results and Discussion

Sources: The history of toxaphene production and use in the United States has been chronicled by Li² and modeled by MacLeod et al.³. Of the 5.34×10^5 t of toxaphene that were used in North America (includes the United States and Mexico), 1.5×10^4 t (3%) was estimated to remain in active circulation as of the year 2000. Most of the toxaphene in active circulation resides in the soils of the southern U.S. and Mexico (83%). Using their regional scale long range transport model, MacLeod et al.³ estimated that approximately 70% of the loadings to the Great Lakes basin came from continental-scale transport mainly from the southern states while loadings from local usage were less than 30% of the total due to the relatively small amount of toxaphene applied.

Air: Toxaphene concentrations in Great Lakes air are dependent on air transport pathways and temperature. Short-term studies have found higher toxaphene levels in air during warmer months. James and Hites⁴ and Hoh and Hites⁵ reported toxaphene concentrations at 288 °K were 160 pg m^{-3} at Lubbock, Texas, $710\text{-}950 \text{ pg m}^{-3}$ at Rohwer, Arkansas, $25\text{-}39 \text{ pg m}^{-3}$ at Bloomington, Indiana and $11\text{-}27 \text{ pg m}^{-3}$ at Sleeping Bear Dunes on Lake Michigan, in 2000-2001 and 2003-2004, confirming the southern states as an ongoing source region. Higher concentrations were found over Lake Superior in August 1996 ($28 \pm 10 \text{ pg m}^{-3}$) than May 1997 ($12 \pm 4.6 \text{ pg m}^{-3}$)⁶. Similar air concentrations were found over Lake Ontario in July 1998 ($19 \pm 4 \text{ pg m}^{-3}$) and June 2000 ($25 \pm 20 \text{ pg m}^{-3}$), although there was only a 5-8 degree difference in air or water temperatures during those months⁷. Whereas measurements of toxaphene in water by different laboratories agreed within a factor of two or better, those in air at a particular site varied by factors of 2-5⁸.

Precipitation: Precipitation has not been extensively investigated as an input pathway for toxaphene to the Great lakes but recent work suggests it is important⁹. Maximum concentrations and fluxes for all homologues at the IADN Point Petre sampling site on Lake Ontario generally occurred in the spring (March-April-May). Hepta- and octachlorobornanes were the predominant homolog groups. Toxaphene was one of the most prominent organochlorines in Great Lakes precipitation in the 1990s exceeding all except total HCH and PCBs at Point Petre on Lake Ontario⁹.

Surface water: Several groups have made measurements of toxaphene in surface water of the Great Lakes between 1996 and 2000 using XAD-2 resin column extractions followed by determination using GC-ECNI-MS^{6, 10-13}. Toxaphene concentrations were highest in Lake Superior ($910 - 1120 \text{ pg L}^{-1}$), intermediate in lakes Michigan and Huron ($380 - 470 \text{ pg L}^{-1}$), and lowest in lakes Erie and Ontario ($81 - 230 \text{ pg L}^{-1}$). There was significant variability in dissolved concentrations with season that corresponded to whether the lakes were stratified or not. During stratified conditions, there was significant volatilization loss from the epilimnion, and then concentrations increased when the lakes vertically mixed in the fall¹⁴. Enantiomer ratios of toxaphene congeners have been measured to examine degradation and sources of toxaphene in water and air^{7,15}. Karlsson et al.¹⁵ found that ERs of B7-515, B8-1412 B8-1414, and B8-806/809 were close to racemic (ER=1) while B8-1945 was non-racemic (ERs of 1.13-1.20) in air and

water of Lake Superior. ERs for B8-1945 were also non-racemic in tributaries. The results suggest that B8-1945 is undergoing biodegradation within the Lake Superior water column and watershed. The similar ERs in air and water supports the hypothesis that volatilization of toxaphene from lake water into air is the main source of the air borne toxaphene over the lake in August ⁷.

Dated Sediment cores: Profiles of toxaphene in dated sediment cores have been used to infer historical deposition and degradation of toxaphene in Lake Superior and nearby inland lakes ^{11, 16}, Michigan ^{16,17} and Ontario ^{16, 18-20}. There is sufficient detail from these studies to infer the history of inputs of toxaphene to three of the five Great Lakes reasonably accurately. The onset of toxaphene inputs into the Great Lakes occurs in sediment horizons dated to the mid-1940s and is quite consistent in all three lakes. However, the dates of maximum concentrations and fluxes vary over a 15 to 20 year period. In Lake Ontario maximum inputs occurred in the 1970s, while maxima in cores from central basins of lakes Michigan and Superior generally occur in the mid- to late 1980s and fluxes were significantly lower than in Lake Ontario ¹⁶. Two small lakes Siskiwit (WI) and Outer Island (WI) near the western end of Lake Superior, had maxima in the early 1970's ¹⁶, as did Clay Lake in northwestern Ontario ¹⁹. Sediment core profiles in Lake Ontario show a mean decline $3.2 \pm 0.6\%$ per year ^{18,19}. The average decline was similar in Lake Michigan, averaging $3.1 \pm 1.2\%$ per year. Annual % declines in toxaphene in Lake Superior were generally more rapid than in Michigan and Ontario, averaging $4.6 \pm 2.8\%$ per year. The overall degradation of toxaphene is very low in Great Lakes sediments with half-lives estimated to range from 40 to >100 years ¹⁶. While toxaphene degradation can be difficult to discern at the homolog level, at the congener level distinctive increases in the hexachlorobornane B6-923 and heptachlorobornane B7-1001, as well as their dechlorination products, are discernable in Great Lakes sediments. Ruppe et al.²¹ demonstrated that the toxaphene profile in the sediment sample from western Lake Ontario was dominated by the known major metabolites B6-923 and B7-1001. These authors were also able to identify transformation products of B7-1001. They concluded that only small amounts B7-1001 and B6-923 had been metabolized based on the ratios to their transformation products identified *in vitro* using an anaerobic bacterial culture. Marvin ²⁰ found that B6-923 and B7-1001 constituted 100% of Σ CHB in sediments dated to the 1940s and 50s from the central Niagara basin of Lake Ontario suggesting that the earliest deposited residues had been significantly transformed.

