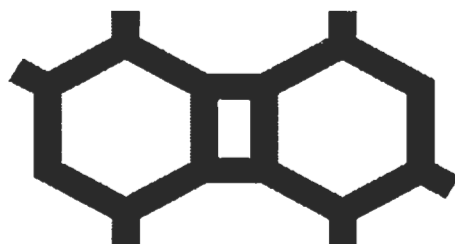


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1994 State of the Lakes Ecosystem Conference Background Paper



Toxic Contaminants

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State of The Lakes Ecosystem Conference

Background Paper

**TOXIC CONTAMINANTS
IN
THE GREAT LAKES**

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Table of Contents

EXECUTIVE SUMMARY	1
1.0 INTRODUCTION	3
2.0 TRANSPORT AND FATE	7
3.0 CONTAMINANT LOADINGS	9
4.0 AMBIENT CONCENTRATIONS AND TRENDS	13
4.1 Concentrations and Trends in the Water Column	13
4.2 Concentrations and Trends in Open Lake Fish	14
4.3 Concentrations and Trends in Herring Gulls	21
4.4 Atmospheric Concentrations	21
5.0 LINKAGE WITH OTHER ECOSYSTEM COMPONENTS	23
6.0 KEY ISSUES TO CONSIDER	25
7.0 REFERENCES	27
Appendix A: Existing Monitoring Programs	29
Appendix B: Descriptions of Contaminants	33
List of Figures	37
Figures	39

NOTICE TO READER

These Background Papers are intended to provide a concise overview of the status of conditions in the Great Lakes. The information presented has been selected as representative of the much greater volume of data. They therefore do not present all research or monitoring information available. The Papers were prepared with input from many individuals representing diverse sectors of society.

The Background Papers were first released as Working Papers to provide the basis for discussions at the first State of the Lakes Ecosystem Conference (SOLEC) in October, 1994. Information provided by SOLEC discussants was incorporated into these final SOLEC Background Papers. SOLEC was intended to provide key information required by managers to make better environmental decisions.

Executive Summary

The overall contaminant picture for the Great Lakes has improved dramatically since the mid-1970s, with significant declines in environmental concentrations of most of the critical contaminants for which data are available.

This is best illustrated with PCBs, for which we have the most extensive data base. PCB concentrations in Lake Superior water declined from 1.73 ng/l to 0.18 ng/l between 1978 and 1992. In southern Lake Michigan water column PCB concentrations declined from 1.8 ng/l in 1980 to 0.2 ng/l in 1993. These declines are also observed in biota, with concentrations in Lake Michigan lake trout declining from 22.9 ng/g in 1974 to 2.77 ng/g in 1990. Declines were also observed in DDT, 2,3,7,8-TCDD, mirex (in Lake Ontario), mercury, lead, dieldrin, and oxychlorane. Concentrations of HCB and BaP were very low.

While most contaminants have declined substantially since first monitored, declines in PCB, DDT and, possibly, other organochlorines in Great Lakes biota appear to have ceased or, in some cases, reversed in recent years. The reason for this is uncertain, although continued declines in PCB concentrations in the water columns of Lakes Superior and Michigan suggest that factors other than contaminant loadings are responsible. One possibility is that major changes in the food web, which were observed concurrent with the slowing and reversals in contaminant declines, may be responsible. Such changes may alter the pathways that chemical contaminants follow as they bioaccumulate up the food chain to top predator species. If changes in the food chain are responsible for the recent trends, we would expect future declines in biota once the food web stabilizes.

While contaminant concentrations have declined, several water quality objectives and fish tissue criteria for the protection of human health are still exceeded. PCB concentrations in fish across much of the basin exceed the IJC objective of 0.1 g/g for the protection of biological resources, and exceedences of state and provincial human health criteria result in fish consumption advisories for each of the lakes. Meeting existing and proposed future objectives will require further decreases in contaminant concentrations.

1.0 Introduction

The Great Lakes have been exposed to a large number and volume of contaminants known to have an adverse impact on plant and animal life, including humans. Scientists have detected 362 contaminants in the Great Lakes ecosystem, including 32 metals, 68 pesticides and 262 other chemicals. About one-third of the chemicals found in the Great Lakes can have acute or chronic toxic effects (IJC 1991).

Under the Great Lakes Water Quality Agreement (GLWQA), both the United States and Canada are committed to restoring and maintaining the chemical, physical, and biological integrity of the Great Lakes Basin ecosystem. As part of this commitment, the Parties agree that "the discharge of toxic substances in toxic amounts be prohibited and the discharge of any or all persistent toxic substances be virtually eliminated" (US and Canada 1987).

A variety of criteria have been used in past studies to develop lists of toxic chemicals relevant to the Great Lakes. Each list has been developed with a particular purpose in mind, involving the types of information desired, the critical values associated with the criteria, and the relative importance of the criteria. For the purposes of this review, we will focus on the list of 11 critical pollutants identified by the International Joint Commission (IJC) (Table 1). These pollutants have been selected because they are persistent and bio-accumulative, may interact with other chemicals to produce synergistic, additive or antagonistic effects, are known to cause detrimental effects on biota and/or human health, and are present in the Great Lakes. Table 2 includes some selected criteria or action levels for these compounds in different media.

Table 1: Critical pollutants in the Great Lakes

2,3,7,8- TCDD (tetrachlorodibenzo-p-dioxin)	DDT and metabolites
2,3,7,8- TCDF (tetrachlorodibenzofuran)	Alkylated Lead
Total PCBs	Mirex
HCB (Hexachlorobenzene)	Toxaphene
Mercury	Dieldrin
Benzo(a)pyrene	

Source: IJC (1991)

Table 2. Selected criteria, action levels or guidelines for critical pollutants in the Great Lakes

<u>Contaminant</u>	<u>US FDA (1)</u>	<u>Health Canada (2)</u>	<u>IJC (3)</u>	<u>IJC (4)</u>	<u>NYDOH (5)</u>	<u>OMEE (6)</u>
2378-TCDD	25 pg/g	20 pg/g			10 pg/g	
DDT	5 ug/g	5 ug/g	0.003 ug/l	1 ug/g (a)	5 ug/g	5 ug/g in fish
PCB	2 ug/g	2 ug/g		0.1 ug/g (a)	2 ug/g	0.001 ug/l
Aldrin/ Dieldrin	0.3 ug/g		0.001 ug/l	0.3 ug/g	0.3 ug/g	0.001 ug/l
Toxaphene	5 ug/g		0.008 ug/l			0.008 ug/l
Mirex	0.1 ug/g	0.1 ug/g	Ld	Ld	0.1 ug/g	0.001 ug/l
Mercury	1 ug/g	0.5 ug/g	0.2 ug/l	0.5 ug/g	1 ug/g	0.2 ug/l
Lead			25 ug/l			X

Ld Less than detectable.

X Between 1 and 5 ug/l depending on water hardness.

a Whole fish.

(1) US Food and Drug Administration action levels in edible portions of fish for regulation of interstate commerce.

(2) Health Canada consumption guidelines for edible portions of fish.

(3) (4) International Joint Commission objectives for protection of aquatic life and wildlife.

(5) New York State Department of Health criteria for edible portions of fish.

(6) Ontario Ministry of Energy and Environment water quality guidelines for protection of human consumers of fish.

It is important to recognize that the IJC list of 11 priority pollutants is not the only list that has been compiled in order to address persistent toxic substances in the Great Lakes. Table 3 includes a list of the more commonly targeted pollutants in the Great Lakes and some of the programs through which they are being addressed.

Table 3: Targeted pollutants of the Great Lakes

Aldrin (1 5 7)	Benzo(a)pyrene (1 3 5 7 8)
Chlordane (1 2 3 6 7)	Copper (1 2 3)
DDT and metabolites (1 2 3 5 6 7)	Dieldrin (1 2 3 6 7)
Furans, including 2,3,7,8-TCDF (1 3 5 7)	Heptachlor (1 2 3)
Heptachlor epoxide (1 3)	Hexachlorobenzene (1 2 3 5 6 7)
Alkylated Lead (1 3 4 5 7)	Hexachlorocyclohexane (1 3 8)
β Hexachlorocyclohexane (1 3 8)	Mercury (1 2 3 4 5 6 7)
Mirex (1 3 5 7)	Octachlorostyrene (1 3 6 7)
Polychlorinated biphenyls (1 2 3 5 6 7)	2,3,7,8-TCDD & other dioxins (1 2 3 5 6 7)
Toxaphene (1 2 3 5 6 7)	

- References:
- 1 = GLWQA Annex One, list 1 (173 total pollutants in list)
 - 2 = GLWQI guidance list of 33 pollutants
 - 3 = LAMPS critical pollutants lists (Lake Michigan 15 total)
 - 4 = Pollution Prevention (Industrial Toxics Project, 17 total)
 - 5 = Eleven Critical Pollutants (IJC, 1985)
 - 6 = Lake Superior Lakewide Management Plan (9 total)
 - 7 = Canada-Ontario Agreement Tier I list of 13 virtual elimination contaminants
 - 8 = Canada-Ontario Agreement Tier II list of 26 (including 17 PAHs)

This paper will review the current data on toxic contaminants found in the air, water, sediments, fish and wildlife of the Great Lakes with emphasis on the IJC critical pollutants. The review primarily surveys information available to December 1993. The goal of this review is to provide sufficient information on contaminant levels and trends to stimulate discussion among interested parties, and to assist future decision-making on Great Lakes environmental quality issues. The paper has been organized into discussions of 1) transport and fate; 2) loadings; 3) concentrations and trends in various media; 4) linkage issues to other stressors and to environmental effects; and 5) knowledge gaps and key issues in dealing with persistent toxic chemicals in the Great Lakes. Because of space limitations, we have not attempted to include all available data, but have, instead, attempted to bring together those data which describe the status and trends of contaminants from a Great Lakes Basin perspective.

2.0 Transport and Fate

Contaminant transport and fate is complex. Chemical contaminants enter the Great Lakes from a variety of sources, including direct point source discharges, tributary loadings, and atmospheric deposition. These loadings originate from both current and past releases to the environment. For example, tributaries discharge not only chemicals currently in use, but also those which were discharged in the past and have accumulated in their sediments. A large proportion of the present tributary loadings of chemicals such as PCB, DDT, dieldrin, and mirex are probably the result of contaminated tributary sediments, rather than current discharges. Atmospheric deposition includes chemicals discharged to the atmosphere from point and non-point sources, as well as chemicals that are volatilized from other aquatic and terrestrial ecosystems, or from the Great Lakes themselves. Contaminants reaching the lakes via the atmosphere may have traveled long distances through a series of steps wherein they are released, deposited on terrestrial or aquatic systems, then volatilized and returned to the atmosphere. During each atmospheric residence, they are moved further from the original source.

While in the lake system, contaminants move between media. They sorb to particles, primarily algae, where they may be bioaccumulated up the food chain, or sink toward the bottom sediments. Contaminants on sinking particles may be effectively removed from the system by burial in the bottom sediments, or they may be returned to the water column to repeat the cycle. Both the bottom sediments and the atmosphere represent boundaries across which contaminants are exchanged, in both directions. The relative magnitude of these processes can be seen in a recent PCB mass budget for Lake Superior (Table 4). Atmospheric deposition, tributaries and "other sources" contributed approximately 307 kg to the water column. This joined the ~10,100 kg already present from previous inputs. Of this mass, approximately 3,000 kg sorbed to particles and began the process of sedimentation and burial. However, nearly all (2,890 Kg) of this was returned to the water column, either prior to reaching the bottom sediments, or from the bottom sediments. This budget indicates that, in Lake Superior, very little of the PCB mass was permanently buried in the sediments and that the atmosphere was the primary route by which PCBs left the Lake, with approximately 1,900 kg volatilizing. Sedimentation and burial would be expected to be a more important removal pathway in a shallower, more productive, lake such as Erie. Table 4 also illustrates that PCBs were declining in Lake Superior with approximately 307 kg entering and over 2,000 kg (1,900 kg to the atmosphere and 110 kg to the sediments) leaving the water column in 1986.

Table 4. Approximate PCB Mass Budget for Lake Superior Water Column in 1986

	Inputs (kg/yr.)	Outputs (kg/yr.)
Atmosphere	157	1900
Tributaries	110	60
Other Discharges	40	0
Bottom sediments	2890	3000

From Jeremiason et al. (1994).

Typically, metals and high molecular weight organic compounds, such as chlorinated dioxins, furans and higher chlorinated PCBs will ultimately be deposited in the sediments. Lower molecular weight organic chemicals (such as lower chlorinated PCBs) will volatilize to the atmosphere. While Table 4 illustrates the inputs and movement of PCBs in Lake Superior for a single year (1986), Table 5 provides estimates for the long term fate of PCBs and lead for each of the Great Lakes.

Table 5. Estimated fate of PCB and Pb in the Great Lakes

Lake	% Volatilized		% to Sediments		% to Outflow	
	PCB	Pb	PCB	Pb	PCB	Pb
Superior	87	0	11	99	2	1
Michigan	68	0	31	98	1	2
Huron	75	0	19	93	6	7
Erie	46	0	45	90	9	10
Ontario	53	0	30	80	17	20

From Strachan and Eisenreich (1988)

3.0 Contaminant Loadings

The term, contaminant loadings, refers to chemicals entering a system from outside sources via atmospheric deposition, tributary discharge, as well as point and non point discharges to the lakes. Of these, atmospheric deposition and tributary discharge are the primary routes by which chemicals enter the Great Lakes system.

Unfortunately, our estimates of both atmospheric and tributary loadings to most areas of the Great Lakes are inadequate. There are difficulties in measuring the low contaminant concentrations in many tributaries which may, nevertheless, deliver significant masses of contaminants over time. Tributaries may also deliver a large portion of their annual load during storm events that last only a few hours or days. Thus tributary loadings studies usually require intensive, event-related sampling. Adequate sampling designs are further complicated by occasional influxes of lake water (flow reversals) into the lower reaches of tributaries due to weather related conditions. These factors result in tributary monitoring being very expensive and, because of the high cost, there are few reliable estimates.

Estimating atmospheric loadings also presents significant monitoring challenges. Chemicals entering the lakes from the atmosphere are delivered through precipitation (rain and snow fall), as dry particulates, and by direct gas exchange across the air-water interface. There are difficulties inherent in measuring the parameters necessary to estimate the contribution of each of these processes. In addition it is difficult, with current monitoring networks, to estimate the local inputs from urban areas.

Previously published estimates of tributary and atmospheric loadings to the Great Lakes are presented in Table 6. These estimates suffer from several significant shortcomings. Tributary estimates may be quite old, based on very limited data, and were calculated using different methods. As a result the error ranges are large. The atmospheric estimates are consensus values derived from several data bases in 1992 (Eisenreich and Strachan 1992). They are also subject to substantial error. **The reader is strongly advised to consult the original reference prior to use of any of the values in Table 6.**

Table 6. Tentative estimates of selected critical contaminant loadings to the Great Lakes (kg/yr.). (a)

Chemical	Source	LAKE				
		Superior	Michigan	Huron	Erie	Ontario
TCDD	Tributary	NA	NA	NA	0.1-0.5 (2)	NA
	Atmosphere (1)	0.019(w)	0.014(w)	0.014(w)	0.0065(w)	0.0052(w)
TCDF	Tributary	NA	NA	NA	0.1-0.5 (2)	NA
	Atmosphere (1)	0.37(w)	0.27(w)	0.27(w)	0.13(w)	0.10(w)
PCBs	Tributary	28(2)-110(4)	650(2)	236(2)	741(2)	609(2)
	Atmosphere (1)	157	114	114	53	42
Hg	Tributary	124(3)	NA	NA	2584(3)	NA
	Atmosphere (1)	2181	1568	1584	723	568
BaP	Tributary	NA	NA	NA	425(2)	148(2)
	Atmosphere (1)	115	84	1584	723	568
Pb	Tributary	NA	NA	NA	NA	NA
	Atmosphere (1)	67055	25920	10488	96574	47610

NA No data available for estimate.

(a) These estimates are partially based on old or limited data, and they should be viewed as only approximations of current loadings. The reader is strongly advised to consult the original source prior to use.

(w) Based on wet deposition only

Sources:

- (1) Eisenreich and Strachan (1992)
- (2) USEPA estimate
- (3) IJC (1993)
- (4) Jeremiason et. al (1994)

Indirect Loadings Measurements

While direct measures of contaminant loadings are desirable, knowledge of the transport and fate of these chemicals allows substantial information to be derived from indirect means. Dated sediment cores reflect historical contaminant loadings because mixing and mobility processes do not generally occur rapidly enough to erase contaminant profiles in the sediments. Recent studies of dated sediment cores from depositional areas in Lakes Michigan and Ontario show the declining concentrations of PCB and total DDT, which have resulted from regulations on the manufacture and use of these contaminants (Figure 1). Similarly, sediment cores from Lakes Superior, Michigan and Ontario indicate that loadings of both Pb and Hg have been declining for several years (Figure 2).

Sediment core data may also be compared with atmospheric deposition estimates to calculate the relative importance of atmospheric and tributary loadings. Sitarz et al. (1993) used sediment fluxes and atmospheric deposition data from the International Atmospheric Deposition Network (IADN) to calculate the approximate atmospheric contribution to Cd, Hg and Pb loadings (Table 7). While these are approximations, they demonstrate the importance of atmospheric loadings to the upper Great Lakes. These types of data may allow limited resources to be efficiently directed toward remedial or regulatory programs in the absence of direct measurements of loadings.

Table 7. Approximate relative contribution of atmospheric loadings to total loads (% atmospheric) based on three data sources.

