

Past and Present Accumulation of Polychlorinated Bornanes in Great Lakes Sediments

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I. INTRODUCTION

The contamination of the Great Lakes by toxic organic contaminants has long been recognized, but efforts to stop inputs or reduce contamination levels have been met with limited success. Despite outright bans of some chemicals, inputs from the atmosphere have continued due to volatilization from large environmental reservoirs and long-range transport. Thus it has become increasingly important to understand the extent of atmospheric inputs of toxic chemicals, and their contribution relative to non-atmospheric inputs, so that appropriate and cost-effective decisions can be made about the management, regulation, and remediation of the Great Lakes.

Inputs from the atmosphere to water surfaces such as the Great Lakes include dry fallout of particulate-associated contaminants, washout of gas phase and particulate phase contaminants by precipitation events, and gas transfer across the air-water interface. Air measurements of contaminants are routinely done (e.g. the Integrated Atmospheric Deposition Network, or IADN, of the U.S. and Canada), but estimates of deposition are highly uncertain because of the uncertainty of the mass transfer coefficients needed to convert a concentration into a transfer rate. Another limitation is that these measurements only provide instantaneous information, and not any indication of changes over time, or changes historically, in inputs. Because many of the chemicals of concern are hydrophobic, they associate with particles in the water and are removed to the bottom, where their accumulation is recorded over time in the sediments. Thus the sediment record can be used to assess the accumulation of a given contaminant over time, changes in inputs over time, and can provide an estimate of the total mass inventory of the chemical since it began accumulating. We can compare these sediment records across the Great Lakes, and compare the Great Lakes record to lakes receiving only atmospheric inputs of these chemicals, to assess the relative contribution of atmospheric vs. non-atmospheric sources to the Great Lakes.

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Toxaphene is one of the Chemicals of Concern in the Great Lakes identified by the International Joint Commission due to its persistence and its ability to bioaccumulate. It is a pesticide comprised of a complex mixture of chlorinated bornenes and bornanes having from 4 to 10 chlorines. First manufactured for commercial use in the 1940's, it was used as a piscicide for removing rough fish from inland lakes in the upper midwest and Canada in the 1950's. Following the ban of DDT in 1972, it became the replacement chemical of choice for cotton crops, and to a lesser extent corn and soybean crops. It was the most widely used chlorinated pesticide in the history of U.S. agriculture¹. However, concerns about its toxicity and persistence led to its ban in the U.S. in 1982. Despite the ban, toxaphene in fish in Lake Superior and Lake Michigan contribute to the need for consumption advisories for several sport fish species. Past and present sources to the Great Lakes have not been clearly delineated. However, it is thought that toxaphene had limited application in the Great Lakes drainage basin. Because of the many forms of toxaphene and compositional changes due to environmental weathering, it will be referred to here as chlorinated bornanes (CBs).

II. OBJECTIVES OF STUDY

The purpose of this study was to investigate the history of accumulation and evaluate atmospheric and non-atmospheric sources of CBs to the Great Lakes from a series of sediment cores from lakes Superior, Michigan, Ontario, and from "control" inland lakes receiving these compounds only by atmospheric deposition. Using these sediment records, we met the following objectives:

1. Determine the concentrations of contaminants over time in each of the lakes;
2. Determine the rate of accumulation and changes in accumulation rate of the contaminants in each of the lakes;
3. Determine the time of onset of accumulation of the contaminants in each of the lakes;
4. Determine the current accumulation rate of the contaminants in each of the lakes;
5. Determine the total burden of contaminant in each lake, and estimate the atmospheric contribution of the burden by comparison to "control" lakes.

III. METHODOLOGY

The sediments were obtained by either box corer (Great Lakes) or by SCUBA diver (remote lakes). Sediments were vertically sectioned into appropriate intervals and subsamples (or core sections from duplicate cores) were analyzed using ²¹⁰Pb dating techniques to establish the age of each section, and for dry weight and porosity.

Sediments were analyzed for organochlorines by Soxhlet extraction in methanol and dichloromethane (DCM). Extracts were cleaned using silica gel and alumina column chromatography, and copper filings to remove elemental sulfur. Surrogate recovery standards were added to each sample at the time of extraction to evaluate the efficiency of the laboratory procedures for each sample. Prior to instrumental analysis, internal standards were added to each extract which were used in the final quantitation.

The extracts were analyzed by gas chromatographic mass spectrometry in electron capture negative ionization mode (Hewlett Packard 5988A). Total chemical class and homolog composition were calculated using the method of Swackhamer et al.² All accumulations and inventories were corrected for sediment focusing using the ²¹⁰Pb inventories.

