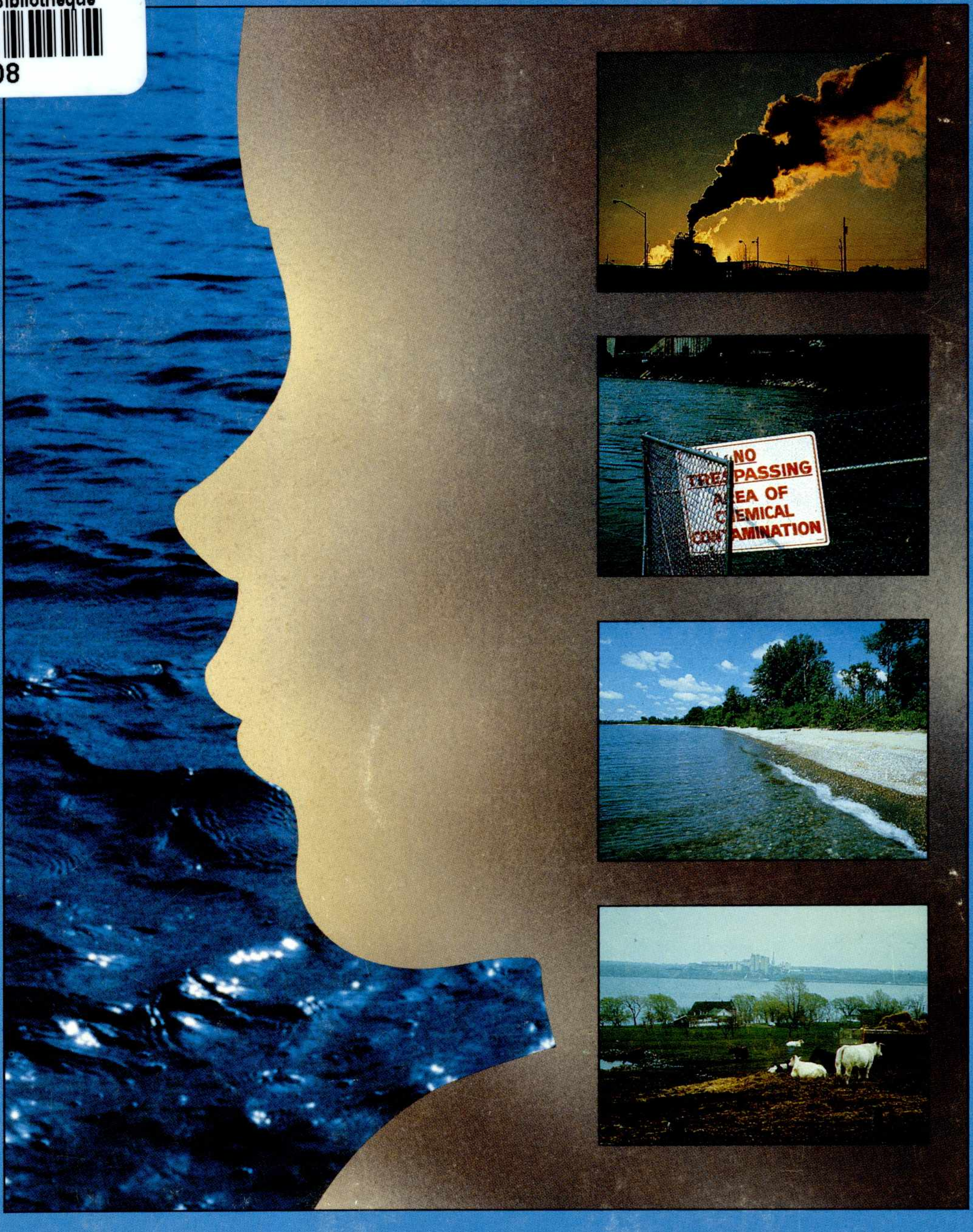
Toxic Chemicals in the Great Lakes and Associated Effects

VOLUME I — Contaminant Levels and Trends



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TOXIC CHEMICALS IN THE GREAT LAKES AND ASSOCIATED EFFECTS

VOLUME I
CONTAMINANT LEVELS AND TRENDS

March 1991

ENVIRONMENT CANADA
DEPARTMENT OF FISHERIES AND OCEANS
HEALTH AND WELFARE CANADA

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INTRODUCTION

The increased commercial production and widespread use of synthetic toxic chemicals and metals since the 1940s have resulted in the contamination of the environment. While the presence of persistent toxic chemicals in the Great Lakes has been known for some time, concerns have been directed in recent years towards the environmental and human health effects of these chemicals.

During the past two and a half years, Environment Canada, the Department of Fisheries and Oceans, and Health and Welfare Canada have worked together to compile the scientific literature on the levels, trends and effects of persistent toxic chemicals in the Great Lakes basin. This has resulted in a two volume technical document entitled *Toxic Chemicals in the Great Lakes and Associated Effects*. Volume I of this report is divided into four parts. It summarizes data on the concentrations of toxic chemicals in water and sediments, invertebrates and fish, wildlife, and humans. Volume II also contains four parts. It reviews what is known about the effects of persistent toxic chemicals on fish, wildlife and people and presents a concluding synthesis which interprets the significance of the levels and effects information in the two volumes. Each part of the report begins with an executive summary.

Based on our knowledge of chemicals and their toxicology, a pattern is emerging that suggests that persistent chemicals in the environment have a significant effect on fish and wildlife species. We still know very little about the effects of a person's lifetime exposure to toxic organic chemicals and metals. Despite some uncertainties, it is clear that toxic chemicals are a threat to the entire ecosystem. As a result, the principle of "virtual elimination" of persistent toxic substances from the lakes has been adopted in the Canada-US Great Lakes Water Quality Agreement. The national governments of both countries together with the province of Ontario, the eight Great Lake states and the large municipalities are moving towards this goal using the regulatory processes, pollution prevention strategies and public education. In the meantime, government programs continue to monitor the health of the ecosystem, assess the extent to which it is impaired by toxic chemicals and develop means to reduce the impact of exposures.

TOXIC CHEMICALS IN THE GREAT LAKES AND ASSOCIATED EFFECTS

VOLUME I PART 1

CONCENTRATIONS OF CONTAMINANTS IN WATER AND SEDIMENTS

EXECUTIVE SUMMARY

This part of the report reviews the available information on concentrations and trends of chemicals in Great Lakes water and sediment. Published reports have been used whenever possible and uninterpreted data have not been included.

The most recent data on chemicals in water are the most reliable and show that ambient concentrations are in the low parts per trillion range. This is much lower than concentrations measured in the past. Presently, most concentrations of toxic chemicals in water from the Great Lakes are below the Great Lakes Water Quality Agreement objectives.

Data on chemical concentrations in sediment cores indicate that the major loadings of persistent toxic chemicals to the Great Lakes aquatic ecosystem took place between the 1950s and the early 1970s. Major influxes of several individual chemicals occurred several years before they were first detected in biota. Concentrations of chemicals have decreased and are lower than they were 10 to 15 years ago. In some lakes, these decreases in sediment concentrations have been dramatic and correlate with bans or restriction on the manufacture and use of chemicals including PCBs and mirex.

Lakes Ontario, Michigan, and Erie are the most chemically contaminated of the Great Lakes. Lake Superior is the least contaminated. The chemical concentrations are affected by physical characteristics of the lakes and connecting channels and the types of source. The atmosphere is relatively a greater source of most of the critical pollutants (e.g., PCBs, DDT and alkyl lead) to the upper Great Lakes than to the lower lakes. The large surface areas and drainage basins of the upper lakes are major contributing factors. Conversely, the lower lakes receive larger inputs from their main tributaries, industries, municipalities and agriculture than the upper lakes.

Concentrations of contaminants in water are higher in the nearshore areas. In contrast, higher concentrations are found in sediments in the depositional basins, harbours and deltas. These include Saginaw, Georgian, Duluth-Superior and Green Bays, western Lake Erie and adjacent to the Niagara River in Lake Ontario. In the connecting channels, higher levels are usually found along the shore downstream from sources. Concentrations of some chemicals in the sediments are still increasing along the St. Clair-

Detroit River corridor and the Niagara River. Spills are a major problem in the St. Clair River.

Although 362 xenobiotic chemicals have been detected in the waters of the Great Lakes, no new ubiquitous, persistent and highly toxic contaminants have been detected since 1982. Future control actions will have to take into account point sources that have not yet been adequately controlled (e.g., sewage treatment plants) and non-point sources of chemicals, such as the atmosphere; chemicals remobilised from contaminated sediment; agricultural, forestry and urban runoff sources; and groundwater.

In the 1978 Great Lakes Water Quality Agreement, Canada and the U.S. agreed to the virtual elimination of all persistent toxic substances from the Great Lakes with an eventual goal of zero discharge. Since 1978, programs have been initiated to reduce or eliminate inputs of contaminants to the Great Lakes at locations such as the Niagara Frontier, the Detroit and St. Clair Rivers, and many Areas of Concern. These and other programs should be expedited so that the goals of virtual elimination and zero discharge can be realised.

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1. INTRODUCTION

The Great Lakes constitute the largest body of freshwater on earth. Ranked by surface area, Lake Superior is the second largest lake in the world, Lake Huron is the fifth largest, Lake Michigan the sixth largest, Lake Erie the thirteenth largest, and Lake Ontario the seventeenth largest (Beeton, 1984). The Great Lakes are one of the planet's great natural resources. In spite of the size of these waterbodies, they have been contaminated with toxic chemicals. The sources of the chemicals are agricultural, urban and industrial development. Some toxic chemicals are distributed throughout the entire Great Lakes ecosystem.

This report reviews the available information on concentrations of chemicals in the water and bottom sediments of the open Great Lakes and their connecting channels. Spatial and temporal trends are discussed where possible.

The introductory section consists of background information about toxic chemicals in the water and sediments of the Great Lakes. This includes the sources, pathways and fate of the chemicals in the system, a discussion of the main chemicals of concern, a history of Great Lakes contamination, and a description of water and sediment sampling and analysis. The overall organization of this report is by geographic location; that is, the data for each lake and connecting channel are presented in sequence from Lake Superior to the international section of the St. Lawrence River. For each body of water, the conditions of the water and then the sediments are discussed. The water sections are divided into two parts. The first reviews data on the aqueous phase and in total water and the second discusses concentrations in the suspended sediment phase. The sediment sections are also divided into two parts: surficial sediment concentrations and concentrations in sediment cores. In each of these four sections, concentrations of metals are discussed before those of organic contaminants. The main chemicals discussed are lead (Pb), mercury (Hg), cadmium (Cd), arsenic (As), DDT and metabolites, dieldrin, alpha-BHC, lindane, mirex, toxaphene, benzo(a)pyrene (B[a]P), dioxins and furans, HCB, HCBD and PCBs. There is a list of chemical abbreviations in Appendix 2. There are tables showing the concentrations of these chemicals in the water and sediments for each of the Great Lakes and the Niagara River. Representative core profiles for each of the Great Lakes show sediment concentration trends. Summaries of geographic patterns of contaminant distribution and concentration changes over time are given in the conclusion. There is a glossary in Appendix 3.