	Cd	Hg	Pb
Lake Superior	>90	>90	>90
Lake Michigan	~50	>90	<10
Lake Ontario	<50	<10	<10

Adapted from Sitarz et al. (1993)

Comparison of sediment data from differing environments within the Great Lakes Basin may provide additional information on sources of loadings. It has long been thought that the primary source of the complex pesticide, toxaphene, was long range atmospheric transport from the southeastern US. Recent sediment data for toxaphene have raised questions regarding this. In Figure 3, toxaphene deposition rates are displayed from three sites in the Great Lakes Basin: northern Lake Michigan, Lake Superior, and an inland lake in the Apostle Islands of Lake Superior. The Apostle Islands site is a small lake, without tributaries, that is only influenced by atmospheric loadings. Notable is the lack of significant decline in toxaphene in sediment cores from northern Lake Michigan and Lake Superior (the opposite of what we observed for PCB, DDT, Hg and Pb). Efforts are currently underway to discover the sources of this contaminant.

Because of the technical difficulties and high cost of load monitoring, it is unlikely that agencies will be able to establish and maintain intensive load monitoring programs across the entire Great Lakes Basin, and operate them for extended periods of time. Fortunately, the behavior and fate of contaminants is predictable. Thus, intensive monitoring efforts on specific portions of the Great Lakes ecosystem may allow the construction of models capable of predicting both the changes in concentrations in the lakes resulting from changes in loadings, and given ambient concentrations, calculating the loadings. Such efforts will improve our ability to launch targeted contaminant track down and remediation efforts. Brief descriptions of some of the monitoring and modeling programs currently underway presently in place are presented in Appendix A.

4.0 Ambient Concentrations and Trends

4.1 Concentrations and Trends in the Water Column

The concentrations of IJC Critical Pollutants in the water column are quite low and the available data are limited. Table 8 contains recent estimates of the total water column concentrations of these chemicals in each lake. The data represent studies undertaken between 1986 and 1991 by Environment Canada, USEPA and researchers funded by the USEPA.

Table 8. Recent contaminant concentrations in the Great Lakes waters (ng/l).

<u>Chemical</u>	LAKE						
	Superior	Michigan	Green Bay	Huron	Georgian Bay	Erie	Ontario
PCB	0.18(1)	0.20(2)	17.1(4)	0.9(3)	0.69(5)	1.22(3)	1.20(3)
p,p'-DDE	<0.06(3)	NA	NA	<0.06(3)	0.03(5)	<0.06(3)	<0.06(3)
Dieldrin	0.26(3)	NA	NA	0.32(3)	0.35(5)	0.38(3)	0.28(3)
HCB	<0.04(3)	NA	NA	0.07(3)	0.04(5)	0.05(3)	0.04(3)
B(a)P	<0.46(3)	NA	NA	<0.46(3)	NA	<0.46(3)	<0.46(3)

NA=No data available.

(1) Jeremiason and Eisenreich (1994)

(2) USEPA, Great Lakes National Program Office, unpublished data

(3) L'Italien (1993)

(4) De Vault (1992)

(5) Stevens and Neilson (1989)

The technology required to measure contaminants at the trace concentrations found in the water column of the Great Lakes has become widely available only recently. As a result, meaningful

trend data are limited. However, research studies conducted for the USEPA and the US National Oceanographic and Atmospheric Administration by the University of Minnesota and University of Wisconsin provide insight into water column trends for PCBs (Table 9). Total PCB concentrations in the Lake Superior water column declined from 1.73 ng/l in 1978 to 0.18 ng/l in 1992. Comparable data from Lake Michigan are only available for the open waters of the southern Basin. These data indicate substantial declines from 1.8 ng/l in 1980 to 0.2 ng/l in 1992 (Table 9).

Table 9. Total PCB Concentrations in lakes Superior and Michigan (mean ng/l).

Year	Lake Superior (1)	Lake Michigan
1978	1.73	
1979	4.04	
1980	1.13	1.8(2)
1983	0.80	
1986	0.56	
1988	0.33	
1990	0.32	
1991		0.4(3)
1992	0.18	0.2(4)

(1) Jeremiason et al. (1994)

(2) Swackhamer and Armstrong (1987)

(3) Swackhamer and Pearson (1994)

(4) USEPA, Great Lakes National Program Office, unpublished data

4.2 Concentrations and Trends in Open Lake Fish

Contaminant concentrations in fish from the open waters of the Great Lakes have been monitored for over 20 years, and provide one of the most extensive data bases on trends in environmental contaminants available anywhere in the world. These programs were originally implemented due to concern over the effects of contaminants on fish consumers (both wildlife and human) and on the fish themselves, and because the technology was not available to directly measure the trace levels present in the water column. It was assumed that top predator fish species would, over the long term, reflect changes in water column concentrations, thus providing a cost effective surrogate to expensive water column monitoring. They are continued

across the Great Lakes today for similar reasons, i.e., cost effectiveness and continuing concerns about human and wildlife health. Comparison of PCB trends in open lake fish with the available water column PCB trend data, indicates that, over the long term, trends of contaminants (PCBs) in fish have followed those in the water column (De Vault and Hesselberg, 1994) and thus provide a measure of trends in the Great Lakes ecosystem.

The data below are primarily the result of three monitoring programs. Lake trout and smelt are monitored by Fisheries and Oceans Canada, using individual whole lake trout of a consistent age (4+) and composites of smelt. Lake trout and walleye (Lake Erie only) from US waters are monitored cooperatively by US EPA- Great Lakes National Program Office, US National Biological Service (NBS), and the Great Lakes States. The US program utilizes whole fish composite samples of a consistent size (600-700 mm lake trout, 400-500 mm walleye). Coho salmon fillets are monitored in US. waters through a cooperative program involving the Great Lakes States, US Food and Drug Administration and US EPA- Great Lakes National Program Office, using five fish composites of age 2+ coho. These programs are complimentary in that together they control for the two primary variables, other than exposure, which affect contaminant concentrations within an individual species; age and size. While the data can not be directly compared across these monitoring programs, the general trends may.

PCBs

Data collected in southeastern Lake Michigan provide insight into the history of PCB contamination (Figure 5). PCB concentrations in Lake Michigan lake trout increased from 12.86 $\mu\text{g/g}$ in 1972 to 22.91 $\mu\text{g/g}$ in 1974. Between 1974 and 1990, PCB concentrations declined, by nearly an order of magnitude, to 2.72 $\mu\text{g/g}$, approximating a first order decay. During the period 1977-1990, PCB concentrations declined significantly in lake trout in the Lakes Superior, Huron, and Ontario, and in walleye from Lake Erie (Figure 5), following the same general trend observed in Lake Michigan. While there have been substantial declines in PCB concentration since the mid 1970s, concentrations have been relatively constant since the mid 1980s, with the exception of Lake Ontario, where declines continue through the most recent data available.

PCB trends in coho salmon fillets from Lake Michigan differ somewhat from those observed in lake trout. PCB concentrations in coho fillets declined from 1.9 $\mu\text{g/g}$ in 1980 to 0.38 $\mu\text{g/g}$ in 1983, after which they increased steadily to 1.09 $\mu\text{g/g}$ in 1992. Coho salmon fillets from Lake Erie declined from 1.07 $\mu\text{g/g}$ in 1980 to 0.53 $\mu\text{g/g}$ in 1992. In both lakes, the decline in PCB concentrations in the coho was statistically significant, as was the increase in Lake Michigan coho PCB concentrations (Figure 6).

The lack of recent decline in PCB concentrations (and DDT, see below) in lake trout and their increase in coho salmon from Lake Michigan is problematic in light of continued declines in PCB concentrations in the water columns of Lakes Superior and Michigan (see section 4.1 Concentrations and Trends in the Water Column). PCB trends in lake trout from both Lake Michigan and Lake Superior followed trends observed in the water column very closely through the mid 1980s after which the rate of decline in fish began to slow or even stopped entirely.

Because top predators such as lake trout receive over 90 percent of their PCB burden through food, it is likely that the lack of decline in PCBs in lake trout and walleye, as well as the increases in coho, are the result of changes in the food chain. The Great Lakes have been invaded by numerous exotic species, some of which have the potential to alter food chains in a manner which could affect contaminant transport to top predator fish species. If this is the case, concentrations of contaminants in the fish should begin to decline again, once the effect of the new species has stabilized in the food chain.

While PCB concentrations in open lake fish have declined dramatically in response to regulatory activity, concentrations in top predator fish species from all lakes were still well above the IJC objective of 0.1 µg/g (in whole fish) (Table 2) in 1990.

DDT

Declines in total DDT (the sum of DDT plus metabolites) concentrations were noted in Lake Michigan lake trout as early as the 1970's (Figure 7). DDT concentrations in Lake Michigan lake trout declined from 19.19 µg/g in 1970 to 1.39 µg/g in 1990 following the same pattern of decline that was observed for PCBs. DDT also declined significantly over the period of record in fish from Lakes Superior, Huron, Ontario and Erie. As was observed for PCBs, DDT concentrations appear to have leveled off in Great Lakes fish in recent years. Little significant change has been observed in DDT concentrations in lake trout from Lakes Superior or Lake Michigan since the mid 1980s. Similarly there has been little change in fish from Lake Erie since the early 1980s (Figure 7). Only in Lake Huron lake trout is total DDT continuing to decline at approximately the same rate over the period of record.

DDT concentrations in filets from Lake Michigan coho salmon (Figure 8) follow the pattern observed for PCBs. That is, statistically significant declines from 1980 through 1983, then statistically significant increases through 1992. Levels of DDT in Lake Erie coho declined significantly from 1980 through 1984, after which there was no statistically significant change. The strong correlation between trends in DDT and PCB suggests that changes in composition of the food web may be at least partly responsible for the lack of recent declines, and for observed increases in contaminant concentrations in the fish.

In spite of dramatic declines in DDT concentrations in Great Lakes fish, they still exceeded the IJC objective of 1.0 µg/g (Table 2) in Lake Michigan, and were very near the objective in Lake Ontario.

Dieldrin

Dieldrin concentrations in Lake Michigan lake trout increased from a mean of 0.27 µg/g in 1970 to 0.58 µg/g in 1979, then they declined to 0.17 µg/g in 1986 and 0.18 µg/g in 1990 (Figure 9). While concentrations varied between lakes, the pattern observed in Lake Michigan was also

observed in Lakes Superior, Huron and Ontario, i.e., a general decline, but with peaks in 1979 and 1984. In Lake Erie walleye, mean dieldrin concentrations decreased from 0.10 µg/g in 1977 to 0.04 µg/g in 1982, then increased to 0.07 µg/g in 1984, then declined again to 0.03 µg/g in 1990. Between 1979 and 1990, mean dieldrin concentrations declined significantly in the top predator fish from Lakes Michigan, Huron and Erie (Figure 9).

Dieldrin concentrations are well below the IJC objective of 0.3 µg/g in whole fish.

Toxaphene

Unlike PCBs and DDT, which are typically highest in Lakes Michigan and Ontario and lowest in Lake Superior, toxaphene concentrations in lake trout are highest in the fish from Lakes Michigan and Superior (1.91 µg/g and 1.27 µg/g, respectively, in 1990) and lowest in Lakes Erie and Ontario (Figure 10). It is currently the dominant contaminant in Lake Superior lake trout, and it is second to PCBs in Lake Michigan lake trout. Significantly lower (<0.5 µg/g) concentrations were found in walleye and lake trout from Lakes Erie and Ontario.

While toxaphene in fish tissue has not been measured long enough to detect trends, limited sediment data suggest that toxaphene may not be declining in Lake Michigan and Superior (see Section 3, Contaminant Loadings).

TCDD and TCDF

There has been substantial monitoring of Great Lakes fish for 2,3,7,8-TCDD and 2,3,7,8-TCDF. However, with the exception of Lake Ontario, these parameters have not been routinely included in open lake trend monitoring programs because of the low concentrations and the high cost of analysis. Tables 10 and 11 contain a subset of the open lake data. Because the sampling location, age and size of fish analyzed vary between studies, **the data can not be directly compared between years**. However, the data sets are comparable across lakes within a given year, and the 1978 and 1988 data bases are comparable both between years and across lakes.

Lake Ontario lake trout have the highest concentrations of 2,3,7,8-TCDD and Lake Superior the lowest. Because data were collected using differing strategies, these data are of limited use in detecting trends. However, the 1978 and 1988 samples were collected and analyzed following similar protocols. The results suggest a basin wide decline between 1978 and 1988.

Table 10. 2,3,7,8-TCDD Concentrations in whole lake trout from Lakes Superior, Michigan, Huron and Ontario, and in walleye from Lake Erie, pg/g (*)

<u>Year</u>	<u>Lake</u>				
	<u>Superior</u>	<u>Michigan</u>	<u>Huron</u>	<u>Erie</u>	<u>Ontario</u>
1978 (1)	2.19	7.37	22.2	2.9	78.6
1984 (2)	1.0	4.7	8.6	1.8	48.9
1988 (1)	Ld	2.83	19.7	Ld.	22.1
1990 (3)	2.8	Na	Na	Na	44.3
1992 (4)	2.29	2.95	2.92	2.32	40.36

(*) Data are not comparable between years and the original reference should be consulted prior to use.

Na=Not analyzed

Ld = below limit of detection

(1) USEPA, Great Lakes National Program Office, unpublished data.

(2) De Vault et al. (1989)

(3) Whittle et al. (1992)

(4) Fisheries and Oceans Canada, unpublished data.

2,3,7,8-TCDF concentrations in these same samples are presented in Table 11. Czuczwa and Hites (1984, 1986) suggest that the atmosphere is the primary route by which these chemicals reach the Great Lakes. There is also evidence for localized sources, i.e., the high concentrations reported for Lake Ontario. De Vault et al. (1989) also found evidence for both localized and broad homogeneous (probably atmospheric) sources of both dioxins and furans in Lake Michigan lake trout. Localized sources were found to be impacting portions of Lake Michigan, possibly because of PCDFs associated with PCB contamination in Green Bay. Comparison of the 1978 and 1988 data suggest that TCDF concentrations declined in fish from all five Great Lakes during that time interval.

Table 11. 2,3,7,8-TCDF Concentrations in lake trout from Lakes Superior, Michigan, Huron and Ontario, and in walleye from Lake Erie, pg/g.

<u>Year</u>	<u>LAKE</u>				
	<u>Superior</u>	<u>Michigan</u>	<u>Huron</u>	<u>Erie</u>	<u>Ontario</u>
1978(1)	32.7	27	31.5	24.5	54.8
1984(2)	14.8	39.5	22.8	11.3	18.5
1988(1)	7.2	13.4	11.2	7.8	8.9
1990 (3)	20.7	Na	Na	Na	72.1
1992 (4)	24.1	16.1	11.5	15.5	40.25

Na Not analyzed.

- (1) Great Lakes National Program Office, unpublished data
- (2) De Vault et al. (1989)
- (3) Whittle et al. (1992)
- (4) Fisheries and Oceans Canada, unpublished data.

Trends in 2,3,7,8 TCDD in whole lake trout have been monitored in the waters of Lake Ontario since 1977 by Fisheries and Oceans Canada. Results from this program indicate that there has been little, if any change in mean 2,3,7,8 TCDD concentrations over the period 1977 through 1992 (Table 12)

Table 12. 2,3,7,8 TCDD concentrations in whole lake trout from Lake Ontario.

<u>Year</u>	<u>TCDD (pg/g)</u>	<u>Standard Error</u>	<u>Number of Samples</u>
1977	13.0	3.0	2
1978	32.5	1.5	2
1979	39.6	6.8	9
1980	34.4	6.7	10
1981	29.4	2.7	16
1982	40.8	10.6	9
1983	31.6	5.0	14
1984	11.4	2.0	17
1985	34.1	1.7	25
1986	42.7	6.9	10
1987	37.4	2.75	7
1988	53.1	3.88	17
1989	34.0	3.32	16
1990	44.3	3.14	18
1991	40.3	4.94	13
1992	49.9	5.72	12

Fisheries and Oceans Canada.

For more information on 2,3,7,8-TCDD trends in Lake Ontario see section 4.3 Concentrations and Trends in Herring Gulls

HCB

Hexachlorobenzene has been monitored in coho salmon fillets and in whole lake trout from the Great Lakes for several years. These data indicate that concentrations are below detection limits of 0.005 µg/g in coho salmon fillets and 0.01 µg/g in lake trout.

B(a)P and Pb.

Because B(a)P is metabolized by fish and other vertebrates, and Pb is not significantly bioaccumulated, these compounds are not routinely monitored in fish tissue. Special studies for both compounds indicate very low concentrations in most Great Lakes fish.

Mirex

Mirex was reported in water samples from Lake Ontario during the mid-1980's at concentrations on the order of 10-50 pg/l (Sergeant et al., 1993). Although historical discharges to the Niagara and Oswego Rivers are known sources, mirex was used elsewhere in the basin and other potential source areas are believed to exist. In 1988, mirex concentrations in lake trout from Lake Ontario Ranged from 0.6 to 0.9 µg/g (Sergeant et al., 1993). Lake trout from Lakes Erie and Huron also contained detectable quantities of mirex, but at concentrations 100-200 times lower than in trout from Lake Ontario (Sergeant et al., 1993). Fish tissue residues of mirex in Lake Ontario fish have declined significantly since the early 1980s.

FORAGE FISH

Rainbow smelt from Lakes Superior, Huron, Erie and Ontario have been routinely monitored by Fisheries and Oceans Canada since 1977. These data provide a view of contaminant trends one trophic level below the lake trout, walleye and coho salmon discussed above. Over the period of this program, concentrations of PCB, total DDT, and Hg have declined significantly in smelt from Lakes Superior, Huron, Erie and Ontario (Figures 11, 12, 13). Samples from Lake Ontario consistently have the highest concentrations of PCBs and total DDT, while those from Lake Superior have the highest Hg concentrations.

