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Great Lakes Water Quality Board Report to the International Joint Commission

> GD ZZ., IJC. 70 83N564 1983 Report on Great Lakes Water Quality Appendix Great Lakes Surveillance

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Great Lakes Water Quality Board Report to the International Joint Commission

1983 Report on Great Lakes Water Quality

Appendix

Great Lakes Surveillance

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Great Lakes Water Quality Board

Report to the International Joint Commussion.

1983 Report on Great Laker Writer Quality

Appendix

Great Lakes Surveillance

Table of Contents

CHAPTER	TITLE	PAGE
	LIST OF TABLES	v
	LIST OF FIGURES	ix
1.0	INTRODUCTION	T
2.0	ASSESSMENT	5
Α.	Lake Superior	6
Β.	Lake Michigan	10
С.	Lake Huron	10
D.	Lake Erie	35
Ε.	Lake Ontario	42
F.	Connecting Channels	51
	St. Marys River Detroit River Niagara River St. Lawrence River	5 1 53 57 58
	References Cited	59
3.0	EMERGING ISSUES AND DEVELOPMENTS	61
Α.	Dioxin and Furan	61
Β.	РАН	66
С.	Toxaphene	82
	References Cited	87
4.0	WATER QUALITY ASSURANCE	95
5.0	PHOSPHORUS LOADINGS 1981 AND 1982	105
6.0	SURVEILLANCE ACTIVITIES AND INITIATIVES	121
	MEMBERSHIP LIST	127
	ACKNOWLEDGEMENTS	129

Table of Contents

-

List of Tables

TABLE	TITLE	PAGE
2.0-1	PCB and DDT Levels in Lake Trout from Four of the Great Lakes	7
2.0-2	Selected Organochlorine Contaminant Residues in Whole Fish Rainbow Smelt, 1981	8
2.0-3	Selected Organochlorine Contaminant Residues in Herring Gull Eggs from the Great Lakes, 1980	9
2A-1	Mean Organochlorine Contaminant Concentrations in Lake Superior Lake Trout	11
2A-2	Mean Concentration Of Selected Organochlorine Contaminants in Herring Gull Eggs From Two Lake Superior Colonies	12
2B-1	Mean Organochlorine Contaminant Concentrations in Lake Michigan Lake Trout	13
2B-2	Mean Concentration of Selected Contaminants in Herring Gull Eggs from Big Sister Island, Lake Michigan, 1971-1980	13
2C-1	Annual Means of Selected Physico-Chemical Variables from Lake Huron Historical Data Base	15
20-2	Summary of 1980 Estimated Phosphorus Loading to Lake Huron	16
2C-3	Comparisons of Nutrient Concentration in Lake Huron Between 1971 and 1980 and Georgian Bay Between 1974 and 1980	18
2C-4	Summary of 1980 Lake Huron Median Trace Metal Concentrations in Water and the Partioning of Trace Metals Between the Dissolved and Particulate Fractions	21
20-5	Evaluation of Toxic Unit Concept as Applied to 1980 Total Trace Metal Concentration of Lake Huron Water	22
20-6	Comparison of Metal Concentrations in Recent Sediments with Those in Older Sediments	23
20-7	Mean Organochlorine Contaminant Concentrations in Lake Huron Lake Trout	25
20-8	Mean Concentration of Selected Trace Metal and Organochlorine Contaminants in Lake Huron Rainbow Smelt	26

List of Tables - cont'd.

TABLE	TITLE	PAGE
2C-9	Mean Concentration of Selected Organochlorine Contaminants in Herring Gull Eggs from Two Lake Huron Colonies	27
2C-10	Pairwise Comparisons for Perch PCB Body Burden Caught in Different Segments of Saginaw Bay, 1977-1980	34
20-11	Bioconcentration Factors for A1242, A1260 and TPCB in Saginaw Bay Yellow Perch, 1977-1980	34
2D-1	Mean Concentration of Selected Trace Metals and Organochlorine Contaminants in Lake Erie Walleye	а 36
2D-2	Mean Concentration of Selected Trace Metal and Organochlorine Contaminants in Lake Erie Rainbow Smelt	37
2D-3	Mean Organochlorine and Mercury Contaminant Concentrations for Young-of-the-Year Spottail Shiners from Selected Sites in the Lower Great Lakes	38
2D-4	Mean Concentration of Selected Organochlorine Contaminants in Herring Gull Eggs from Two Lake Erie Colonies	41
2E-1	Evaluation of Toxic Unit Concept as Applied to 1979 Trace Metal Concentration of Lake Ontario Water	48
2E-2	Mean Concentration of Selected Trace Metals and Organochlorine Contaminants in Lake Ontario Age 4 ⁺ Lake Trout	49
2E-3	Mean Concentration of Selected Trace Metal and Organochlorine Contaminants in Lake Ontario Rainbow Smelt	50
2E-4	Mean Concentration of Selected Organochlorine Contaminants in Herring Gull Eggs from Two Lake Ontario Colonies	52
2F-1	Water Quality of Range DT 3.9 Located at the Mouth of the Detroit River	54
2F-2	Loadings to Lake Erie from the Detroit River	55
3A-1	Possible Number of Positional PCDD and PCDF Isomers	62
3A-2	Dibenzofuran Residues in Parts Per Trillion in Samples from the Great Lakes	64
3A-3	Dibenzo-P-Dioxin Residues in Parts Per Trillion in Samples from the Great Lakes	65
3A-4	2,3,7,8-Tetrachlorodibenzo-P-Dioxin Residue in Parts Per Trillion in Whole Fish Composite Samples of Young-of-the-Year Spottail Shiners from the Niagara River	67

List of Tables - cont'd.

1-

TABLE	TITLE	PAGE
3B- 1	Summary of Water Solubility and Partitioning Information	71
3B-2	Atmospheric Flux of PAH to the Great Lakes	73
3B-3	Range of Concentrations of PAH in Great Lakes Surficial Sediments	74
3B-4	Lake Michigan Sediment PAH	74
3B-5	Human Exposure to PAH from Various Environmental Sources	78
3B-6	Population Data for the Great Lakes States	79
3B-7	Estimated PAH Emissions	80
3C-1	Toxaphene in Great Lakes Whole Fish Residues	84
3C-2	Concentration of Toxaphene in Cold-Water Fish Samples from the Upper Great Lakes, 1977 and 1979	85
3C-3	Concentrations of Toxaphene-Like Compounds in Composited Samples of Lake Michigan Lake Trout	86
4.0-1	Median Values for Total Phosphorus in Water	97
4.0-2	Total Phosphorus in Water, Summary of Performance by Study by Laboratory	98
4.0-3	Comparisons of Medians Obtained for a Sample on Study No. 42 to Medians Obtained on the Same Sample in Studies No. 33 and 29	99
4.0-4	Comparison of Medians Obtained for Two Samples on Study No. 42 to Medians Obtained on the Same Two Samples in Study 39	100
4.0-5	Comparison of Median Results for Unpreserved Samples of Major Ions and Nutrients in Water Used in Two Interlaboratory Studies	5 101
5.0-1	Summary of 1981 Estimated Atmospheric, Industrial, Municipal and Tributary Phosphorus Loading Data to the Great Lakes	107
5.0-2	Summary of 1981 Estimated Phosphorus Loading Data to Lake Superior	108
5.0-3	Summary of 1981 Estimated Phosphorus Loading Data to Lake Michigan	109
5.0-4	Summary of 1981 Estimated Phosphorus Loading Data to Lake Huron	110

List of Tables - cont'd.

TABLE	TITLE	PAGE
5.0-5	Summary of 1981 Estimated Phosphorus Loading Data to Lake Erie	111
5.0-6	Summary of 1981 Estimated Phosphorus Loading Data to Lake Ontario	112
5.0-7	Summary of 1981 Estimated Phosphorus Loading Data to the International Portion of the St. Lawrence River	113
5.0-8	Summary of 1982 Estimated Atmospheric, Industrial, Municipal and Tributary Phosphorus Loading Data to the Great Lakes	114
5.0-9	Summary of 1982 Estimated Phosphorus Loading Data to Lake Superior	115
5.0-10	Summary of 1982 Estimated Phosphorus Loading Data to Lake Michigan	116
5.0-11	Summary of 1982 Estimated Phosphorus Loading Data to Lake Huron	117
5.0-12	Summary of 1982 Estimated Phosphorus Loading Data to Lake Erie	118
5.0-13	Summary of 1982 Estimated Phosphorus Loading Data to Lake Ontario	119
5.0-14	Summary of 1982 Estimated Phosphorus Loading Data to the International Portion of the St. Lawrence River	120

List of Figures

FIGURE	TITLE	PAGE
2C-1	Comparison of the Distribution of <u>Fragilaria</u> <u>capucina</u> in Southern Lake Huron in 1974 and 1980	19
2C-2	Segments in Saginaw Bay used for Data Analysis of Interpretation	29
2C-3	Comparison of Dissolved Ortho-Phosphate Phosphorus in Segment 2 of Saginaw Bay in 1974 and 1980	30
2C-4	Comparison of Nannoplankton Less Filaments and Colonies in Segment 2 of Saginaw Bay in 1974 and 1980	31
2C-5	Comparison of the Nitrate-Plus-Nitrite/Phosphate Phosphorus Ratio in Segment 2 of Saginaw Bay in 1974 and 1980	32
2C-6	Comparison of Phytoplankton Crop Composition vs. Time in Segment 2 of Saginaw Bay	33
2E-1	Function Map of Lake Ontario used for Data Analysis and Interpretation	43
2E-2	Area - Weighted Mean Whole Lake Spring Total Phosphorus Concentrations	44
2E-3	Box Plots of Whole Lake Spring Total Phosphorus Concentrations	45
2E-4	Box Plots of Whole Lake Spring Nitrate-Plus-Nitrite Concentrations	47
2F-1	Long-Term Water Quality Trends at the Detroit River Mouth, Water Years 1967 Through 1980	56
3A-1	Ring Structures of Polychlorinated Dibenzofurans and Polychlorinated Dibenzo-p-Dioxins	62
3A-2	2,3,7,8-TCDD Concentration in Herring Gull Eggs in 1980 from Selected Great Lakes Nesting Colonies	68
3B-1	Ring Structures of the Most Common PAH in Environmental Samples	69
3B-2	The Equilibrium Distribution of PAH (and other organic contaminants) Within the Water Column of the Great Lakes	71
3B-3	The Distribution of Fluoranthene in the Surficial Sediments of Lake Michigan	75

List of Figures - cont'd.

FIGURE	TITLE	PAGE
3B-4	Lake Michigan Benzo(a)pyrene Budget	76
3B-5	Atmospheric Concentration of Benzo(a)pyrene in the Great Lakes Region	81
6-1	Sampling Grid for the Monitoring and Surveillance Stations in Lake Ontario	122
6-2	Prevalence of Lip Papillomas in White Suckers from Lakes Huron and Ontario as the Percent of Total Male and Female Fish Greater than 40 cm in Fork Length Collected by Electrofishing During Spring Spawning Runs for the Years 1981 Through 1983.	125

- x -

I. Introduction

Surveillance and monitoring activities are conducted in each of the Great Lakes to establish the degree to which jurisdictional pollution control requirements are being met, to determine achievement of the general and specific objectives given in Articles III, IV and Annex 1 of the 1978 Great Lakes Water Quality Agreement, to provide information for measuring local and whole lake response to control measures and to identify emerging problems. Specifically, these are the requirements of Annex 11 of the Agreement. The Great Lakes International Surveillance Plan (GLISP) has been the "model" framework for providing this information.

The Surveillance Work Group notes that despite some shortcomings in implementation by the jurisdictions, GLISP nonetheless has provided a mechanism for accruing considerable compatible information on the environmental quality of the Great Lakes. A substantial effort has gone into surveillance and monitoring activities over the last five years and much more compatible and usable data now exist as a result of this effort.

An important feature of the GLISP was a 9-year cycle of intensive surveys for each of the lakes. The intensive years for Lake Michigan were 1976/77, Lake Erie 1978/79, Lake Huron 1980, Lake Ontario 1981/82 and for Lake Superior 1983. The final report for Lake Michigan was released in 1980. The final reports for the intensive surveys on Lakes Erie, Huron and Ontario are still in various stages of preparation. Highlights of available data have been incorporated into assessments of the environmental quality of these lakes in Chapter 2 of this report.

These intensive surveys represent the most comprehensive surveillance and monitoring studies conducted on the Great Lakes in over a decade. Moreover, surveillance and monitoring activities conducted within the GLISP framework have provided a mechanism to detect long-term trends in the lakes, specifically relating to particular control measures (e.g., control of phosphorus, PCBs, DDT, etc.).

In many ways, 1983 is a landmark year for Great Lakes surveillance activities. Implementation of the Lake Superior study this year represents completion of the intensive lake-by-lake rotational cycle originally outlined in the GLISP. As reported in Chapter 6 of this report, the Surveillance Work Group, on the basis of the additional knowledge and experience gained through these studies, is currently improving the planning and implementation of binational surveillance and monitoring activities on each of the Great Lakes and Connecting Channels. In this regard, the Surveillance Work Group is particularly cognizant of the shift in emphasis which has occurred since the signing of the 1972 Agreement from eutrophication to concern with toxic substances contamination of the Great Lakes basin. These new issues and changing priorities are placing additional demands on the program for surveillance information. Nevertheless, monitoring efforts on eutrophication must not be jeopardized. In particular, there is need to continue trend analyses for phosphorus to monitor water quality improvements achieved through phosphorus abatement programs.

The Surveillance Work Group recognizes that the ability to detect toxic substances has increased substantially in recent years primarily because of advancements in analytical technology. This fact is readily apparent by examining the comprehensive data in this year's Appendix E. Unfortunately, the ability to ascertain the environmental and/or human health significance of these compounds has not kept pace with the improvements in analytical capability. The presence of organic compounds such as TCDDs, PCDFs, toxaphene and PAHs which are known to be deleterious to the aquatic ecosystem must be incorporated into planned surveillance activities despite the high analytical costs. The Surveillance Work Group is working with other Committees within the IJC structure trying to develop priorities for these substances for both monitoring and control purposes.

Further, the Surveillance Work Group notes that these more sensitive analytical procedures have established better baseline measurements that are, in certain instances, difficult to compare with historical values generated by less sensitive methods available at the time of their collection. This is especially true for organics and trace metals in water. These new data will be useful in establishing new baselines for determining future trends. The Surveillance Work Group cautions, however, that results generated by these more sensitive analtyical techniques must be scrutinized carefully. Although a low detection capability is important given the toxicity of some of these chemicals at extremely low concentrations (for example, TCDD) it is essential that errors resulting from missed or misidentified chemicals be kept to a minimum. In addition, results at such low sensitivity levels tend to exhibit greater analytical variation which makes the interpretation of trends more difficult. These factors reinforce the need for increased overall quality assurance programs. At the time of this writing, the format of such a program is currently being reviewed.

The Surveillance Work Group recognizes that there are many ongoing surveillance and monitoring activities conducted by the individual jurisdictions which do not directly form a part of the GLISP effort, but which, nonetheless, are often a valuable source of information on environmental quality. The Work Group will continue to compile these reports, where possible, for use in reporting to the Board and the Public.

Finally, it will be noted that this year's Surveillance Appendix to the Board Report has changed somewhat in the degree of detail and format from that presented in previous years. Chapter 2 provides only highlights of the environmental quality in each of the Great Lakes since the more detailed reports as a result of the intensive studies will be available in the near future. Chapter 3 provides a review of those compounds which the Surveillance Work Group feels there is need to emphasize in future surveillance and monitoring programs. This Chapter is a new addition to the Surveillance Appendix but it is one which the Work Group feels is within its mandate "to identify emerging problems" as required in Annex 11. Many continuing and emerging problems are associated with Areas of Concern previously identified by the Board; the status of Class "A" Areas of Concern are discussed in Appendix A of the Board Report. Chapter 4 reports on the activities, in particular, the round robin studies conducted by the Data Quality Work Group over the period 1982 - 1983. Chapter 5 presents the annual phosphorus loadings to the lakes for 1981 - 1982. Chapter 6 outlines a number of current initiatives which the Surveillance Work Group believes will improve the responsiveness of surveillance and monitoring activities to Agreement requirements and to the changing priorities and issues that have surfaced since the development of the Great Lakes International Surveillance Plan which was endorsed by the Water Quality Board in 1980.



2. Assessment

Since the 1972 Water Quality Agreement there has been a major effort on behalf of both governments to reduce phosphorus loadings and curtail inputs of certain toxic chemicals. Concomitantly, there has been a coordinated effort to measure the success of these remedial programs. This coordinated effort formally became known as the Great Lakes International Surveillance Plan (GLISP) which was endorsed by the Water Quality Board in 1980.

The current status of each of the Great Lakes with respect to eutrophication and contaminants is reported in this chapter based on results of certain efforts related to the Great Lakes International Surveillance Plan (GLISP). While these data, in some instances, have not been collected over a sufficient number of years to establish long-term trends, there is nevertheless adequate information to permit statements on changes. Relevant data are summarized briefly below for selected parameters on a basinwide perspective followed by a more detailed lake-by-lake assessment.

Results from open lake studies show that Lake Ontario has exhibited a consistent decline in total phosphorus concentrations over the last 13 years. This trend has occurred without significant reductions in phosphorus loading from Lake Erie. The lower concentrations in Lake Ontario may reflect a singular or combined outcome of lower inputs from point sources other than the Niagara River or a function of some as yet unexplained lakewide process. Results from Lake Erie have been subjected to several interpretive schemes, and while there is as yet no universal agreement to the absolute meaning of these data, there is agreement that total phosphorus values apparently have stabilized. Given the increased trend of total phosphorus in the early to mid-1970's, this stabilization is an encouraging sign. Concentrations of total phosphorus in Lake Huron have not increased significantly since earlier observations in 1974 and results from Saginaw Bay indicate a substantial decline in the eutrophication process within this important embayment.

The trend for nitrogen (nitrate plus nitrite) concentrations in the Great Lakes basin appears to be the reverse of phosphorus. Results from Lakes Ontario and Huron indicate a steady increase in nitrogen which has been calculated at 9.4 and 5.4 μ g/L/yr, respectively. Nitrogen concentrations in Lakes Michigan and Erie similarly show an increasing trend with values in all three Lake Erie basins having doubled over the last 20 years. Given this consistent trend there is reason to anticipate the 1983 Lake Superior survey will likewise show an increase in nitrogen. Suspected cause for these increases include: changes in biological activity (community shifts); changes in agricultural practices (fertilizers); or increasing atmospheric deposition. Regardless of the cause, these increases may be of concern and some attention should be directed toward an explanation of this observation and its potential impact, if any.

Results from the Great Lakes fish contaminants monitoring program indicated that Lake Michigan had the highest concentration of PCBs and Σ DDT in 1980. In 1981, the Agreement objectives for PCBs in all lakes and for Σ DDT in all lakes except Lake Superior were exceeded (Tables 2.0-1 and 2.0-2). Using the latest year from which complete data are available, results demonstrate that there is little difference in PCB concentrations in herring gull eggs from Lakes Ontario, Michigan and Erie. For Σ DDT, however, Lake Michigan eggs maintain the highest concentrations when compared to the other four lakes (Table 2.0-3).

In every instance reported, the observed concentrations of the routinely analyzed organochlorines in fish and gulls indicate that recent values are lower than historical high values. For some substances, however, the absolute concentrations have increased over the last two to three years. If these higher values are attributable to some additional uncontrolled source, then there is cause for concern. If, on the other hand, these observations merely represent a variation for substances that are approaching some environmental equilibrium, then such aberrations would not necessarily be cause for concern. Any definitive conclusions cannot as yet be made and must await the results from additional collections.

A. LAKE SUPERIOR

The Board approved the 1983 intensive surveillance plan for Lake Superior. The plan has been forwarded to the jurisdictions for implementation. This represents the last of the intensive surveillance plans on each of the lakes according to the 9-year binational strategy originally outlined in the GLISP. The 1983 intensive surveillance study was designed to provide updated baseline information on the current trophic status and degree of contamination of the lake with toxic substances, particularly those for which Agreement objectives presently exist.

Eutrophication

The concentration of nutrients in the open waters of Lake Superior was last measured intensively in 1973 as part of the Upper Lakes Reference Group (1976) study. The Reference Group reported that there was little evidence of nutrient enrichment or long-term changes in general water quality in the lake. The lake was classified as oligotrophic with deteriorated water quality being generally restricted to a few localized areas along the shoreline. Factors contributing to the oligotrophic status of the lake are its large volume to surface area ratio, low water temperatures and low nutrient loadings. The 1983 intensive surveillance study was designed to determine changes in lake water quality, if any, over the last decade.

Contaminants in Biota

During the 1960's and early 1970's, it was apparent that organic contaminants were occurring at elevated levels in several species of Lake Superior fish. Studies by the Upper Lakes Reference Group in 1973 detected such persistent compounds as PCBs, hexachlorobenzene, heptachlor epoxide, methoxychlor and toxaphene. Toxaphene was highlighted as a major toxic substance of concern by the Board in its 1982 Report to the Commission. It is further addressed in Chapter 3 of this report.

TABLE 2.0-1

PCB AND DDT LEVELS (µg/g Wet Weight) IN LAKE TROUT (Whole Fish Composites) FROM FOUR OF THE GREAT LAKES

	Ί ΣΡCΒ	977 ΣDDT	19 ΣΡCΒ	278 ΣDDT	19 ΣPCB	79 ΣDDT	198 ΣΡCΒ	80 ΣDDT	198 ΣΡCΒ	81 ΣDDT
Ontario ⁺	8.0	4.4	5.1	1.3	4.7	2.0	4.8	0.81	3.7	1.5
Michigan*	5.8	3.8	6.0	3.3	4.5	2.8	5.3	2.8	ençî en	3.4 (1.0)
Huron + *	2.0	1.8	2.6	2.0	2.9	1.7	2.4	1.2	1.7	0.81 1.2
Superior ⁺ *	1.7	0.97	0.96	0.64	0.68	0.76	0.90	0.35	0.46	0.31

+ Data Source: Department of Fisheries and Oceans, Burlington, Ontario. Mean of individual age 4⁺ fish; N is variable.

* Data Source: U.S. Fish and Wildlife Service, Ann Arbor and U.S. EPA, GLNPO, Chicago, IL cooperating - mean of 10 fish composites T.L. 450-640 mm; N = 4.

TABLE 2.0-2

SELECTED ORGANOCHLORINE CONTAMINANT RESIDUES IN µg/g WET WEIGHT (± S.E.) IN WHOLE FISH RAINBOW SMELT, 1981

3.7		ONTARI O	ERIE	HURON	SUPERIOR
	N*	47	36	36	12
	Weight (g)	28.27 (3.18)	31.55 (2.85)	27.69 (1.85)	30.50 (2.27)
	% Lipid	5.55 (0.22)	4.76 (0.22)	4.30 (0.14)	3.39 (0.16)
	РСВ	0.90 (0.06)	0.23 (0.02)	0.13 (0.01)	0.11 (0.00)
	pp'DDE	0.33 (0.02)	0.03 (0.00)	0.07 (0.01)	0.06 (0.00)
	ΣDDT	0.49 (0.03)	0.06 (0.00)	0.10 (0.01)	0.07 (0.00)
	Mirex	0.04 (0.00)	ND	ND	ND

Data Source: Department of Fisheries and Oceans, Burlington, Ontario

*Each sample consists of a composite of five fish.

TABLE 2.0-3

SELECTED ORGANOCHLORINE CONTAMINANT RESIDUES IN μ g/g WET WEIGHT (± S.D.) IN HERRING GULL EGGS FROM THE GREAT LAKES, 1980

	LAKE ONTARIO	LAKE ERIE	LAKE HURON	LAKE SUPERIOR	LAKE MICHIGAN
	(SNAKE IS.)	(MIDDLE IS.)	(CHANTRY IS.)	(AGAWA ROCKS)	(BIG SISTER)
N	10	10	10	10	10
% Lipid	7.9 (0.6)	7.1 (1.0)	9.4 (0.07)	8.3 (0.7)	8.4 (1.0)
РСВ	53	54	23	24	56
	(23)	(12)	(14)	(12)	(12)
Mirex	1.60	0.09	0.16	0.17	0.07
	(0.77)	(0.08)	(0.15)	(0.11)	(0.04)
НСВ	0.15	0.09	0.08	0.08	0.08
	(0.08)	(0.02)	(0.03)	(0.02)	(0.02)
Dieldrin	0.20	0.16	0.24	0.35	0.65
	(0.09)	(0.06)	(0.07)	(0.21)	(0.22)
pp'DDT	0.14	0.10	0.04	0.15	0.17
	(0.13)	(0.08)	(0.02)	(0.13)	(0.05)
pp'DDE	7.4	2.6	2.8	3.8	11.0
	(4.1)	(0.66)	(1.4)	(3.5)	(2.6)

Data Source: Canada Wildlife Service, Burlington, Ontario

Analysis of lake broat whole fish composites from 1977 through 1990 indicates that no consistent patters in levels of PCBs, DDT, dielevin, and chlorence has amarged (Table 22-11). These data do indicate, however, diel take Hichigan has the highest contabinant levels of PCBs and PDT compared to the other Great Lakes. Tissue concentrations for these compounds still exce the Agreement ejectives. Continued surveillance efforts will be required before a consistent patters or Verd can be determined

Analysis of herring will eggs from (31) through (350 hadicates a significant dooline in 1905a and stDT (1961a 28-3). No consistent pattern (a evident for disidrift and MSE, but mires spentre to nare declined. Mires and ACB had values in 1950 that seprendent the tourst recorded to date

The Upper Lakes Reference Group (1976) concluded that Lake Huron, Georgian bay and the North Chalmel ware of rothing in seture but the Incasts of roth's

Only three years of data on a consistent basis are available for contaminants in Lake Superior fish. Data on lake trout (Salvelinus namaycush) whole fish composites are presently insufficient to determine any statistically significant trends (Table 2A-1). Several additional years of collection and analysis will be required before trends can be determined. Nevertheless, these data do demonstrate that tissue concentration of PCBs still exceed the Agreement objective.

