Analysis of Toxaphene Behavior in the Great Lakes

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Abstract

This paper is a summary of the data interpretation and modeling research performed in an effort to interpret existing data on toxaphene in the Great Lakes and to understand its past and present behavior. The analysis has provided scientifically plausible explanations for the somewhat disputable conclusions related to the observations of toxaphene behavior in the Great Lakes. We have shown that understanding the effects of lake geometry, hydrology, sediment/sorbent dynamics, and food web structure and function on the transport and fate of toxaphene in the Great Lakes is sufficient to explain the *in situ* observations without invoking the influence of local point sources. We have also shown that toxaphene is behaving no differently from other historically banned chemical mixtures (PCB's, DDT), which continue to cycle within the environment and, therefore, persist in the Great Lakes for times dependent on the above lake-specific factors and the pattern of historical use both inside and outside the Great Lakes Basin.

Introduction

Toxaphene is a complex mixture of chlorinated bornane, bornene, and camphene compounds. Technical toxaphene, produced by chlorinating camphene, was first produced in 1947 and sold in the United States for use as a pesticide. Between the 1960's and mid-1970's, toxaphene was the most heavily used insecticide in the United States.[1)] Toxaphene was most frequently used on cotton; however, it was also applied to a variety of grains and vegetables, used as a miticide for scabies control on cattle and other livestock, and used as a piscicide to kill off rough fish in lakes. Concern over toxaphene bioaccumulation and toxicity eventually led to a review by the U.S. EPA, and by 1982 most registrations for toxaphene were canceled with the provision that existing stocks could be used until 1986.[2)]

Toxaphene is a contaminant of concern in the Great Lakes; it has been listed among the *bioaccumulative chemicals of concern* (BCC) in the Great Lakes Water Quality Guidance.[3)] The properties of toxaphene which make it a contaminant of concern include its extensive use in the environment, its persistence in the environment, its potential to be transported long distances in the atmosphere, its propensity to bioaccumulate in aquatic biota, and its toxicity and carcinogenicity. In spite of its ban in the mid-1980's, it is still present in unacceptably high levels in many parts of the Great Lakes basin and is not decreasing in some systems as quickly as expected. In particular, there are some observations, summarized quite nicely in report from an expert panel workshop on toxaphene in the Great Lakes,[4)] that have led to various speculations about historic and current sources of toxaphene to the Great Lakes. Among the observations that have given rise to some uncertainty about the sources and behavior of toxaphene are:

1. Toxaphene concentrations in the water column and sediments of Lakes Michigan and Superior (upper Great Lakes) appear to be higher than those in the lower Great Lakes (Erie and Ontario) and in small, isolated lakes located near or on islands in the upper Great Lakes. These levels in the upper Great Lakes do not appear to be decreasing as rapidly as in the other systems.

2. The distribution of toxaphene homologs in water and sediment samples varies among lakes.
3. Higher toxaphene levels and rates of accumulation have been found in sediment cores taken from northern Lake Michigan than in those taken from the southern basin of the lake.[5)]
4. Lake Superior lake trout have higher body burdens of toxaphene than those in other lakes and, unlike other lakes, the 1992 mean level appears to be unchanged relative to the 1982 level.[6)]

This paper summarizes our attempt to utilize what we know about the transport and fate of this type of chemical in large lakes to help explain these observations and to draw conclusions about the behavior of toxaphene in the Great Lakes that are consistent with the observed data.

Whole-lake Mass Balance Model

A process-oriented mass balance modeling framework, which has been used extensively to analyze PCB fate and transport in the Great Lakes, [7,8)] was applied to provide an understanding of the differences that might be expected in toxaphene concentrations among lakes and among chemical properties within a lake. The model is developed to compute long-term (year-to-year) changes (or steady-state values) in lake-wide average water column and upper mixed sediment layer concentrations of hydrophobic organic chemicals (HOCs), such as toxaphene. It includes processes for chemical equilibrium partitioning to solids in the water column and bottom sediments, sediment and associated chemical deposition, resuspension, and deep burial, hydrologic flushing, and air-water mass transfer (absorption and volatilization).

The model was applied to five different lakes: Lake Superior, Lake Michigan, Lake Erie, Lake Ontario, and a "small" lake that is representative of a lake like Basswood Lake on the Apostle Islands of Lake Superior. When the specific geometric, hydrologic, and sediment transport properties of these lakes are incorporated into our modeling framework, [9)] one can see that these lakes represent a wide range of surface area to volume ratio, hydraulic retention time, overflow rate, suspended solids concentration, and solids dynamics (as exemplified by the solids residence times in the water column and sediments. Our hypothesis is that each of these lakes has specific characteristics that will control their processing of an HOC so that the quantitative relationship between its external loading and its in-lake concentration is not *a priori* expected to be the same.

