

Dioxin '97, Indianapolis, Indiana, USA

Toxaphene in Great Lakes Fish and Air

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Abstract

Toxaphene is a complex mixture of at least 600 hexa- through decachlorinated norbornanes and norbornenes. Like PCBs and other environmentally persistent organochlorine compounds, toxaphene is ubiquitous in the environment, probably because of its atmospheric transport away from areas of use. Work in our laboratory has shown that toxaphene levels are now higher in lake trout (*Salvelinus namaycush*) and rainbow smelt (*Osmerus mordax*) taken from Lake Superior as compared to levels in the four other Great Lakes. This suggests that there is either more toxaphene entering the Lake Superior basin or that the loss rates are significantly lower as compared to the other Lakes. To determine the atmospheric deposition of toxaphene to Lake Superior, bimonthly air samples have been taken at a remote shore-based site (Eagle Harbor, Michigan) and periodically over the lake itself (on the US Environmental Protection Agency research vessel, the *Lake Guardian*). The concentrations of toxaphene in these atmospheric samples are similar to those found in a recent study of Lake Ontario. This may indicate that all of the Great Lakes are receiving the same atmospheric burden. Additionally, the concentrations appear to be strongly correlated with air temperature.

Introduction

In the late 1940's, the Hercules Company introduced toxaphene in the United States as an insecticide.¹ Toxaphene was produced by the chlorination of champhene, which can take place to varying degrees and on various carbon atoms. There are 32,768 theoretically possible congeners,² of which more than 600 have been found in commercial toxaphene.³ Due to the complexity of the mixture, less than 30 of these congeners have been isolated and structurally identified.⁴

The primary use of toxaphene, estimated at 67 to 90% of its total U. S. consumption,^{1,5} was as an insecticide to treat cotton pests.⁶ The remainder was used as an insecticide and a herbicide on soybeans and peanuts, as a treatment for scabies on livestock, and as a piscicide to remove rough fish from lakes.^{1,7,8} The majority of this usage occurred in the southeastern United States; uses in the Midwest accounted for less than 1% of the total annual use.⁹ Toxaphene's use was encouraged after the U. S. Environmental Protection Agency (EPA) banned DDT in 1972.¹⁰

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The U. S. EPA canceled the registrations for most of toxaphene's uses in 1982, but allowed the existing stocks to be used in limited circumstances until 1986.¹¹ Toxaphene has not been registered in Canada since 1983.¹² In addition to the US and Canada, its use has been banned in England, Sweden, Finland, Denmark, France, Germany, Switzerland, Hungary, Italy, Egypt, India, China, and Algeria.¹³

Experimental Methods

Archival fish samples were collected in 1977, 1982, 1983, 1984, 1985, 1988, 1992, 1993, and 1994 and provided to us by the US EPA and by the US National Biological Survey (NBS) through the Great Lakes Fish Contaminate Monitoring Program. Through this program, lake trout (*Salvelinus namaycush*) were collected at one site each on Lakes Superior, Huron, Michigan, and Ontario in 1982 and 1992. Additional lake trout samples from the other years mentioned above from Lakes Superior and Michigan were also analyzed. Walleye (*Stizostedion vitreum vitreum*) were collected from Lake Erie. For the exact fish collection sites, see Figure 1. Rainbow smelt (*Osmerus mordax*) were collected by gill net from the same five sites in 1982 and from Lakes Superior, Huron, and Erie in 1994. At the NBS, the fish were composited (five whole fish per sample), homogenized, and stored frozen at less than -30 °C. The air samples were collected at Eagle Harbor, MI (see Figure 1), using a high volume air sampler. Particulates were collected on quartz fiber filters, but they were not analyzed due to the very low concentrations of toxaphene in that phase. The vapor phase was collected on Amberlite XAD-2 resin. The 24 hour air samples for this project were taken every 12 days beginning in September 1996.

The analytical method employed for toxaphene was based on that of Swackhamer *et al.*¹⁴ Both the ground fish tissue (blended with 80 grams of sodium sulfate) and the XAD-2 were loaded into a glass wool plugged glass thimble, placed in a Soxhlet extractor, spiked with the internal standard (³⁷Cl₆-*trans*-nonachlor), and extracted for 24 hours with 1:1 acetone in hexane. With every batch of 5 to 6 samples, a procedural blank was prepared and similarly extracted. To ensure adequate recovery, a procedural blank spike, was extracted with every other batch.

For the tissue samples, the lipid concentrations were determined through gravimetric measurement. The majority of the lipids were removed using a gel permeation chromatography system. The solvent was 3:2 cyclohexane in dichloromethane. Both matrixes were subjected to further chromatographic clean up on 1% water deactivated silica. Four solvent fractions were collected: hexane, 1:9 dichloromethane in hexane, dichloromethane, and methanol. The first three fractions were combined, solvent exchanged into hexane through rotary evaporation, reduced to 200 µL under a steady stream of nitrogen, and analyzed by electron capture, negative ionization, gas chromatographic mass spectrometry (ECNI GC/MS).