Analysis of herring gull (Larus argentatus) eggs from 1974 to 1979 indicate a decline in the levels of the six persistent organochlorine substances investigated. These declines continued through 1981 but at a slightly diminished rate. The decline between 1981 levels and those when concentrations were greatest for each compound are as follows: DDE-74%, DDT-94%, dieldrin-23%, HCB-52%, mirex-85% and PCBs-56% (Table 2A-2).

B. LAKE MICHIGAN

Two reports describing the results from intensive surveillance on Lake Michigan in 1976 and 1977 were issued by the U.S. EPA (Rockwell et al., 1980; Bowden et al., 1981). Efforts to describe changes in open water nutrient chemistry are scheduled for 1983.

Eutrophication

The U.S. EPA reports focused on differences in physicochemical conditions between 1976 and 1977. Phosphorus concentrations were around 7 μ g/L in 1976 and substantially decreased to near 5 μ g/L in 1977. Concurrently, improved trophic conditions were indicated by narrower nearshore zones of mesotrophic waters along the entire shoreline in 1977, as determined by phosphorus reductions and other physicochemical and biological trophic indicators. Eutrophic zones were especially noted near Milwaukee Harbor and Indiana Harbor Canal. These reports caution that the apparent declining trends may be due to shortterm annual variation between the two years and may not necessarily indicate a continuing downward trend in phosphorus concentrations.

Contaminants in Biota

Analysis of lake trout whole fish composites from 1977 through 1980 indicates that no consistent pattern in levels of PCBs, DDT, dieldrin, and chlordane has emerged (Table 2B-1). These data do indicate, however, that Lake Michigan has the highest contaminant levels of PCBs and DDT compared to the other Great Lakes. Tissue concentrations for these compounds still exceed the Agreement objectives. Continued surveillance efforts will be required before a consistent pattern or trend can be determined.

Analysis of herring gull eggs from 1971 through 1980 indicates a significant decline in Σ PCBs and Σ DDT (Table 2B-2). No consistent pattern is evident for dieldrin and HCB, but mirex appears to have declined. Mirex and HCB had values in 1980 that represent the lowest recorded to date.

C. LAKE HURON

The Upper Lakes Reference Group (1976) concluded that Lake Huron, Georgian Bay and the North Channel were oliotrophic in nature but the impacts of man's

TABLE 2A-2

MEAN CONCENTRATION (in $\mu g/g$ Wet Weight \pm S.D.) OF SELECTED ORGANOCHLORINE CONTAMINANTS IN HERRING GULL EGGS FROM TWO LAKE SUPERIOR COLONIES

Data Source: Canada Wildlife Service, Burlington, Ontario

LAKE SUPERIOR	N	% FAT	DDE	DDT	DIELDRIN	НСВ	MIREX	ΣPCBs
MAMAINSE HA AGAWA ROO	ARBOUR CKS*	1						
1974	10	8.7 + 1.0	14.0 + 4.1	0.84 + .48	0.42 + .15	0.29 + .13	0.76 + 0.66	50 + 10
1975	10	7.2 + 1.4	22.0 + 8.6	0.72 + .67	0.32 + .11	0.24 + .08	1.3 + 1.7	70 + 37
1977	10	9.3 + 0.9	12.0 + 4.3	0.07 + .06	0.40 + .17	0.13 + .06	0.42 + 0.79	56 + 20
1978	9	9.3 + 0.8	9.7 + 4.8	0.10 + .10	0.40 + .43	0.09 + .05	0.15 + 0.16	37 + 16
* 1979	10	9.3 + 0.7	7.3 + 5.4	0.09 + .04	0.56 + .31	0.14 + .08	0.33 + 0.44	58 + 33
* 1980	10	8.3 + 0.7	3.7 + 3.5	0.15 + .13	0.35 + .21	0.08 + .02	0.17 + 0.11	24 + 12
* 1981	10	8.9 + 1.1	6.3 + 3.1	0.05 + .03	0.49 + .32	0.14 + .09	0.20 + 0.35	36 <u>+</u> 13
GRANITE ISI	AND							
1974	9	8.8 + 0.9	19.0 + 7.0	0.83 + .44	0.61 + .17	0.22 + .12	1.3 + .73	75 + 18.0
1975	10	8.2 + 0.9	24.0 + 11.0	0.25 + .12	0.44 + .34	0.12 + .08	0.62 + .37	82 + 33.0
1977	10	9.2 + 0.8	12.0 + 6.9	0.06 + .03	0.35 + .16	0.12 + .07	0.24 + .23	55 + 22.0
1978	10	9.7 + 0.4	9.6 + 3.3	0.12 + .05	0.39 + .17	0.14 + .06	0.39 + .48	45 + 11.0
1979	10	9.2 + 1.7	6.4 + 3.6	0.09 + .06	0.64 + .53	0.15 + .06	0.19 + .15	59 + 17.0
1980	10	6.9 + 1.1	3.6 + 1.0	0.13 + .05	0.33 + .12	0.08 + .03	0.09 + .11	27 + 9.3
198 1	10	8.4 + 1.0	5.2 + 0.9	0.02 + .01	0.38 + .19	0.09 + .02	0.09 + .06	31 + 5.6

1

TABLE 2B-1

MEAN (RANGE) OR GANOCHLOR INE CONTAMINANT CONCENTRATIONS IN µg/g WET WEIGHT IN LAKE MICHIGAN LAKE TROUT (Whole Fish Composites) BETWEEN 450-600 mm TOTAL LENGTH

Data Source: U.S. EPA (GLNPO), Chicago, Illinois in cooperation with U.S. Fish and Wildlife Service, Ann Arbor, Michigan

YEAR	N*	DIELDRIN	ΣΡCΒ	ΣDDΤ
1977	4	0.42 (0.35 - 0.55)	5.8 (4.2 - 7.3)	3.8 (3.4 - 4.2)
1978	4	0.52 (0.28 - 0.82)	6.0 (4.2 - 8.3)	3.3 (0.5 - 7.6)
1979	4	0.43 (0.29 - 0.73)	4.5 (3.5 - 5.7)	2.8 (2.2 - 3.8)
1980	3	0.23 (0.20 - 0.25)	5.3 (4.6 - 6.4)	2.8 (2.4 - 3.4)

*Ten fish composites.

TABLE 2B-2

MEAN CONCENTRATION (in µg/g Wet Weight ± S.D.) OF SELECTED CONTAMINANTS IN HERRING GULL EGGS FROM BIG SISTER ISLAND, LAKE MICHIGAN, 1971-1980

Data Source: Canada Wildlife Service, Burlington, Ontario in cooperation with Dr. R. Faber, St. Marys College, Winona, Minnesota

YEAR	N	DDE	DDT	ΣDDT	DIELDRIN	НСВ	MIREX	ΣPCBs
1971 1973 1976 1978 1980	9 10 10 10 10	61±34.0 64±16.0 33±10.0 21± 8.0 11± 2.6	0.98±0.43 0.70±0.21 0.27±0.19 0.14±0.05 0.17±0.05	62±34.0 65±16.0 34±11.0 22± 8.0 12± 2.6	0.83±0.36 0.59±0.35 0.82±0.35 0.90±0.57 0.65±0.22	0.45±0.66 0.11±0.05 0.14±0.06 0.12±0.05 0.08±0.02	0.68±1.4 0.21±0.31 0.36±0.54 0.26±0.25 0.07±0.04	140±64 170±50 120±28 90±37 56±12

activities were clearly evident. The main goal of the 1980 Lake Huron Intensive Study was to provide a detailed assessment of lake conditions which would allow a statistical comparison with earlier baseline data (1971 and 1974) so that changes, if any, in overall water quality could be determined. Of major interest in the 1980 study was the improvements in Saginaw Bay and the resultant impact on southern Lake Huron. Saginaw Bay is discussed separately at the end of this section.

Eutrophication

Nutrients

Nutrient concentrations measured in 1980 were low compared to Lake Michigan and the Lower Great Lakes. Mean concentrations for the major nutrients such as phosphorus, nitrogen and silica still indicate an oligotrophic system (Table 2C-1). Water quality conditions were generally better in the northern vs southern part of the lake although the southern part of the lake has improved considerably as a result of improvements in Saginaw Bay. Some nearshore areas continue to exhibit deteriorated water quality conditions for limited periods of time. Included are such regions as the Ontario shoreline of southern Lake Huron, Thunder Bay, Michigan, and the mouth of Saginaw Bay.

Phosphorus. Ambient concentrations of phosphorus in Lake Huron vary directly with point source loadings. The largest contributions of total phosphorus were derived from tributaries but the atmosphere also contributed a significant amount (Table 2C-2).

Levels of total phosphorus were low, averaging 5.0 μ g/L (area weighted mean) in the surface waters of Lake Huron and 4.2 μ g/L in Georgian Bay over the period April to November 1980. In contrast, concentrations in Lake Ontario are nearly three times higher averaging approximately 14.0 μ g/L.

<u>Nitrogen</u>. Principal sources of nitrogen to the lake are atmospheric loading, nitrogen fixation and inputs from surface and groundwater drainage. Lakewide mean (area-weighted) values for nitrate + nitrite-N averaged over the six cruises were greater in Lake Huron (274 μ gN/L) and the North Channel (271 μ gN/L) than in Georgian Bay (253 μ gN/L). Ammonia levels were low throughout most of the Lake Huron/Georgian Bay system ranging from 1-4 μ gN/L during the six cruises with the exception of the spring concentrations measured in the North Channel which were due to inputs from the St. Marys River.

Silica. Lake Superior, via the St. Marys River was by far the principal source of soluble reactive silica (SRS) with levels consistently exceeding 2 $\mu g \ SiO_2/L$ throughout the study period. In contrast, SRS concentrations in the remaining surface waters of Lake Huron exhibited large spatial and temporal variations but were generally less than 1.6 $\mu g \ SiO_2/L$.

ANNUAL MEANS (STANDARD DEVIATIONS) OF SELECTED PHYSIOCHEMICAL VARIABLES FROM LAKE HURON HISTORICAL DATA BASE

Data Source: Compiled from United States and Canadian agencies: Available on U.S. EPA STORET System

YEAR	TEMPERATURE °C	CONDUCTIVITY µmho/cm	CHLORIDE mg/L	SULFATE mg/L	SILICA mgSiO2/L	NITRATE + NITRITE mgN/L	SOLUBLE P µgP/L	TOTAL P µgP/L
1954	12.1(5.8)	166(14)			2.2(0.6)			
1956	12.0(5.2)	177(9)	6.5(2.2)	12.7(2.4)	2.0(0.4)			
1966	14.6(6.2)	117(44)		14.3(2.4)	2.4(1.9)		2.7(1.4)	
1967	17.8(3.9)	173(13)	7.8(0.8)	17.4(0.6)	1.4(0.5)		1.6(2.6)	
1968	11.5(6.1)	200(15)	6.2(2.1)	17.1(1.5)	1.2(0.4)	.0.21(.06)	0.5(2.6)	7.6(7.1)
1969	9.0(5.2)	184(39)	4.6(2.8)	11.5(6.0)	0.9(0.4)	0.20(.05)	0.8(1.6)	6.8(2.6)
1970	15.5(5.2)	208(25)	6.7(2.7)	11.4(1.4)	1.1(0.3)	0.13(.06)	3.4(3.6)	
1974	14.6(6.6)	211(13)	6.2(0.8)	12.4(1.8)	1.0(0.4)	0.30(.04)	3.0(1.9)	4.5(2.1)
1980	7.8(5.3)	193(20)	5.2(0.7)	15.1(1.6)	1.4(0.4)	0.27(.04)	0.8(.4)	5.0(2.0)

SUMMARY OF 1980 ESTIMATED PHOSPHORUS LOADING (metric tonnes/year) TO LAKE HURON

BAR SHALL	MICHIGAN	ONTARIO	TOTALS	
Direct Industrial Discharge	2	1	2	
Direct Municipal Discharge	18	103	121	
Tributary: Monitored (standard error)	559 (13)	994 (134)	1,553 (134)	
Subtotals	579	1,098	1,676	
Unmonitored (standard error) ²	315 (25)	328 (43)	643 (50)	
Atmospheric			<u>1,495</u> 1	
TOTAL				
Estimated inputs from Lak	e Superior 730 (1	46), Lake Michigar	n 255 ³ 985	-
Total estimated input to	Lake Huron		4,799	
Target Load, 1978 Great L	y Agreement	4,360		

Data Source: Compiled from United States and Canadian agencies: Available on U.S. EPA STORET System

Totals may not sum due to rounding.

¹Estimate uses Canadian monitoring sites only.

²This estimate is based on the proportion of unmonitored basin area. Standard errors calculated from tributary loading estimates were used in making adjustments.

³Upper Lakes Reference Group 1974-1975 estimates.

Inter-year comparison. A principal objective of the 1980 Lake Huron Intensive Surveillance Program was to document any change in water quality by comparing current results with the baseline data sets for 1971 and 1974. The mean and standard deviation for total phosphorus, nitrate + nitrite and soluble reactive silica for the 1971 and 1980 spring cruises on Lake Huron and the 1974 and 1980 spring cruises on Georgian Bay are presented in Table 2C-3.

Statistical analysis using a Student's t-test indicated that total phosphorus exhibited no significant increase (p less than 0.05) since 1971 in Lake Huron and 1974 in Georgian Bay. These results are in keeping with the non-degradation management concept for the Upper Lakes as stated in the 1978 Great Lakes Water Quality Agreement. Soluble reactive silica showed a significant increase (12%) from 1971 to 1980 in Lake Huron. In contrast, SRS levels in Georgian Bay decreased significantly (13.5%) between 1974 and 1980. Nitrate + nitrite demonstrated a significant increase in both Lake Huron and Georgian Bay. If a constant annual rate of increase can be assumed, then nitrate + nitrite has increased at approximately 5.4 μ g N/L/yr in Lake Huron and 4.5 μ g N/L/yr in Georgian Bay.

It should be stated that when nutrient data from this study became available, several investigators undertook to analyze and interpret it. Their results are in general agreement, however, there are some discrepancies in details but these do not affect the conclusions about the change in nutrient concentrations in Lake Huron. For example, data in Table 2C-1 are annual means based on all stations for Lake Huron. Data in Table 2C-3 are spring (April) means and are based on only those stations that were common to both years in the comparison.

Phytoplank ton

Phytoplankton data were available only for southern Lake Huron, but this area has been historically the most impacted by Saginaw Bay. The 1980 algal measurements indicate an increase of the smaller microflagellates relative to other groups of algae. Also, nearshore areas in southern Lake Huron often had phytoplankton assemblages more characteristic of offshore waters. This was not true in 1974. The open lake stations south of Saginaw Bay in 1980 did not exhibit the extent of influence from Saginaw Bay as they did in 1974 (Figure 2C-1). These observations tend to corroborate the improvements in the southern half of the lake as a result of improvements in Saginaw Bay.

Zooplank ton

Zooplankton sampling was conducted on four of the six main Lake Huron cruises (April-July). Zooplankton standing stocks were characteristic of oligotrophic to meso-oligotrophic conditions. Species included <u>Cyclops</u> <u>bicuspidatus thomasi, Diaptomas ashlandi., D. minutus and D. sicilis.</u> Crustacean standing stocks were low, ranging from a May cruise mean of 14,000 to a July high of 75,600 individuals per m³. Species considered indicators of eutrophic waters such as <u>Mesocyclops edax</u>, <u>Eurytemora affinis</u>, <u>Cyclops</u> <u>vernalis</u>, <u>Chydorus sphaericus</u>, and <u>Eurycercus</u> lamellatus were either rare or not detected.

COMPARISONS OF SPRING NUTRIENT CONCENTRATION IN LAKE HURON BETWEEN 1971 AND 1980 AND GEORGIAN BAY BETWEEN 1974 AND 1980

REGION	VARIABLE	YEAR	MEAN ± STANDARD DEVIATION	COEFFICIENT OF VARIABILITY(%)
Lake Huron	Total	1980	4.6± 0.71 N.S.	14.4
	Phosphorus (µg/L)	1971	4.1± 1.50	35.5
	Nitrate +	1980	283.8±10.01**	3.5
	Nitrite (µg/L)	1971	235.0±18.62	7.9
	Soluble Reactive	1980	1,497.0± 0.096**	6.4
	Silica (µg/L)	1971	1,395.0± 0.058	4.2
Georgian Bay	Total	1980	5.1± 2.03 N.S.	40.0
	Phosphorus (µg/L)	1974	4.7± 3.02 N.S.	64.7
	Nitrate +	1980	267.1±26.82**	10.0
	Nitrite	1974	248.3±20.39**	8.5
	Soluble Reactive	1980	1,248.0± 0.176**	14.1
	Silica (µg/L)	1974	1,444.0± 0.184	12.7

Data Source: Compiled from United States and Canadian agencies: Available on U.S. EPA STORET System

**Significant difference (5% level). N.S. = No significant difference (5% level).



- 19 -

Rotifer species such as Notholca squamula and Synchaeta spp. also indicative of oligotrophic or meso-oligotrophic conditions had abundances ranging from 4,500 in June to 15,000 individuals per m³ in July. Again, species considered indicators of eutrophic waters were rare (Filinia, Ploesoma, and Trichocerca) or not detected (Brachionus and Euchlanis).

The most productive area of Lake Huron was the southern nearshore region, particularly in the Goderich/Bayfield and Harbor Beach/Lexington areas. Zooplankton standing stocks in these areas were high for all cruises, apparently due to the stimulation of primary productivity from nutrient runoff. In July, high production also occurred in the St. Marys River/North Channel area. In general, zooplankton productivity was higher in nearshore waters than offshore.

Contaminants

Metals

An extensive sampling effort for 14 trace metals in water was conducted as part of the Lake Huron Intensive Study in 1980. Results for many of these metals were lower than historical values. This may be due to improved instrumentation and methodology. Table 2C-4 summarizes the results for these metals.

Because of the more sensitive analytical methodologies employed in the 1980 metals survey, comparison with historical results to determine changes in metal concentrations since 1971 is difficult. These new data, however, provide a valuable baseline for determining future changes in concentrations and the methodologies used, despite some equipment contamination problems with a few of the metals, should be employed in future surveillance efforts for determining metal concentrations in each of the lakes.

The Aquatic Ecosystem Objectives Committee (AEOC) of the Great Lakes Science Advisory Board has recently developed a "toxic unit concept" to ascertain what metals (in a metals mixture in water) may be cause for concern (AEOC, 1981). In simplified terms, this concept states that if the sum of the ratios of the observed concentrations of a particular metal to the specific objective outlined in Annex 1 of the 1978 Agreement exceeds one and any particular metal ratio exceeds 0.25 then this metal may be cause for concern. Table 2C-5 presents these calculations for several stations in Lake Huron. On the basis of this concept, there may be concern for the concentrations of selenium, mercury, cadmium and silver at several locations in Lake Huron. Research efforts have indicated, however, that the dissolved fraction represents the most toxic form of the metal and concern over these reported values should be viewed in this context. The calculated ratio of particulate to particulate plus dissolved concentrations appears in Table 2C-4.

The 1980 survey results also showed that recent (surficial) sediments in certain locations in the lake were consistently found to be enriched in cadmium, copper, lead, nickel and zinc (Table 2C-6). This is consistent with the findings of the ULRG (1976) study of this lake in 1974.

SUMMARY OF 1980 LAKE HURON MEDIAN TRACE METAL CONCENTRATIONS IN WATER AND THE PARTIONING OF TRACE METALS BETWEEN THE DISSOLVED AND PARTICULATE FRACTIONS

METAL	DISSOLVED (μg/L) <.5 μm	PARTICULATE (μg/L) >.5 μm	PARTICULATE PARTICULATE + DISSOLVED
Fe	.80	6.4	.89
Cd	0.	.012	1.00
Cu	.28	. 12	.30
Cr	.11	.017	. 13
Pb	.0089	.041	.82
Ni	.49	.034	.06
Zn	. 17	.33	.66
Mn	.28	.58	.67
На	.0042	1 2 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1	.62
As	.25	.0086	.03
AT	3.1	15.	.83
Aq	.0058	.0013	. 18
V	.24	.014	.06
Se	.48	0.	.00

Data Source: Rossmann (1982)

EVALUATION OF TOXIC UNIT CONCEPT (AEOC, 1981) AS APPLIED TO 1980 TOTAL TRACE METAL CONCENTRATION (µg/L) OF LAKE HURON WATER. A REPRESENTATIVE STATION WITHIN A GEOGRAPHICAL LOCATION WAS USED TO CALCULATE Mi/Oi, WHERE Mi IS THE OBSERVED CONCENTRATION AND OI IS THE WATER QUALITY OBJECTIVE

IJC WATER QUALITY OBJECTIVE UPPER L. HURON STA. 61 NORTH OT GEORGIAN STA. 84 CENTRAL OT LOWER L. HURON STA. 44 STATIONS HIGHEST OT STATIONS MEDIAN VALUE Fe 300 7.2 0.02 5.0 0.02 3.1 0.01 2.2 0.007 22 0.07 25 (NC) 0.08 4.8 Cd 0.2 0.061 0.30 0.016 0.08 0.017 0.085 0.016 0.06 0.033 0.16 0.061 0.033 0.16 0.061 0.033 0.16 0.061 0.033 0.16 0.061 0.033 0.16 0.061 0.033 0.16 0.061 0.033 0.16 0.061 0.033 0.16 0.061 0.033 0.16 0.061 0.13 0.4 Cr 50 0.14 0.003 0		CURRENT	CURRENT			LUCA	1 1 0 11	AND	511	A I I O N	н о.			ALL			ALL	
Fe 300 7.2 0.02 5.0 0.02 3.1 0.01 2.2 0.007 22 0.07 25 (NC) 0.08 4.8 Cd 0.2 0.061 0.30 0.016 0.08 0.017 0.085 0.016 0.06 0.033 0.16 0.061 (UH) 0.30 0.015 Cu 5 0.40* 0.08 0.47 0.09 0.50 0.1 0.23 0.05 0.64 (NC) 0.13 0.4 Cr 50 0.14 0.003 0.12 0.002 0.047 0.001 0.16 0.003 0.19 (CH) 0.004 0.13 Pb 3 0.051 0.02 0.022 0.007 0.039 0.013 0.10 0.03 0.19 (CH)<0.004 0.022 Ni 25 0.74 0.03 3.8 0.15 1.2 0.05 0.54 0.02 0.31 0.01 3.8 (NC) 0.15 0.	METALS	IJC WATER QUALITY OBJECTIVE	UPPER L. HURON STA. 61	Mi Di	NORTH CHANNEL STA. 84	Mi Oi	GEORGIAN BAY STA. 114	Mi Oi	CENTRAL L. HURON STA. 44	Mi Oi	LOWER L. HURON STA. 10	Mi Di	STATIONS HIGHEST VALUE	S T	Mi Oi	STATIONS MEDIAN VALUE	Mi Oi	
	Fe Cd Cu Cr Pb Ni Zn Hg As Ag Se	300 0.2 5 50 3 25 30 0.2 50 0.1 1	7.2 0.061 0.40* 0.14 0.051 0.74 0.79 0.10* 0.20 0.042 0.58	0.02 0.30 0.08 0.003 0.02 0.03 0.03 0.5 0.004 0.42 0.58	5.0 0.016 0.64 0.11 0.022 3.8 0.56 0.099 0.16 0.002 0.41	0.02 0.08 0.13 0.003 0.007 0.15 0.02 0.5 0.003 0.02 0.41	3.1 0.017 0.47 0.12 0.039 1.2 0.21 0.012 0.072 0.011 0.62	0.01 0.085 0.09 0.002 0.013 0.05 0.007 0.06 0.001 0.11 0.62	2.2 0.016 0.50 0.047 0.10 0.54 0.28 0.21 0.37 0.01 0.43	0.007 0.06 0.1 0.001 0.03 0.02 0.009 1.05 0.007 0.10 0.43	22 0.033 0.23 0.0 0.0 0.31 0.38 0.097 0.27 0.013 0.86	0.07 0.16 0.05 0.003 0.00 0.01 0.01 0.48 0.005 0.13 0.86	25 0.061 0.64 0.19 0.11 3.8 0.56 0.35 0.53 0.042 1.2	(NC) (UH) (NC) (CH) (UH) (NC) (UH) (CH) (UH) (UH)	0.08 0.30 0.13 0.004 0.04 0.15 0.02 1.75 0.01 0.4 1.2	4.8 0.015 0.4 0.022 0.54 0.29 0.011 0.21 0.009 0.48	0.02 0.08 0.003 0.007 0.02 0.01 0.055 0.004 0.09 0.48	
Σ Mi/Oi 2.25 1.34 1.05 1.81 1.78 4.08	Σ Mi/Oi			2.25		1.34		1.05		1.81		1.78			4.08		0.86	

Data Source: Rossmann (1982)

* In accordance with author's recommendation the reported values of 1.7 and 2.8 were ignored and replaced by value of next closest station, respectively. **Contribution greater than 0.2 toxic units.