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

1.1 TOXIC CHEMICAL SOURCES, PATHWAYS AND FATE

The Great Lakes system flows from Lake Superior and Lake Michigan through the other Great Lakes and the St. Lawrence River to the Atlantic Ocean (Figure 1). The lakes are one unit and are connected by short narrows at Mackinac and by the short connecting channels of the St. Clair, Detroit and Niagara Rivers. These channels have extremely high discharges of approximately 6,000 m^3/sec, putting them on a scale with the world's largest rivers. The massive transfers of water into and out of Lakes Erie and Ontario are important for the fate of toxic chemicals in the lower Great Lakes. Less than 1% of the total volume of water in the system flows out annually through the St. Lawrence River. The residence times of the lower Great Lakes are strongly influenced by the flows of the connecting channels (Table 1).

The connecting channels, other tributaries and the atmosphere are major sources of many toxic chemicals to the lower Great Lakes (Strachan and Eisenreich, 1988). Canadian industry is concentrated along the shore of the St. Clair River. Detroit and Windsor are located on the shores of the Detroit River. Buffalo is located immediately upstream of the Niagara River. There has been major industrial development on the side of the Niagara River. Effluents from these cities and industries have introduced toxic chemicals into the connecting channels and thus to the downstream lakes (NRTC, 1984; UGLCCS, 1989). The connecting channels rapidly transfer chemicals discharged into them to the downstream lakes. For example, there is little or no long term removal of chemicals by burial in the bottom sediments of the Niagara River (Mudroch and Williams, 1989). Another important result of the high discharge rate of the channels is that chemical inputs are quickly diluted to extremely low concentrations in the water phase. But, because of the high discharge rates, these extremely low concentrations represent large loadings to the downstream lakes.

The two largest conurbations in the Great Lakes basin are the Gary-Chicago-Milwaukee area of southwestern Lake Michigan and the Hamilton-Toronto area of northwestern Lake Ontario. Contaminants are introduced to the lakes by urban runoff, via storm sewers and by many sewage treatment plants.

Today, non-point sources of chemical contamination, such as the atmosphere, agricultural runoff, and contaminated bottom sediments are recognized sources of contaminants to the lakes. Agricultural practices are sources of pesticides to tributaries of Lakes Michigan, Erie and Ontario, in particular. Because of their surface area, atmospheric deposition is a major source of chemicals to the Great Lakes (Strachan and Eisenreich, 1988).

The Great Lakes are frequently referred to as inland seas yet the processes such as sedimentation, photodegradation and bioaccumulation which control the fate of chemicals in these large lakes are similar to those in smaller lakes. Hydrophobic contaminants are found at the interfaces between water and other aquatic compartments such as inorganic and organic solids in the water column, or at surface microlayers between the water and the atmosphere. If they are associated with particulates, toxic chemicals become subject to limnological processes, such as sedimentation and accumulation in depositional basins. Burial in bottom sediments is a major process for aquatic ecosystem self-cleansing. In the deep lakes (Superior, Michigan, Huron and Ontario) toxic chemicals which have accumulated in bottom sediments are eventually buried beneath cleaner sediments and are removed from bioaccumulation pathways. The depth and size of the lakes also affects their biological productivity and thus the fate of the contaminants. Nutrient loads to the lakes also affect productivity. The relationship between nutrient status and the fate of toxic chemicals is not well established but it has been hypothesised that chemical concentrations at the top of aquatic food webs may be lower in nutrient rich lakes. The response of each lake to contamination is thus unique. The fate of toxic chemicals in the lakes is also governed by the physicochemical characteristics of the chemicals. These include solubility, volatility, hydrophobicity, lipophilicity, the degree of partitioning onto suspended solids, and the susceptibility to photo- and biodegradation. Once released to aquatic ecosystems, some chemicals rapidly disappear by degradation or volatilization to the atmosphere. Chemicals degradation can take place by a variety of chemical and biological processes including hydrolysis, photolysis, and bacterial or fungal dechlorination. Even short lived chemicals can be highly toxic while they are in the water column.

1.2 MAIN CHEMICALS OF CONCERN

Concern about the contamination of the Great Lakes have focused on persistent toxic chemicals. Toxic metals include lead, mercury, cadmium and arsenic, and persistent toxic organic chemicals include chlorinated pesticides such as DDT and mirex, chlorinated benzenes, chlorinated dioxins and furans, and PCBs.

In 1983, the IJC published a comprehensive inventory of chemical substances identified in the Great Lakes ecosystem. The 1986 working list of chemicals in the Great Lakes basin (IJC Comprehensive Track chemicals) was produced from this inventory. It contains 362 chemicals (IJC 1987b). Of these chemicals, 11 critical pollutants were chosen by the IJC for its Primary Track. Information used in deriving priority lists tends to include chemical stability leading to persistence in the environment, the quantities in use, the types of use, the tendency to accumulate in living organisms, and the biological effects associated with acute or chronic exposure (Hamilton *et al.*, 1987). In this report, all of the Primary Track chemicals are discussed as well as several of the Comprehensive Track chemicals.

In Canada, there are several sets of objectives and guidelines established for concentrations of toxic chemicals in water. Two of these are shown in Table 2. When developing and using guidelines for the protection of aquatic life, there should be complete information on the parameter of concern, including its form and fate in the aquatic environment, quantitative exposure/effect relationships, and its fate within organisms over a wide range of exposure concentrations. The relevant information base for a particular chemical is rarely complete. In general, water quality guidelines used in

Canada are based on unfiltered water samples (CCREM, 1987). The first set of objectives shown are the 1978 Great Lakes Water Quality Agreement specific objectives. These were amended by the 1987 Protocol. Although the Protocol stated that the discharge of toxic substances in toxic amounts should be prohibited and the discharge of any or all persistent toxic substances should be virtually eliminated (IJC 1988), the specific objectives listed in the revised 1978 Agreement were adopted in 1987 as interim objectives for persistent toxic substances. The second set of guidelines has been proposed by the Canadian Council for Resource and Environment Ministers. In 1984, CCREM approved a recommendation from the Task Force on Water Quality Guidelines that Canadian water quality guidelines be harmonized (CCREM, 1987). The guidelines are presented here for comparison with the IJC objectives. The introduction to the Task Force report states that the guidelines should not be regarded as blanket values for national water quality and that variations in environmental conditions across Canada will affect water quality in different ways so that many of the guidelines will need to be modified according to local conditions (CCREM, 1987).

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

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

1.3 HISTORY OF CONTAMINATION

In the early 1960s, pesticides, such as DDT, were detected in the Great Lakes. This was followed by the detection of other organochlorine pesticides and industrial chemicals, such as PCBs (Williams, 1975; D'Itri, 1988). In 1968, mercury (Hg) was detected in high concentrations in sediments from

Lakes Ontario and Huron (Thomas, 1972; 1973). Concurrently, high concentrations of mercury were discovered in Lake St. Clair fish (Fimreite *et al.*, 1971) at levels which resulted in a ban on commercial fishing in the lake in 1970. The source of mercury to Lake St. Clair was upstream chlor-alkali plants on the St. Clair River. In 1971, the Michigan Public Health Department issued a consumption advisory because of PCBs in lake trout and salmon in Lake Michigan. Soon after, in 1974, mirex was discovered in fish in the Bay of Quinte, Lake Ontario. In late 1979, chlorinated dioxins were detected in herring gull eggs from colonies in Saginaw Bay, Michigan. In 1982, toxaphene was first detected in fish from Lake Superior. Subsequent sampling showed that most of these chemicals were present throughout the Great Lakes system. Also, analyses of Great Lakes media for metals, such as lead and cadmium, showed that these were also ubiquitous contaminants. Thus, the scientific and public awareness of the level of toxic chemical pollution of the Great Lakes developed over approximately 25 years. The period of greatest public concern was around 1980 and was related to the discovery of 2, 3, 7, 8-tetrachloro-dibenzo-(p)-dioxin, in herring gull eggs. Another major event occurred in 1985 when there was a perchloroethylene spill into the St. Clair River.

Chemical analyses of radiodated sediment cores showed that contamination of the Great Lakes began only after World War II, concurrently with the expansion in urban and industrial development. PAHs were detected in lake sediments deposited at the turn of the century. Some chlorinated organics such as PCBs and chlorinated benzenes (CBs) were produced before the war. However, peak inputs of these chemicals and chlorinated pesticides took place much later in the 1950s, 1960s and early 1970s. During the 1970s, it became apparent that bottom sediments were contaminated with organochlorine pesticides and PCBs.

1.4 SAMPLING AND ANALYSIS

The chemicals discussed in this report are those traditionally analyzed for in most media. However, recent attempts to calculate mass balances for the Great Lakes have shown that the data bases are quite inadequate, with the possible exception of PCBs (Strachan and Eisenreich, 1988). Since about 1979, concentrations of hydrophobic chemicals have been measured in suspended particulates. Previously, water column concentrations and trends had been assessed by analysis of suspended solids, for example, in the connecting channels such as the Niagara River. However, at the low suspended solids concentrations common in the Great Lakes system, even the most hydrophobic organic chemicals are primarily in the dissolved phase. At that time, reliable quantitative data for toxic contaminants in water were scarce. Nearly all historical results were below the existing detection limits. Concentrations in water are often an order of magnitude or more, less than the minimum detection levels in routine sample volumes of 1 to 2 litres. Only since 1980 has it been possible to determine concentrations of some of these chemicals in water in the open lakes and connecting channels. Large volumes of water (200 litres) are now extracted to detect concentrations in the low ppt and ppq ranges. Measurements of ambient concentrations in water are complex and have become semi-routine only since 1983. Because of these complex, time consuming and costly procedures for sample collection, preparation and analyses, few measurements for toxic organic chemicals have been made in all parts of the Great Lakes. The values for whole water, and especially for the dissolved phase are highly variable in space and time and must still be viewed with caution as they are often near limits of analytical detection. Despite these problems, it is important to measure concentrations in water because such data can provide information on:

(1) The relationship of chemical concentrations in water to those in fish;
(2) The several orders of magnitude higher concentrations of these chemicals in bottom sediments in cause-effect linkages;
(3) The burial of chemicals in lake sediments as a self-cleansing process; and
(4) Model chemical fate or concentrations for mass balances so as to determine major sources of toxic chemicals and prioritize control actions.

