# Environment Canada Water Science and Technology Directorate

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An Overview of Toxic Contaminant Concentrations in Water and Sediments of the Great Lakes By: R.J. Allan & A.J. Ball

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#### AN OVERVIEW OF TOXIC CONTAMINANT CONCENTRATIONS IN WATER AND SEDIMENTS OF THE GREAT LAKES

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#### EXECUTIVE SUMMARY

This report presents the chemical concentrations and trends in Great Lakes water and sediment. It has been prepared as a contribution to the Government of Canada Interdepartmental report "Synopsis of Chemical Pollution of the Great Lakes and Associated Health Effects". Results presented here are taken, whenever possible, from published documents. Uninterpreted data was not used.

The most recent data, obtained for both toxic metals and organic chemicals in water is considered the most reliable and shows that ambient concentrations are very low, much lower than historically measured and thus believed. The concentrations of chemicals in water are much less than in fish. For example, in 1985/86, the amount of PCBs consumed in half a kilogram of lake trout (mean value of 2.9 ppm for 1985) from Lake Ontario (open water mean value of 1.41 ppt for 1986) is equivalent to that acquired by drinking two litres of Lake Ontario water a day for 1,410 years. Presently, most water concentrations of toxic chemicals are below the Great Lakes Water Quality Agreement objectives throughout the Great Lakes.

From the available sediment data, the trends for the chemicals discussed all seem to be downwards at least relative to the concentrations 10 and 15 years ago. Thus, the historical trends of chemical concentrations in lake bottom sediment cores indicate that the major influx of toxic metals and persistent toxic organic chemicals to the Great Lakes aquatic ecosystem took place in the nineteen sixties and early seventies. Some of these recent declines have been dramatic, once control action has taken place (PCBs; Mirex). Often, these periods of peak input of several chemicals to the Great Lakes occurred several years prior to their first detection in lake biota.

In the last five years (1982 to 1987) no new contaminants which fit the criteria of widespread occurrence, high toxicity, and long persistence, similar to the chemicals discussed in this report, have been detected in any of the Great Lakes. However, to

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#### INTRODUCTION

1.0

1

The Great Lakes constitute the largest body of freshwater on earth. Ranked by surface area, Lake Superior is the second largest lake in the world. Lake Huron comes fifth, Michigan sixth, Erie thirteen, and Ontario seventeenth (Beeton, 1984). The Great Lakes are viewed as one of the planets great natural resources, not only by the Canadians and Americans who live in their drainage basin (Figure 1) but by people around the world. In spite of the size of these waterbodies, man has contaminated them with toxic chemicals. The sources of the chemicals are urban and industrial development and agriculture. Some of the toxic chemicals are distributed throughout the entire Great Lakes ecosystem.

The purpose of this report is to present published results of selected toxic chemical concentrations in the water and bottom sediments of the open Great Lakes and their connecting channels. Spatial patterns and temporal trends in these abiotic media are presented where possible.

The introductory section consists of background information about toxic chemicals in the water and sediments of the Great Lakes. This includes sources, pathways and fate of the chemicals in the system, a discussion of the main chemicals of concern, a history of Great Lakes contamination, and a description of water and sediment sampling and analysis. The overall organization of this report is by geographic location; that is, the data for each lake and connecting channel is presented in sequence from Lake Superior to the international section of the St. Lawrence River. For each body of water, the conditions of the water and then the sediments are discussed. The water sections are divided into two sections. The first section includes concentrations in the aqueous phase and in total water and the second section includes concentrations in the suspended sediment phase. The sediment sections are also divided into two parts: surficial sediment concentrations and concentrations in sediment cores. In each of

these four sections, concentrations of metals are discussed before those of organic toxic contaminants. The main chemicals included for discussion in this report are lead (Pb), mercury (Hg), cadmium (Cd), arsenic (As), DDT and metabolites, dieldrin, a-BHC lindane, mirex, toxaphene, B(a)P, dioxins and furans, HCB, HCBD, and PCBs. There is a list of chemical abbreviations in Appendix 1. For each of the Great Lakes and the Niagara River, there are extensive tables of concentrations of these chemicals in the water and Representative core profiles for each of the Great sediments. The summaries for Lakes show sediment concentration trends. geographic patterns of contaminant distribution and concentration changes over time are presented in the conclusion. There is a glossary in Appendix 2.

Presently, the available information on toxic chemical contamination of the Great Lakes is greater than exists for any other set of freshwater lakes in the world (Allan, 1988). This report is the most comprehensive document prepared to date on the concentrations of toxic contaminants in the water and sediments of all of the Great Lakes and their connecting channels. The sources used to prepare this literature review included journal articles, journal issues, reports, conference papers and proceedings, dissertations, monographs, and chapters. When possible, only primary published sources were used.

## 1.1 TOXIC CHEMICAL SOURCES, PATHWAYS AND FATE

The Great Lakes system flows from Lake Superior and Lake Michigan through the other Great Lakes and the St. Lawrence River to the Atlantic Ocean. The lakes are one unit in that they are connected by short narrows at Mackinac and by the short connecting channels of the St. Clair, Detroit and Niagara Rivers. These channels have extremely large discharges of approximately 6,000  $m^3$ /sec, putting them on a scale with the world's largest rivers. The massive transfers of water into and out of lakes Erie and Ontario are a critical factor in toxic chemical fate in the lower

					<u> </u>	. <u></u>
Elevation (km)	Superior 183	Michigan 176	Huron 176	Erie 173	Ontario 74	Totals
ength (km) Breadth (km Average Depth (m)	563 257 147	494 190 85	332 245 59	388 92 19	311 85 86	· ·
Maximum Depth (m) Volume (km <sup>3</sup> ) Area:	405 12,100	281	229 3,540	64 484	244 1,640	22,684
Vater (km <sup>2</sup> ) Land Drainage	82,100	57,800	59,600	25,700	18,960	244,160
Area (km)	127,700	118,000	134,100	78,000	64,030	521,830
Fotal (km <sup>2</sup> )	209,800	175,800	193,700	103,700	82,990	765,900
Shoreline Length (km)	4,385	2,633	6,157	1,402	1,146	17,017
Retention Time (years)	191	99	22	2	.6 6	
Population: U.S. (1980) Canada (1981)	558,100 180,440	13,970,900		11,347,500 1,621,106		
Totals	738,540	13,970,900	2,372,119	12,968,606	6,662,175	36,692,340
Dutlet St	. Mary's River	Straits of Mackinac	St. Clair River		St. Lawrence River	
			· / ·	Canal	KIA6T	•

## TABLE 1 PHYSICAL FEATURES OF THE GREAT LAKES (after Botts and Krushelnick, 1987).

highly toxic while they are in the water column.

1.2

MAIN CHEMICALS OF CONCERN

It is the toxic metals and persistent toxic organic chemicals which have generated most concern about contamination of the Great Lakes. The latter includes chlorinated pesticides such as DDT and Mirex, chlorinated benzenes, chlorinated dioxins and furans, and PCBs. The former includes Pb, Hg, Cd, and As.

In 1983, a comprehensive Inventory of Chemical Substances Identified in the Great Lakes Ecosystem was published by the IJC. Produced from this inventory was the 1986 Working List of Chemicals in the Great Lakes Basin (IJC Comprehensive Track chemicals) which contains 362 chemicals (IJC 1987b). Of these chemicals, 11 critical pollutants were chosen by the IJC for their Primary Track. Information used in deriving priority lists tends to include chemical stability leading to persistence in the environment, the quantities in use, the types of use, the tendency to accumulate in living organisms, and the biological effects associated with acute or chronic exposure (Hamilton et al., 1987). In this report, all of the Primary Track chemicals.

In Canada, there are several sets of objectives and guidelines set for concentrations of toxic chemicals in water. Two of these are presented in Table 2. When developing and using guidelines for the protection of aquatic life, there should be complete information on the parameter of concern, including form and fate quantitative exposure/effect environment; in the acuatic relationships; and fate within organisms over a wide range of The relevant information base for a exposure concentrations. particular chemical is rarely complete and there are often many gaps in knowledge. In general, water quality guidelines used in Canada are based on an unfiltered water sample (CCREM, 1987).

The first set of objectives listed are the 1978 Great Lakes Water Quality Agreement Specific objectives. These were amended

by the 1987 Protocol. Although the Protocol stated that the discharge of toxic substances in toxic amounts be prohibited and the discharge of any or all persistent toxic substances be virtually eliminated (IJC 1988), the Specific Objectives listed in the revised 1978 Agreement were adopted in 1987 as interim objectives for persistent toxic substances.

The second set of guidelines are those proposed by the Canadian Council for Resource and Environment Managers. In 1984, CCREM approved the recommendation by the Task Force on Water Quality Guidelines that Canadian water quality guidelines be harmonized (CCREM 1987). The guidelines are presented here as a comparison to the IJC objectives. The introduction to the Task Force report states that the guidelines should not be regarded as blanket values for national water quality and that variations in environmental conditions across Canada will affect water quality in different ways such that many of the guidelines will need to be modified according to local conditions (CCREM, 1987).

Because the role of sediments as a source of chemical contaminants to the aquatic environment is poorly understood, criteria and standards are still being developed. The existing criteria for open lake disposal of dredged materials were developed as a guide to determining appropriate disposal techniques for dredged materials, not for ambient water quality evaluation and/or ecosystem risk assessment. The guidelines are as follows: Hg, 0.3 ppm; Pb, 50 ppm; Cd, 1.5 ppm; As, 8 ppm; and PCBs, 0.05 ppm. For other organic contaminants, the guideline is below detection using best available technology.

In this report concentrations are reported in ppm, ppb, ppt or ppq. Examples of the wet and dry weight concentrations these represent are given in Table 3.

## HISTORY OF CONTAMINATION

The recent history of toxic chemical pollution events began in the early 1960s with pesticides such as DDT, followed by detection of other organochlorine pesticides and industrial chemicals such as PCBs (Williams, 1975; D'Itri, 1988). In 1968, Hg was detected in high concentrations in sediments from lakes Concurrently, high Ontario and Huron (Thomas, 1972; 1973). concentrations of Hg were discovered in Lake St. Clair fish (Fimreite et al., 1971) at levels which resulted in implementation of a ban on commercial fishing in that lake in 1970. The source of Hg to Lake St. Clair was upstream chlor-alkali plants on the St. Clair River. In 1971, the Michigan Public Health Department issued a warning on PCBs in lake trout and salmon in Lake Michigan. Soon thereafter, in 1974, Mirex was discovered in fish in the Bay of In late 1979, chlorinated dioxins were Lake Ontario. Ouinte, detected in herring gull eggs from colonies in Saginaw Bay, Michigan. In 1982, toxaphene was first detected in fish from Lake Superior. Between these major chemical crises, subsequent sampling revealed that most of these same chemicals were found throughout the Great Lakes system. Also, analyses of Great Lakes media for toxic metals such as Pb and Cd, showed that these were also Thus the scientific and ubiquitous pollutants of the system. public awareness of the level of toxic chemical pollution of the Great Lakes has developed over a period of some 25 years from DDT; to Hg; to PCBs; to Mirex; to dioxins; to toxaphene. The period of greatest public concern was around 1980 and related to the discovery of 2,3,7,8-TCDD, in herring gull eggs. Another major event occurred in 1985 with a perchloroethylene spill into the St. Clair River.

Chemical analyses of radiodated sediment cores was eventually to show that the serious toxic chemical pollution of the Great Lakes began only after World War II, with the expansion in urban and industrial development. PAHs were detected in lake sediments deposited at the turn of the century. Some chlorinated organics

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revealed that the data bases are quite inadequate, with the possible exception of PCBs (Strachan and Eisenreich, 1988).

Since about 1979, the collection of suspended particulates has permitted detection of toxic metals and hydrophobic toxic organic chemicals. Historically water column concentrations and trends have been assessed more commonly by analysis of suspended solids, for example, in the connecting channels such as the Niagara River. However, at the low suspended solids concentrations common in the Great Lakes system, even the most hydrophobic organic chemicals are primarily in the dissolved phase.

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It should be clearly stated that reliable quantitative data for toxic contaminants in water are scarce. Nearly all historical results were below then existing detection limits. Concentrations in water are often an order of magnitude or more beneath detection levels in routine sample volumes of 1 to 2 litres. Only since 1980 has it been possible to determine some of these chemicals in water in the open lakes and connecting channels. Large volumes of water (200 litres) are now extracted to detect concentrations in the low Measurements of ambient concentrations of ppt and ppg ranges. toxic metals and organic chemicals in water are complex and have Because of these complex, become semi-routine only since 1983. time consuming and costly procedures for sample collection, preparation and analyses, few measurements for toxic organic chemicals have been made in all parts of the Great Lakes. The values for whole water and especially for the dissolved phase are highly variable in space and time and must still be viewed with caution as they were and still are often near limits of analytical detection.

The requirements to detect extremely low water concentrations has been driven mostly by an objective to (1) understand the relationship of chemical concentrations in water to those in fish; (2) include the several orders of magnitude higher concentrations of these chemicals in bottom sediments in cause-effect linkages; (3) quantify the burial of chemicals in lake sediments as a self-

even pre-colonial periods.

Given the above brief overview of the toxic chemical contamination of the Great Lakes; the availability of data in different abiotic media; and the problems described for the dissolved phase; the chemicals to be discussed here fall into two general categories :

- 1) Toxic chemicals for which there is a reasonably extensive data base. These are usually the chemicals which have been those of greatest significance in the development of our knowledge of the extent of contamination of the complete Great Lakes systems. They include Pb, Hg, Cd, and As, DDT and metabolites, dieldrin, BHCs, HCB, Dioxins, and PCBs
- 2) Toxic chemicals for which there is a data base but which is restricted geographically because the chemicals were associated with some particularly serious sub-area of contamination e.g. the Niagara River. Such chemicals include: CBs (e.g. Lake Ontario); toxaphene (e.g. Lake Superior); octachlorostyrene (OCS) (e.g. Lake St. Clair); Mirex (e.g. St. Lawrence River); chlorinated volatile organics (e.g. the lower Great Lakes and Connecting channels); and PAHs (e.g western Lake Erie).

Lakes Superior, Huron, Erie and Ontario during 1986 and examined for toxic organic chemicals (Stevens and Neilson, in press). The results of these studies appear in the summary tables for each of the Great Lakes and the Niagara River.

#### 2.1 LAKE SUPERIOR

Lake Superior has a greater surface area than any other lake in the world. By volume it represents half of the water stored in all the Great Lakes and is the second largest lake in the world by volume after Lake Baikal in Siberia. The main tributaries to Lake Superior are the Nipigon, St. Louis, Pigeon, Pic, White, Michipicoten and Kaministikquia Rivers. The lake discharges via the St. Marys River. It is primarily surrounded by the forested, Precambrain terrain of the Canadian Shield.

Chemical mass balance calculations have shown that the atmosphere is a major source of contaminants such as PCBs, DDT, B(a)P and Pb to Lake Superior (Young et al., 1987). There are several reasons for this. Compared with the other Great Lakes, agriculture, population and industrialization of the Lake Superior basin are much less. This results in lower overall contamination from these sources. Also, the surface of the lake is about 40% of its drainage basin; the precipitation over the lake accounts for more than 50% of the total water input; and the lake has a long rapid circulation low combined with and time residence sedimentation (Chan, 1984).

Some of the chemicals of concern in the St. Marys River are PAHs and PCBs. The zone of greatest impact is along the Canadian shore downstream of industrial and municipal discharges.

#### 2.1.1 CHEMICAL CONCENTRATIONS IN WATER

The historical concentrations of toxic metals and organic chemicals in the waters of Lake Superior are presented in Table 4. As discussed earlier, much of the historical data, especially for metals, has been questioned. Rossmann (1986) compared his 1983 data on concentrations of metals in the dissolved, particulate and total water phases to earlier data for Lake Superior. The results for Pb, Hg, Cd, and As are discussed here. He concluded that the historical data could only be used to determine trends for total

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E 4 TOXIC CHEMICAL CONCENTRATIONS IN LAKE SUPERIOR WATER (ppt)

	Chemical	Sample	Testing	#	Min	Max	Mean	SD	Median	DL	~% ∕∠Di	Ref.	
	Chemical	Jampie	Date	#		Max	(TREGIT)	30	Meu Ian		NDL.	Rei.	
	Pb	dis.	1983	22	ND	100	14	31	6	27	41	(1)(5)	
	Pb	dis.	<1986				75					(11)	
	Pb	part.	1977	7	50	4,700	770	1,700	100			(2)	•
	Pb	part.	1983	22	. 11	48	25	10	23	2	0	(1)(5)	
	Pb	part.	<1986				25	, · · ·				(11)	
	Pb	whole	1975	5			`400	200				(4)	,
	Pb	whole	1977	7	<300	3,200	1,500	1,300	1,500		·	(2)	
	Pb	whole	<1981		1000	1,500							
•	Pb	whole	1983	22	ND	130	-39	34	29	27		(1)(5)	
	Hg	dis.	1983	22	ND	56	0.91	18	0	6.9	95	(1)(5)	
	Hg	dis.	<1986				7					(11)	
	Hg	part.	1983	2Ž	ND	100	7.6	34	· 1	:		(1)	
	Hg	part.	<1986				3				·	(11)	
	Hg	whole	1970-71	226	ND	470	180	130		50		(3)	
	Hg	whole	<1981		50	100					÷		
	Hg	whole	1983	22	NĎ	120	9.8	34	2	6.9	90	(1)(5)	
	Cd	dis.	1983	22	ND	12	6.6	3	6	2	64	(1)(5)	
	Cd	dis.	<1986				20					(11)	
	Cd	part.	1977	7	2	40	10	10	4			(2)	
	Cd	part.	1983	22	ND	38	21	10	21	3.9	23	(1)(5)	
	Cd	part.	<1986				20		1			(11)	
	Cd	whole	1977	7	<20	250	120	100	130			(2)	
	Cd	whole	<1981				<200					(12)	
	Cd	whole	1983	22	70	44	27	10	27	2		(1)	`
	As	dis.	1983	22	400	900	550	130	520	29	0	(1)(5)	
	As	part.	1983	22	ND	50	11	25	10	50	91	(1)(5)	
	As	whole	1969	47	ND	1,000	230			100		(13)	
	As	whole	1975	5			800	100				(4)	
	As	whole	1983	22	430	900	560	130	520	29		(1)	
	As	whole	<1986				600					(11)	
	tDDT	dis.	<1986				0.1				· .	(11)	
	tDDT	part.	<1986				0.1		. 1			(11)	
	p,p'-DDT	whole	1983	11	0.01	0.513	0.227	0.189	0.39			(6)	
	o,p'-DDT	whole	1983	3	0.016	0.195	0.113	0.09	0.05			(6)	
	p,p'-DDT	whole	1986	19		ND	0.110	0.00		0.007	100		
	o,p'-DDT	whole	1986	19		ND	· ,			0.007			
										¥.901	, 99	(1)	
	p,p'-DDE	whole	1983	15	0.007	0.041	0.02	0.009				(6)	
•	p,p'-DDE	whole	1983	17	0.005	0.024	0.012	0.006				(8)	
	p,p'-DDE	whole	1986	19		ND				0.007	100	(7)	•
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TABLE 4 cont.

- 1. Rossmann 1986. Particulate conc.: ppt=ng/L. Filter: 0.5 um pore size. Particulate conc. + dissolved conc. = whole water concentration.
- 2. Eisenreich 1982. Particulate conc.: ppt=ng/L. Filter: 0.4 um pore size.

3. Chau and Saitoh 1973

- 4. Poldoski et al. 1978
- 5. Rossmann and Barres 1988. The number presented for "% below detection" actually represents the percent of analyses below the limit or criterion of detection. Particulate concentrations are ng/l.
- 6. Chan 1984
- 7. Stevens and Nielson in press
- 8. Baker et. al. 1985. All samples were from the same site in western Lake Superior.
- 9. Sullivan and Armstrong 1985
- 10. Eisenreich 1987
- 11. Strachan and Eisenreich 1988. Mean value based on assessment of historical data up to 1985-86. These values were used in mass balance models. Part. conc.: ppt=ng/L. Particulate conc. + dissolved conc. = whole water conc.
- 12. Sonzogni and Simmons 1981. Typical concentration ranges. These values are designed only to illustrate the types of values and the relative range of concentrations reported.

13. Traversy et al. 1975

14. Baker and Eisenreich 1989

15. Capel and Eisenneich 1985

concentrations in suspended solids from the nepheloid layer of western Lake Superior in 1983 as 0.005 to 0.024 ppt. They also found that the concentrations of particulate associated PCBs in the benthic nepheloid layer were not that different from those in the epilimnion. In 1980, the range of PCB concentrations in suspended solids was 30 to 2,770 ppb (ng/g) (Capel and Eisenreich, 1985). They pointed out that the fraction associated with particulates versus the dissolved phase changed, with time and with depth. By 1986, the particulate associated PCB concentration had dropped dramatically to 33 +/- 16 ppb (ng/g) (Baker and Eisenreich, 1989). Concentrations of some PCBs and some PAHs in Lake Superior were greater in suspended solids collected by sediment traps than when collected by centrifugation (Baker and Eisenreich, 1988). This was considered to be related to biological processing of the contaminants. They found that the flux rates of PCBs to the bottom waters of Lake Superior were up to two orders of magnitude higher than the net accumulation rates of PCBs in the bottom sediments, implying high benthic organism recycling rates. Particulate total PCB concentrations could thus be higher than those found in lake bottom sediments. When surficial Lake Superior was stratified, the fraction of total PCB's associated with particulate phases at all depths was around 13 - 14% (Baker et al., 1985). The highest concentrations of particulate PCBs were in the eastern basin of the lake in 1980 (Capel and Eisenreich, 1985). In 1986, individual particulate PAH concentrations ranged from less than one to a few hundred ppb (Baker and Eisenreich, 1989).

#### 2.1.2 CHEMICAL CONCENTRATIONS IN BOTTOM SEDIMENTS

The most extensive sampling of bottom sediments of Lake Superior was in 1973 as part of multi-year program to map chemical distributions in the surficial bottom sediments of all five Great Lakes. Although individual element distribution maps, particularly for Hg, were published in separate papers, the report by Thomas and Mudroch (1979) released nearly all of the toxic metal and organic

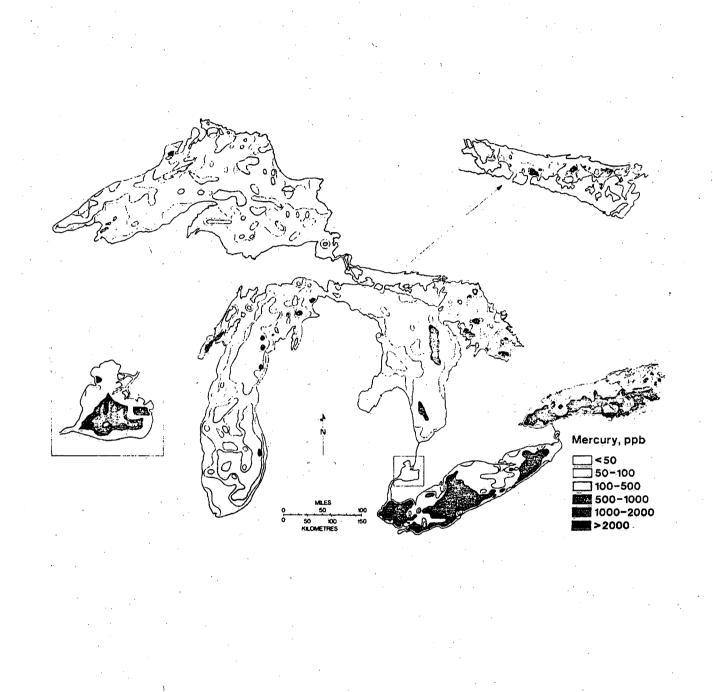


FIGURE 2 Hq IN GREAT LAKES SEDIMENT (Thomas and Mudroch, 1979)

		SEDIM	ENTS (	ppb)	·	· · · ·	<u></u>					<b>.</b>
			Testing			-	•	•			*	
	Chemica]	Sample	Date	#	Min	Max	Mean	SD	Median	DL	<dl< th=""><th>Ref.</th></dl<>	Ref.
	РЬ РЬ РЬ РЬ РЬ	3 cm 1 cm	1973 1973 <1981 <1984 <1986	404 5	<50,000	143,900 150,000 138,210	44,000 120,000 50,000 100,000	27,000 25,607	133,400		•	(11) (1) (8) (10) (9)
	Hg Hg Hg Hg Hg	3 cm 1 cm	1973 1973 <1981 <1984 <1986	404 5	94 30 94	356 300 160	83 190 100 100	56 91	160	•		(11) (1) (8) (10) (9)
	Cd Cd Cd Cd Cd Cd	3 cm 1 cm	1973 1973 <1981 <1984 <1986	<b>404</b> 5	1,400 500 1,400	2,500 2,500 2,500	1,200 2,200 1,000 600	800 445	2,500			(11) (1) (8) (10) (9)
	As As	3 cm 3 cm	1973 1973	404 15	500	8,000	1,700 2,033	2,500 2,429	800	٩		(11) (2)
	tDDT p,p'-DDE DDE	3 cm 3 cm	<1986 1973 1983	405 6	ND 2.2	23 7.6	8 0.71 4.6	1.65 1.9	·	0.25	66	(9) (5) (3)
	dieldrin dieldrin	3 cm	1973 <1986	405	ND	1.9	<0.25 20			0.25	95	(5) (9)
	a-BHC	•	<1986				0.8					(9)
	lindane		<1986		·••.	,	<i>г</i> <b>б.1</b>					(9)
	B(a)P B(a)P B(a)P	•	<1986 1986	1 3	32	<b>4</b> 0	28 30 45	14				(7) (9) (12)
	HCB HCB HCB	3 cm 3 cm	1980 1983 <1986	13 6	0.02 0.7	0.7 1.8		0.4		1	•	(4) (3) (9)
-	HCBD	3 cm	1983	6	0.1	0.1	0.1					(3)
	PCBs PCBs PCBs PCBs PCBs	3 cm 0.5 cm 3 cm	<1981 1983	405 18 6	ND 5 14	57 390 53	3.3 130 200 27	5.7 110 12		2.5	78	(5) (6) (8) (3)
	PCBs PCBs		<1986 1986	3	5.32	11.73	30 8.62	2.62	j.	•		(9) (12)

CONCENTRATIONS IN LAKE SUPERIOR BOTTOM

TABLE 5

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TOXIC CHEMICAL

<u>al.</u> (1980) concentrations are for the top 0.5 cm only. Eisenreich and Baker (1989) reported that the mean total PCB concentration in 1986 (8.6 ppb) was significantly lower than that of 1978 (74 ppb). This reflects lower PCB burdens in the water column. The mean HCB concentration of 0.2 ppb in surficial sediments in 1980 was at least an order of magnitude lower than in lakes Huron, Erie and Ontario (Oliver and Nicol, 1982). In 80 samples collected in 1973, Frank <u>et al.</u> (1980) did not detect Mirex at a detection limit of 0.3 ppb. PAH concentrations in sediments are about ten times lower than the other Great Lakes reflecting both its remote location and the primarily atmospheric source (Baker and Eisenreich, 1989).