COMPARISON OF METAL CONCENTRATIONS IN RECENT SEDIMENTS WITH THOSE IN OLDER SEDIMENTS (mg/kg Dry Weight)

		TRATIONS	RECENT SEDIMENTS ²			
METAL	KEMP AND THOMAS (1976)	ROBBINS (1980) ¹	LAKE HURON BASINS	GEORGIAN BAY AND NORTH CHANNEL BASINS		
As	ANTER AND	6.0	1.88	7.19		
Cd	1.0	1.5	1.3	2.0		
Со		12.2	17.0	24.0		
Cr		55.0	43.0	176.0		
Cu	38.0	30.0	46.0	60.0		
Hg	0.15	0.03	0.277	0.392		
Ni		35.0	51.0	119.0		
Pb	39.0	30.0	66.0	67.0		
٧		120.0	54.0	77.0		
Zn	94.0	65.0	86.0	146.0		

¹Derived from his data. ²Konasewich, <u>et al</u>. 1978.

Organics

For the first time in 1980, concentrations of selected organic compounds were measured in lake waters. Concentrations for most of these compounds were in the low ng/L range. For example, concentrations of PCBs ranged from 0.1 ng/L in Georgian Bay to 3.2 ng/L in the North Channel. Mean concentrations in Lake Huron, the North Channel and Georgian Bay were 0.4, 1.7 and 1.4 ng/L, respectively. The mean value reported in 1981 for Lake Huron was 0.6 ng/L which agrees reasonably well with the 1980 data. Open lake concentrations of chlorobenzenes range from .003 to .009 ng/L for pentachlorobenzenes and .002 to .004 ng/L for hexachlorobenzenes for 1980 and 1981, respectively.

As is the case with metals, these data provide a baseline from which future changes can be determined. Perhaps the significance of these data at the present time is not so much the absolute value of their concentrations in water but the fact that they can be detected at all, substantiating their ubiquity in all compartments of the lake ecosystem. The "virtual elimination" of these substances from discharges entering the Great Lakes is required by the 1978 Agreement. Therefore, the very presence of these man-made chemicals in the ecosystem is of concern and is cause for further controls.

Contaminants in Biota

Concentrations of Σ DDT and Σ PCBs in lake trout whole fish composite samples apparently peaked in 1978 and 1979, respectively, while levels of dieldrin show no consistent pattern since 1977 (Table 2C-7). Both PCB and DDT still exceeded the Agreement objectives for these compounds in 1981. Smelt (Osmerus mordax) samples were collected and analyzed from 1979 to 1981 (Table 2C-8). Only PCB showed an apparent significant decline. These data, however, are from an insufficient number of years to allow a rigorous statistical treatment of the results.

Long-term trends in six organochlorine residues in herring gull eggs from nesting colonies representing southern Lake Huron (Chantry Island) and the North Channel (Double Island), showed a significant decrease for the period 1974 through 1979 (Table 2C-9). During the period 1979 through 1981 levels of DDE from Double Island and mirex from Chantry Island increased significantly. Except for a slight increase in DDE from Chantry Island, all remaining compounds showed continued declines with the declines in DDT from Chantry Island and HCB from both monitoring colonies being statistically significant. Excluding the above three observations, data for the other compounds suggest that the calculated half-lives of these compounds have increased over the period from 1974 to 1981. This would indicate that the rate of decrease of these trends has started to level off.

SAGINAW BAY

Eutrophication

As reported previously in the 1982 Water Quality Board Report and the 1981 Appendix B, the loading of total phosphorus to Saginaw Bay from the Saginaw River has decreased over the period 1974-1980 due to phosphorus removal efforts by municipal treatment works. Although the proposed target load of

MEAN (RANGE) ORGANOCHLORINE CONTAMINANT CONCENTRATIONS IN µg/g WET WEIGHT IN LAKE HURON LAKE TROUT (Whole Fish Composites) BETWEEN 450-600 mm TOTAL LENGTH

Data Source: U.S. EPA (GLNPO), Chicago, Illinois in cooperation with U.S. Fish and Wildlife Service, Ann Arbor, Michigan

YEAR	N*	DIELDRIN	ΣΡCΒ	ΣDDT
1977	4	0.20	2.0	1.8
10.00 TS.9		(0.13 - 0.32)	(1.5 - 2.2)	(1.5 - 2.2)
1978	4	0.14	2.6	2.0
		(0.12 - 0.15)	(1.9 - 3.5)	(1.9 - 2.1)
1979	4	0.14	2.9	1.7
		(0.12 - 0.16)	(2.5 - 4.0)	(1.5 - 1.8)
1980	4	0.11	2.4	1.2
		(0.09 - 0.13)	(2.2 - 2.6)	(0.9 - 1.3)
1981	4	0.14	2.2	1.2
		(0.12 - 0.18)	(1.9 - 2.6)	(1.0 - 1.3)

*Ten fish composites.
TABLE 2C-8

MEAN CONCENTRATION IN μg/g WET WEIGHT (± S.E.) OF SELECTED TRACE METAL AND ORGANOCHLORINE CONTAMINANTS IN LAKE HURON RAINBOW SMELT (Whole Fish Composites)

TOTAL LENGTH % YEAR N* WEIGHT (mm) ΣРСВ ΣDDT As Se Hq (q) RANGE LIPID 1979 26.33 164.6 4.24 12 0.19 0.07 0.06 0.27 0.64 (1.72) (145-188) (0.16)(0.02)(0.02)(0.01)(0.02)(0.01)1980 36 20.68 154.2 3.46 0.11 0.07 0.07 0.26 0.69 (1.51) (124-204)(0.14)(0.01)(0.01)(0.01)(0.01) (0.02)1981 27.69 36 161.3 4.30 0.13 0.10 0.06 0.31 0.68 (1.85) (125-195) (0.14)(0.01)(0.01)(0.00) (0.01) (0.00)

Data Source: Department of Fisheries and Oceans, Burlington, Ontario

*Each sample consists of a composite of five fish.

TABLE 2C-9

MEAN CONCENTRATION (in µg/g Wet Weight ± S.D.) OF SELECTED ORGANOCHLORINE CONTAMINANTS IN HERRING GULL EGGS FROM TWO LAKE HURON COLONIES

Data Source: Canada Wildlife Service, Burlington, Ontario

LAKE HURON	N	% FAT	DDE	DDT	DIELDRIN	НСВ	MIREX	ΣPCBs
CHANTRY ISLAND	on con	Num a						
1974	10	8.2 + 1.1	21.0 + 8.6	0.63 + .23	0.47 + .18	0.47 + .23	2.2 + 2.1	86 + 22
1975	10	8.6 + 0.8	12.0 + 4.4	0.15 + .12	0.31 + .20	0.18 + .05	0.48 + 0.56	39 + 17
1977	10	9.4 + 0.8	13.0 + 4.6	0.09 + .05	0.57 + .25	0.17 + .08	0.34 + 0.22	64 + 16
1978	10	11.0 + 1.3	6.0 + 2.5	0.05 + .03	0.22 + .09	0.14 + .07	0.26 + 0.33	32 + 12
1979	10	7.7 ± 0.8	2.5 + 1.7	0.06 + .02	0.28 + .09	0.10 + .07	0.20 + 0.33	31 + 23
1980	10	9.4 + 0.7	2.8 + 1.4	0.04 + .02	0.24 + .07	0.08 + .03	0.16 + 0.15	23 + 14
198 1	10	9.2 <u>+</u> 1.5	4.1 + 1.9	0.03 ± .01	0.25 + .09	0.07 + .03	0.35 + 0.37	28 + 10
DOUBLE ISLAND								
1974	10	9.3 + 0.9	14.0 + 6.7	0.55 + .28	0.53 + .16	0.30 + .08	0.52 + 0.22	56 + 17.0
1975	10	7.3 + 1.1	16.0 + 8.5	0.17 + .10	0.41 + .18	0.24 + .08	0.55 + 0.67	46 + 15.0
1977	10	9.4 + 2.9	15.0 + 13.0	0.09 + .07	0.45 + .23	0.21 + .05	0.55 + 0.57	77 + 48.0
1978	10	9.0 + 0.5	7.0 + 2.6	0.09 + .02	0.22 + .12	0.09 + .05	0.16 + 0.22	33 + 9.5
1979	10	8.7 + 1.0	2.1 + 0.76	0.06 + .04	0.32 + .18	0.10 + .04	0.17 + 0.16	26 + 7.4
1980	10	9.1 + 1.5	2.6 + 1.3	0.05 + .02	0.24 + .18	0.06 + .02	0.06 + 0.05	17 + 7.8
198 1	10	9.6 ± 0.9	3.6 <u>+</u> 1.4	0.04 + .01	0.23 + .09	0.07 ± .03	0.17 ± 0.15	23 + 7.6

440 metric tonnes was approached (and actually met in 1979), the total phosphorus concentrations in inner Saginaw Bay still remain above 20 μ g/L while the objective is set at 15 μ g/L. Mathematical modelling of the total phosphorus loads and concentrations over the entire period indicates that this delayed response is due to sediment resuspension of particulate phosphorus.

Nevertheless, Saginaw Bay has responded favorably as indicated by changes in nutrient concentrations and in the biological community structure in specific areas in the bay. Data from Segment 2 (Figure 2C-2) is especially illustrative. Soluble reactive phosphorus levels in Segment 2 of Saginaw Bay have declined dramatically (Figure 2C-3). Nannoplankton, which are small phytoplankton (less than 20μ in diameter) and are considered to be a prime food source for the herbivorous zooplankton, have increased sixfold (Figure 2C-4). The available nitrogen:phosphorus ratio over the period of study was observed to be below 29:1 for a six week period (Figure 2C-5). This observation is significant, since according to Smith (1983), ratios of less than 29:1 are favorable to nuisance causing blue-green algae. The species composition of the phytoplankton community has also improved dramatically from 1974 to 1980 to one indicative of improved water quality (Figure 2C-6).

All these indicators corroborate that nutrient control measures have been successful in this embayment of Lake Huron.

Contaminants

Water

Saginaw Bay was studied intensively for contaminants (PCBs and metals) over the period 1976-1980. The results of metals concentrations have been reported previously. The 1979 results for PCBs are the most complete and these are summarized here.

The loading of total PCBs to Saginaw Bay in 1979 was 1.4 kg/day with approximately half from the atmosphere and half from the tributaries (mainly the Saginaw River). As with phosphorus, the sediments in Saginaw Bay are currently a source of PCBs to the water column. The total PCB concentrations for inner and outer Saginaw Bay were approximately 25 and 17 ng/L, respectively.

Biota

A study of PCBs in various species of fish in Saginaw Bay was conducted from 1977-1980. The most complete information is available for yellow perch. Results indicate that there is a distinct geographical gradient for body burden of Aroclor 1260 in whole perch from inner to outer Saginaw Bay after length of fish is taken into account (Table 2C-10). Calculated bioconcentration factors for perch are presented in Table 2C-11. Aroclor 1242 does not appear to bioconcentrate differently depending on the area of the bay, whereas Aroclor 1260 does. This empirical finding is in agreement with the laboratory results of Oliver and Niimi (1983) which indicated that the bioconcentration factor increases dramatically as the degree of chlorine substitution becomes greater. No trends in PCB body burden in perch over time were observed.



FIGURE 2C-2 Segments in Saginaw Bay used for data analysis of interpretation. Data Source: U.S. EPA Storet System.



FIGURE 2C-3 Comparison of dissolved ortho-phosphate phosphorus (mg/L) in segment 2 of Saginaw Bay in 1974 and 1980. Date Source: Canada Centre for Inland Waters and U.S. EPA Storet System.



FIGURE 2C-4 Comparison of nannoplankton (20 u) less filaments and colonies (#/L) in segment 2 of Saginaw Bay in 1974 and 1980. Data Source: Stoermer et al., 1982.



FIGURE 2C-5 Comparison of the nitrate-plus-nitrite/phosphate phosphorus ratio in segment 2 of Saginaw Bay in 1974 and 1980. Data Source: Canada Centre for Inland Waters and U.S. EPA Storet System.





FIGURE 2C-6 Comparison of phytoplankton crop composition vs. time in segment 2 of Saginaw Bay. Data Source: Stoermer et al., 1982.

TA	DI	E.	20	1	0
IA	DL	L	26	- 1	U

PAIRWISE COMPARISONS FOR PERCH PCB BODY BURDEN CAUGHT IN DIFFERENT SEGMENTS OF SAGINAW BAY, 1977-1980

Data Source: Matthews and Dolan, in preparation

SEGMENT*	LENGTH ADJUSTED MEAN AROCLOR 260	SEGMENTS DIFFERING SIGNIFICANTLY**
1	1.29 µg/g	3 and 5
2	1.23 μg/g	all but 4
3	1.53 µg/g	3 and 5
4	1.21 µg/g	none
5	0.98 µg/g	all but 4

Grand mean = $1.24 \mu g/g$ Aroclor 1260.

*See Figure 2C-3 for location of segments. ** $\alpha = 0.05$.

TABLE 2C-11

BIOCONCENTRATION FACTORS (BCFs) FOR A1242, A1260 AND TPCB IN SAGINAW BAY YELLOW PERCH, 1977-1980

Data Source: Matthews and Dolan, in preparation

OF ONE NT	BI	OCONCENTRATION FAC	TORS*	
SEGMENT	A 1242	A 1260		
1	47390	60700	53600	
2	50750	93850	72350	
3	48820	109380	78900	
4	44300	130770	95580	
5	48040	119660	88890	

*Based on concentrations of A1242 and A1260 in total water as reported by Richardson et al., 1983.

D. LAKE ERIE

Intensive surveillance on Lake Erie occurred during the years of 1978 and 1979. A report has been prepared under contract to U.S. EPA Great Lakes National Program Office which summarizes the findings of this effort. The Surveillance Work Group has reviewed this report in addition to several others and expects to issue its findings by early 1984.

Eutrophication

According to a report prepared for the Surveillance Work Group, spring total phosphorus concentrations from 1974 through 1980 in the west-central basin showed a downward linear trend with time. No significant relationships were detected for the west, east-central or east basins over the same time period. Fall total phosphorus concentration from 1974 through 1980 likewise showed no significant trends in any of the four sub-basins. However, an analysis of typical concentrations of fall chlorophyll a did indicate a downward trend in concentrations which is considered the most severe season for eutrophication. This report, however, represents but one of several that have recently been issued. While there is some disagreement among the various authors, there appears to be some agreement that neither increasing nor decreasing phosphorus trends are apparent through 1981. Further studies combined with sophisticated analyses will be required before a definitive statement can be made.

Contaminants in Biota

Walleye was the top predator fish species collected most consistently in Lake Erie (Table 2D-1). Mirex was not detected in any samples analyzed. The concentration of PCB in 1979 samples was significantly greater (p less than 0.001) than in other years sampled. Concentrations of Σ DDT, pp'DDE and dieldrin decreased significantly (p less than 0.001) by 1981 but considerable variation occurred within the period from 1977 to 1981. Mercury levels declined consistently from 1977 through 1981 with 1981 levels significantly lower (p less than 0.001) than any preceding year.

Contaminant levels in Lake Erie rainbow smelt showed very few consistent trends (Table 2D-2). As in walleye, mirex was not detected in any samples analyzed. Maximum concentrations of PCB occurred in 1979 with a significant decline occurring subsequently. Analysis of variance of other contaminants measured failed to define any other significantly consistent trends. Only PCB levels in walleye exceeded the whole fish Agreement objective.

Contaminant levels in spottail shiners (Notropis hudsonius) indicate a general decline in both DDT and PCBs along the north shoreline. Mirex was not detected in any of the samples analyzed. Chlordane and its metabolites continue to show declining concentrations as does mercury, although the latter has tended to begin leveling off (Table 2D-3).

Analysis of herring gull eggs from 1974 to 1979 indicate a decline in levels for all six of the persistent organochlorines investigated (Table 2D-4). While not statistically significant, absolute levels of PCBs, DDT, and DDE have nevertheless shown increases since 1979, as have mirex levels from a Lake Erie colony (Pt. Colborne) close to Lake Ontario. Since 1979,

MEAN CONCENTRATION (in µg/g Wet Weight ± S.E.) OF SELECTED TRACE METALS AND ORGANOCHLORINE CONTAMINANTS IN LAKE ERIE WALLEYE (Whole Fish)

YEAR	N	WEIGHT (g)	TOTAL LENGTH (mm Range)	% LIPID	ΣΡCΒ	pp'DDE	2DD T	DIELDRIN	Hg	Zn	As	Se
1977	9	1,032.1 (222.9)	436.7 (230-570)	11.01 (1.24)	1.61 (0.42)	0.36 (0.10)	0.50 (0.13)	0.07 (0.01)	0.20 (0.04)	12.93 (0.62)	-	0.26 (0.01)
1978	56	806.3 (90.1)	388.1 (193-571)	6.23 (0.59)	1.47 (0.18)	0.14 (0.02)	0.26	0.05 (0.01)	0.15 (0.01)	12.34 (0.22)	0.22 (0.01)	0.35 (0.01)
1979	30	1,481.7 (155.9)	490.2 (325-655)	9.87 (0.57)	3.05 (0.39)	0.21 (0.04)	0.49	0.10 (0.01)	0.15 (0.02)	12.99 (0.25)	0.32 (0.01)	0.37 (0.01)
1980	40	1,123.3 (138.9)	451.4 (244-655)	9.72 (0.67)	1.40 (0.12)	0.19 (0.04)	0.45 (0.09)	0.04 (0.01)	0.13 (0.01)	13.76 (0.50)	0.33 (0.01)	0.33 (0.01)
1981	44	1,226.2 (163.3)	441.7 (214-726)	8.80 (0.64)	1.16 (0.11)	0.04 (0.00)	0.10 (0.01)	0.02 (0.00)	0.10 (0.01)	11.03 (0.37)	0.38 (0.01)	0.44 (0.01)

Data Source: Department of Fisheries and Oceans, Burlington, Ontario

Lat B

MEAN	CONCEN	TRATIC)N (in	$\mu g/g$	Wet	Weight	<u>+</u>	S. E.) (DF SEL	ECTED
TRAC	E METAL	_ AND	ORGANO	CHLOR	INE	CONTAM	INA	NTS	IN	LAKE	ERIE
		F	AINBOW	SMEL	T (W	hole Fi	ish)			

Data Source: Department of Fisheries and Oceans, Burlington, Ontario

	TOTAL										
DATE	LEN GTH (mm) RAN GE	N(1)	WEIGHT	% LIPID	ΣPCB	pp ' DD E	ΣDDT	Hg	Pb	As	Se
1977	111.5 (13-220)	78	18.45 (1.69)	2.74 (0.10)	0.18 (0.01)	0.04 (0.00)	0.06 (0.00)	0.05 (0.00)	*		0.29 (0.01)
1978	164.3 (122-211)	44	30.24 (1.90)	4.45 (0.18)	0.27 (0.03)	0.04 (0.00)	0.06 (0.01)	0.05 (0.00)	*	0.15 (0.01)	0.36 (0.01)
1979	170.5 (132-241)	35	32.38 (3.15)	4.65 (0.25)	0.38 (0.04)	0.05 (0.00)	0.10 (0.01)	0.04 (0.00)	*	0.23 (0.01)	0.31 (0.01)
1980	161.6 (115-240)	42	25.56 (2.10)	3.48 (0.11)	0.26 (0.02)	0.06 (0.00)	0.12 (0.01)	*	0.21 (0.03)	0.16 (0.01)	0.37 (0.01)
1981	164.1 (109-210)	36	31.55 (2.85)	4.76 (0.22)	0.23 (0.02)	0.03 (0.00)	0.06 (0.00)	0.04 (0.00)	*	0.23 (0.01)	0.35 (0.01)

(¹)Each sample consists of a composite of five fish. *>50% results below detection limit.

MEAN ORGANOCHLORINE AND MERCURY CONTAMINANT CONCENTRATIONS (in ng/g Wet Weight ± S.D.) FOR YOUNG-OF-THE-YEAR SPOTTAIL SHINERS FROM SELECTED SITES IN THE LOWER GREAT LAKES

Data Source: Ontario Ministry of the Environment, Rexdale, Ontario

SAMPLING SITE	YEAR	NO. OF* SAMPLES	TOTAL LENGTH (mm)	% LIPID	ΣΡCΒ	ΣDDT	MIREX	ΣCHLOR – DANE	MERCURY
LAKE ST. CLAIR				19/33 21/23			101001		
Mitchell Bay	1978 1979 1982	8 7 7	54 + 255 + 558 + 4	$ \begin{array}{r} 1.8 + 0.2 \\ 1.0 + 0.2 \\ 2.2 + 0.2 \end{array} $	94 <u>+</u> 50 33 <u>+</u> 14	$ \begin{array}{r} 21 + 16 \\ 3 + 1 \\ 4 + 4 \end{array} $	nd nd nd	$\begin{array}{c}4 + 2\\3 + 2\\\overline{tr}\end{array}$	70 + 1080 + 2056 + 5
Thames River	1977 1979 1982	8 4 7	59 + 1 70 + 5 62 + 5	1.5 + 0.32.4 + 0.11.8 + 0.2	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	nd nd nd	$\begin{array}{r}4 + 3\\12 + 4\\tr\end{array}$	$\begin{array}{c} 62 + 6 \\ 50 + 16 \\ 31 + 4 \end{array}$
Pike Creek	1978 1979 1980 1982	8 4 7 7	57 + 263 + 662 + 661 + 6	2.0 + 0.22.1 + 0.51.2 + 0.21.7 + 0.2	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	nd nd nd nd	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	50 + 838 + 1041 + 946 + 8
LAKE ERIE									
Big Creek	1977 1978 1980 1981 1982	7 7 7 7 7 7	57 + 355 + 266 + 560 + 457 + 7	$\begin{array}{c} 0.9 + 0.1 \\ 1.0 + 0.2 \\ 1.1 + 0.2 \\ 2.1 + 0.3 \\ 1.7 + 0.2 \end{array}$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	75 + 1542 + 2226 + 1331 + 152 + 1	nd nd nd nd	nd 7 + 5 7 + 3 8 + 3 nd	$\begin{array}{r} 93 + 16 \\ 40 + 7 \\ 47 + 26 \\ na \\ 61 + 7 \end{array}$

INSTE SO-S

Table 2D-3 - cont'd.

GTH GTH n) 2			10 NOG			+ + +	
¢ LIPID		+ 3 1.8 + 0.2 + 1 1.6 + 0.3 + 1 1.7 + 0.3 + 4 3.4 + 0.5 + 4 1.4 + 0.3	+ - + 0.3 + 5 1.6 + 0.3 + 5 1.8 + 0.1 + 4 2.8 + 0.6 + 8 2.6 + 0.5	+ 2 2.6 + 0.3 + 3 1.5 + 0.2 + 7 2.0 + 0.5 + 4 1.8 + 0.4	$\begin{array}{c} + 2 \\ + 2 \\ + 7 \\ + 7 \\ + 7 \\ + 7 \\ + 7 \\ + 7 \\ + 6 \\ + 6 \\ + 0.7 \\ + 0.4 \\ + 0.4 \\ \end{array}$	$\begin{array}{c} + 4 & 2.3 + 0.3 \\ + 3 & 2.5 + 0.6 \\ + 1 & 1.9 + 0.2 \end{array}$	+ 2 2.4 + 0.4 + 2 2.1 + 0.4 + 3 1.9 + 0.1 + 3 2.2 + 0.1
ΣPCB		844 + 403 467 + 113 528 + 55 337 + 79 150 + 37	236 + 38 236 + 30 50 + 30 33 + 36 33 + 36 30 + 36	70 70	$157 + 28 \\ 31 + 12 \\ 95 + 29 \\ 60 + 17 \\ 17 \\ 17 \\ 17 \\ 17 \\ 17 \\ 17 \\ 17$	$\begin{array}{r} 690 + 195 \\ 654 + 170 \\ 320 + 49 \end{array}$	$ \begin{array}{r} 153 + 23 \\ 266 + 51 \\ 327 + 62 \\ 255 + 24 \\ \end{array} $
ΣDDT		92 + 22 133 + 45 47 + 10 18 + 4 21 + 4	24 + 10 16 + 4 16 + 4 16 + + 4 16 + + 6 16 + 7 16 +	42 + 13 12 + 13 5 + 4	$\begin{array}{c} 33 + 12 \\ 9 + 7 \\ 24 + 14 \\ 19 + 8 \\ 19 + 8 \end{array}$	$\begin{array}{rrrr} 244 + 52 \\ 157 + 38 \\ 99 + 49 \end{array}$	26 + 9 41 + 9 73 + 15 82 + 14
MIREX		prrr.		pre	pu pu pu	na 13 + 4 29 + 8	11 tr 10 ++ 2 6 ++ 3 10 3 10 3 10 4 10 3 10 4 10 3 10 4 10 3 10 4 10 3 10 4 10 4 10 4 10 4 10 4 10 4 10 4 10 4
2CHLOR- DANE	14	27 nd 27 + 8 18 + 5 14	+ + + + + + + + + +	9 + 1 9 + 1 1 + 1	20 + 4 20 + 2 20 + 2 10 10	01 + 19 61 + 10	21 + 18 24 + 6 11 + 4 17 + 7
MER CUR Y	10 m	56 + 7 50 + 5 16 + 5 12 + 5	29 + 4 29 + 4 22 + 8 na 25 + 5	23 ± 3 54 + 10 37 + 18 22 ± 4 22 ± 4	$ \begin{array}{r} 40 + 5 \\ 30 + 10 \\ \hline na \\ 49 + 7 \end{array} $	77 + 13 50 + 8	$ \begin{array}{r} 50 + 12 \\ 23 + 5 \\ \hline na \\ 43 + 13 \\ \hline and \\ 43 + 13 \\ \hline and \\ an$

Table 2D-3 - cont'd.