A Hewlett Packard 5989A mass spectrometer was used to analyze the samples. The samples were injected into a Hewlett Packard 5890 Series II gas chromatograph containing a 30 m DB-5MS™ column (film thickness 0.25 µm, 250 µm i.d., J&W Scientific, Folsom, Ca). Helium was used as the carrier gas. The 1 µL injections were made in the splitless mode, with a vent time of 1.9 min. The injection port temperature was maintained at 285 °C to ensure complete volatilization of the sample. The temperature program for the column began with a 1 minute hold at 40 °C, followed by a 10 °/min ramp to 200 °C, a 1.5 °/min ramp to 230 °C and a 10 °/min ramp to 300 °C, which was held for 5 min. After eluting from the column, the effluent was carried through a 300 °C transfer line into the ion source of the mass spectrometer, which was held at 125 °C. Methane was used as the reagent gas in the ion source; its pressure was maintained at 0.43 Torr. The electron capture GC/MS analysis procedure, using selected ion

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monitoring, was developed by Swackhamer *et al.*¹⁴ The only notable difference in our procedure is that quantitation was based on the M^+ ions (quantitation ion $m/z = 344$, confirmation ion $m/z = 342$) for the hexachlorinated homologues; as in the earlier paper, the $(M-Cl)^+$ ions of the hepta- through decachlorinated norbornanes and norbornenes were monitored. Four time windows, each monitoring a subset of the ions, were used to increase sensitivity relative to monitoring all of the ions all of the time.

Results and Discussion

In the 10 years between 1982 and in 1992, toxaphene was banned by the US EPA. Presumably this action should have lowered the concentrations of the pesticide in the environment. To test this hypothesis, we examined the differences in concentrations over time for each species. As shown in Figure 2, toxaphene concentrations in lake trout from Lakes Michigan, Huron and Ontario and walleye from Lake Erie declined significantly between the two time periods. Likewise, toxaphene concentrations in smelt from Lakes Michigan and Ontario declined significantly. Only in Lake Superior was there no statistically significant change in toxaphene concentrations in either lake trout or smelt.

There are at least three hypothesis that might explain why the toxaphene concentrations have not decreased in Lake Superior over time as they have in the other lakes. These are: (a) The relatively older (12 year old lake trout in Superior vs. 4 year old lake trout in Ontario) fish in Lake Superior have not had time to respond to the 1982 ban. (b) Physical characteristics of Lake Superior (primarily the colder summer water temperatures and resulting lower volatilization rates, the great depth, and the very low sedimentation rates) result in lower loss rates than in the other Great Lakes. (c) There are current or recent basin-specific sources of toxaphene to Lake Superior.

Of the above hypothesis, there are sufficient data to adequately test only the first. De Vault *et al.*¹⁵ and Miller *et al.*¹⁶ reported decreases in PCB and DDT concentrations in lake trout (similar in size and age to this study) from Lake Superior in response to banning these chemicals. In fact, PCBs were already declining when monitoring began in 1977 following the 1975 ban. In addition, our smelt samples are about the same age in all of the lakes. It would appear that age of our Lake Superior lake trout is not a major contributor to the lack of decline.

While there are not sufficient data to fully test the second (slower loss rate) hypothesis, some extrapolations from PCB trends may be made. Water column PCB data from Lake Superior¹⁷ and from Lake Michigan¹⁸⁻²⁰ indicate that between 1980 and 1990, PCB loss rates were similar for the water columns of both lakes. PCB loss rates in lake trout from Lakes Superior and Michigan were also similar between 1980 to 1990.¹⁵ The similarity in PCB loss rates in both water and lake trout between lakes argues against lake-specific physical characteristics as the cause for the lack of a decline in toxaphene in Lake Superior. It is possible, however, that the physical chemical properties of toxaphene render extrapolations from particle mediated pollutants, such as PCBs, inappropriate. Recent water column data for toxaphene in the Great Lakes indicates the over 90% is present in the dissolved ($<0.7 \mu m$) phase.²¹ Because toxaphene is primarily in the dissolved phase, the lower summer water temperatures and subsequently lower volatilization rates in Lake Superior could be a factor in lower loss rates. Unfortunately, data are not available to quantitatively evaluate this idea.

Because the sampling sites in this study were specifically selected to avoid localized sources of contaminants, the third, local source hypothesis can not be completely evaluated here. However, continuing

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work in our laboratory has begun to examine toxaphene's burden to Lake Superior from atmospheric sources.