Historical trends in toxic metal loads to Lake Superior have been investigated by collection, sectioning, age dating, and analysis of lake bottom sediment cores. Kemp et al. (1978), calculated sediment enrichment factors for several metals in Lake Superior. The mean values for Pb, Hg, Cd, and As were 4.6, 1.8, 2.9 (n = 6) and 0.7 (n = 1) respectively. The sediment enrichment value is the ratio of the surficial sediment concentration to the historical, pre-settlement concentration below the Ambrosia Cores analyzed by Rossmann (1986) show that there has horizon. been an increase in Pb concentrations in the most recent sections of sediment cores (Figure 4). Because most Pb introduced to Lake Superior comes from the atmosphere, it is likely that concentrations in the surface sediments will now decline as they have, for example in Lake Ontario (Rossmann, 1986). Anthropogenic enrichment of Pb in Lake Superior has been less than for the other Great Lakes (Hodson et al., 1984). Concentrations of Hg reached peak values at a depth of 3 cm and decreased to the surface (Figure 4).

The distribution of PCBs in sediment cores for 9 sites in Lake Superior was described by Eisenreich (1987). Each of the top 1 cm of sediment represented approximately 10 years of time. At all sites, the concentrations of PCBs began to increase at a depth corresponding to the late 1940's. Peak concentrations varied at

each of the sites but were either at the very surface or at a depth of 1 cm representing a time in the early 1970's. In general, Lake Superior has the lowest sedimentation rate of all of the Great Lakes (Thomas and Frank, 1983). In 7 of the 9 cores, the top 0.25 cm had concentrations of total PCB that were 20 to 100% less than the next 0.25 cm section. This could be evidence of a recent decrease in the sedimentary PCB flux. The mean value for the whole lake in the top 0.5 cm was 53 ppb total PCBs. Charles and Hites (1987) determined the average PCB concentration as a function of year in three sediment cores from Lake Superior (Figure 4). The distribution shows a slow increase from around 1943 to 1955; a rapid rise from 1955 to a peak value of 110 ppb in 1972-73; followed by a decline to 75 ppb by 1975. This decline should continue as North American bans and restrictions on PCBs take greater effect. Most of the PCB input to Lake Superior is from the atmosphere (Strachan and Eisenreich, 1987).

The historical distribution of some PAHs in Lake Superior sediment cores show that inputs of these chemicals to the lake began after the turn of the century. The highest B(a)P concentration in a Lake Superior core was around 30 ppb at a depth of 0.25 (Gschwend and Hites, 1987). Although CM B(a)P concentrations in Lake Superior bottom sediments more than tripled between 1900 and 1980, concentrations are still an order of magnitude lower than in the lower Great Lakes because the region around Lake Superior is far less industrialized (Eadie, 1984). In Lake George, part of the St. Mary's River connecting channel between Lake Superior and Lake Huron, B(a)P concentrations in sediment cores show recent declines (Figure 4).

#### 2.2 LAKE MICHIGAN

Lake Michigan is the only Great Lake to lie completely within the United States. It is the sixth largest lake in the world both by area and volume. Downstream, it is connected to Lake Huron by the Straits of Mackinac. The lake is essentially two basins, a southern basin with depths to 170 m and a northern basin with depths to 280 m.

Lake Michigan and Lake Ontario were the two most contaminated Great Lakes based on combined historical contamination by toxic metals, toxic chlorinated pesticides, and industrial toxic organic chemicals, especially Pb, Cd, DDT and PCBs. The contamination of Lake Michigan by organochlorine chemicals began, as for the other Great Lakes in the 1920's and 30's but increased rapidly after World War II. Contamination of the southern end of the lake has been more severe than the northern end.

One of the main tributaries of the lake is Fox River which empties into Green Bay. The bay is about 8% of the surface area of the lake but it has about one third of the lakes's watershed (Harris <u>et al.</u>, 1987). There has been concern about water quality in Green Bay since the 1920s.

#### 2.2.1 CHEMICAL CONCENTRATIONS IN WATER

Published data on chemical concentrations in Lake Michigan waters are given in Table 6. Historical data on total Pb concentrations in Lake Michigan waters as determined by many investigators was reviewed by Rossmann (1984). The values for both total Pb and dissolved Pb as determined by Rossmann in 1981 are much less than many of the historical levels measured in the 1970s and 1960s because of sample contamination problems. The mean values obtained by Rossmann of 260 ppt total Pb and 150 ppt of dissolved Pb (n = 11) are considered the most realistic. Earlier measurements of total Pb had ranged up to 170 ppb with a mean of 18 ppb (n = 30) in 1976 (Wisconsin Electric Power Company and TABLE 6 cont.

		Testing							· ·	*	
Chemical	Sample	Date	#	Min	Max	Mean	SD	Median	DL	<dl ref.<="" th=""><th></th></dl>	
PCBs	dis.	<1986				1.4		×	14.1	(8)	
PCBs	part.	<1986				0.6			•	(8)	
PCBs	whole	<1981				<100	•			(3)	
PCBs	whole	1980	7			6.36	1.3			(7)	
PCBs	whole	1980	19	0.4	7.9	1.8	1.8	1.8		(6)	
•			÷ .							(-)	
	: detecte				•						
			ater;	dis. = a	queous p	phase; par	rt.≓ş	uspended	parti	culate pha	se.
# : numb	per of sa	mples		- * *				-			
SD : sta	andard de	viation								*	
DL : det	ection 1	imit				•					
名 <dl :<="" td=""><td>percent</td><td>below th</td><td>e dete</td><td>ection li</td><td>nit</td><td></td><td></td><td></td><td></td><td></td><td></td></dl>	percent	below th	e dete	ection li	nit						
ومانيةا فيدخية بتلوجيه وتصحب	سابياتك ب منترجة تقاات					. <u> </u>				·	
1. Rossn	nann 1984	. Partic	ulate	conc.: p	pt=ng/L.	Filter:	0.5 um	porë st	ze.		

Particulate conc. + dissolved conc. = whole water concentration.

2. Muhlbaier and Tisue 1981

3. Sonzogni and Simmons 1981. Typical concentration range. These values are designed only to illustrate the types of values and the relative range of concentrations reported.

4. Sullivan and Armstrong 1985

5. Rossmann and Barres 1988. The number presented for "% below detection" actually. represents the percent of analyses below the limit or criterion of detection. Particulate concentrations are ng/L.

6. Swackhammer and Armstrong 1987

7. Eadie et al. 1983

8. Strachan and Eisenreich 1988. Mean value based on assessment of historical data up to 1985-86. These values were used in mass balance models.

Part. conc.: ppt=ng/L. Particulate conc. + dissolved conc. = whole water conc.

In 1980, Swackhammer and Armstrong (1987) reported an open lake average of 1.2 ppt total PCB, lower than the nearshore average of 3.2 ppt. They found little vertical variability in PCB concentration with lake depth.

Data on toxic chemical concentrations in Lake Michigan particulates is given in Table 6. Rossmann's results (1984) indicated that in the water column, the percentage of Cd and As present in the dissolved and total fractions were such that the particulate fraction did not make a significant contribution to the total concentration.

#### 2.2.2 CHEMICAL CONCENTRATIONS IN BOTTOM SEDIMENTS

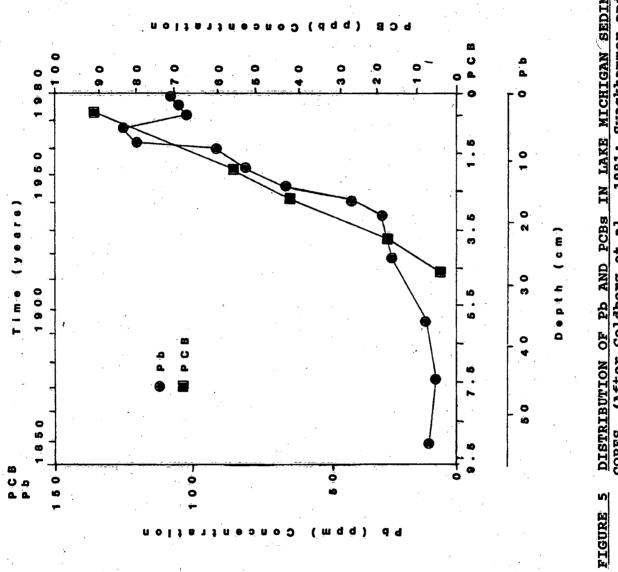
The distribution of toxic chemical concentrations is closely related to depositional basins in that concentrations are markedly higher in these basins. Not all of the total metal content is anthropogenic in origin, whereas all of the toxic organic chemicals are. Data on bottom sediment toxic chemical concentrations is given in Table 7. The most extensive surficial sediment survey of Lake Michigan was done in 1975. The distributions of Pb, Hg and As in the surficial sediments were similar. Based on 1973 samples, the concentration range of Cd in surficial sediments was reported as 0.09-1.93 ppm (Cline and Chambers, 1977). In northeastern Lake Michigan, the mean value was 0.47 ppm and in Green Bay in northwestern Lake Michigan it was 1.3 ppm (n = 5) (Lum, 1987). Only very small areas of the lake exceeded 300 ppb Hg (Cahill and Shrimp, 1984). The highest values for As were found in Green Bay.

In 1963, early sampling had indicated that some sediments in Lake Michigan had up to 20 ppb of DDE (Hickey <u>et al.</u>, 1966). In 1975, mean total DDT in surficial lake bottom sediments was 11.9 ppb (Table 7). The mean for the depositional basins was 24.4 ppb (n = 92) (Frank <u>et al.</u>, 1981a). The corresponding mean concentrations for p,p'-DDT, o,p'-DDT, p,p'-TDE and p,p'-DDE were 2.9 ppb and 5.4 ppb; 0.37 ppb and 0.73 ppb; 3.25 ppb and 7.65 ppb; and 5.43 ppb and 10.58 ppb respectively. The distribution of total TABLE 7 cont.

ND : not detected Sample : depth of surficial sediment sample # : number of samples SD : standard deviation DL : detection limit % <DL : percent below the detection limit

- 1. Sonzogni and Simmons 1981. Typical concentration range. These values are designed only to illustrate the types of values and the relative range of concentrations reported.
- 2. Strachan and Eisenreich 1988. Mean value based on assessment of historical data up to 1985-86. These values were used in mass balance models.
- 3. Cahill 1981. Depositional and non-depositional zones.
- 4. Czuczwa and Hites 1986
- 5. Eadie 1984

- 6. Helfrich and Armstrong 1986. Southern Lake Michigan.
- 7. Frank et al. 1981a. Depositional and non-depositional zones.
- 8. Mudroch et al. 1988. These numbers are a summary of concentration ranges taken from reports published between 1974 and 1984. Concentrations are from surface samples of deposititional zones.



DISTRIBUTION OF PD AND PCBS IN LAKE MICHIGAN SEDIMENT CORES. (After Goldberg et al., 1981; Swackhammer and Armstrong, 1986)

#### 2.3 LAKE HURON

Lake Huron is 59,600 km<sup>2</sup> in area. By volume, it is the seventh largest lake in the world and the third largest Great Lake at 3,540 km<sup>3</sup>. Its drainage basin is 134,100 km<sup>2</sup>. The maximum depth is 229 m and water retention time is 22 years. The major inflows are the Straits of Mackinac and the St. Marys River, followed by the Mississagi, Saginaw, French, and Spanish Rivers. It discharges to the St. Clair River. Manitoulin Island and the Bruce Peninsula divide the body of the lake from the North Channel and Georgian Bay, respectively. The lake is used for both commercial and recreational fishing. The catchment area in 1978 was mainly natural landscape. Toxic chemical inputs to Lake Huron come from municipal point sources, combined sewer overflows, rural and urban nonpoint sources, leachates from municipal and hazardous waste landfill disposal sites and from the atmosphere. Problems related to industrial sources are most apparent in industrialized harbors and embayments such as Saginaw Bay.

Lake Huron has 2 large bays. Saginaw Bay extends 82 km from the main body of the lake. The city of Saginaw, at the head of the bay and on the Saginaw River, was historically a lumbering centre. It now supports agriculture and diversified manufacturing. The bay is used for commercial fishing and summer recreation. Georgian Bay is 190 km long and 80 km wide. The surrounding area is mainly forested with some agriculture in the south. There are several important commercial shipping ports located on Georgian bay.

## 2.3.1 CHEMICAL CONCENTRATIONS IN WATER

Toxic chemical concentration data for Lake Huron water is summarised in Table 8. Rossmann (1983) reviewed toxic metal concentrations in Lake Huron. Rossmann (1983) compared his 1980 Pb data to those from previous studies and concluded that the trend in dissolved Pb concentration appeared to be downward. Available data for Hg, Cd and As prior to 1980 could not be used to establish

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	Chemica]	Sample	Testing Date	#	Min	Max	Mean	SD.	Median	DL.	<b>%</b> <dl< th=""><th>Ref.</th><th></th></dl<>	Ref.	
	Pb	dis.	1980	23	ND	81	1,9 -	26	8.9	23		(2),(5)	
	Pb Pb Pb	dis. part. part.	<1986 1980 <1986	23	ND	140	150 50 50	34	41	12	4	(1) (2),(5) (1)	
	Pb Pb	whole whole	<1981 1980	23	ND	110	<1000 38	35	22	34		(10) (2),(5)	
	Hg Hg	dis. dis.	1980 <1986	23	ND	360	50 7	90	4.2	200	87	(2),(5) (1)	
	Hg Hg		<1986 1970-71	387	50	380	3 170	110	· · ·	50		(1 <sup>°</sup> ) (6)	
	Hg Hg	whole whole	<1981 1980	23	<40 ND	150 350	6Ò	92	11	<b>` 8</b> 9	61	(10) (2),(5)	
	Cd Cd	dis. dis.	1980 <1986	23	ND	46	3.8 20	10	0	17	91	(2),(5) (1)	
	Cd Cd Cd	part. part. whole	1980 <1986 <1981	23	ND	150	21 20 <20	31	12	0.83	13	(2),(5) (1) (10)	
	Cd	whole	1980	23	ND	61	16	13	15	5.5	13	(2),(5)	
•	As As As As As	dis. part. whole whole whole	1980 1980 1969 1980 <1986	23 23 155 23	ND ND ND 72	1750 17 700 53	240 8 410 250 700	190 4.6 120	250 8.6 210	20 1.4 100 14	61 0	(2),(5) (2),(5) (3) (2),(5) (1)	
	tDDT tDDT tDDT	dis. part. whole	<1986 <1986 <1981				0.1 0.1 <4					(1) (1) (10)	
;	p,p'-DDT p,p'-DDT p,p'-DDT o,p'-DDT p,p'-DDT	whole whole whole whole whole	1980 1981 1984 1984 1986	15 5 16 16 17	0.01 0.007	0.062 0.027 ND ND ND	0.028 0.014	0.013	0.029 0.01	0.007	.100 100	(8)	-
	o,p'-DDT		1986	17	0.04	ND		0.004	ô 001	0.007	100	(8)	
:	p,p'-DDE p,p'-DDE p,p'-DDE p,p'-DDE	whole whole whole whole	1980 1981 1984 1986	15 5 16 17	0.01 0.006 <0.002 0.018	0.09 0.019 0.016 0.046	0.031 0.013 0.024	0.024 0.005	0.021 0.012	0.007	61	(7) (7) (8) (8)	
	dieldrin dieldrin dieldrin	dis. part. whole	<1986 <1986 <1981	·	. • •		0.2 0.1 <1		)		•	(1) (1) (10)	
	dieldrin dieldrin	whole whole	1984 1986	16 17	0.197 0.202	0.366 0.688	0.368			0.007	0	(8) (8)	

TOXIC CHEMICAL CONCENTRATIONS IN LAKE HURON WATER (ppt) TABLE 8

TABLE 8 cont.

	Chemical	Sample	Testing Date 1	ţ.	Min	Max	Mean	SD	Median	DL	% <dl< th=""><th>Ref.</th><th></th></dl<>	Ref.	
	aBHC aBHC aBHC aBHC	dis. part. whole whole	<1986 <1986 1984 1986	16 17	4.32 2.504	12.19 10.647	9 1 6.16			0.007	O	(1) (1) (8) (8)	
	lindane lindane lindane lindane	dis. part. whole whole	<1986 <1986	16 17	0.475	0.835	0.6 0.1 0.805			0.007		(1) (1) (8) (8)	
	mirex	whole	1986	17		ND			•	0.007	100		
	toxaphèné toxaphène toxaphène	part.	<1986 <1986 1980-81	· .	· ·		0.4 0.2 1.6					(1) (1) (9)	
	B(a)P B(a)P	dis. part.	<1986 <1986	,			0.07 0.03		• • •		`	(1) (1)	
•	HCB HCB HCB HCB HCB HCB	dis. part. whole whole whole whole whole	<1986 <1986 1980 1980 1981 1984 1986	15 5 5 16 17	0.003 0.02 0.002 0.003 0.018	0.019 0.1 0.007 0.032 0.073	0.01 0.009 0.04 0.005 0.033	0.005 0.002	0.007 0.004	0.01	6	<ol> <li>(1)</li> <li>(1)</li> <li>(7)</li> <li>(4)</li> <li>(7)</li> <li>(8)</li> <li>(8)</li> </ol>	`
	PCBs PCBs PCBs PCBs PCBs PCBs PCBs	dis. part. whole whole whole whole whole	<1986 <1986 1980 1981 <1981 1984 1986	15 5 16 17	0.282 0.135 1 0.076 0.186	3.232 0.78 10 0.394 2.342	0.7 0.3 0.929 0.4 <100 0.631	0.837 0.234	0.572 0.349	÷	O	(1) (1) (7) (7) (10) (8) (8) (8)	
~													

ND : not detected

Samplë : whole = whole water; dis. = aqueous phase; part. = suspended particulate phase. # : number of samples

SD : standard deviation

DL : detection limit

% <DL : percent below the detection limit

#### TABLE 8 cont.

- 1. Strachan and Eisenreich 1988. Mean value based on assessment of historical data up to 1985-86. These values were used in mass balance models. Part. conc.: ppt=ng/L. Particulate conc. + dissolved conc. = whole water conc.
- 2. Rossmann 1982. Including Georgian Bay and the North Channel. Particulate conc.: ppt=ng/L. Filter: 0.5 um pore size. Particulate conc. + dissolved conc. = whole water concentration.
- 3. Traversy et al. 1975. Excluding Georgian Bay and the North Channel.
- 4. Oliver and Nicol 1982
- 5. Rossmann and Barres 1988. The number presented for "% below detection" actually represents the percent of analyses below the limit or criterion of detection. Particulate concentrations are ng/L.
- 6. Chau and Saitch 1973. Excluding Georgian Bay and the North Channel.
- 7. Filkins and Smith 1982. Including Georgian Bay and the North Channel.
- 8. Stevens and Nielson in press. The 1986 results exclude Georgian Bay and the North Channel. The 1984 results are based on centrifuged samples and include Georgian Bay and the North Channel.
- 9. Swain 1978 as quoted in Kreis and Rice 1985
- 10. Sonzogni and Simmons 1981. Typical concentration range. These values are designed only to illustrate the types of values and the relative range of concentrations reported.

In 1980, dissolved Cd concentrations in Lake Huron were trends. significantly lower than those of lakes Erie and Michigan and there was no significant difference between the Lake Huron levels and those of lakes Superior and Ontario (Rossmann and Barres, 1988). Total Cd levels were significantly less than in lakes Erie and Ontario. In Saginaw Bay, very limited data from 1985 suggest that water column values for Pb and Cd were at or below levels measured in 1976-1978 (IJC, 1987a). The 1980 dissolved As levels in Lake Huron were significantly lower than those of lakes Michigan, Ontario and Superior but not significantly different from Lake Erie. levels (Rossmann and Barres, 1988). For total As, Lake Huron median concentration was significantly lower than that of Lake Michigan but not significantly different from that of Lake Erie.

Concentrations of toxic organic chemicals in Lake Huron water are summarised in Table 8. In 1974 and 1975, concentrations of DDT in Saginaw Bay had exceeded the GLWQA objective of 3.0 ppt. However, all subsequent reported concentrations were substantially below the objective level (Kreis and Rice, 1985). In a review of historical data, Kreis found that and Rice (1985) all concentrations for the dieldrin-aldrin sum were below the GLWQA objective concentration of 1.0 ppt. A single concentration of 0.5 ppt had been reported for Lake Huron in 1975, considerably below the GLWQA objective of 10.0 ppt. The IJC (1981) reported that toxaphene levels in Lake Superior and Lake Huron water ranged from 0.1 to 1.0 ppt. In Lake Huron the highest PCB concentration of 191 ppt was observed in 1979 at Harbor Beach, Michigan (Anderson et al., 1982). The highest PCB concentrations measured in 1980 were in the North Channel (1.56 ppt) and Georgian Bay (1.17 ppt) (Filkins and Smith, 1982).

A survey in 1980 was made of toxic metal concentrations in suspended solids in Lake Huron (Rossmann, 1982) (Table 8). Particulate Pb levels were somewhat lower in the southern part of the lake and in Georgian Bay than in the rest of the lake. Highest particulate Cd concentrations were found in Georgian Bay and the

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North Channel. The particulate Cd level in Lake Huron was significantly less than in lake Ontario but not significantly different from lakes Superior and Michigan (Rossmann and Barres, 1988). Rossmann (1982) concluded that 100% of the total Cd and 62% of the total Hg were associated with particulate matter. In 1980, particulate As concentrations were highest in southern Lake Huron and in Georgian Bay. Only 3% of the As was in the particulate form.

Most data on toxic organic chemicals in Lake Huron is based on whole water analyses. Some data on particulate concentrations for some toxic organic chemicals is given in Table 8. In 1974, among nine streams sampled around Lake Huron, only one showed unusually high concentrations of total DDT on suspended solids (Frank <u>et al.</u>, 1981b). That was the Beaver River on the south shore of Georgian Bay with a level of 1.3 ppm . Total DDT in the remaining streams ranged from less than 0.5 to 44 ppb. In 1974 and 1975, the mean levels for total DDT and dieldrin and PCBs were 7.2 and 8.7 ppb; 0.4 ppb and 0.3 ppb, and 36 and 63 ppb. Mirex was not detected.

#### 2.3.2 CHEMICAL CONCENTRATIONS IN BOTTOM SEDIMENTS

Data on toxic chemical concentrations in bottom sediments is presented in Table 9.

In the studies done by both Thomas and Robbins, most Pb concentrations in surficial sediments were less than 100 ppm. Mudroch et al.'s (1988) review described surface sediment in depositional basins to have up to 151 ppm Pb with surface sediments in embayments to be somewhat higher at up to 230 ppm. Fitchko and Hutchinson (1975) found elevated Pb levels near Parry Sound and in the sediments of the Cheboygan River. Increased concentrations of the Bruce Peninsula may near be due to sphalaerite Hq Mudroch et al. mineralization (Fitchko and Hutchinson, 1975). (1988) found surface sediment concentrations of Hg in depositional basins to be up to 0.805 ppm and in embayments to be up to 9.5 ppm.

		SEDIM	IENTS	(ppb)			U IN LA	NE HURL	UN BUILC				
	Chemical	Sample	Testir Date	ng : #	Min	Ma×	Mean	SD	Median	DL	% DL>	Ref.	
	Pb Pb Pb Pb Pb	3 cm 1-2 cm	1969 ?1969 <1981 <1984 <1986	197 6	50,000	151,400 150,000 151,400	49,000 123,100 50,000 70,000	34,000 23,000	132,000			(6) (5) (1) (3) (2)	
	Hg Hg Hg Hg Hg	3 cm 1-2 cm	1969 ?1969 <1981 <1984 <1986	197 6	90 100 10	297 500 805	217 157 200 300	160 72	122	• •		(6) (5) (1) (3) (2)	•
	Cd Cd Cd Cd Cd	3 cm 1-2 cm	1969 ?1969 <1981 <1984 <1986	197 6	1,400 1,000 300	2,600 2,000 4,300	1,400 2,000 1,500 1,000	3,900 450	2,000	•		(6) (5) (1) (3) (2)	
	As As As As As	3 cm 3 cm 1-2 cm	1969 19697 ?1969 <1984 <1986	197 10 3	19,000 14,700	24,000 54,000	1,090 2,300 21,000 5,000	2,160 1,100 2,000	19,000			(6) (4) (5) (3) (2)	
	tDDT tDDT tDDT p,p'-DDE DDE DDE	3 cm 3 cm 3 cm	1969 <1981 <1986 1969 1980 1980	174 174 9 5	ND ND 2 4	220 21 15 28.9	10.2 <30 40 3 10 20.6	9	23	0.2		(11) (1) (2) (11) (12) (10)	
í	dieldrin dieldrin dieldrin	3 cm	1969 <1981 <1986	174	ND	1.3	<0.2 <10 20		• •	0.2	94.3	(11) (1) (2)	
	Mirex Mirex	3 cm 3 cm	1969 1980	9		ND ND						(11) (12)	
	a-BHC a-BHC	3 cm	1980 <1986	9	. <sup>.</sup>	Jow	1	•	۰.	0.2	0	(12) (2)	
a.	lindane lindane	3 cm	1980 <1986	9		Jow	0.5			·0.1	0	(12) (2)	
	B(a)P B(a)P		<1986	1			294 200	• •				(8) (2)	

## TOXIC CHEMICAL CONCENTRATIONS IN LAKE HURON BOTTOM TABLE 9

TABLE 9 cont.

		Testing			, 					*
Chemical	Sample	Date	#	Min	Max	Mean	SD	Median	DL	<dl ref.<="" td=""></dl>
HCB	3 cm	1980	42	0-4	5	2			1	(9)
HCB	3 cm	1980	9	0.5	3.3	1.5				(12)
HCB	3 cm	1980	5	1.7	3.1	2.4	0.46	2.3	·.	(10)
HCB		<1986				2		• •		(2)
HCBD	3 cm	1980	9	0.04	0.1	0.08				(12)
HCBD	3 cm	1980	5	0.05	0.6	0.3	0.2	0.3		(10)
PCBs	3 cm	1969	174	3	90	13	10			0 (11)
PCBs	3 cm .	1980	9	12	51	34				(12)
PCBs -	3 cm	1980	5	64	390	152	121			(10)
PCBs	· ·	<1981		<10	>100	100				(1)
PCBs		<1986				100				(2)
OCDD		1975-81	4			. 880				(7)
N	<b>\</b>				•			-	,	·

ND : not detected

Sample : depth of surficial sediment sample

# : number of samples

SD : standard deviation

DL : detection limit

% <DL : percent below the detection limit

1. Sonzogni and Simmons 1981. Typical concentration range. These values are designed only to illustrate the types of values and the relative range of concentrations reported.

2. Strachan and Eisenreich 1988. Mean value based on assessment of historical data up to 1985-86. These values were used in mass balance models.