Concentrations of chemicals in waters and suspended solids can change rapidly depending on sources, bottom sediment resuspension, internal productivity, currents and many other seasonal and limnological processes. In nearshore areas and in the connecting channels, concentrations of chemicals in water and suspended particulates can vary considerably over short periods of time.

Much of the historical data on dissolved metals in water from the open lakes have recently been questioned. Metals are ubiquitous and found in sampling platforms such as boats, and in dust from laboratories. This suggests that samples could have been contaminated, particularly with lead and cadmium. The bottom sediment and most suspended solids chemical data which follow are reliable. Sectioned, radiodated sediment cores have shown long term trends in chemical inputs to the lakes. These trends can be extended to pre-industrial and even pre-colonial periods. Bearing in mind these problems, two types of chemicals are discussed in this report:

1) Toxic chemicals for which there is a reasonably extensive data base. They include lead, mercury, cadmium, and arsenic, DDT and metabolites, dieldrin, BHCs, HCB, dioxins, and PCBs .

2) Toxic chemicals for which there is a geographically restricted data base. Such chemicals include: chlorobenzenes (e.g., Lake Ontario); toxaphene (e.g., Lake Superior); octachlorostyrene (OCS) (e.g., Lake St. Clair); mirex (e.g., St. Lawrence River); chlorinated volatile organics (e.g., the lower Great Lakes and connecting channels); and PAHs (e.g., western Lake Erie).

2. TOXIC CHEMICALS IN WATER, SUSPENDED SOLIDS, AND BOTTOM SEDIMENTS OF THE GREAT LAKES AND THEIR CONNECTING CHANNELS

There have been several comprehensive studies of toxic chemicals in different regions of the Great Lakes. These include:

Allan *et al.* (1983), Niagara River Toxics Committee Report (NRTC, 1984), Chau *et al.* (1985), Lawrence (1986), Canada - Ontario St. Clair River Pollution Investigation report (1986), and the Upper Great Lakes Connecting Channels Study (UGLCCS, 1989). Information on the concentrations and fate of toxic chemicals in the connecting channels (the St. Clair, Detroit and Niagara Rivers) and the fate of these chemicals downstream in Lakes St. Clair, Erie and Ontario, has added significantly to the rapidly expanded data base.

There have also been several studies which covered all or most of the lakes. Between 1968 and 1975, bottom sediment surveys of some metals and organic chemicals were conducted on each of the lakes and composite geochemical maps were produced. These were extremely valuable for inter-lake comparisons. The interpretation of the distributions must, however, be related specifically to the years of sample collection. This type of survey has not been repeated. During the 1980s, Rossman (1982, 1983, 1984, 1986, 1988) studied metals in the waters of each of the Great Lakes. He attempted to determine temporal trends and made inter-lake comparisons. In 1981, Sonzogni and Simmons presented typical concentration ranges for lakes. Mudroch *et al.* (1988) summarized sediment concentrations of some metals and PCBs in each lake. Strachan and Eisenreich (1988) recently attempted to provide representative values for toxic chemical concentrations in Great Lakes water and sediments. They assessed the best available values in early 1986 when they attempted to calculate mass balances for several toxic chemicals in each lake. Concurrently, Stevens and Neilson (in press) collected large volume (37 to 55.5 L) surface water samples from Lakes Superior, Huron, Erie and Ontario and examined them for toxic organic chemicals (Stevens and Neilson, in press). The results of these studies are in the summary tables for each of the Great Lakes and the Niagara River.

2.1 LAKE SUPERIOR

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

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

2.1.1 Water and Suspended Solids

The historical concentrations of toxic metals and organic chemicals in the waters of Lake Superior are shown in Table 4. As discussed earlier, much of the historical data, especially on metals, has recently been questioned. Rossmann (1986) compared his 1983 data on concentrations of metals in the dissolved, particulate and total water phases to earlier data for Lake Superior. The results for lead, mercury, cadmium and arsenic are discussed below. He concluded that the historical data could only be used to determine trends for total mercury and total arsenic. The decline in concentrations of mean total arsenic was 28 ppt/year based on data from 1973-1983 (Rossmann, 1986). His metal results were all below the IJC Great Lakes Water Quality objectives. Rossmann and Barres (1988) compared the 1983 results for Lake Superior with similar studies on the other Great Lakes done between 1980 and 1985. Generally, the mean concentrations of lead, mercury, cadmium and arsenic in dissolved and total water samples from Lake Superior were significantly (0.05 level of significance) less or not significantly different from concentrations in the other Great Lakes. However, the concentration of dissolved arsenic was significantly higher in Lake Superior than Lake Huron. High levels of lead, mercury and cadmium have been reported in the harbours and bays of Lake Superior in the 1980s (Simpson, 1987; Kirby, 1986; Glass *et al.*, 1988).

There have been several studies of toxic organic chemicals in Lake Superior. The results are shown in Table 4. The most recent results show (Stevens and Neilson, in press) that concentrations of all detectable organic contaminants in 1986 were slightly higher in the north than the south of the lake, especially in the vicinity of Nipigon Bay, Jackfish Bay, Peninsula Harbour and Michipicoten Bay. Concentrations of chlorobenzenes, dieldrin, and PCBs were not significantly different from those in Lake Huron and they were consistently ranked lower than those in Lake Ontario. The mean concentrations of some of the organic contaminants studied by Stevens and Neilson are given in Table 4.

The most frequently detected persistent, toxic, chlorinated organic chemical in most of the lakes and connected channels is total PCBs. There are considerable variations in PCB concentrations in lake waters due to ice cover, ice melt, spring overturn and evaporation (Capel and Eisenreich, 1985). Capel and Eisenreich (1985) reported mean total PCB concentrations at the centre of Lake Superior as 1.30 ppt (1978), 3.8 ppt (1979), and 0.9 ppt (1980). Baker *et al.* (1985) reported mean concentrations of 0.95 ppt (1978), 3.3 ppt (1979), 0.75 ppt (1980), and 0.63 ppt (1983). Their overall conclusion was that lake-wide PCB concentrations in water are probably decreasing. The results in Table 4 for whole water lead to a similar conclusion. Eisenreich (1987) estimated the decrease from 1978 to 1983 to be 54%. The residence time for PCBs in Lake Superior waters was estimated as 2 to 6 years, compared with to the hydraulic residence time of 170 to 180 years. On this basis, it was predicted that concentrations of total PCBs would decline in Lake Superior water to about 0.2 ppt by 1990 (Eisenreich, 1987). The latest measurements in 1986 were 0.3 ppt in whole water (Stevens and Neilson, in press) and 0.55 +/- 0.37 ppt in the dissolved phase (Baker and Eisenreich, 1989). The highest values in 1986 were 0.56 and 0.58 ppt in Duluth - Superior Harbour and South of the Apostle Islands respectively. The higher values reported by Chan (1984) for 1983 (Table 4) may be the result of analytical artifacts.

The concentrations of toxic chemicals in particulates in Lake Superior are given in Table 4. The benthic nepheloid layer has been described by Baker *et al.* (1985) and Baker and Eisenreich (1989). Rossmann (1986) reported that in 1983, particulate arsenic concentrations were significantly higher in the eastern region than in the central region. The 1977 data discussed above cannot be compared with the 1983 data because of sample contaminations and the use of different analytical procedures. Rossmann and Barres (1988) compared the 1983 results of metal particulate concentrations for Lake Superior with similar studies on the other Great Lakes done between 1980 and 1985. Generally, the mean concentrations of lead, mercury, cadmium and arsenic in particulates of Lake Superior were significantly less, or not significantly different from concentrations in the other Great Lakes. The exception was the concentration of particulate cadmium which was significantly higher in Lake Superior than in Lake Michigan.

There are limited data on toxic organic chemicals in suspended solids, other than those for PCBs. Most concentrations were measured in whole water samples (Table 4). Baker *et al.* (1985) reported DDE concentrations in suspended solids from the nepheloid layer of western Lake Superior in 1983 as being from 0.005 to 0.024 ppt. They also found that the concentrations of particulate-associated PCBs in the benthic nepheloid layer were not that different from those in the epilimnion. In 1980, the range of PCB concentrations in suspended solids was 30 to 2,770 ppb (ng/g) (Capel and Eisenreich, 1985). Capel and Eisenreich pointed out that the fraction associated with particulates versus the dissolved phase changed with time and with depth. By 1986, the particulate-associated PCB concentration had dropped dramatically to 33 +/- 16 ppb (ng/g) (Baker and Eisenreich, 1989). Concentrations of some PCBs and PAHs in Lake Superior were greater in suspended solids collected by sediment traps than when collected by centrifugation (Baker and Eisenreich, 1988). This was thought to be related to biological processes. They found that the flux rates of PCBs to the bottom waters of Lake Superior were up to two orders of magnitude higher than the net accumulation rates of PCBs in the bottom sediments, implying high benthic organism recycling rates. Particulate concentrations of total PCBs could thus be higher than those found in surficial sediments. When Lake

Superior was stratified, the fraction of total PCBs associated with particulate phases at all depths was around 13 - 14% (Baker *et al.*, 1985). The highest concentrations of particulate PCBs were in the eastern basin of the lake in 1980 (Capel and Eisenreich, 1985). In 1986, individual particulate PAH concentrations ranged from less than one to a few hundred ppb (Baker and Eisenreich, 1989).

2.1.2 Bottom Sediments

The most extensive sampling of bottom sediments of Lake Superior was conducted in 1973 as part of multi-year program to map chemical distributions in the surficial bottom sediments of all five Great Lakes. Although distribution maps for different chemicals were published in separate papers, the report by Thomas and Mudroch (1979) contained nearly all of the distribution maps for metals and organic chemicals for all five lakes. This survey has not been repeated. The maps represent the distribution of chemicals in the bottom sediments only for the period when the samples were collected. The top 3 cm of sediment were used in the analysis to produce the maps. This depth can represent different numbers of years of sediment accumulation depending on the lake and location in the lake. The present day surficial concentrations and distributions of toxic metals and organic chemicals will be probably quite different from those represented by samples taken in the late 1960s and early 1970s. Two maps are included in this report. The first is for mercury which may be the most serious metal contaminant of the lakes (Figure 2). The second is for total PCBs, because this is the most extensively studied toxic organic chemical in the Great Lakes (Figure 3).

In Lake Superior, the concentrations and distributions of metals were principally related to the geology of the area surrounding the lake. Thomas and Mudroch (1979) proposed that copper was an exception and that concentrations of this metal were related to inputs from mines. Surface sediment concentrations of lead were usually less than 100 ppm and less than 4 ppm for cadmium (Table 5). Information on the arsenic content of Lake Superior bottom sediments showed that the concentrations in the Thunder Bay basin were 2.0 ppm (n = 15) with a range of 0.5 to 8.0 ppm in 1973 (Traversy *et al.*, 1975). In general, information about arsenic concentrations in Great Lakes sediments is scarce (Mudroch *et al.*, 1985).