In addition to using top predator fish species and their forage fish species to assess toxic contamination in the Great Lakes, contaminant concentrations in young of the year spottail shiners are also monitored by the Ontario Ministry of Environment and Energy (OMEE). These fish do not travel extensively during their first year of life, so they provide a measure of contaminant exposure in local, near-shore areas. At most collection sites, PCBs and total DDT concentrations declined significantly from the mid-1970's to 1990 (Suns et al., 1993). Even so, concentrations of PCBs in spottail shiners in 1991/1992 exceeded the Great Lakes Water Quality objective of 100 ng/g at most of the sites studied in the Niagara River and Lake Ontario (Figure 14).

4.3 Concentrations and Trends in Herring Gulls

In the early 1970s, fish-eating birds (gulls, terns, cormorants, herons, etc.) on the Great Lakes suffered widespread reproductive failure, declining population levels and eggs with very thin shells. These phenomena were largely attributed to high concentrations of toxic contaminants in their diet. The Canadian Wildlife Service has been monitoring contaminants in herring gull eggs and in the adults since 1974. This monitoring program provides important data on a terrestrial species which is closely tied to the aquatic food web. Data for several, representative colonies are discussed below. These data are a subset of a much larger data base.

Between 1974 and 1993, the concentrations of PCBs and DDT/DDE declined significantly at most sites (Figures 15 and 16). In eastern Lake Ontario (Figure 17), 2,3,7,8 TCDD declined significantly from the high concentrations observed in 1971 and 1972. As was observed for fish tissue concentrations, most of the decrease in these compounds occurred between 1974 and the mid 1980s. Since then the rate of decrease of these contaminants in gull eggs has been much slower.

Contaminant concentrations in herring gull eggs from around the Great Lakes in 1992 tended to follow a geographical distribution similar to that of top predator fish. PCB concentrations in the eggs were generally higher in Lakes Erie and Ontario, although one site in Lake Huron contained the greatest concentrations (Figure 18). Concentrations of 2,3,7,8-TCDD (Figure 19) and mirex (Figure 20) were the highest in Lake Ontario eggs.

4.4 Atmospheric Concentrations

We have limited data and understanding of atmospheric concentrations and processes. However, a series of workshops involving researchers from across the US. and Canada has resulted in consensus atmospheric concentrations for several contaminants in the early 1990s (Table 13). Work is underway to improve our knowledge in this area. The US. and Canada are cooperating on the International Atmospheric Deposition Network (IADN) which is designed to measure atmospheric deposition of a long list of organic and metal contaminants. In addition, research studies conducted by government and university laboratories are rapidly advancing our understanding in this important component of the contaminant picture. Studies are underway to improve our understanding of the geographical distribution of contaminants, as well as processes such as volatilization and large particle transport.

Table 13. Consensus atmospheric concentrations of toxic organic contaminants in the Great Lakes region during the early 1990's (ng/m³ for air and ng/l for rain).

Contaminant	Air Concentration			Rain
	Summer	Fall/Spring	Winter	
PCBs	0.4	0.2	0.1	2.0
HCB	0.15		0.1	0.06
Dieldrin	0.08		0.02	0.4
DDT	0.05-0.1		0.02	
Toxaphene	0.06		0.01	
B[a]P	0.005			2.0

From Eisenreich and Strachan (1992).

Recent studies of PCB concentrations over the Great Lakes in 1991-1992 (Figure 21) suggest that, with the exception of urban areas such as Chicago and Detroit/Windsor, concentrations are relatively uniform across the Basin. Most notable in Figure 21 is the nearly ten-fold increase in atmospheric PCB concentrations that occurs as one moves from north to south down Lake Michigan toward the Chicago-Milwaukee area.

5.0 Linkages With Other Ecosystem Components

Toxic contamination is but one of several stressors impacting the Great Lakes ecosystem. As all elements of the Great Lakes ecosystem are ultimately linked, so are contaminants linked to other factors. The links between contaminants and aquatic community health, human health, nutrients, the economy, and habitat (including wetlands) are very briefly explored below.

Aquatic Community Health

Toxic contaminants can result in unhealthy aquatic communities by causing disease, deformities, abnormal behavior, and reproductive failure, all of which can impair the fitness of a population. As more becomes known about the interactive effects of toxic contaminants, the potential adverse effects of these chemicals on both fish and fish-eating birds becomes more evident. In spite of major reductions in the environmental concentrations of most toxic contaminants, deformities and reproductive impairments are still observed in fish-eating birds certain areas (Giesy et al. 1994).

Human Health

The human population of the Great Lakes Basin is exposed to contaminants through water, air, and food. Because of the very low concentrations in water and air, fish consumption is the major route of human exposure to contaminants. To reduce this exposure, the Great Lakes States and the Province of Ontario issue Sport Fish Consumption Advisories, at least, annually. While the contaminant concentrations which trigger advisories vary between jurisdictions, they all advise reduced consumption of those species and sizes of fish with the highest contaminant concentrations.

Traditional health analyses have focused on risks of contracting cancer. However, reproductive toxicity and outcomes have been studied recently because they may be more sensitive indicators of chemical impacts. Studies conducted in the late 1970s and early 1980s documented effects such as reduced head circumference and subtle behavioral deficits among infants of mothers who consumed large quantities of Great Lakes fish. Recent studies conducted in the area of Green Bay, Lake Michigan, found no adverse effects among offspring born to fish consumers. The Green Bay results appear to be due to decreases in fish tissue concentrations and the fact that the public appears to be following fish consumption advisories, both of which result in decreased exposure.

Nutrients

Toxic contaminants accumulate in or adsorb onto phytoplankton as part of the bioaccumulation process. The abundance and species composition of phytoplankton populations are highly

dependent on the nutrient concentrations and on the ratio of nitrogen, phosphorus, and silica. The reduction in the amount of phytoplankton and the restoration of algal species compositions more typical of oligotrophic communities are desired results of nutrient control programs. However, they may have the undesirable effect of increasing concentrations of hydrophobic contaminants in fish. This ironic phenomenon may come about in two ways. First, the larger phytoplankton populations associated with more eutrophic systems provide a more direct pathway for plankton-bound contaminants to reach the sediments, thereby removing them from the water column. Secondly, the energy transfer up the food chain is more efficient in more oligotrophic systems. This low nutrient-high contaminant situation has been observed in Scandinavian lakes (Larsson et al., 1992) and higher bioaccumulation factors were observed in the oligotrophic/mesotrophic northern Green Bay, Lake Michigan compared to the hypereutrophic southern Green Bay in 1989 (David De Vault, USEPA, personal communication 1994). While an increase in contaminants in fish could result from successful nutrient control, this would be short lived as contaminant loadings continue to decline.

Economy

The presence of contaminants in the Great Lakes ecosystem has both direct and indirect costs. These include in reduced revenue from sport and commercial fisheries, increased costs for treating drinking water and disposal of dredge spoils. Indirect costs can include increased costs for health care and loss of tourist revenue due to concern over contaminant exposure.

Because environmental contaminants are the result of industrial and agricultural activity, the discharge of many contaminants are directly tied to economic cycles. Discharges of currently used chemicals will typically decline if the industries using those chemicals are in a recession period, and the discharges will increase during periods of economic growth.

Habitat and Wetlands

Toxic contaminants can exert deleterious effects on all biotic components of the Great Lakes ecosystem, not just fish, birds and humans. The productivity of aquatic plants, invertebrates, amphibians, reptiles and mammals can also be significantly reduced upon exposure to toxic substances. Contaminants can exert their effects both directly and indirectly on the aquatic community. For example, contaminated sediments can directly inhibit successful spawning of some fish species as well as severely limit the survival of a benthic community.

6.0 Key Issues to Consider

Continuing Problems and Concerns

Concentrations of most toxic contaminants in the Great Lakes ecosystem have decreased substantially since the 1970s. However, contaminants are still present throughout the Great Lakes, often at levels above standards or guidelines. Issues to consider:

- Fish consumption restrictions continue in all of the Great Lakes.
- Hot spots of contaminated sediments remain.
- Elevated levels of contaminants continue in fish and wildlife.
- Deformities in wildlife continue to occur in localized areas such as Green Bay and Saginaw Bay.
- Levels of contaminants appear to be leveling off in some fish and avian species. While these findings may be the result of changes in food webs, they bear further attention.
- The source and chemistry of some contaminants, such as toxaphene, are not sufficiently understood to reduce or eliminate sources.

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APPENDIX A: Existing Monitoring Programs

CONTAMINANT MONITORING PROGRAMS

Contaminant Loadings

Since 1987, the United States has tracked the emissions of certain pollutants through the Toxics Release Inventory, and Canada has recently started a similar program, the National Pollutants Release Inventory. These programs require dischargers to report the release to the environment of certain chemicals above threshold amounts.

In 1989 the U.S. conducted a pilot load monitoring program on Green Bay, Lake Michigan, as part of the Green Bay Mass Balance Study. Building on the Green Bay study, the USEPA, in cooperation with other federal and Great Lakes State agencies, has implemented an enhanced monitoring program to estimate atmospheric and tributary loadings of a wide range of toxic substances to Lake Michigan. The U.S. enhanced tributary monitoring programs are linked to monitoring in other media to provide data for the calibration of mathematical models. These models are intended to provide environmental managers with the ability to evaluate effects of potential regulatory and remedial actions.

On the Canadian side, there are various programs run by both the Federal and Provincial government agencies. Some of these programs include the binational Niagara River Toxics Management Plan and St. Clair River Management Plan, St. Lawrence River Vision 2000, Great Lakes 2000 and the OMEE Tributary Monitoring Program.

Substantial research is also being conducted under the sponsorship of USEPA, Environment Canada and the OMEE to understand the processes of volatilization and short range atmospheric transport.

Water

Large volume surface water samples were collected each spring between 1986 and 1990 throughout the Great Lakes by the Ontario Region of Environment Canada, Inland Waters Directorate. Because of the need to provide information for mass balance models, a new approach was initiated on Lake Ontario in 1992 and 1993. This involves processing large volumes of water at six stations each spring, summer and fall.

In 1993 USEPA established an annual program to assess organic contaminants at a limited number (5 to 6) of sites on each of the Great Lakes in the early spring. These data will assist the interpretation of data on contaminants in fish tissue, support mass balance modeling efforts, and over time, allow assessment of trends in the concentrations of contaminants in the open waters.

In 1994, USEPA and partner agencies began an intense study of contaminants in all media (water, air, sediments, biota) in Lake Michigan to develop and calibrate a predictive mathematical model.

Sediments

In 1990, the Ontario Ministry of Environment and Energy (OMEE) began a program to periodically monitor sediment quality, among other environmental quality features, at a network of inshore stations for the purpose of identifying changes over time, detecting emerging problems and providing reference information. Trace metals and organic contaminants are also measured annually in suspended solids and benthic samples from 17 large Ontario tributaries to the Great Lakes.

USEPA periodically sponsors studies of sediments in the depositional areas of the Great Lakes to determine the historical loading profiles and to develop a better understanding of the source of chemicals to the lakes, as well as the impact of contaminated sediments on water column concentrations.

Fish

US. EPA, Great Lakes National Program Office in cooperation with the US. National Biological Service and Great Lakes States annually collects and analyzes whole lake trout from Lakes Superior, Huron, Michigan and Ontario and walleye from Lake Erie for pesticides, PCBs and other industrial contaminants. This program began in 1970 on Lake Michigan and in 1977 on the other lakes. The Canadian Department of Fisheries and Oceans annually collects and analyzes whole lake trout and smelt from multiple sites on Lakes Superior, Huron, Erie and Ontario for PCBs, pesticides and metals. This program began in 1977. Both programs maintain fish tissue archives which are used to provide retrospective analyses. These archives have provided data on historical levels of contaminants such as dioxin, furans and planar PCBs. The open lake sampling programs provide data to assess long term trends in contaminant concentrations, the relative severity of contamination between lakes, the impacts of near-shore controls on the open lake, and of non-point source contributions to the toxic contamination of the lakes.

The U.S. Environmental Protection Agency, in cooperation with the U.S. Food and Drug Administration and the Great Lakes States, also annually collects and analyzes fillets of coho or chinook salmon from each of the lakes. These data are useful not only to monitor trends in organic contaminants in fish, but they also provide a measure of potential exposure to contaminants by fish-eating human populations.

The Ontario Ministry of Environment and Energy and the Ministry of Natural Resources cooperate to monitor contaminants in lean, dorsal, skinless, boneless muscle tissue from Great Lakes fish to provide consumption advice to sport anglers. The Great Lakes States also monitor contaminant residues in fillets of several sport fish species to provide consumption advice to sport anglers.

Contaminant residues in spottail shiners have been monitored by the Ministry of Environment and Energy since 1975 to assess the effectiveness of remediation and to monitor trends. Over a 17 year period, shiners have been collected and tested at more than 150 sites on the Great Lakes and their connecting channels. Forage fish such as shiners provide a link in contaminant transfers to higher trophic levels such as fish-eating wildlife birds and predatory fish. Comparable monitoring has been conducted by New York for their jurisdictional waters in Lakes Erie and Ontario, the Niagara and St. Lawrence Rivers. Following initial studies in 1984-1987, analysis of spottail shiners is being conducted every five years as an indicator of trends and remedial success.

Birds

The Canadian Wildlife Service of Environment Canada annually collects and analyzes eggs from up to 15 herring gull colonies around the Great Lakes. Biological parameters such as eggshell thickness, reproductive success, behavior, physiological markers and population size have also been measured. This program has been ongoing since the early 1970s.

Mathematical Models

Screening-level models have been developed for PCB and Hg in Lakes Ontario and Superior. USEPA recently built a state of the art model for Green Bay, Lake Michigan (De Vault and Harris, 1989), and is currently working to adapt this to the main body of Lake Michigan. The Green Bay model predicts the behavior of individual PCB congeners from loadings through top predator fish. The model incorporates the ability to predict concentrations which will likely occur as a result of changes in toxic substance loadings, and can incorporate the linkages to changes in other environmental components such as changes such as nutrient and solids loadings.

APPENDIX B: Descriptions of Contaminants

Aldrin and Dieldrin

These chemicals were used primarily as insecticides. Most uses have been banned, although dieldrin is still used in limited amounts for termite control in the Great Lakes basin (IJC, 1991). Aldrin naturally degrades to dieldrin in the environment, while dieldrin is persistent. The uses of both pesticides have been eliminated or severely restricted.

DDT and its breakdown products, including p,p'-DDE

DDT is an insecticide which was introduced to North America in 1946. Its use was restricted beginning in 1968 and is now banned. DDT and its breakdown products, including p,p'-DDE, are still found in the Great Lakes. They probably originate from a number of sources including lake bottom sediments, contaminated tributary sediments, runoff from sites of historical use, leaking landfill sites, illegal use of old stocks, and long range transportation through the atmosphere from countries still using DDT.

DDT can disrupt the hormone and enzyme systems. It gained notoriety in the late 1970s for causing eggshell thinning in birds, and it is associated with embryo mortality and sterility in wildlife. Recent research in the Great Lakes indicates that p,p'-DDE and o,p'-DDT possess estrogenic activities, and they have the potential to feminize wildlife embryos, i.e., to alter the hormonal balance and reproductive structures.

Dioxins

Dioxins, which comprise a family of 75 related chemicals, are the unwanted byproducts of combustion and some industrial processes that use chlorine. The most significant dioxin sources are the wood preservative, pentachlorophenol, municipal incinerators, and pulp and paper mills using chlorine for the bleaching process (Canada 1993). One member of this family, 2,3,7,8-tetrachloro-di-benzo-dioxin (TCDD), is considered to be the most toxic synthetic chemical (IJC, 1991). TCDD can act as an endocrine disrupter, and may suppress various immune systems components. Recent process changes in the pulp and paper industry have greatly reduced this source of dioxins.

Furans

This family of 135 related chemicals are unwanted byproducts of combustion, industrial processes that use chlorine, the manufacture of pentachlorophenol and as contaminants in PCBs. One member, 2,3,7,8 TCDF, is similar to 2,3,7,8 TCDD but is considered to be about one tenth as toxic (NATO, 1988). Furans can also act as endocrine disrupters (IJC, 1993).

Hexachlorobenzene

Hexachlorobenzene (HCB) is a member of the chlorobenzene family. Chlorobenzenes are widely used and are found in industrial wastes, atmospheric discharges and municipal waste water.

Hexachlorobenzene was used as a fungicide on cereal crops in Canada between 1948 and 1972. It is also created during the manufacture of other pesticides, and is still used in limited applications. HCB is persistent in the environment and can interfere with enzymes that control the production of hemoglobin, a component of blood, and can be an endocrine disrupter. HCB can also affect the nervous system, liver, reproductive system and produce cancer in laboratory animals.

Lead

Lead is an industrial metal which has been used in a variety of purposes including gasoline, plumbing, leaded glass, paints, and batteries. Lead is released as a result of coal and oil combustion, metal mining, smelting and manufacturing, cement manufacturing, fertilizer production and waste incineration (IJC, 1993b).

Lead can exist in inorganic and organic forms such as triethylead and tetraethyl lead. Tetraethyl lead or (organoleads) are volatile, easily partitioned into lipids, adsorbed into particulates and volatilized to the atmosphere (Wong et al., 1989).

Lead is a neurotoxin which causes nervous system damage. It is also immunotoxic and can depress the antibody response in mammals.

Mirex

Mirex (Dichlorane) was used as an insecticide and fire retardant. Mirex is extremely persistent, and has been shown to cause reproductive problems and cancer in laboratory animals (IJC, 1991).