SAMPLING SITE	YEAR	NO. OF* SAMPLES	TOTAL LENGTH (mm)	% LIPID	ΣΡCΒ	ΣDDT	MIREX	ΣCHLOR- DANE	MERCURY
LAKE ONTARIO - cont'd.	8861 0061	the Areas	Rea La	1.9 ¥ 0.7	11 E 00			19 .SQ 11 7	40 4 1 19
Twelve Mile Creek	1978 1979 1980 1981 1982	8 8 7 6 7	51 + 3 51 + 4 48 + 6 54 + 5 41 + 5	2.9 + 0.42.1 + 0.41.9 + 0.32.5 + 0.51.6 + 0.3	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{r} 20 + 12 \\ nd \\ tr \\ tr \\ 21 + 5 \end{array}$	$ \begin{array}{r} 24 + 10 \\ \hline nd \\ 7 + 2 \\ 6 + 2 \\ 8 + 2 \\ \end{array} $	$\begin{array}{c} 40 + 8 \\ 20 + 7 \\ 14 + 5 \\ na \\ 29 + 4 \end{array}$
Credit River	1976 1978 1979 1980 1982	10 8 8 7 7 7	$\begin{array}{r} 62 + 3 \\ 60 + 3 \\ 56 + 3 \\ 62 + 4 \\ 52 + 7 \end{array}$	$na \\ 2.6 + 0.3 \\ 3.7 + 0.6 \\ 2.7 + 0.6 \\ 3.2 + 0.2 \\ \end{cases}$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{r} 278 + 106 \\ 96 + 12 \\ 69 + 12 \\ 59 + 20 \\ 66 + 32 \end{array}$	$ \begin{array}{r} 32 + 13 \\ 28 + 8 \\ nd \\ tr \\ 7 + 2 \end{array} $	55 + 2137 + 836 + 624 + 521 + 7	na 40 + 6 24 + 10 33 + 5 39 + 4
Humber River	1977 1978 1979 1980 1981 1982	8 8 6 6 6	$\begin{array}{r} 62 + 3 \\ 58 + 5 \\ 60 + 6 \\ 62 + 5 \\ 62 + 5 \\ 62 + 5 \\ 58 + 2 \end{array}$	7.3 + 0.4 5.8 + 0.5 4.0 + 1.3 4.0 + 0.4 5.0 + 0.8 3.7 + 0.4	$\begin{array}{r} 2218 + 263 \\ 2938 + 391 \\ 1223 + 347 \\ 621 + 66 \\ 954 + 45 \\ 353 + 70 \end{array}$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	5 + 2 $15 + 4$ nd nd nd nd	$58 + 16 \\ nd \\ 47 + 9 \\ 35 + 6 \\ 26 + 9 \\ 22 + 1$	$\begin{array}{r} 44 + 5 \\ 40 + 7 \\ 30 + 19 \\ 22 + 4 \\ \hline na \\ 30 + 0 \end{array}$
Outlet River	1979 1980 1982	8 7 7	53 + 353 + 449 + 1	$\begin{array}{r} 4.3 + 1.2 \\ 4.8 + 0.4 \\ 4.8 + 0.3 \end{array}$	$ \begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$

TOITON-

tr - Trace.

na - Not analyzed.

nd - Non-Detectable.

* - Each sample is a composite of 10 fish.

- 40 -

MEAN CONCENTRATION (in μ g/g Wet Weight ± S.D.) OF SELECTED ORGANOCHLORINE CONTAMINANTS IN HERRING GULL EGGS FROM TWO LAKE ERIE COLONIES

Data Source: Canada Wildlife Service, Burlington, Ontario

LAKE ERIE	N	% FAT	DDE	DDT	DIELDRIN	НСВ	MIREX	PCBs
PT. COLBORNE LIGHTHOUSE							134820	
1974	10	8.5 + 1.0	8.7 + 3.3	0.23 + 07	0.37 ± 13	0 21 + 05	0.04 . 51	72 . 00
1975	10	8.3 + 0.6	7.9 + 1.8	0.10 + 06	$0.37 \pm .13$ 0.38 ± 14	$0.21 \pm .05$	$0.84 \pm .51$	73 + 20
1977	10	9.8 + 1.6	7.6 + 1.7	0.06 + 03	0.50 + .14	0.17 + .05	$0.42 \pm .17$	54 + 14
1978	10	9.0 + 1.0	5.6 + 1.3	0.00 ± .05	0.30 + .20	$0.19 \pm .03$	0.51 + .20	59 + 13
1979	10	8.6 + 0.5	3.4 + 1.0	$0.03 \pm .00$	0.28 + .09	$0.09 \pm .02$	0.38 + .16	46 + 11
1980	9	7.6 + 0.5	3.4 + 1.5	0 11 + 10	0.24 + .00	$0.10 \pm .02$	$0.25 \pm .09$	38 + 6
198 1	10	9.6 ± 1.0	4.7 + 1.7	0.05 ± .02	$0.27 \pm .13$ $0.24 \pm .09$	$0.09 \pm .02$ $0.08 \pm .03$	$0.28 \pm .18$ $0.42 \pm .37$	38 <u>+</u> 16 44 <u>+</u> 13
MIDDLE ISLAND								
1974	10	8.5 + 0.9	5.6 + 1.6	0.32 + .17	0.34 + .14	0.38 + .12	0.44 + 43	72 + 14
1975	10	8.4 + 0.8	6.9 + 1.7	0.10 + .07	0.28 + .07	0.23 ± 09	0 22 + 06	72 + 14
1977	10	9.0 + 1.1	7.4 + 2.2	0.05 + .03	0.31 + 09	0.19 + 06	0.30 + 34	71 + 13
1978	10	8.8 + 1.1	3.0 + 1.0	0.05 + .03	0.21 ± 06	0.09 ± .00	0.03 + .54	70 + 24
1979	10	8.1 + 1.1	2.8 + .59	0.03 ± 01	0.27 ± 11	0.12 1 02	0.02 + .05	42 + 11
1980	10	7.1 + 1.0	2.6 + .66	0.10 ± 08	0 16 + 06	0.02 + .02	0.10 + .04	59 + 13
198 1	10	8.6 ± 0.9	3.1 + .93	0.04 + .02	0.20 ± .05	$0.10 \pm .02$	$0.09 \pm .08$ $0.07 \pm .07$	54 <u>+</u> 12 69 <u>+</u> 16

concentrations of dieldrin, HCB, and mirex on the Middle Island colony have shown a persistent declining trend and HCB on the Pt. Colborne colony has shown a significant declining trend.

E. LAKE ONTARIO

The years 1981-1982 were designated in the Great Lakes International Surveillance Plan (GLISP) as the intensive field years for Lake Ontario. A report on these studies is currently in preparation. This section covers only highlights of presently available material.

Eutrophication

Nutrients

To adequately summarize the large volume of data on phosphorus and nitrogen, two techniques were employed in the analyses: a) the box plot (McGill et al., 1978) and b) ALDAR which is a computer program producing area-weighted mean values for each of 17 zones into which the lake has been divided for the purpose of analyses (Figure 2E-1). These zones, based on temperature profiles and geographic considerations, have been used since 1977 in Board Reports to summarize data and report trends. Currently, a new regionalization of the lake is being devised based on statistical analysis of 1977, 1981 and 1982 data and future Lake Ontario status reports will be based on this new zonation scheme. Only spring data (i.e., collected while the lake was still isothermal) have been used in the trend analyses. During this period, vertical gradients of chemical parameters are at a minimum with the result that surface conditions (1 m) are representative of that found throughout the entire water column (Scavia and Bennett, 1980).

<u>Total Phosphorus</u>. The area weighted mean total phosphorus concentration for the 1981 and 1982 spring periods were compared using a Student's t-test to determine if there has been any change in phosphorus concentrations between the two years. While no significant difference (p less than 0.05) was found, the large spatial variations associated with each year tend to mask any true differences. In an attempt to eliminate the sources of this variability, results were reanalyzed using only data from the mid-lake region (zone 17). Variability was subsequently reduced from 22.3% to 4.7% and 22.7% to 10.0% for 1981 and 1982, respectively, but there was still no significant difference (p less than 0.05) found in the concentrations between the two years. The actual change in concentration between 1981 and 1982 was 0.5 μ gP/L which is approximately a 3.5% decrease.

Available data indicate that phosphorus concentrations have declined since about 1973. Such data have previously been reported using area weighted mean total phosphorus concentrations (Figure 2E-2). Although these data indeed show this trend, a new "box plot" is a more informative technique and will be used to report future trends.

Specifically, Figure 2E-3 shows that since 1977 the median value has continued to decrease, although during 1978-1980, 50% of the samples were within the same approximate range of concentrations (15.0 - 19.0 μ g P/L). In 1981, 25% of the samples were reported at less than 13.3 μ g P/L (i.e.,







Data Source: Neilson (1983a).

45 -

the lower quartile concentration) while in 1982, almost 50% of the samples were less than this median (median = 13.5 μ g P/L). Furthermore, the median concentration of 13.5 μ gP/L reported in 1982 was the lowest reported in the last 13 years. The annual decrease in phosphorus was not constant from year to year (i.e., not linear).

Nitrate + Nitrite (Filtered). Data for whole lake spring (surface) filtered nitrate + nitrite concentrations are presented in Figure 2E-4. With the exception of 1980, the median concentrations have increased each year since 1975. The median value increased significantly (p less than 0.05) from 0.335 μ g N/L to 0.359 μ g N/L between 1981 and 1982. Linear regression analysis of the data over the period 1970 to 1982 indicates that nitrate + nitrite-N has been increasing at a rate of approximately 9.4 μ g N/L/yr (r² = 0.86).

Contaminants

Metals

Trace metals were sampled during three 1979 cruises. Water quality objectives were exceeded for silver, cadmium, iron, lead and selenium but not at the frequency encountered during 1972-1973 collections (Waller and Lee, 1979). Concentrations were generally greater in the western end of the lake and in localized areas near the influence of the Credit, Humber, Etobicoke, Don, Genesee, and Black Rivers and in the vicinity of Hamilton Harbour. Results from the 1982 survey were not available in time for this report.

Based on a toxic unit analysis of total metals in water (see section 2C -Metals) cadmium (Cd), copper (Cu) and, silver (Ag) may be contributing a deleterious impact to the entire lake (Table 2E-1).

Contaminants in Biota

Age 4⁺ lake trout samples were utilized to describe annual contaminant trends (Table 2E-2). One way ANOVA was used to compare mean contaminant levels between years. PCB concentrations declined steadily from 1977 to a significantly lower level (p less than 0.001) in 1981. Preliminary 1982 data indicate an increase of 67.3% over 1981 PCB levels. Additional years of collection will be needed to determine the significance of this observation. Dieldrin, mirex, pp'DDE and Σ DDT have all shown significant declines (p less than 0.001) from 1977 levels but the declines have not been consistent from year to year. Levels of Σ DDT and PCB were consistently above the IJC whole fish Agreement objective. Trace metal levels were nominally consistent from year to year with mercury (Hg) showing a significant (p less than 0.05) decline over the period 1977 to 1981. Trace metal data are not yet available for 1982 samples.

Levels of PCB and Σ DDT in rainbow smelt samples varied considerably from year to year while average weight increased consistently from 1977 to 1982 (Table 2E-3). Mirex levels decreased consistently with 1982 concentrations significantly lower (p less than 0.001) than all previous years (Table 2D-3). Of all trace metals measured, only lead (Pb) levels have increased significantly (p less than 0.001) from 1978 to 1981. Only PCB levels exceeded the whole fish Agreement objective of 0.1 µg/g.



TABLE 2E-1

EVALUATION OF TOXIC UNIT CONCEPT (AEOC, 1981) AS APPLIED TO 1979 TRACE METAL CONCENTRATION (µg/L) OF LAKE ONTARIO WATER. MEAN VALUES WITHIN EACH OF FOUR ZONES WERE USED TO CALCULATE Mi/Oi, WHERE Mi IS THE OBSERVED CONCENTRATION AND Oi IS THE WATER QUALITY OBJECTIVE.

Data Source: Neilson (1983b)

METALS	CURRENT IJC WATER QUALITY OBJECTIVES	ZONE 1	Mi Oi	ZONE 2	Mi Di	ZONE 3	Mi Oi	ZONE 4	Mi Oi
Fe Cd Cn Cr Pb Ni Zn Hg As Ag Se	300.0 0.2 5.0 20.0 3.0 25.0 30.0 0.2 50.0 0.1 1.0	61.2 0.07 1.71 1.16 0.59 2.81 2.20 0.026 0.54 0.08 0.08	0.20 0.35 0.34 0.02 0.20 0.11 0.07 0.13 0.01 0.80 0.08	32.4 0.05 1.27 0.53 0.36 1.58 1.30 0.025 0.52 0.08 0.08	0.11 0.25 0.25 0.01 0.12 0.06 0.04 0.125 0.01 0.80 0.08	12.3 0.05 1.31 0.44 0.33 1.35 0.90 0.025 0.62 0.08 0.07	0.04 0.25 0.26 0.009 0.11 0.05 0.03 0.125 0.01 0.80 0.07	9.3 0.05 1.10 0.34 0.34 1.23 0.80 0.025 0.52 0.52 0.07 0.08	0.03 0.25 0.22 0.007 0.11 0.05 0.03 0.125 0.01 0.70 0.08
Σ Mi/Oi			2.31		1.86		1.75		1.61
*		Cd, C	u, Ag	Cd, C	u, Ag	Cd, Cu	u, Ag	Cd, C	u, Ag

*Contribution greater than 0.2 toxic units.

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YEAR	N	WEIGHT (g)	TOTAL LENGTH (mm Range)	% LIPID	ΣΡCΒ	pp'DDE	ΣΟΟΤ	DIELDRIN	MIREX	Hg	Zn	As	Se
1977	3	2,102.3 (458.2)	543.3 (475-580)	21.30 (3.00)	8.00 (0.91)	2.58 (0.38)	4.35 (0.53)		0.49 (0.08)	0.25 (0.04)	11.67 (1.20)	1.00	0.44 (0.01)
1978	11	1,199.5 (121.3)	471.5 (375-557)	17.75 (0.99)	5.06 (0.63)	1.01 (0.11)	1.27 (0.15)	0.21 (0.02)	0.15 (0.04)	0.18 (0.01)	8.88 (0.64)	-	0.33 (0.03)
1979	75	2,067.9 (49.8)	559.6 (457-622)	20.23 (0.34)	4.73 (0.30)	1.50 (0.10)	1.99 (0.12)	0.23 (0.01)	0.25 (0.01)	0.20 (0.01)	10.52 (0.15)	0.57 (0.01)	0.42
1980	82	1,791.7 (51.1)	553.0 (405-646)	18.42 (0.34)	4.77 (0.28)	0.64 (0.08)	0.81 (0.09)	0.12 (0.01)	0.14 (0.01)	0.20 (0.00)	7.96 (0.20)	0.55 (0.01)	0.43
1981	83	1,538.0 (62.2)	517.9 (330-635)	19.09 (0.50)	3.67 (0.22)	0.89 (0.04)	1.51 (0.05)	0.19 (0.01)	0.15 (0.01)	0.16 (0.00)	9.64 (0.12)	0.50 (0.01)	0.40 (0.01)
1982	22	1,734.7 (90.4)	541.4 (405-613)	19.48 (0.66)	6.14 (0.42)	0.82 (0.06)	1.23 (0.06)	0.17 (0.01)	0.16 (0.01)	-	-	-	-
and the state of the													

Data Source: Department of Fisheries and Oceans, Burlington, Ontario

MEAN CONCENTRATION (in µg/g Wet Weight ± S.E.) OF SELECTED TRACE METALS AND ORGANOCHLORINE CONTAMINANTS IN LAKE ONTARIO AGE 4⁺ LAKE TROUT (Whole Fish)

TABLE 2E-2

1 1

MEAN	CONCENTRATION	(in µg/g W	let Weigh	nt ± S.E.) OF SELECTED	TRACE METAL	AND ORGANOCHLORINE
	00	NTAM IN AN TS	IN LAKE	ONTARIO	RAINBOW SMEL	T (Whole Fish)

TABLE 2E-3

YEAR	N(1)	WEIGHT (g)	TOTAL LENGTH (mm Range)	% LIPID	РСВ	pp'DDE	ΣDDT	DIELDRIN	MIREX	· Hg	РЪ	As	Se
1977	38	22.69 (1.93)	149.6 (100-280)	4.87 (0.19)	1.50 (0.18)	0.44 (0.05)	0.60 (0.06)	0.02 (0.00)	0.11 (0.01)	0.08 (0.01)	Sadt-	15381-	0.35 (0.01)
1978	73	24.44 (2.30)	152.1 (69-242)	5.41 (0.18)	1.74 (0.16)	0.33 (0.03)	0.39 (0.03)	0.05 (0.01)	0.05 (0.00)	0.06 (0.00)	0.11 (0.01)	0.43 (0.01)	0.36
1979	73	24.20 (2.28)	150.8 (100-243)	5.64 (0.17)	0.80 (0.05)	0.33 (0.04)	0.39 (0.04)	0.04 (0.00)	0.05 (0.00)	0.06 (0.00)	0.17 (0.01)	0.62 (0.01)	0.33
1980	33	28.65 (3.63)	160.4 (108-245)	6.18 (0.27)	1.12 (0.10)	0.21 (0.02)	0.25 (0.02)	0.04 (0.00)	0.04 (0.00)	0.09 (0.01)	0.22 (0.02)	0.59 (0.03)	0.33
1981	47	28.27 (3.18)	159.9 (86-241)	5.55 (0.22)	0.90 (0.06)	0.33 (0.02)	0.49 (0.03)	0.06 (0.00)	0.04 (0.00)	0.07 (0.00)	0.26 (0.03)	0.53 (0.01)	0.31 (0.00)
1982	44	31.66 (3.75)	164.7 (176-250)	4.65 (0.25)	1.68 (0.13)	0.35 (0.02)	0.44 (0.03)	0.05 (0.00)	0.02 (0.00)	-	-	-	-

Data Source: Department of Fisheries and Oceans, Burlington, Ontario

 $(\ {}^1)Each$ sample consists of a composite of five fish.

Analysis of spottail shiner composites demonstrates that while there is a significant residue reduction (p less than 0.01) of PCBs, *EDDT*, total chlordane and mirex at most of the sites sampled, PCBs, *EDDT* and mirex residues have remained relatively constant at Twelve Mile Creek and PCBs have not declined at Outlet River. All 1982 PCB residue values still exceed the Agreement objective. Mercury residue levels have remained relatively unchanged (see Table 2D-3).

Analysis of herring gull eggs from 1974 through 1979 indicate an overall decline in levels of six organochlorine contaminants investigated (Table 2E-4). The decline between 1981 levels and those when concentrations were greatest for each compound are as follows: DDE-50%, DDT-91%, dieldrin-44%, HCB-57%, mirex-62%, and PCBs-52%. While the 1981 values are less than those reported in 1974/75, a pattern of increasing values beginning in 1980 has emerged. The significance of such increases must await several more years of collection and analysis.

F. CONNECTING CHANNELS

Each of the Connecting Channels has been designated by the Water Quality Board as Class "A" Areas of Concern. As stated in the introduction to this report, significant environmental changes in Class "A" Areas of Concern have been incorporated into a separate Appendix to this year's Board Report (Appendix A). The sections below provide a brief summary of the issues and some additional information that may not have been incorporated into Appendix A for each of the Connecting Channels.

ST. MARYS RIVER

The St. Marys River has historically received effluents from Algoma Steel, Abitibi Paper, and municipal wastewaters. These point sources have been responsible for high river concentrations of iron, zinc, phenol, cyanide, oil, and bacteria. The river was intensively studied in 1980 to assess and evaluate progress of remedial actions that were instituted largely as a result of the 1974 studies conducted under the Upper Lakes Reference Group. Additional water quality information on the St. Marys River will appear in the Lake Huron 1980 Intensive Survey Summary Report.

Phenol concentrations of less than 10 μ g/L were recorded from 3 km or more downstream from the Algoma Steel outfall. While these values represent a significant improvement over historical data, the recorded concentration still exceeds the Agreement objective of 1 μ g/L. Transboundary pollution occurs to some degree as values in excess of 5 μ g/L were observed in United States waters.

Ammonia levels in 1980 were in compliance except in close proximity to the Sault Ste. Marie, Ontario sewage treatment plant. There is some limited transboundary movement of ammonia resulting from this discharge but concentrations are generally less than the Agreement objective of 0.5 mg/L.

While concentrations of iron were below the Agreement objective at a distance greater than 300 m below the Algoma Steel outfall, values exceeding the objective were consistently recorded near the effluent discharge area.

TABLE 2E-4

MEAN CONCENTRATION (in µg/g Wet Weight ± S.D.) OF SELECTED ORGANOCHLORINE CONTAMINANTS IN HERRING GULL EGGS FROM TWO LAKE ONTARIO COLONIES

Data Source: Canada Wildlife Service, Burlington, Ontario

LAKE ONTARIO	N	% FAT	DDE	DDT	DIELDRIN	НСВ	MIREX	ΣPCBs
SNAKE ISLAND								
1974	10	7.2 + 1.4	21.0 + 9.1	1.0 + 1.1	0.47 + .25	0.56 + .39	6.6 + 2.8	141 + 49
1975	10	7.8 + 1.7	24.0 + 6.1	0.23 + 0.17	0.35 + .20	0.22 + .20	6.0 + 2.3	181 + 51
1977	10	9.6 + 1.5	17.0 + 4.7	0.11 + 0.06	0.50 + .10	0.50 + .11	2.9 + 1.1	121 + 33
1978	10	9.7 + 1.6	10.0 + 2.9	0.07 + 0.02	0.28 + .10	0.35 + .12	1.7 + 0.51	71 + 20
1979	10	8.6 + 0.8	8.8 + 3.0	0.06 + 0.03	0.19 + .10	0.22 + .12	2.0 + 0.61	63 + 18
1980	10	7.9 + 0.6	7.1 + 4.1	0.14 + 0.13	0.20 + .09	0.15 + .08	1.6 + 0.77	53 + 23
198 1	10	9.5 + 0.8	12.0 + 4.5	0.11 + 0.05	0.27 ± .16	0.26 + .11	2.8 + 1.6	86 + 41
MUGG'S ISLAND								
1974	9	7.8 + 1.2	23.0 + 5.5	1.2 + 0.79	0.46 + .13	0.60 + .36	7.4 + 4.7	171 + 48
1975	10	7.7 + 0.8	22.0 + 5.5	0.13 + 0.06	0.24 + .16	0.45 + .26	3.4 + 1.4	111 + 21
1977	10	8.8 + 1.0	13.0 + 2.5	0.12 + 0.05	0.27 + .08	0.34 + .06	2.1 + 0.4	87 + 19
1978	8	8.6 + 1.0	11.0 + 3.0	0.10 + 0.05	0.25 + .05	0.28 + .06	1.4 + 0.7	75 + 17
1979	10	8.7 + 0.5	9.0 + 3.5	0.08 + 0.06	0.22 + .13	0.21 + .08	1.8 + 0.9	76 + 30
1980	9	7.9 + 0.8	8.7 + 6.0	0.10 + 0.04	0.18 + .10	0.20 + .10	1.7 + 1.1	60 + 29
198 1	10	8.9 ± 0.8	10.0 + 5.2	0.08 ± 0.03	0.28 ± .21	0.23 ± .08	2.5 <u>+</u> 1.1	72 ± 30

DETROIT RIVER

Water

Quality of water in the Detroit River has been monitored since 1967 by the Michigan Department of Natural Resources (MDNR). Data are used to compare characteristics of ambient water quality over time and to calculate pollutant loadings to Lake Erie.

Data from 1982 have not been compiled. Data from 1981, not previously reported, show that water quality and pollutant loads, as indicated by standard indexing parameters (turbidity, solids, nutrients) have generally improved. Tables 2F-1 and 2F-2, and Figure 2F-1, illustrate this trend. Analyses for organochlorine and other persistent toxic organic compounds were not performed.

Sediments

In 1980, the Ontario Ministry of the Environment (Thornley and Hamdy, 1983) assessed bottom sediments and associated macrobenthos to compare with conditions observed in 1968. In 1982, the MDNR, (Fallon and Horvath, 1983) analyzed sediment core samples for 129 "priority pollutants" from throughout the river.

The OMOE data indicate a balanced community structure, reflective of satisfactory water quality, along the entire Canadian shoreline both in 1968 and 1980. Canadian point sources had not seriously disrupted the macrobenthos. Along the United States shoreline, however, serious disruption was evident. Macrobenthos populations near the mouth of the Rouge River were greatly reduced in abundance and diversity. Immediately downstream from the Rouge, pollution-tolerant aquatic worms numbered over one million per square meter of river bottom in both 1968 and 1980 demonstrating long-term, severe organic enrichment. Further downstream to the Detroit River mouth relatively high numbers of worms, representing a lesser degree of enrichment, persisted along the United States shore.

In general, an increase in the types (diversity) of benthic organisms occurred between 1968 and 1980, particularly along the Canadian shoreline. The burrowing mayfly <u>Hexagenia limbata</u> was found at 70% of the OMOE stations in 1980 compared to 26% in 1968. The recovery of the mayfly was most evident in the center of the river and along the Canadian shoreline. Along the United States shoreline, however, mayfly numbers were still low although somewhat improved since 1968.

Both the 1980 OMOE and 1982 MDNR sediment data indicate high concentrations of heavy metals along the United States shoreline downstream of the Rouge River. Mercury levels generally declined between 1968 and 1980, but OMOE data show significant increases in cadmium, chromium, copper, lead, nickel and zinc in the vicinity of the Rouge River.

Sediment contaminants along the Canadian shoreline were localized and attributed to known sources, such as the Little River, West Windsor Sewage Treatment Plant, Turkey Creek, and River Canard. Sediments around Fighting Island showed contaminant levels well below OMOE dredging guidelines.

TABLE 2F-1

WATER QUALITY OF RANGE DT 3.9 LOCATED AT THE MOUTH OF THE DETROIT RIVER

Data from the Detroit Monitoring Program carried on by Michigan were used to prepare the table shown below. Ten stations across the mouth range 3.9 were used in calculating the averages for each Water Year.