The distribution of several organochlorines in bottom sediments was determined in 1973 (Frank *et al.*, 1980) (Table 5). The mean values (n = 406) for total PCBs and p,p'-DDE were 3.3 ppb and 0.71 ppb, respectively, for all basins. Eisenreich *et al.* (1980) sampled Lake Superior bottom sediments in 1977 and 1978. Whereas Frank *et al.* (1980) analyzed the top 3 cm, concentrations reported in Eisenreich *et al.* (1980) are for the top 0.5 cm only. Eisenreich and Baker (1989) reported that the mean total PCB concentration in 1986 (8.6 ppb) was significantly lower than that in 1978 (74 ppb). This reflects lower PCB burdens in the water column. The mean HCB concentration of 0.2 ppb in surficial sediments in 1980 was at least an order of magnitude lower than that in Lakes Huron, Erie and Ontario (Oliver and Nicol, 1982). Frank *et al.* (1980) did not detect mirex in any of 80 samples collected in 1973, at a minimum detection limit of 0.3 ppb. PAH concentrations in sediments are about ten times lower than in the other Great Lakes, reflecting both its remote location and that the atmosphere is the primary source (Baker and Eisenreich, 1989).

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

The distribution of PCBs in sediment cores from nine sites in Lake Superior was described by Eisenreich (1988). The top 1 cm of sediment represented approximately 10 years. At all sites, the concentrations of PCBs began to increase at a depth corresponding to the late 1940s. Peak concentrations varied at each of the sites but were either at the surface or at a depth of 1 cm, representing the early 1970s. In general, Lake Superior has the lowest sedimentation rate of all of the Great Lakes (Thomas and Frank, 1983). In seven of the nine cores, the top 0.25 cm had concentrations of total PCB that were 20 to 100% less than the next 0.25 cm section. This could be evidence of a recent decrease in the sedimentation of PCBs. The mean value for the whole lake in the top 0.5 cm was 53 ppb total PCBs. Charles and Hites (1987) determined the average PCB concentration as a function of time in three sediment cores from Lake Superior (Figure 4). The distribution shows a slow increase from around 1943 to 1955; a rapid rise from 1955 to a peak value of 110 ppb in 1972-73; followed by a decline to 75 ppb by 1975. This decline should continue as North American bans and restrictions on PCBs take greater effect. Most of the PCB input to Lake Superior is from the atmosphere (Strachan and Eisenreich, 1987).

The historical distribution of some PAHs in Lake Superior sediment cores show that inputs of these chemicals to the lake began after the turn of the century. The highest B[a]P concentration in a Lake Superior core was around 30 ppb at a depth of 0.25 cm (Gschwend and Hites, 1981). Although B[a]P concentrations in Lake Superior bottom sediments more than tripled between 1900 and 1980, concentrations are still an order of magnitude lower than in the lower Great Lakes because the region around Lake Superior is far less industrialized (Eadie, 1984). In Lake George, which is part of the St. Marys River connecting channel between Lake Superior and Lake Huron, B[a]P concentrations in sediment cores show recent declines (Figure 4).

2.2 LAKE MICHIGAN

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

The contamination of Lake Michigan by organochlorine chemicals began at the same time as for the other Great Lakes, in the 1920s and 1930s, but increased rapidly after World War II. Contamination of the southern end of the lake has been more severe than the northern end. One of its main tributaries is Fox River which empties into Green Bay. The bay is about 8% of the surface area of the lake but it has about one third of the lake's watershed (Harris *et al.*, 1987). There has been concern about water quality in Green Bay since the 1920s.

2.2.1 Water and Suspended Solids

Published data on chemical concentrations in Lake Michigan water are shown in Table 6. Historical data on total lead concentrations in Lake Michigan waters were reviewed by Rossmann (1984). The values for both total and dissolved lead as determined by Rossmann in 1981 are much less than many of the historical levels measured in the 1960s and 1970s because of sample contamination problems. Rossmann's mean values of 260 ppt total lead and 150 ppt of dissolved lead (n = 11) are considered the most accurate. Earlier measurements of total lead had ranged up to 170 ppb with a mean of 18 ppb (n = 30) in 1976 (Wisconsin Electric Power Company and Wisconsin Michigan Power Company, 1977, as cited in Rossmann, 1984). Reported historical mean mercury values were as high as 4.3 ppb (Rossmann, 1984) but these earlier values are now considered to be invalid. All of the cadmium measured by Rossmann in 1981 at 11 sites was in the dissolved phase. Earlier mean cadmium values as high as 2,800 ppt (n = 42) in 1974 are now considered to be erroneous. Owen and Meyers (1984) reported total cadmium concentrations in the mid-lake subsurface in the late 1970s were 70 ppt and nearshore subsurface as 80 ppt. In southern Lake Michigan, the mean concentration of total cadmium was 26.6 ppt with a range of 12.0 to 45.6 ppt (Lum, 1987). These values are similar to Rossmann's (Table 6). Rossmann considered historic arsenic concentrations to be valid for comparison with recent results. Values of just over 1,000 to 2,000 ppt were measured in the mid to late 1970s and compared to Rossmann's whole water mean value in 1981 of 790 ppt. Much higher values for mean total arsenic were reported prior to 1970 (up to 40 ppb in 1969) but these were almost certainly analytical artifacts.

There is little published information available on organochlorines in Lake Michigan water (Table 6). From 1968 to 1970, total DDT values were reported as 3 to 151 ppt (Sonzogni and Simmons, 1981). Open water samples collected in 1968 and analyzed for dieldrin by three independent laboratories contained a mean value for dieldrin of 1.0 ppt. In the late 1970s, dieldrin was undetected at 0.1 ppt using better detection methods (Sonzogni and Simmons, 1981). Analyses of nearshore samples for toxaphene from 1972 to 1976 failed to detect the chemical at the 1.0 ppb level. The data on PCB concentrations in Lake Michigan waters are more extensive than those on other toxic organics because this chemical is one of the main contaminants. Rare measurements from the early 1970s indicated that total PCB concentrations in water may have been from 30 to 40 ppt (Swackhammer and Armstrong, 1987). These were probably a result of analytical problems which were not resolved until the early 1980s . Rodgers and Swain (1983) reported water column PCB concentrations of 3 to 9 ppt for 1976. In 1980, Swackhammer and Armstrong (1987) reported an open lake average of 1.2 ppt total PCB, lower than the nearshore average of 3.2 ppt. They found little variability in PCB concentration with lake depth.

Data on concentrations of toxic chemicals in Lake Michigan particulates are shown in Table 6. Rossmann's results (1984) indicated that in the water column, the percentage of cadmium and arsenic present in the dissolved and total fractions were such that the particulate fraction did not make a significant contribution to total concentrations.

2.2.2 Bottom Sediments

Concentrations of toxic chemicals are significantly higher in the depositional basins. Not all of the metals are anthropogenic, but all of the toxic organic chemicals are. Data on concentrations of toxic chemicals in bottom sediments are shown in Table 7. The most extensive surficial sediment survey of Lake Michigan was done in 1975. The distributions of lead, mercury and arsenic were similar. Based on 1973 samples, concentrations of cadmium ranged from 0.09 to 1.93 ppm (Cline and Chambers, 1977). In northeastern Lake Michigan, the mean value was 0.47 ppm and in Green Bay in northwestern Lake Michigan it was 1.3 ppm (n = 5) (Lum, 1987). Only very small areas of the lake exceeded 300 ppb mercury (Cahill and Shrimp, 1984). The highest concentrations of arsenic were in Green Bay.

In 1963, sampling had indicated that some sediments in Lake Michigan had up to 20 ppb of DDE (Hickey *et al.*, 1966). In 1975, mean total DDT in surficial lake bottom sediments was 11.9 ppb (Table 7). The mean for the depositional basins was 24.4 ppb (n = 92) (Frank *et al.*, 1981a). The corresponding mean concentrations of p,p'-DDT, o,p'-DDT, p,p'-TDE and p,p'-DDE were 2.9 ppb and 5.4 ppb, 0.37 ppb and 0.73 ppb, 3.25 ppb and 7.65 ppb, and 5.43 ppb and 10.58 ppb, respectively. The distribution of total DDT was similar to that of the heavy metals. Persistent, hydrophobic organic chemicals are associated with the fine particulate phases which accumulate in the major depositional basins. Most samples had dieldrin concentrations of less than 1.1 ppb. Prior to 1977, dieldrin levels in sediments from southern Lake Michigan of less than 0.5 to 10.4 ppb were reported (Sonzogni and Simmons, 1981). Lake Michigan has high sediment concentrations of PAHs (Table 7). In 1979 to 1980, the mean concentration of B[a]P in Lake Michigan sediments from the depositional basins and non-depositional areas was 462 and 62 ppb respectively (Eadie *et al.*, 1983). Two major sources of PCBs in the south west part of the lake drainage basin at Milwaukee and at Waukegan are easily discernible from the concentrations in surficial sediments (Figure 3). The mean PCB concentration in the depositional basins of the lake in 1975 was 17.3 ppb (Frank *et al.*, 1981a). Lake Michigan contains some of the areas most heavily contaminated with PCBs. They include Waukegan Harbour (500,000 ppm), North Ditch (250,000 ppm), and Milwaukee Harbour (6.4 ppm) (Simmons, 1984).

The distribution of chemicals in sediment cores from Lake Michigan suggests that inputs have decreased. Lake Michigan has low sedimentation rates which range from 0.1 to 4 mm/year (Cahill and Shrimp, 1984). Concentrations of metals in sediment cores from Lake Michigan show that lead, cadmium and other metal contamination started in the 1890s in the southern part of the lake and in about 1920 further north (Christensen and Goetz, 1987). The major increase in lead (Figure 5) began in about 1930 and rose rapidly to a peak between 1960 and 1970. Lead concentrations in the immediate surface decreased to levels similar to those between 1950 and 1960 (Goldberg *et al.*, 1981). This agrees with Christensen and Goetz (1987) who calculated that the period of maximum lead inputs was 1954-1969 and that present inputs have decreased by 35-45% from these maxima. Maximum cadmium pollution occurred between 1939 and 1954 and current levels are 35 to 45% less than these maxima. Goldberg *et al.* (1981)

determined the period of maximum cadmium input to be in the late 1960s. Measurable amounts of PCBs were detected in a core at 3-4 cm depth (Swackhammer and Armstrong, 1986). This corresponds to a period from 1920 to 1950 and indicates that inputs to the lake began soon after commercial sales of PCBs started in the U.S. in 1929. The largest loadings to the sediments took place between 1960 and the early 1970s. Sediment cores have also shown that the initial inputs of dioxins and furans to Lake Michigan began around 1940 (Czuczwa and Hites, 1986).