3. Mudroch et al. 1988. These numbers are a summary of concentration ranges taken from reports published between 1974 and 1984. Concentrations are from surface samples of deposititional zones.

4. Traversy et al. 1975

5. Kemp et al. 1978

6. IJC 1977b. Excluding Georgian Bay and the North Channel.

7. Czuczwa and Hites 1986

8. Eadie 1984

9. Oliver and Nicol 1982. Depositional and non-depositional zones.

10. Bourbonniere et al. 1986. Excluding Georgian Bay and the North Channel.

11. Frank et al. 1979b. Excluding Georgian Bay and the North Channel. Depositional and nondepositional zones.

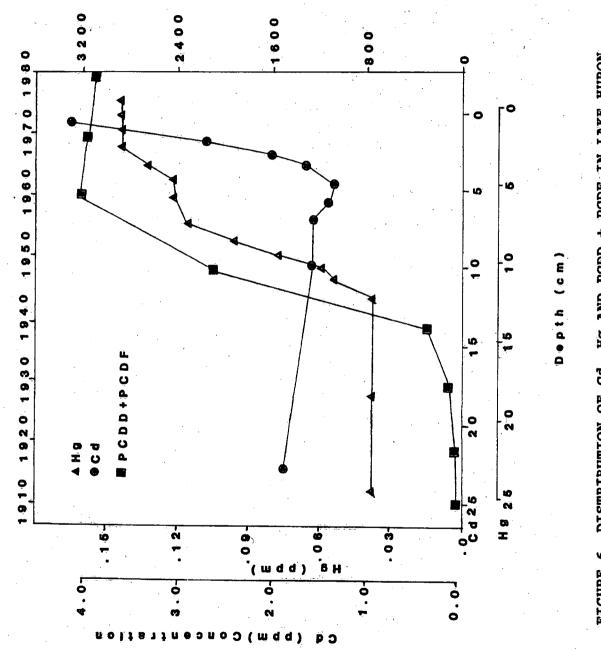
12. Oliver and Bourbonniere 1985. Southern Lake Huron. "Low" concentrations: all concentrations were above but close to the detection limit. Most areas of Lake Huron have Cd concentrations of less than 4 ppm, although a few discreet areas in Georgian Bay have concentrations greater than 6 ppm (Thomas, 1981). There was an indication of anthropogenic input to the southern part of the lake but no trends were observed in Georgian Bay. Mudroch <u>et al.</u> (1988) found a range of <0.3-4.6 ppm Cd in embayments.

The highest organic chemical residues in surficial sediments from Lake Huron were in Saginaw Bay. Some other nearshore localities also exhibit higher concentrations. In the open lake, the highest concentrations of toxic organic chemicals are in the depositional basins, due to the previously described relationship between hydrophobic organic chemicals and fine-grained sediments. Data on toxic organic chemical concentrations in bottom sediments are given in Table 9. In 1969, Frank et al. (1979b) found levels of DDT to be higher in depositional (18.4 ppb) rather than nondepositional zones (3.8 ppb). Of the six basins in Lake Huron, the highest concentrations of DDT were in the Goderich Basin (31.3 ppb). The parent compound was the highest component of DDT followed by DDE and TDE. Although the inputs were primarily from diffuse sources, three point sources were identified as Saginaw Bay, Wasaga Beach, and the central part of eastern Georgian Bay.

In 1969, dieldrin was identified in only 5.7% of the surface sediment samples with residues at or below 1.3 ppb (Frank et al., 1979b). Samples containing dieldrin came from the Goderich and Mackinac Basins and in the non-depositional zone near Saginaw Bay. Dieldrin was identified in 30% of the sediments from Georgian Bay in 1973 and 15% of those from the North Channel (Frank et al., 1979b). Kreis and Rice (1985) reported that mean dieldrin concentrations were high in Georgian Bay, particularly in Lions Trough and the nearshore zone at Owen Sound. Some samples from Saginaw Bay also showed high concentrations whereas the main lake and the North Channel had lower concentrations. Mirex was not detected by Frank et al. (1979b) in 1969 sediments nor by Oliver and Bourbonniere (1985) in 1980. In 1969, unlike DDT, the PCB

residues (11 ppb) in the non-depositional zones of Lake Huron were similar to the levels observed in the depositional basins (15 ppb) (Frank et al., 1979b). Saginaw Basin contained the highest mean residue (33 ppb) and Alpena Basin the lowest (9 ppb) (Figure 3). The mean concentration for Georgian Bay was 13 ppb while the mean for the North Channel was 8 ppb. In Georgian Bay, substantial inputs of PCBs appeared to come from the northeast shore (Frank et al., 1979b). In the review by Mudroch et al. (1985), surface concentrations of PCBs ranged from 10-20 ppb in the open lake. Ín the embayments, they ranged from beneath detection to a high of 490 ppb. Rice and Evans (1984) reported that no data exists for toxaphene in bottom sediments of Lake Huron. In 1981, Czuczwa and Hites (1984) found that concentrations of PCDDs and PCDFs were ubiquitous in 1 cm surface sediment samples and higher closer to urban centres than in the open lake. There was a predominance of They concluded that the municipal and/or OCDD and HpCDF. industrial combustion of chlorinated organic products present in various wastes was probably the source of the dioxins and furans to the Great Lakes. Average OCDD in the surface sediments was 880 ppt (Czuczwa and Hites, 1984).

Sedimentation rates in Lake Huron are generally lower than in Lakes Erie and Ontario (Kemp and Thomas, 1976a) but higher than in Lake Superior (Thomas, 1983). For Pb, Hg, Cd, and As, there has been a marked enrichment at the sediment-water interface relative This was related to increasing to low background values. anthropogenic inputs of these metals to the sediments in recent years or to postdepositional processes (Kemp et al., 1978). Robbins (1980), Thomas (1981), and Kemp and Thomas (1976a) all found lead to be consistently enriched in surficial sediments (Figure 6). Surface sediments were also enriched in Cd over background levels (Kemp <u>et al.</u>, 1978; Kemp and Thomas, 1976a; Robbins, 1980). Kemp and Thomas (1976a) reported that recent average Cd concentrations (2 ppm) were double that of pre-colonial Robbins (1980) found surficial enrichment of levels (1 ppm).



DISTRIBUTION OF Cd, Hq AND PCDD + PCDF IN LAKE HURON **SEDIMENT CORES. (After Robbins, 1980; Czuczwa and Hites, 1984)** FIGURE 6

PCDD + PCDF(ppt) Concent

D+PCDF TIMe (years)

P C D D + P C D F

mercury in only a few cores in 1974-75. Most concentrations were less than 0.2 ppm and all were less than 0.30 ppm (Figure 6). In the early 1970s, Kemp <u>et al.</u> (1978) found surficial levels of As to be 19-26 ppm corresponding to enrichment factors of 2.7-6.2. Robbins (1980) found As to only occasionally show surficial enrichment in the cores sampled in 1974-75.

The resolution of total DDT and PCB profiles in cores proved to be insufficient to provide a good estimate of the onset of their input to the lake but Frank <u>et al.</u> (1979b) inferred a period in the early 1950's. Cores analysed by Czuczwa and Hites (1986) indicated that there has been a considerable increase in input of total PCDD and PCDF since around 1940 (Figure 6).

# 2.4 ST. CLAIR RIVER/LAKE ST. CLAIR/DETROIT RIVER

The St. Clair River drains Lake Huron and flows south into Lake St. Clair. Its length is 64 kilometers. The river is an important international shipping channel and serves as the source of water for commercial, industrial, and domestic uses.

The St. Clair River receives discharges from several refineries and petrochemical plants and the volume of these discharges is about 0.5% of the total river flow (DOE and MOE, 1985). The industrial inputs of contaminants are much greater than the municipal ones (Marsalek, 1986). The U.S. has 32 permitted discharges to the river, including 6 municipal sewage treatment plants (IJC, 1987a). There are 12 industrial and 6 municipal dischargers on the Canadian side of the river. Non-point sources, including contaminated sediments, along with the point sources have led to the degradation of river water and sediments. Many toxic chemicals are confined primarily to a 100 meter wide area along the Ontario shore near Sarnia's chemical industrial area. Contaminants found in elevated levels in sediments include chlorinated organics such as PCBs, and volatile hydrocarbons, and heavy metals, such as mercury and lead. Spills remain a significant problem in this area. Between 1972 and 1984, 175 spills were recorded of which 161 discharged directly into the river or a tributary (IJC, 1987b). In 1986 there were 48 spills, 10 of which were on the U.S. side of the river (UGLCCS, 1989).

The St. Clair River flows into Lake St. Clair. The average depth of Lake St. Clair is about 3.4 meters. Mean inflow from the St. Clair River accounts for 98 percent of the outflow to the Detroit River. The theoretical flushing time of the lake is 7.3 days. The lake supports the spawning grounds for over 30 species of fish and is one of the most heavily used sport fishing and recreation areas of the Great lakes. Until recently, the lake also supported a commercial fishery. The Detroit River is a 51 kilometer long connection between Lake St. Clair and Lake Erie. It is used extensively for shipping, recreation and public and industrial water supply. Contamination of the water and sediments by metals and a variety of organic chemicals from municipal, agriculture and industrial waste has led to significant degradation. The majority of the sources, particularly PCBs, appear to be located along the U.S. shore (UGLCCS, 1989). The Rouge River is a major source of contaminants to the Detroit River. Many industrial outfalls, landfill spoil areas, municipal, hydro, and combined sewer facilities are found along the shores of the Detroit River.

# 2.4.1 CHEMICAL CONCENTRATIONS IN WATER

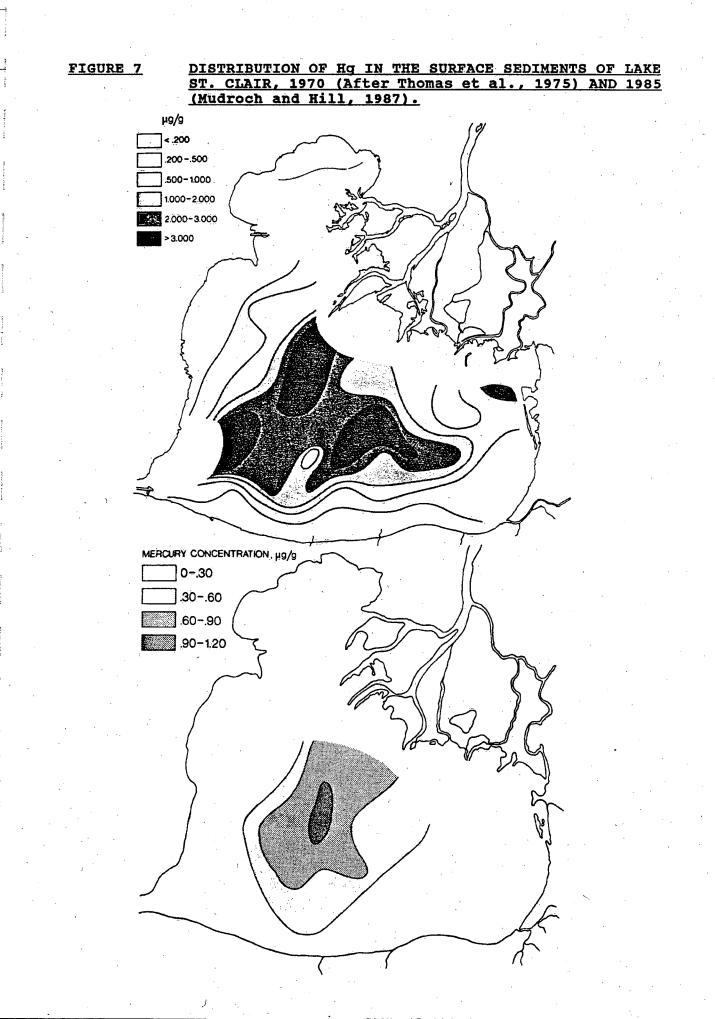
There were marginal increases of Pb and Hq along the St. Clair River (UGLCCS, 1989). Toxic metal levels were consistently below the GLWQA guidelines except for Pb near Sarnia and Corunna. Elevated levels of alkyllead and Pb were found in the water near Ethyl Corporation, an alkylead production plant at Corunna (Chau <u>et al.</u>, 1985). Typical Pb and Hg levels in the river are 10-100 ppt and 0.1-1.0 ppb (UGLCCS, 1989). In unfiltered water near industrial outfalls, levels of Pb were up to 2.7 ppb in the St. Clair River. Concentrations of Hg in the Detroit River were relatively constant from 1984-1986. Some elevated Hg levels have been reported for tributaries of the Detroit River. Concentrations of Cd did not change significantly over the course of the St. Clair River (UGLCCS, 1989). The mean concentration of Cd downstream of the Sarnia industrial area was 10 ppt with a maximum level of 90 Over the course of the Detroit River in 1987, Cd increased ppt. from 23 to 35 ppt (UGLCCS, 1989) and a concentration of 2,060 ppt was recorded in the Rouge River.

In 1985, very low levels of DDT, dieldrin, a-BHC, and lindane were found in the St. Clair River (Kauss and Hamdy, 1985; Oliver and Kaiser, 1986; Chan <u>et al.</u>, 1986). Even distributions indicated non-point sources. No active sources of DDT or metabolites were identified in the Detroit River in 1983 (Kaiser <u>et al.</u>, 1985). Detectable levels of lindane were reported in Lake St. Clair (UGLCCS,1989). Active sources of dieldrin and lindane have been reported in the Rouge River and the Trenton Channel (Kaiser <u>et al.</u>, 1985).

Several studies (Kauss and Hamdy, 1985; Oliver and Kaiser, 1986; Chan et al., 1986; Chan and Kohli, 1987) have identified point sources of HCB and HCBD near Sarnia. A plume emanating from this area is found along the Canadian shore and exits the river via the Chenal Ecarte. Similar distributions were found in water for (Chan and Kohli, OCB and OCS 1987). Mean whole water concentrations above and below the source, in 1985, were 0.03 and 0.8 ppt for HCB and 0.09 and 2.3 ppt for HCBD (Chan and Kohli, 1987). The percent of HCB in the dissolved phase was much greater (90%) at the head of the river than at Port Lambton (41%). The percent of HCBD in the dissolved phase at each end of the river was very similar (95% head, 96% Port Lambton). Maximum levels near industrial outfalls on the St. Clair River (unfiltered) were 2.4 ppm HCB and 1.3 ppm HCBD both of which are much greater than CCREM Water Quality Guidelines of 6.5 ppb and 100 ppb respectively (UGLCCS, 1989). Low concentrations were also identified upstream of this major source on the American side of the river (Oliver and Kaiser, 1986). The typical range of concentrations reported for HCB in the St. Clair River by the UGLCCS (1989) is 0.1-1.0 ppt.

Concentrations of HCB and HCBD in the mid 1980s were less in water at the head of the Detroit River than at the St. Clair River mouth indicating that some of these contaminants are retained, degraded or volatilized in Lake St. Clair but also that some are carried through to the Detroit River (UGLCCS, 1989). CBs concentrations in 1986 were higher in the western basin area of Lake Erie than in southern Lake Huron (Stevens and Neilson, in press). HCB enters the Detroit River from Michigan point sources including the Rouge River (UGLCCS, 1989). In 1983, total CB concentrations were highest in the Rouge River and at the mouths

In 1985, Chan et al. (1986) determined concentrations of HCBD, QCB, HCB, and OCS in suspended solids in the St. Clair River. There was a dramatic increase in chemical concentrations in suspended solids over the course of the river. The mean concentrations at the St. Clair River head and at Port Lambton were 2.0 and 130 ppb (ng/g) respectively for HCB. For HCBD, concentrations were 1.0 and 20 ppb. In 1985, Oliver and Kaiser (1986) analyzed water samples near industrial outfalls for HCE, HCBD, HCB, OCS, and CBs. The highest concentrations were discovered downstream from the township ditch and near Dow and Polysar. In that area, the concentrations for HCB ranged from 23 to 40 ppm and for HCBD from 9.3 to 24 ppm. These levels are, very roughly, two orders of magnitude greater than levels at the head of the river and downstream. In Lake St. Clair, concentrations of HCB and HCBD in the particulate fraction, were higher in the central corridor of the lake connecting the two rivers (Charlton and Oliver, 1986). Mean concentrations in 1985 were 20 ppb for HCB and 4 ppb for HCBD. Elevated levels of total CBs in the particulate phase were found at the head of the Detroit River, 0.9 ppt, downstream of Belle Isle, 2 ppt, and at the mouth of the Detroit River, 1.2 ppt in 1983 (Kaiser et al., 1985). In 1985, in Lake St. Clair, the mean particulate concentration of PCBs was 36 ppb (Charlton and Oliver, 1986) with higher concentrations consistently on the west side of the lake. In the mid 1970s PCB concentrations in suspended solids were higher in the Detroit River than in Lake St. Clair (Frank et al., 1977) and ranked with the Niagara River as the highest levels in the Great Lakes (Frank et al., 1981b). The short residence time of the Detroit River may result in an uncharacteristically high fraction of PCBs in the aqueous phase. In 1983, the highest levels of PCBs in the particulate phase, 2.8 ppt, were identified just downstream from Belle Isle and at the mouth of the Trenton Channel (Kaiser et al., 1985) and levels were 10 times higher at the Rouge River and Trenton channel than on the Canadian side.



Contaminated sediments in the Detroit River occur mainly along the American side of the river downstream from the city of Detroit. The sediment deposited at the mouth of the Detroit River is ultimately resuspended and transported to the depositional zones of Lake Erie.

Lead levels in sediments of the St. Clair River and Lake St. Clair are generally low. Exceptions occur adjacent to (1) the Ethyl Corporation on the St. Clair River where levels up to 339 ppm Pb have been reported in sediment samples, (2) in sediments of the Black River, (3) across the river from the Lambton Generating Station, and (4) in the eastern distributary of the St. Clair Delta (UGLCCS, 1989, Mudroch et al., 1985).

Pb levels in bottom sediments in the Detroit River are often higher than the dredge spoil guideline of 50 ppm. In 1980, elevated levels were found adjacent to Windsor and along the Michigan side of the river (Hamdy and Post, 1985). Concentrations at the mouth of the Rouge River (200 ppm) were higher in 1980 than in 1970 (50 ppm). In two studies done in 1982, the highest levels were found in the southern part of the river (Lum and Gammon, 1985; Fallon and Horvath, 1985). In 1983, levels of Pb in Detroit River sediments were found to be higher than those of Lakes St. Clair and Erie (Mudroch, 1985). The highest concentration (700 ppm) in 1983 was in the surficial sediments at the Rouge River mouth and elevated levels were also found to the west of Fighting Island and In 1982 and 1985, concentrations of Pb were highest Belle Isle. (> 200 ppm) in the upper part of the river (above the Rouge River) and in the Trenton Channel (UGLCCS, 1989). Some of the maximum levels found in the river have been 960 ppm in 1982 (Lum and Gammon, 1985), 704 ppm and 546 ppm in 1983 (Mudroch, 1985; Chau et al., 1985), and 1,750 ppm in 1982 and 1985 (UGLCCS, 1989).

Mercury has been one of the main trace contaminants in this connecting channel. Levels of Hg in the bottom sediments of the St. Clair River peaked in the late 1960s and early 1970s with maximum levels of 1,470 ppm. The main source, the Dow chlor-alkali plant, ceased production in 1973 but some mercury is still entering the river from that area. In the early 1970s, elevated levels were also found at the mouth of the Black River (Fitchko and Hutchinson, 1975). By 1977, the concentration at the Dow site had dropped to However, concentrations up to 51 ppm were 58 ppm (IJC, 1987a). found in the mid-1980s indicating that inputs remain (UGLCCS, Sediments at the lower end of the river still have 1989). concentrations of Hg in excess of dredge spoil guidelines (UGLCCS, 1989). Decreases in Hg concentrations in the Detroit River from 1970 to 1980 reflect the reduction of Hg loadings upstream. The upper section of the river, above Zug Island has seen the largest changes in concentrations. The mean concentrations in bottom sediments were 3.73 ppm in 1970 and 0.4 ppm in 1980 (Hamdy and Post, 1985). In the mid 1980s, the highest Hg levels in bottom sediments were in the Trenton Channel (> 3.0 ppm) and adjacent to Belle Isle (> 2.5 ppm) (UGLCCS, 1989).

Cadmium in the sediments of the St. Clair River is generally low and not indicative of point sources (UGLCCS, 1989). Concentrations of Cd are greater in Lake St. Clair sediments than in Lake Huron sediments (UGLCCS, 1989). In 1980, concentrations of >6 ppm Cd were recorded at several locations along the Michigan side of the Detroit River (Hamdy and Post, 1985). In 1982, levels of Cd >10 ppm were detected at the mouths of the Detroit and Rouge Rivers (Lum and Gammon, 1985). Also in 1982, Fallon and Horvath (1985) reported that the highest concentrations of Cd were at the southern part of the Trenton Channel. In the mid 1980s, peak concentrations of Cd were found adjacent to Belle Isle and the Rouge River and in the Trenton Channel (UGLCCS, 1989). Maximum levels ranged from 25 to 96 ppm and continuing sources of Cd to the Detroit River were indicated (UGLCCS, 1989).

In 1970 and 1974, the mean concentrations of As in the bottom sediments of Lake St. Clair were 2.5 and 3.4 ppm respectively (Thomas <u>et al.</u>, 1975). In the Detroit River, the mean concentration of As in the mid 1980s was 10 ppm and the peak level

Six locations in the river and four in the lake had 1985). concentrations of OCS greater than 10 ppb. Oliver and Bourbonniere (1985) reported that in 1982, bottom sediment concentrations of HCB in southern Lake Huron were about 1 ppb and concentrations in Lake St. Clair had a mean level of 68 ppb (top 3 cm). The difference for HCBD was 0.08 ppb in Lake Huron and a mean level of 7.3 ppb in In 1985, mean concentrations in Lake St. Clair Lake St. Clair. were 21 ppb (top 1 cm) for HCB and 5 ppb for HCBD (Charlton and Oliver, 1986). The concentrations of HCB and HCBD in Lake St. Clair are still increasing or at least not dropping significantly (UGLCCS, 1989). Elevated levels of HCB, up to 140 ppb, were found in 1985 in the Detroit River adjacent to the Rouge River, in the Trenton Channel and at the mouth of the Detroit River but no major point sources have been identified (UGLCCS, 1989). A similar distribution was found in 1983 for total CBs with the exception of a high concentration west of Fighting Island of 3,500 ppb (Kaiser et al., 1985).

Mirex was not detected in Lake St. Clair in 1982 (Oliver and Bourbonniere, 1985) or the Detroit River in 1980 (Hamdy and Post, 1985). Dioxins and furans were detected in the sediment samples in the mid-1980s in the St. Clair River (DOE and MOE, 1985, 1986; UGLCCS, 1989). Highest concentrations were found at the Township ditch and the 1st Street sewer. The octa-and hepta- congeners predominated and 2,3,7,8-TCDD was not detected.

A review of PCBs in St. Clair River sediments concluded that a trend over time could not be stated because of the variability of the studies (Pugsley <u>et al.</u>, 1985). In 1983 and 1985, along the Canadian shore of the St. Clair River, there appeared to be an increase in concentrations at the Polysar-Dow area of the river (DOE and MOE, 1986) (Figure 8). The maximum levels were considerably higher than the dredge spoil guideline of 0.05 ppm. Additional regions of PCB concern are in the vicinity of Ontario Hydro's Lambton generating station on both sides of the river and in the Belle River (UGLCCS, 1989). The range of concentrations along the American shore was relatively low. Oliver and Bourbonniere (1985) did not detect an increase in the concentration of PCBs in sediments between southern Lake Huron and Lake St. Clair. In 1982, mean concentrations of PCBs in Lake St. Clair sediments were much lower than those reported for western Lake Erie (Oliver and Bourbonniere, 1985).

The Detroit River is a major source of PCBs to Lake Erie (Oliver and Bourbonniere, 1985). PCBs enter the river from Lake St. Clair and there are several point sources along the river. In 1980, PCBs were found in 78% of the bottom sediment samples (Hamdy and Post, 1985). The highest concentrations (> 500ppb) were found along the Michigan shore south of the city of Detroit. In 1982, the highest levels were found at the head of the river (Fallon and Horvath, 1985). This was thought to reflect the effect of Lake St. Clair and a nearby wastewater treatment plant. In 1983, Pugsley et al. (1985) reported higher concentrations of PCBs in 10 cm bottom sediments from Lake St. Clair than in the Detroit River. Kaiser et al. (1985) found highest concentrations, 200 to 23 ppb, to be at the mouth of the Rouge River, southeast of Belle Isle, and at the mouths of the Trenton Channel and Detroit River in 1983. High levels, and possibly sources, are also indicated downstream of Belle Isle (IJC, 1987a) and adjacent to the Ecorse River (UGLCCS, 1989).

In 1985, PAHs were detected in bottom sediments of the St. Clair River adjacent to Dow at levels up to 60.79 ppm and averaging 3.31 ppm (Nagy <u>et al.</u>, 1986). Levels up to 140 ppm were reported in the UGLCCS (1989). Elevated levels of PAHs have been identified across the river from Lambton Generating Station and in some tributaries on the American side of Lake St. Clair (UGLCCS, 1989). Elevated levels of PAHs were found in the 1980s in the Detroit River, especially downstream of Belle Isle, in the vicinity of Grosse and Fighting Islands, and in the lower Rouge River (Fallon and Horvath, 1985; Kaiser <u>et al.</u>, 1985; UGLCCS, 1989). The highest concentrations reported by Kaiser <u>et al.</u> (1985) were 20 to 33 ppb.