Mercury

Mercury is an industrial metal with a large number of uses ranging from slime prevention to electrical components. It is still used in paints, switches, thermostats, batteries and some lights. World mine production of mercury in 1989 ranged from 5,800 to 7,000 tons, and estimates of global annual emissions from anthropogenic sources vary between 11,000 and 20,000 tons (IJC, 1993b). Much of the mercury entering the Great Lakes results from the combustion of fossil fuels, particularly coal, which releases mercury as a vapor. Mercury is also released from natural sources such as emissions from vegetation, forest fires, soils and water (IJC, 1993b). Mercury exists in many different forms (elemental, inorganic ion, and organic) which interconvert, each with different properties and toxicities. Mercury accumulates rapidly in fish,

and can accumulate in the human brain, kidney and liver, and cause nervous system disorders (IJC, 1991).

Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls are a family of 209 related chemicals, many of which have toxic properties. Some members of this family are of particular concern because they have chemical structures and biochemical characteristics similar to dioxins. PCBs have been used since the 1930s in electrical and hydraulic equipment, which accounts for about 60% of the total usage. They were also used in various plasticizers (25% of total use), hydraulic fluids and lubricants (10%) and in consumer products such as carbonless copy paper, inks, adhesives, flame retardants and fluorescent lights (5%). After 1971, PCB use was restricted to closed electrical systems. In 1975, the manufacture and importation of PCBs was prohibited in the United States.

Although the manufacture of PCBs stopped in the late 1970s, 65% of the world's 1,200,000 tons of PCBs are still in use in electrical products, or deposited in landfill sites. As of 1982, only 3% of PCBs in the US had been destroyed, with 140,000 tons in landfills and 70,000 tons in the environment (IJC, 1993b). In 1988, over 280,000 tons of PCBs were still in use in the US (IJC, 1993b) and over 16,000 tons of PCBs were in use in Canada, where another 12,000 tons were in storage (IJC, 1993b).

PCBs are among the most ubiquitous chemicals in the Great Lakes ecosystem. They are very persistent, accumulate rapidly in the food chain, and have been linked to health problems such as embryo mortality and wildlife deformities. PCBs possess estrogenic activities, and can act as hormone mimics.

Polynuclear Aromatic Hydrocarbons (PAHs)

Benzo(a)pyrene (BaP), is a PAH which has been linked to cancer in wildlife and humans. BaP is produced during combustion of fossil fuels and wood, and during incineration.

Toxaphene

Toxaphene is a poorly characterized mixture of several hundred individual chemicals. Toxaphene was the most common substitute for DDT after its ban in 1971 and was used extensively in the southern United States on cotton crops. Its use has been restricted in the US since 1982. Toxaphene was removed from general use in Canada in 1974, although small amounts are still allowed for use in Canada (Government of Ontario, 1993; IJC, 1991). Toxaphene is acutely toxic to fish, but relatively non toxic to mammalian species. It has, however, been identified as an animal carcinogen, (US EPA, 1980).

Analytical methods for toxaphene are imprecise and most data is for "Toxaphene like" mixtures. recent evidence suggests that there may be sources other than the pesticide for many components of this mixture.

LIST OF FIGURES

1. Sediment Cores showing PCB and DDT profiles
2. Anthropogenic Pb and Hg Sediment Profiles in Dated Sediment Cores from the Great Lakes
3. Accumulation Rates of Toxaphene in Lake Michigan, Lake Superior and the Apostle Islands
4. Toxaphene mass in sediments from in Lake Michigan, Lake Superior and the Apostle Islands, adjusted for sediment-focusing.
5. PCBs in lake trout, all lakes, combined US and Canadian data. Walleye for Lake Erie instead of lake trout.
6. PCBs in coho salmon, all lakes, US data
7. DDT in lake trout, all lakes, combined US and Canadian data. Walleye for Lake Erie instead of lake trout.
8. DDT in coho salmon, all lakes, US data
9. Dieldrin in lake trout, all lakes, US data. Walleye in Lake Erie instead of lake trout.
10. Toxaphene in lake trout, all lakes US data.
11. PCB trends in smelt. Canadian data
12. DDT trends in smelt. Canadian data
13. Mercury trends in smelt. Canadian data
14. PCBs in spottail shiners, 1990-1991.
15. PCB trends in herring gull eggs
16. DDE trends in herring gull eggs
17. Dioxin trends in herring gull eggs
18. PCB, dieldrin, DDE, HCB geographic distribution in herring gull eggs

19. Dioxin geographic distribution in herring gull eggs
20. Mirex, oxychlorane and heptachlor-epoxide geographic distribution in herring gull eggs
21. PCB concentrations in air over the Great Lakes.

PCBS AND DDT IN LAKE MICHIGAN AND LAKE ONTARIO SEDIMENTS

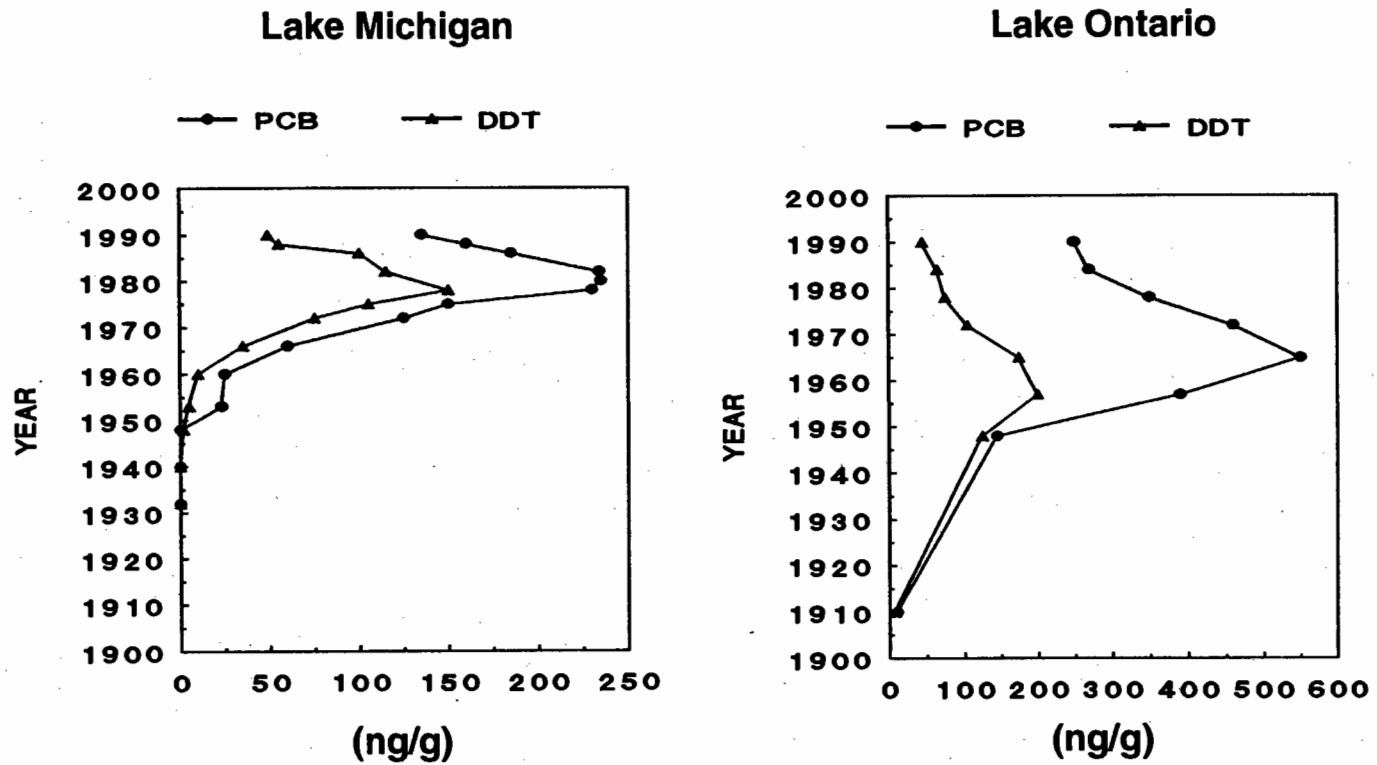


Figure 1. Concentrations of PCBs and DDT in sediment cores from Lake Michigan and Lake Ontario, dry mass (data from S. Eisenreich, University of Minnesota).

LEAD AND MERCURY IN GREAT LAKE BOTTOM SEDIMENTS

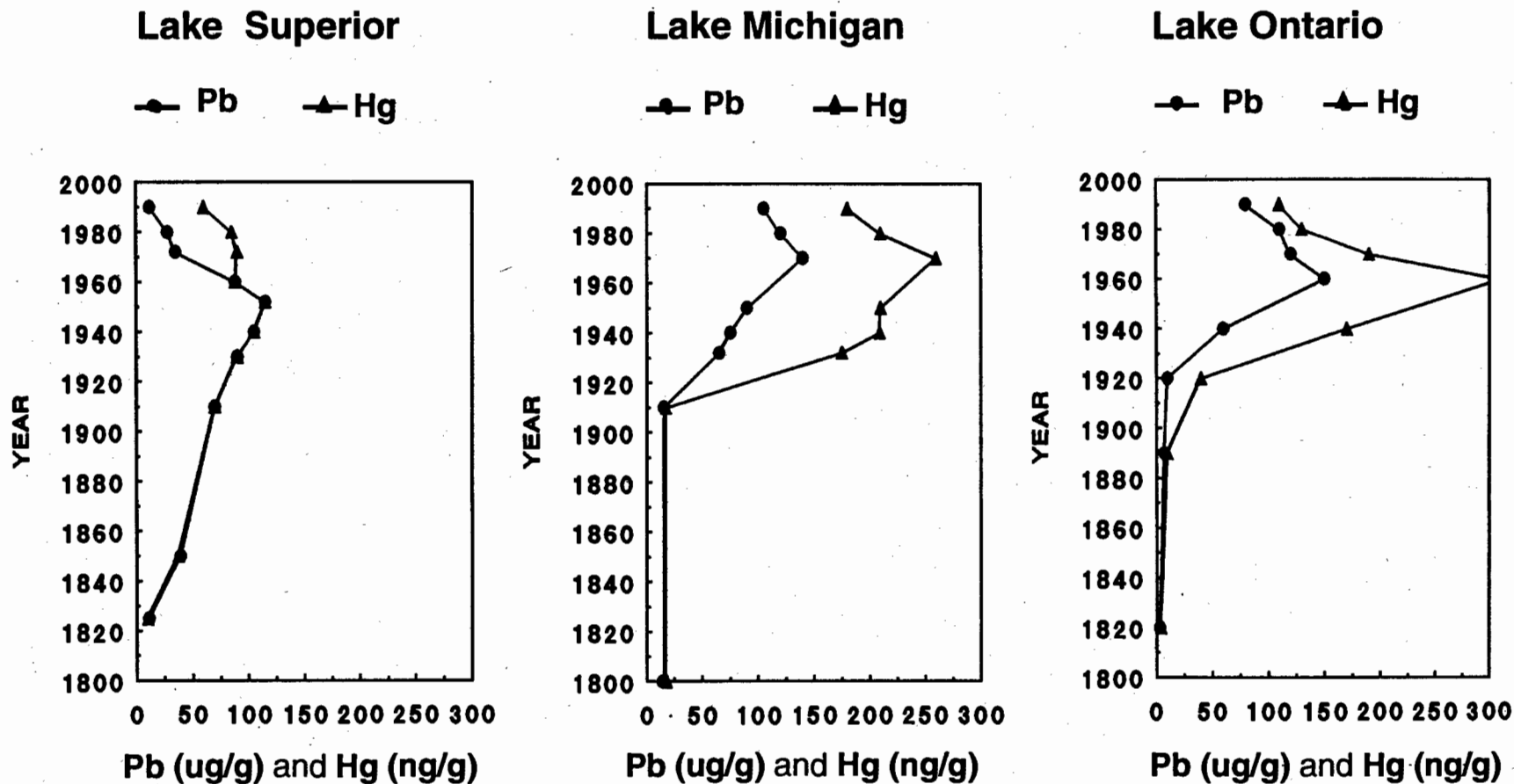


Figure 2. Anthropogenic lead (Pb) and mercury (Hg) in dated sediment cores from Lakes Superior, Michigan, and Ontario (data from D. Long, Michigan State University).

ACCUMULATION RATES OF TOXAPHENE IN THE GREAT LAKES

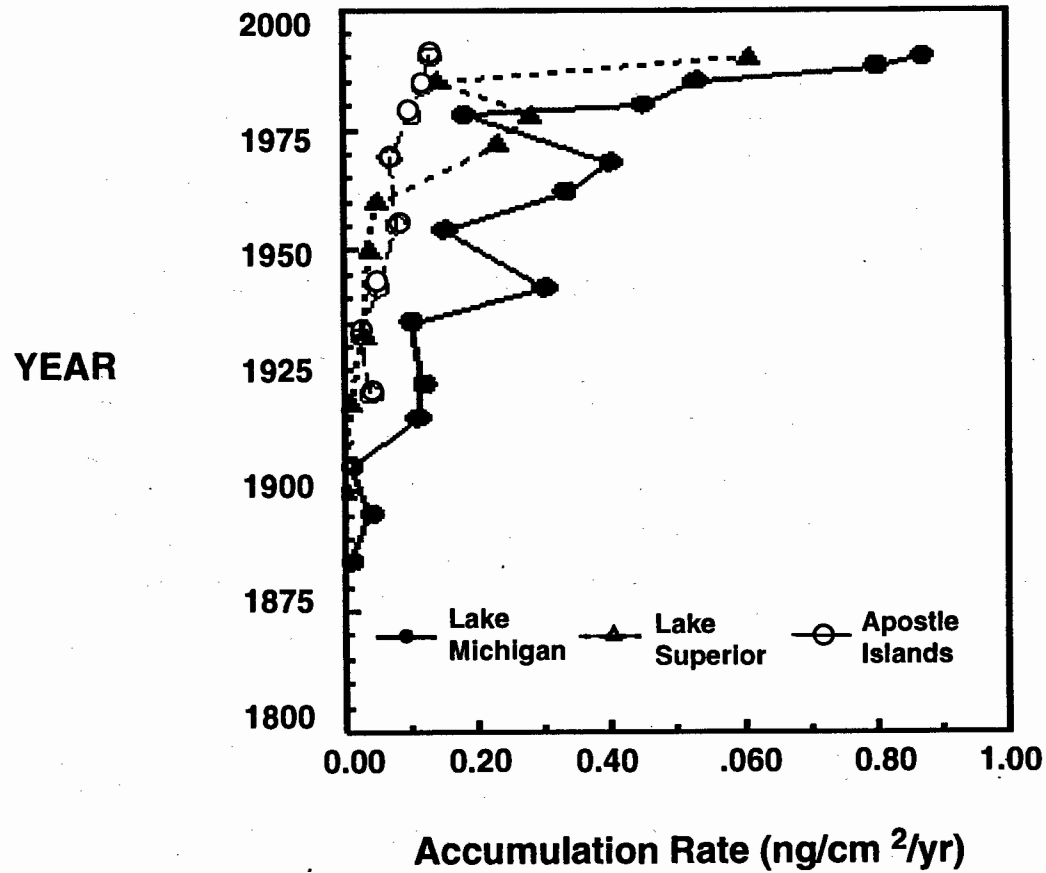


Figure 3.

Rates of accumulation of toxaphene in sediments from Lakes Michigan and Superior, and from the Apostle Islands (data from D. Swackhamer, University of Minnesota).