The mean concentrations were developed by weighting individual concentrations across the range for flcw. The weighting factors used were based on the percentage of river flow presented at each station on the range.

MEAN WATER QUALITY DATA - WATER YEAR BASIS

PARAMETERS	WATER YEAR 69	WATER YEAR 70	WATER YEAR 71	WATER YEAR 72	WATER YEAR 73	WATER YEAR 74	WATER YEAR 75	WATER YEAR 76	WATER YEAR 77	WATER YEAR 78	WATER YEAR 79	WATER YEAR 80	WATER YEAR 81
Phenols (µg/L)	1.7	6.1	1.7	1.8	1.5	2.0	2.1	2.7	2.9	1.7	1.2	0.7	0.8
Total Iron (mg/L)	0.56	0.52	0.37	0.60	0.39	0.35	0.11	0.55	0.42	0.39	0.35	0.30	0.27
Chloride (mg/L)	18	18	16	17	16	16	15	15	15	15	13	13	11
Sol. Phosphorus (mg/L)	0.07	0.08	0.04	0.03	0.02	0.02	0.03	0.02	0.01	0.02	0.00	0.01	<0.00
Tot. Phosphorus (mg/L)	0.14	0.14	0.08	0.07	0.08	0.05	0.06	0.05	0.04	0.04	0.03	0.02	0.02
Ammonia Nitrogen (mg/L)	0.13	0.13	0.16	0.15	0.10	0.12	0.13	0.10	0.10	0.10	0.08	0.07	0.08
Nitrate Nitrogen (mg/L)	0.17	0.27	0.28	0.32	0.27	0.27	0.35	0.30	0.25	0.28	0.31	0.32	0.30
pH (low value/ high value)	7.3/ 8.2	7.3/ 8.2	7.6/ 8.3	7.0/ 8.3	7.0/ 8.3	7.0/ 8.1	7.5/ 8.3	7.5/ 8.2	7.7/ 8.6	7.3/ 8.6	7.4/8.5	7.6/ 8.6	7.7/ 8.2
Diss. Cxygen (mg/L)	8.6	7.7	7.8	9.1	7.9	8.9	9.8	8.8	8.7	8.8	9.3	9.5	9.6

TABLE 2F-2

LOADINGS TO LAKE ERIE FROM THE DETROIT RIVER

Data from the Detroit River Monitoring Program carried on by Michigan were used to prepare the table below. The table shows the mean daily loading rate of ten water quality parameters at approximately 3.9 miles upstream of the mouth of the Detroit River. Data at 10 stations across Range 3.9 were used to calculate the loadings, which represent the amounts of the various materials entering Lake Erie.

The monthly concentration was multiplied by the average daily flow for the month to yield a loading product. These individual products were weighted for flow by taking into account the percentage of total river flow represented by the sampled station. These weighted loading rates were summed to yield a mean daily loading rate for the year. Also given is the standard deviation of the loading, enclosed in parentheses, for each parameter.

> PERIOD OF RECORD - WATER YEAR BASIS Mean Daily Loadings as kg/day¹ Passing Range DT 3.9 at the Mouth of the Detroit River Standard Deviation Expressed as kg/day are in parentheses

WATER YEAR	TOTAL ² SOLIDS (kg/day)	DISSOLVED SOLIDS (kg/day)	SUSPENDED SOLIDS (kg/day)	CHLORIDE (kg/day)	TOTAL PHOSPHORUS (kg/day)	SOLUBLE PHCSPHORUS (kg/day)	NITRATE ³ NITROGEN (kg/day)	AMMONIA NITROGEN (kg/day)	TOTAL IRON (kg/day)	PHENOLS (kg/day)	FLOW ⁵ (m ³ /Sec)
1969	NA	NA	8,400,000 (540,000)	9,400,000 (660,000)	72,000 (8,300)	37,000 (7,200)	90,000 (7,000)	68,000 (9,900)	290,000 (16,000)	900 (100)	6,030
1970	NA	NA	8,000,000 (490,000)	9,500,000 (630,000)	71,000 (6,200)	42,000 (6,600)	140,000 (12,000)	68,000 (10,000)	270,000 (18,000)	3,100 (1,400)	6,060
1971	87,000,000	81,000,000 (2,300,000)	6,400,000 (300,000)	8,900,000 (630,000)	42,000 (4,200)	19,000 (2,300)	150,000 (17,000)	84,000 (12,000)	200,000 (11,00C)	910 (120)	6,260
1972	98,000,000	90,000,000 (2,200,000)	7,700,000 (610,000)	9,100,000 (560,000)	40,000 (4,100)	18,000 (2,500)	170,000 (14,000)	84,000 (9,300)	330,000 (29,000)	990 (150)	6,350
1973	100,000,000	98,000,000 (2,000,000)	4,700,000 (270,000)	9,500,000 (530,000)	45,000 (2,600)	12,000 (1,100)	160,000 (9,500)	60,000 (8,000)	230,000 (13,000)	880 (120)	6,790
1974	100,000,000	96,000,000 (1,900,000)	5,100,000 (310,000)	9,500,000 (500,000)	31,000 (3,000)	12,000 (1 500)	160,000 (6,800)	73,000 (8,900)	308,000 (11,000)	1,200 (170)	6,820
1975	100,000,000	93,000,000 (1,600,000)	8,800,000 (510,000)	8,600,000 (390,000)	33,000 (3,600)	14,000 (1,800)	200,000 (12,000)	76,000 (9,000)	240,000 (18,000)	1,300 (6C)	6,640
1976	100,000,000	89,000,000 (1,800,000)	9,000,000 (610,000)	8,400,000 (430,000)	28,000 (2,400)	8,900 (820)	170,000 (11,000)	59,000 (6,70C)	320,000 (17,000)	1,600 (84)	6,640
1977	82,000,000	77,000,000 (1,500,000)	5,400,000 (280,000)	7,100,000 (390,000)	17,000 (1,800)	6,100 (790)	120,000 (6,400)	50,000 (6,500)	200,000 (11,000)	1,400 (81)	5,640
1978	85,000,000	79,000,000 (1,600,000)	6,500,000 (270,000)	7,000,000 (400,000)	17,000 (1,400)	8,300 (3,900)	136,000 (4,600)	49,000 (6,200)	188,000 (10,000)	800 (69)	5,740
1979	86,000,000	80,000,000 (1,600,000)	6,300,000 (290,000)	6,700,000 (400,000)	14,000 (1,000)	2,600 (260)	160,000 (6,800)	43,000 (5,900)	186,000 (8,900)	630 (60)	6,100
1980	85,000,000	80,000,000 (1,900,000)	4,700,000 (320,000)	6,400,000 (440,000)	13,000 (800)	3,800 (290)	164,000 (6,000)	38,000 (5,000)	152,000 (9,500)	340 (30)	5,940
1981	80,000,000	75,000,000 (1,400,000)	4,600,000 (200,000)	5,400,000 (330,000)	9,700 (500)	2,100 (160)	154,000 (4,400)	40,000 (5,300)	140,000 (15,000)	390 (30)	5,904

 1 lbs/day = kg/day *2.21.

²Summation of dissolved solids and suspended solids. ³Nitrate nitrogen for Water Year 1969 through 1972. Nitrate plus nitrite nitrogen to present.

"Not available.

⁵Represents Detroit River flow on days samples were obtained.



Data Source: Michigan Department of Natural Resources

56 -

Highest levels of organochlorine pesticides and PCBs were observed on the United States side of the river in the Fort Wayne, Zug Island, Rouge River and Trenton areas. PCB levels 10 times higher than those along the Canadian shore were prevalent on the United States side.

NIAGARA RIVER

Water, sediment, and fish from the Tonawanda Channel of the Upper Niagara River are severely contaminated. The lower Niagara River also exhibits extensive contamination.

Almost all sediments from the Tonawanda Channel are heavily contaminated with conventional pollutants, heavy metals, and PCBs in excess of acceptable concentrations for open water disposal of dredged materials. Many sediments are also contaminated with high concentrations of other organic substances primarily from industrial sources. Nine potential or positive carcinogens and eight organic substances having a potential for chronic aquatic toxicity were identified. Each was present in at least one sampling location and at a concentration of at least 5 mg/kg; the concentrations of some substances exceeded 50 mg/kg. Sediments from the lower Niagara River generally exceeded acceptable levels for heavy metals. A number of organic compounds have also been identified in sediment and water samples taken from the river near industrial landfills.

Numerous organic chemicals of industrial or agricultural origin have been identified in fish. For those substances for which U.S. Food and Drug Administration action levels or Canadian federal consumption guidelines have been established, concentrations are such that most fish are suitable for unrestricted consumption. Advisories are in place for larger specimens of American eel and coho salmon, because of elevated levels of PCBs and mirex; although found in the lower Niagara River, these species are generally resident in Lake Ontario.

Agreement or Ontario objectives were exceeded in some water samples for PCB, aldrin/dieldrin, DDT, endrin, phenolics, heptachlor/heptachlor epoxide, endosulfan, fecal and total coliform, and several heavy metals. Most of the observed exceedences were in the Tonawanda Channel and in the lower Niagara River.

The benthic fauna is disrupted in the Tonawanda Channel and in the lower Niagara River. Toxicity was a limiting factor along the shoreline of the upper Niagara River and was also a problem in the lower Niagara River.

In response to the growing shared concerns about toxic substances prevention of the Niagara River, a joint Canada-United States Niagara River Toxics Committee (NRTC) was formed in February 1981 with representation from federal, provincial and state environmental agencies. The objectives of the Committee were to: 1) identify sources of pollution, 2) make recommendations for remedial action, and 3) make recommendations for a long-term monitoring program on the river which would determine the effectiveness of the remedial programs. The Committee is nearing completion of its three-year task and a final report on the status of the river and recommendations for controls and monitoring will be available in early 1984.

ST. LAWRENCE RIVER

Elevated mercury and PCB levels in larger sizes of some fish species continue to necessitate advisories or restrictions on the consumption and commercial sale of these fish. However, the prospects are for declining levels because of in place or planned controls. The mercury problem is residual in nature. Some reduction of PCB levels in forage fish has occurred over the last three years, in response to initial controls on industrial sources in the Massena area.

Elevated fecal and total coliform levels have resulted in recreational use restrictions at some beaches downstream of Cornwall. There are also localized violations on both sides of the river for some Agreement or jurisdictional objectives including phosphorus, total phenolics, certain heavy metals, PCB, and two organochlorine pesticides.

Contaminants in sediments collected from the mouth of the Grasse River, at Massena, and along the Cornwall, Ontario waterfront exceed jurisdictional guidelines for open water disposal of dredged materials for nutrients, heavy metals, oil and grease, and/or PCBs. This contamination is primarily residual.

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3. Emerging Issues And Developments

The 1978 Water Quality Agreement (Annex 11(1)(d)) specifically states the need for surveillance activities to "...determine the presence of new or hitherto undetected problems in the Great Lakes basin." The reporting of emerging problems has been a perplexing one, historically for the Surveillance Work Group (SWG), as the Agreement requirement seems to imply the need for programs to monitor for unknown or undetected substances. There is presently a dichotomy of opinion within the SWG as to whether it is a function of surveillance and monitoring programs to purposely search for, identify and quantify hitherto unidentified substances in the Great Lakes ecosystem. Given the high cost of toxic substances analyses, the Work Group feels that efforts must be more focused on identified substances of concern. The Work Group has concluded that an efficient compromise to resolving the conflict of undetected substances is through active communication between its members, the Toxic Substances Committee, the Aquatic Ecosystem Objectives Committee, and the research community.

While the mere presence of certain extremely toxic chemicals is of concern and, therefore, connotes a problem, the Surveillance Work Group is equally concerned with changes in the concentration trends of all such chemicals. In particular, the Work Group deems increases in these trends after a period of substantial decline, as was noted in Chapter 2 for some substances, as an equally important definition of an emerging problem as is the discovery of "new" substances in the ecosystem.

This chapter will focus on three chemicals of concern. These chemicals, due to their existence in the basin, are no longer emerging problems. They do, nonetheless, represent additional concern if their concentrations are determined to be increasing within the environment. While trends can not as yet be determined, their inclusion on the routine surveillance parameter list will ensure that future reports will address any pattern of change.

A. DIOXIN AND FURAN

The presence of dioxins in Great Lakes biota was first reported in the Board's 1978 report. In the 1981 and 1982 Water Quality Board Reports, the presence of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) was summarized in fish from the Saginaw Bay area and herring gull eggs from the Great Lakes. This year's report elucidates work completed on concentrations of 2,3,7,8-TCDD and polychlorinated dibenzoflurans (PCDFs) in whole fish and herring gull eggs.

Polychlorinated dibenzofurans and polychlorinated dibenzo-p-dioxins (PCDDs) are two groups of toxic aromatic compounds (Figure 3A-1) composed of 135 and 75 individual isomers, respectively (Table 3A-1). Selected isomers are extremely toxic, particularly those with chlorine substitutes in the 2,3,7,8-positions of the aromatic ring (Moore et al., 1979).



FIGURE 3A-1 Ring structures of polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxins (PCDDs)

T	Δ	R	11	F	3	Δ	-	1	
1 1			-	-	5	\neg		- 1	

The second se	NO. OF ISOMERS					
CHLORINE SUBSTITUTION	PCDDs	PCDFs				
Mono-	2	4				
Di-	10	16				
Tri-	14	28				
Tetra-	22	38				
Penta-	14	28				
Hexa-	10	16				
Hepta-	2	o 4				
Octa -	<u>_</u>	_1				
	75	135				

POSSIBLE NUMBER OF POSITIONAL PCDD AND PCDF ISOMERS*

*From Rappe and Buser 1980.

PCDFs occur as trace contaminants in polychlorinated biphenyls (PCBs) and can be formed from pyrolysis or incomplete combustion of PCBs. PCDFs and PCDDs also occur as contaminants in the manufacture of chlorinated phenols (Buser and Bosshardt, 1976).

Fewer toxicological studies have been conducted with 2,3,7,8-TCDF than with TCDD, thus the toxicity of TCDF to fish from water exposures is not well established (McConnell, 1980). The similarities of these compounds, however,
give reason for concern about the impact of PCDFs on aquatic resources. Bioaccumulation factors of 2 to 2.6×10^4 have been observed for snails, fish and daphnids (Isensee and Jones, 1975).

Stalling, et al. (1983) undertook an assessment of the isomer distribution and total concentration of PCDFs and PCDDs in the Great Lakes. Whole fish samples were largely obtained from the National Pesticide Monitoring Program of the U.S. Fish and Wildlife Service but the U.S. EPA, Michigan DNR, New York Department of Environmental Conservation and the Department of Fisheries and Oceans also contributed fish samples. The distribution and concentration of these chemicals are listed in Tables 3A-2 and 3A-3.

Concentrations of PCDFs were lowest in lake trout samples from Lake Siskiwit on Isle Royale, Lake Superior, and in walleye from Lake St. Clair (Table 3A-2). Levels of PCDFs were greater in fish from Lakes Erie, Ontario, Michigan and Superior. The greatest PCDF concentrations were observed in fish from Saginaw Bay (153 ng/L) and the Tittabawassee River near Midland, Michigan (290 ng/L). The ratio of PCDF residues to PCB content strongly suggest the PCDF residues are correlated with PCB residues in the samples (Table 3A-3).

Except for the recent discovery of TCDD from Peninsula Harbour, Lake Superior, (OMOE, 1983), fish from Lakes Superior and Siskiwit do not apparently contain measurable levels of TCDD or other PCDDs. Samples from Lake Michigan and Erie showed low levels of PCDDs (Table 3A-3). Those fish analyzed from Lake Ontario and Huron (except Saginaw Bay) showed moderate levels relative to Saginaw Bay and the Niagara River. The fish from Saginaw Bay and Niagara River, including the tributary stream Cayuga Creek, had high levels of PCDDs, including 2,3,7,8-TCDD.

Stalling, et al. (1983) stated that measurable isomer specific analyses confirmed that the tetrachlorodioxin residues are composed predominately, or exclusively, of the 2,3,7,8-tetrachlorodibenzo-p-dioxin isomer.

Samples from Saginaw Bay, Tittabawassee River, Niagara River and Cayuga Creek contain the most complex mixture of PCDD and PCDF congeners. The residue data suggest a somewhat different distribution of congeners in samples from Saginaw Bay and the Niagara system than in samples from the other Great Lakes. Pollution with PCDDs is low in the Great Lakes except for Lakes Ontario and Huron. However, PCDFs were detected in all of the Great Lakes fish analyzed. Stalling, et al. (1983) cites trace occurrences of methylated chlorophenoxyphenols in their samples as a suggestion that commercial chlorophenols may contribute to the environmental pollution of PCDDs and PCDFs in Lakes Ontario and Superior.

The occurrence of low levels of PCDFs in fish from Lake Siskiwit suggests that atmospheric transport of PCDFs and PCBs may be involved. With the occurrence of PCDDs in material from various combustion sources (Bumb, et al., 1980; Rappe, et al., 1979), the absence of PCDDs in the fishes in Lake Siskiwit and the area waters of Lake Superior is a curious phenomenon.

TABLE 3A-2

DIBENZOFURAN RESIDUES IN PARTS PER TRILLION (ng/kg) IN SAMPLES FROM THE GREAT LAKES

M alona								4 017 101112
	LAKE SUPERIOR	100.00	6.6	. 21	108	10.0	Care	Tigunta I
all 1979	Bloater Keweenaw Bay	26	9	2	1	2	40	26/40=0.65
	Lake Trout							
linter 1979	Isle Royale, Lake Siskiwit	10	5	ND	ND	trace	15	10/15=0.67
all 1979	Apostle Islands	19	5	5	4	3	36	19/36=0.53
	LAKE MICHIGAN							
	Lake Trout							
all 1979	Saugatuck, Sample #1	35	41	8	1	1	86	35/86=0 41
- hanna and a	Sample #2	33	61	10	4	2	110	33/110=0.30
	Common Carp							
all 1980	*Waukegan	29	3	ND	ND	ND	32	29/32=.91
all 1980	Largemouth Bass *Waukegan	68	28	2	ND	ND	98	68/98=.69
	LAKE HURON							
	Lake Trout							
Summer 1980	*Burnt Island	19	9	242	<1	<1	270	19/270=0.07
all 1979	Rockport, MI	32	28	16	9	6	91	32/91=0.35
	(Duplicate analyses)	19	29	16	4	2	70	19/70=0.27
linter 1979	Common Carp Saginaw Bay at Bay City	27	44	34	44	4	153	27/153=0.18
all 1979	Bay Port	5	12	5	6	1	29	5/29=0.17
all 1978	Tittabawassee River,				~	1-4	1.2.3	games est
	Midland, MI	37	/3	145	31	4	290	37/290=0.13
	LAKE ST. CLAIR							
all 1979	Malleye Anchor Bay	4	4	0.7	0.7	3	12	4/12=0.33
	LAKE ERIE							
	Common Carp							
all 1979	Port Clinton	5	5	2	4	2	18	5/18=0.28
all 1979	Walleye Cedar Point, OH	18	9	6	5	2	40	18/40=0.45
	Brown Bullhead							
inter 1981	Mouth of Black River	2	ND	ND	ND	ND	2	1
	NIAGARA RIVER							
Ma la	Common Carp							
ummer 1979	Niagara River at Fort Niagara	6	75	139	49	6	275	6/275=.02
ummer 1980	Cayuga Creek, Trib. to Niagara River	5	80	215	324	388	1,012	5/1,012=.00
	LAKE ONTARIO							
	Lake Trout							
all 1980	*Burlington	40	24	10	ND	ND	74	40/74=0.54
all 1980	Rainbow Trout *Toronto Harbour	39	10	2	ND	ND	51	39/51=0.76
er traicoli	Brown Trout							
all 1979	Roosevelt Beach	19	4	3	3	3	32	19/32=0.59
	Labor Torrest							

Data Source: U.S. Fish and Wildlife Service, Columbia, Missouri

*Single whole fish samples collected at these locations. ND = Not Detected.

Suns (1983) reported additional data on 2,3,7,8-TCDD in the Niagara River. Five locations in the river were sampled from the upper to the lower part. Two composites of young-of-the-year spottail shiners were analyzed from each location except Frenchman Creek where one composite was tested (Table 3A-4). The residue levels at all sample locations appear to be elevated above background. Indications are that the TCDD in the Niagara River is from one or more local point sources.

Eggs from an additional colony of herring gulls has been analyzed for 2,3,7,8-TCDD since this information was last reported in the 1981 Appendix B (WQB). Eggs from Fighting Island located in the Detroit River, contain approximately 40 ng/kg (Figure 3A-2). This concentration of 2,3,7,8-TCDD is well above background, as measured in some other locations of the Great Lakes. With the addition of these data it appears that Saginaw Bay of Lake Huron, the Detroit River and Lake Ontario may have point source contamination of TCDD.

The residue data presented for fish tissue and herring gull eggs suggest that the presence of PCDDs in biota within the Great Lakes basin is strongly influenced by point source discharges. This was also the conclusion presented in the Board's 1981 and 1982 reports.

This discussion of levels of PCDFs and PCDDs in the fish of the Great Lakes presents the most recent information available. The potential adverse effects on reproduction and survival of Great Lakes fish and other aquatic organisms remains unknown.

B. A PERSPECTIVE ON POLYCYCLIC AROMATIC HYDROCARBONS IN THE GREAT LAKES

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are a class of compounds with a basic structure consisting of carbon and hydrogen atoms arranged in two or more fused aromatic (benzene) rings. They are of concern because many of the congeners can be carcinogenic and/or mutagenic. The term also covers fused aromatic systems containing a cyclopentene ring or hetero atoms of sulfur or nitrogen. This report will consider only the hydrocarbons, which range from the two-ring compound naphthalene $(C_{10}H_8)$ to the seven-ring compound coronene $(C_{2+}H_{12})$. Permutations of the spatial orientation of the rings and multiple types of substitution lead to a large number of PAH congeners. Of this large group, those most often reported in environmental samples are illustrated in Figure 3B-1.

PAHs are products of the incomplete combustion of organic materials, for example, forest fires or the burning of fossil fuels. As is to be expected from such commonly available source material, PAH are ubiquitous in the environment (Hites et al., 1980), with elevated concentrations reported near urban areas (Laflamme and Hites, 1978; Wakeham et al., 1980a). The predominant compounds found in atmospheric samples (Gordon, 1976; Strand and Andren, 1980) and sediments (Laflamme and Hites, 1978) are the unsubstituted parent compounds (Figure 3B-1). These are primarily generated at temperatures in excess of 400°-500°C. At lower combustion temperatures, alkyl-substituted

TABLE 3A-4

2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN RESIDUE IN PARTS PER TRILLION (ng/kg) IN WHOLE FISH COMPOSITE SAMPLES OF YOUNG-OF-THE-YEAR SPOTTAIL SHINERS FROM THE NIAGARA RIVER

Data Source: Ontario Ministry of the Environment, Rexdale, Ontario

COLLECT	COLLECTION SAMPLE		CONCENT	RATION
	DATE SITE		2,3,7,8	-TCDD
8	Enter	Upper Niagara		
Sept. 1	981 Frenchma	n Creek	Composite	1 15
Sept. 1	981 102nd St	reet	Composite	1 4
	Nîagara	Falls, New York	Composite	2 11
Sept. 1	981 Cayuga C	reek	Composite	1 60
	(Conflue	nce with Little River)	Composite	2 58
		Lower Niagara		
Sept. 1	981 Peggy's	Eddy	Composite	1 3
	(New Yor	k side)	Composite	2 11
Sept. 1	981 Niagara-	on-the-Lake	Composite	1 13
	(at Lake	Ontario)	Composite	2 14



selected Great Lakes nesting colonies.

Data Source: Canada Wildlife Service, Burlington, Ontario

- 88 -



FIGURE 3B-1 Ring structures of the most common PAH in environmental samples. By convention, symbols representing the aromatic character of the rings are omitted.

PAH begin to predominate. This trend is carried to an extreme in the low temperature (100°-150°C) maturation of oil, which contains complex mixtures of substituted PAH (Youngblood and Blumer, 1975).

In the atmosphere, PAHs generated in the combustion process are primarily associated with fine particles (Neff, 1979). Recent work indicates that most of the mass of PAH is attached to submicron particles (Miguel and Rubenich, 1979). Particles this size could be expected to have an atmospheric residence time of weeks to months, although this is considerably reduced by washout during precipitation. This still leaves time (days to weeks) for long range atmospheric transport of PAH, contributing to their wide distribution.

There are other sources for some of the PAH. In sediments, perylene concentration has been shown to increase with depth within the core, and it often becomes the most abundant PAH (Wakeham et al., 1980b). Laflamme and Hites (1978) describe some possible quinone pigment precursors that might form perylene in reducing sedimentary environments. Alkylated phenanthrenes occasionally appear in large quantities and are postulated to have two sources in addition to combustion: terpenes associated with pine forests (Laflamme and Hites, 1978) and dehydrogenation of steroids (Wakeham et al., 1980b) within the sediment.