# 2.5.1 CHEMICAL CONCENTRATIONS IN WATER

The summarised data on toxic chemical concentrations in water in Lake Erie is given in Table 10. Rossmann (1984) reviewed the available data for total and dissolved Pb in Lake Erie water. For water collected at unrecorded depths, the 1974 and 1980 medians were at the limit of detection at that time (5 to 10 ppb) (n = 6). Total Pb in epilimnion water, taken at depths of less than 5 m, revealed no trend. Mean concentrations in 1967, 1973, 1975, 1978 and 1979 ranged from 0 to 9 ppb. This early data and that in Table 10 cannot be taken as evidence of a decrease in Pb concentrations but rather reflects that true metals concentrations are less than had been estimated by earlier sampling and analytical techniques. Sonzogni and Simmons (1981) arrived at the same conclusion when comparing data from 1967 with that from 1970 to 1977. In 1978. dissolved Pb mean values as high as 23 ppb and a maximum of 840 ppb (n = 717) had been recorded. Again, this historical data is unlikely to be accurate (Rossmann, 1984). Earlier Hg data from the 1970's recorded mean total Hg concentrations of up to 370 ppt (median 37 ppt and maximum 130 ppb (n = 618) in 1978). There may be a trend, for example for total Hg, which was a mean of 170 ppt (n = 170) in 1970-71; 370 ppt (n = 618) in 1978; 81 ppt (n = 596); in 1979; and 42 ppt (n = 11) in 1981. Rossmann (1984) calculated that total Hg concentrations in epilimnetic water appeared to be declining at a mean rate of 12 ppt/year. The reason for the changes is more likely the improvement in analytical accuracy. Mean values for dissolved Cd in 1963 and 1964 were reported as 10 ppb (n = 49) (the detection limit). In the 1970's, mean dissolved Cd concentrations were reported as 1.1 ppb (1970; n = 9); 0.7 ppb (1971; n = 112); 2.5 ppb (1978; n = 708); 0.7 ppb (1979; n = 567).The latter value for 1979 is still an order of magnitude higher than the mean dissolved concentration of 71 ppt measured in 1981 In 1978, Lum and Leslie (1983) reported that 87% of (Table 10). the total Cd in Lake Erie water was in the dissolved phase. İn 1981, Rossmann (1984) found dissolved Cd to be lowest in the waters

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# TOXIC CHEMICAL CONCENTRATIONS IN LAKE ERIE WATER (ppt) 0

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	•		Testing								~ %		
	Chemica ]	Sample	Date	#	Min	Max	Mean	SD	Median	DL		Ref.	
	Pb	dis.	1981	11	ND	500	220	140	170		q	(2),(5	>
	Pb	dis.	<1986				750				9	(4)	/
	Pb	part.	1981	11					190		•	(5)	
	Pb	part.	<1986				250					(4)	
	Pb	whole	1978-79				1,180-26	.310				(1)	
	Pb	whole	<1981		<1,000	5,000		, _ , _		10 S S		(7)	
	Pb	whole	1981	11	150	3,000	910	1,000	340		- 0	(2),(5	)
	Hg	dis.	1981	11	ND	80	34	29	24	* .	55	(2),(5	
	Hg	dis.	<1986				30				0,0	(4)	/
	Hg	part.	1981	.11			•••	•	2			(5)	
	Hg	part.	<1986				10		£			(4)	
	Hg	whole		170	ND	400	170	110		50		(6)	
	Hg	whole	1978-79				10-730	110				(1)	
	Hġ	whole	<1981				<1,000					(7)	
	Hg	whole	1981	.11	ND	14	42	44	33		27	(2),(5	)
	Cd	dis.	1981	11	41	120	71	27	67		0	(2),(5	$\sim$
	Cd	dis.	<1986	, ,		120	50	21	U r	. *	. 0	(2), (3)	1
	Cd	part.	<1986			·	50					(4)	
	Cd	whole	1978-79				370-10,6	60				$(1)^{-1}$	
	Cd	whole	<1981				<200	~~				(7)	
	Cd	whole	1981	11	39	320	98	81	72		'n	(2),(5	1
					00				12		0	(2),(0	/
•	As	dis.	1981	11	ND	800	380	190	420		55	(2),(5	)
	As	part.	1981	11					. 87			(5)	
	As	whole	1969	17	ND	.600	250			100	35	(3)	
	As	whole	1978-197				ND-2,290		,			(1)	
	As	whole	1981	11	280	920	490	200	430		0	(2),(5	)
	As	whole	<1986				500			•		(4)	
	tDDT	dis.	<1985				0.1					(4)	
	tDDT	part.	<1986				° 0.1					(4)	
	tDDT	whole	<1981				<1			·		(7)	
	p,p'-DDT	whole	1986	21		ND				0.011	100	(8)	
	o,p'-DDT	whole	1986	21		ND				0.011	100	(8)	·
	p,p'-DDÈ	whole	1986	21	0.028	0.096	0.053			0.011	48	(8)	
	dieldrin	dis.	<1986				0.3					(4)	
	dieldrin	part.	<1986				0.1					(4)	
	dieldrin	whole	<1981				<1			· .		(7)	
	dieldrin	whole	1986	21	0.082	1,111	0.402			0.011	0	(8)	
	aBHC	dis.	<1986			• .	9				:	(4)	
	a-BHC	part.	<1986				1			. '		(4)	
	a-BHC	whole	1986	21	2.576	6.513	3.962			0.011	0	(8)	
	-				· · .					-			

TABLE 10 cont.

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Chemical	Sample	Testing Date	#	Min	Max	Mean	SD	Median	DL	~ 名L	Ref.	
lindane lindane lindane	dis. part. whole	<1986 <1986 1986	21	0.581	2.554	2.0 0.2 1.075			0.011	0	(4) (4) (8)	
mirex	whole	1986	21		ND				0.011	100	(8)	
toxaphène toxaphène toxaphène	part.	<1986 <1986 1981				0.4 0.2 0.7	· .		· · . · .		(4) (4) (9)	
B(a)P B(a)P	dis. part.	<1986 <1986				0.2	•	•	. ·		(4) (4)	
HCB HCB HCB	dis. part. whole	<1986 <1986 1986	21	0.025	0.26	0.04 0.02 0.078			0.011	24	(4) (4) (8)	
PCBs PCBs PCBs PCBs	dis. part. whole whole	<1986 <1986 <1981 1986	21	1 0.341	10 3.513	0.7 0.3 ≪100 1.378	•	•	0.24	D	(4) (4) (7) (8)	
									•			;

ND : not detected

Sample : whole = whole water; dis. = aqueous phase; part. = suspended particulate phase. # : number of samples

SD : standard deviation

DL : detection limit

% <DL : percent below the detection limit

- 1. Rathke 1984. The range represents the mean concentrations for the 2nd to 4th quarters of 1978 and 1979 along the south shore.
- 2. Rossmann 1984. Particulate conc.: ppt=ng/L. Filter: 0.5 um pore size.

Particulate conc. + dissolved conc. = whole water concentration.

3. Traversy et al. 1975.

- 4. Strachan and Eisenreich 1988. Mean value based on assessment of historical data up to 1985-86. These values were used in mass balance models. Part. conc.: ppt=ng/L. Particulate conc. + dissolved conc. = whole water conc.
- 5. Rossmann and Barres 1988. The number presented for "% below detection" actually represents the percent of analyses below the limit or criterion of detection. Particulate concentrations are ng/L.

6. Chau and Saitch 1973.

7. Sonzogni and Simmons 1981. Typical concentration range. These values are designed only to illustrate the types of values and the relative range of concentrations reported.

8. Stevens and Nielson in press.

9. Sullivan and Armstrong 1985

of the central basin, but insufficient samples were collected to justify this statistically. Lum (1987) compared Rossmann's (1984) data for 1981 (71 +/-27 ppt) with his data for 1978 (40 +/- 20 ppt) and for 1984 (29 +/- 15 ppt). Because all of this Cd data is considered to be reliable, there may be a decreasing trend, although the differences may still be methodological. For 1975, Rossmann quotes a value of 1.0 ppb (n = 2) total As in water from unrecorded depths. In 1980, a mean value of 10 ppb As (n = 6) was recorded but in this case this was the detection limit. Mean concentrations in 1981 were about 50% of what mean values were thought to be by measurements made in the late 1970s. Rossmann arrived at a total As rate of decrease of 310 ppt/year between 1978 to 1981.

There is limited data available on the concentrations of toxic organic chemicals in the waters of Lake Erie (Table 10). Nearly all early values were beneath the detection limits prior to the implementations of new sampling and analytical techniques developed For DDT, Konasewich et al. (1978) reported in the early 1980's. open lake water values close to or less than the detection of 1 ppt. McCrea et al. (1985) using newly developed large water value extraction procedures reported that in 1981 p,p'-DDT was detectable at all of his sample stations and was present almost exclusively in the aqueous phase. Between 1981 and 1983, DDE was detected at concentrations of some 0.1 ppt (Oliver and Nichol, 1984). In 1981. Filkins et al. (1983) reported p,p'-DDT and p,p'-DDE concentrations ranging from 0.007-0.022 ppt and 0.006-0.018 ppt respectively (n In 1986 Lake Erie surface water DDE concentrations ranged = 5). from beneath detection to 0.08 ppt (IJC, 1987). For 1981, McCrea et al. (1985) reported that 94% of the dieldrin in Lake Erie surface water was in the aqueous phase. Concentrations were reported as between 0.069 and 0.0934 ppt. McCrea et al., (1985) reported that 100% of lindane was present in the aqueous phase. At Fort Erie in 1981 to 1983, Oliver and Nicol (1984) reported total concentrations of 4.2 ppt a-BHC and 0.38 ppt g-BHC. No Mirex

predictive models. The most recent data relied on is that of Stevens and Neilson (in press).

### 2.5.2 CHEMICAL CONCENTRATIONS IN BOTTOM SEDIMENTS.

Chemical concentration data for Lake Erie bottom sediment is summarised in Table 11. Two studies of toxic chemical concentrations in bottom sediment have been carried out in Lake Erie, one in 1971 (Frank et al., 1977; Thomas and Mudroch, 1979) and one in 1979 (Rathke, 1984). The 1971 samples were the surface 3 cm while the 1979 samples used the surface 10 cm. Direct comparison is thus not possible. However, because the more contaminated sediments of 1971 were being buried by less contaminated sediments by the late seventies, the collection of a 3 cm sample in 1979 might well have revealed an even greater decrease in concentrations than are seen in the 10 cm samples. Toxic metal concentrations in the surface 3 cm of surficial sediments, shows that Pb, Cd and Hg concentrations in the lower Great Lakes are higher over greater areas of the lake bottom than for the three upper Great Lakes. In 1971 (Thomas, 1981) large areas of the lake bottom had concentrations of Pb greater than 150 ppm whereas in 1979 only small areas had greater than 100 ppm (Rathke, 1984). In the central basin, where concentrations in 1971 had been greater than 100 ppm, levels have declined to less than 75 ppm, presumably by burial, dilution, or dispersion downstream of the historically contaminated sediments or downstream transport. The 1971 survey revealed two Pb plumes, one from Detroit to the western basin and one from Cleveland to the Central basin (Thomas, In 1970, Konasewich et al. (1978) reported levels of 340 1981). and 420 ppm Pb for Cleveland and Buffalo harbours respectively. effect is seen for Cd (Figure 9). Background The same (pre-colonial) bottom sediment concentrations of Cd in Lake Erie are 0.1 to 1.7 ppm. Surface sediment Cd concentrations in near shore areas were 0.1 - 8.3 ppm and in harbours 0.2 -0.3 ppm (Fitchko and Hutchinson 1975; Mudroch et al., 1985). The lake

	0201		( PPD									
Chemical	Sample	Testing Date	#	Min	Max	Mean	SĎ	Median	DL.	。 そDL	Ref.	
Pb Pb Pb Pb Pb Pb	3 cm 1 cm 10 cm	1971 1971 1979 <1981 <1984 <1986	258 6	83,000 <50,000 <50,000	299,000 146,000 >140,000 >150,000 299,000	107,000	50,000 23,000	100,000			(5) (11) (13) (1) (3) (2)	
Hg Hg Hg Hg Hg Hg	3 cm 1 cm 10 cm	1971 1971 1979 <1981 <1984 <1986	258 6	8 330 <300 <50 45	2,929 1,430 <2,000 2,000 4,800	578 860 500	554 340	850			(5) (11) (13) (1) (3) (2)	
Cd Cd Cd Cd Cd Cd Cd	3 cm 1 cm 10 cm	1971 1971 1979 <1981 <1984 <1986	258 6	100 2,500 <3,000 800	10,800 4,500 >4,000 13,700	2,400 3,500 <8,000 1,000	1,500 720	3,500			(5) (11) (13) (1) (3) (2)	
As As As	3 cm 3 cm	1971 1971 <1984	10 258	2,000 200 450	4,000 60,000 12,300	3,200 1,300	1,100 4,300	3,200	•	•	(4) (5) (3)	
tDDT tDDT tDDT p,p'-DDE	3 cm 3 cm	1971 <1981 <1986 1971	259 259		322 30 136	27.9 30 8.2	32.6	1	0.1-0.		(14) (1) (2) (14)	
p,p'-DDE DDE	3 cm 3 cm	1982 1982	· 46 5	2.6 5.7	17 21	3.8-8 10.7	5.4	9.8			(12) (10)	
dieldrin dieldrin dieldrin	3 cm	1971 <1981 <1986	259	NÖ	5	1.2 <3 20	0.9		0.2	14	(14) (1) (2)	
Mirex Mirex	3 cm 3 cm	1982 1982	46 5	·	ND ND			: :			(12) (10)	
aBHC aBHC	3 cm	1982 <1986	46		low	2			0.2	Q	(12) (2)	
lindane lindane	3 ếm	1982 <1986	46		low	1		• •	0.1	0	(12) (2)	
B(a)P B(a)P		<1986	3	•	· .	255 200	152		· ·		(8) (2)	

# TABLE 11 TOXIC CHEMICAL CONCENTRATIONS IN LAKE ERIE BOTTOM SEDIMENTS (ppb)

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TABLE 11 cont.

		Testing							. 1	ጜ		
Chemical	Sample	Date	#	Min	Мах	Mean	SD	Median	DL	<dl< th=""><th>Ref.</th><th></th></dl<>	Ref.	
HCB	3 cm	1980	5	0.7	12	3					(9)	
HCB	3 cm	1982	5	2.5	20	7.6	6.8	2.8			(10)	
HCB	3 cm	1982	46	1.2	17	2.4-9.1		ţ			(12)	
HCB	$X^{-1}$	<1986		•		4		· · ·	-		(2)	
HCBD	3 cm	1982	5	0.1	2.4	0.86	0.84	0.5			(10)	
HCBD	3 cm	1982	46	0.1		0.2-1.6					(12)	,
PCBs	3 cm .	1971	231	4	800	95	114				(14)	
PCBs		<1981		<10	>100	100	-				(1)	•
PCBs	Зст	1982	46	37	660	91-300			· .		(12)	
PCBs	3 cm	1982	5	150	1099	428	355.3	242.2			(10)	
PCBs	2	<1986			,	60					(2)	
OCDD		1981-83	2	1700	2000	•					(7)	
											-	

ND : not detected

Sample : depth of surficial sediment sample

# : number of samples

SD : standard deviation

DL : detection limit

% <DL : percent below the detection limit

1. Sonzogni and Simmons 1981. Typical concentration range. These values are designed only to illustrate the types of values and the relative range of concentrations reported.

2. Strachan and Eisenreich 1988. Mean value based on assessment of historical data up to 1985-86. These values were used in mass balance models.

3. Mudroch et al. 1988. These numbers are a summary of concentration ranges taken from reports published between 1974 and 1984. Concentrations are from surface samples of deposititional zones.

4. Traversy et al. 1975

5. Thomas and Mudroch 1979.

7. Czuczwa and Hites 1986

8. Eadie 1984. Adjacent to Raison River in the Western Basin.

9. Oliver and Nicol 1982. Depositional and non-depositional zones.

10. Bourbonniere et al. 1986. Excluding Georgian Bay and the North Channel.

11. Kemp and Thomas 1976b

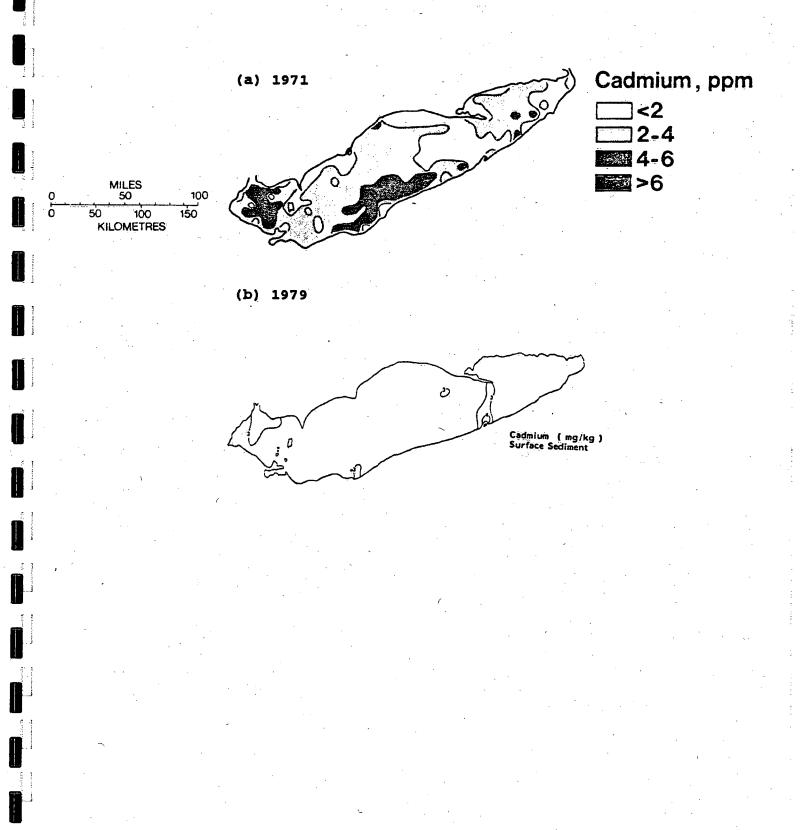
12. Oliver and Bourbonniere 1985. Mean concentrations were given for the Western, Central and Eastern zones.

13. Rathke 1984

14. Frank et al. 1977. Depositional and non-depositional zones.

# FIGURE 9 Cd IN SURFICIAL BOTTOM SEDIMENTS OF LAKE ERIE (a) 1971 (After Thomas and Mudroch, 1979) AND (b) 1979 (Rathke, 1984)

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reported as 6.6 ppm (Nriagu et al., 1979). The pattern for Hg in Lake Erie sediments is again similar. In 1971, a small area of the western basin of Lake Erie had bottom sediment concentrations of greater than 2 ppm Hg and a large area of over 1 ppm (Thomas and Jacquet, 1976). By 1979, the anomaly was farther out into the west basin away from the inflow of the Detroit River and the area of greater than 1 ppm Hg had decreased considerably indicating a rapid recovery from earlier Hg contamination (Rathke, 1984). Suspended solids entering Lake Erie from the Detroit River had shown little change in Hg concentration during 1974 (Thomas and Jacquet, 1976) when the mean value was 1.06 ppm. In 1971, mean surficial sediment Hg concentrations in the west basin were 1.14 +/- 1.28 ppm compared to 0.60 +/- 0.42 ppm in 1979. The comparable values for Pb, Cd and As were 86 +/- 48 and 56 +/- 36 ppm; 5.6 +/- 3.5 and 3.0 +/- 2.4 ppm; and 7.9 +/- 2.5 and 6.5 +/- 3.0 ppm respectively.

Data on the concentrations of toxic organic chemicals in Lake Erie surficial sediment is given in Table 11. In 1971 the distribution of toxic organic chemicals in Lake Erie surficial sediments showed that the highest concentrations for hydrophobic compounds such as DDE and dieldrin were found in a plume originating from the Detroit River. In the top 3 cm bottom sediment samples from 1971, TDE was the predominant compound of the The mean TDE lake value was 18.4 ppb with a DDT group present. range of 0.3 to 186 ppb. Both TDE and DDE concentrations were 2 to 3 times higher in the depositional basins than in the other parts of the lake. The highest value of TDE was 46.5 ppb in the western basin. DDE was 22.1 ppb giving a total TDE and DDE value In 1980 at a site in the western basin, DDE was 8 of 68.6 ppb. ppb, DDE was 2 ppb and DDT was 1 ppb (a total of 11 ppb) in the upper 3 cm of sediment (Anderson, 1980). Oliver and Bourbonniere (1985) reported that p,p'-DDD were evenly distributed across Lake Erie. The sum of dichloro through hexachlorobenzenes in Lake Erie sediment was some 26 ppb, less than in both Lake Huron (38 ppb) and Lake Ontario sediment (560 ppb) (Oliver and Nicol, 1982). In 1982,

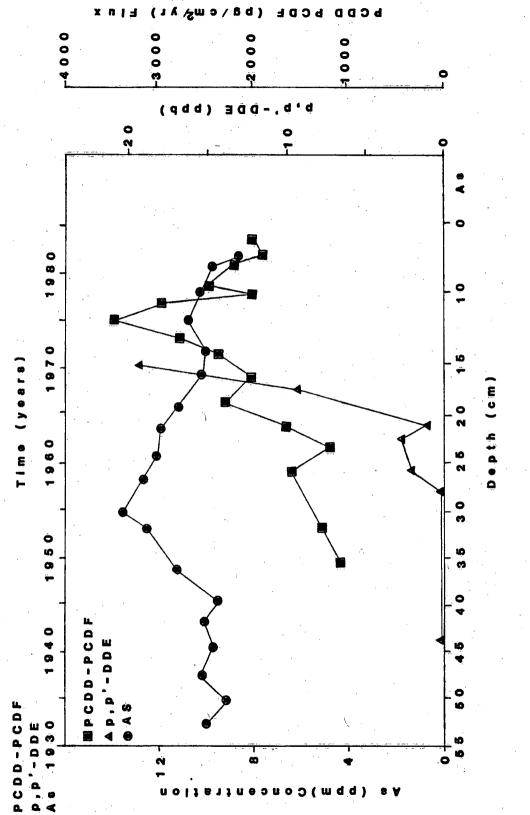
• .

HCB in 3 cm samples from the western, central and eastern basins of Lake Erie had concentrations of 9.1 ppb (range 4.6 - 17 ppb); 2.4 ppb (range 1.2 - 3.7 ppb); and 2.7 ppb (range 1.4 ppb - 5.2 ppb) respectively (Oliver and Bourbonniere, 1985). In the same samples, they detected HCBD at concentrations of 1.6 ppb (0.7 - 3.2 ppb); 0.2 ppb (0.1 - 0.4 ppb); and 0.2 ppb (0.1 - 0.6 ppb) respectively, or an overall depositional basin mean of some 0.7 ppb. In 1982, total PAH's in the adjacent Raison River in western Lake Erie ranged from 530-770 ppb (Eadie et al., 1982). Extreme concentrations of 4.8 to 390 ppm PAH were found in the sediments of the Black River near steel industries. The distribution of PAHs in the three basins of Lake Erie (Nagy et al., 1989) showed that B(a)P had highest concentrations of some 200 ppb in the central Surface sediment PCDD and PCDF concentrations for Lakes basin. Erie, Ontario, Huron, and Michigan were determined by Czuczwa and Hites (1986). The main isomer present was OCDD followed by H7CDF. Lake Erie concentrations of OCDD were 1,700 and 2,000 ppt; compared to 4,800 ppt for Lake Ontario; 780 and 960 ppt for Lake Michigan; and 880 ppt for Lake Huron. OCDF concentrations were much lower than in Lake Ontario. The surficial lake bottom sediment data on PCBs is the most extensive for toxic organic chemicals (Table 11). The highest levels were in the western basin and associated with inputs from the Detroit River.

In cores collected in 1971, rapid increases occurred in Hg and Pb concentrations after 1935 and especially after 1955 for Hg. Based on these analyses, the sediment concentration of Hg in 1971 was some 12.4 times that in pre-colonial sediments (Kemp and Thomas, 1976a). In surface sediments, Pb was 4.4 times and Cd was 3.6 times the precolonial concentrations. More recent data shows that this trend has been reversed. Distribution of Pb in a dated core from the eastern basin of Lake Erie showed that concentrations of this metal began to increase slowly from about 3 ppm at the turn of the century, increased in the 1940's, rose rapidly from around 30 ppm in 1950, peaked at 58 ppm in the early 1970's, and have

since declined to values of 30 ppm similar to those of around 1955 (Eddie and Robbins, 1987) (Figure 10). In cores collected in 1985, recent declines from 13 to 9 ppm in As concentrations in bottom sediment have also been recorded (Legault, 1986). Peak As concentrations occured around 1955 and since then have declined to concentrations similar to those which were recorded around 1945. Lake Erie sediment cores analyses initiated that there has been a recent recovery from earlier previous contamination by toxic organic chemicals. In 1971, p,p'-DDE was found to a depth of 10-12 cm or to around 1958-60 (Figure 10) (Frank et al., 1977). TDE in the same core was first detected at a depth of 6-8 cm, representing 1961-1963. DDE and TDE then increased rapidly to surface concentrations of 19 and 53 ppb respectively. Ten years later, Anderson (1980) reported that the upper 3 cm of sediment in a core from the eastern basin had DDT, DDE and DDD concentrations of 1 ppb, 2 ppb and 8 ppb respectively. The highest concentrations of total DDTs was 23 ppb at a depth of 15 cm. Beneath this depth, concentrations fell to 15 ppb total DDTs at 35 cm depth. For dioxins and furans, the high sedimentation rates of Lake Erie allow good resolution of historical input trends. In two cores, the maximum input of PCDD and PCDF was in the mid-1970S (Czuczwa and Following the mid-1970s, inputs declined (Figure Hites, 1986). Extrapolation to deeper layers and times of sediment 10). deposition indicated that initial inputs of PCDDs and PCDFs to Lake Erie probably occurred in the mid to late 1930's.

In 1971, in a core from near Toledo, PCBs were in sediment deposited during 1954-1956. The upper layers had progressively rapidly increasing PCB concentrations of up to 340 ppb for the layers being deposited in 1971 (Frank et al., 1977). In 1982, the surface 3 cm of sediment for the western, central and eastern basins of Lake Erie had PCB concentrations of 300 ppb (range of 140-660 ppb); 131 ppb (range 38-190 ppb); and 91 ppb (range 37-140 ppb) (Oliver and Bourbonniere, 1982). These values can be compared with the mean western basin, surficial 3 cm of sediment



DISTRIBUTION OF AS, DDE AND PCDD + PCDF IN LAKE ERIE SEDIMENT CORES. (After Czuczwa and Hites, 1986a; Legault, 1986; Frank et al., 1977) FIGURE 10

concentration of 252 ppb in 1971 (Frank et al., 1977). The reasons may be that the surficial sediments of the western basin are thoroughly mixed as proposed by Eadie and Robbins (1987) or the inputs of PCB's have not significantly declined.

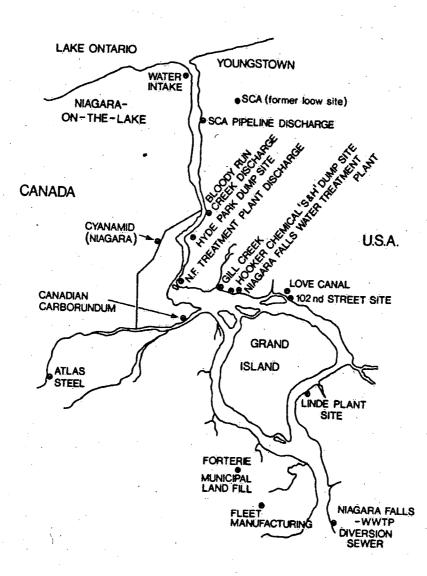
# 2.6 THE NIAGARA RIVER

The Niagara River connects Lake Frie to Lake Ontario. It is a short connecting channel of about 60 km length with a very large The river is divided into upper and lower reaches by discharge. Niagara Falls. The main sources of pollution to the river were point source discharges from steel and petrochemical industries and municipal wastewater treatment plants (Figure 11). These treatment plants often received discharged effluents from industries. The large petrochemical industries on the United States side of the river have produced a variety of chlorinated industrial organic chemicals and pesticides. Most of the wastes from these petrochemical industries have been buried in waste landfills such as Hyde Park and Love Canal. These sites now produce leachates which enter the Niagara River.