TOXAPHENE INVENTORY LAKES MICHIGAN AND SUPERIOR, AND THE APOSTLE ISLANDS

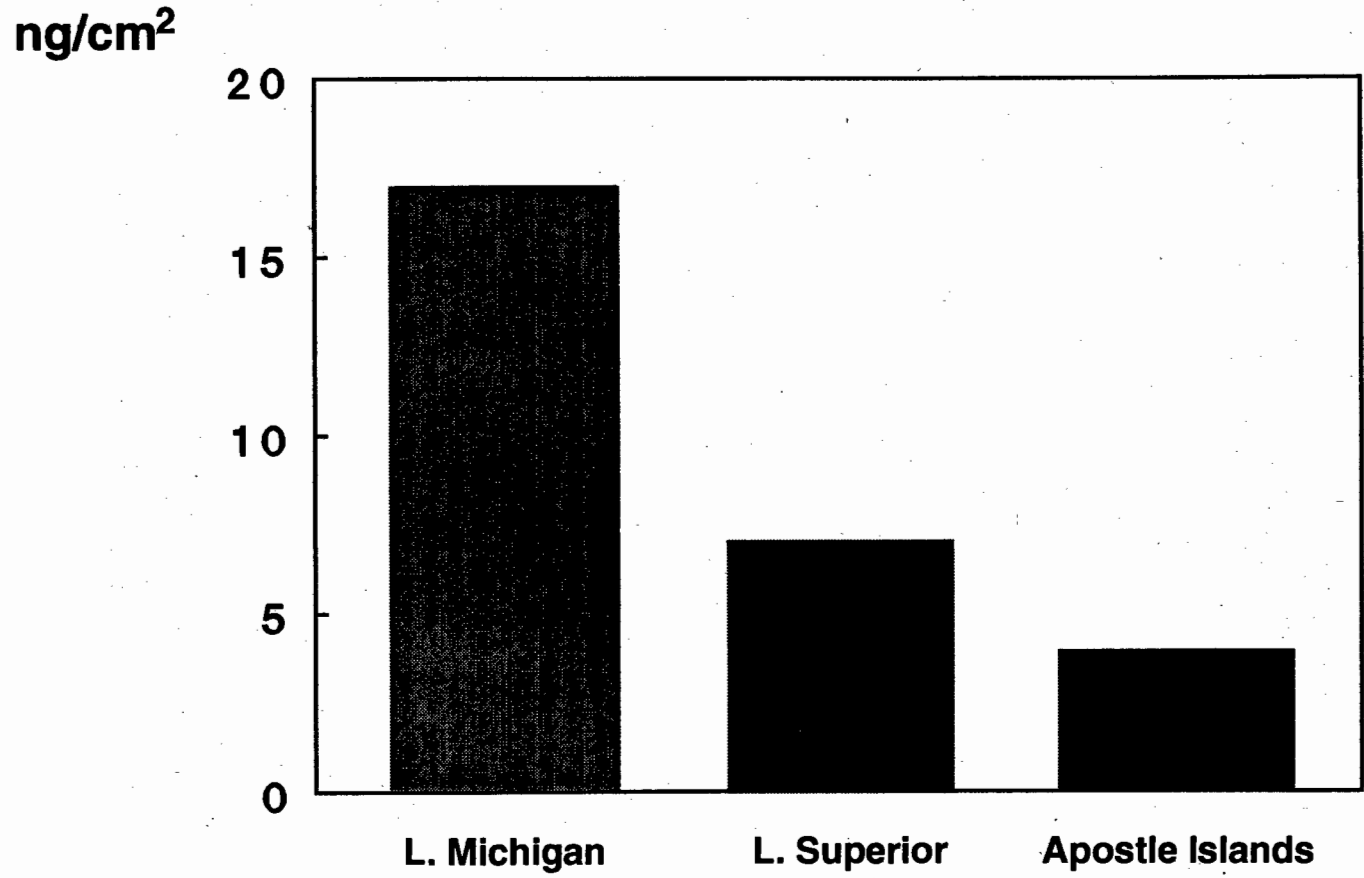


Figure 4. Toxaphene mass in sediments from Lakes Michigan and Superior, and the Apostle Islands Outer Island, adjusted for sediment distribution (focusing) (data from D. Swackhamer, University of Minnesota).

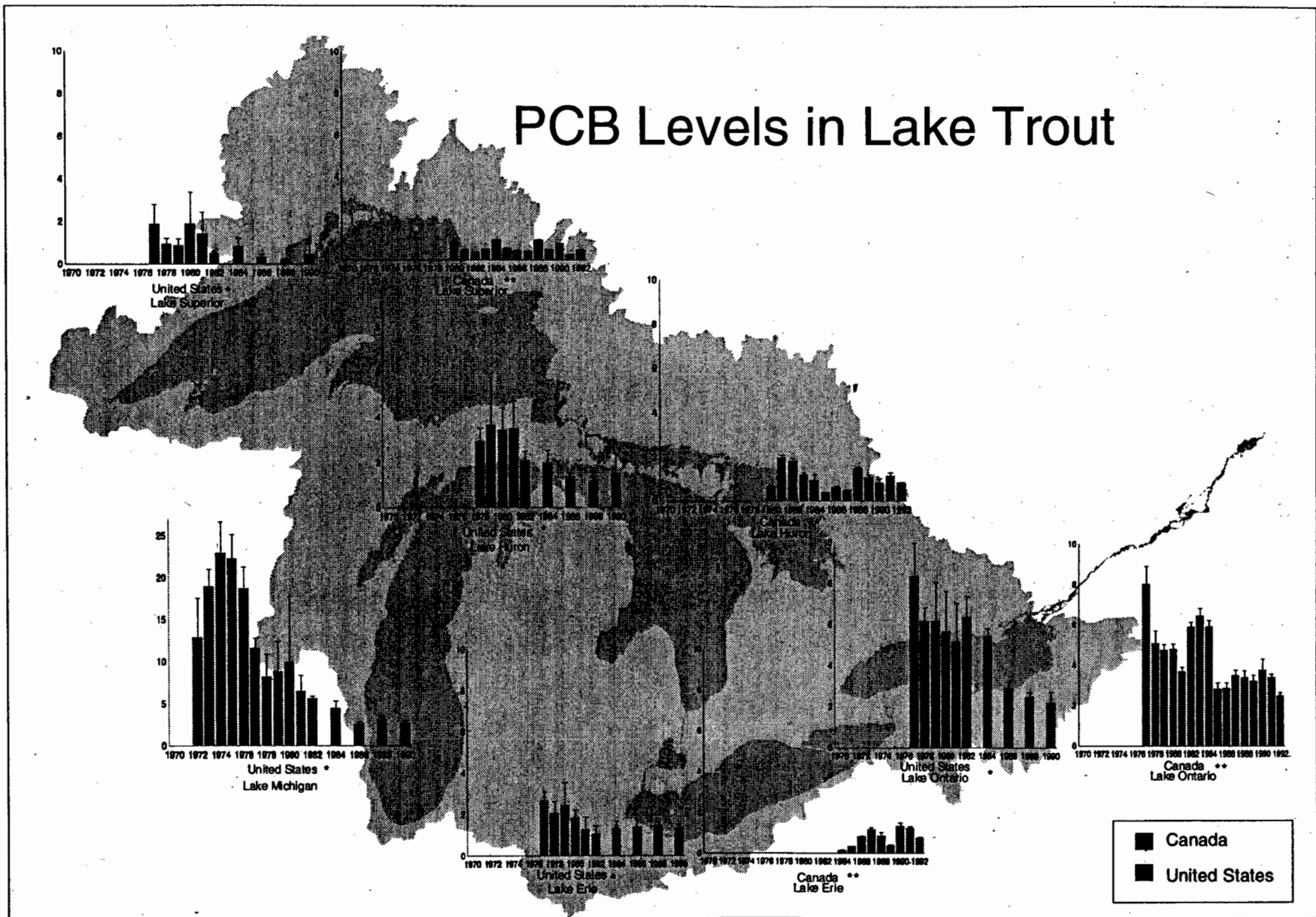


Figure 5. PCB levels (µg/g wet weight) in whole lake trout

Data Source: * US Environmental Protection Agency, Great Lakes National Program Office -- 10 fish composite samples, 600-700 mm. T.L.. ($\bar{x} \pm 95\%$ C.I.) (Lake Erie data are for wallye)

** Canadian Department of Fisheries and Oceans -- Individual fish age 4+ yrs., $\bar{x} \pm$ S.E.

PCB in Coho Salmon

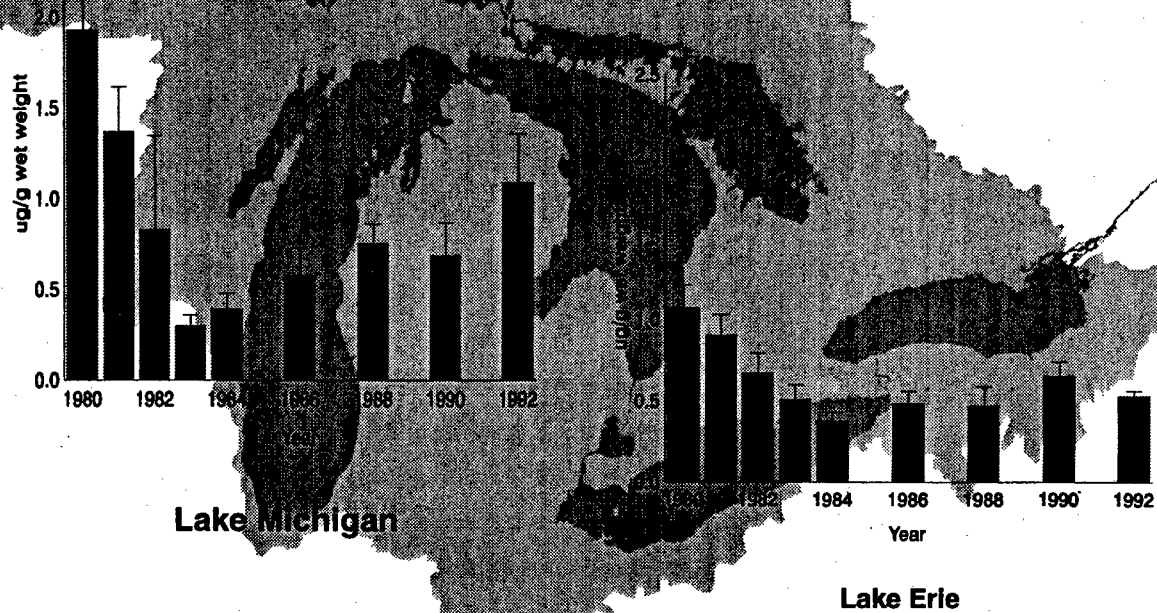


Figure 6. PCB levels ($\mu\text{g/g}$ wet weight $\bar{x} \pm \text{S.E.}$) in coho salmon skin-on filet

Data Source: US Environmental Protection Agency, Great Lakes National Program Office

Total DDT Levels in Lake Trout

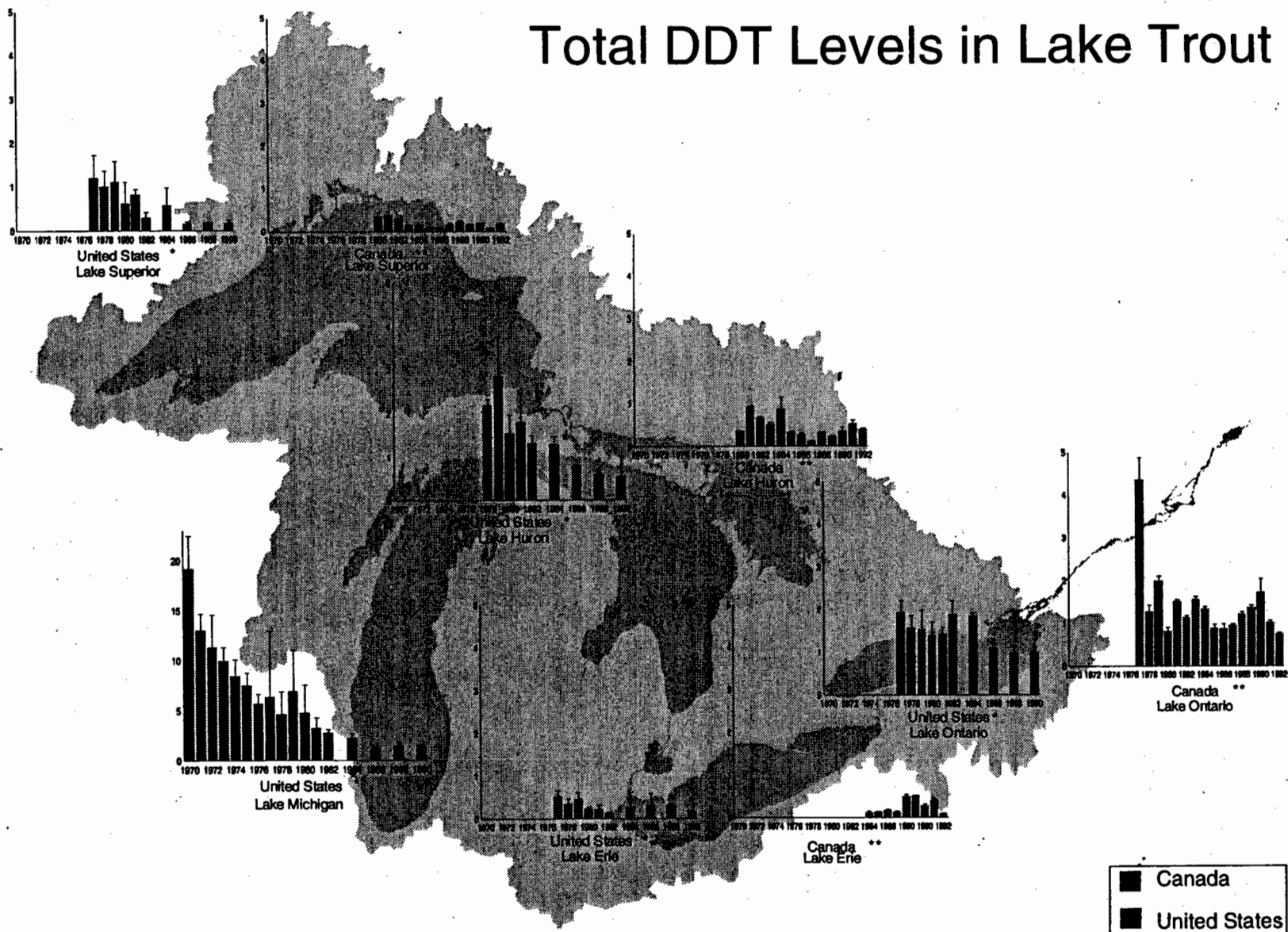


Figure 7. DDT levels (µg/g wet weight) in whole lake trout

Data Source: * US Environmental Protection Agency, Great Lakes National Program Office -- 10 fish composite samples, 600-700 mm. T.L.. ($\bar{x} \pm 95\%$ C.I.) (Lake Erie data are for walleye)

** Canadian Department of Fisheries and Oceans -- individual fish age 4+ yrs., $\bar{x} \pm$ S.E.

Total DDT in Coho Salmon

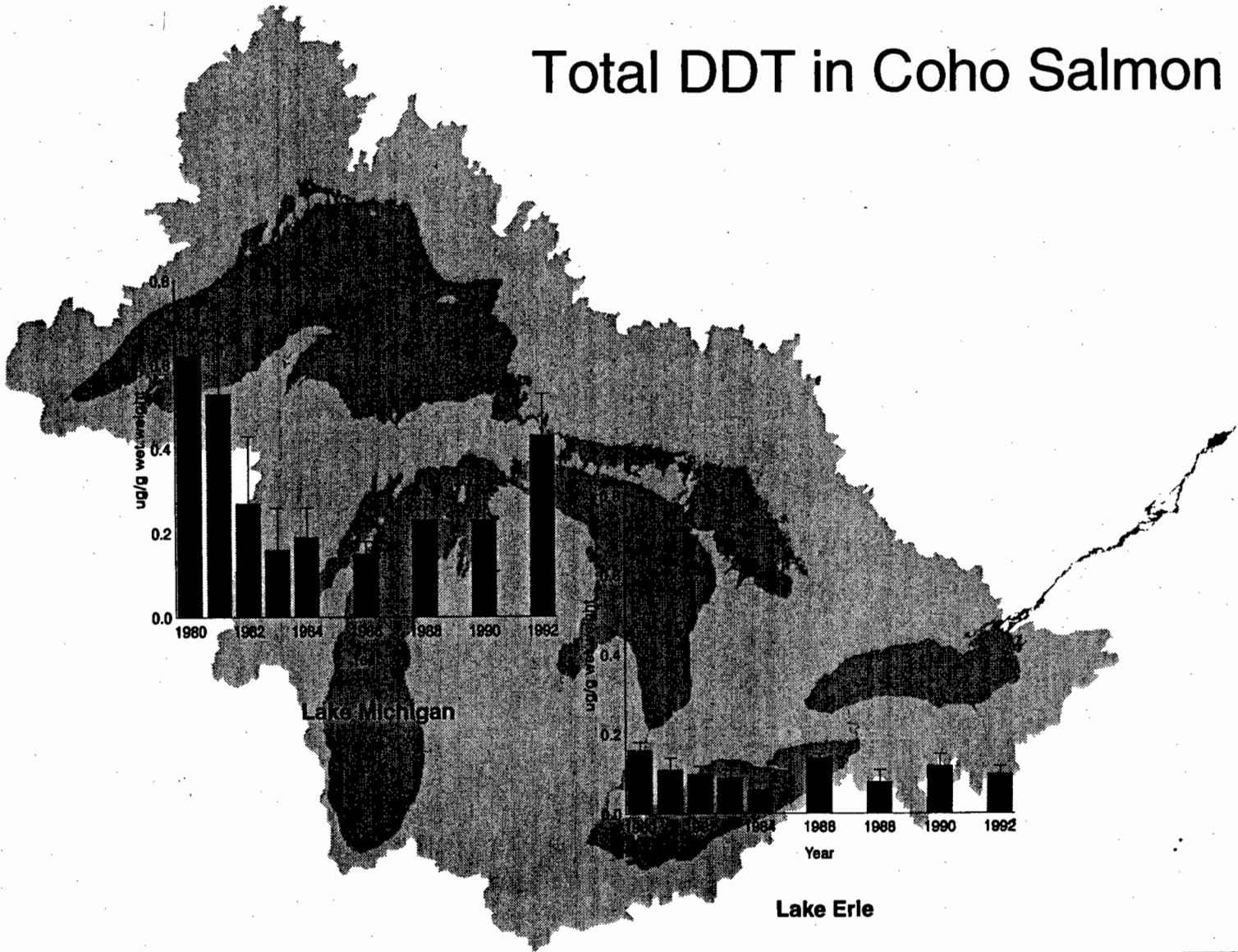


Figure 8. Total DDT levels ($\mu\text{g/g}$ wet weight $\bar{x} \pm \text{S.E.}$) in coho salmon skin-on filet

Data Source: US Environmental Protection Agency, Great lakes National Program Office