Behavior of PAH in the Aquatic Environment

Solubility dominates the behavior and fate of persistent organic contaminants in the Great Lakes (and other aquatic systems). The distribution of the contaminant within the system is defined by its equilibrium partition coefficient (K_p) :

 $K_p = \frac{\text{concentration in particulate phase (mg/L)}}{\text{concentration in dissolved phase (mg/L)}}$

Several investigators have recently published on this topic (Chiou et al., 1977; Herbes, 1977; Means et al., 1979; and Karickhoff et al., 1979). The most comprehensive of these studies was a review by Kenaga and Goring (1979), who derived the following relationship:

> $\log K_{oc} = 3.64 - 0.55 \log WS$ n = 106 compounds r = -0.84,

where WS = solubility in water (mg/L) and $K_{oc} = (100 \times K_p)/(\% \text{ organic carbon of the substrate}).$

Reported solubilities of PAH in distilled water (tabulated in Neff, 1979, and in Lee and Grant, 1982) range from approximately 1 mg/L for phenanthrene to 0.1 μ g/L for coronene. Mean solubilities and K_{oc} values calculated from the expression above are listed in Table 3B-1. Log K_{oc} values for pyrene measured by Means et al. (1979) averaged 4.82 and those measured by Karickhoff et al. (1979) on silts and clay averaged 5.05. These results indicate that the calculated K_{oc} values in Table 3B-1 may be 10 times too low.

The equilibrium distribution of PAH in the water column of the Great Lakes, calculated from this information, is illustrated in Figure 3B-2. The fraction of contaminant associated with the dissolved phase is equal to:

$$fd = \frac{1}{1 + K_p * TSM}$$

where TSM represents the concentration of total suspended matter (g/g). The Great Lakes vary in their open lake TSM concentrations as shown below (Bell, 1982):

Lake	Approximate TSM (mg/L)
Superior	0.5-1
Michigan	1-2
Huron	1-2
Frie	4-8
Ontario	2-4

In shallow nearshore regions, TSM concentrations are generally greater by a factor of two or more. The range of TSM illustrated in Figure 3B-2 (1-10 mg/L) is correct over most of the Great Lakes. In the upper three lakes,

TABLE 3B-1

C OMPO UND	MEAN OF REPORTED SOLUBILITIES (mg/kg) ¹	CALCULATED LOG10 K _{oc}
Naphthalene	31.3	2.82
Phenanthrene	1.24	3.59
Anthracene	0.062	4.30
Pyrene	0.142	4.11
Chrysene	0.0018	5.15
Fluoranthene	0.242	3.98
Benzo (a) pyr ene	0.0039	4.97
Pervlene	0.0004	5.51
Benzo (dhi) per vlene	0.00026	5.61
Coronene	0.00014	5.76

SUMMARY OF WATER SOLUBILITY AND PARTITIONING INFORMATION

¹Compiled data from Lee and Grant (1982).



FIGURE 3B-2

The equilibrium distribution of PAH (and other organic contaminants) within the water column of the Great Lakes. The fraction of dissolved contaminant is defined as $fd = 1/(I + K_p * TSM)$. $K_{oc}(10)$ represents the partition coefficient assuming 10% substrate organic carbon, equivalent to 10^*K_p . The water solubility is calculated from the expression of Kenaga and Goring (1979). (See text). The region of PAH partitioning is indicated. At equilibrium the PAH are predominately in the dissolved form.

approximately 90% of the water column inventory of PAH will be in the dissolved phase. Only in nearshore regions or western Lake Erie will a substantial fraction of the low solubility PAHs be associated with particles.

Decomposition of PAH in the water column is primarily through photo-oxidation (National Academy of Science, 1982). Benzo(a)pyrene (BaP), for example, has a half-life of less than 1.0 hour when exposed to sunlight; however, the near-ultraviolet light that supplies the energy for these reactions is rapidly attenuated within the first few meters of the water column, greatly reducing the amount of BaP removed by this process.

Transport of PAH out of the water column occurs through sorption to particles and particle settling. Fecal pellets were identified as the primary transport vehicle for PAH in a marine bay (Prahl and Carpenter, 1979). Preliminary evidence suggests that fecal pellets play a similar role in Lake Michigan (M. Evans, University of Michigan, personal communication). These are relatively large and have settling speeds of tens of meters per day, rapidly removing PAH from the euphotic zone. Biological decomposition is at a maximum near the sediment/water interface (Gardner et al., 1979; Lee et al., 1981) and competes with burial as the predominant removal mechanism in the Great Lakes.

The distribution of PAH in various sedimentary environments around the world, although complex (Laflamme and Hites, 1978; Hites et al., 1980), is usually dominated by fluoranthene and pyrene in about equal concentrations and is consistent with the hypothesis of a combustion source. Concentrations of these compounds range from a few μ g/kg in regions remote from urban environments up to approximately one mg/kg in sediments from the New York Bight. Similarly high concentrations (\neg 1 ppm) were reported for Lake Washington (Seattle, WA) and three Swiss lakes (all close to urban sources) (Wakeham et al., 1980a).

PAH In The Great Lakes

The Great Lakes are the focus of a heavily populated and industrialized region and, as previously described, such areas are expected to receive large loads of PAH. Estimates of the load of PAH to the Great Lakes (Table 3B-2) are similar to maximum estimates of PCB and DDT loads to the same region. Load estimates are based on a very sparse data base, and thus are subject to improvement as more information becomes available. In addition to atmospheric input, tributary input can be estimated from suspended solids load data of Sonzogni et al. (1979) and Sullivan et al. (1980) and an estimate of 50 μ g/kg fluoranthene or pyrene for soil from Hites et al. (1980). Based on these assumptions, PAH via tributary input is approximately 10% of the level attributed to atmospheric input. Shoreline erosion and diffuse sources would also contribute small amounts, but direct atmospheric input appears to be the major source of PAH to the Great Lakes.

Because of their low solubility and concentration, data on PAH in the water column are very limited. Worldwide concentrations of BaP ranged from approximately 0.1 to 100 ng/L (Neff, 1979). BaP (0.3 ng/L) and total PAH (4.7 ng/L) were found in Lake Erie near Buffalo (Basu and Saxena, 1979). Large volumes of treated municipal drinking water taken from 12 plants using Great

TABLE 3B-2

			LAKE			
COMPOUND	SUPERIOR 1	MICHIGAN ¹	MICHIGAN ²	HURON 1	ER IE ¹	ONTARIO ¹
Phenanthrene	4.8	3.4	2.1	3.5	1.5	1.1
Anthracene	4.8	3.4	2.1	3.5	1.5	1.1
Fluoranthene	no - sha	1. 1. 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1	3.6	-	-	-
Pyrene	8.3	5.9	4.0	6.1	2.6	1.9
Benzo(a)anthracene	4.1	2.9	3.3	3.0	1.5	1.1
Benzo(a)pyrene	7.9	5.6	4.0	5.8	2.5	1.8
Perylene	4.8	3.3	2.1	3.4	1.5	1.1
Benzo(a)anthracene Benzo(a)pyrene Perylene	4.1 7.9 4.8	2.9 5.6 3.3	3.3 4.0 2.1	3.0 5.8 3.4	1.5 2.5 1.5	

ATMOSPHERIC FLUX OF PAH TO THE GREAT LAKES (MT/yr)

¹Eisenreich et al. (1981). ²Andren and Strand (1981).

Lakes water yielded relatively high concentrations of pyrene (11.2 \pm 20.0 and 3.9 \pm 10.2 ng/L)* and fluoranthene (9.2 \pm 12.0 and 10.6 \pm 25.0) Williams et al., 1982). Fluoranthene (15 \pm 9 ng/L), pyrene (14 \pm 6 ng/L), and BaP (7 \pm 4 ng/L) were found in filtered offshore waters of southern Lake Michigan (Eadie, 1983). The concentration of these compounds on suspended particles was 2-4 μ g/g. At a concentration of 1 mg/L of TSM, more than 75% of these PAH are estimated to be in the dissolved phase.

PAH concentrate in the sediments, and there have been several analyses of Great Lakes sediments for these compounds (Table 3B-3). In general, high sediment PAH concentrations are associated with fine-grained, organic rich sediments whereas low values are from nearshore, sandy environments.

PAH in Lake Superior sediments are 10 times lower than those in the lower lakes. Lake Michigan sediments have the highest PAH concentration. This observation supports the hypothesis of localized urban sources, since the Lake Superior region is heavily forested and undeveloped, while the region around southern Lake Michigan (where six of the sediments were collected) is heavily industrialized. The distribution of measured PAH congeners in Great Lakes sediments is similar in a gross sense to concentrations in sediments reported by Hites et al. (1980), Laflamme and Hites (1978), Wakeham et al. (1980a), Tan and Heit (198T), and Eadie et al. (1982a,b) for environments that receive PAH from anthropogenic sources. Characteristically, these are highest in unsubstituted fluoranthene and pyrene, with large concentrations of phenanthrene, chrysene (plus triphenylene), and BaP.

*The numbers in parenthesis represent the mean ± 1 standard deviation for winter and summer samples, respectively.

TABLE 3B-3

COMPOUND	SUPERIOR ¹ (n=1)	MICHIGAN ² (n=10)	L A K E HURON ² (n=3)	ERIE ² , ³ (n=4)	ONTARIO ² , ⁴ (n=5)
Phenanthrene	34	6-1268	11-272	18-431	40- 205
Fluoranthene	88	9-1564	33-487	65-285	210-1000
Pyrene	53	8-1430	36-256	57-287	56-1182
BaP	28	4-944	23-294	56-173	76- 306

RANGE OF CONCENTRATIONS OF PAH IN GREAT LAKES SURFICIAL SEDIMENTS (ng/g dry)

¹Gischwend and Hites (1981). ²Eadie et al. (1982b, 1983). ³Eadie et al. (1982a). ⁴IJC (1977).

More detailed information on the distribution of PAH in Lake Michigan sediments is presented in Table 3B-4. Stations Tl and T6 are located in regions where sediments are not accumulating (Cahill, 1981). The other seven stations are in regions of recent sediment deposition. The distribution of the fluoranthene concentrations for these nine stations (Figure 3B-3) is in general agreement with the map of chlorinated organic contaminants (whose source is also primarily atmospheric) (Frank et al., 1981). It appears that

TABLE 3B-4

Contraction of the local division of the loc	STATION	PHENANTHENE	FLUORANTHENE	PYRENE	CHRYSENE + TRIPHENYLENE	BaP
	T1 T2 T3* T4 T5 T6 T7 T8 T11	28 809 1,268 308 537 19 298 245 263	34 906 1,564 445 794 62 620 419 431	30 733 1,430 363 665 38 421 319 318	36 1,128 319 522 41 554 348 543	33 450 944 251 248 26 572 571 324

LAKE MICHIGAN SEDIMENT PAH (µg/kg dry)

*Calculated PAH coefficients of variation (%) for replicate (3-4) analyses of replicate (3) extracts from station T3 are: 27.6, 13.0, 11.6, 19.4, 18.5, respectively. Data Source: Great Lakes Environmental Research Laboratory (NOAA), Ann Arbor, Michigan.



FIGURE 3B-3

The distribution of fluroanthene (ng/g) in the surficial sediments of Lake Michigan. Data Source: Great Lakes Environmental Research Laboratory (NOAA), Ann Arbor, Michigan. the final sedimentary distribution of PAH and other hydrophobic organics will be controlled by processes that affect the movement of the fine-grained, organic rich sediments to which they are attached.

The information from the previous discussion can be used to estimate a simple steady-state mass balance for PAH in the Great Lakes. Figure 3B-4 illustrates such a calculation for BaP in Lake Michigan. The numbers should be considered uncertain to about \pm 50% at this time. The loss of 2.8 metric tonnes (MT) of BaP per year (calculated by difference) indicates decomposition of approximately 50% of the load. If the concentration in the water is divided by the load, the result indicates a relatively long apparent residence time of approximately seven years for BaP in Lake Michigan water. The large reservoir of BaP in the surficial sediments may act as an important source for the water column through resuspension and diffusion. The load of 5 MT/yr, equivalent to 8.5 ng/cm²/yr, is higher (by a factor of 35) than that calculated by Gischwend and Hites (1981) from a core in Lake Superior, but lower than their reported fluxes for urban sites.



Lake Michigan BaP Budget

FIGURE 3B-4 Lake Michigan benzo(a)pyrene budget. The input (~5MT/yr) is from Table 3B-2. Concentration in the water column (7 ng/L, 80% dissolved) is from Eadie (1983) multiplied by the volume of the lake and distributed as 27 MT dissolved and 7 MT associated with particulate matter. Sedimentation is estimated from recent accumulation data (Robbins and Edgington, 1975) and trap fluxes (Chambers and Eadie, 1981), both of which are approximately 7 mg/cm²/yr. This figure was multiplied by the lake area and a BaP concentration of 500 ng/g (Table 3B-4). Sediment inventory was estimated for the upper 3 cm (well mixed 2.6 g/cm³, 80% porosity). The losses of approximately 2.8 MT/yr were calculated by difference.

Biological Effects

The complex mixtures and relatively high concentration of PAH in lake sediment has raised questions regarding the exposure of benthic organisms to these compounds, resultant bioconcentration factors, and the transfer of these compounds up the food chain to fish. In general, fish and some invertebrates have inducible, mixed-function oxidase systems capable of oxidizing PAH, resulting in low bioconcentration factors. Other invertebrates may lack the appropriate enzymes for biotransformation, resulting in large bioconcentration factors. Neff (1979) summarizes a great deal of information on biological uptake, accumulation, and degradation in the aquatic environment. Recent analyses of oligochaete worms and chironomids from Lake Erie and Pontoporia from Lake Michigan (Eadie et al., 1982a,b) have shown that the PAH concentrations in these organisms are similar to those found in the fine-grained fraction of their sedimentary environment. Bioconcentration factors in Pontoporia hoyi, the most aboundant benthic organism (by mass) in Lake Michigan, ranged from 10^4 to 10^5 with respect to the overlying water concentrations of seven measured PAH. Recent laboratory experiments with this organism confirm these bioconcentration factors for anthracene and BaP (Landrum, 1982). In Pontoporia from recent (fine-grained) sediments, concentrations of several PAH exceeded T mg/kg (wet wt.) (Eadie et al., 1982b).

Do these concentrations present a serious threat to Great Lakes fish? The primary concern is the ability of PAH to cause cancer (Jones and Leber, 1979; Gelboin and Ts'o, 1978). Acute toxicity from these compounds is of major significance only in the immediate area of an oil spill. In addition, Leversee et al. (1982) recently described a high acute mortality rate for sunfish exposed to μ g/L concentrations of anthracene in the presence of sunlight. Benzo(a)pyrene adversely affected the hatching and early development of flatfish (Hose et al., 1980) at very low μ g/L levels.

The limited amount of work on the chronic response of aquatic organisms has been summarized in Neff (1979) and Malins and Hodgins (1981). Both reviews agree that measurable effects of chronic exposure are probably limited to polluted coastal environments or locations of oil spills and that these locations are usually contaminated with a wide variety of pollutants, making it difficult to distinguish between cause and effect.

Since fish can enzymatically oxidize PAH, monitoring the ambient levels of PAH in fish tissue does not measure their exposure. Payne and Fancey (1982) found elevated levels of mixed function oxidase in fish exposed to moderate levels of petroleum hydrocarbons, and they advocate monitoring this enzyme to determine if fish are being stressed by PAH.

Are PAH causing cancer in fish? Sonstegard (1977) found very high incidences of tumorous tissue in Great Lake fish that feed primarily on bottom organisms; yet he did not detect any such malformations in an analysis of a museum collection of similar Great Lakes fish collected in 1952. The implication is that some carcinogenic or mutagenic agent(s) have been introduced into the Great Lakes since the early 1950's. Many compounds or possible combinations of compounds could be those agents; PAH are certainly among them. Further discussion on this subject can be found in Chapter 6 of this report.

High incidences of tumorous tissue in the carp and goldfish hybrids of Lake Erie tributaries have been correlated with high concentrations of PAH in sediments (Black et al., 1980a,b). Liver tumors were found in the brown bullhead of the Black River, an input to Lake Erie that is highly contaminated with PAH (Baumann et al., 1982). As mentioned above, these regions are usually contaminated with multiple pollutants that may have additive or synergistic effects with PAH. However, PAH in laboratory studies have induced tumors in fish (Jones and Hoffman, 1957; Schultz and Schultz, 1982; Black, 1982), and fish enzyme systems have been shown to produce carcinogenic metabolites (Neff, 1979). Thus, there is evidence of both chronic effects and carcinogenic/mutagenic responses in fish populations exposed to PAH. These effects are most severe near urban areas and for fish that live or feed on the bottom.

How does this exposure of fish to PAH affect human health? Since fish have the enzymes to biotransform PAH, exposure of bioaccumulated parent compounds will be minimal. While it has been reported that marine fish have levels of BaP up to 5,000 ng/kg dry wt., the one reported level in fresh water fish (lake trout) was less than 4 ng/kg dry wt. (Neff, 1979). Based on a consumption of 0.5 kg of fish per day and the daily intake of PAH from other sources (Table 3B-5) (Lee and Grant, 1981), lake trout would contribute less than 2% of the total intake of PAH. Since fish can biotransform PAH, the level of metabolites in fish may be quite high, depending on exposure. Research has not yet been performed to examine these levels, nor has the toxicity of these biotransformation products of PAH been determined. Therefore, the hazards and the extent of exposure to the biotransformation products of PAH are unknown.

TABLE 3B-5

SOURCE	BaP	μg/day CARCINOGENIC PAH	TOTAL PAH
Air	0.00095-0.0435	0.038	0.207
Water	0.0011	0.0042	0.0270
Food	0.16-1.6		1.6-16

HUMAN EXPOSURE TO PAH FROM VARIOUS ENVIRONMENTAL SOURCES

The Future of PAH in the Great Lakes

Although the seriousness of the exposure of benthic organisms and fish to PAH is currently supported only by circumstantial evidence, it appears that the load of PAH to the Great Lakes and consequent exposure will increase over the next few decades. This will result from increasing population and consequent increasing energy consumption. Regional population data are given in Table 3B-6. Population for the year 2000 is estimated to be approximately 10% larger than the current population, a somewhat slower rate of growth than the country as a whole. It is expected that growth on the Canadian side will be similar.

A study by the National Academy of Sciences (1979, p. 204) has concluded that, because of its availability, coal will be a key element in the United States energy policy well beyond the end of the century. They estimate that three times the present level of production, or about 45 quads (1 quad = 10¹⁵ BTU), annually will provide one-third to one-half of the nation's energy compared to 18% (14 quads of 78 quads) in 1978. A regional study (Great Lakes Basin Commission, 1981) estimates that, by the year 2000, the use of coal will increase with respect to oil and gas, and that energy production within the basin will increase from 3.1 quads (1975) to 3.9 quads by 1990 (see also SAB, 1982).

TABLE 3B-6

	1970 ¹	1980 ²	1990 ³	2000 ³	2050 *
U.S. Total	203,000	222,000	243,000	260,000	3 16,000
Illinois Indiana Ohio Michigan New York Pennsylvania Minnesota Wisconsin	11,113 5,196 10,657 8,882 18,241 11,801 3,806 4,418	11,418 5,490 10,797 9,258 17,557 11,913 4,077 4,705	12,015 5,804 11,570 10,302 18,528 12,272 4,382 5,156	12,491 6,069 11,999 10,970 18,816 12,465 4,637 5,476	
GL States Total	73,394	75,215	80,029	82,923	

POPULATION DATA FOR THE GREAT LAKES STATES (MILLIONS)

¹U.S. Bureau of Census, 1979.

²U.S. Bureau of Census, 1981.

³U.S. Bureau of Census (1979), Projection IIA.

⁴Schurr et al. (1979), p. 110; no estimates given by state.

Information summarized for the United States in the late sixties (National Academy of Sciences, 1972) indicates that over 1200 MT/yr of BaP were emitted each year. This amount was apparently reduced to approximately 300 MT/yr by the mid-1970's (Table 3B-7). This 75% reduction in emissions supports the National Air Surveillance Network's (NASN) estimate of a 75% reduction in the atmospheric concentration of BaP at 26 urban sites throughout the United States from 1966 to 1977 (Faoro and Manning, 1981). This decline has been observed at the Great Lakes basin atmospheric monitoring stations (Figure 3B-5). The decline has been attributed to a reduction in the use of coal and wood in residential heating, although with the recent rise in the price of oil and gas, coal and wood use is again increasing (Peters et al., 1981). Considering changes in sample collection and analysis techniques, it is not clear whether the reported decline in PAH is real or an artifact of the methods employed. Potvin et al. (1981) found no significant differences in atmospheric BaP measured between 1971 and 1975 and that between 1975 and 1979 at a site in northern Ontario. What is obvious from the four emission estimates in Table 3B-7 is that there is considerable disagreement about the relative importance of even major sources of BaP. In the late 60's, the major sources were perceived to be open burning of refuse, followed closely by the

combustion of coal for heat and power. By the mid 70's, this was altered to coke production in both the United States and Ontario. In the case of total PAH estimates, the major source for this period was the combustion of wood for heat and power. These estimates are rather weak since sampling procedures and analytical intercomparisons are not yet standardized or uniformly efficient for various environments. Bennett et al. (1979) found order of magnitude ranges in the PAH concentrations of oil fired power plant emissions (23-2550 ng PAH/m³) and coal fired power plant emissions (24-378 ng PAH/m³); thus the use of an average emission factor for each source type is only a gross

TABLE 3B-7

			the same so that we do not not the same so we are so so that an area so that an area of the same so that a	
PERIOD	BaP U.S. ¹ LATE 60's	BaP U.S. ² 1975	BaP ONTARIO ³ 1976	TOTAL PAH U.S. ⁴ mid-70's
Heat and Power		tet, er gan e	198,01	or do
Coal Oil Gas Wood	431.0 2.0 2.0 40.0	27.0 2.7 1.0 73.0	0.013 0.052 0.048 -	184.0 9.0 12.2 7,674.0
Open burning	450.0	>52.0	101.27 163	2,547.0
Coke production	20.0	110.0	9.33	632.0
Forest fires	140.0	11.0	8.16	1,478.0
Mobile sources	22.0	13.0	0.323	2,266.0
Grams emitted per capita	6.6	1.4	2.2	⊙ 70.5

ESTIMATED PAH EMISSIONS (MT/yr)

¹NAS (1972). ²Faoro and Manning (1981). ³MOE (1979). ⁴Peters et al. (1981).

approximation. In a literature review, Junk and Ford (1980) found 109 organics in coal combustion products and 331 in coal and refuse combustion, but stated that there are probably many more as yet uncollected or unidentified compounds. Many of these could have caused interference in earlier, less specific analytical procedures.

At this time it is unclear to what extent PAH emissions will increase with projected increased fossil fuel combustion. The fact that PAH are associated with submicron particles makes them very difficult to remove from stack

gases. Increased use of "dirty" fuels, such as coal and wood, will further increase the potential for PAH production. If regional energy production increases by 25% (3.1 quads to 3.9 quads) as estimated by the Great Lakes Basin Commission (1981) report and if this increase is primarily in the form of coal and wood combustion, then based on the figures in Table 3B-7, we can conservatively estimate an increase of 10% in the loads of PAH to the lake.



FIGURE 3B-5

Atmospheric concentration of benzo(a)pyrene in the Great Lakes Region. Data for United States cities are from the U.S. EPA/NASN (Faoro and Manning, 1981; Ackland, 1982). Data for 10 Canadian cities on the Great Lakes are from the Ontario Ministry of the Environment (MOE) (1979). Each of the 2-year averages falls within the gray zone; the grand mean for all the data is also shown. The Toronto data for 1976 is from Katz et al. (1978). The Lake Michigan data are from Strand and Andren (1980). The Sault Ste. Marie point is from the MOE (1979). Youngstown and Milwaukee both show recent increases in BaP concentrations.

As long as rates of removal from the ecosystem remain the same or even decrease because of a reduction in primary productivity caused by the Great Lakes phosphorus abatement program, concentrations of PAH within the Great Lakes ecosystem will increase.

C. TOXAPHENE

INTRODUCTION

On 29 November, 1982 the U.S. EPA officially cancelled most uses of toxaphene but permitted existing stocks of the chemical to be used through 31 December, 1986. This action, coupled with the Canadian ban of 31 October 1980 would seemingly reduce this persistent contact pesticide from entering the Great Lakes ecosystem in quantity. Assuming the ban is effectively implemented, especially after 1986, and quantities of the substance do not enter the water column through long range atmospheric transport or hazardous waste site leachate, the Great Lakes ecosystem should begin to show signs of improvement as indicated by reduced body burdens in fish over the next several years.

The IJC was first advised of the presence of this pollutant in 1976 (URLG) when toxaphene or toxaphene-like substances were detected in lake trout from Lake Superior at values ranging between 0.1 - 1.0 mg/L. Since that report, the Commission has been periodically updated as to the Great Lakes levels in biota and recently water concentrations of Lake Huron. The Surveillance Work Group will continue reporting to the Water Quality Board toxaphene values as derived from routine monitoring in the Great Lakes fish contaminant program.

What follows is a brief synopsis of values found within fish along with a general description of the chemical. There are several thorough general reviews on toxaphene (U.S. EPA, 1980; Cohen et al., 1982, and U.S. FWS, 1982) and these should be referenced for more details.

OVERVIEW

Toxaphene is a common trade name for chlorinated camphene. Commercial toxaphene has a maximum pesticidal activity when the chlorine content ranges from 67-69%, resulting in a typical empirical formula of $C_{10}H_{10}Cl_{18}$ and an average molecular weight of 414. Technical grade toxaphene consists of 177 components, of which 20 to 40 have been isolated in Great Lakes fish. According to Cohen et al., 1982, annual toxaphene production during the 1970's varied between 45 x 10° and 106 x 10° kg. The chemical was extensively used in the Dakotas, California and the southern states on sunflower, vegetables and cotton crops, respectively. According to Seiber et al., (1979) quantities in excess of 50% can be lost to the atmosphere through volatilization and dust. Furthermore, whole fish residues of 2.3 to 3.2 $\mu g/g$ were detected in lake trout collected from Lake Siskiwit which is hydrologically isolated from Lake Superior proper. Taken together this evidence implicates long range atmospheric transportation as a primary vehicle for toxaphene contamination of the Great Lakes.