Research results on the Niagara River and downstream Lake Ontario were published in a special volume of the Journal of Great Lakes Research (Allan et al., 1983). Numerous research and monitoring papers and reports have also been since published on the Niagara River pollution status. The Niagara River was the subject of a major bi-national study Niagara River Toxics Committee Study (NRTC, 1984) which has described the pollution of the river in far more detail than can be described here. The NRTC (1984) reported, amongst other conclusions, that 261 man-made chemicals were identified in the ecosystem; 1400 kg of pollutants were discharged to the river from municipal and industrial point sources; 89% of the total came from U.S. sources; 61 U.S. hazardous waste disposal sites and 5 Canadian landfills have the potential to contaminate the river (and downstream); 28 of these 61 sites have or are contributing contaminants to the river; and general groundwater contamination covers a large area along the U.S. side of the river. Since release of the this, Canada and the United States have agreed to a plan which has a goal of 50% reduction of selected persistent toxic chemicals from both point and non-point sources by 1996.

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# FIGURE 11 MAJOR EFFLUENT OUTFALLS AND WASTE DUMPS ADJACENT TO THE NIAGARA RIVER. (Allan et al., 1983)



In general, the longer term monitoring data on suspended solids on the Niagara River and the more recent water analyses comprise the best long term (1979 for metals) (1980 for organics) water quality data for toxic chemicals available anywhere in the Great Lakes. The data indicate an overall decline in concentration of many contaminants. This decline is recorded downstream in the bottom sediments of Lake Ontario and will be discussed later.

Between 1981/2 and 1986/7, the point source loadings to the Canadian side were estimated to have decreased by 60% (MOE, 1987). On the United States side, an 80% reduction in total organic and inorganic priority pollutants from point sources was estimated to have taken place between 1981/82 and 1985/86 (NYDEC, 1987). Α significant fraction was related to plant closings or process shutdowns (NYDEC, 1987). In 1984, no assessment could be made of the loadings of toxic chemicals via groundwater from 215 hazardous waste sites (NRTC, 1984). Further study concluded that 61 of the 164 sites within 5 km of the river have the potential tó contaminate it (NRTC, 1984). Of the 17 landfill sites on the Canadian side, 5 were identified with a potential to contaminate the Niagara River (Koszalka et al., 1985). Although estimates of inputs have been made, they are extremely tenuous and considerably greater sampling and modelling will be needed to arrive at meaningful loadings. The existing estimates are based on 70 sites on the U.S. side of the river and arrive at a total of 180 kg/day of organic compounds. Thus, there is a possibility that non-point groundwater sources of chemicals could be as high as point source inputs to the Niagara River. The four major superfund sites of 102nd Street, Love Canal, S-area and Hyde Park collectively hold 304,000 tonnes of chemical waste; are hydraulically connected to the river; and have been associated with off-site migration of chemicals (Brooksbank, 1987). Several of the small tributaries to the Niagara River contain bottom sediments with elevated concentrations of toxic contaminants and these could be a longer term source of pollutants to the river.

The Niagara River has been the most intensely studied part of the Great Lakes system for toxic metals and organic chemicals. This has occurred because the Niagara River was the first major area (1980) of crisis due to toxic organic chemical contamination, following closely on the exposure of Love Canal as a major chemical Monitoring for toxic metals using suspended solids waste site. went into effect in Canada in the late 1970's. By the early 1980s, this method had been extended to toxic organic chemicals in suspended solids at the mouth of the Niagara River. Later, in the mid-1980s. more sophisticated aqueous phase analyses were All of these developments required new sampling and performed. analytical techniques which have since been extended both up and downstream in the Great Lakes system.

By 1984, both upstream (Fort Erie) and downstream (Niagaraon-the-Lake (NOTL) monitoring had been implemented to calculate mass balances of specific toxic chemicals in the river by Federal agencies in Canada. Meanwhile, several special studies of chemical distribution in and sources to the river have been carried out by both Federal and Provincial (Ontario) Canadian agencies. A summary of the differential concentrations between Fort Erie and NOTL (Table 13) is based on values agreed to by the Canadian and U.S. agencies responsible for the program. There has, of course, been considerable debate about sampling, analytical and data reduction techniques to arrive at these estimates. Loadings of 25 chemicals or elements were considered to be significantly higher at the NOTL location, either in the water or suspended sediment fractions or both in 1984/86 and 1986/87. Regardless of the exact numbers for specific compounds, even if these are accurate, it is clear that large amounts of chemicals have been or are still being introduced to the Niagara River along its shores.

Between 1984 and 1987, Environment Canada collected data on water and suspended solids concentrations at NOTL and Fort Erie. Two reports have been released, the first for Dec. 1984 to March 1986 and the second for April 1986 to March 1987. Collectively,

the data in these reports on organic chemicals concentrations in the water and suspended solids at NOTL and Fort Erie represent the most comprehensive data base of its type anywhere in the world. Suspended solids are sampled by high speed centrifugation. Concentrations in the aqueous fraction are based on a continuous extraction system over a 24 hour period. The objective has been to assess the differential loads of toxic organic chemicals added along the course of the Niagara River. Of more importance in this report are the mean and range of concentrations recorded at both sites. A value for recombined water (RWW) was calculated from the aqueous concentration combined with the suspended solids concentrations based on the suspended solids content of the water. Using these values for RWW, 21 of the organic chemicals exceeded the strictest water quality criteria at least once, 15 at both NOTL and Fort Erie, 3 at Fort Erie only, and 3 at NOTL only. This data base reveals the extremely low concentrations of those chemicals present in the raw waters of connecting channels and Great Lakes.

# 2.6.1. CHEMICAL CONCENTRATIONS IN WATER

Between 1975 and 1979 less than 10% of the samples analysed at the mouth of the Niagara River exceeded the 1978 Water Quality Agreement (GLWQA) objectives, yet the river was a source of toxic metals and organic chemicals to Lake Ontario (DOE and MOE, 1981). The main compounds of concern were DDT, PCBs, Mirex and Hg. Most organic chemicals were beneath the detection limits for water, which in turn are usually beneath the GLWQA objectives. In 1980, PCBs, a-BHC and lindane; and a and g-chlordane, HCB, dieldrin, heptachlor epoxide, and p,p'-DDE were observed in 80% of ambient waters collected over a 10 day period at the mouth of the Niagara River (Kuntz, 1983).

Partitioning of organic chemicals between aqueous and particulate fractions varies considerably with respect to location in the river and with time. The majority of the toxic organic chemical load in this river with a low (5 to 10 mg/L) suspended solids concentration, is in the aqueous phase. Collection and analyses of suspended solids at the mouth of the Niagara has been of great importance in establishing long term concentration trends. However, Kuntz and Warry (1983) found that only 40% of the total loadings to Lake Ontario of p,p'-DDE, Mirex and PCB's, all extremely hydrophobic organic chemicals, were in the particulate phase. The percentage was significantly less for most other toxic organics.

The general pattern of toxic chemical concentrations, at least in the Niagara River above Niagara Falls, results primarily from sources along the United States side of the River (IJC, 1987b). The presence of compounds such as dioxins and furans which were never produced commercially but are known to be present in chemical waste disposal sites implies active leaching from these to the Niagara River. This conclusion was arrived at by both the NRTC (1984) and from results showing that specific compounds associated only with specific waste disposal sites are widespread downstream in Lake Ontario sediments (Kaminsky, <u>et al.</u>, 1983).

Between 1984 and 1987, Environment Canada collected whole water samples for metal analyses from NOTL and Fort Erie. The mean concentrations and ranges are given for Pb, Cd, and As in Table In 1981, the highest levels of Pb in water were 2, 3, and 5 13. ppb (Kuntz, 1984b). These were found just downstream of Buffalo. Between 1975 and 1983, the 12-month moving average of total lead concentrations seems to show a decrease and translates into loading reductions of from some 430 tonnes/annum in 1975 down to some 200 tonnes/annum in 1983 (Kuntz, 1988b). Between 1979 and 1980, Kauss (1983) reported that mean Hg concentration in the Tonawanda Channel were 100 ppt as opposed to 60 ppt in the Chippawa Channel. Mercury concentrations (MOE and DOE, 1981) were from 60 to 110 ppt in In 1986, Hg was beneath the waters of the upper Niagara River. detection limit at NOTL and at FE. In 1982 to 1983, the analytical detection limit for Cd was 10 ppb which is above the GLWQA objective of 2 ppb (Kuntz, 1984a). In 1985, the Cd concentrations

at both NOTL and Fort Erie were beneath the detection limit of 2 ppb at 1.5 m depths. During 1980, As concentrations in the upper Niagara River were 1 or less than ppb but 1 ppb was the detection limit.

Because of the major focus on the Niagara River as a source of toxic organic chemicals to Lake Ontario, the organic chemical data base waters is on more extensive than elsewhere. Concentrations of toxic organic chemicals in the Niagara River are found in Table 12. For total DDT plus metabolites; endrin; heptachlor/heptachlor epoxide; and endosulphan, the 1978 GLWQA objectives have been exceeded occasionally in less than 10 % of the water samples (DOE and MOE, 1981). Most concentrations were less than 1 or 5 ppt depending on the detection limit of the compound. Most PCB concentrations were less than the detection limit of 20 ppt. (In 1979, the highest values recorded were 80 ppt total PCB's; 20 ppt dieldrin, 7 ppt a-BHC; 1 ppt lindane; 5 ppt total DDT and metabolites; and 15 ppt HCB (MOE and DOE, 1980). Most of these elevated concentratios were from the U.S. side of the upper Niagara River.

Kuntz (1984b) found that concentrations of total DDT were 1-2 times greater at NOTL than at Fort Erie between 1975 to 1982. El-Shaarawi <u>et al.</u> (1985) said there was a significant difference in mean concentrations between Fort Erie and at NOTL for sixteen toxic chemicals. For whole water, some of these were PCBs, a-BHC, Mirex, and some CBs including HCB. Lindane and p,p'-DDE in the aqueous phase and Hg in the suspended phase also increased. McCrea <u>et al.</u> (1985) found the a-BHC, lindane and dieldrin, and to a lesser extent p,p'-TDE were mainly in the aqueous phases.

Over a two year period for 1981 to 1983, weekly water samples from Niagara-on-the-Lake were analyzed by Oliver and Nicol (1984) for several organic compounds and isomers. The distribution of the concentrations of a-BHC; total PCBs; 1,2,3,4-TeCB; and HCB show that maximum concentrations occurred as short-lived (one sample) peaks (Figure 12). The peak concentrations were as follows: 50

	Chemical	Sample	Place	Testing Date	#	Min	Max	Mean	SD	Median	ÔĻ	°% ≺DL	Ref.
•	Pb Pb	whole whole	UNR NOTL		168 394	•	.!	1,000		<1,000-2,000		23	(4) (2)
	Pb Pb Pb Pb	whole whole whole whole	FE NOTL	1985 1985 <1986 1986-87	48	800	2,100	5	1,000 1,000 1,360,00	0		29	<ul> <li>(7)</li> <li>(7)</li> <li>(5)</li> <li>(1)</li> </ul>
- -	Pb Hg Hg Hg Hg Hg Hg	whole whole whole whole whole whole	NOTL UNR NOTL NOTL FE NOTL	1986-87 1979 1979-82 1983 1985 1985 <1986	45 144 202 50	900	2,600	1,600 10 <20 <20 70	1,402,00	<50 <20.	•		<ol> <li>(1)</li> <li>(4)</li> <li>(2)</li> <li>(2)</li> <li>(7)</li> <li>(7)</li> <li>(5)</li> </ol>
	Cd Cd Cd Cd Cd Cd Cd Cd Cd	whole whole whole whole whole whole	UNR NOTL FE NOTL FE NOTL	1979 1976-83 1985 1985 <1986 1986-87 1986-87	165 394 48 45	90 100	120 170		659,000 918,000	<1,000			<ul> <li>(4)</li> <li>(2)</li> <li>(7)</li> <li>(7)</li> <li>(5)</li> <li>(1)</li> <li>(1)</li> </ul>
	As As As As As As As	whole	UNR NOTL FE NOTL FE NÖTL	1979 1980-83 1985 1985 <1986 1986-87 1986-87	94 211 49 48	590 690	640 840		200 400 168,000 385,000	500- 1,100			(4) (2) (7) (7) (5) (1) (1) (1)
	tDDT p,p'-DDT p,p'-DDT p,p'-DDT p,p'-DDT p,p'-DDT p,p'-DDT	whole whole dis. dis. dis. whole	UNR NOTL FE NOTL	<1986 1979 1980-82 1981 1981 1981 1985-86	72 75 43	0.01	0.05	0.4 <1 0.2 0.015 0.02 11.2	0.5	<0.1	1	60	<ul> <li>(5)</li> <li>(4)</li> <li>(4)</li> <li>(4)</li> <li>(10)</li> <li>(8)</li> <li>(1)</li> </ul>
	p,p'-DDT p,p'-DDT	part. part.	FE NOTL	1986-87 1986-87	45 42	0.14 0.026	0.21 0.05	0.17	0.74 0.64				(1) (1) -

# TABLE 12 TOXIC CHEMICAL CONCENTRATIONS IN NIAGARA RIVER WATER (ppt)

TABLE 12 cont.

	, . 			Testing								¥	
	Chemical	Sample	Place	Date	#	Min	Ma×	Mean	SD	Median	DL	<dl< th=""><th>Ref.</th></dl<>	Ref.
	p,p'-DDE p,p'-DDE p,p'-DDE p,p'-DDE	whole whole dis. dis.	UNR NOTL FE	1979 1980-82 1981 1981	72 75			<1 0.3 ND	0.5	0.1	1		(4) (4) (4)
	p,p'-DDE p,p'-DDE p,p'-DDE p,p'-DDE p,p'-DDE	whole whole part. part.	NOTL NOTL FE NOTL	1981 1981 1985-86 1986-87 1986-87	5 43 45 42	0.1 0.32 0.044	ND 33.5 0.48 0.052	0.015 2.9 0.39 0.048	8.5 0.75 0.31		0.5		(4) (9) (8) (1) (1)
	dieldrin	whole	UNŔ	1979	72			<1	0101	·	1		(4)
	dieldrin dieldrin dieldrin	whole dis. dis.	NOTL FE NOTL	1980-82 1981 1981	75	х <sup>7</sup> х		0.6 0.26 0.27	0.3	0.6	3		(4) (4)
	dieldrin	dis. whole whole	NOTL NOTL	1981 1981 1985–86	5 43	0.2 ND	0.35		, , ,		0.5	60	(4) (10) (9)
,	dieldrin dieldrin	whole dis.	FE	<1986 1986-87	44	0.3	8.2 0.34	2.9 0.6 0.32	4.6 0.3	. *	•		(8) (5) (1)
	dieldrin dieldrin dieldrin	dis. part. part./	NOTL FE NOTL	1986-87 1986-87 1986-87	38 45 42	0.28 0.013 0.015	0.34 0.029 0.023	0.31 0.02 0.019	0.36 1.2 0.46		•	82	(1) (1) (1)
	a-BHC a-BHC	whole whole	UNŘ NOTL	1979 1980-82	72 75			7 10.5	5.2	9.7	: <b>1</b>		(4) (4)
	a-BHC a-BHC .a-BHC	dis. dis. dis.	FE NQTL:	1981 1981 1981		<1	8	2.89 5.5	•				(4) (4) (10)
	a-BHC a-BHC a-BHC	whole whole whole	LO NOTL	1981 1982 1985-86	5 244 43	ND 1 0.5	7 84 3.6	1.7	1.1	· · · · · ·	0.5	20	(9) (11)
	a-BHC a-BHC	whole dis.	FE	<1986 1986–87	. 4.9	2.71	2.33	10 2.51	0.3			2	(8) (5) (1)
	a-BHC a-BHC	dis.	NOTL	1986-87 1986-87	38		2.65 0.043	2.44	0.31	• .	-	<u></u> 3	(1) (1) (1)
	lindane lindane lindane lindane	dis. dis.	UNR NOTL FE NOTL	1979 1980–82 1981 1981	72 75			1 2.1 0.59 1.5	1.5	1.8	, 1	1	(4) (4) (4) (4)
	lindane lindane lindane lindane	dis. whole whole whole	LO	1981 1981 1982 <1986	5 245	0.5 ND <1	1.8 0.9 28	2		•	0.5	40	(10) (9) (11) (5)
	lindane lindane	dis.	FE NOTL	1986-87 1986-87	44 38	0.6 0.6	0.68 0.7	0.64	0.25 0.28				(1) (1)
	Mirex- Mirex Mirex	whole whole part.	NOTL	1980-82 <1986 1986-87	75 42	0.016	0.03	<0.1 0.3 0.022	0.74	<0.1			(4) (5) (1)
											-		

TABLE 12 cont.

	Chemical	Sample	Place	Testing Date	#	Min	Max	Mean	SD	Median	DL	%; <dl ref.<="" th=""><th></th></dl>	
	Toxaphene	whole	, <i>•</i>	<1986				0.6	•	· · ·		(5)	
	B(a)P B(a)P	whole part.	NOTL	<1986 1986–87	42	1.05	2.28	0.3 1.59	0.63			(5) 88 (1)	
	TeCB TeCB	dis. part.	NOTL NOTL	1986-87 1986-87	38 42	0.56 0.19	0.92 0.45	0.72	0.82 1.29			11 (1) 7 (1)	
	HCB HCB HCB HCB HCB HCB	whole whole whole whole whole dis.	UNR NOTL NOTL LO NOTL	1979 1980-82 1981 1982 1985-86 <1986 1986-87	72 75 5 245 43	<1 0.1 0.11	ND 8 4.3 0.13	<1 0_8 1_5 0_4 0.12	0.9 1.5 0.36	0.5	1 0.5	97 (4) 5 (4) 100 (9) 88 (11) (8) (5) 8 (1)	
-	HCB HCBD HCBD HCBD	part. whole dis. part.	NOTL NOTL NOTL NOTL	1986-87 1985-86 1986-87 1986-87	42 43 38 42	0.11 0.1 0.09 0.035	0.23 0.2 0.12 0.11	0.17 0.2 0.11 0.066	1.11 0.1 0.45 1.45	• • • • • •		28 (1) (8) 29 (1) 60 (1)	•
	PCBs PCBs PCBs PCBs PCBs PCBs PCBs PCBs	whole dis. dis. dis. whole whole dis. part. part.	UNR NOTL FE NOTL NOTL FE FE NOTL	1979 1980-82 1981 1981 1981 1981 <1986 1986-87 1986-87 1986-87	72 75 5 44 45 42	0.2 ND 2.57 0.88 1.42	1.3 39 3.26 1.14 1.91	5 19.9 0.26 0.8 10 2.9 1.0 1.66	34.7 0.09 0.49 0.54	11	20 5	81 (4) 3 (4) (4) (10) 50 (9) (5) 93 (1) 36 (1) 2 (1)	•
	TCDD TCDD PnCDD PnCDD HxCDD HxCDD HpCDD HpCDD OCDD OCDD OCDD TCDF TCDF PnCDF HxCDF HxCDF HxCDF HxCDF	dis. part. dis. part. dis. part. dis. part. dis. part. dis. part. dis. part. dis. part. dis. part. dis.		1984 1984 1984 1984 1984 1984 1984 1984	6 8 6 8 6 8 6 8 6 8 6 8 6 8 6 8 6 8 6 8	ND ND ND ND ND ND ND ND ND ND ND ND ND	ND ND 0.3 76 0.4 177 1.4 238 3.6 228 156 412 317 300 14 495 1.5					100 (3) 100 (3) 83 (3) 75 (3) 67 (3) 38 (3) 38 (3) 38 (3) 17 (3) 12 (3) 83 (3) 12 (3) 33 (3) 12 (3) 67 (3) 25 (3) 83 (3)	•

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TABLE 12 cont.

Chemical	Sample Place	Testino Date	<b>∃</b> #	Min	Max	Mean	SD	Median	DL	% <dl ref.<="" th=""></dl>
HpCDF	part.	1984	· . 8	ND	2,450					25 (3)
OCDF	dis.	1984	6	ND	0.5					33 (3)
OCDF	part.	1984	8	2.2	2,530					0 (3)

ND : not detected

Sample : whole = whole water; dis. = aqueous phase; part. = suspended particulate phase. Place : testing place

# : number of samples

SD : standard deviation

DL : detection limit

% <DL : percent below the detection limit

FE : Fort Erie

NOTL : Niagara-on-the-Lake

LNR : Lower Niagara River, north of Niagara Falls.

UNR : Upper Niagara River, south of Niagara Falls

LO : Samples taken from the Niagara River plume in Lake Ontario.

1. DOE, USEPA, MOE & NYDEC 1988. Minimum and maximum values represent 90% confidence intervals. Particulate concentration: Equivalent water concentration for particulate phase calculated as product of mean contaminant concentration on particulate and mean suspended sediment concentrations. Particulate conc. + dissolved concentration = whole water concentration.

ND: not detected or not analysed for.

2. Kuntz 1988b. Weekly samples.

3. Hallett and Brooksbank 1986

4. Kuntz 1984b. Weekly sampling.

5. Strachan and Eisenreich 1988. Mean value based on assessment of historical data up to 1985-86. These values were used in mass balance models.

6. DOE and MOE 1981.

7. Kuntz and Biberhofer 1986

8. Maguire and Tkacz 1988

9. Maguire et al. 1983. Samples taken at 5 stations along the river in July, 1981.

10. McCrea et al. 1985. Concentrations listed here are approximations.

11. Fox and Carey 1985. Samples from the Niagara River plume in Lake Ontario.

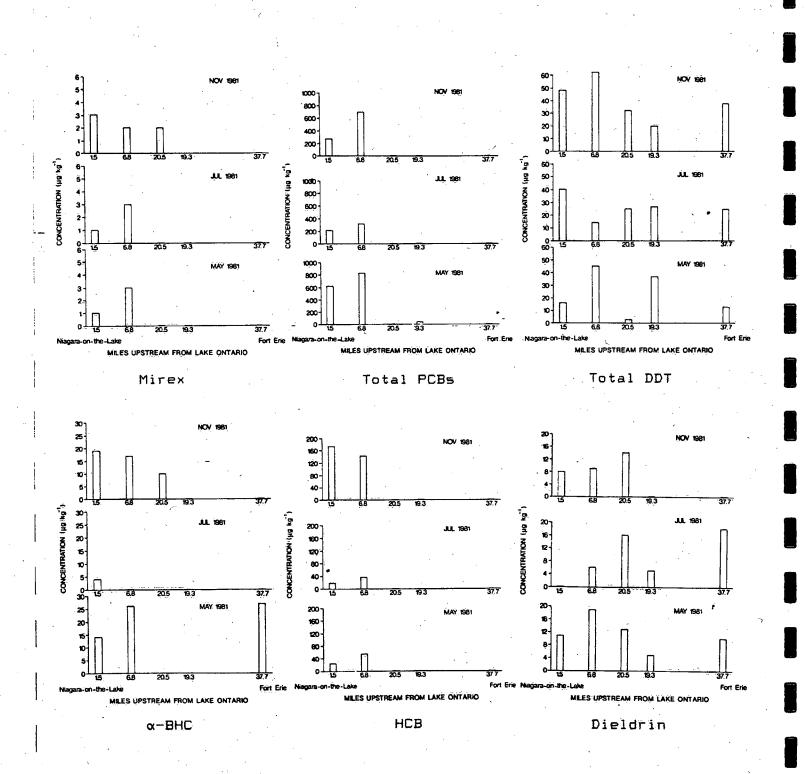
12. Warry and Chan 1981a

TABLE 13 cont.