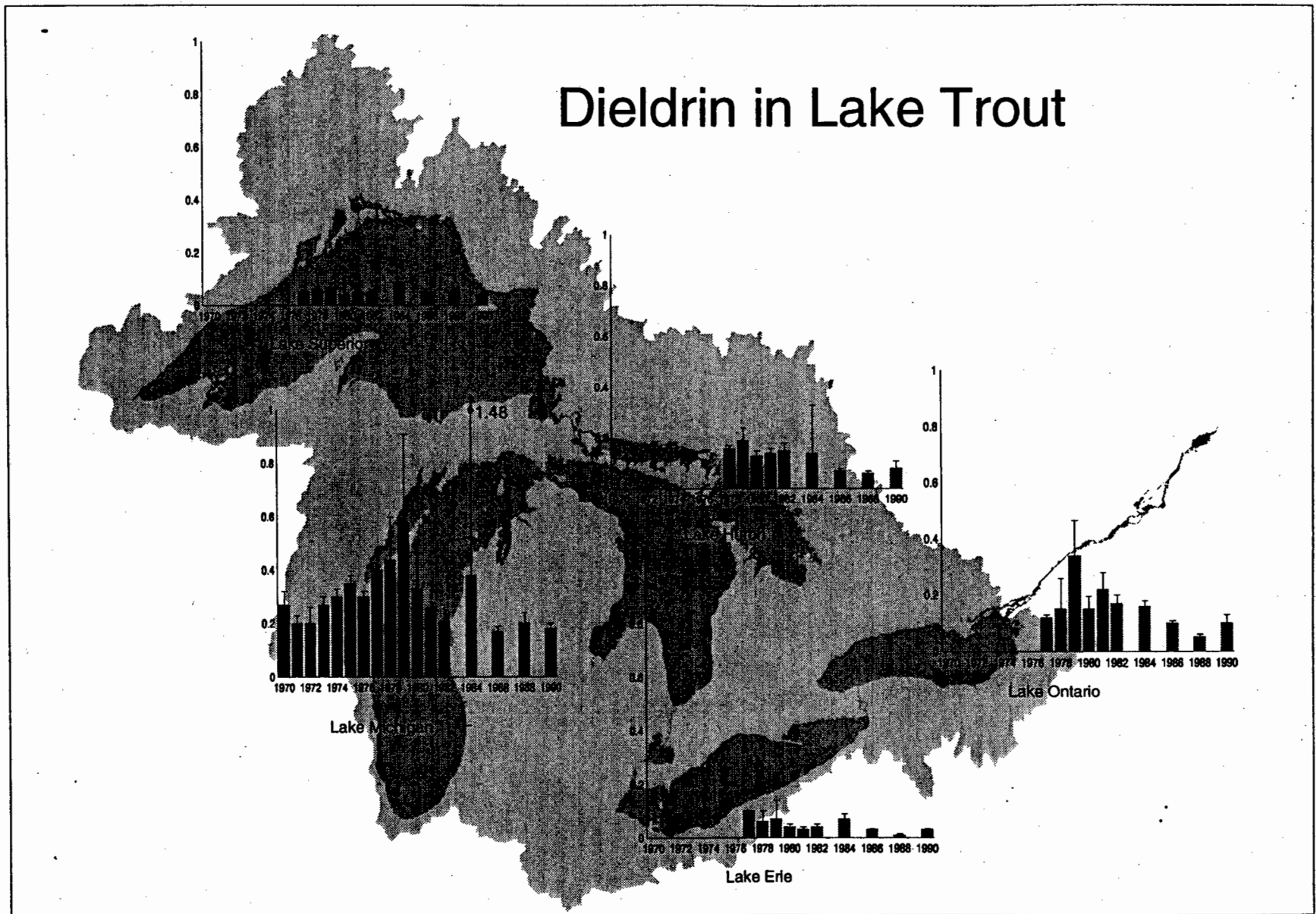


Figure 9. Dieldrin levels (µg/g wet weight) in whole lake trout

Data Source: US Environmental Protection Agency, Great Lakes National Program Office -- 10 fish composite samples, 600-700 mm T.L.. ($\bar{x} \pm 95\% \text{ C.I.}$)
 (Lake Erie data are for wallye)

Toxaphene in Lake Trout

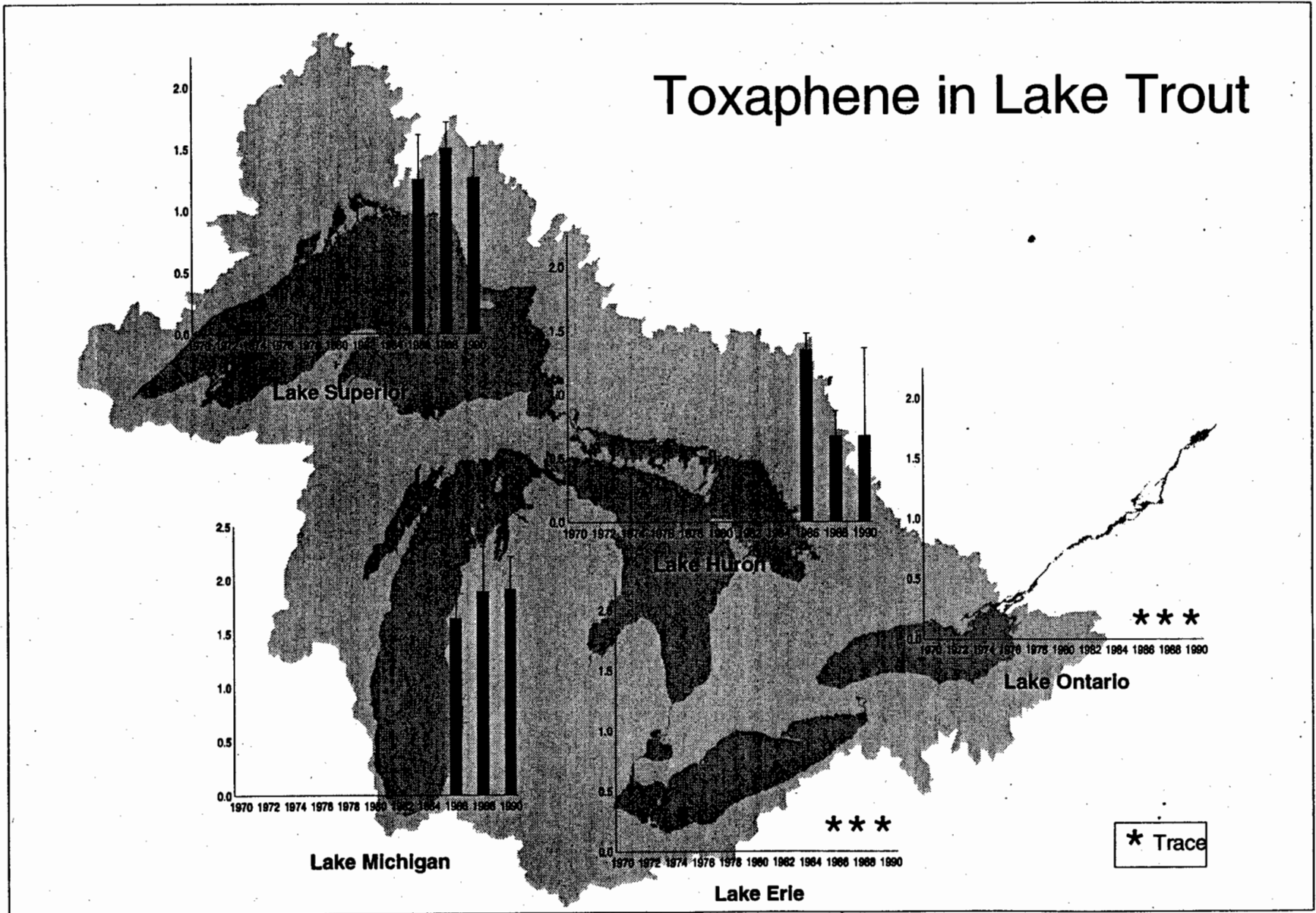


Figure 10. Toxaphene levels ($\mu\text{g/g}$ wet weight $\bar{x} \pm 95\%$ C.I.) in 10 fish composite samples, 600 - 700 mm T.L.

Data Source: US Environmental Protection Agency, Great Lakes National Program Office

PCB Trends in Smelt

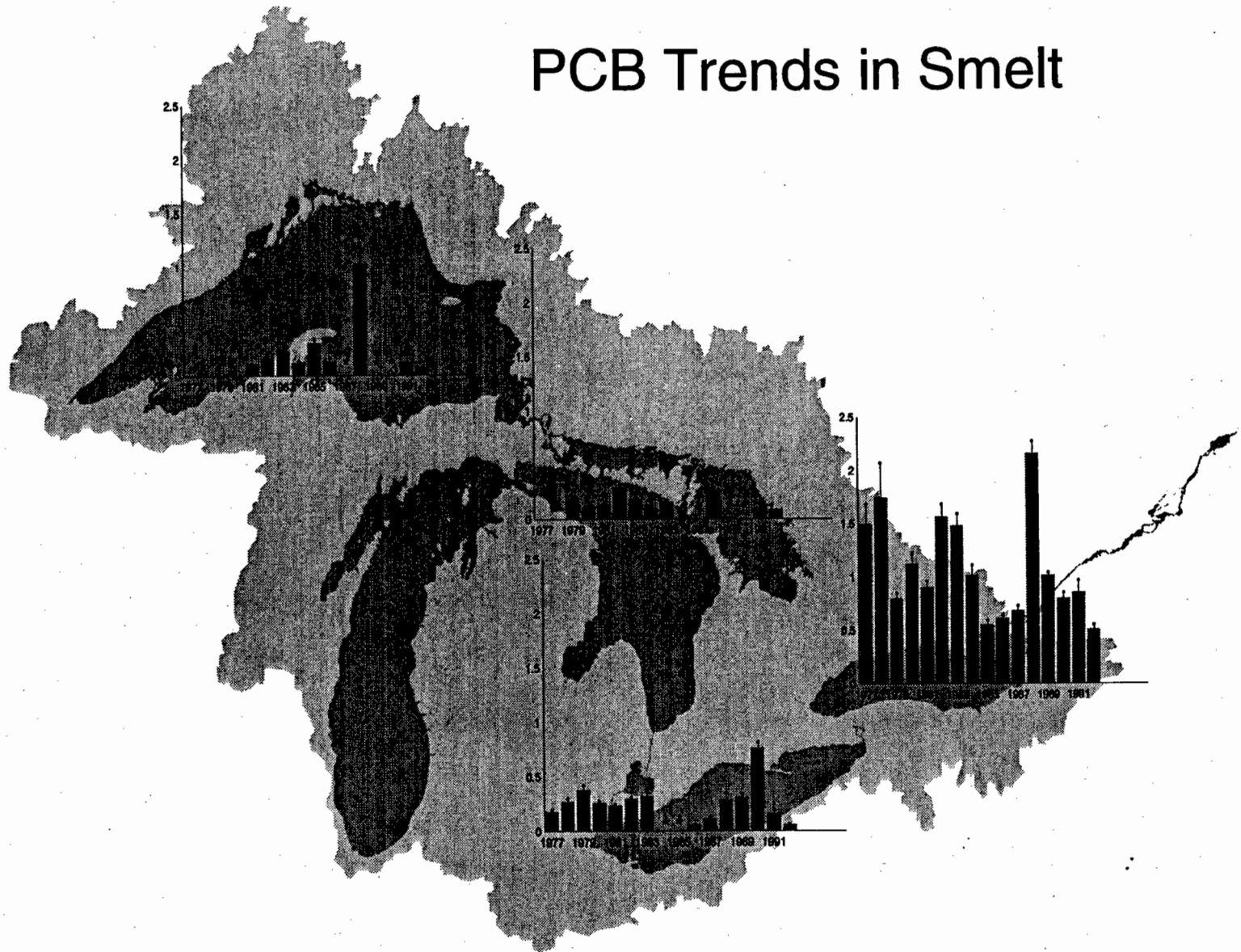


Figure 11. PCB levels ($\mu\text{g/g} \pm \text{S.E.}$) in rainbow smelt whole fish (wet weight) in the Great Lakes, 1977-1992.

* >50% results below detection limit (0.10 $\mu\text{g/g}$)

Data Source: Canadian Department of Fisheries and Oceans

Total DDT in Smelt

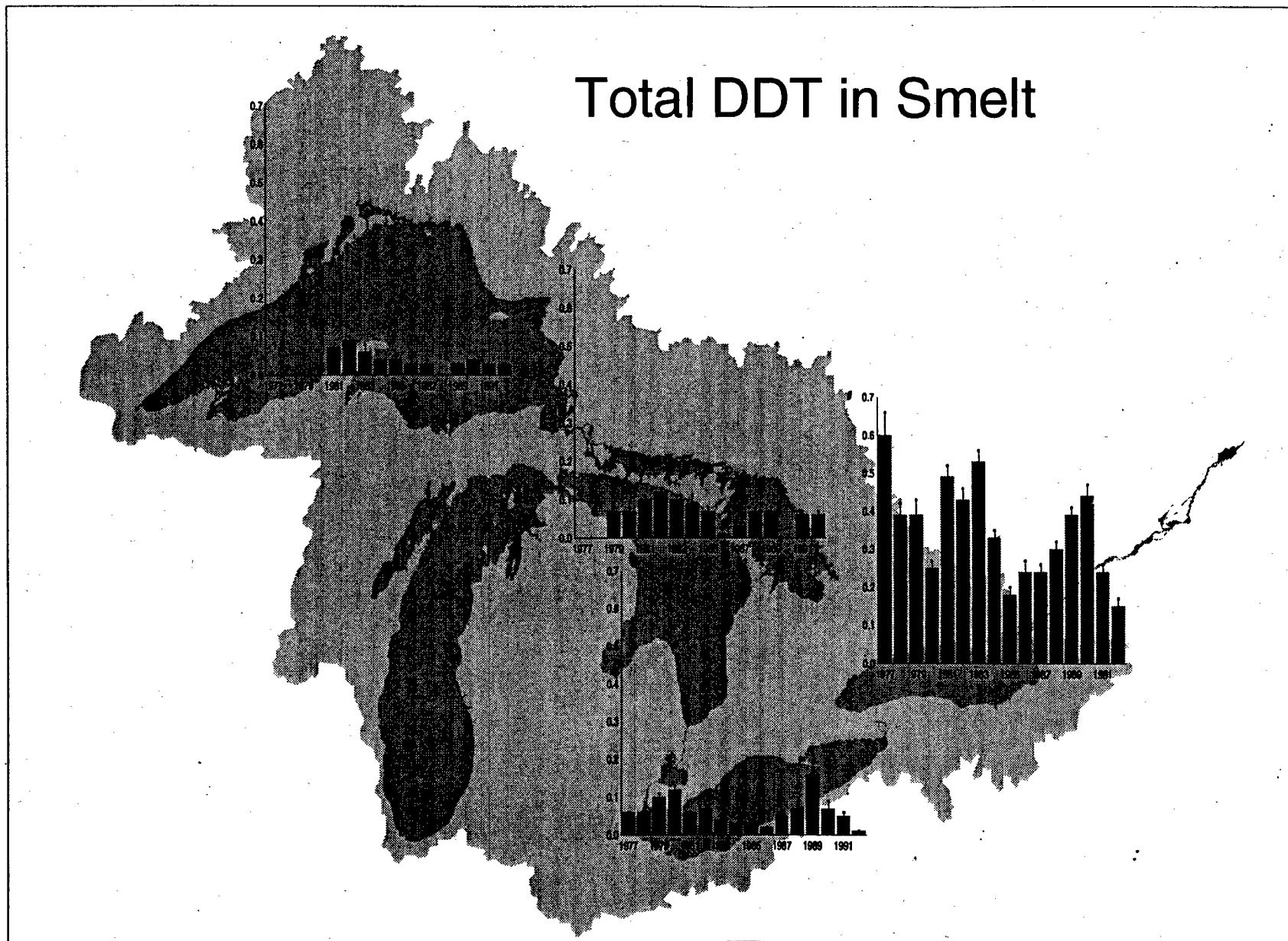


Figure 12. Total DDT levels ($\mu\text{g/g} \pm \text{S.E.}$) in rainbow smelt whole fish (wet weight) in the Great Lakes, 1977-1992.

