

A Mass Balance of Toxaphene in the Great Lakes of North America

Deborah L. Swackhamer, Roger F. Pearson, and Shawn Schottler

Environmental and Occupational Health, School of Public Health, Box 807 UMHC, University of Minnesota, Minneapolis, MN, 55455, USA.

1. Introduction

Toxaphene is a broad-spectrum pesticide that is the most widely used chlorinated agricultural chemical in U.S. history ¹⁾. It was the replacement for DDT when the latter was banned in 1972, and was used primarily on cotton, peanuts, soybeans, and grains, and as a cattle dip. It was first introduced in 1947 by Hercules, and was used in the 1950's and 1960's as a piscicide to kill rough fish from inland lakes in the upper mid-west and Canada. It eventually was registered with 180 producers, and was contained in over 800 different products ²⁾. Various estimates of total cumulative use in the U.S. range from 1 to 3×10^9 kg ^{2,3)}. World use can be estimated as twice this figure. It was banned in 1982 following concerns about its toxicity and widespread environmental distribution. Despite this action, toxaphene is the contaminant found in the highest concentration of all organochlorine compounds measured in fish from Lake Superior, including PCBs and EDDT ^{4,5)}.

Toxaphene is a complex mixture of chlorinated bornanes and bornenes, made by the chlorination of terpenes from pine tree roots. It was produced either by chlorinating pinenes (Strobane) or camphenes (toxaphene), and more than 670 different components have been estimated to comprise these mixtures ⁶⁾.

Approximately 85% of the toxaphene used in the U.S was on cotton crops in the southern states from Texas eastward to Georgia. Approximately 1% or less was used in the Great Lakes basin ⁷⁾. The rate of use in the basin (including Ontario) was approximately 1 million kg/yr in the early 1970's, and would have peaked in approximately 1977. Thus the presence of toxaphene in the Great Lakes has largely been attributed to long-range atmospheric transport from the southern U.S. or Central America, followed by wet and dry deposition to the lakes. This assumption has been supported by the finding of toxaphene in fish in Siskiwit Lake, on Isle Royale in Lake Superior ^{8,9)}; bog measurements made from Minnesota, southern Ontario, and Maine ¹⁰⁾; and air measurements coupled to trajectory analysis ¹¹⁾. Total inputs to Lake Superior were estimated to be 12.5 kg/yr (0.15 ug/m² yr) wet deposition, 6.3 kg/yr (0.07 ug/m² yr) dry deposition, and between +225 kg/yr and -1100 kg/yr (+2.7 to -13 ug/m² yr) by gas exchange ¹¹⁾. The huge uncertainties in the gas exchange reflect that there were no published measurements of toxaphene

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in Lake Superior water until now. The estimated range in gas flux represents a water concentration range of 0.1 - 1.0 ng/L.

We have recently completed the first known determinations of toxaphene concentrations in Great Lakes water and its accumulation in sediment. Using these data and published air concentration data, we have constructed first order mass balance models of toxaphene in three of the Great Lakes. We also have used these data in a dynamic model to estimate the historical air profile, and evaluate the potential for non-atmospheric sources of toxaphene to the lakes.

2. Methods

Multiple sediment cores were obtained from lakes Superior, Michigan, and Ontario in 1991-1993. We determined the current and historic accumulation rates and the total cumulative burden of toxaphene in each of the cores, accounting for sediment focusing and compaction. The historical record was determined by ^{210}Pb dating.

More recently, we analyzed 5 water samples from Lake Superior, 7 from Lake Michigan, and 9 from Lake Ontario collected in 1992 by the U.S. EPA using a continuous flow counter-current extraction, and extracts were provided courtesy of Dr. Steven Eisenreich, Rutgers University. Samples were preserved in such a way as to allow for toxaphene determinations.

Samples were extracted, and interferences removed by alumina and silica gel liquid-solid chromatography. Extracts were analyzed by electron capture negative ion gas chromatographic mass spectrometry (ECNI-GCMS) in selected ion mode for homologs and total toxaphene ¹².

3. Results and Discussion

Concentrations of toxaphene in Great Lakes water in 1992 were as follows:

	Lake Superior	Lake Michigan	Lake Ontario
diss. toxaphene conc., ng/L	0.29 ± 0.04	0.13 ± 0.05	0.061 ± 0.022
% in dissolved phase	> 90	90	90

These values show that Lake Superior has the highest concentrations in water in the Great Lakes, which is consistent with the observed trends in fish data from Lake Superior to Lake Ontario. These elevated concentrations may be a result of non-atmospheric inputs of toxaphene to Lake Superior, or they may be a result of slower loss mechanisms operating within Lake Superior.

These water values can be used to estimate the air-water exchange of toxaphene, assuming that they are all exposed to the same air concentrations (and the available data indicate that they are; 11,13,14). Calculations indicate that the net flux for all lakes is from air to water. Lake Superior, Lake Michigan and Lake Ontario are 100 %, 72% and 33% saturated, respectively. The annual fluxes, adjusting for seasonal temperature changes and differences among lakes, are 400, 2200, and 3900 ng/m² yr, respectively. A first order mass balance can be constructed from these

estimates and the total atmospheric inputs (net gas exchange plus wet and dry deposition). Connecting channels flow in the upper lakes is small and is not included.

	L. Superior	L. Michigan	L. Ontario
atmospheric inputs	+52	+149	+96
sedimentation loss	-90	-290	-98
Niagara River input	--	--	+18
net	-38	-141	-16

This first order exercise indicates that Lake Ontario is near steady state regarding toxaphene, but that the other two lakes are not in steady state, or have or once had addition inputs. To help answer this, we constructed a dynamic model of lakes Superior and Michigan using the STELLA II modelling framework. The sediment data were used to calculate the best-fit estimate of historical atmospheric concentrations, which were consistent with the few historical air data available. However, given the high uncertainties in the data used in the model, we cannot definitively rule in or out non-atmospheric sources to the upper lakes.

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