III. RESULTS

The key parameters that can be compared across lakes are summarized in Table 1. Given the low resolution of the assignment of dates to the cores, it appears that CBs began to accumulate in each of the Great Lakes and in the control lakes sometime in the 1940's. This is consistent with the beginning of commercial manufacture of this compound in North America. An exception is the northern basin of Lake Michigan, where accumulation was detected as far back as 1906 and accumulation rates were the highest. The mixed depth in this core was less than 1 cm, so mixing does not explain this observation. Downward diffusion may explain this, but comparable diffusion was not seen in the other cores. A source specific to the northern basin is implicated due to its high accumulation rate and inventory. Another exception is the date of onset observed in both Lake Superior cores, which was in the 1920's. A full explanation for these exceptions is not forthcoming at this time.

The time period where accumulation was highest was generally in the early 1970's, except for Lake Michigan which shows maximum accumulations around 1980 or later. The latter is consistent with the period of most intense use (1972-1984). The maxima observed in Lake Superior and Lake Ontario are earlier than would be expected, perhaps indicating downward mixing. In some cores the accumulation rates have not decreased to present day; these include the Basswood core from Lake Superior, and the northern basin of Lake Michigan. The Basswood core, in a non-depositional location, may reflect only an atmospheric source signal and not have captured non-atmospheric signals retained in the depositional core (NOAA3). The increased accumulation at the surface of the core from northern Lake Michigan (68k) implies that there is still a current source of CBs to this part of the lake.

The maximum accumulations were in the order : Lake Ontario \cong Lake Michigan > Lake Superior > control lakes. If the control lakes represent accumulation from atmospheric deposition only, then all of the Great Lakes have received non-atmospheric sources of CBs at one time. The magnitude of the loadings indicates that, particularly for Lake Michigan and Lake Ontario, these loadings were substantial. The current accumulation rates may be of greater interest. The current rates are 2X, approximately 5X, and approximately 10X greater than the control lakes for Lake Superior, Lake Michigan, and Lake Ontario, respectively. Thus *current* loadings to Lake Michigan and Lake Ontario are still substantially greater than those due to atmospheric deposition.

The total accumulation of CBs is represented by the inventory, in ng/cm². The inventory is 3 in Outer Island, 4-8 in Lake Superior, 8-27 in Lake Michigan, and 34-22 in Lake Ontario. If the inventory of Outer Island represents the total cumulative mass of CBs received from atmospheric sources, it follows that the Great Lakes have received significant quantities of CBs from non-atmospheric sources. The homolog compositions support this conclusion. The pattern seen in the control lakes is dominated by the hepta-

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and hexachlorobornanes. Cores from Lake Superior and Lake Michigan are dominated by the octa- and heptachlorobornanes, which show a closer resemblance to the parent compound. The control lakes look like toxaphene that has been weathered by volatilization and subsequent redeposition, or that has been subjected to reductive dechlorination. Lake Ontario also shows a dominance of hepta- and hexachlorobornanes. These cores have evidence of reductive dechlorination.

Based on these observations, it appears that the common notion that CBs in the Great Lakes is due mostly to long-range transport and atmospheric deposition of CBs is incorrect. Significant quantities of non-atmospheric CBs have been and are currently accumulating in Great Lakes sediments.

1. Saleh, M.A. 1991. Toxaphene: chemistry, biochemistry, toxicity, and environmental fate. *Rev. Environ. Contam. Toxicol.* 118:1-86.

2. Swackhamer, D.L., M.J. Charles, and R.A. Hites. 1987. Quantitation of toxaphene in environmental samples using negative ion chemical ionization mass spectrometry. *Anal. Chem.* 59:913-917.

Table 1. Summary of accumulations and inventories for CBs in the Great Lakes

	Date of Onset	Maximum Accum, ng/cm ² yr	Date of Maximum Accum	Present Accum, ng/cm ² yr	Inventory ng/cm ²
<i>Control Lakes</i>					
Siskiwit	<1933 ± 9	0.08	1966	0.05	NA
Outer Isl	1949 ± 6	0.07	1972	0.05	3.0
<i>L. Superior</i>					
Basswood	1922 ± 14	0.10	1990	0.10	3.5
NOAA3	1925 ± 8	0.16	1962; 1975	0.11	7.9
<i>Lake Michigan</i>					
LM-18	1949 ± 3	0.32	1978	0.24	7.9
LM-47s	1950 ± 4	0.66	1980	0.52	15
LM-68k	1906 ± 5	1.17	1992	1.17	27
<i>Lake Ontario</i>					
LO-40	1949 ± 2	1.0	1971	0.60	34
LO-19	1942 ± 5	0.69	1969	0.39	22