In order to understand how chemicals with different properties behave in lakes with different properties, we have used our model to produced the steady-state analyses depicted in Figure 1. The model was applied to each of the five lakes for three hypothetical non-polar chemicals with different properties representing a range of partition coefficients (K_{ow}) and Henry's Law Constants (H_e) that might be seen for toxaphene-like compounds. A reasonable range of K_{ow} values was obtained from the synthesis of field data in the toxaphene workshop report[4)] and from the measurement of H_e for a standard toxaphene mixture by Murphy, *et al.*[11)] All five lakes for all three chemical types received the same area-normalized load and gas phase boundary condition, thus simulating equivalent exposure to an atmospheric source of the chemical. In general, these results illustrate how chemicals with different properties behave differently within the same lake and chemicals with the same property will behave differently from one lake to the next. Specifically, the results suggest:

1. Even for the exact same area-normalized loading and chemical properties, the steady state concentration in water or sediments is not same for all lakes. Lake Superior and Lake Michigan, because of their smaller overflow rates and lower net sedimentation rates, would be expected to have the highest concentrations in water (followed by Lake Ontario and then Lake Erie and Small Lake). Lake Superior water column predictions would be even higher if we had adjusted H_e values for temperature differences between lakes, but in this case all lakes are assumed to have the same average temperature.

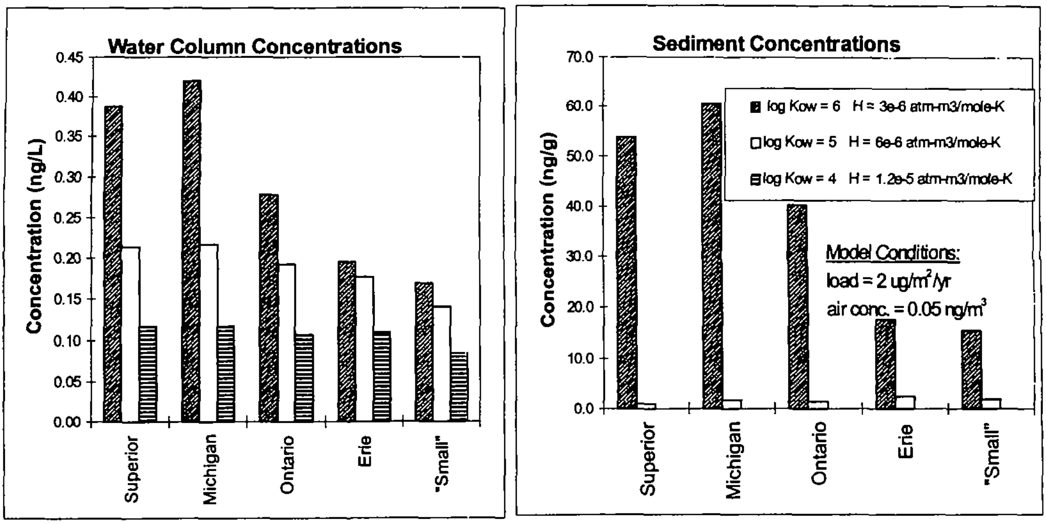

Figure 1. Steady-state mass balance model of three hypothetical chemicals in five lakes, all exposed to the same area-normalized loading and atmospheric boundary conditions.

2. Another observation above is that there are different toxaphene homolog ratios among lakes and that is used to suggest that there are different homolog ratios in the loadings. The results in Figure 1 demonstrate that the ratio between chemicals of different properties will vary within a lake as well as among lakes even though the external sources enter at the same 1:1:1 distribution.

This analysis also demonstrates the sensitivity of water column toxaphene levels to H_e and the sensitivity of sediment toxaphene levels to the water column partition coefficient. There have been very few measurements of these important parameters (and they have only been performed on a total toxaphene basis); considerable effort on the measurement of toxaphene physical-chemical properties is required to reduce uncertainty in the analysis of this mixture of compounds.

Analysis of Lake Michigan

The third observation above, that toxaphene concentrations and accumulation rates are higher in northern Lake Michigan sediments than in the southern basin, has led to hypotheses about the role of relatively local sources that impact the northern part of the lake to a greater extent than the south. In particular, one might hypothesize that Green Bay is and has been the source of this additional contamination in the north. Because the Green Bay watershed is so large (30% of the entire Lake Michigan watershed and 72% of the northern lake drainage area) and because sediment core analyses for PCBs and organochlorine pesticides showed the same spatial trend as toxaphene, [10)] we decided to investigate the hypothesis that historical use of toxaphene within the Green Bay watershed has and perhaps still is contributing a significant load to northern Lake Michigan.

Analysis of the records of the Wisconsin Agricultural Statistics Service its was estimated that 224,000 Kg of toxaphene was used in the Green Bay watershed between 1950-1980. Most of use was as a pesticide on cropland; however, there was some use on livestock and in lakes for rough fish control. Even if only 1% of this toxaphene usage (2240 Kg) ran off into Green Bay, it would represent a significant fraction of the estimate of the current inventory of toxaphene in all of Lake Michigan (11,000 Kg).[4)] This analysis, although uncertain, adds credibility to the hypothesis that higher toxaphene (and other pesticide) levels in northern Lake Michigan sediments are probably the result of historical pesticide use in the Green Bay watershed.