Chemical	Sample Place	Testing Date	#	Min	Max	Mean	SD	Median	DL	。 くDL	Ref.
HCB HCB	part.* NOTL part.* FE	1979 <del>-</del> 81 1981	70			124	320	49		0	(1) (1)
НСВ	part.* NOTL	1981				73		,			(1)
PCBs	part.* NOTL	•	70	•		718	597	500			(1)
PCBs	part.* NOTL	1979-80	41			961	2,196			· 0	(2)
PCBs	part.* FE					ND					(1)
PCBs	part.* NOTL	1981				367					(1)
Sample : Place : t	whole = whole	water; c	is.	= aqueou:	s phase	• nart		ndod nan	+	- <b>1</b> - <b>4</b>	· · ·

3. DOE and MOE 1981.

FIGURE 13 DISTRIBUTIONS OF TOTAL DDT; DIELDRIN; MIREX; PCBs; α-BHC; HCB; AND PCBs (ALL ppb) IN SUSPENDED SEDIMENTS IN THE NIAGARA RIVER IN 1981. (Kuntz, 1984b)



SEDIMENTS	<u>(ppb)</u>						`.		
	Testing			• .				R	
Sample Pláce	Date	#	Min	Max	Mean	SD	Median	DL <dl< td=""><td>Ref.</td></dl<>	Ref.
3 cm UNR	1979	15	4,000	200.000			11 000	··· n	(2)
									(2)
					98.000	180.000			(1)
3 cm UNR	1979	15	<10	670			90	7	(2)
3 cm LNR	1979	9	30	3,200			340		(2)
2.54 cm	1981	16	20	2,450	607	754			(1)
					•		r.		
									(2)
							650	11	(2)
2.54 cm	1981	16	<100	19,000	2,200	4,400			(1)
	4070	4 5	1 000	14 000			0.000	~	(0)
•									(2)
						E 400	3,500	U	(2)
2.04 CM	1981	10	3,000	20,000	1,800	5,100			(1)
	1070	15	٦	51	7		R	n.	(2)
	1010	U	. 4	150			,0		1-1
3 cm UNR	1979	15		ND				100	(2)
			ND		. `		ND		(2)
2.54 cm	1981		<u> </u>		× ' .		<1		(1)
		•	,			,			
3 cm UNR	1979	15	1	19	,		3	0	(2)
3 cm LNR	1979	.8	4	36			· 9		(2)
2.54 cm	1981	16	<1	280			2.5		(1)
							ND		(2)
							5	28	(2)
2.54 cm	1981	16	<1	10			<1		(1)
0 (1940)	4000						-		(8)
									(2) (2)
								38	(2)
2.54 CM	1981	. ID	< 1	890			<1	4 - 1	(1)
3 cm UNP	1970	15	ND	1		•	ND	02	(2)
							ND		
							. 2		(2) (1)
		19	•1	-,			<b>د</b>		
3 cm UNR	1979	14		ND				100	(2)
			ND				ND		(2)
2.54 cm			<1						(1)
				, -					
3 cm UNR	1979	15	ND	. 22		•	ND:	93	(2)
3 cm LNR	1979		1				32		(2)
	Sample Place 3 cm UNR 3 cm UNR 2.54 cm 3 cm UNR 3 cm UNR 2.54 cm 3 cm UNR 3 cm UNR	Testing           Sample Place         Date           3 cm         UNR         1979           3 cm         LNR         1979           2.54 cm         1981           3 cm         UNR         1979           3 cm         UNR         1979           3 cm         UNR         1979           3 cm         UNR         1979           2.54 cm         1981           3 cm         UNR         1979	Testing Date #         3 cm UNR LNR LNR 1979 9       15         3 cm UNR LNR 1979 9       15         2.54 cm       1981 16         3 cm UNR LNR 1979 9       15         3 cm UNR LNR 1979 9       15         3 cm UNR 1979 15       16         3 cm UNR 1979 15       16         3 cm UNR 1979 8       16         3 cm UNR 1979 15       17         3 cm UNR 1979 15       16         3 cm UNR 1979 15       16         3 cm UNR 1979 15       17         3 cm UNR 1979 15       16         3 cm UNR 1979 15       16         3 cm UNR 1979 15 <td>Testing Sample Place         Testing Date         Min           3 cm         UNR         1979         15         4,000           3 cm         LNR         1979         9         6,000           2.54 cm         1981         16         9,000           3 cm         UNR         1979         9         6,000           3 cm         UNR         1979         9         6,000           3 cm         UNR         1979         9         6,000           3 cm         UNR         1979         9         30           2.54 cm         1981         16         20           3 cm         UNR         1979         9         4400           2.54 cm         1981         16         100           3 cm         UNR         1979         9         1,500           2.54 cm         1981         16         3,000           3 cm         UNR         1979         15         1           3 cm         UNR         1979         15         1           3 cm         UNR         1979         15         1           3 cm         UNR         1979         15         ND      <tr< td=""><td>Testing Sample Place Date         #         Min         Max           3 cm UNR 3 cm UNR 3 cm UNR 3 cm UNR 3 cm UNR 1979         1979 1981         15 6,000         4,000 60,000 2.54 cm         200,000 60,000 9,000           3 cm UNR 3 cm UNR 3 cm UNR 3 cm UNR 3 cm UNR 1979         1979 9         15 400         400 880 880 880 880 880 880 880 82.54 cm           3 cm UNR 3 cm UNR 1979         197 9         15 400         400 880 880 800 880 2.54 cm         880 880 800 880 800 880 2.54 cm           3 cm UNR 3 cm UNR 3 cm UNR 1979         197 15 1,900         14,000 8,200 20,000           3 cm UNR 1979         15 1,900         14,000 8,200 20,000           3 cm UNR 1979         15 1,900         14,000 8,200 20,000           3 cm UNR 1979         15 1         1 24 190           3 cm UNR 2.54 cm         1979 15 16         ND 74 2.54 cm           3 cm UNR 2.54 cm         1979 15 16         1 981           3 cm UNR 1979         15 1981         10 6           3 cm UNR 2.54 cm         1979 15 16         ND 640 2.54 cm           3 cm UNR 3 cm LNR 2.54 cm         1979 15 16         ND 16 640 2.54 cm           3 cm UNR 3 cm LNR 2.54 cm         1979 15 16         1 2.260           3 cm UNR 2.54 cm         1979 15 16         1 2.260           3 cm UNR 3 cm LNR 2.54 cm         1979 15 16</td><td>Testing DateMinMaxMean3 cmUNR1979154,000200,0003 cmLNR197996,00060,0002.54 cm1981169,000767,00098,0003 cmUNR197915&lt;10</td>6703 cmLNR19799303,2002.54 cm198116202,4506073 cmUNR197915&lt;400</tr<></td> 8803 cmLNR19799<400	Testing Sample Place         Testing Date         Min           3 cm         UNR         1979         15         4,000           3 cm         LNR         1979         9         6,000           2.54 cm         1981         16         9,000           3 cm         UNR         1979         9         6,000           3 cm         UNR         1979         9         6,000           3 cm         UNR         1979         9         6,000           3 cm         UNR         1979         9         30           2.54 cm         1981         16         20           3 cm         UNR         1979         9         4400           2.54 cm         1981         16         100           3 cm         UNR         1979         9         1,500           2.54 cm         1981         16         3,000           3 cm         UNR         1979         15         1           3 cm         UNR         1979         15         1           3 cm         UNR         1979         15         1           3 cm         UNR         1979         15         ND <tr< td=""><td>Testing Sample Place Date         #         Min         Max           3 cm UNR 3 cm UNR 3 cm UNR 3 cm UNR 3 cm UNR 1979         1979 1981         15 6,000         4,000 60,000 2.54 cm         200,000 60,000 9,000           3 cm UNR 3 cm UNR 3 cm UNR 3 cm UNR 3 cm UNR 1979         1979 9         15 400         400 880 880 880 880 880 880 880 82.54 cm           3 cm UNR 3 cm UNR 1979         197 9         15 400         400 880 880 800 880 2.54 cm         880 880 800 880 800 880 2.54 cm           3 cm UNR 3 cm UNR 3 cm UNR 1979         197 15 1,900         14,000 8,200 20,000           3 cm UNR 1979         15 1,900         14,000 8,200 20,000           3 cm UNR 1979         15 1,900         14,000 8,200 20,000           3 cm UNR 1979         15 1         1 24 190           3 cm UNR 2.54 cm         1979 15 16         ND 74 2.54 cm           3 cm UNR 2.54 cm         1979 15 16         1 981           3 cm UNR 1979         15 1981         10 6           3 cm UNR 2.54 cm         1979 15 16         ND 640 2.54 cm           3 cm UNR 3 cm LNR 2.54 cm         1979 15 16         ND 16 640 2.54 cm           3 cm UNR 3 cm LNR 2.54 cm         1979 15 16         1 2.260           3 cm UNR 2.54 cm         1979 15 16         1 2.260           3 cm UNR 3 cm LNR 2.54 cm         1979 15 16</td><td>Testing DateMinMaxMean3 cmUNR1979154,000200,0003 cmLNR197996,00060,0002.54 cm1981169,000767,00098,0003 cmUNR197915&lt;10</td>6703 cmLNR19799303,2002.54 cm198116202,4506073 cmUNR197915&lt;400</tr<>	Testing Sample Place Date         #         Min         Max           3 cm UNR 3 cm UNR 3 cm UNR 3 cm UNR 3 cm UNR 1979         1979 1981         15 6,000         4,000 60,000 2.54 cm         200,000 60,000 9,000           3 cm UNR 3 cm UNR 3 cm UNR 3 cm UNR 3 cm UNR 1979         1979 9         15 400         400 880 880 880 880 880 880 880 82.54 cm           3 cm UNR 3 cm UNR 1979         197 9         15 400         400 880 880 800 880 2.54 cm         880 880 800 880 800 880 2.54 cm           3 cm UNR 3 cm UNR 3 cm UNR 1979         197 15 1,900         14,000 8,200 20,000           3 cm UNR 1979         15 1,900         14,000 8,200 20,000           3 cm UNR 1979         15 1,900         14,000 8,200 20,000           3 cm UNR 1979         15 1         1 24 190           3 cm UNR 2.54 cm         1979 15 16         ND 74 2.54 cm           3 cm UNR 2.54 cm         1979 15 16         1 981           3 cm UNR 1979         15 1981         10 6           3 cm UNR 2.54 cm         1979 15 16         ND 640 2.54 cm           3 cm UNR 3 cm LNR 2.54 cm         1979 15 16         ND 16 640 2.54 cm           3 cm UNR 3 cm LNR 2.54 cm         1979 15 16         1 2.260           3 cm UNR 2.54 cm         1979 15 16         1 2.260           3 cm UNR 3 cm LNR 2.54 cm         1979 15 16	Testing DateMinMaxMean3 cmUNR1979154,000200,0003 cmLNR197996,00060,0002.54 cm1981169,000767,00098,0003 cmUNR197915<10	Testing         #         Min         Max         Mean         SD           3 cm         UNR         1979         15         4,000         200,000         3         3         0         180         100         180,000         180,000           2.54 cm         1981         16         9,000         767,000         98,000         180,000           3 cm         LNR         1979         15         <10	Sample Place Date         #         Min         Max         Mean         SD         Median           3 cm         LNR         1979         15         4,000         200,000         11,000         16,000           3 cm         LNR         1979         15         4,000         200,000         16,000           3 cm         LNR         1979         9         30         3,200         340           3 cm         LNR         1979         9         30         3,200         340           2.54 cm         1981         16         20         2,450         607         754           3 cm         UNR         1979         9         <400	Testing Sample Place Date         #         Min         Max         Mean         SD         Median         DL <dl< th=""> <dl< th="">           3 cm         UNR         1979         15         4,000         200,000         11,000         0           3 cm         UNR         1979         9         6,000         60,000         18,000         0           2.54 cm         1981         16         9,000         767,000         98,000         180,000         0           3 cm         UNR         1979         15         &lt;10</dl<></dl<>

# TABLE 14 TOXIC CHEMICAL CONCENTRATIONS IN NIAGARA RIVER BOTTOM SEDIMENTS (ppb)

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TABLE 14 cont.

Chemical	Sample Place	Testing Date #	Min	Max	Mean	SD	Median	DL.	∜ <dl ref.<="" th=""></dl>
PCBs	3 cm UNR	1979 13	ND	960			220	<i></i>	8 (2)
PCBs	3 cm LNR	1979 8	66	2,700		• •	280		0(2)
PCBs	2.54 cm	1981 16	<10	17,900		•	210		(1)

Tr: trace abundance
ND : not detected
Sample : depth of surficial sediment sample
Place : testing place
# : number of samples
SD : standard deviation
DL : detection limit
% <DL : percent below the detection limit
LNR : Lower Niagara River, north of Niagara Falls.
UNR : Upper Niagara River, south of Niagara Falls</pre>

1. Kuntz 1984b.

2. DOE and MOE 1981.

inputs to the delta were in 1950-54 followed by a leveling off after the older style rocking Hg electrodes were replaced in the After 1970, both Niagara Falls chloralkali chloralkali plants. plants began to reduce Hg concentrations in effluents. By 1971-72, they were down to a third of the peak in the early 1950's. By 1978 to 1979, the levels were about 12% of the 1969 to 1970 values and were approaching the levels representing the early 1940's (Breteler et al., 1984). In 1975 to 1981, high concentrations were found in the bottom sediments at nearly every station on the United States side between the Buffalo River and Love Canal. Values over 1 ppm Hg were observed in the Black Rock Canal and near Love Canal (Kuntz, 1984b). The Cd and As concentration distributions were similar to those for Pb and Hg. Many high values of Cd, above the MOE open water dredge spoil guilelines of 1 ppm were found in the Black Rock Canal, the Buffalo River, near Love Canal and at one site in the lower river. In the late 1960s-early 1970s, the As concentrations in sediments from the Niagara Basin of Lake Ontario were 13 times higher than those from the Eastern Basin of Lake Erie (NRTC, 1984). Levels of As in the Niagara River bottom sediments were generally below the MOE open water dredge disposal guideline of 8 ppm except in the Buffalo River and Black Rock Canal (Kuntz, 1984b).

The distribution of toxic chemicals in the bottom sediments of the Niagara River were last determined systematically in 1981 (Kuntz, 1984b). Parent DDT was found at 5 of 16 stations sampled. The highest DDT values were at the Black Rock Canal. Dieldrin was beneath the detection limit of 1 ppb at all but two sites. Mirex values were low throughout the entire river system except at one site near Love Canal where the concentration was 890 ppb. Based on bottom sediment analyses in 1981, Jaffe (1985) concluded that the 102nd Street waste site is a source of Mirex to the river. Kuntz (1984b) also reported on several other organic chemicals including methoxychlor, a and g-chlordane, various CB congeners, other DDT metabolites and a and g-endosulfan. No ambient water or sediment data has been reported for toxaphene in either the Niagara River or Lake Ontario (Strachan and Edwards, 1984).

### 2.7 LAKE ONTARIO

Lake Ontario, with a surface area of 19,000 km<sup>2</sup>, is the 5th largest of the Great Lakes. Its volume of 1,640 km<sup>3</sup> also ranks 5th in the Great Lakes but 11th in the world. With a maximum depth of 244 metres, it is the 2nd deepest of the Great Lakes. Retention time is about 8 years. By far the largest inflow of some 5,700  $m^3/s$  is from the Niagara River. In decreasing order of discharge, other main tributaries are the Oswego, Trent, Black, and Genesee Rivers. The lake's discharge rate is approximately 7,700 m<sup>3</sup>/s via the St. Lawrence River. Circulation in the southern section of Lake Ontario is to the east. The flow then turns north and travels west across the middle of the lake. South of Toronto, the current turns north and then east along the north shore. In the southwest, there is a counterclockwise circulation pattern. The Niagara River plume usually splits as it enters the lake with a smaller section joining the southwest counterclockwise circulation pattern and a larger section joining the easterly current along the south shore of the lake.

There has been extensive historical pollution of Lake Ontario from industrial, agricultural. and municipal sources. Industrialized harbours and embayments generally show the highest contaminant levels. Some of the main contaminants investigated in Lake Ontario are Hg, Mirex, PCBs, and CBs. Lake Ontario has the highest volume of Canadian urban runoff of persistent toxic substances (Marsalek and Schroeter, 1984). The main industrial centres are Toronto, Hamilton, and Rochester and other important ports are Kingston and Oswego. Seven areas, four in Canada, plus the Niagara River, have been designated as Lake Ontario Areas of Concern by the International Joint Commission.

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Constraints and Constraints an

### 2.7.1 CHEMICAL CONCENTRATIONS IN WATER

Toxic metals concentrations in Lake Ontario water (Table 15) are less than in lakes Erie and Michigan and greater than lakes Huron and Superior (Rossmann and Barres 1988). Concentrations of Pb in the waters of Lake Ontario are low and uniform with a small zone of higher concentrations at the extreme west end of the lake (Schmidt and Andren 1984, Neilson 1983). Lake Ontario has significantly less total and dissolved Pb than Lake Erie and significantly less dissolved Pb than Lake Michigan (Rossmann and Barres, 1988). Hq levels in Lake Ontario water are low (Table 15). Levels of total Hg in Lake Ontario were significantly less than those in Lakes Erie and Michigan while levels of dissolved mercury were significantly less than those of Lake Michigan (Rossmann and Barres 1988). In the late 1960s, Lake Ontario had the highest As concentrations of all the Great Lakes a maximum value of 1,200 ppt (Traversy et al., 1975) (Table 15). When dissolved and particulate As fractions are reported, the dissolved phase was at least 60% of the total concentration (Rossmann and Barres, 1988).

DDT was banned in the early 1970s but still enters the lake via the atmosphere, from the regional use of dicofol which contains traces of DDT and metabolites, and as a photolytic product of methoxychlor which is still used in the Great Lakes basin (Biberhofer and Stevens, 1987). In 1981, McCrea <u>et al.</u> (1985) found p,p'-DDT to be exclusively in the aqueous phase with an average concentration of just less than 0.04 ppt. In 1986, the mean concentration of p,p'-DDE in Lake Ontario (Table 15) was the same as in Lake Erie and about twice the concentration in Lake Huron.

In 1981, dieldrin concentrations of just less than 0.04 ppt in Lake Ontario were 100% in the aqueous phase (McCrea <u>et al.</u>, 1985). In 1983, Biberhofer and Stevens (1987) reported that the highest levels of dieldrin were in the mid-lake area rather than at near-shore stations. The average concentration of dieldrin in 1986 was similar to that of Lakes Erie, Huron, and Superior and

# TABLE 15 TOXIC CHEMICAL CONCENTRATIONS IN LAKE ONTARIO WATER (PPt)

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	Chemical	Sample	Testing Date	#.	Min	Max	Mean	SD	Median	DL	ିଞ୍ଚ <dl< th=""><th>Ref.</th><th></th></dl<>	Ref.	
	Pb	dis.	1985	22					· ND		91	(5)	
	Pþ	dis.	<1986				300	· · · ·				(11)	
	Pb	part.	1978	19	78	970						(2)	
	Pb	part.	1985	22					28		41		
	Pb	part.	<1986			· .	100					(11)	
	Pb	whole	1979	532	)	3,000	310-400			·, 500	67		
	Pb	whole	<1981		1,000	5,000			•	}		(12)	
	Pb	whole	1982	55		,	<500					(4)	
	Pb	whole	1985	22	•		• •		40			(5)	
	Hg	dis.	1985	22					11	-	96	(5)	
	Hg	dis.	<1986				20	1 e		·		(11)	
	Hg	part.	1985	22					ND			(5)	
	Hg	part.	<1986				5			•		(11)	
	Hg	whole	1970-71	132	ND	300	130	70				(6)	
	Hg	whole	1979	528		160	25-27			50	98	(1)	
	Hg	whole	<1981				<200						
	Hg	whole	1982	55			<10					(4)	
	Hg	whole	1985	22					10		73	(5)	
	Cd	dis.	1985	22					24		41	(3)	
	Cd	dis.	<1986				60					(11)	
	Cd	part.	1978	15	4.4	58				•		(2)	
	Cd	part.	1985	22					69		0	(5)	
	Cd	part.	<1986				60					(11)	
	Cd	whole	1979	532		300	50-60			100	.92	(1)	
	Cd	whole	<1981	,	<1,000	15,000			· ~			(12)	
	Cd	whole	1982	55			<200					(4)	
	Cd	whole	1985	22			4		96			(5)	
	As	dis.	1985	22			•		490		Q	(5)	
	As	part.	1985	22					24		86	(5)	
	As	whole	?1968	24	600	- 1;200	910			100	0	(3)	
	As	whole	1979	525			570-720			100		(1)	
	As	whole	1982	55			980		1		<i></i>	(4)	
	As	whole	1985	22					500	· .		(5)	
	As	whole	<1986				500					(11)	
	tDDT	dis.	<1986				0.1					(11)	
	tDDT	part.	<1986				0.1	۰,	· · ·			(11)	
	t DDT	whole	<1981		<10	60	35					(6)	
	tDDT	whole	1983	14	0.069	0.271	0.144	0.069	0.124			(10)	
	p,p'=DDT	whole	1986	31		ND				0.011	100		
•	o,p'-DDT	whole	1986	31		ND				0.011	100		
	p,p'-DDE	whole	1986	31	0.023	0.139	0.053			0.011		(8)	
		• •				· .				•			

TABLE 15. cont.

	Chemical	Sample	Testing Date	<b>#</b>	Min	Max	Mean	SD	Median	DĹ	% <dl< th=""><th>Ref.</th></dl<>	Ref.
•	dieldrin dieldrin dieldrin dieldrin dieldrin	dis. part. whole whole whole	<1986 <1986 <1981 1983 1986	14 31	1 0.259 0.075	10 0.631 0.514	0.3 0.1 4 0.405 0.331	0.14	0.48	0.011	• •	(11) (11) (12) (10) (8)
	a-BHC a-BHC a-BHC a-BHC	dis. part. whole whole	<1986 <1986 1983 1986	14 31	4.36 1.173	8.81 5.919	6.0 1.0 6.68 4.115	1.28	6.86 (	0.011	0	(11) (11) (10) (8)
	lindane lindane lindane lindane	dis. part. Whole Whole	<1986 <1986 1983 1986	1 <b>4</b> 31	0.806 0.311	1.85 2.276	2.0 0.2 1.3 1.313	0.34	1.26	0.011		(11) (11) (10) (8)
	Mirex Mirex Mirex Mirex	dis. part. whole whole	<1986 <1986 1983 1986	14 31		0.03 0.03 ND ND			4 .  	0.011	10 100	(11) (11) (10) (8)
	toxăphene toxaphene toxaphene toxaphene	part. whole	<1986 <1986 1981 1983	14	· ·	ND	0.4 0.2 0.6				100	(11) (11) (9) (10)
	B(a)P B(a)P	dis. part.	<1986 <1986	, 		•	0.2				•	(11) (11)
	HCB HCB HCB HCB	dis. part. whole whole whole	<1986 <1986 1980 1983 1986	5 14 31	0.02 0.017 0.02	0.1 0.103 0.113	0.04 0.02 0.06 0.052 0.063		0.042	0.01		(11) (11) (7) (10) (8)
	PCBs PCBs PCBs PCBs PCBs	dis. part. whole whole whole	<1986 <1986 <1981 1983 1986	14 31	2 0.32 0.484	50 3.1 5.189	0.6 0.3 0.95 1.41	0.71	0.78	0.24	0	(11) (11) (12) (10) (8)

ND : not detected

Sample : whole = whole water; dis. = aqueous phase; part. = suspended particulate phase.
# : number of samples

SD : standard deviation

DL : detection limit

% <DL : percent below the detection limit

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#### TABLE 15 cont.

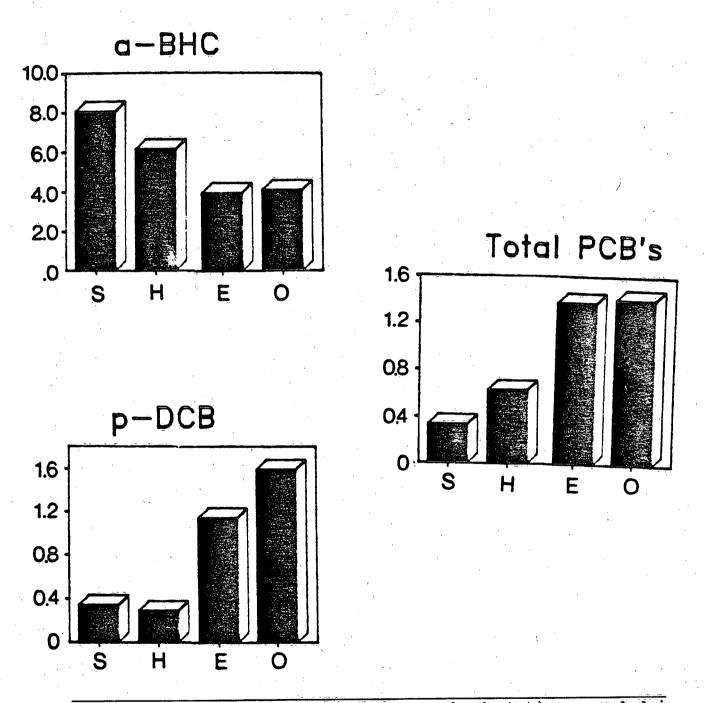
Construction of the second seco

- 1. Neilson 1983. The range represents the mean concentrations for 3 cruises.
- 2. Nriagu et al. 1980. Particulate conc.: ppt=ng/L.
- 3. Traversy et al. 1975.
- 4. Stevens 1987. Offshore waters.
- 5. Rossmann and Barres 1988. The number presented for "% below detection" actually represents the percent of analyses below the limit or criterion of detection. Particulate concentrations are ng/L.
- 6. Chau and Saitch 1973.
- 7. Oliver and Nicol 1982
- 8. Stevens and Nielson in press.
- 9. Sullivan and Armströng 1985
- 10. Biberhofer and Stevens 1987
- 11. Strachan and Eisenreich 1988. Mean value based on assessment of historical data up to 1985-86. These values were used in mass balance models. Part. conc.: ppt=ng/L. Particulate conc. + dissolved conc. = whole water conc.
- Sonzogni and Simmons 1981. Typical concentration range. These values are designed only to illustrate the types of values and the relative range of concentrations reported.

indicated that input is historical, atmospheric, or from resuspension of contaminated sediments (Stevens and Neilson, in In 1981, McCrea et al. (1985) found a-BHC and lindane press). completely in the aqueous phase at concentrations of 9 and 8 ppt In 1986, the mean concentration for a-BHC was respectively. similar to that of Lake Erie but lower than consentrations in Lakes Lindane concentrations were Huron and Superior (Figure 14). similar throughout the lakes (Stevens and Neilson, in press). The mean concentration of HCB in 1986, was lower than that of Lake Erie and higher than in lakes Huron and Superior (Stevens and Neilson, Mirex is extremely insoluble and was not detected in in press). the aqueous phase in 1977, 1981 and 1983 (Strachan and Edwards, 1984; McCrea et al., 1985; Biberhofer and Stevens, 1987) or in whole water samples in 1986 (Stevens and Neilson, in press). Mirex was detected in 1982 in water from Oswego Harbour (Mudambi <u>et al.</u>, 1983) where concentrations in the dissolved phase, ranged from beneath the detection limit (0.005 ppt) to 0.130 ppt. Strachan and Eisenreich (1988) calculated whole water concentration of Mirex in Lake Ontario to be 0.060 ppt. The mean toxaphene concentration of 0.6 ppt in Lake Ontario was the same as the average for all the Great Lakes for that year (Sullivan and Armstrong, 1985). Strachan and Edwards (1984) reported that there are no data for dioxins in the waters of Lake Ontario. Strachan and Eisenreich (1988) used a value of 3 ppt total water B(a)P concentration for their mass balance calculations. In 1981, the concentration of PCBs in the aqueous phase of Lake Ontario was 0.5 (McCrea et al., 1985). Ninety-one percent of the total PCBs was in the aqueous phase In 1983, the highest total PCB (McCrea et al., 1983). concentration (Table 15) was detected adjacent to Hamilton Harbour (Biberhofer and Stevens, 1987). Concentrations of PCBs in Lakes Ontario and Erie were significantly higher than those of Lakes Locations identified as having high PCB Huron and Superior. concentrations in 1983 were Black River Bay (1.9 ppt) and the Niagara River plume (1.1 ppt) (Biberhofer and Stevens, 1987). The central area of the lake in 1986 had PCB concentrations of 1.5 to 2.5 ppt, higher than values nearer the north and south shores (Stevens and Neilson, in press). Chlorinated benzenes were higher in Lake Ontario waters in 1986 than in any other of the Great Lakes. In particular there are major differences in concentrations of di, tri, and tetra chlorobenzenes between Lake Erie at its inflow to the Niagara River and Lake Ontario off and to the east of the mouth of the Niagara River (Figure 14) (Steven and Neilson, in press).

An extensive nepheloid layer was described in Lake Ontario (Sandilands and Mudroch, 1983) for depths greater than 60 m. Oliver and Charlton (1984) and Oliver <u>et al.</u> (1987) stated that resuspension occurred, especially during the winter months. At that time, Lake Ontario is unstratified and frequent violent storms can penetrate the lake to great depths. Oliver and Charlton (1984) found that given the amount of particulate matter available, the adsorption was low compared to theoretical partition coefficients and that concentrations of organic chemicals were generally higher in the suspended sediment fraction at deeper depths, indicating resuspension of bottom surface sediments. In 1981, Sandilands and Mudroch (1983) found that the suspended particulate concentrations of Pb were similar to the surface bottom sediment concentrations at the same locations.