* >50% results below detection limit (0.01 $\mu\text{g/g}$)

Data Source: Canadian Department of Fisheries and Oceans

Mercury Trends in Smelt

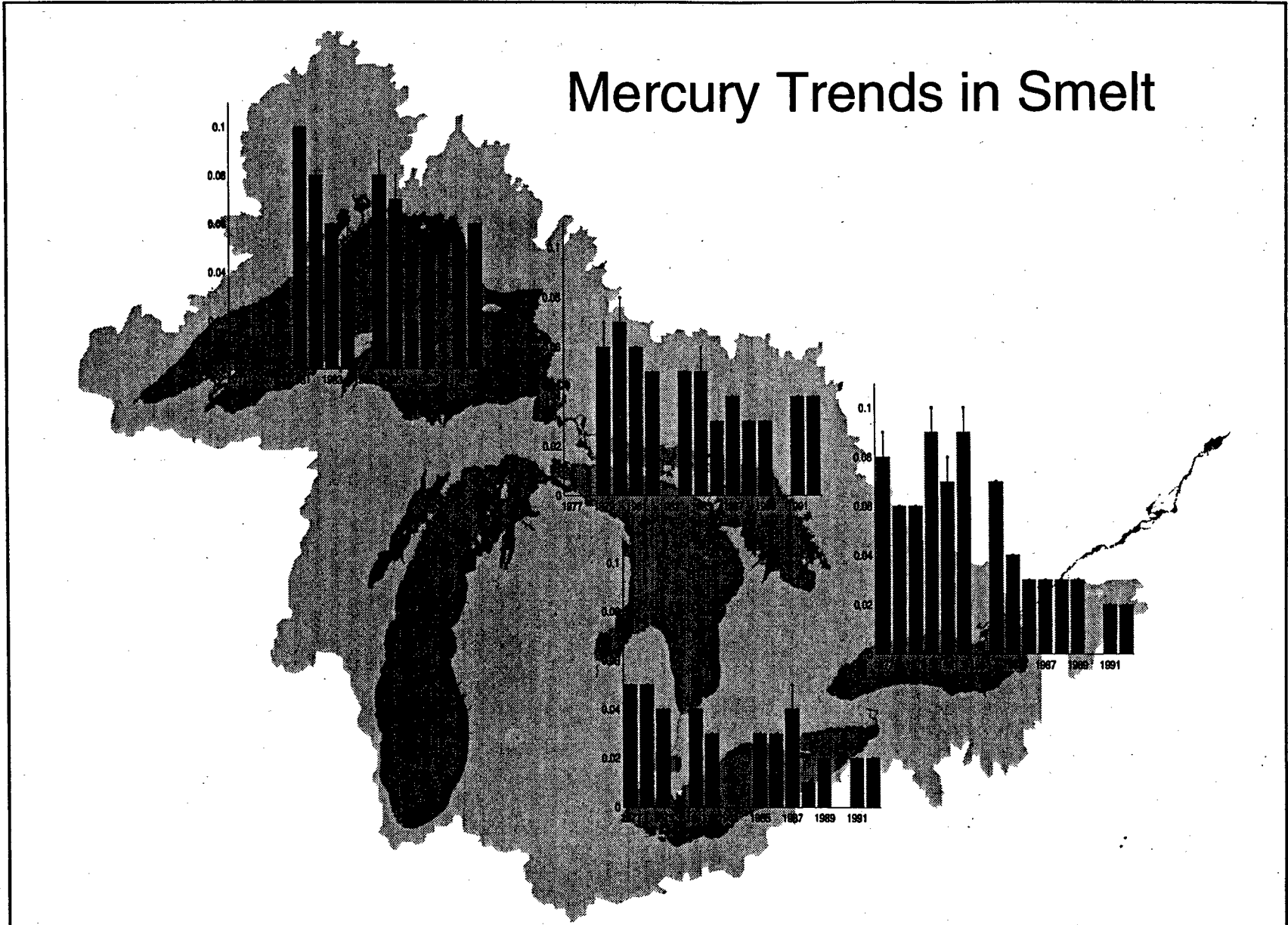


Figure 13. Mercury levels ($\mu\text{g/g} \pm \text{S.E.}$) in rainbow smelt whole fish (wet weight) in the Great Lakes, 1977-1992.

* >50% results below detection limit (0.03 $\mu\text{g/g}$)

Data Source: Canadian Department of Fisheries and Oceans

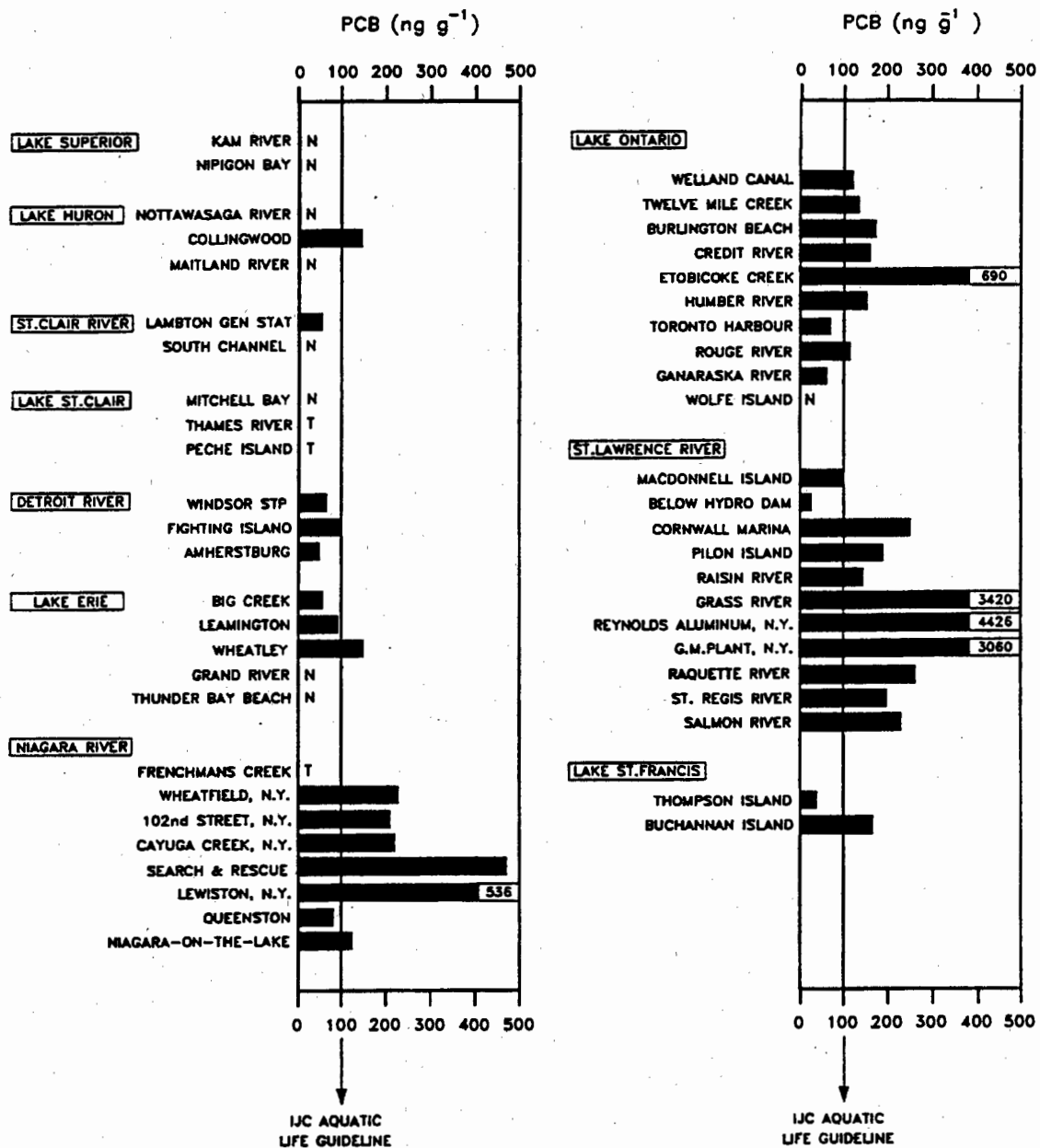


Figure 14. Total PCB concentrations in young-of-the-year spottail shiners from the Great Lakes and connecting channels for the most recent year, 1990 or 1991. IJC Aquatic Life Guideline for PCB = 100 ng/g. (N = not detected; T = trace)

(Data Source: Karlis R. Suns, et al., Ontario Ministry of Environment and Energy)

PCB Trends in Herring Gull Eggs

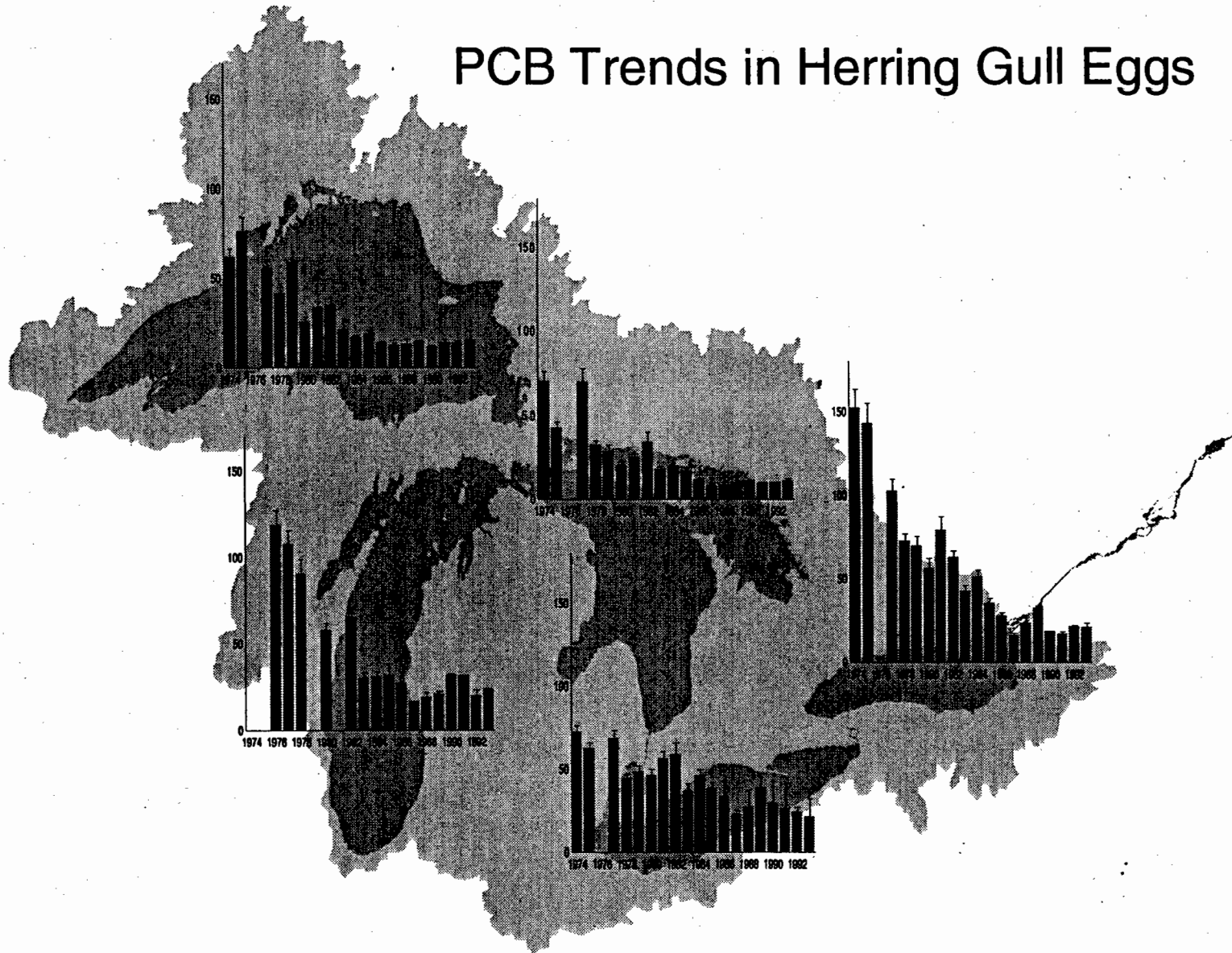


Figure 15. PCB levels ($\mu\text{g/g}$ wet weight \pm S.E.) in Herring Gull eggs in the Great Lakes, 1974-1993.

Data Source: Canadian Wildlife Service, adapted from Bishop et al. 1992 and Petit et al. 1994)

p,p'-DDE Trends in Herring Gull Eggs

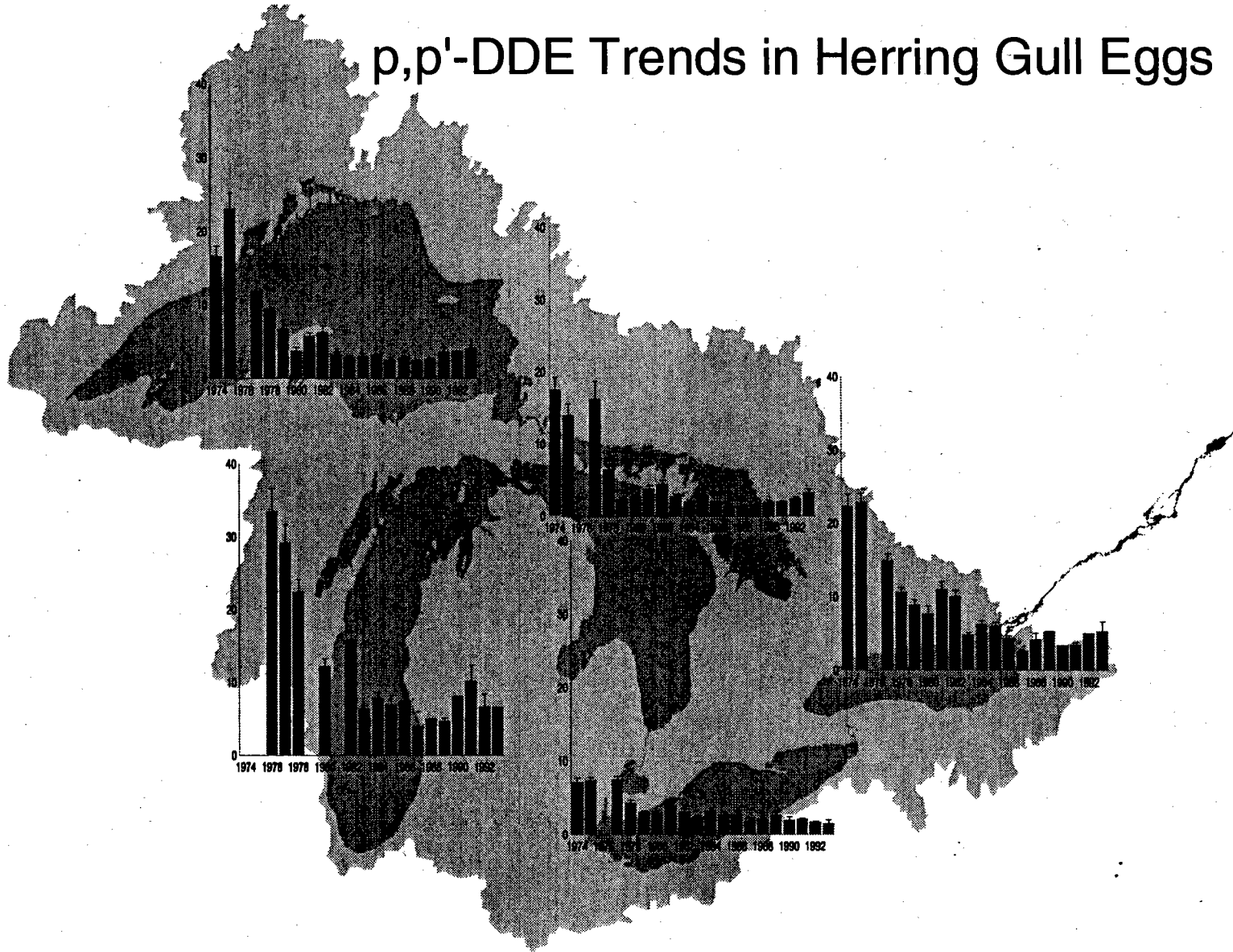
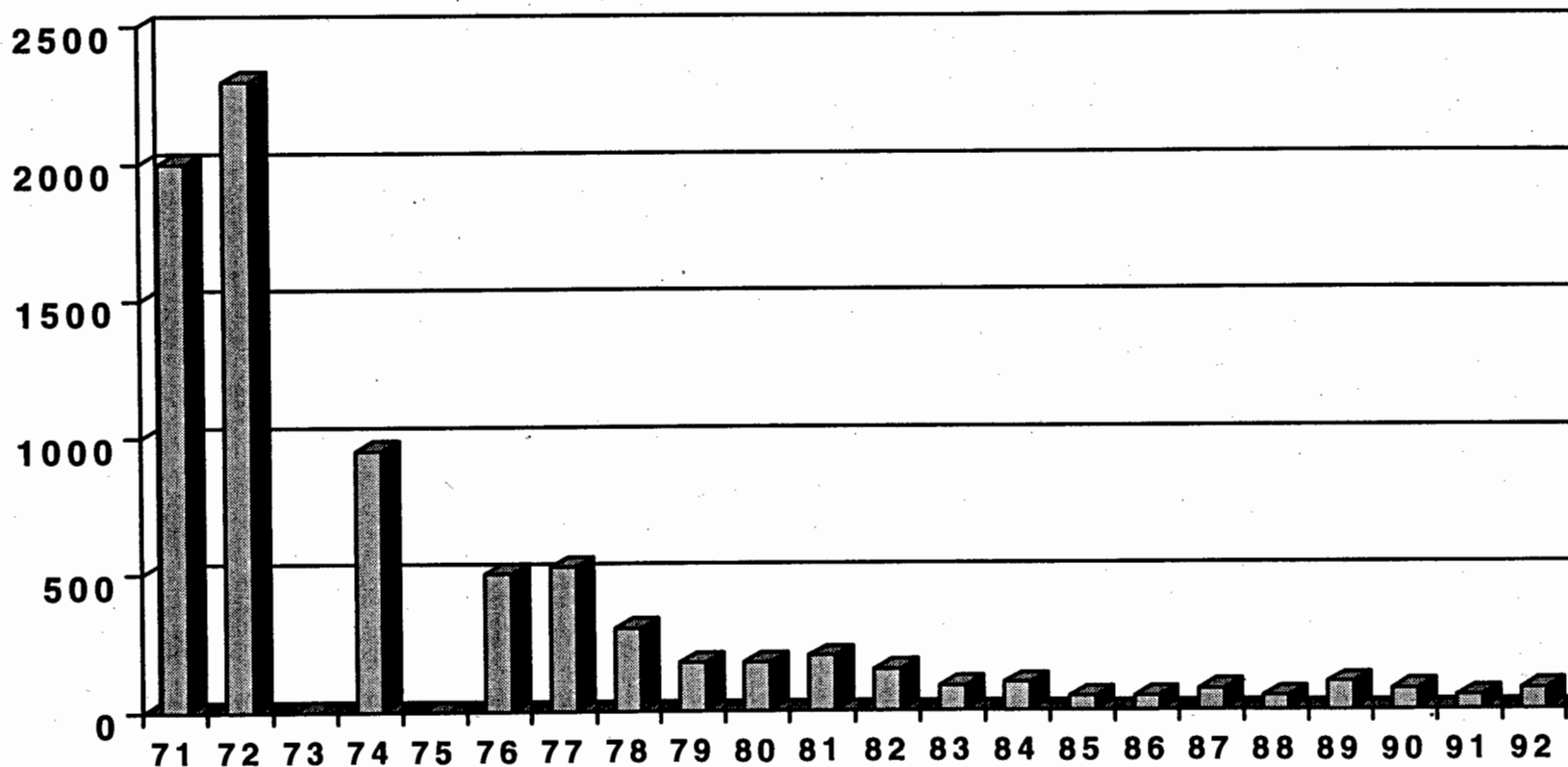


Figure 16. p,p'-DDE levels (µg/g wet weight±S.E.) in Herring Gull eggs in the Great Lakes, 1974-1992

Data Source: Canadian Wildlife Service, Adapted from Bishop et al. 1992 and Petit et al. 1994.