2.3 LAKE HURON

The surface area of Lake Huron is 59,600 km². By volume, it is the seventh largest lake in the world and the third largest Great Lake at 3,540 km³. Its drainage basin is 134,100 km². The maximum depth is 229 m and water retention time is 22 years. The major inflows are the Straits of Mackinac and the St. Marys River, followed by the Mississagi, Saginaw, French and Spanish Rivers. It discharges to the St. Clair River. Manitoulin Island and the Bruce Peninsula divide the body of the lake from the North Channel and Georgian Bay, respectively. The lake is used for both commercial and recreational fishing. In 1978, the catchment area was mainly natural landscape. Toxic chemical inputs come from municipal point sources, combined sewer overflows, rural and urban nonpoint sources, leachates from municipal and hazardous waste landfill disposal sites and from the atmosphere. Problems related to industrial sources are most apparent in industrialized harbours and embayments such as Saginaw Bay. Saginaw Bay extends 82 km from the main body of the lake. The city of Saginaw is at the head of the bay and on the Saginaw River. It was historically a lumbering centre and now supports agriculture and diversified manufacturing. The bay is used for commercial fishing and summer recreation. The other large bay on Lake Huron is Georgian Bay, which is 190 km long and 80 km wide. The surrounding area is mainly forested although there is some agriculture in the south. There are several important commercial shipping ports located on Georgian Bay.

2.3.1 Water and Suspended Solids

Data on concentrations of contaminants in Lake Huron water are summarised in Table 8. Rossmann (1983) reviewed toxic metal concentrations in Lake Huron. He compared his 1980 lead data to those from previous studies and concluded that there was a downward trend in dissolved lead concentrations. Data on mercury, cadmium and arsenic prior to 1980 could not be used to establish trends. In 1980, concentrations of dissolved cadmium in Lake Huron were significantly lower than those of Lakes Erie and Michigan and there was no significant difference between the Lake Huron levels and those of Lakes Superior and Ontario (Rossmann and Barres, 1988). Total cadmium levels were significantly less than in Lakes Erie and Ontario. In Saginaw Bay, very limited data from 1985 suggest that lead and cadmium concentrations in the water column were at or below levels measured in 1976-1978 (IJC, 1987a). The 1980 dissolved arsenic levels in Lake Huron were significantly lower than those of Lakes Michigan, Ontario and Superior but not significantly different from levels in Lake Erie (Rossmann and Barres, 1988). The median concentration of total arsenic in Lake Huron was significantly lower than that of Lake Michigan but not significantly different from that of Lake Erie.

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

In 1980, a survey of toxic metal concentrations in suspended solids was conducted in Lake Huron (Rossmann, 1982) (Table 8). Particulate lead levels were somewhat lower in the southern part of the lake and in Georgian Bay than in the rest of the lake. The highest particulate cadmium concentrations were found in Georgian Bay and the North Channel. The particulate cadmium level in Lake Huron was significantly less than in Lake Ontario but not significantly different from Lakes Superior and Michigan (Rossmann and Barres, 1988). Rossmann (1982) concluded that 100% of the total cadmium and 62% of the total mercury were associated with particulate matter. In 1980, particulate arsenic concentrations were highest in southern Lake Huron and in Georgian Bay. Only 3% of the arsenic was in the particulate form.

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

2.3.2 Bottom Sediments

Data on toxic chemical concentrations in bottom sediments are shown in Table 9. In the studies done by both Thomas and Robbins, most lead concentrations in surficial sediments were less than 100 ppm. Mudroch *et al.*'s (1988) review described surface sediment in depositional basins as having up to 151 ppm lead with surface sediments in embayments to be somewhat higher at up to 230 ppm. Fitchko and Hutchinson (1975) found high lead levels near Parry Sound and in the sediments of the Cheboygan River. Increased concentrations of mercury near the Bruce Peninsula may be due to sphalaerite mineralization (Fitchko and Hutchinson, 1975). Mudroch *et al.* (1988) found surface sediment concentrations of mercury in depositional basins to be up to 0.805 ppm and in embayments to be up to 9.5 ppm. Most areas of Lake Huron have cadmium concentrations of less than 4 ppm, although a few discrete areas in Georgian Bay have concentrations greater than 6 ppm (Thomas, 1981). An anthropogenic source in the southern part of the lake was suspected but no trends were observed in Georgian Bay. Mudroch *et al.* (1988) found a range of <0.3-4.6 ppm cadmium in embayments.

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

In 1969, dieldrin was identified in only 5.7% of the surface sediment samples. Concentrations were at or below 1.3 ppb (Frank *et al.*, 1979b). Samples containing dieldrin came from the Goderich and Mackinac Basins and in the non-depositional zone near Saginaw Bay. Dieldrin was identified in 30% of the sediments from Georgian Bay in 1973 and 15% of those from the North Channel (Frank *et al.*, 1979b). Kreis and Rice (1985) reported that mean dieldrin concentrations were high in Georgian Bay, particularly in Lions Trough and the nearshore zone at Owen Sound. Some samples from Saginaw Bay also had high concentrations, whereas the main lake and the North Channel had lower concentrations. Mirex was not detected by Frank *et al.* (1979b) in sediments collected in 1969 nor by Oliver and Bourbonniere (1985) in 1980. In 1969, unlike DDT, the PCB residues (11 ppb) in the non-depositional zones of Lake Huron were similar to the levels observed in the depositional basins (15 ppb) (Frank *et al.*, 1979b). Saginaw Basin contained the highest mean residue (33 ppb) and Alpena Basin the lowest (9 ppb) (Figure 3). The mean concentration in Georgian Bay was 13 ppb while in the North Channel, it was 8 ppb. In Georgian Bay, substantial loadings of PCBs probably came from the northeast shore (Frank *et al.*, 1979b). In the review by Mudroch *et al.* (1985), surface concentrations of PCBs ranged from 10-20 ppb in the open lake. In the embayments, they ranged from less than the minimum detection level to a maximum of 490 ppb. Rice and Evans (1984) reported that there were no data on toxaphene concentrations in bottom sediments from Lake Huron. In 1981, Czuczwa and Hites (1984) found that PCDDs and PCDFs were ubiquitous in 1 cm surface sediment samples and concentrations were higher closer to urban centres than in the open lake. There was a predominance of OCDD and HpCDF. They concluded that the source of the dioxins and furans was probably the municipal and/or industrial combustion of wastes containing chlorinated organic products. Average OCDD in the surface sediments was 880 ppt (Czuczwa and Hites, 1984).

Sedimentation rates in Lake Huron are generally lower than in Lakes Erie and Ontario (Kemp and Thomas, 1976a) but higher than in Lake Superior (Thomas, 1983). There has been a significant enrichment of lead, mercury, cadmium and arsenic at the sediment-water interface, relative to background concentrations. This was related to increasing anthropogenic inputs of these metals to the sediments in recent years or to post-depositional processes (Kemp *et al.*, 1978). Robbins (1980), Thomas (1981), and Kemp and Thomas (1976a) all found lead to be consistently enriched in surficial sediments (Figure 6). Surface sediments were also enriched in cadmium over background levels (Kemp et al., 1978; Kemp and Thomas, 1976a; Robbins, 1980). Kemp and Thomas (1976a) reported that recent average cadmium concentrations (2 ppm) were double that of pre-colonial levels (1 ppm). Robbins (1980) found surficial enrichment of mercury in only a few cores in 1974-75. Most concentrations were less than 0.2 ppm and all were less than 0.30 ppm (Figure 6). In the early 1970s, Kemp *et al.* (1978) found surficial levels of arsenic to be between 19 and 26 ppm. This corresponds to enrichment factors of between 2.7 and 6.2. Robbins (1980) found only occasional surficial enrichment of arsenic in cores sampled in 1974-75.

There was insufficient resolution of total DDT and PCB profiles in cores to provide a good estimate of when inputs to the lake started but Frank *et al.* (1979b) suggested that it occurred in the early 1950s. Cores analyzed by Czuczwa and Hites (1986) indicated that there has been a considerable increase in input of total PCDDs and PCDFs since approximately 1940 (Figure 6).

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

The St. Clair River drains Lake Huron and flows south into Lake St. Clair. It is 64 kilometres long. The river is an important international shipping channel and is used for commercial, industrial, and domestic purposes. Several refineries and petrochemical plants discharge to the St. Clair River and the volume of these discharges is about 0.5% of the total river flow (DOE and MOE, 1985). The industrial inputs of contaminants are much greater than the municipal ones (Marsalek, 1986). There are 32 permitted discharges to the river in the U.S., including 6 municipal sewage treatment plants (IJC, 1987a). There are 12 industrial and 6 municipal dischargers on the Canadian side of the river. These point sources and non-point sources, including contaminated sediments, have led to the degradation of river water and sediments. Many toxic chemicals have been identified in a 100 metre wide area along the Ontario shore near Sarnia's chemical industrial area. High levels of chlorinated organics such as PCBs, and volatile hydrocarbons, and heavy metals such as mercury and lead have been found in sediments. Spills are a significant problem in this area. Between 1972 and 1984, 175 spills were recorded, of which 161 discharged directly into the river or a tributary (IJC, 1987b). In 1986, there were 48 spills, 10 of which were on the U.S. side of the river (UGLCCS, 1989).

The St. Clair River flows into Lake St. Clair. The average depth of Lake St. Clair is about 3.4 metres. Mean inflow from the St. Clair River accounts for 98% of the outflow to the Detroit River. The theoretical flushing time of the lake is 7.3 days. The lake supports the spawning grounds for over 30 species of fish and is one of the most heavily used sport fishing and recreation areas of the Great lakes. Until recently, the lake also supported a commercial fishery.

The Detroit River is 51 kilometres long and connects Lake St. Clair and Lake Erie. It is used extensively for shipping, recreation and public and industrial water supplies. Contamination of the water and sediments by metals and a variety of organic chemicals from municipal, agriculture and industrial waste has led to significant degradation. The majority of the sources, particularly of PCBs, are located along the U.S. shore (UGLCCS, 1989). The Rouge River is a major source of contaminants to the Detroit

River. There are many industrial outfalls, waste disposal sites, municipal, hydro, and combined sewer facilities along the shores of the Detroit River.

2.4.1 Water and Suspended Solids

Concentrations of lead and mercury increased slightly along the St. Clair River (UGLCCS, 1989). Concentrations of metals were consistently below the GLWQA objectives except for lead near Sarnia and Corunna. High levels of alkyl lead and lead were found in the water near Ethyl Corporation, an alkyl lead production plant at Corunna (Chau *et al.*, 1985). Typical lead and mercury levels in the river are between 10 and 100 ppt and between 0.1 and 1.0 ppb, respectively (UGLCCS, 1989). In unfiltered water near industrial outfalls in the St. Clair River, levels of lead were up to 2.7 ppb. Concentrations of mercury in the Detroit River were relatively constant from 1984 to 1986. Some high mercury levels have been reported for tributaries of the Detroit River. Concentrations of cadmium did not change significantly over the course of the St. Clair River (UGLCCS, 1989). The mean concentration of cadmium downstream of the Sarnia industrial area was 10 ppt, with a maximum level of 90 ppt. Over the course of the Detroit River, concentrations of cadmium increased from 23 to 35 ppt in 1987 (UGLCCS, 1989) and a concentration of 2,060 ppt was recorded in the Rouge River.