Although the initial use of toxaphene dates to 1948, recently developed sample preparation procedures coupled with capillary GC and election capture detection have hastened its quantification in the Great Lakes biota. Earlier attempts to isolate and quantify ambient environmental toxaphene levels were hampered because conventional packed column GC yielded chromatograms with peaks that overlapped other ubiquitous contaminants, most notably, DDT and its homologues, PCBs, and certain chlordane components (Ribick <u>et al.</u>, 1982). Toxaphene is soluble in water in the range of 0.4 to 3.0 mg/L (Paris et al., 1977; Brooks, 1974) and has a partition coefficient between 1.995 x 10^3 to 2.512 x 10^6 (Paris et al., 1977; Magnuson et al., 1979). Mean 96-h LC₅₀, acute toxicity levels in juvenile fish range from a low of 2 µg/L for large-mouth bass (Micropterus salmoides) to 18 µg/L for fathead minnows (Pimphales promelas) (Johnson and Finley, 1980). Several studies have yielded bioaccumulation factors ranging from 2,000 to 69,000 (10 to 140 days) in various species of freshwater fish (Mayer et al., 1977; Terriere et al., 1966). The 48-h LC₅₀'s at 17°C for the cladocerans Bosmina longirostris, Daphnia magna, and D. pulex were 1.4, 5.4, and 11.3 μ g/L respectively (U.S. FWS, 1983).

Although there is an Agreement objective for toxaphene in water (0.008 μ g/L, for the protection of aquatic life), there is no objective for fish tissue concentration. Smith, (Cranbrook Institute of Science) has measured concentrations in the range of 0.0005 - .002 μ g/L from Lake Huron waters. The U.S. Food and Drug Administration action level for toxaphene in edible portions of fish is 5 mg/kg. Although the values reported recently exceed this action level, it must be understood that these results are for whole fish and thus are higher than would be expected from analysis of edible portions.

Toxaphene in Great Lakes Fish

Samples of individual and composite whole fish homogenates have been analyzed to describe historical levels of toxaphene or toxaphene-like substances. The results were provided by the Department of Fisheries and Oceans (DFO), Burlington, Ontario and U.S. FWS laboratories in Ann Arbor, Michigan and Columbia, Missouri.

Results from DFO include whole fish toxaphene levels for top predator salmonid samples from each of the Canadian Great Lakes (Table 3C-1). In addition, a range of age classes from 1982 lake trout collected in Lake Ontario were analyzed to determine toxaphene accumulation patterns. Historical samples were chosen to represent the eldest individual of that species available at the time of collection. These fish also contained the highest lipid levels of all fish collected at that time. With the exception of two separate eel samples from Lake Ontario, there was a positive relationship between lipid levels and toxaphene concentration.

Current data (1982) from Lake Ontario indicate that toxaphene accumulates in the same manner as other lipophilic compounds. Concentrations increase with both lipid content and age. Generally, toxaphene concentrations are similar throughout the lakes monitored with physiological conditions rather than geographic location being the most influential variable.

Results from the U.S. FWS demonstrates that toxaphene contamination is not restricted to the top predatory fish. Values for planktivorous species were generally about half the concentration recorded for lake trout (Table 3C-2). Toxaphene concentration from samples of large Lake Michigan lake trout were comparable to specimen collected from Lakes Superior and Huron (Table 3C-3).

TABLE 3C-1

TOXAPHENE IN GREAT LAKES WHOLE FISH RESIDUES

Data Source: Department of Fisheries and Oceans, Burlington, Ontario

	COLLECTION YEAR	SPECIES	AGE	% LIPID	TOXAPHENE (µg/g)
Lake Ontario	1977	Lake Trout	5+	26.35	3.53
		Rainbow Trou Coho	t 5+ 3+	12.67 12.50	1.69 2.04
	1978	Lake Trout	3+	20.93	11.50
	1980	Lake Trout	5+	25.48	0.19
	1982	Lake Trout	10+	26.73	3.56
		Lake Irout	6+	25.49	2.95
		Lake Trout	6+	17.99	2.04
		Lake Trout	5+	26.61	1.38
		Lake Trout	4+	14.26	0.61
		Rainbow Trout	t 7+	9.06	1.59
		Coho	3+	4.74	0.72
		Eel	te la contrar	32.26	1 74
		Ee1	-	34.53	1.71
Lake Erie	1977	Rainbow Trout	t 5+	18.00	2.66
		Coho	3+	5.45	2.09
Lake Huron	1979	Splake	3+	20.00	2.54
	1980	Lake Trout	8+	18.85	3.53
	1982	Lake Trout	8+		1.69
		Lake Trout	7+	-	1.25
		Lake Trout	7+	(SC-1)96268	2.93
		Lake Trout	6+	o ter monder	1.93
		Lake Trout	6+	19.30	4.90
Lake Superior	1978	Lake Trout*	7+	59.68	10.00
		Lake Irout*	/+	37.25	9.68
		Lake Trout	3+	19.05	2.15
Lake Superior	1980	N X	S.E.	Ran	ge
	Toxaphene	10 1.90	0.58	(0.37 -	6.18)
	% Lipid	10 26.60	1.56	(20.60 -	36.80)

* Siscowet.

TABLE 3C-2

CONCENTRATION (µg/g WET WEIGHT) OF TOXAPHENE IN COLD-WATER FISH SAMPLES FROM THE UPPER GREAT LAKES, 1977 AND 1979 COMPOSITE SAMPLES (FIVE ADULT FISH/SAMPLE), (TOTAL LENGTH IN mm)

YEAR MEAN TOXAPHENE LAKE COLLECTED LOCATION SPECIES LENGTH CONCENTRATION Michigan 1977 Sheboygan, MI 257 3.5 Bloater Michigan 1977 Sheboygan, MI 3.3 Bloater 254 Michigan 1977 Sheboygan, MI Lake Trout 698 7.8 Michigan 1979 Sheboygan, MI Bloater 284 2.7 1979 Michigan Sheboygan, MI Bloater 269 2.3 1979 Michigan Sheboygan, MI Lake Trout 612 7.1 Michigan 1977 287 6.4 Beaver Is., MI Bloater Michigan 1977 Beaver Is., MI Lake Trout 653 8.1 1979 Michigan Beaver Is., MI Bloater 307 3.3 Michigan 1979 Beaver Is., MI Bloater 282 3.1 1979 Michigan Beaver Is., MI Lake Trout 610 5.5 1977 290 3.7 Michigan Saugatuck, MI Bloater 1977 0.6 Michigan Saugatuck, MI Bloater 287 Michigan 1977 Lake Trout Saugatuck, MI 627 7.0 1979 Saugatuck, MI Saugatuck, MI Michigan Bloater 287 3.4 1979 Michigan Bloater 297 3.4 663 6.8 Michigan 1979 Saugatuck, MI Lake Trout Huron 1977 594 9.0 Alpena, MI Lake Trout 627 5.2 Super ior 1977 Lake Trout Bayfield, WI 516 2.3 Superior 1977 Bayfield, WI Lake Whitefish Super ior 1979 Bayfield, MI Lake Trout 630 2.2 0.9 1979 Lake Whitefish 335 Super ior Bayfield, WI 0.6 Super ior 1979 Bayfield, WI Lake Whitefish 328 1977 Keeweenaw Pt., 264 2.8 Superior Bloater 2.9 262 Super ior 1977 MI Bloater 11 1977 11 Lake Trout 559 3.0 Super ior Keweenaw Pt., 277 3.6 1979 Bloater Super ior 295 2.8 1979 Bloater Super ior MI 11 11 Lake Trout 605 7.3 Super ior 1979 Whitefish Pt., 488 1.4 1977 Lake Whitefish Superior 503 2.1 Lake Whitefish 1977 Super ior MI 11 11 Lake Trout 607 3.1 1977 Superior 1.2 Whitefish Pt., Lake Whitefish 566 1979 Superior 495 Lake Whitefish Super ior 1979 MI 1.9 561 11 11 1979 Lake Trout Superior

Data Source: U.S. Fish & Wildlife Service, Columbia, Missouri

TABLE 3C-3

CONCENTRATIONS OF TOXAPHENE-LIKE COMPOUNDS IN COMPOSITED SAMPLES OF LAKE MICHIGAN LAKE TROUT (20 ADULT FISH/SAMPLE)¹ ALL RESULTS REPORTED AS µg/g TOXAPHENE (WHOLE FISH)

Data Source: U.S. Fish and Wildlife Service, Ann Arbor, Michigan

SPECIES	YEAR COLLECTED	MEAN LENGTH (mm)	LOCATION	TOXAPHENE CONCENTRATION
Lake Trout	1977a ²	697	Charlevoix, MI	7.2
Lake Trout	1977b	697	Charlevoix, MI	6.1
Lake Trout	1978a	671	Charlevoix, MI	8.4
Lake Trout	1978b	671	Charlevoix, MI	8.1
Lake Trout	1978a	717	Sturgeon Bay, WI	10.5
Lake Trout	1978b	717	Sturgeon Bay, WI	10.9
Lake Trout	1979a	688	Sturgeon Bay, WI	6.5
Lake Trout	1979b	688	Sturgeon Bay, WI	6.9
Lake Trout ³	1977a	653	Saugatuck, MI	6.6
Lake Trout ³	1977b	653	Saugatuck, MI	7.3
Lake Trout	1978a	701	Saugatuck, MI	7.7
Lake Trout	1978b	701	Saugatuck, MI	7.4
Lake Trout	1979a	694	Saugatuck, MI	7.3
Lake Trout	1979b	694	Saugatuck, MI	6.5

¹Represents the 20 largest fish collected.
²a or b denotes duplicate analysis of the same sample.
³18 fish composited.

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4. Water Quality Assurance

(Note: This Chapter was prepared by the Data Quality Work Group. Comments or inquiries regarding this Chapter's contents should be directed to the Data Quality Work Group Secretary.)

Annex 11 of the Agreement calls for quality assurance programs in support of Great Lakes surveillance and monitoring activities. As described in Annex 11, these programs include standard sampling and analytical methodology, interlaboratory comparisons, and compatible data management. The execution of proper quality assurance programs permits valid assessment of surveillance and monitoring data and help substantiate the evaluations and conclusions which are derived from these data. In order to help ensure the production of environmental data of acceptable quality to meet the surveillance and monitoring requirements of the the Agreement, the Water Quality Board established a Data Quality Work Group.

Under the Work Group's Terms of Reference, the Work Group performs the following tasks:

- 1. In collaboration with the Surveillance Work Group recommends the quality assurance requirements for field, laboratory, and data management activities undertaken in support of the Agreement and monitors the meeting of the requirements;
- Conducts interlaboratory studies and, as needed, assists participants in implementing remedial action;
- 3. Compiles and updates information on the analytical characteristics of methods used by participants in interlaboratory studies. Evaluates and recommends necessary changes to those methods if such methods do not produce comparable results and;
- 4. Reports to laboratory directors, project officers, agency representatives, report writers and others with, as needed, on laboratory performance.

SUMMARY

During 1982 and 1983, the Work Group conducted six interlaboratory studies, has planned one or two more, overviewed the development of reference materials to meet specific quality assurance requirements, continued compiling an inventory of archived Great Lakes basin environmental samples, maintained a compendium of analytical methods by laboratory, and continued its efforts to assist laboratories in implementing adequate intralaboratory quality control programs. In response to a cooperative International Joint Commission/Water Quality Board inquiry regarding the Work Group's activities and responsibilities, a review task force was formed. The composition of the task force and its recommendations are discussed later in this chapter.

INTERLABORATORY STUDIES

The Work Group is convinced that interlaboratory studies are an essential element in determining if laboratories produce comparable analytical results. The six interlaboratory studies conducted for this purpose include: two for phosphorus in water, one for metals in water, one for major ions and nutrients in water, one for total phosphorus in sewage treatment plant effluent, and one for chlorinated hydrocarbon pesticides and PCBs in fish and ampuls.

A typical round robin consists of submitting samples of ambient environmental constituents levels to laboratories which contribute to the measurement of the Great Lakes basin samples. Distributed with the samples are a transmittal letter, a methods questionnaire, a report form, a discussion on reporting low level data, and a description of the Work Group's recommended minimum intralaboratory quality control program.

After the results are received by the Work Group, they are individually evaluated by comparing them to the medians, which serve as target values. Bias of the set of results from each laboratory is assessed using a modification of a method developed by Youden (1969).

After the results are evaluated, each laboratory receives a report on its performance, a glossary of terms used in the evaluation, and a table of all results so that its performance can be compared to that of others. Frequently the methods used by the laboratories are cited or listed with the report. Descriptions and findings from these studies follow.

Phosphorus in Water - Studies 40 and 43

Two studies on phosphorus in water were conducted in 1982 with 34 laboratories (15 samples) participating in the first one and 36 laboratories (15 samples) in the second one. The samples used for these studies consisted of water from open lake, nearshore, harbor areas, lake tributary, and laboratory standard solutions.

The median (target) values ranged from 2.0 μ g/L to 621 μ g/L, admittedly a wide range. The laboratories, however, included in these studies measure tributary water high in phosphorus concentrations as well as nearshore and open lake waters with low phosphorus values.

In order to demonstrate sample stability, several samples were redistributed over three round robins, but their identities were not known to the participants. The median values for these samples from all results for each study in 1981 and 1982 are given in Table 4.0-1.

TABLE 4.0-1

SAMPLE SOURCE	STUDY 38	STUDY 40	STUDY 43
	SEPTEMBER '81	SEPTEMBER '82	JANUARY '83
Lake Superior Rain Water Lake Erie Lake Ontario Grand River Hamilton Harbor Spike (124) Spike (187) Spike (248)	2.0 4.0 - 10.9 12.3 - 124.0 187.5 253.5	2.5 - 11.0 - 90.5 127.0 188.5 255.5	2.0 4.1 10.6 11.0 13.0 88.0 127.5 189.0 253.5

MEDIAN VALUES FOR TOTAL PHOSPHORUS IN WATER, µg/L

The nearly constant medians, which the participating laboratories collectively provide, indicate that the samples derived from the various sources were quite stable and can be used for performance comparisons over time.

The performance of laboratories on total phosphorus in water analyses over the past five years is documented in Table 4.0-2. While several laboratories generally performed well, there were many which were erratic or produced biased data. For a few laboratories, there was some deterioration in performance (e.g., laboratories 5 and 9) while some (e.g., laboratories 4 and 27) showed improvement in the last study.

The Work Group finds it particularly discouraging that the level of performance by some laboratories varies so widely from test to test. This wide variation clearly indicates that either the internal quality control programs for these laboratories are not working or that there are no such programs at all. The Work Group has emphasized the critical importance of a sound laboratory quality control program using a widely circulated recommended practice.

Total Phosphorus in Sewage Treatment Plant Effluent - Study No. 44

At the request of the Municipal Abatement Task Force of the Water Quality Board, the Work Group conducted an interlaboratory study among select sewage treatment laboratories. On April 25, 1983 ten samples comprised of standards, effluent, and effluent plus standards were distributed to 36 sewage treatment plant laboratories and to the four OMOE laboratories which analyze effluents for total phosphorus.

TABLE 4.0-2

TOTAL PHOSPHORUS IN WATER SUMMARY OF PERFORMANCE BY STUDY BY LABORATORY

	all the second			STUDY NO.				
LAB. NO.	?1	2.2.	24	27	2.8	38	40	43
1 2	S S	S-1FH	S S	S-1FH	S 3FL-LB	S-1FL	S-1FL	S-1FH
3 4 5 6 7 8 9 11 12 12 14 15	S 2FH, VHB S S 2FH 2FL S Q 2FL S	NR 7FH, VHB S S NR S, -1FH S 1FL 1FH, 0 S, -1FH NR	S,-1FH NR S 2FH NR 1 OFL,1FH,LB S NR 6FL-LB S NR	4FL,1FH 5FL,1FH 4FL,-LB 1FL,2FH 10FH,-HB 7FH,-HB S 8FH,-HB 1FL,6FH S NR	SFEED SFE, 7FL S 2FL 4FH, -HB S, -1FH 5FH, -HB NR 3FH, 7FL 2FH 4FH, 1FL	S-1FH S 2FL-LB S 9FL,1FH,-LB S-1FL 3FH 4FH S	3FH S 5FL,1FH 6FL,1FH S-1FL 10FH,-HB 5FL,2FH S	S-1FH 2FH 7FL,-LB S-1FL 3FH,2FL 3FL,2FH 3FL,-LB 2FL
16 17 18 20	1FH S S	2FL Q -	2FL 12FH-HB	S 1FL,3FH	S, -1FH 1FH, 2FL	6FL,1FH 3FL,4FH	8FL,-LB 5FH,3FL	2FH 6FH,4FL
21 22 23 24		NR Q 3E H	3FH,1FL NR 3FH, HR	NR NR	4FL, 2FH NR	S S	S	S
25 26 27 28		Q NR 5FH	S, -1FL S 3FH, 3FL	2FL, 2FH S 10FH,1FL,HB	S 7FH, -НВ	3FL,1FH S 10FH,-HB	2FH, FFL 6FH, 4FL 7FL, -LB 14FH, -VHB	8FL,-LB 9FL,3FH S 2FH
29 30						1FH,1FL	4FH,2FL	3FL
31 32 33				IFL,IFH	1FH,4FL,-LB	2FH 11FH,1FL,-HB 11FH,1FL,-HB	S-1FH	IFL,IFH
34 35 39 47						S-IFH 11FL,-VLB	7FH,1FL 2FL,2FH 9FH,3FL 8FH,-HB	S-1FL 2FH,-HB
56 57 59						13FH, -VHB	5FL,1FH,-LB	
60 62						Urn, or L	3FL	S 11 FH, -VHB

Key: NR - Received samples but never reported values.

HB - High bias.

LB - Low bias.

XFL - Number of results flagged low. XFH - Number of results flagged high.

Q - Method insufficient for the test at hand.

S - Satisfactory.

VHB - Very high bias.

*Laboratory 2 has combined with another laboratory.

TA	RI	F	Λ	n	-1
IM	DL		To	U	

COMPARISON OF MEDIANS (µg/L) OBTAINED FOR TWO SAMPLES ON STUDY NO. 42 TO MEDIANS OBTAINED ON THE SAME TWO SAMPLES IN STUDY 39

	A1	Cd	Со	Cr	Cu	Fe	Mn	Мо	Ni	Pb	۷	Zn
Study 42	200.0	3.0	4.8	26	13	154	50	25.0	5.8	49.0	4.1	59.5
Study 39	177.5	3.0	4.9	25	15	150	50	26.8	5.4	53.8	5.3	51.0
Study 42	382	5.0	9.0	52.0	9.0	205	25.1	50.0	4.0	91.0	20.3	111
Study 39	362	4.8	9.2	46.5	8.3	192	25.8	51.5	3.9	92.2	19.3	95

Findings from this round robin confirm previous findings: most laboratories performed fairly well on the higher level samples, but many of the analytical methods used by the laboratories were insufficient to quantify metal levels at low concentrations expected in open lake waters. A metals round robin emphasizing open lake samples is planned for this fall, in order to provide an assessment of the laboratory work on samples from Lake Superior.

Major Ions and Nutrients in Water - Study No. 41

Fourteen samples were distributed to each of 33 laboratories. The samples were determined for calcium, magnesium, sodium, potassium, chloride, sulfate, pH, alkalinity, hardness, nitrate plus nitrite, total Kjeldahl nitrogen, reactive silicate, specific conductivity, and color.

The samples comprised Great Lakes open lake waters, harbor waters, tributary waters, tap water (Burlington, Ontario), and laboratory standards. As was done in other round robins, some of the samples had been used in a previous test. The median values for these samples generally compared well over the two tests (Table 4.0-5).

Those laboratories that did well for a few constituents generally performed well on all of them. Further, the laboratories that routinely measure major ions and nutrients produced the most consistent results. Several laboratories demonstrated high or low biases. Surprisingly, some laboratories produced poor pH and conductivity results, either biased high or low, indicating calibration problems. Total Kjeldahl nitrogen was one of the more troublesome measurements.

Chlorinated Hydrocarbon Pesticides and PCBs in Fish and Ampuls - Study No. 35

Eight wet fish homogenate samples, four freeze-dried fish flesh samples, and eight ampuls of standard solutions were distributed to 21 laboratories. Although not all the results are in, some laboratories clearly have
TABLE 4.0-5

	TAP	WATER	TAT	١K	LAKE M	ICHIGAN
A CTAL TE LOSOS	1982	1981	1982	1981	1982	1980
ant a discre	ST	UDY	STL	JDY	S	TUDY
	No.41	No. 37	No. 41	No. 37	No. 41	No. 32
Toofseld, off	NO. OF	SAMPLES	NO. OF	SAMPLES	NO. OF	SAMPLES
CONSTITUENT	10	5	9	6	13	3
	10.5	10.1	40.5	10.0	24.1	24.0
Ca	40.6	40.1	42.5	43.0	34.1	34.0
Mg	1.1	8.2	9.5	9.5	11.0	10.5
Na	14.7	14.0	19.1	19.0	4.58	4.60
К	1.60	1.51	0.91	0.90	1.19	1.09
C1	29.0	29.5	105.0	105.0	8.2	8.3
S04	29.0	28.9	36.9	36.6	22.1	20.6
рН	8.0	8.0	5.70	. 5.78	8.00	7.85
Alkalinity	93.1	92.0	2.0	2.0	104.0	105.4
Hardness	134.0	136.0	146.0	146.0	130.0	127.0
NO 3+NO 2 µg/L	400.0	400.0	40.0	38.0	299.5	302.0
TKN	210.0	183.5	20.0	30.0	145.0	130.0
Si	0.36	0.35	0.01	0.01	0.28	0.24
Conductance (µmho)	344.0	344.0	446.0	.448.5	274.0	270.0
Color (units)	1.0	2.60	1.0	3.0	5.0	2.0

COMPARISON OF MEDIAN RESULTS (mg/L unless otherwise mentioned) FOR UNPRESERVED SAMPLES OF MAJOR IONS AND NUTRIENTS IN WATER USED IN TWO INTERLABORATORY STUDIES

> e is a need to clarify the process of selecting pu a robins by conseivation among the Water Quality)

demonstrated difficulties with calibration, and some laboratories failed to identify constituents in several of the ampuls. Others misidentified the PCBs that were in the ampuls.

Several of the laboratories that have not yet reported have stated a reluctance to report based on the complexity of these analyses and the need to modify their standard procedures to accommodate these samples. The Work Group regrets that there has been so much reluctance to report results since it wishes to help identify problems with the analyses and assist in remedial action when requested.

A recent review of the Data Quality Work Group activities resulted in a recommendation that the Work Group stress toxic organic analyses and conduct more round robins on priority pollutants in environmental samples. The Work Group will require better cooperation from participating laboratories to accomplish this task.

INTRALABORATORY QUALITY CONTROL AND REPORTING LOW LEVEL DATA

As mentioned earlier, the Data Quality Work Group frequently distributes its recommendations on a minimum intralaboratory quality control program and a discussion on reporting low level data. The Work Group considered these matters essential to reporting adequate data for Great Lakes ecosystem assessments.

Further, as a result of this work, the recommendations and discussion were combined as a single document and have now become an American Society for Testing and Materials Standard Practice (ASTM, 1983). The Work Group believes that this wider circulation will assist many laboratories in the proper measurement of industrial waste treatment and environmental samples.

DATA QUALITY WORK GROUP ACTIVITY REVIEW

As a result of various questions on Work Group activities by Commission staff and some members of the Water Quality Programs Committee, a review task force was struck. The membership was made up from representatives from the two Commission Sections, the Water Quality Programs Committee, and the Surveillance Work Group. One technical advisor and four expert external reviewers were also consulted.

The Task Force reported the following findings as summarized by its secretary:

- o There needs to be greater interaction among the Water Quality Programs Committee, Surveillance Work Group, and the Data Quality Work Group, especially in work-planning.
- o There is a need to clarify the process of selecting parameters for round robins by consultation among the Water Quality Programs Committee, Surveillance Work Group, and the Data Quality Work Group.

- Further evaluation of analytical methods are required but the Review Group was not certain this evaluaton should be conducted by the Data Quality Work Group for limited resource reasons.
- Sample collection and handling procedures need to be evaluated and necessary changes recommended.

REFERENCES CITED

ASTM. 1983. Standard practice for intralaboratory quality control procedures and a discussion on reporting low-level data. American Society for Testing and Materials, Committee D-19 on Water. ASTM D-4210-83, p. 7-16.

Youden, W. J. 1969. Ranking laboratories for round-robin tests, p. 165-169. In: Ku, H. H. (ed.), Precision Measurement and Calibration, Selected NBS papers on statistical concepts and procedures, National Bureau of Standards, NBS Special Publ. 300-Vol. 1, Washington, D.C.

5. Phosphorus Loadings 1981 And 1982

PHOSPHORUS LOADING ESTIMATES

This chapter contains phosphorus loading estimates for water years 1981 and 1982. Summaries of estimated loadings to the Great Lakes by basin are given in Table 5.0-1 for 1981 and in Table 5.0-8 for 1982. Tables 5.0-2 through 5.0-7 give the 1981 estimates for each basin by jurisdiction, and Tables 5.0-9 through 5.0-14 give this information for 1982.

Basins are defined as before: the Lake Huron basin begins at the head of the St. Marys River, the Lake Erie basin begins at the head of the St. Clair River, and the Lake Ontario basin begins at the head of the Niagara River and includes the Buffalo River estimate. Estimated inputs to the downstream basins from the basins upstream are provided.

ATMOSPHERIC LOADINGS

Loading estimates are based on data from wet collectors at landbased stations. These data do not include dry deposition for which few measurements are available. In these estimates, the contribution of the dry component is assumed to be equal to that of wet deposition. For estimates from Canadian collectors, this means that the loading rate was doubled to give a total rate. The loading rates calculated from United States collectors were not doubled since there is some question about exposure time for many data points. The loading rates to the portions of the lakes belonging to each country. The Lake Michigan estimate is based solely on United States data. The Lake Ontario estimate is based solely on Canadian data.