Data on particulate metal concentration is given in Table 15. Most of the Pb in Lake Ontario water (approximately two thirds) was in the particulate fraction in 1978 (Nriagu <u>et al.</u>, 1980) and 1985 (Rossmann and Barres, 1988). In 1981, Sandilands and Mudroch (1983) found that the suspended particulate concentrations of mercury were less than the surface sediment concentrations at the same locations. Nriagu <u>et al.</u> (1980) reported higher particulate Cd concentrations in nearshore than offshore waters. When metal levels in each of the Great Lakes were compared (Rossmann and Barres, 1988), Lake Ontario was found to have significantly higher particulate Cd than Lakes Superior, Michigan, and Huron. Generally FIGURE 14 INTER LAKE COMPARISON OF MEAN CONCENTRATIONS OF a-BHC, TOTAL PCBS, AND p-DCB (ng.L<sup>-1</sup>). (STEVENS AND NEILSON, IN PRESS)



 All compounds were detected at a 100% of stations sampled in each lake. S=Lake Superior; H=Lake Huron; E=Lake Erie; O=Lake Ontario the concentration of particulate Cd in Lake Ontario decreases from west to east due to sedimentation (Lum, 1987). In 1981, Sandilands and Mudroch (1983) found that the suspended solids concentrations of As were less than the surface sediment concentrations at the same locations.

In 1981, one hundred percent of p,p'-DDT, 60% of p,p'-DDE, and 100% of dieldrin were in the aqueous phase in Lake Ontario (McCrea <u>et al.</u>, 1985). Among all the chlorobenzenes, HCB has the highest tendency to become associated with suspended sediments and most of the HCBs in Lake Ontario are in the bottom sediments (Oliver, 1984). Where Mirex was found in the lake, it was almost exclusively in the particulate phase (McCrea <u>et al.</u>, 1985). In Lake Ontario surface water, 91% of the PCBs were in the dissolved phase (McCrea <u>et al.</u>, 1985). Concentrations of toxaphene and B(a)P in Lake Ontario were calculated by Strachan and Eisenreich (1988). No information was found for dioxins/furans in the particulate phase. McCrea <u>et al.</u> (1985) reported that a-BHC and lindane were almost exclusively in the aqueous phase.

### 2.7.2 CHEMICAL CONCENTRATIONS IN BOTTOM SEDIMENTS

There are four sedimentation basins in Lake Ontario, named from west to east, Niagara, Mississauga, Rochester and Kingston. The major source of suspended sediment to the lake is the Niagara River. At the mouth of the river, sedimentation occurs off the Niagara Bar.

Concentrations of toxic chemicals in Lake Ontario bottom sediments are summarised in Table 16. Background levels of lead in Lake Ontario bottom sediments are 18-32 ppm. (Mudroch <u>et al.</u>, 1985). In 1968, surface sediments were enriched approximately six times above background Pb levels (Thomas and Mudroch, 1979). High concentrations of over 150 ppm conformed to the depositional basins indicating diffuse, rather than point sources (Thomas <u>et al.</u>, 1988). Levels of lead in the bottom sediments of the depositional basins of Lake Ontario were significantly higher than those of Lake

			CHHN CHHN								
Chemical	Sample	Testing Date	#	Min	Max	Mean	SD	Median	DL	% ≺DL	Ref.
 Pb Pb Pb Pb Pb	3 cm 1 cm	1968 ?1968 <1981 <1984 <1986	275 5	176,000 <50,000	287,000 285,000 >150,000 285,000	220,000	65,000 36,000	216,000		T	(5) (11) (1) (3) (2)
Hg Hg Hg Hg	3 cm 1 cm	1968 ?1968 <1981 <1984 <1986	275 5	25 540 25 140	2,100 3,950 3,900 3,950	651 2,350 800	511 130	2,650		· ·	(5) (11) (1) (3) (2)
Cd Cd Cd Cd	3 cm 1 cm	1968 ?1968 <1984 <1986	275 5	100 3,700 100	20,600 6,200 6,200	2,500 5,100 1,000	1,900 320	5,100			(5) (11) (3) (2)
As As As	3 cm 3 cm	1968 ?1968 <1984	275 8	200 1,500 200	22,500 14,000 17,000	3,300 4,100	4,700 3,800	2,800			(5) (4) (3)
tDDT tDDT tDDT p,p'-DDE DDE	3 cm 3 cm 3 cm	1968 <1981 <1986 1968 1981	229 229 6	0.5 0.5 26.8	218 70 130	42.8 <50 50 12.7 82	42.4 12.5 42	86	0.4		(14) (1) (2) (14) (10)
dieldrin dieldrin dieldrin	3 cm	1968 <1981 <1986	229		6.7	0.6 <3 10		· · · · · · · · · · · · · · · · · · ·	0.1	61	(14) (1) (2)
Mirex Mirex Mirex Mirex Mirex	3 cm 3 cm 3 cm	1968 1980 1981 1981 <1986	229 8 35 6	Ťr 3	62 65	33	8.3 16 25	95.5	1	67	(12) (15) (13) (10)
a-BHC	e station	<1986		· · ·		2	1 1		•		(2)
lindane		<1986				5	•				(2)
B(a)P B(a)P	•	<1986			· · ·	306 300			<b>~</b> .		(8) (2)

# TABLE 16 TOXIC CHEMICAL CONCENTRATIONS IN LAKE ONTARIO BOTTOM SEDIMENTS (ppb)

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Chemical Sam HCB HCB 3 ( HCB 3 ( HCB 3 ( HCB 3 ( HCB 3 ( HCB 2 ( HCB 2 ( HCB 3	cm 1981 cm 1981 <1986 1980 cm 1981 cm 1981 cm 1968 <1981 cm 1981 cm 1981 cm 1983 cm 1984 cm 1984 cm 1984 cm 1985 cm 1985 c	# 12 11 35 6 9 4 6 9 229 35 6 9 35 5 5 5	Min 7.6 9 16 150 62 Tr 24 12 ND 30 200 630 260 ND	Max 89 320 250 380 840 8.7 45 120 280 100 1200 1,500 840 0.004	Mean 97 112 226 220 10 34 35 57 80 606 844 570 100 4800	SD 63 73 230 7 32 56 256 420 220	Mēd i an 205 34 975	DL	0 0 4 0	Ref. (15) (9) (13) (10) (16) (2) (10) (16) (14) (13) (10) (16) (16) (2) (7) (6)
HCB HCB 3 ( HCB 3 ( HCB 3 ( HCB 3 ( HCB 2 ( HCB 2 ( HCB 2 ( HCB 2 ( HCB 2 ( HCB 3 ( HCB 2 ( HCB 3 ( HCB 2 ( HCB 2 ( HCB 2 ( HCB 2 ( HCB 3 ( HCB 2 ( HCB 3 ( HCB 2 ( HCB 3 ( HCB 2 ( HCB 3 ( HCB 2 ( HCB 2 ( HCB 2 ( HCB 3 ( HCB 2 ( HCB 2 ( HCB 3 ( HCB 3 ( HCB 2 ( HCB 3 ( HC	ample Date 1980 cm 1980 cm 1981 cm 1981 cm 1981 cm 1981 cm 1981 cm 1981 cm 1981 cm 1981 cm 1981 cm 1983 cm 1984 cm 1984 cm 1985 cm	# 12 11 35 6 9 4 6 9 229 35 6 9 35 5 5 5	7.6 9 16 150 62 Tr 24 12 ND 30 200 630 260 ND	89 320 250 380 840 8.7 45 120 280 100 1200 1,500 840 0.004	97 112 226 220 10 34 35 57 80 606 844 570 100	63 73 230 7 32 56 256 420	205 34		<dl 0 4 0</dl 	<pre>(15) (9) (13) (10) (16) (2) (10) (16) (14) (13) (10) (16) (2) (7)</pre>
HCB3 dHCB3 dHCB3 dHCB2 dHCB1 dHCBD3 dHCBD2 dHCBD3 dHCBD2 dPCBs3 dPCBs3 dPCBs3 dPCBs3 dPCBs2 dPCBs3 dPCBs3 dPCBs2 dPCBs2 dPCBs1 dTr:trace abuND : not deteSample : dept# : number ofSD : standardDL : detectio% <dl :="" perce<="" td="">1. Sonzogni a</dl>	cm 1980 cm 1981 cm 1981 cm 1981 <1980 cm 1981 cm 1981 cm 1981 cm 1981 cm 1981 cm 1981 cm 1981 cm 1983 cm 1984 cm 1984 cm 1984 cm 1984 cm 1985 cm 19	11 35 6 9 4 6 9 229 35 6 9 5 5	9 16 150 62 Tr 24 12 ND 30 200 630 260 ND	320 250 380 840 8.7 45 120 280 100 1200 1,500 840 0.004	112 226 220 10 34 35 57 80 606 844 570 100	73 230 7 32 56 256 420	34	5	0 4 0	<pre>(9) (13) (10) (16) (2) (10) (16) (14) (13) (10) (16) (2) (7)</pre>
HCBD3 dHCBD2 dPCBs3 dPCBs3 dPCBs3 dPCBs3 dPCBs2 dPCBs2 dPCBs1 dTr:trace abuND :not deteSample :dept# :number ofSD :standardDL :detection% <dl :<="" td="">percent1.Sonzognia</dl>	cm 1981 cm 1981 cm 1988 <1981 cm 1981 cm 1981 cm 1981 <1986 1983 cm 1987 bundance tected pth of surf of samples rd deviatio	6 9 229 35 6 9 5 	24 12 ND 30 200 630 260 ND	45 120 280 100 1200 1,500 840 0.004	35 57 80 606 844 570 100	32 56 256 420		5	4	<pre>(16) (14) (1) (13) (10) (16) (2) (7)</pre>
PCBs 3 c PCBs 3 c PCBs 2 c PCBs 2 c PCBs OCDD TCDD 3 c Tr: trace abu ND : not dete Sample : dept # : number of SD : standard DL : detectio % <dl :="" perce<="" td=""><td>&lt;1981 cm 1981 cm 1981 cm 1981 &lt;1986 1983 cm 1987 cm 1987 cm 1987 cm 1987 cm 1987 cm 1987 cm 1987 cm 1983 cm 1983 cm 1983 cm 1983 cm 1983 cm 1984 cm 1981 cm 1983 cm 1983 cm 1985 cm 19</td><td>35 6 9 5 </td><td>30 200 630 260 ND</td><td>100 1200 1,500 840 0.004</td><td>80 606 844 570 100</td><td>256 420</td><td>975</td><td>5</td><td>0</td><td><pre>(1) (13) (10) (16) (2) (7)</pre></td></dl>	<1981 cm 1981 cm 1981 cm 1981 <1986 1983 cm 1987 cm 1987 cm 1987 cm 1987 cm 1987 cm 1987 cm 1987 cm 1983 cm 1983 cm 1983 cm 1983 cm 1983 cm 1984 cm 1981 cm 1983 cm 1983 cm 1985 cm 19	35 6 9 5 	30 200 630 260 ND	100 1200 1,500 840 0.004	80 606 844 570 100	256 420	975	5	0	<pre>(1) (13) (10) (16) (2) (7)</pre>
TCDD 3 c Tr: trace abu ND : not dete Sample : dept # : number of SD : standard DL : detection % <dl :="" percent<br="">1. Sonzogni a</dl>	cm 198? bundance tected pth of surf of samples rd deviatio	icial se			4800				80	
ND : not dete Sample : dept # : number of SD : standard DL : detectio % <dl :="" perce<br="">1. Sonzogni a</dl>	tected pth of surf of samples rd deviatio		ediment s	sample					====	
	and Simmon	the dete s 1981.	Typica	l concent	ration r	ànge. T	hese valu	Jes a	re de	 esigne
only to i reported. 2. Strachan a up to 1985 3. Mudroch et from repor	illustrate and Eisenr 85-86. The	the type eich 198 se value . These hed betw	es of va 88. Mear es were u e numbers ween 1974	lues and n value k used in m s are a s	the rela based on bass bala summary o	assessme ince mode of concern	ge of con nt of his ls. tration (	ncent stori range	ratic cal c s tak	ons data ken
4. Travensy e 5. Thomas and 6. Onuska et 7. Czuczwa ar	nd Mudroch t al. 1983. and Hites 1	1979. De Wester	eposition	nal and r	-depositi non-depos	onal zon itional	es. zones.	· ·		
8. Eadie 1984 9. Oliver and 10. Bourbonn 11. Kemp and 12. Holdrinet 13. Oliver et 14. Frank et 15. Kaminsky	nd Nicol 19 niere et al d Thomas 19 et et al 19 et al. 1987	. 1986. 76b 78. Deposi . Deposi	sitiona itional ; sitional	l and nor zones. and non-	-deposit	ional zo	nes.		· · · ·	

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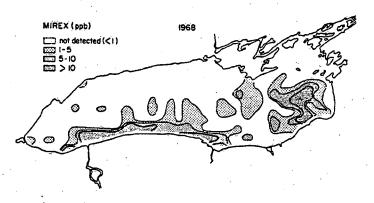
Huron and Lake Superior; and higher than those of Lakes Erie (Hodson et al., 1984). In a review of 1974-84 data, Mudroch et al. (1988) calculated that the range of Pb concentrations reported for the depositional zones for both Lake Ontario and Lake Erie were Also, the range of concentrations completely almost identical. enclosed (with much higher maximum values) those of Lakes Huron, However, they noted that comparison of Michigan and Superior. concentrations should be viewed with caution because of different sampling techniques employed. Background levels of mercury in sediments in depositional zones of Lake Ontario are 30-90 ppb (IJC, Background concentrations in the Niagara and Rochester 1987b). Basins are more than twice that of the Mississauga Basin (IJC, 1987b). The major source of anthropogenic Hg to Lake Ontario has Because of the effect of been the Niagara River (Thomas, 1972). the lake currents on the Niagara River plume, the highest concentrations of Hg were found in sediment along the south shore and in an area to the northwest of the river mouth (Figure 3). Eadie et al. (1983) suggested that, as well as the Niagara River, significant local sources of mercury could also be involved. The range of background levels of Cd in Lake Ontario is 0.9-3.7 ppm (Mudroch et al., 1985). There has been an obvious post-industrial rise of Cd in bottom sediments. In 1968, there were many areas with concentrations greater than 6 ppm Cd in bottom sediments from both depositional and non-depositional areas (Thomas and Mudroch, As of 1970-71, Cd levels were still increasing in the 1979). depositional basin sediments (Kemp and Thomas, 1976a). Lake Ontario has the highest sediment Cd concentration of the Great Lakes (Lum, 1987), approximately twice that of Lakes Michigan and Erie. Generally, Cd concentrations are higher in non-depositional zones and embayments (maximum levels of 18.6, 20.6, and 22.0 ppm respectively) than in the depositional zones (maximum level of 6.2 ppm) (Mudroch <u>et al.</u>, 1985). Background levels of As in Lake Ontario are not available. Mudroch et al. (1985) reported that surface sediment levels in depositional and non-depositional zones

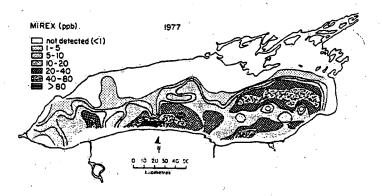
from the late 1960s early 1980s were 0.2-17.0 and 0.2-24.0 ppm respectively.

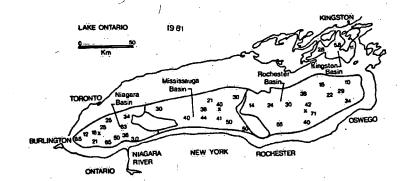
In 1968, Frank et al. (1979a) found **DDT** and dieldrin mainly in the surface bottom sediments of the depositional basins of the lake (Table 16). In 1981, the highest concentrations of DDT were found in bottom sediments along the western shore of the Kingston Basin (Stevens, 1987). In 1980, Oliver and Nicol (1982) reported CB concentrations in Lake Ontario sediments (Table 16) to be much higher than in Lakes Superior, Huron, and Erie (10-38 ppb). Also, the higher chlorinated CBs, associated with industrial activity, were more common in Lake Ontario than in the other lakes. In a surficial sediment survey, Oliver et al. (1987) found mean 1981 concentrations of HCB for the Niagara, Mississauga, Rochester and Kingston Basins to be 110, 130, 100, and 14 ppb respectively. In 1968, Holdrinet et al. (1978) observed areas of sediment with Mirex concentrations of over 10 ppb extending from the Niagara and Oswego Rivers (Figure 15). The mean concentration of Mirex in surficial sediments in 1968 was 7.5 ppb (Holdrinet et al., 1978). By 1977, large areas of the lake had concentrations of Mirex over 20 ppb (Thomas et al., 1988). The mean concentration in 1981 was 33 ppb (Oliver et al., 1987) based on fewer samples all from the depositional basins. Pickett and Dossett (1979) predicted that by 1989 the highest concentrations of Mirex would be in two plumes: at the mouth of the Niagara River and along the southern shore and adjacent to the mouth of the Oswego River, respectively. Eadie et al. (1983) predicted that the plume would move from the southern shore to the south-eastern shore and then to the Niagara and The predictions made by Eadie et al. (1983) are Rochester basins. closer to the results reported by Oliver et al., (1987), namely that by 1981 Mirex was becoming more evenly distributed in the sedimentary basins. No toxaphene values have been reported for Lake Ontario sediments (Strachan and Edwards, 1984). Onuska et al. (1983), calculated that PAHs introduced to the lake from the Niagara River generally moved to the east.

FIGURE 15

### CONCENTRATION OF MIREX (ppb) IN 3 cm SURFICIAL SEDIMENTS OF LAKE ONTARIO. (a) 1968 (Holdrinet et al., 1978); (b) 1977 (Thomas et al., 1988); AND (c) 1981 (Oliver et al., 1987).



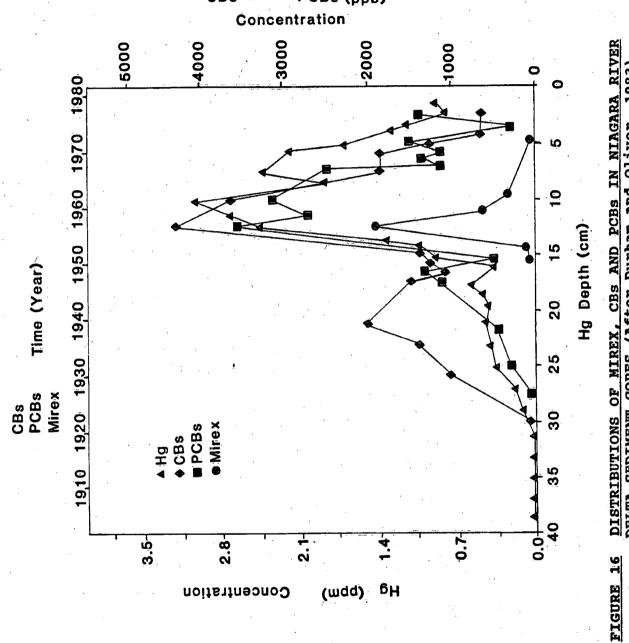




The congener profiles of PCDDs and PCDFs in Lake Ontario sediments were different from the other Great Lakes because of the high concentration of OCDF present (Czuczwa and Hites, 1986). The presence of OCDF indicates a local source which could be from the production of HCB and pentachlorophenol (PCP). HCDF, HpCDF, OCDF, and 2,3 7,8-TCDD were all detected in sediments offshore from the mouth of the Niagara River in the early 1980s (Onuska <u>et al.</u>, 1983; Kaminsky <u>et al.</u>, 1983). The maximum concentration for 2,3,7,8-TCDD in bottom sediment was 13 ppt (Onuska <u>et al.</u>, 1983).

In 1968 mean PCB concentration was generally higher (85 ppb) in the depositional than non-depositional (28 ppb) basins. The mean value for the whole lake was 58 ppb (n=216). A plume of >200 ppb PCBs extended from the mouth of the Niagara River. Minor plumes indicated other local sources along the north and south shores (Frank <u>et al.</u>, 1979a; Thomas and Frank, 1983) (Figure 4). The 1981 mean PCB concentrations (Oliver <u>et al.</u>, 1987) were considerably higher (570 ppb) than those of 1968 (58 ppb). Improved extraction and analytical techniques are the probable explanation.

sediment cores showed anthropogenic surface In 1970-71 enrichment of Hg, Pb, Zn, Cd, and Cu at all five stations in Lake Ontario (Kemp and Thomas, 1976a). In 1981, two cores taken from the eastern end of the lake were shown to have subsurface maximum concentrations of Hg (Figure 16) and Pb. However, surface levels (120-150 ppm) were still considerably higher than background (Eadie et al., 1983). The cores indicated that the average Pb flux to Lake Ontario increased 680% from the early 1800s to the time of maximum lead usage in the mid-1970s (Eadie <u>et al.</u>, 1983). Surface sediment Pb levels are still elevated at 100-200 ppm near the Niagara River mouth in the early 1980's (Mudroch, 1983). Recovery from mercury pollution, as seen in sediment cores, was the most dramatic for the toxic metals (Mudroch, 1983; Mudroch et al., In a core taken in 1970, mercury contamination was shown 1988). to increase rapidly between the turn of the century and the early



CBs Mirex PCBs (ppb)

DELTA SEDIMENT CORES (After Durham and Oliver, 1983)

AND DISTRIBUTION OF HG IN AN EASTERN LAKE ONTARIO

SEDIMENT CORE (After Eadie et al., 1983)

1940s. Between then and 1970, mercury concentrations increased at a slower rate and were in the range of 1-1.5 ppm (Thomas, 1972). This dramatic increase was also seen in cores sampled 1970-71 from the depositional basins. Surface concentrations were reported as being higher for the Niagara and Rochester Basins than for the Mississauga Basin. The surface sediment concentration range for the three basins was 2.6-3.9 ppm (Kemp et al., 1974). Cores taken in 1981, from both ends of the lake showed a reversal of this trend (Eadie et al., 1983; Mudroch, 1983) (Figure 16). Îmmediately adjacent to the mouth of the Niagara River, subsurface maximum Hg concentrations ranged from 4-7 ppm. Surface levels were approximately 1 ppm. Ranges in the eastern cores were slightly lower. The Hg distribution shows that this site of former maximum surficial sediment Hg concentration now has surface sediment concentrations less than those of surficial sediments farther out in the lake. The presently more contaminated sediments remain well within benthic organism mixing depths, whereas the former maximum concentrations near the Niagara River mouth are now below this depth (Allan, 1986).

In 1976, cores showed the highest concentrations of  $\Sigma DDT$  in the surface sediments and first appearance in the late 1950s (Frank <u>et al.</u>, 1979a). In a 1982 core, peak levels of **DDT** were again seen in the late 1950s to the early 1960s, in good agreement with usage patterns (Oliver et al., 1987). Oliver and Nicol's (1982) core showed that increases of CBs in sediment began in the early 1940s and began to decline by the late 1960s (Figure 16). This corresponds to the use of CBs in the production of phenols. There was little, if any, change in the the proportions of the various chlorobenzenes down this core. Cores analysed by Onuska et al., (1983) also showed that there may have been a decrease in chlorobenzene loading from the Niagara River during the 1970s. HCBD and OCS concentrations in cores also peaked (160 ppb and 550 ppb respectively) in the 1960s and 1970s respectively. Low concentrations of HCBD occurred prior to the late 1950s and after

the early 1970s, with high concentrations during the 1960s (Durham and Oliver, 1983). Sediment core analyses reflected Mirex production in the Niagara River area (Durham and Oliver, 1983; Eadie <u>et al.</u>, 1983) (Figure 16). Because concentrations continued to increase and expand in the lake sediments after production ceased (in 1976), remobilization of contaminated Niagara River sediments has been suspected (Thomas <u>et al.</u>, 1988). Durham and Oliver (1983) found the highest concentrations of PCBs to be at sediment depths corresponding to early 1960s (Figure 16). Sediment core samples showed up to a 100 times increases in PAH's in the surface over deeper sediments, indicating extensive loading in the late 1970s.

### 2.8 ST. LAWRENCE RIVER

The St. Lawrence River drains Lake Ontario and thus the Great Lakes to the north Atlantic ocean. The St. Lawrence River has a massive flow out of Lake Ontario of some 7,700 m<sup>3</sup>/sec. The mean concentration of suspended solids in the river at its source in Lake Ontario was 1.3 mg/L (mean of four years of data). The international section of the river included in the Great Lakes Water Quality Agreement stretches from Lake Ontario to the Province of Quebec and thus does not include Lake St. Francis. Major industries are located on the Canadian and United States shores of the river just upstream from Quebec. They include a major foundry, automobile plant, and two large aluminium plants. In the Cornwall ärea, a former chor-alkali plant released Hg to the St. Lawrence and resulted in high Hg levels in downstream bottom sediments. Near Maitland, a former tetraethylead plant was a source of alkylleads to the river.

### 2.8.1 CHEMICAL CONCENTRATIONS IN WATER

In the St. Lawrence River in 1977, the mean concentrations of the metals discussed here were 0.50 to 1.01 ppb Pb; ND - 0.004 ppb Hg; beneath detection for Cd; and 0.55 - 0.73 ppb As between Kingston and Cornwall (Chan, 1980). These results were based on unfiltered water. Between 1977 and 1983, water samples from the St. Lawrence outflow from Lake Ontario were routinely analysed for inorganic chemicals (Sylvestre et al., 1987). Values less than the detection limit were taken as equal to the detection limit for calculation of means. The mean concentrations for Pb between 1977 to 1983 was 1.2 ppb (n= 341). No data was given for Hg, Cd or As. Between 1979 and 1982 filtered water samples showed that Hg concentrations at Cornwall - Massena were below 0.2 ppb. The metal most studied recently in the river has been Cd. Lum and Kaiser (1986) reported dissolved Cd concentrations of 3 - 23 ppt (mean = 10ppt; n=11).

In 1977, lindane and a-BCH, were detected in water in the St. Lawrence between Kingston and Cornwall at concentrations from 3 to 7 ppt and 3 to 8 ppt respectively (Chan, 1980). In 1982, water and suspended sediments collected at the source of the St. Lawrence River near Wolfe Island, began to be analysed routinely for toxic organic chemicals (Sylvestre, 1987). The chemicals determined were PCBs, PAHs, CBs and organochlorine pesticides. In whole water, only 3 of the 18 organochlorine pesticides measured were detected in more than 40% of the samples. Mean concentrations for 1982 to 1984 were 5.8 ppt a-BHC; 1.0 ppt lindane; and 0.4 ppt dieldrin (Sylvestre, 1987). The results for <40% detection were not considered meaningful to calculate means using the detection limit as the lower value. When larger volume samples (200 L versus 2 L) were extracted in 1983, other chemicals were detected above the improved detection limit. The results from this 1983 study were 4.8 ppt a-BHC, 1.2 ppt lindane; 0.54 ppt dieldrin (all similar to the above); 0.17 ppt total DDT; and 0.43 ppt total PCBs. Mirex remained beneath detection. McCrea et al., (1985) found that DDT and its metabolites were from 38 to 100% in the aqueous phase in the St. Lawrence River. Concentration of pp-DDT was 0.065 ppt in the aqueous phase and 0.02 ppt in the suspended solids, while PCB's were present at 2.0 ppt in the aqueous phase and at less than 0.1 ppt in suspended solids. In 1977, PCB's were detected in water at the mouth of the Grassé River at concentrations of 60 and 180 ppt. Levels of 20 to 70 ppt in water and up to 660 ppb PCBs in suspended solids were measured at the mouth of the Grassé River between 1979 and 1982 (MOE, 1988a).