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

Several studies (Kauss and Hamdy, 1985; Oliver and Kaiser, 1986; Chan *et al.*, 1986; Chan and Kohli, 1987) have identified point sources of HCB and HCBD near Sarnia. There is a plume emanating from this area along the Canadian shore which exits the river via the Chenal Ecarte. Similar distributions were found in water for QCB and OCS (Chan and Kohli, 1987). Mean whole water concentrations above and below the source, in 1985, were 0.03 and 0.8 ppt for HCB and 90.09 and 2.3 ppt for HCBD (Chan and Kohli, 1987). The percent of HCB in the dissolved phase was much greater (90%) at the head of the river than at Port Lambton (41%). The percent of HCBD in the dissolved phase at each end of the river was very similar (95% head, 96% Port Lambton). Maximum levels near industrial outfalls on the St. Clair River (unfiltered) were 2.4 ppm HCB and 1.3 ppm HCBD, both of which are much greater than the CCREM Water Quality Guidelines of 6.5 ppb and 100 ppb, respectively (UGLCCS, 1989). Low concentrations were also identified upstream of this major source on the U.S. side of the river (Oliver and Kaiser, 1986). The typical range of concentrations reported for HCB in the St. Clair River by the UGLCCS (1989) was between 0.1 and 1.0 ppt.

Concentrations of HCB and HCBD in the mid 1980s were less in water at the head of the Detroit River than at the St. Clair River mouth. This suggests that some of these contaminants are retained, degraded or volatilized in Lake St. Clair and also that some are carried through to the Detroit River (UGLCCS, 1989). Chlorobenzene concentrations in 1986 were higher in the western basin area of Lake Erie than in southern Lake Huron (Stevens and Neilson, in press). HCB enters the Detroit River from point sources in Michigan including the Rouge River (UGLCCS, 1989). In 1983, total chlorobenzene concentrations were highest in the Rouge River and at the mouths of the Trenton Channel and the Detroit River (Kaiser *et al.*, 1985). The concentrations were 25.9, 2 and 2 ppt, respectively. HCBD was not found in the aqueous phase in the Detroit River. PCBs are ubiquitous in St. Clair River water (Kauss and Hamdy, 1985; Oliver and Kaiser, 1986; Chan *et al.*, 1986).

Typical concentrations are between 1 and 10 ppt (UGLCCS, 1989). Levels higher than those generally found in the St. Clair River have been observed on the west side at the head of the river (Chan and Kohli, 1987). In Lake St. Clair, the mean PCB concentration was reported as 1.2 ppt (UGLCCS, 1989). There was no significant difference in concentration between the outlet of the St. Clair River and the inlet for the Detroit River. In 1983, the highest levels of PCBs in the Detroit River were 2.1 ppt in the Rouge River and 3.4 and 2.1 ppt at the mouth of the Trenton Channel (Kaiser *et al.*, 1985). Several industrial volatile halocarbons are present in the Detroit River. High concentrations of these compounds coincide with zones of industrial and municipal pollution (Comba and Kaiser, 1985). For example, the highest total levels of industrial volatile halocarbons were detected at Connors Creek, 5,121 ppt, just north of Amherstburg, 3,844 ppt, and at the Detroit Sewage Treatment Plant, 3,820 ppt. The concentration range of PAHs in the St. Clair River is 1-10 ppt (UGLCCS, 1989). The Sarnia township ditch is a major source of PAHs to the river. In the Detroit River in 1983, three major sources were identified (Kaiser *et al.*, 1985) downstream of major steel manufacturing plants. The two highest concentrations of 6,100 and 5,200 ppt were detected downstream from the Rouge River. The third highest concentration was 3,900 ppt at the mouth of the Detroit River.

The St. Clair River has a high suspended sediment load. This is because of the amount of shore erosion in Lake Huron (Charlton and Oliver, 1986). Because Lake St. Clair is shallow, bottom sediments are constantly resuspended by wind and swept down the Detroit River (Charlton and Oliver, 1986).

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

A higher proportion of PAHs was associated with suspended solids in the Detroit River than PCBs, probably because some PAHs enter the river as particles (Kaiser *et al.*, 1985). The highest concentrations of particulate PAHs in 1983 were downstream from Belle Isle (1.3 ppt), adjacent to Fighting Isle (1 ppt) and at the mouth of the Detroit River (1.3 ppt) (Kaiser *et al.*, 1985).

2.4.2 Bottom Sediments

Sediment accumulation is low in the St. Clair and Detroit Rivers. Less than 1% of contaminant movement is by bottom sediment movement (UGLCCS, 1989). High concentrations of certain toxic chemicals were found consistently in the sediments adjacent to the Sarnia industrial complex on the Canadian side of the St. Clair River. There was a major chemical release in 1985 which consisted mainly of perchloroethylene and carbon tetrachloride. Because these chemicals are volatile, they are only found in sediments near major source (Oliver and Pugsley, 1986). After the spill, high concentrations were observed in the bottom sediments mainly on the Canadian side of the river. During the investigation of this spill, a large area of non-aqueous puddles overlying the sediments was found downstream of Dow (Carey and Hart, 1986).

In Lake St. Clair, the centre of the lake is the area of greatest recent accumulation of chemicals. The sediments are only a temporary reservoir before they are resuspended and moved down the Detroit River. Because of the non depositional nature of Lake St. Clair, the sediments are responsive to changes in loadings. Usage of PCBs, mercury and DDT was curtailed in the early 1970s. Following this, there was a significant decrease in mean concentrations of these compounds between 1970 and 1974 (Thomas *et al.*, 1975). Mean concentrations of mercury in bottom sediments decreased from

1.5 to 0.6 ppm, mean DDT from 3.6 to 1.5 ppb and mean PCBs from 19 to 10 ppb. By 1985, the decrease in concentrations of mercury was more pronounced (Figure 7).

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

Lead levels in sediments of the St. Clair River and Lake St. Clair are generally low. Exceptions occur adjacent to:

(1) The Ethyl Corporation on the St. Clair River where levels up to 339 ppm lead have been reported in sediment samples;
(2) In sediments of the Black River;
(3) Across the river from the Lambton Generating Station; and
(4) In the eastern distributary of the St. Clair Delta (UGLCCS, 1989, Mudroch *et al.*, 1985).

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

Mercury has been one of the main contaminants in this connecting channel. Levels of mercury in the bottom sediments of the St. Clair River peaked in the late 1960s and early 1970s with maximum levels of 1,470 ppm.

The main source, was the Dow chlor-alkali plant, which ceased production in 1973. However, some mercury is still entering the river from the area. In the early 1970s, high levels were also found at the mouth of the Black River (Fitchko and Hutchinson, 1975). By 1977, the concentration at the Dow site had dropped to 58 ppm (IJC, 1987a). However, concentrations up to 51 ppm were found in the mid-1980s indicating that there are still inputs (UGLCCS, 1989). Sediments at the lower end of the river still have concentrations of mercury in excess of dredge spoil guidelines (UGLCCS, 1989). Decreases in mercury concentrations in the Detroit River from 1970 to 1980 reflect reduced upstream loadings of mercury. The largest changes in concentrations occurred in the upper section of the river, above Zug Island. The mean concentrations in bottom sediments were 3.73 ppm in 1970 and 0.4 ppm in 1980 (Hamdy and Post, 1985). In the mid 1980s, the highest mercury levels in bottom sediments were in the Trenton Channel (> 3.0 ppm) and adjacent to Belle Isle (> 2.5 ppm) (UGLCCS, 1989).

Cadmium concentrations in the sediments of the St. Clair River are generally low and suggest that there are no point sources (UGLCCS, 1989). Concentrations of cadmium are greater in Lake St. Clair sediments than in Lake Huron sediments (UGLCCS, 1989). In 1980, concentrations of >6 ppm cadmium were recorded at several locations along the Michigan side of the Detroit River (Hamdy and Post, 1985). In 1982, levels of cadmium >10 ppm were detected at the mouths of the Detroit and Rouge Rivers (Lum and Gammon, 1985). Also in 1982, Fallon and Horvath (1985) reported that the highest concentrations of cadmium were in the southern part of the Trenton Channel. In the mid 1980s, peak concentrations of cadmium were found adjacent to Belle Isle and the Rouge River and in the Trenton Channel (UGLCCS, 1989). Maximum levels ranged from 25 to 96 ppm and the data suggested that there were still sources of cadmium to the Detroit River (UGLCCS, 1989).

In 1970 and 1974, the mean concentrations of arsenic in the bottom sediments of Lake St. Clair were 2.5 and 3.4 ppm respectively (Thomas *et al.*, 1975). In the Detroit River, the mean concentration of arsenic in the mid 1980s was 10 ppm and the peak level was 54 ppm in the Rouge River (UGLCCS, 1989).

In Lake St. Clair, concentrations of DDT decreased from 6.6 ppb to 2.4

ppb between 1970 and 1974. The highest concentrations were found at the outlet of the lake at both times. In 1982, Oliver and Bourbonniere (1985) found that mean levels of DDT and its metabolites were lower in Lake St. Clair than in southern Lake Huron or Lake Erie.

In 1970 and 1974, 24% of sediment samples from Lake St. Clair had detectable levels of dieldrin (Frank *et al.*, 1977). In the Detroit River, in 1980, dieldrin was detected in only 22% of the samples (Hamdy and Post, 1985) and the maximum level was 35 ppb. In 1985, the highest levels of up to 55 ppb were found adjacent to the Canard River mouth (UGLCCS, 1989).

Alpha-BHC and lindane tend to remain in the aqueous phase so sediment concentrations are low. Oliver and Bourbonniere (1985) detected low concentrations in 1982 in southern Lake Huron, Lake St. Clair and Lake Erie. In an earlier study by Frank *et al.* (1977), lindane was not detected in any samples from Lake St. Clair. In 1980, in the Detroit River, alpha-BHC and lindane were detected in 52% and 27% of the sediment samples respectively (Hamdy and Post, 1985). In a 1984 study, concentrations of HCB and HCBD in St. Clair River sediments were reported to be highest in areas adjacent to the Sarnia industrial zone (Figure 8)(DOE and MOE, 1986). For example, the highest concentrations of HCB in bottom sediments near Dow were 24 ppm with an average concentration of 5.2 ppm. Mean concentration of HCB for the reach 35 km downstream was 370 ppb. The maximum HCBD concentration was 46 ppm with a mean concentration of 750 ppb and a downstream level of 190 ppb. Similar results were found in 1985. Concentrations of HCBD in near shore sediments rose from less than the minimum detection level to more than 1 ppm downstream of the town ditch (Oliver and Kaiser, 1986).