The loading estimates for Lakes Superior, Michigan, Huron and Erie are all well below the 1979 loading estimates. To what extent these differences reflect true large year-to-year fluctuations rather than the difficulties in obtaining accurate estimates is not clear.

DIRECT INDUSTRIAL AND MUNICIPAL DISCHARGES

These data were provided by the states and the province of Ontario. The point source coordinators of the two countries have continued to work with the jurisdictions to insure comprehensive reporting.

TRIBUTARY LOADINGS

Tributary loading estimates were prepared as in previous years. The methodology employed is discussed in the Surveillance Subcommittee Report of 1977.

The Ontario Ministry of the Environment has continued its augmented sampling program of major tributaries. EPA Region V supported an event monitoring program for some Ohio, Michigan, and New York tributaries in 1982. Due to this event monitoring, the 1982 estimates for Lakes Erie and Ontario provide more reliable results than do the 1981 estimates for these lakes.

ESTIMATES AND TARGET LOADS

In the discussion which follows the estimates for 1981 and 1982 are compared to the target phosphorus loads given in the 1978 Water Quality Agreement.

The estimates for Lake Superior in 1981 and 1982 are quite similar, 3,412 and 3,160 tonnes, respectively. The major differences between the two estimates is the much higher adjustment for unmonitored area in 1981. Both estimates compare favorably to the target load of 3,400 tonnes. However, this comparison depends on the low atmospheric estimates used in the calculations.

The estimates for Lake Michigan in 1981 and 1982 are almost identical, being 4,091 and 4,084 tonnes, respectively. Both estimates are well below the target load of 5,600 tonnes. Again, the favorable comparison is related to a very low atmospheric estimate.

The 1981 and 1982 estimates to Lake Huron of 3,481 and 4,689 tonnes differ by over 1,200 tonnes. Almost half the difference is due to the much larger 1982 atmospheric estimate. Most of the remaining difference stems from a much higher 1982 adjustment for unmonitored area. The 1981 estimate is well under the target load of 4,360 tonnes, while the 1982 estimate is over 300 tonnes above it.

The estimates for Lake Erie in 1981 and 1982 of 10,452 and 12,349 tonnes, respectively, have a substantial difference of almost 1,900 tonnes. Over half this difference is attributable to the much higher Ohio tributary estimate in 1982. The 1982 Ontario tributary estimate also exceeds the corresponding 1981 estimate by the substantial amount of almost 900 tonnes. The meeting of the target load of 11,000 tonnes by the 1981 estimate should be viewed with caution, while the 1982 estimate, which exceeds the target by over 1,300 tonnes, probably presents a truer picture.

The 1982 estimate to Lake Ontario, 8,891 tonnes exceeds the 1981 estimate of 7,437 tonnes by 1,454 tonnes. Almost 500 tonnes of this difference is due to an inexplicable increase in the loading from Lake Erie. An additional portion of the increase is attributable to more extensive sampling of the New York tributaries, although the estimate for the Ontario tributaries increased comparably. The estimates for both years are above the target load of 7,000 tonnes.

SUMMARY OF 1981 ESTIMATED ATMOSPHERIC, INDUSTRIAL, MUNICIPAL AND TRIBUTARY PHOSPHORUS LOADING DATA TO THE GREAT LAKES (All values are in metric tonnes/year)

R10 (101ALS	SUPERIOR	MICHIGAN	HURON	ERIE	ONTAR IO	ST. LAWRENCE RIVER	TOTAL
						Industrial	1 sestio
Atmospheric ¹ (standard error)	506 (188)	306 (47)	613 (132)	729 (371)	328 (171)		2,481 (471)
Direct Industrial Discharge	36	42	3	55	62	36	234
Direct Municipal Discharge	116	243	141	1,843	1,756	202	4,302
Tributary: Monitored (standard error)	1,259 (189)	2,966 (329)	1,638 (129)	5,582 (426)	1,822² (79)	129 (13)	13,397 (590)
Adjustment for Unmonitored Area (standard error)	³ (470)	534 (56)	429 (64)	1,163 (109)	613 (44)	119 (11)	4,353 (492)
Within lake Totals	3,412	4,091	2,824	9,372	4,581	486	24,767
From Connecting Channels	-	-	657	1,080	2,856	2,765	
TOTALS	3,412	4,091	3,481	10,452	7,437	3,251	
Target Loads ⁴	3,400	5,600	4,360	11,000	7,000		

Totals may not sum due to rounding.

¹U.S. atmospheric estimates combine 1981 and 1982 data, but are predominantly made from 1981 data.

²Includes Buffalo River.

³Standard errors calculated from tributary loading estimates used in making adjustments.

⁴Annex 3, 1978 Water Quality Agreement.

SUMMARY OF 1981 ESTIMATED PHOSPHORUS LOADING DATA TO LAKE MICHIGAN

(All values are in metric tonnes/year)

21410)	WISCONSIN	MICHIGAN	ILLINOIS	INDIANA	TOTALS
Directy Locasterial					
Direct Industrial Discharge	29	11	-	1	42
Direct Municipal Discharge	211	32	-	0	243
Tributary: Monitored (standard error)	769 (80)	1,748 (301)	-	449 (105)	2,966 (329)
Subtotals	1,009	1,791	-	450	3,251
Atmospheric (standard error)					306 ¹ (47)
Tributary: Adjustment for Unmonitored Area (standard error) ²	United St	tates			534 (56)
TOTAL					4,091
tal asles hopur trole	Lare ndron		000 101190	2 add may	A sharks

Target Load, Annex 3, 1978 Great Lakes Water Quality Agreement 5,600

Totals may not sum due to rounding.

¹Atmospheric estimates combine 1981 and 1982 data, but are predominantly made from 1981 data.

²Standard errors calculated from tributary loading estimates used in making adjustments.

SUMMARY OF 1981 ESTIMATED PHOSPHORUS LOADING DATA TO LAKE HURON

2 DEDT AMATOMI PIE	MICHIGAN	ONTARIO	ORTARIO	TOTALS
Direct Industrial Discharge	2	1		3
Direct Municipal Discharge	18	123		141
Tributary: Monitored (standard error)	776 (118)	863 (52)		1,638 (129)
Subtotals	796	987		1,782
Atmospheric (standard error)				613 ¹ (132)
Tributary: Adjustment for Unmonitored Area (standard error) ²	United States	154, Canada (62)	276 (18)	429 (64)
TOTAL				2,824
190,6				lator
Inputs from Lake Super Lake Michigan are es	ior and timated at 402 and	255, respectivel	у	657 ³
Total estimated input	to Lake Huron			3,481
Target Load, Annex 3,	1978 Great Lakes W	later Quality Agre	ement	4,360

(All values are in metric tonnes/year)

Totals may not sum due to rounding.

¹U.S. atmospheric estimates combine 1981 and 1982 data, but are predominantly made from 1981 data.

²Standard errors calculated from tributary loading estimates used in making adjustments.

³Upper Lakes Reference Group 1974-1975 estimates.

SUMMARY OF 1981 ESTIMATED PHOSPHORUS LOADING DATA TO LAKE ERIE

(All values are in metric tonnes/year)

2.18705	MICHIGAN	OHIO	PENNS VAN I	YL- NEW YORK	ONTARIO	TOTALS
Direct Industrial Discharge	27	2	ж та :	2 0	25	55
Direct Municipal Discharge	1,125	530	8	0 38	69	1,843
Tributary: Monitored (standard error)	306 (25)	3,939 (412)	8) 85.3	- 260 - (96)	1,077 (45)	5,582 (426)
Subtotals	1,458	4,471	8	2 298	1,171	7,480
Atmospheric (standard error)						729 ¹ (371)
Tributary: Adjustment for Unmonitored Area (standard error) ² TOTAL	United	States (939, 108)	Canada 224 (9) JATOT JUGAT SES	1,163 (109) 9,372
Estimated input ³ from	m Lake Huron	1 11 11 11 11 11 11 11 11 11 11 11 11 1	(in) (in)	ex 3, 1976 Ge	nnA .bso.]	1,080
Total estimated inpu	t to Lake Er	ie				10,452
Target Load, Annex 3	, 1978 Great	Lakes Wa	ter Qua	lity Agreemen	t	11,000

Totals may not sum due to rounding.

¹U.S. atmospheric estimates combine 1981 and 1982 data, but are predominantly made from 1981 data.

²Standard errors calculated from tributary loading estimates used in making adjustments.

³Upper Lakes Reference Group 1974-1975 estimates.

SUMMARY OF 1981 ESTIMATED PHOSPHORUS LOADING DATA TO LAKE ONTARIO

(All values are in metric tonnes/year)

NTOT OTALITA TOTAL	NEW YORK	ONTARIO	TOTALS
Direct Industrial Disch	arge 30	32	62
Direct Municipal Discha	-ge 813	942	1,756
Tributary: Monitored (standard error)	898 (53)	924	1,822 ¹ (79)
Subtotals	1,741	1,898	3,640
Atmospheric (standard error)			328 ² (171)
Tributary: Adjustment for Unmonitored Area (standard error) ³ TOTAL	United States 332, (37)	Canada 281 (24) <u>613</u> (44) 4,581
Estimated input ⁴ from L	ake Erie	1	2,856
Total estimated input t	o Lake Ontario		7,437 ¹

Totals may not sum due to rounding.

¹Includes Buffalo River.

²Canadian data.

³Standard errors calculated from tributary loading estimates used in making adjustments.

⁴This estimate is derived from extensive sampling data at the mouth of the Niagara River, and adjusted by subtraction of estimated tributary loadings and reported municipal and industrial discharges to the Niagara.

SUMMARY OF 1981 ESTIMATED PHOSPHORUS LOADING DATA TO THE INTERNATIONAL PORTION OF THE ST. LAWRENCE RIVER (All values are in metric tonnes/year)

and and and another		NEW YORK	Maria .	ONTARIO	a (SETAR)	TOTALS
A3VIA						
Direct Industrial Discharge		0	306 (47))	36		36
Direct Municipal Discharge		131		71		202
Tributary: Monitored (standard error)		79 (8)		51 (10)		129 (13)
Subtotals		210		158		367
Tributary: Adjustment for Unmonitored Area (standard error) ²	United	l States	84 (9)	Canada	35 (7)	119 (11)
TOTAL						486
From Lake Ontario ¹ (standard error)	080, f	657	-			2,765 (92)
Total estimated input to t St. Lawrence River	the inter	national	portion	of the		3,251

¹Based on sampling of the St. Lawrence River near Kingston, Ontario.

²Standard errors calculated from tributary loading estimates used in making adjustments.

SUMMARY OF 1982 ESTIMATED ATMOSPHERIC, INDUSTRIAL, MUNICIPAL AND TRIBUTARY PHOSPHORUS LOADING DATA TO THE GREAT LAKES (All values are in metric tonnes/year)

	SUPERIOR	MICHIGAN	HURON	ERIE	ONTARIO	ST. LAWRENCE RIVER	TOTAL
Atmospheric ¹ (standard error)	653 (186)	306 (47)	1,174 (359)	660 (135)	600 (223)	t. Indus tri charge	3,393 (483)
Direct Industrial Discharge	33	53	5	67	54	27	239
Direct Municipal Discharge	128	246	113	1,388	1,589	190	3,654
Tributary: Monitored (standard error)	1,338 (87)	2,808 (239)	1,921 (140)	7,483 (197)	2,581 ² (84)	232 (68)	16,362 (367)
Adjustment for Unmonitored Area (standard error)	1,008 (227)	671 (62)	819 (162)	1,671 (103)	737 (261)	232 (73)	5,138 (407)
Within lake Totals	3,160	4,084	4,032	11,269	5,561	681	28,786
From Connecting Channels	_	-	657	1,080	3,330	3,162	
TOTALS	3,160	4,084	4,689	12,349	8,891	3,843	
Target Loads ⁴	3,400	5,600	4,360	11,000	7,000		

Totals may not sum due to rounding.

¹U.S. atmospheric estimates combine 1981 and 1982 data, but are predominantly made from 1981 data.

²Includes Buffalo River.

³Standard errors calculated from tributary loading estimates used in making adjustments.

⁴Annex 3, 1978 Water Quality Agreement.

SUMMARY OF 1982 ESTIMATED PHOSPHORUS LOADING DATA TO LAKE SUPERIOR (All values are in metric tonnes/year)

INGTANA TOTALS	M	INNESOT	A WIS	CONSTN	MT	CHIGAN	ONTARTO	TOTALS
				00110111		OTTUAN	ONTARIO	TUTALS
Direct Industrial Discharge		0		0		0	33	33
Direct Municipal Discharge		1		3		8	115	128
Tributary: Monitored (standard error)		203 (19)		224 (65)	806. (03.()	158 (30)	752 (44)	1,338 (87)
Sub to tals		204		227		166	900	1,499
Atmospheric (standard error)								653 ¹ (186)
Tributary: Adjustment for Unmonitored Area (standard error) ²		United	States	806, (227)	st fati	Canada	202 (13)	1,008 (227)
TOTAL								3,160

Target Load, Annex 3, 1978 Great Lakes Water Quality Agreement 3,400

Totals may not sum due to rounding.

¹U.S. atmospheric estimates combine 1981 and 1982 data, but are predominantly made from 1981 data.

²Standard errors calculated from tributary loading estimates used in making adjustments.

SUMMARY OF 1982 ESTIMATED PHOSPHORUS LOADING DATA TO LAKE MICHIGAN (All values are in metric tonnes/year)

OUTARIO TOTALS		VISCONSIN	MICHIGAN	ILLI	NOIS	INDIANA	TOTALS
Direct Industrial Discharge		44	8		0	dustrial gal	53
Direct Municipal Discharge		213	33		0	0	246
Tributary: Monitored (standard error)		1,008 (140)	1,488 (162)		-	312 (105)	2,808 (239)
Subtotals		1,265	1,529		0	313	3,107
Atmospheric (standard error)							306 ¹ (47)
Tributary: Adjustment for Unmonitored Area (standard error) ²		United S	tates				671 (62)
TOTAL							4,084
Target Load, Annex	3, 19	078 Great L	akes Water	Qualit	y Agre	ement	5,600

Totals may not sum due to rounding.

¹Atmospheric estimates combine 1981 and 1982 data, but are predominantly made from 1981 data.

²Standard errors calculated from tributary loading estimates used in making adjustments.

SUMMARY OF 1982 ESTIMATED PHOSPHORUS LOADING DATA TO LAKE HURON

(All values are in metric tonnes/year)

NEW YORK ONTARIU 1013	MICHIGAN	ONTARIO	TOTALS
Direct Industrial Discharge	5	0	
Direct Municipal Discharge	26	86	113
Tributary: Monitored (standard error)	999 (135)	922 (38)	1,921 (140)
Subtotals	1,030	1,008	2,039
Atmospheric (standard error)			1,174 ¹ (359)
Tributary: Adjustment for Unmonitored Area (standard error) ²	United States 500 (161	, Canada)	319 819 (14) <u>(162)</u>
TOTAL			4,032
Inputs from Lake Superio	or and	Quality Agree	
Lake Michigan are est	imated at 402 and 255	, respectively	y 657 ³
Total estimated input to	b Lake Huron		4,689

Target Load, Annex 3, 1978 Great Lakes Water Quality Agreement 4,360

Totals may not sum due to rounding.

¹U.S. atmospheric estimates combine 1981 and 1982 data, but are predominantly made from 1981 data.

²Standard errors calculated from tributary loading estimates used in making adjustments.

³Upper Lakes Reference Group 1974-1975 estimates.

SUMMARY OF 1982 ESTIMATED PHOSPHORUS LOADING DATA TO LAKE ERIE

TOTALS	MICHI	GAN OHIO	D PENNSYL VANIA	NEW YORK	ONTARIO	TOTALS
Direct Industrial Discharge	2	29	2 1	0	34	67
Direct Municipal Discharge	7(07 523	3 73	22	63	1,388
Tributary: Monitored (standard error)	39(3	98 4,992 35) (172	2 0 8) <u>–</u>	129 (32)	1,964 (70)	7,483 (197)
Subtotals	1,13	34 5,51	7 74	151	2,061	8,938
Atmospheric (standard error)						660 ¹ (135)
Tributary: Adjustment for Unmonitored Area (standard error) ²	u oberno Ui	nited State	s 1,251 (103)	Canada 420 (13) 3)	1,671 (103)
TOTAL					TOTAL	11,269
Estimated input ³ fr	om Lake	Huron			2	1,080
Total estimated inp	out to La	ke Erie				12,349
Target Load, Annex	3, 1978	Great Lakes	Water Qual	ity Agreemen	nt	11,000

(All values are in metric tonnes/year)

Totals may not sum due to rounding.

¹U.S. atmospheric estimates combine 1981 and 1982 data, but are predominantly made from 1981 data.

²Standard errors calculated from tributary loading estimates used in making adjustments.

³Upper Lakes Reference Group 1974-1975 estimates.

SUMMARY OF 1982 ESTIMATED PHOSPHORUS LOADING DATA TO LAKE ONTARIO

(All values are in metric tonnes/year)

	NEW YORK	ONTARIO	TOTALS
Direct Industrial Discharge	29	25	54
Direct Municipal Discharge	732	857	1,589
Tributary: Monitored (standard error)	1,270 (66)	1,311 (51)	2,581 ¹ (84)
Subtotals	2,031	2,193	4,224
Atmospheric (standard error)			600 ² (223)
Tributary: Adjustment for Unmonitored Area Unit (standard error) ³ TOTAL	ted States 463, (260)	Canada 275 (18)	737 (261) 5,561
Estimated input ⁴ from Lake Eri	ie		3,330
Total estimated input to Lake Ontario			8,891 ¹
Target Load, Annex 3, 1978 Great Lakes Water Quality Agreement			7,000

Totals may not sum due to rounding.

¹Includes Buffalo River.

²Canadian data.

³Standard errors calculated from tributary loading estimates used in making adjustments.

⁴This estimate is derived from extensive sampling data at the mouth of the Niagara River, and adjusted by subtraction of estimated tributary loadings and reported municipal and industrial discharges to the Niagara.

SUMMARY OF 1982 ESTIMATED PHOSPHORUS LOADING DATA TO THE INTERNATIONAL PORTION OF THE ST. LAWRENCE RIVER (All values are in metric tonnes/year)

2 18007 01307	and the second second second second		
	NEW YORK	ONTARIO	TOTALS
25 Fairstaubri 64mmin 68			
Direct Industrial Discharge	0	27	27
Direct Municipal Discharge	123	67	190
Tributary: Monitored (standard error)	198 (68)	34 (5)	232 (68)
Subtotals	32 1	128	449
Tributary: Adjustment for Unmonitored Area (standard error) ¹ TOTAL	United States 212 (73)	Canada 20 (3) <u>232</u> (73) 681
From Lake Ontario ² (standard error)	Contactor	ines of steph is	3,162 (93)
Total estimated input to St. Lawrence River	the international portion	on of the	3,843

¹Standard errors calculated from tributary loading estimates used in making adjustments.

²Based on sampling of the St. Lawrence River near Kingston, Ontario.

6. Surveillance Activities Initiatives

In this section, the Surveillance Work Group presents initiatives that it believes may modify future surveillance activities. While these activities do not in themselves constitute guarantees for more efficient surveillance programs, they do represent significant achievements in aiding the Work Group toward meeting its mandate to continually review existing programs or methods of accomplishing the goals outlined in Annex 11 and 12 of the 1978 Water Quality Agreement.

BIOLOGICAL MONITORING RESEARCH PROGRAM

Over the last decade there has been a scientific debate concerning the appropriate number of sampling sites and the frequency with which those sites must be sampled in order to sufficiently describe the chemistry of a particular water body thus allowing for accurate assessment of man's impact. The Surveillance Work Group (SWG) has heard from many scientists the advantages and disadvantages of performing surveillance at a few sites with frequent collection versus numerous sites collected infrequently. Still another faction of science claims that monitoring the biological community structure gives a more accurate and sensitive measure of lake behavior in terms of assessing the effects of various abatement programs.

In conjunction with the 1981-82 Lake Ontario intensive survey, the Great Lakes Fisheries Research Branch (GLFRB) at the Canada Centre for Inland Waters (CCIW) implemented a program with the purpose of supplementing the GLISP related program with data from a limited number of sites collected on a weekly basis during the ice free period (see Figure 6-1). In addition to collecting and analyzing chemical and physical attributes of the water column, the research program has collected and will analyze in a detailed manner the biological community at the selected sites.

This year marks the culmination of the GLFRB three year effort and some preliminary findings suggest that there are differences between the data emanating from this program and that from the intensive study. The significance of these differences may have a bearing on future surveillance activities. Therefore, the SWG looks forward to the complete data interpretation of this effort with the hope that many questions will be answered.

LAKE AND CONNECTING CHANNEL TASK FORCES

Based on a Surveillance Work Group review of the GLISP, the Water Quality Board reported last year that it was considering a proposal to ensure that requisite annual binational planning and implementation of surveillance activities occur in a timely manner. The Surveillance Work Group and the Water Quality Board also anticipated a need for providing a basis for allocating sufficient funds to implement scientifically sound programs.



FIGURE 6-1

Sampling grid for the monitoring and surveillance stations in Lake Ontario. The intensive, weekly sampling program is conducted at the circled stations.

- 122 -

Subsequently, the Water Quality Board approved the Terms of Reference for establishing five lakes and two connecting channels task forces.

To assure that the anticipated work plans would be effective in influencing the budgeting process, it was necessary to ask that the task forces initially produce a three-year plan to commence in field year 1984. The expected three one-year plans were required in order to coincide with the United States federal budgetary process whereby financial requests for 1986 activities must be submitted prior to January 1, 1984.

The work plans for 1984 and 1985 will be used, where appropriate, to re-program allocations for 1984 and 1985 or where financial needs exceed resources, the plans will be used as supporting documentation for additional financial request. As mentioned, the 1986 plan will be used as a guideline and justification for the budget request which is required by the administration on January 1984. The plans are expected to have an identical impact on the Canadian process as effected through the Canada-Ontario Agreement.

In addition to the task of designing future surveillance plans, the terms of reference for the task forces specify two other major areas of activity including, compilation of previous findings and coordination of on-going activities. In total, the task forces functions will be scrutinized by the Surveillance Work Group to assure that such activities are within the scope of the Water Quality Agreement.

The Surveillance Work Group reports that the task forces were formed and have had several meetings to date. The Surveillance Work Group is optimistic that the task forces will meet their target date for submitting their annual work plans in a manner consistent with their terms of reference.

TUMOR MONITORING

Research in aquatic toxicology indicates that many of the substances of anthropogenic origin found in the Great Lakes ecosystem have the potential, through long-term, low level exposure, to produce chronic adverse effects on fish and wildlife. Included in these impacts are disruption of physiological and biochemical function and non-adaptive pathological changes.

Great Lakes biota are exposed to a large number and variety of substances under changing environmental conditions. Indeed, the Appendix E of the 1983 Water Quality Board Report lists over 800 compounds that are presently found in some component of the Great Lakes ecosystem. The prospect of generating toxicological data for each of these chemicals is overwhelming and clearly impractical if all chemical and species interactions are to be considered.

Laboratory induction studies clearly indicate that certain chemicals are carcinogenic to fish. These chemicals may be responsible for the occurrence of neoplastic and non-neoplastic lesions in Great Lakes fish. Freshwater fish health monitoring programs indicate that several species of Great Lakes fish have elevated frequencies of pathological anomalies. The most commonly found anomalies include; epidermal papillomas on white suckers (Catostomus commersoni) and brown bullhead (Ictalurus nebulosus), gonadal tumors on carp

(Cyprinis carpio) and yellow perch (Perca flavescens), liver tumors on brown bullhead and thyroid hyperplasia on coho salmon (Oncorhynchus kisutch). The etiology of these tumors is unknown, but it appears that fish inhabiting waters contaminated with industrial and domestic wastewater show an increased prevalence of tumors, skeletal deformities and fin rot. These findings are supported by empirical observation in the Great Lakes, whereby 35% of three-year old brown bullhead from the Black River, Ohio were affected by clearly observable liver tumors. This figure may be a conservative estimate as histological analyses indicate that upwards of 90% of these fish are affected. The river sediments where these fish were collected are contaminated with high concentrations of polynuclear aromatic hydrocarbons (see Chapter 3 of this report). The relationship between tumor induction and PAH exposure was demonstrated in laboratory studies which induced epidermal hyperplasia and papillomas by repeated application of PAH contaminated sediment extracts from the Buffalo River, New York. In a survey of white sucker papillomas, Canadian nearshore investigations in Lakes Huron and Ontario demonstrate that these fish show elevated papilloma frequencies in geographically separate areas (Figure 6-2). These data may have utility as an indicator of contaminated sites.

Although there is as yet no conclusive evidence confirming the role of ambient chemical carcinogens in wild fish populations, there is increasing data indicating that Great Lakes fish are responding to chemical exposure and that a systematic fish health surveillance program would provide an early warning mechanism to identify sites and species impacted by chemical stress. The Surveillance Work Group is interested in additional advances from these ongoing programs as they show promise of inclusion into the existing surveillance network for measuring the success of or need for abatement programs. This type of monitoring, if acceptable, could provide an appropriate link between contaminated environments and biological responses.



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Prevalence of tip papiliomes in white suckers from Lakes Huron and Ontario as the percent of total male and female fish greater than 40 cm in fork length collected by alectrofishing during spring spawning rune for the years 1931 through 1983. "N" equals number of the collected

> Data Source: Department of Fisheries and Oceans: Buillington: Golatio

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