DIOXIN* IN HERRING GULL EGGS 1971 - 1992 EASTERN LAKE ONTARIO

pg/g (ppt) W et W eight



* 2,3,7,8 - tetra-chloro-benzo-dioxin

Figure 17. Dioxin (2,3,7,8-TCDD) Concentrations in herring gull eggs from eastern Lake Ontario, 1971-1992 (Data from C. Weseloh, Canadian Wildlife Service, adapted from Bishop et al. 1992, Petit et al. 1994, and Hebert et al., 1994).

Contaminants in Herring Gull Eggs - 1992

Spatial Distribution

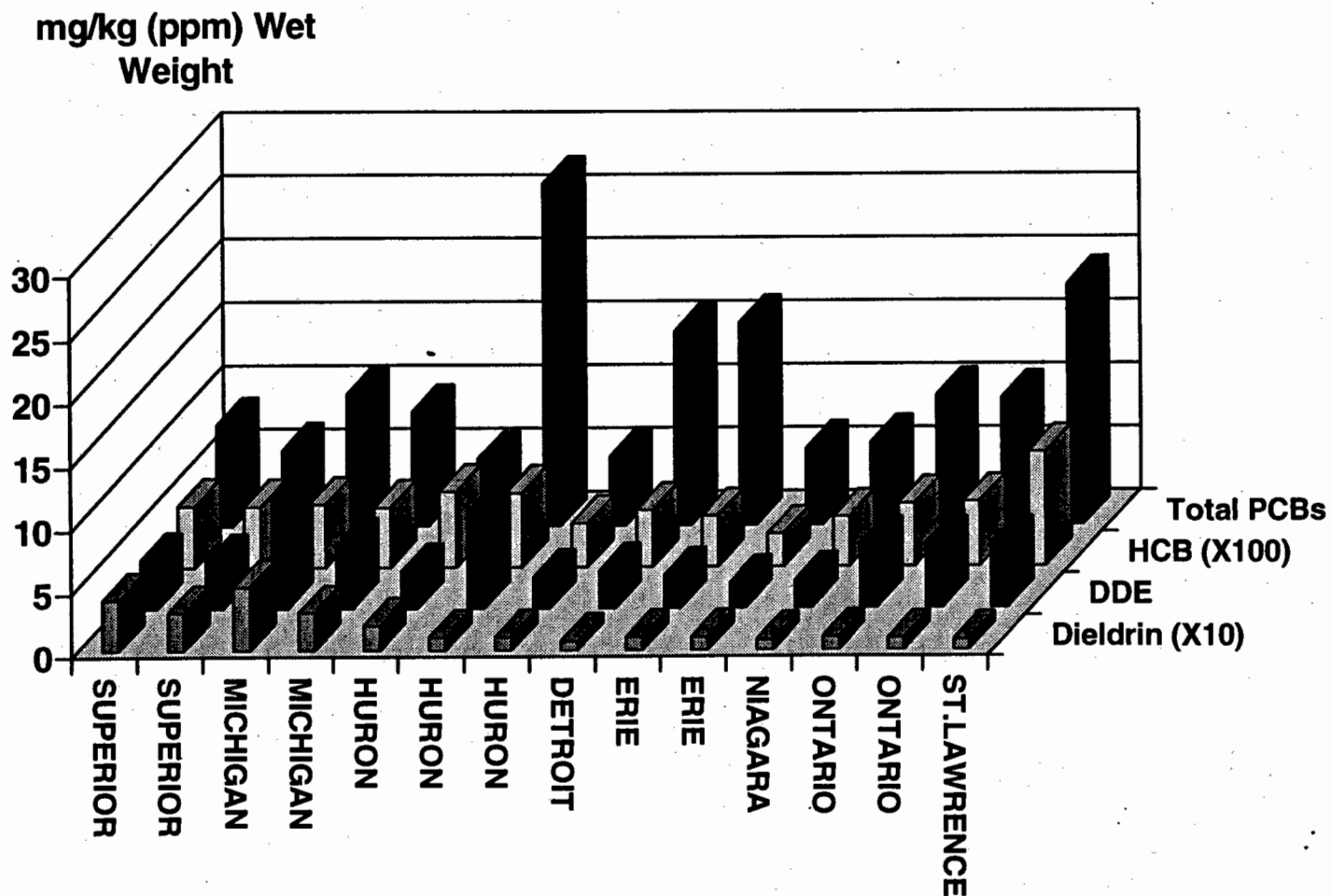


Figure 18. PCBs, DDE, and dieldrin in Herring Gull Eggs collected in 1992 from sites on each Great Lake and the Detroit, Niagara, and St. Lawrence Rivers. (Data from C. Weseloh, Canadian Wildlife Service, adapted from Bishop et al 1992 and Petit et al. 1994)

DIOXIN IN HERRING GULL EGGS - GREAT LAKES 1992

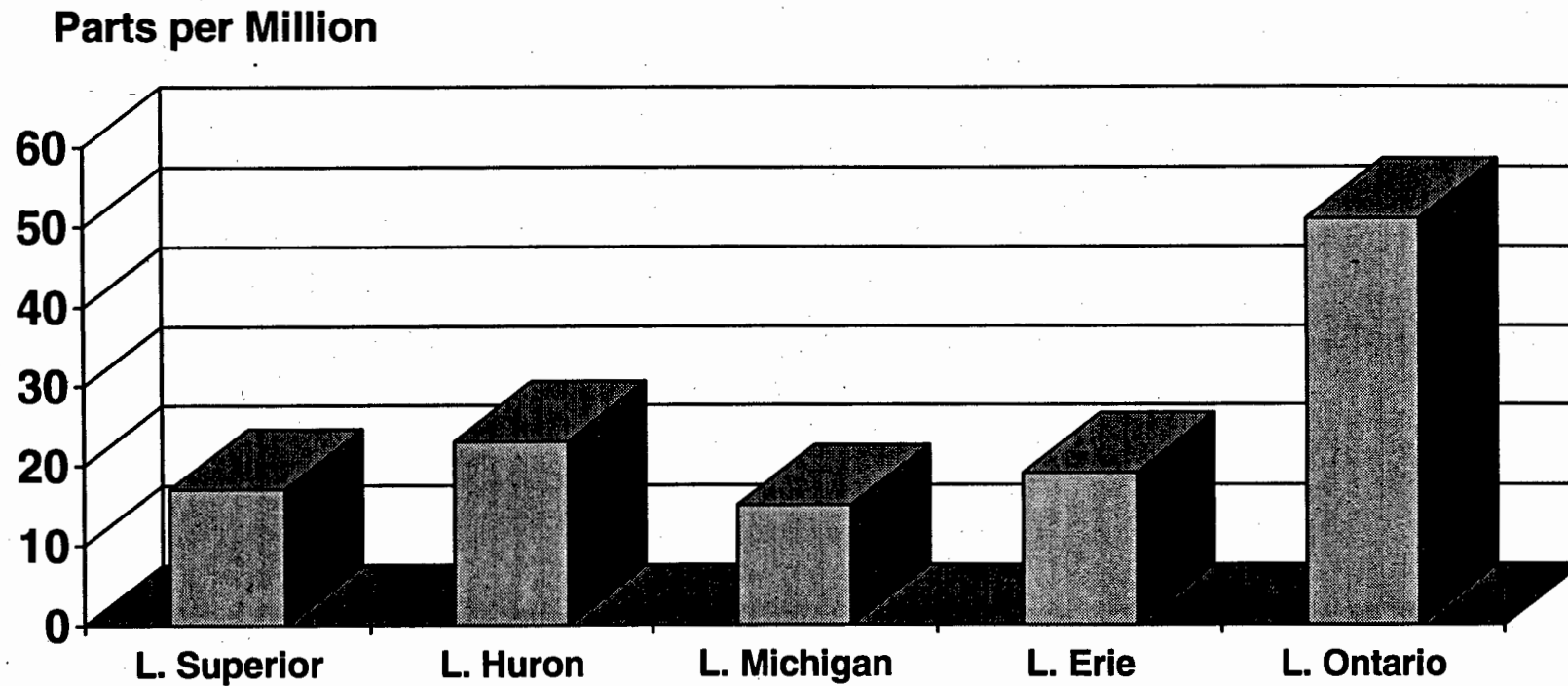


Figure 19. Dioxin (2,3,7,8-TCDD) concentrations in herring gull eggs collected in 1992 from sites on each Great Lake (Data from C. Weseloh, Canadian Wildlife Service, adapted from Bishop et al. 1992, Petit et al. 1994, and Hebert et al., 1994).

CONTAMINANTS IN HERRING GULL EGGS - 1992

SPATIAL DISTRIBUTION

mg/kg (ppm),
Wet Weight

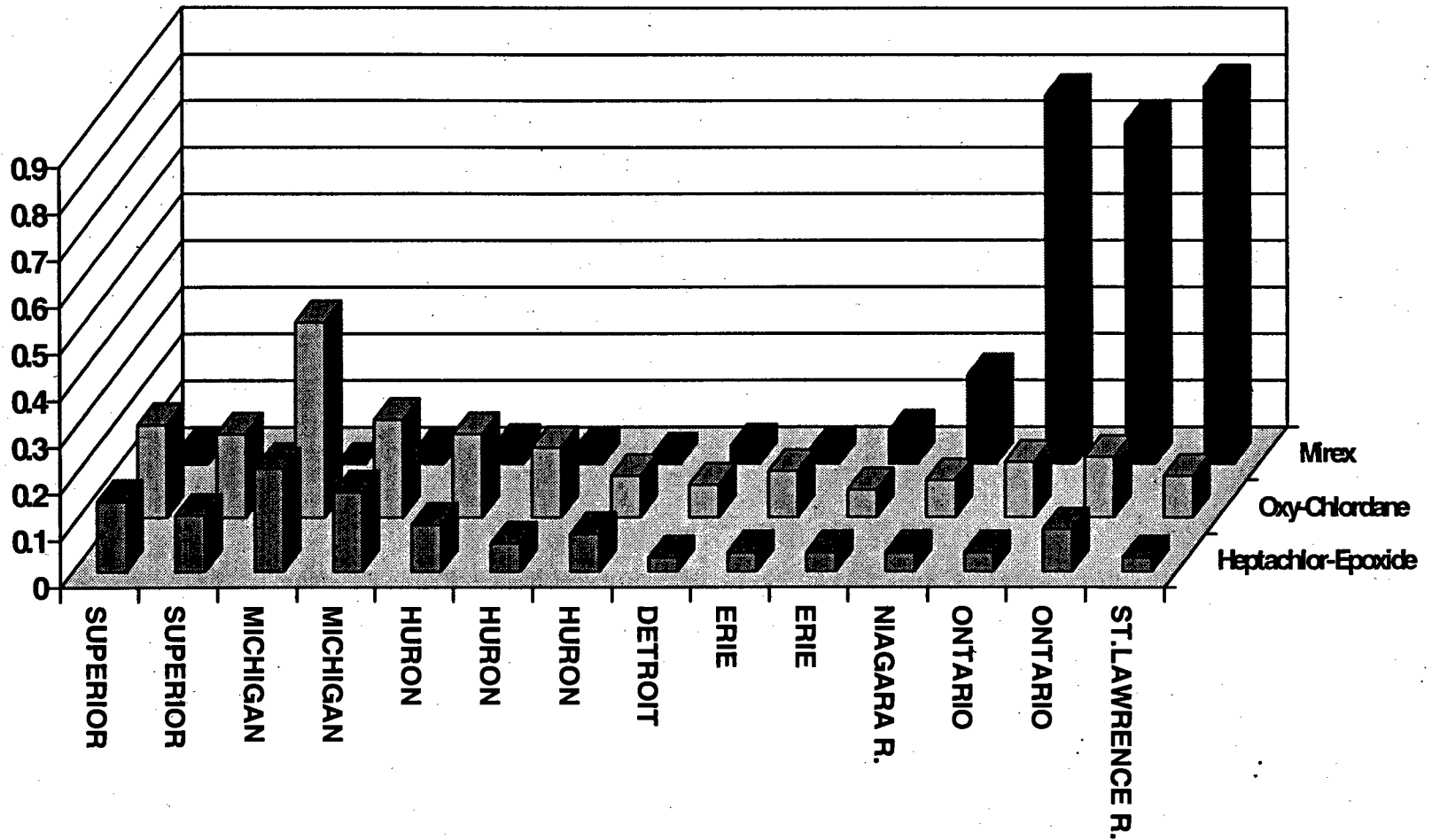


Figure 20. Mirex and other contaminants in herring gull eggs collected in 1992 from sites on each Great Lake (data from C. Weseloh, Canadian Wildlife Service, adapted from Bishop et al. 1992 and Petit et al. 1994).

ATMOSPHERIC PCBs, FALL AND SPRING, 1991 - 1992

(in ng/m^3)

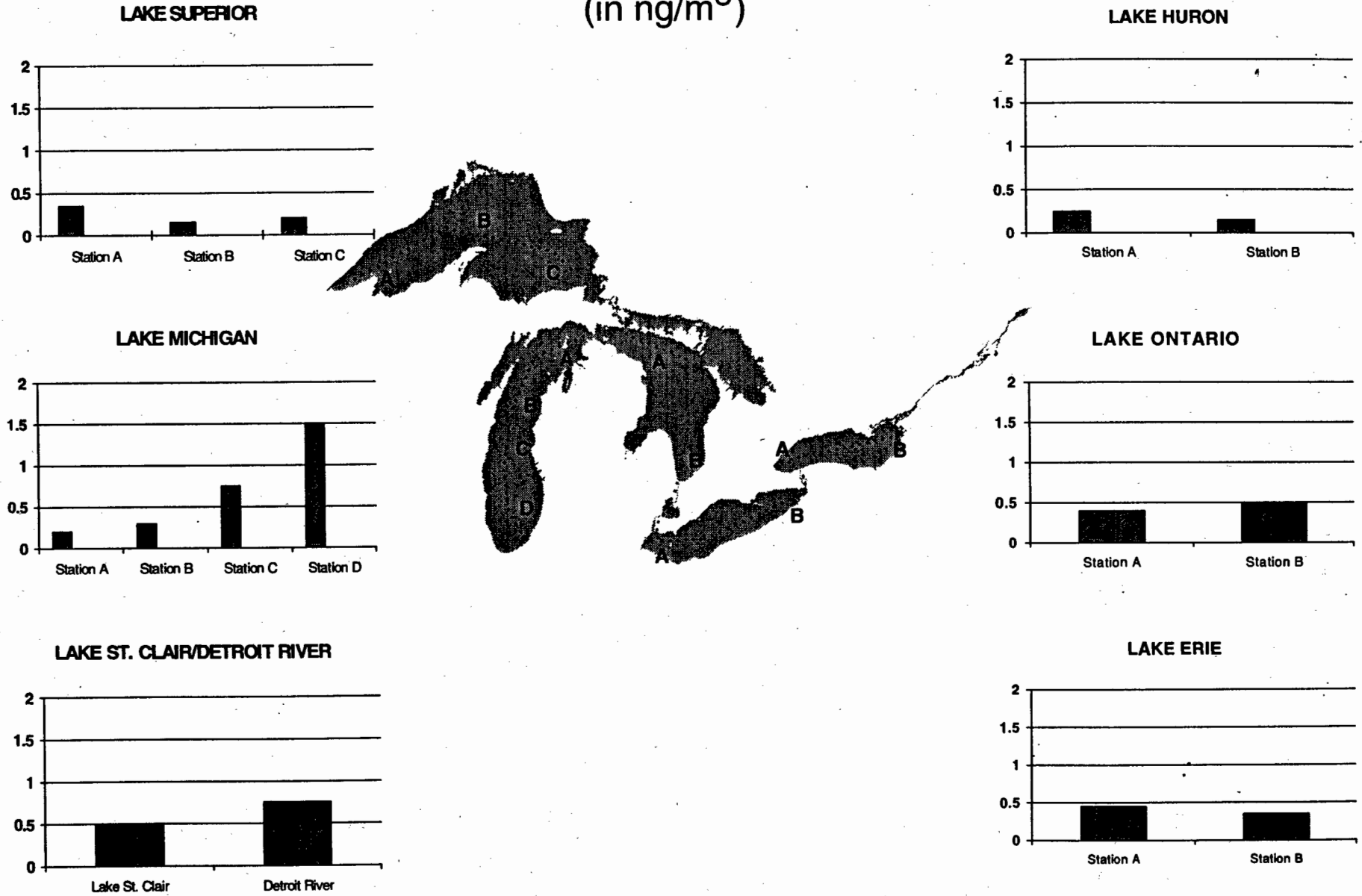


Figure 21. Concentrations of PCBs in the air over the Great Lakes., 1991-1992 (Data from S. Eisenreich, personal Communication).