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

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

A review of PCBs in St. Clair River sediments concluded that a temporal trend could not be assessed because of the variations in the studies (Pugsley *et al.*, 1985). However, there was an increase in concentration at the Polysar-Dow area of the St-Clair River (on the Canadian shore), (DOE and MOE, 1986) (Figure 8). The maximum levels were considerably higher than the dredge spoil guideline of 0.05 ppm. Other areas where there is PCB contamination include the vicinity of Ontario Hydro's Lambton generating station on both sides of the river and in the Belle River (UGLCCS, 1989). The range of concentrations along the American shore was relatively low. Oliver and Bourbonniere (1985) did not detect an increase in the concentration of PCBs in sediments between southern Lake Huron and Lake St. Clair. In 1982, mean concentrations of PCBs in Lake St. Clair sediments were much lower than those reported for western Lake Erie (Oliver and Bourbonniere, 1985).

The Detroit River is a major source of PCBs to Lake Erie (Oliver and Bourbonniere, 1985). PCBs enter the river from Lake St. Clair and there are several point sources along the river. In 1980, PCBs were found in 78% of the bottom sediment samples (Hamdy and Post, 1985). The highest concentrations (> 500 ppb) were found along the Michigan shore, south of Detroit. In 1982, the highest levels were found at the head of the river (Fallon and Horvath, 1985). This was thought to reflect the effect of Lake St. Clair and a nearby wastewater treatment plant. In 1983, Pugsley *et al.* (1985) reported higher concentrations of PCBs in 10 cm bottom sediments from Lake St. Clair than in the Detroit River. Kaiser *et al.* (1985) found the highest concentrations in 1983, 200 to 230 ppb, to be at the mouth of the Rouge River, southeast of Belle Isle, and at the mouths of the Trenton Channel and Detroit River. There are also high levels and possible sources of PCBs downstream of Belle Isle (IJC, 1987a) and adjacent to the Ecorse River (UGLCCS, 1989).

In 1985, PAHs were detected in bottom sediments of the St. Clair River adjacent to Dow at levels up to 60.79 ppm and averaging 3.31 ppm (Nagy *et al.*, 1986). Levels up to 140 ppm were reported in the UGLCCS (1989). High levels of PAHs have been identified across the river from Lambton Generating Station and in some tributaries on the U.S. side of Lake St. Clair (UGLCCS, 1989). High levels of PAHs were found in the 1980s in the Detroit River, especially downstream of Belle Isle, in the vicinity of Grosse and Fighting Islands, and in the lower Rouge River (Fallon and Horvath, 1985; Kaiser *et al.*, 1985; UGLCCS, 1989). The highest concentrations reported by Kaiser *et al.* (1985) were between 20 and 33 ppb. Coal-fired power plants and steel mills are the likely sources.

Subsurface maximum concentrations in most core samples from the connecting channels have been included in this report. Exceptions are mercury in a 1986 core from 1986 Chenal Ecarte (Mudroch and Hill, 1987) and HCB and HCBD in the mid-1980s adjacent to Dow (DOE and MOE, 1986). Even though concentrations are decreasing in many cases, surface levels are far higher than background levels. Cores with decreased surface concentrations are as follows, by chemical, date of sampling, and geographic location: mercury, 1986, adjacent to Sarnia (Mudroch and Hill, 1987); mercury, 1985, central Lake St. Clair (Mudroch and Hill, 1987); DDT, 1985, Lake St. Clair (UGLCCS, 1989); HCB and HCBD, mid 1980s, vicinity of Dow (DOE and MOE, 1986); PCBs, 1985, Lake St. Clair (UGLCCS, 1989); and PAH, 1985, St. Clair River (Nagy *et al.*, 1986).

2.5 LAKE ERIE

Lake Erie is the fourth largest of the Great Lakes by area. It is the smallest by volume and also the shallowest. It is divided into three basins. The western basin, into which the Detroit River flows, is very shallow but has the most important fish spawning and nursery grounds. It is downstream from the Canadian chemical companies on the St. Clair River, downstream from Detroit, and has Toledo on its shores. Thus, this part of Lake Erie is the most likely to be affected by chemical contamination. Limnologically, Lake Erie is different from the other four, deeper and essentially oligotrophic Great Lakes. Lake Erie is mesotrophic and approached a eutrophic status in the 1960s. It has a high nutrient load, relative to its volume. Combined with its shallow depth and high biological productivity, it processes contaminants differently from the other four lakes. The greater productivity in Lake Erie may has several possible consequences: the biomass may dilute the chemicals; the organic-rich suspended particulates may compete for toxic metals and hydrophobic organic chemicals; the sedimentation and burial rates are higher; and photochemical and biological degradation of chemicals is perhaps greater. The rapid flushing of the lake (see Table 1) also accounts for the lower concentration of contaminants in the water column. The net result is that although loads of chemicals such as PCBs to the lake are similar to Lake Ontario (Strachan and Eisenreich, 1988), the bioaccumulation of these chemicals has been less.

Lake Erie has been heavily contaminated by metals. It is probably the second most heavily contaminated with metals of the Great Lakes (after Lake Michigan) based on overall concentrations (Rossmann, 1984). The relative occurrence of dissolved metal concentrations was highest in Lake Erie (Rossmann and Barres, 1988). Lake Erie also had the highest total concentrations of the greatest number of metals.

2.5.1 Water and Suspended Solids

Data on toxic chemical concentrations in water in Lake Erie are shown in Table 10. Rossmann (1984) reviewed the available data on total and dissolved lead in Lake Erie water. For water collected at unrecorded depths, the 1974 and 1980 medians were at the minimum detection level (5 to 10 ppb) (n = 6). There were no trends in total lead in epilimnion water, taken at depths of less than 5 m. Mean concentrations in 1967, 1973, 1975, 1978 and 1979 ranged from 0 to 9 ppb. These early data and those in Table 10 cannot be taken as evidence of a decrease in lead concentrations but probably reflect sample contamination problems in the earlier studies. Sonzogni and Simmons (1981) arrived at the same conclusion when comparing data from 1967 with those from 1970 to 1977. In 1978, mean concentrations of dissolved lead were as high as 23 ppb and a maximum of 840 ppb (n = 717) had been recorded. Again, these historical data are unlikely to be accurate (Rossmann, 1984). Nevertheless, there may be a trend in concentrations of total mercury. Data from the 1970s suggest that mean concentrations of total mercury were as high as 370 ppt (median 37 ppt and maximum 130 ppb (n = 618) in 1978). There was a mean concentration of 170 ppt (n = 170) in 1970-71; 370 ppt (n = 618) in 1978; 81 ppt (n = 596); in 1979; and 42 ppt (n = 11) in 1981. Rossmann (1984) calculated that total mercury concentrations in epilimnetic water were decreasing at a mean rate of 12 ppt/year. The reason for these changes is more likely to be the improvement in analytical accuracy. Mean values of dissolved cadmium in 1963 and 1964 were reported as 10 ppb (n = 49) (the minimum detection level). In the 1970s, mean concentrations of dissolved cadmium were reported as 1.1 ppb (1970; n = 9); 0.7 ppb (1971; n = 112); 2.5 ppb (1978; n = 708); 0.7 ppb (1979; n = 567). The latter value for 1979 is still an order of magnitude higher than the mean dissolved concentration of 71 ppt measured in 1981 (Table 10). In 1978, Lum and Leslie (1983) reported that 87% of the total cadmium in Lake Erie water was in the dissolved phase. In 1981, Rossmann (1984) found the concentration of dissolved cadmium was lowest in the waters of the central basin, but insufficient samples were collected to justify this statistically. Lum (1987) compared Rossmann's (1984) data for 1981 (71 +/-27 ppt) with his data for 1978 (40 +/- 20 ppt) and for 1984 (29 +/- 15 ppt). Cadmium concentration may be decreasing because these data are considered to be reliable, although there may still be methodological problems. Rossmann quotes a value of 1.0 ppb (n = 2) for total arsenic in water from unrecorded depths for 1975. In 1980, a mean value of 10 ppb arsenic (n = 6) was recorded but this was the minimum detection level. Mean concentrations in 1981 were about half of what could have been predicted from measurements made in the late 1970s. Rossmann calculated the rate of decrease of arsenic concentrations was 310 ppt/year between 1978 to 1981.

There are limited data available on the concentrations of toxic organic chemicals in the waters of Lake Erie (Table 10). Nearly all early values were below the minimum detection levels of the analytical techniques used prior to the early 1980s. For DDT, Konasewich *et al.* (1978) reported open lake water values close to or less than the minimum detection level of 1 ppt. In 1981, McCrea *et al.* (1985) used large water volume extraction procedures and reported that p,p'-DDT was detectable at all of his sample stations and was present almost exclusively in the aqueous phase. Between 1981 and 1983, DDE was detected at concentrations of 0.1 ppt (Oliver and Nicol, 1984). In 1981, Filkins *et al.* (1983) reported p,p'-DDT and p,p'-DDE concentrations ranging from 0.007 to 0.022 ppt and from 0.006 to 0.018 ppt respectively (n = 5). In 1986, Lake Erie surface water DDE concentrations ranged from less than the minimum detection level to 0.08 ppt (IJC, 1987). McCrea *et al.* (1985) reported that 94% of the dieldrin in Lake Erie surface water was in the aqueous phase in 1981. Concentrations were reported as between 0.069 and 0.0934 ppt. McCrea *et al.* (1985) reported that 100% of lindane was present in the aqueous phase. Oliver and Nicol (1984) reported total concentrations of 4.2 ppt alpha-BHC and 0.38 ppt gamma-BHC in water from Fort Erie in 1981-1983. No mirex was found in water from the eastern area of Lake Erie by McCrea *et al.* (1985). Eadie (1984) stated that 90% of the PAHs in the waters of Lake Erie were in the dissolved phase and that a substantial portion of the low-solubility PAH was associated with suspended solids only in nearshore areas. Near Buffalo, in 1976, B[a]P and total PAH were found at concentrations of 0.3 ppt and 4.7 ppt, respectively (Basu and Saxena, 1978).