Table I lists the average atmospheric, gas-phase, concentration for the samples collected between September 1996 and February 1997, as well as literature values from Hoff *et al.*²² Vapor phase concentrations dropped with decreasing temperatures. A plot of the log of the concentration versus the inverse of the Kelvin temperature multiplied by 1000 (see Figure 3) shows a significant correlation between these two parameters ($r^2 = 0.976$). Homologue percentages also began to skew towards the lower chlorinated groups with decreasing temperature. Both of these trends were expected. Cooler weather hinders volatilization, thus concentrations are lower. Additionally, the more highly chlorinated congeners are generally less volatile than the lesser chlorinated components, so they would tend to sorb onto particles, out of the gas phase, in cooler weather. The concentrations appear to be slightly higher in the Lake Superior basin, but due to the small sample size of this study, this could be a statistical artifact

Acknowledgments

We thank the U.S. Environmental Protection Agency and the Canadian Atmospheric Environment Service for funding, Robert Hesselberg of the U.S. National Biological Survey (Ann Arbor, MI) for providing the fish samples, Ilora Basu and Matt O'Dell for their work collecting the air samples, and Don Cortes for his help with the temperature data.

TABLE I. Toxaphene concentration in air from Eagle Harbor, MI. All concentrations are in $\mu\text{g}/\text{m}^3$

Date	Temperature	Concentration	Monthly Average	Literature ²²
09/08/96	20.04	127		
09/20/96	12.25	39.2	83.1	50
10/02/96	12.45	35.9		
10/14/96	8.65	22.1		
10/26/96	9.14	15.8	24.6	14
11/07/96	7.17	23.1		
11/19/96	-3.60	5.59		
11/30/96	2.61	11.3	13.3	18
12/12/96	-0.89	9.29		
12/24/96	-6.77	2.92	6.11	2.2
01/17/97	-18.41	0.80		
01/29/97	-16.18	1.35	1.08	0.39
02/10/97	-3.51	5.21		

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Figure 1. Sampling locations. 1) Apostle Islands: lake trout, 1977, 1982, 1984, 1988, 1992; smelt, 1982, 1994. 2) Saugatuck: lake trout, 1982, 1992; smelt, 1982, 1994. 3) Rockport: lake trout, 1982, 1992; smelt, 1982. 4) Middle Bass Island: walleye, 1982, 1992; smelt, 1982. 5) Oswego: lake trout, 1982, 1992; smelt, 1982, 1994. 6) Charlevoix: lake trout 1985, 1993. 7) Door County: lake trout 1984. 8) Sturgeon Bay lake trout 1985, 1993. 9) Eagle Harbor: air samples 1996, 1997.

Figure 2. Mean Concentrations of toxaphene in lake trout, walleye and smelt in the Great Lakes in 1982 and 1992/1994. Error bars represent the 90% confidence level of the average.

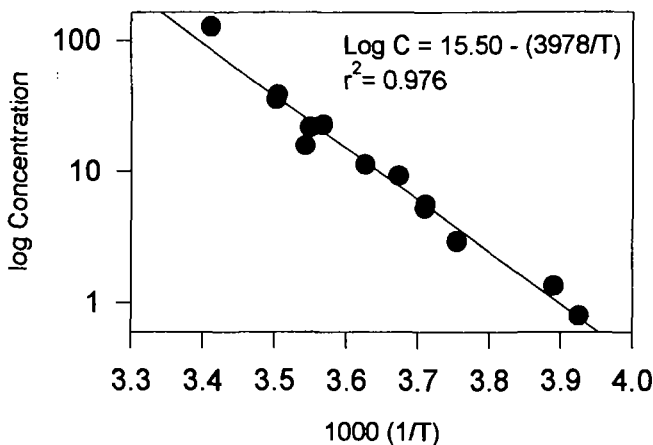
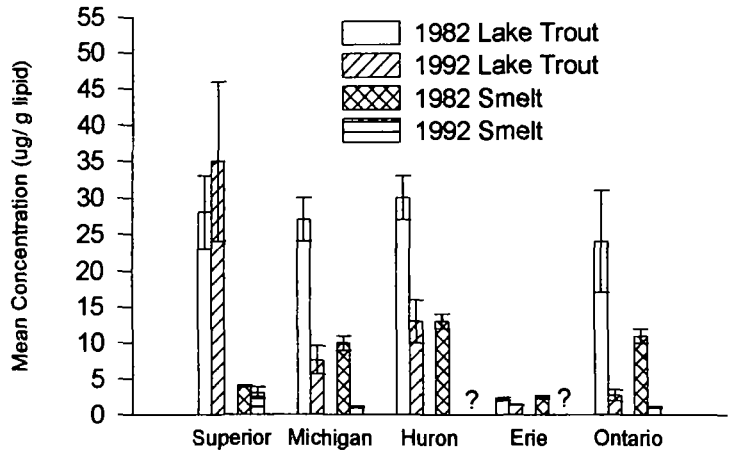


Figure 3. Logarithm of the air concentration of toxaphene versus the inverse of the median air temperature of each sampling period.

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