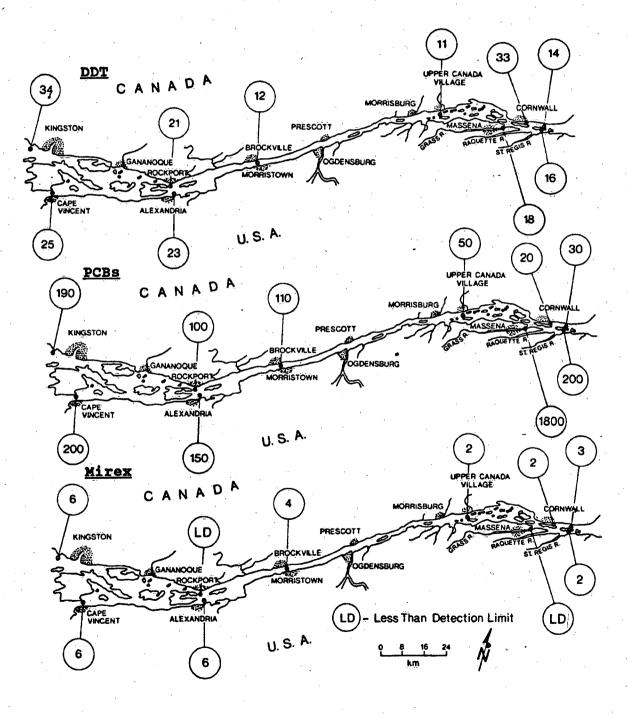
Lum and Kaiser (1986) reported particulate Cd concentrations of 1.0 to 3.8 ppm (mean = 2.1 ppm; n = 12) for 1985. Between Cornwall and Massena, suspended solids had Hg concentrations of up to 2.4 ppt in 1979-82. Between Kingston and Cornwall, Merriman (1987) reported concentration ranges in suspended solids of <1-2 ppb a-BHC; <1 ppb lindane; <1-14 ppb dieldrin; <1-16 ppb p,p'DDT; 7-18 ppb p,p'DDE; 11-34 ppb total DDT and metabolites; <1 to 6 ppb

Mirex; 1-27 ppb HCB; and 30 to 126 ppb total chlorobenzenes in 1981. The spatial distributions of total DDT and metabolites, total PCB's and Mirex are given in Figure 17. Between 1982 and 1984, lindane was beneath the detection limit of 4 ppb while a-BHC and dieldrin were detected in more than 40% of the samples at mean concentrations of 6 ppb and 9 ppb respectively in suspended solids collected at Wolfe Island (Sylvestre, 1987). PCB's were detected in 93% of the samples at a mean value of 162 ppb. Total DDT was found in 90% of the samples at a mean concentration of 18 ppb. Mirex was detected in 33% of the samples and concentrations ranged from beneath the detection limit of 4 ppb to a maximum of 27 ppb. A mean for Mirex could not be reasonably calculated with 33% detection but the mean of the concentrations above detection was 9.8 ppb (n= 26). In 1981, the range of Mirex concentrations had been from beneath detection to 6 ppb (Figure 17). The occurence of some chlorinated benzene congeners in suspended solids was >50%. The mean concentrations, maximum values are in brackets, were 32 ppb (131) 1, 2, 4-tri; 14 ppb (95) 1, 2, 3, 4-tetra; 11 ppb (56) penta; and 13 ppb (54) hexachlorobenzene (Sylvestre, 1987). Most PAH's were not detected in the suspended solids at a detection limit of 50 ppb and the few exceptions were possibly the result of interference in the analyses.

# 2.8.2 CHEMICAL CONCENTRATIONS IN BOTTOM SEDIMENTS

In 1975, Kuntz (1988a) collected bottom sediments between Kingston and Cornwall and Cape Vincent and Masenna on the Canadian and United States sides of the St. Lawrence River. Pb concentrations ranged from the detection limit of 50 ppm up to 190 ppm. Mercury concentrations were usually well below 0.3 ppm, except for a site immediately downstream of Cornwall where the concentration was 4.9 ppm. Concentrations of Cd were generally below the detection limit of 10 ppm. Five of fifty-six samples were above detection and the maximum Cd value was 14 ppm just downstream of the Grassy River. For As, the concentrations ranged

# FIGURE 17 TOTAL DDT AND METABOLITES; PCBs; AND MIREX IN SUSPENDED SOLIDS IN THE ST. LAWRENCE RIVER IN 1981 (Merriman, 1987).



up to 7.6 ppm on the Canadian side and 8.0 ppm on the United States side of the river.

In 1975, p,p'-DDT was not detected in any of the 57 samples analaysed (Kuntz, 1988a). For p,p'-TDE several concentrations above the detection limit, in the range of 3-11 ppb, were observed in the Gananoque-Rockport area; p,p'-DDE was usually below the detection limit of 1 ppb and its maximum concentration was 90 ppb. In 1981, the highest concentration of total DDT and metabolites was 56 ppb just off Kingston (Merriman, 1987) (Figure 17). The maximum HCB concentration detected in 1981 was 13 ppb for the seven sites sampled (Merriman, 1987) and the values were in the Dupont outfall zone near Maitland (MOE, 1988b). The bottom sediment survey of 1975 did not detect Mirex in any of the samples at a detection limit of 1 ppb (Kuntz, 1988a). In 1981, Merriman (1987) detected Mirex at only one site near Kingston at 9 ppb. In 1975, Kuntz (1988a) found levels of PCB's above 50 ppb at 10 of 57 stations. The highest value was 1.5 ppm downstream of the Grassy River. In 1981, the highest bottom sediment PCB concentration was 8.74 ppm (Merriman, <u>1987</u>). Total chlorobenzenes were found in low concentrations of 8-9 ppb in St. Lawrence River bottom sediments (Merriman, 1987). The maximum concentration was 50 ppb.

#### CONCLUSIONS

The purpose of this report was to give an overview of toxic chemical concentrations along with historical concentration trends in water and sediments of the Great Lakes. Until recently we have relied on analyses of bottom sediments and in particular cores of bottom sediments as a surrogate method to detect trends in chemical inputs and concentrations in water in the lakes. This is easier to do for chemicals in sediments than water because of historical problems in analysis of waters for the extremely low ambient concentrations that existed. From the available sediment data, the trends for the chemicals discussed all seem to be downwards at least relative to the concentrations 10 and 15 years ago. Thus, the historical trends of chemical concentrations in lake bottom sediment cores indicate that the major influx of toxic metals and persistent toxic organic chemicals to the Great Lakes aquatic ecosystem took place in the nineteen sixties and early seventies. These peak concentrations are followed by declines into the early eighties. Some of these declines have been dramatic, once control action has taken place (PCBs; Mirex). Often, these periods of peak input of several chemicals to the Great Lakes occurred several years prior to their first detection in lake media. Thus, the overall evidence from the abiotic data is that the maximum inputs of most of those toxic metals and persistent, chlorinated, organic chemicals so far detected occurred in the past and that the inputs of such chemicals have declined, often dramatically in recent There are some exceptions along the St. Clair River years. Detroit River corridor and the Niagara River where concentrations are at a plateau rather than declining.

### 3.1 Trends

Some changes in concentrations of contaminants over time have been determined for each of the lakes and channels. In Lake Superior, historic data for concentrations of Pb, Hg and Cd could not be used to determine trends in the waters. Arsenic concentrations in whole water declined since the 1970s. There has been a dramatic reduction in PCB concentrations in the waters and sediments of Lake Superior since the early to mid-1970s. Of the metals discussed in this report, Pb in sediments had a higher anthropogenic enrichment factor than Hg, Cd and As. In recent core analysis, Pb and Hg are shown to be decreasing in the surface sediments. Historic data for concentrations of Pb, Hg and Cd in Lake Michigan could not be used to determine trends in the waters. Arsenic concentrations in whole water declined since the 1970s. Pb has decreased in the sediments from high levels in the 1950s-Cd has shown similar declines from highs in the 1940s-1960s. PCBs have declined from peak levels in the 1960s-1970s. 1960s. In Lake Huron, historic data for Hg, Cd and As in water could not be used to determine trends. Dissolved Pb concentrations have There are indications that levels of Pb, declined in Lake Huron. Cd and DDT in the water of Saginaw Bay have declined since the 1970s. In cores taken prior to 1980, there was surface enrichment of Pb, Hg, Cd and As. Hg in most parts of the St. Clair River has decreased in the bottom sediments, however, levels are often still above the dredging guideline. Core studies have also shown slight declines in sediment concentrations of HCB, HCBD and PAHs. For Lake St. Clair, PCBs, Hg and DDT decreased in bottom sediments following curtailment of use in the early 1970s. The concentrations of HCB and HCBD in the sediments of Lake St. Clair are still increasing or at least not dropping significantly. Generally, Hg has decreased in the bottom sediments of the Detroit River, however, levels are often still above the dredging guideline. In Lake Erie historic Pb data could not be used to determine trends in the water. Hg, Cd and As concentrations in water are decreasing. PCBs may be decreasing in the water of Lake Erie. Cores collected in the early 1970s showed anthropogenic increases of Pb, Hg and PCBs. More recent cores showed surface declines of Pb, As, DDT and metabolites, dioxins and furans. PCBs may not be declining in the

sediments. During the 1980s, point source loadings to the Niagara River declined by over 60% on each side of the river. Because of changes in analytical methods, water samples from the early 1980s could not be compared to those of the mid-1980s. Between the mid-1970s and the 1980s, Pb loadings from the Niagara River to Lake Ontario were reduced by half. Peak levels of Hg in the sediments of the delta occurred in the early 1950s. By the end of the 1970s, Hg levels were back to pre-1940 levels. From the late 1960s to the early 1980s, Mirex and PCBs in surface sediments of Lake Ontario appeared to increase; however, improved analytical and sampling techniques are the probable explanation because core analyses refute this. Core analysis showed anthropogenic enrichment of Pb, Hg, Cd, DDT, CBs, HCBD, OCS, Mirex, PCBs and PAHs in bottom sediments but concentrations are now declining or levelling off. In the St. Lawrence River, Pb and Hg concentrations in sediments have declined following closure of source industries.

# 3.2 Interlake and Interchannel Comparisons

The most chemically contaminated Great Lakes were lakes Ontario, Michigan, and Erie based on an assessment on overall concentrations of toxic and persistent chemicals in abiotic aquatic media. Lake Superior was and is the least contaminated of the Great Lakes. Lake Huron is one of the least contaminated of the lakes with the exception of some local areas.

# 3.2.1 Sources and Physical Characteristics

The types of sources and the physical characteristics of the lakes and channels influence the relative concentrations in each area. The atmosphere is a greater source of most of the critical toxic chemicals to the upper Great Lakes than the lower lakes; for example, PCBs, DDT and Pb. The large surface areas and drainage basins of the upper lakes are major contributing factors. Conversely, the lower lakes receive greater inputs from their main tributaries, industries, municipalities and agriculture than the Elevated levels of Pb, Hg and Cd have been reported for some of the bays and harbours. All Rossmann's metal concentrations in Lake Superior were below the GLWQA objectives. Highest levels of toxic chemicals in the St. Marys River were generally found along the Canadian shore. For Lake Michigan, concentrations of toxic organic chemicals are usually higher in the southern section of the lake and Green Bay. PCB concentrations are highest in the sediments of the southwest part of the lake. Saginaw and Georgian Bays are the major sources of toxic chemicals to Lake Huron. In the St. Clair River elevated toxic chemical concentrations are confined primarily to a 100 meter wide area along the Ontario shore near Sarnia's chemical industrial area; for example, PCBs, volatile hydrocarbons, Pb and Hg. Spills are a significant problem. Increases in water and/or sediment concentrations over the course of the river have been reported for Pb, Hg, HCB, HCBD, OCS, and PAHS. Levels above the GLWQA objectives have been found for Pb, HCB and HCBD, and above dredging guidelines for OCS, PAHs and PCBs. For Lake St. Clair, PCBs have been reported as highest on the western side. Elevated levels of sediment contaminants have been found in the central depositional basin and at the outlet. In the Detroit River the majority of sources are along the U.S. shore and along the Chemical concentrations in water and/or sediment Rouge River. which have been reported to increase along the river are Cd, PCBs, CBs, dieldrin, lindane, industrial volatile halocarbons and PAHs. Levels above dredging guidelines have been reported for Pb. Hg, Cd, As, PCBs, PAHs, a-BHC, and lindane. The western basin of Lake Erie is the most impacted by toxic chemicals mainly because of inputs from the Detroit River; for example, PCBs and industrial halocarbons in water; PCBs, HCB, HCBD, and PAHs in sediments; and DDT and metabolites, Hg and Cd in sediments in the 1970s. The main sources of toxic chemicals to the Niagara River are along the U.S. shore. Concentrations of many contaminants are higher in the water and sediments of the Tonawanda Channel than the Chippawa Channel. Since there is extensive mixing at Niagara Falls, no plume

develops. Increases along the course of the river were observed in the late 1970s-1980s for PCBs, a-BHC, lindane, CBs (sometimes including HCB), HCBD, Mirex, p,p'-DDE, Hg, Cd, As, PAHs and B(a)P. Sources of dioxins and furans have also been found. Concentrations for Hg, As, PCBs, Mirex, HCB and HCBD are much lower in the sediments of Lake Erie than those of Lake Ontario. DDT and metabolites have recently been shown to decrease between Fort Erie and Niagara-on-the-Lake. For Lake Ontario, the Niagara River has historically been the main source of toxic chemicals. These chemicals initially collect in a pattern in the sediments which Eventually they reside in the reflects lake circulation. depositional basins. Along with other dioxins and furans, 2,3,7,8-TCDD has been detected in the sediments offshore from the mouth of the Niagara River.

### 3.4 Data Reliability

The historically documented higher concentrations for metals in water are now thought to reflect sampling and particularly analysis in non-metal free (dusty) environments. The use of special sampling and clean laboratory techniques is now revealing that dissolved concentrations of Pb, Cd and other metals are much less (in the low ppt range) than previously thought (in the low ppb range). Likewise recent sampling techniques using large volume aqueous phase or continuous flow extraction systems have allowed reliable detection of toxic organic chemicals at extremely low concentrations (< 1 ppt) in water samples. Historical data on toxic organic chemical concentrations in water mostly included nondetected concentrations or resulted in high concentrations which now must be viewed with caution.

If the values recorded are taken at face value then there have been dramatic reductions in some chemicals such as Pb, Cd and PCBs in some of the lakes. Declines in concentrations over the last few years are probably realistic. The most recent data, obtained for both toxic metals and organic chemicals is considered the most reliable and shows that ambient concentrations are very low, much lower than historically measured and thus believed.

### 3.5 Nearshore/Offshore Variations

Data on the types of toxic chemicals discussed here is rare for nearshore areas. There is data for the connecting channels and the concentrations of chemicals in water in these channels can vary considerably over short periods of time. The same would be true at nearshore sites if they were located under the influence of tributaries or effluents from industry or municipalities. Data on the nearshore areas of Canada is in the process of being acquired under the Remedial Action Plans (RAPs) for Areas of Concern (AOCs) and under the Ontario Municipal and Industrial Strategy for Abatement (MISA) Programmes.

There is no simple relationship between raw water toxic chemical content and that of drinking water taken from the Great Drinking water intakes are all located nearshore, often Lakes. within a kilometre or less of the shoreline. Wave action or storms can resuspend nearshore sediments or cause upwelling of deeper lake water on an event basis or can cause small creeks to dramatically increase their sediment load to the nearshore zone. In essence, each site is unique since it may be near a major municipal effluent or a unique industry. Drinking water treatment plants are designed to take these local variations into account by filtering the raw water and by removing suspended and probably colloidal material by flocculation. Thus, from a human exposure viewpoint, nearshore ambient toxic chemical concentrations are best assessed by analyses of treated drinking water. The only entirely Canadian Area of Concern from which drinking water is taken is the Bay of Quinte and toxic chemicals are not the main reason for this Bay being an AOC.

The open water data presented here is a better measure of total lake contamination and can be better used for comparison with information obtained by analysis of open lake fish. However, there is no simple relationship between the concentrations of chemicals in water and sediments and the concentrations in biota in the lakes. Some scientists claim that the majority of chemicals are taken up directly by fish from the water by bioconcentration. Others favour the concept that the chemicals are primarily bioaccumulated in the food chain. For biota which inhabit contaminated sediments or for fish which eat organisms living in such sediments, the sediments or their porewater may be a major source of chemicals. For some fish it may well be all three, i.e. water, sediments, and other biota. The mix will be different for different organisms, at different trophic levels, with different diets and dependent on local contamination.

### 3.6 Present State of the Environment

In the last five years (1982 to 1987) no new contaminants which fit the criteria of widespread occurrence, high toxicity, and long persistence, similar to the chemicals discussed in this report, have been detected in any of the Great Lakes. There are analytical techniques that could detect other chemicals, for example highly toxic but rapidly degraded pesticides, but the scale of the problem in space and time is unlikely to ever be as bad as it once was. To a greater extent than in the past, control actions will have to take into account the non-point sources of the chemicals, especially from atmospheric sources; chemicals recycled internally from in-situ contaminated sediments; agricultural, forestry and urban sources; and groundwater sources. Such control sequencing and in-situ remedial actions will rely heavily on accurate source assessments and mass balances for the connecting The next major steps in the channels and for whole lakes. continued recovery of the Great Lakes from toxic chemical contamination will result from the implementation of Remedial Action Plans for the Areas of Concern and from the application of load based controls as part of Lakewide Management Plans. Thus, with the renewed efforts required by the 1987 Great Lakes Water Quality Agreement Protocol, the recovery of the lakes from chemical

contamination should continue.

In the 1978 Great Lakes Water Quality Agreement, Canada and the United States called for a virtual elimination of persistent toxins from the Great Lakes with an eventual goal of zero discharge of persistent, toxic organic chemicals. Since 1978, action has taken place at many locations, not the least of which is the Niagara Frontier, the Detroit and St. Clair Rivers, and at many Areas of Concern to reduce or eliminate toxic loads to the Great Lakes. Rather than wait for absolute evidence of a link between toxic chemicals and human health effects, Canada and the United States have acted to proceed toward a toxic free Great Lakes environment.

## APPENDICES

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## APPENDIX 1

# 1. CHEMICAL ABBREVIATIONS

*2,3,7,8-TCDD *2,3,7,8-TCDF	2,3,7,8-Tetrachlorodibenzo-p-dioxin 2,3,7,8-Tetrachlorodibenzofuran
AS	Arsenic
*B(a)P	Benzo(a)pyrene
BHCS	hexachlorocyclohexanes
a-BHC	alpha-1,2,3,4,5,6-BHC
g-BHC	gamma-1,2,3,4,5,6-BHC; use Lindane
CBs	Chlorobenzenes
Cđ	Cadmium
DCB	Dichlorobenzene
*DDD (TDE)	Dichlorodiphenyl dichloroethane
*DDE	Dichlorodiphenyl dichloroethylene
*DDT	Dichlorodiphenyl trichloroethane
*Dieldrin	use for HEOD
Dioxins	see PCDD
*HCB	Hexachlorobenzene
HCBD	Hexachlorobutadiene
HCH	use BHC
HEOD	use Dieldrin
*Hg	Mercury .
*Mirex	Dodecachloropentacyclodecane
OCS	Octachlorostyrene
OCDD	Octachlorodibenzo-p-dioxin
OCDF	Octachlorodibenzofuran
PAHS	Polynuclear Aromatic Hydrocarbons
*Pb	Lead
*PCBs	Polychlorinated Biphenyls
PCDD	Polychlorinated dibenzo-p-dioxin
PCDF	Polychlorinated dibenzofuran
PCP	Pentachlorophenols
PERC	Perchloroethylene; use for Tetrachloroethene
QCB	Pentachlorobenzene
TCB	Trichlorobenzene
TCDD	use for 2,3,7,8-TCDD
TCDF	use for 2,3,7,8-TCDF
TCP	Trichlorophenol
TeCB	Tetrachlorobenzene
*Toxaphene	use for Chlorinated Bornane
Zn	Zinc

: Main chemicals discussed in this report. : IJC Primary Track Chemicals.

4.0

# 2. ABBREVIATIONS

AOC CCREM	Area of Concern Canadian Council of Resource and Environmental Ministers
DOE	Environment Canada
FË	Fort Erie
GLWQA	Great Lakes Water Quality Agreement
IJC	International Joint Commission
MISA	Municipal-Industrial Strategy for Abatement
MOË	Ontario Ministry of the Environment
NOTL	Niagara-on-the-Lake
NRC	National Research Council
NRTC	Niagara River Toxics Committee
NYDEC	New York Department of Environmental Conservation
RAP	Remedial Action Plan
RSC	Royal Society of Canada
TSM	Total Suspended Matter
UGLCCS	Upper Great Lakes Connecting Channel Study
USEPA	United States Environmental Protection Agency

#### APPENDIX 2

#### GLOSSARY

Area of Concern: a geographic area that fails to meet the General or Specific Objectives of the Agreement where such failure has caused or is likely to cause impairment of beneficial use of of the area's ability to support aquatic life (IJC 1988)

Bioaccumulation: general term describing a process by which chemical substances are accumulated by aquatic organisms from water directly or through consumption of food containing the chemicals (CCREM 1987)

Bioassay: test used to evaluate the relative potency of a chemical by comparing its effect on a living organism with the effect of a control, without the test chemical, which is run under identical conditions (CCREM 1987).

Bioconcentration: a process by which there is a net accumulation of a chemical directly from water into aquatic organisms resulting from simultaneous uptake (e.g. by gill or epithelial tissue) and elimination (CCREM 1987).

Bioconcentration factor (BCF): a unitless value describing the degree to which a chemical can be concentrated in the tissues of an organism in the aquatic environment. At apparent equilibrium during the uptake phase of a bioconcentration test, the BCF is the concentration of a chemical in one or more tissues of the aquatic organisms divided by the average exposure concentration in the test. (CCREM 1987)

Biomagnification: result of the processes of bioconcentration and bioaccumulation by which tissue concentrations of bioaccumulated chemicals increase as the chemical passes up through two or more trophic levels. The term implies an efficient transfer of chemicals from food to consumer, so that residue concentrations increase systematically from one trophic level to the next (CCREM 1987).

Bioturbation: the physical disturbance of sediments by burrowing and other activities of organisms (CCREM 1987).

Carcinogen: a substance which induces cancer in a living organism (CCREM 1987).

Congener: a different configuration or mixture of a specific chemical usually having radical groups attached in numerous potential locations (UGLCCS 1989).

Contaminant: a substance foreign to a natural system or present at unnatural concentrations (UGLCCS 1989).

Detection Limit: The smallest concentration or amount of a substance which can be reported as present with a specified degree of certainty by a definite, complete analytical procedure (CCREM 1987).

Dioxin: a group of approximately 75 chemicals of the chlorinated dibenzodioxin family, including 2,3,7,8-TCDD which is generally considered the most toxic form (UGLCCS 1989).

Dredging Guidelines: procedural directions designed to minimize the adverse effects of shoreline and underwater excavation with primary emphasis on the concentrations of toxic materials within the dredge spoils (UGLCCS 1989).

Effluent: a complex waste material (e.g. liquid industrial discharge or sewage) which may be discharged into the environment (CCREM 1987).

Great Lakes Water Quality Agreement: a joint agreement between Canada and the United States which commits the two countries to develop and implement a plan to restore and maintain the many desirable uses of the waters in the Great Lakes Basin. Originally signed in 1978, the Agreement was amended in 1987 (UGLCCS 1989).

Guideline (water quality): numerical concentration limit or narrative statement recommended to support and maintain a designated water use (CCREM 1987).

Half-life: the time require for the concentrations of a substance to diminish to one-half of its original value in a lake or water body (1978 Agreement).

Loading: the amount of a substance added per unit of lake area per unit time (CCREM 1987).

Mass-Balance Approach: a management approach in which the aim is to eliminate accumulation of pollutants what will degrade water quality or have adverse affects on living organisms. This approach requires establishment of a mass-balance budget in which the amounts of contaminants entering the system less the quantities stored, transformed, or degraded within the system must equal amounts leaving the system. Application of this approach depends on quantification of sources and effects of contaminants and mathematical modeling to simulate probable longterm consequences (NRC and RSC 1985). Municipal-Industrial Strategy for Abatement: the principal goal of this program is the virtual elimination of toxics discharged from point sources to surface waters in Ontario (UGLCCS 1989).

Mutagen: any substance or effect which alters genetic characteristics or produces an inheritable change in the genetic material (UGLCCS 1989).

Nepheloid Layer: regions of turbid bottom water characterized by a maximum in light scattering and particle concentration. Possible sources of nephloid material are eroded shore material, suspended matter brought in a large river, deep sediments eroded by bottom currents, and organic matter settling from surface layers (Chambers and Eadie 1981; Sandilands and Mudroch 1983).

Nonpoint source: source of pollution in which pollutants are discharged over a widespread area or from a number of small inputs rather than from distinct, identifiable sources (UGLCCS 1989).

Objective (water quality): a numerical concentration limit or narrative statement which has been established to support and protect the designated uses of water at a specified site (CCREM 1987).

Octanol-water partition coefficient  $(P_{ow})$ : the ratio of a chemical's solubility in n-octanol and water at equilibrium. The logarithm of  $P_{ow}$  is used as an indication of a chemical's propensity for bioconcentration by aquatic organisms (CCREM 1987).

Persistent toxic substance: any toxic substance with a half-life in water of greater than eight weeks (1978 Agreement).

Point Source: a source of pollution that is distinct and identifiable, such as an outfall pipe from an industrial plant (UGLCCS 1989).

Primary Track Chemicals: These chemicals are Great Lakes contaminants of known concern, for which abatement and corrective action has been taken, but for which additional measures are required because of their continued presence in the ecosystem at unacceptable levels. They were selected by the IJC. (IJC 1987b)

Range: the difference between the lowest and highest values in a set of data (CCREM 1987).

Remedial Action Plan: this is a plan to be developed with citizen involvement to restore and protect water quality at each of the 42 Areas of Concern in the Great Lakes Basin. The RAP will identify impaired uses, sources of contaminants, desired use goals, target clean-up levels, specific remedial options, schedules for implementation, resource commitments by Michigan and Ontario as well as by the federal governments, municipalities and industries, and monitoring requirements to assess the effectiveness of the remedial options implemented (UGLCCS 1989).

Resuspension: the remixing of sediment particles and pollutants back into the water by storms, currents, organisms and human activities such as dredging (UGLCCS 1989).

Suspended Sediments/Solids: particulate matter suspended in water (UGLCCS 1989).

Teratogen: an agent that increases the incidence of congenital malformations (CCREM 1987).

Toxic Substance: A substance that can cause death, disease, behavioral abnormalities, cancer, genetic mutations, physiological or reproductive malfunctions, or physical deformities in any organisms or its offspring or that can become poisonous after concentration in the food chain or in combination with other substances (NRC and RSC 1985).

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