In addition to the above analysis, a mass balance modeling analysis of the Green Bay/Lake Michigan system was conducted with a spatially segmented (12 water column and 7 sediment segments) screening model (MICHTOX) developed by the EPA-Grosse Ile Laboratory.[12] Although there is insufficient space for presentation of this analysis, it confirmed the Fox River/Green Bay system as a significant source of toxaphene to the northern basin of Lake Michigan. It also suggested that the current measured level of toxaphene in the Lake Michigan water column can be explained by normal resuspension of lake bottom sediments without invoking any current watershed loadings to the system.

Lake Superior Lake Trout Analysis

The final observation for which the interpretation is somewhat uncertain is the observation that lake trout body burdens in Lake Superior might for some reason be behaving anomalously relative to those measurements in the other Great Lakes. Our analysis of this observation is based on the contention that exposure to bioavailable forms of a chemical is not the only determinant of bioaccumulation in top predator fish. Other very important factors include food chain length; food chain structure (dietary composition, benthic feeding habits, prey selectivity); fish migration; bioenergetics of both predator and prey (growth and respiration rates, prey consumption rates and assimilation); and physiology of both predator and prey (size, age, weight, lipid content, chemical assimilation and metabolism). If these factors are considered in analyzing the available data for this system, one can conclude that the observed toxaphene behavior in Lake Superior lake trout is not anomalous and indeed is expected without invoking any unusual or unexpected lake-specific loadings.

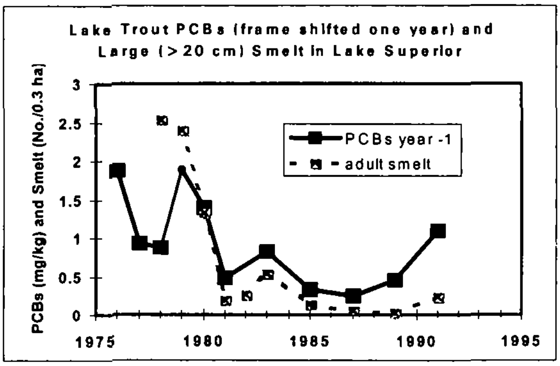

Figure 2. Temporal trends in large smelt per unit area and lake trout PCB levels in Lake Superior.

Our first observation is that, while the lake trout that were analyzed for comparison with those in other Great Lakes were the same size range (600-700 mm), it was determined that the lake trout from Lake Superior were much older than those from the other Great Lakes (12 years vs. 4 years). This longer exposure and slower net growth rate in Lake Superior, in combination with the expected higher bioavailable water column concentrations as discussed above, leads to an expectation that lake trout in Lake Superior should have higher toxaphene body burdens.

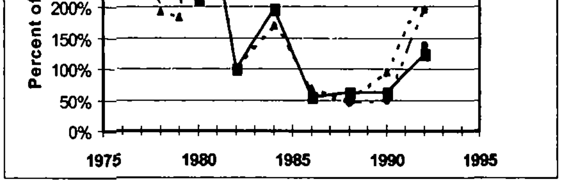

Figure 3. Temporal trends in PCB[15], DDT[15] and Toxaphene[6,15] relative concentrations in Lake Superior lake trout normalized to their respective 1982 levels.

With regard to the comparison of 1992 lake trout toxaphene concentrations with those in 1982, we submit that the dynamics of the smelt population (major prey fish for Lake

Superior lake trout) can explain the apparent lack of decrease from 1982 to 1992. From 1979 to 1981, there was a major perturbation in the smelt population of Lake Superior. A large decline in the number of large (>20 cm) smelt occurred, probably as a result of greatly increased predation pressure because of the rehabilitation of the Lake Superior lake trout population at that time (decreased commercial fishing, lamprey control, restocking).[13,14)] Variations in the age and size structure of the lake trout prey population could easily have repercussions in the bioaccumulation of organochlorine chemicals in the lake trout. Shown in Figure 2 are temporal profiles of the number per 0.3 hectare of smelt and the PCB body burdens in lake trout (after shifting the PCB data by one year to account for a bioaccumulation lag period). This trend analysis graphically illustrates how measurements made in 1982 might produce an unusually low level of lake trout body burdens of bioaccumulative chemicals and how the 1992 data might very well be expected to be higher simply on the basis of changes in the prey fish population.

Shown in Figure 3 is a comparison of the PCB trends with those of DDT and toxaphene, with all concentrations normalized to the levels observed in 1982. By plotting the data in this way, we demonstrate that DDT and toxaphene are behaving virtually identical to PCB's, which in turn track the smelt population waves (shown in Figure 2). Note that all three chemicals are higher in 1992 than in 1982; therefore, toxaphene is not behaving anomalously relative to other historically driven bioaccumulative chemicals of concern.

Acknowledgments

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