Pulp mills as possible toxaphene sources: The persistently high concentrations of toxaphene, observed in Lake Superior lake trout in the 1990s, and apparent lack of decreases in sediment cores in northern Lake Michigan, led to speculation that there might be significant within-basin sources of toxaphene. In the late 1990s several groups investigated the hypothesis that inadvertent toxaphene production could be occurring from chlorination of terpene precursors present in pulp mill effluents. Shanks et al.²² measured toxaphene concentrations in river sediments from Great Lakes tributaries in Wisconsin and Michigan. They found that sediments downstream of pulp and paper mills did not have elevated levels. Rappe et al.^{23,24} 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.²²). The discrepancy could be explained if Rappe et al. used individual congeners rather than technical toxaphene to quantify the small number of peaks observed.

Spatial and temporal trends in Great Lakes fishes: Fish collection surveys in the late 1970s and early 1980s showed that toxaphene was present in all Great Lakes fish with highest concentrations in lake trout (*Salvelinus namaycush*) and coho salmon (*Oncorhynchus kisutch*) ²⁵⁻²⁸. Glassmeyer et al.²⁹ found that toxaphene concentrations in lake trout and rainbow smelt were ranked Lake Superior > Michigan > Huron > Ontario in samples collected in 1992. Muir et al.¹³ found that toxaphene concentrations in lake trout from Siskiwit Lake on Isle Royale were about 15-fold lower than in Lake Superior lake trout when compared on a wet weight or lipid weight basis. Glassmeyer et al.²⁹ found that toxaphene concentrations in lake trout and rainbow smelt declined significantly ($p < 0.05$) in all lakes except Lake Superior. Combined results from several studies ^{13, 29-31} from the 1970s to late 1990s suggest no decline in toxaphene concentrations in Lake Superior ¹. Toxaphene congeners B8-1413, B8-2229, B9-1679 and B9-1025 generally increased in prominence and in concentration (ng g^{-1} lipid wt) up the food chain of Lake Superior. Muir et al. ¹³ found toxaphene and major congeners in lake trout were significantly correlated ($p < 0.05$) with % lipid, age, length and weight but not with nitrogen isotope ratios ($\delta^{15}\text{N}$). Bioaccumulation factors for toxaphene in lake trout were remarkably constant ranging (log BAF) from 6.6 to 7.1 in the Great Lakes and Siskiwit Lake ¹. Biota-sediment accumulation factors for toxaphene in *Diporeia* ranged from 5.2 to 15 compared to 2.1-3.1 for Σ PCBs ¹³. This indicates that toxaphene congeners are highly bioavailable relative to PCBs. Most octa- and nonachlorobornanes were found to have trophic magnification factors (TMF) values >1 in the Lake Superior pelagic food web indicating significant food chain biomagnification ¹³. TMF values for B9-1679 were similar to total

toxaphene and about 80% of those for recalcitrant chemicals, p,p'-DDE and CB153¹³.

Conclusions

Given the long half-lives in fish and the water, elevated toxaphene is likely to remain a contaminant issue until the middle of the 21st century. Modelling by Swackhamer et al.¹² demonstrated that colder temperatures and low sedimentation rates in Lake Superior, and to some extent in Lake Michigan, conspire to maintain high water concentrations. There has been very little study of the possible biological consequences of prolonged elevated toxaphene concentrations on fish and fish-eating wildlife in the Great Lakes. However, Delorme et al.³² reported a study which implies that continued high levels of toxaphene in lake trout may have biological consequences in terms of fish recruitment. The 2003 "Guide to Eating Sport Fish" published by Ontario Ministry of Environment³³ indicates fish consumption advisories for Lake Superior lake trout due to toxaphene levels. As a result of the high toxaphene levels Ontario Ministry of Natural Resources has restricted sale with Ontario (but not the export) of large lake trout harvested from Lake Superior as of 1995. No toxaphene advisories for Great Lakes fish consumption have been issued by the Great Lakes states.

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