There are many sources of PCBs to Lake Erie, including industrial and municipal outfalls, land and urban runoff, landfills, resuspension and translocation of contaminated lake bottom sediments and the atmosphere. From 1972 to 1978, five independent groups reported that concentrations of total PCBs in Lake Erie waters were below the minimum detection level of 100 ppt, while one lake-wide survey in 1972 reported a mean value of 27 ppt (Glooschenko *et al.* 1976). Also, a nearshore mean value of 20 ppt was reported for 1974-75 (Konasewich *et al.*, 1978). Both of these values were at the minimum detection levels (Sonzogni and Simmons, 1981). In 1981, McCrea *et al.* (1985) reported that 100% of the PCBs in Lake Erie water were in the aqueous phase. Between 1981 and 1983 Oliver and Nicol (1984) detected various PCB isomers at 0.49, 0.46 and 0.25 ppt in water from Fort Erie. Clearly, by the early 1980s, the minimum detection level of 100 ppt that had been used in the mid 1970s could not be used for detecting trends of PCB in water. Filkins *et al.* (1983) detected PCBs at 0.13 to 0.78 ppt (n = 5). The spatial distribution of PCBs in Lake Erie showed that the highest concentrations of >2.5 ppt were at the extreme western end of the lake (Stevens and Neilson, in press). Most of the western basin had concentrations higher than those found in Lake Ontario. The IJC (1987b) reported surface water PCB values of 0.29 - 2.96 ppt. If the data for 1972 to 1975 are reliable, then the decrease from approximately 23 ppt in the early 1970 to approximately 1.4 ppt in 1986 could be evidence of a dramatic decrease in PCB concentrations.

Starting in the late 1970s concentrations of the numerous volatile industrial organic chemicals which are present in the dissolved state were determined in water from the lower Great Lakes. Concentrations were highest in the western-central basin of Lake Erie. For example, levels over 30 ppt of carbon tetrachloride were detected in 1978 (Kaiser and Valdmanis, 1980). Continual inputs of volatile chemicals must occur to maintain concentrations. In 1977 and 1978, mean concentrations of dichlorodifluoromethane were 76 and 73 ppt; 34 and 46 ppt trichlorofluoromethane; 15 ppt chloroform; 19 and 37 ppt carbon tetrachloride; and 20 and 11 ppt trichloroethlyene, respectively, in Lake Erie (Kaiser and Valdmanis, 1980).

The available data on contaminants in suspended solids are summarised in Table 11. Suspended material in Lake Erie originates from shoreline erosion, river inputs, aeolian material, autochthonous organic matter production and bottom sediment resuspension. Lake Erie has TSM concentrations of 2-6 mg/L, compared to Lake Ontario (1-4 mg/L), Lakes Huron and Michigan (0.5-2 mg/L), and Lake Superior (0.2-1 mg/L) (Eadie and Robbins, 1987). As discussed in the introduction, this may reduce bioaccumulation in Lake Erie. This is supported by Rossmann and Barres (1988), who reported that Lakes Erie and Ontario had the highest concentrations of toxic metals in the particulate fraction. Lake-wide concentrations of particulate cadmium were 2.4 ppm (n = 54) in 1978 and 1984 compared to 1.7 ppm (n = 14) measured at the Niagara River inflow at Lake Erie, indicating a retention of some particulate cadmium in the lake, most likely in the deep eastern basin (Lum, 1987).

Data on organic chemical in suspended solids are scarcer than on toxic metals (Table 10). Most of the concentration data on organic chemicals are from Strachan and Eisenreich (1988) who carefully reviewed all published values to select reliable values for use in predictive models. The most recent reliable data are those of Stevens and Neilson (in press).

2.5.2 Bottom Sediments

Data on chemical concentration for Lake Erie bottom sediment are summarised in Table 11. Two studies on concentrations of toxic chemicals in bottom sediment have been conducted in Lake Erie, one in 1971 (Frank *et al.*, 1977; Thomas and Mudroch, 1979) and one in 1979 (Rathke, 1984). The 1971 samples were the surface 3 cm, while the 1979 samples used the surface 10 cm. Therefore, direct comparison between the studies is not possible. However, because the more contaminated 1971 sediments were being buried by less contaminated sediments in the late 1970s, the collection of a 3 cm sample in 1979 might have revealed an even greater decrease in concentrations than that seen in the 10 cm samples. Data on metals in the surface 3 cm of surficial sediments show that lead, cadmium and mercury concentrations in the lower Great Lakes are higher over larger areas of the lake bottom than in the three upper Great Lakes. In 1971, large areas of the lake bottom had concentrations of lead greater than 150 ppm (Thomas, 1981), whereas in 1979 only small areas had concentrations greater than 100 ppm (Rathke, 1984). In the central basin, where concentrations in 1971 had been greater than 100 ppm, levels have decreased to less than 75 ppm, presumably because of downstream transport burial, dilution or dispersion downstream of the historically contaminated sediments. The 1971 survey showed two lead plumes, one from Detroit to the western basin and one from Cleveland to the central basin (Thomas, 1981). In 1970, Konasewich *et al.* (1978) reported levels of 340 and 420 ppm for Cleveland and Buffalo Harbours respectively. The same effect can be seen in cadmium (Figure 9). Background (pre-colonial) bottom sediment concentrations of cadmium in Lake Erie are 0.1 to 1.7 ppm. Surface sediment concentrations of cadmium in nearshore areas were between 0.1 and 8.3 ppm and between 0.2 and 0.3

ppm in harbours (Fitchko and Hutchinson 1975; Mudroch *et al.*, 1985). The average concentration of cadmium in lake bottom sediment for western Lake Erie was reported as 6.6 ppm (Nriagu *et al.*, 1979). The pattern for mercury in Lake Erie sediments is also similar. In 1971, a small area of the western basin of Lake Erie had concentrations of mercury in bottom sediments of greater than 2 ppm mercury and a large area was over 1 ppm (Thomas and Jacquet, 1976). By 1979, the anomaly was farther out into the west basin away from the inflow of the Detroit River and the area with a concentration greater than 1 ppm mercury had decreased considerably, indicating a rapid recovery from earlier contamination (Rathke, 1984). There was little change in the mercury concentration in suspended solids entering Lake Erie from the Detroit River during 1974 (Thomas and Jacquet, 1976), when the mean value was 1.06 ppm. In 1971, mean surficial sediment mercury concentrations in the west basin were 1.14 +/- 1.28 ppm compared to 0.60 +/- 0.42 ppm in 1979. The comparable values for lead, cadmium and arsenic were 86 +/- 48 and 56 +/- 36 ppm; 5.6 +/- 3.5 and 3.0 +/- 2.4 ppm; and 7.9 +/- 2.5 and 6.5 +/- 3.0 ppm respectively.

Data on the concentrations of organic chemicals in surficial sediment from Lake Erie are shown in Table 11. In 1971, the distribution of organic chemicals in surficial sediments showed that the highest concentrations of hydrophobic chemicals, such as DDE and dieldrin, were found in a plume originating from the Detroit River. TDE was the predominant compound of the DDT group in the top 3 cm of bottom sediment samples from 1971. The mean TDE lake value was 18.4 ppb with a range of 0.3 to 186 ppb. Both TDE and DDE concentrations were 2 to 3 times higher in the depositional basins than in the other parts of the lake. The highest concentration of TDE was 46.5 ppb in the western basin. The concentration of DDE was 22.1 ppb, giving a total TDE and DDE value of 68.6 ppb. In 1980, DDE was 8 ppb, DDE was 2 ppb and DDT was 1 ppb (a total of 11 ppb) in the upper 3 cm of sediment from a site in the western basin. (Anderson, 1980). Oliver and Bourbonniere (1985) reported that p,p'-DDD were evenly distributed across Lake Erie. The sum of dichloro- through to hexachlorobenzenes in Lake Erie sediment was 26 ppb, less than in Lake Huron (38 ppb) and Lake Ontario sediment (560 ppb) (Oliver and Nicol, 1982). In 1982, 3 cm samples from the western, central and eastern basins of Lake Erie had concentrations of HCB of 9.1 ppb (range 4.6 - 17 ppb); 2.4 ppb (range 1.2 - 3.7 ppb); and 2.7 ppb (range 1.4 ppb - 5.2 ppb), respectively (Oliver and Bourbonniere, 1985). In the same samples, they detected HCBD at concentrations of 1.6 ppb (0.7 - 3.2 ppb); 0.2 ppb (0.1 - 0.4 ppb); and 0.2 ppb (0.1 - 0.6 ppb) respectively, or an overall depositional basin mean of some 0.7 ppb. In 1982, concentrations of total PAHs in the adjacent Raisin River in western Lake Erie ranged from 530 to 770 ppb (Eadie *et al.*, 1982). Extreme concentrations of between 4.8 to 390 ppm PAH were found in sediments from the Black River, near steel industries. The distribution of PAHs in the three basins of Lake Erie (Nagy *et al.*, 1989) showed that the highest concentrations of B[a]P were 200 ppb in the central basin. Concentrations of PCDDS and PCDFs in Lakes Erie, Ontario, Huron and Michigan were determined by Czuczwa and Hites (1986). The main isomer present was OCDD, followed by H7CDF. Concentrations of OCDD in Lake Erie were 1,700 and 2,000 ppt compared to 4,800 ppt for Lake Ontario, 780 and 960 ppt for Lake Michigan, and 880 ppt for Lake Huron. OCDF concentrations were much lower in Lake Erie than in Lake Ontario. Data on PCBs in surficial lake bottom sediments are the most extensive (Table 11). The highest levels were in the western basin and were associated with inputs from the Detroit River.

Concentrations of mercury and lead increased rapidly after 1935 in cores collected in 1971. Concentrations of mercury increased most rapidly after 1955. Based on these analyses, the sediment concentration of mercury in 1971 was 12.4 times that in pre-colonial sediments (Kemp and Thomas, 1976a). In surface sediments, concentrations of lead were 4.4 times and concentrations of cadmium were 3.6 times precolonial levels. More recent data show that this trend has been reversed. Data on lead in a dated core from the eastern basin of Lake Erie show that concentrations began to increase slowly from about 3 ppm at the turn of the century to the 1940s, rose rapidly to approximately 30 ppm in 1950, peaked at 58 ppm in the early 1970s, and have since decreased to 30 ppm. This is similar to concentrations in about 1955 (Eddie and Robbins, 1987) (Figure 10). Cores collected in 1985 have shown that concentrations of arsenic have decreased from 13 to 9 ppm in bottom sediments (Legault, 1986). Peak arsenic concentrations occurred in approximately 1955 and since then have decreased to concentrations similar to those which were recorded in 1945. Thus, sediment cores from Lake Erie indicate that there has been a recovery from earlier contamination. In 1971, p,p'-DDE was found at a depth of 10-12 cm (corresponding to about 1958-60) (Figure 10) (Frank *et al.*, 1977). In the same core TDE was first detected at a depth of 6-8 cm, representing 1961-1963. Concentrations of DDE and TDE then increased rapidly to surface concentrations of 19 and 53 ppb, respectively. Ten years later, Anderson (1980) reported that the upper 3 cm of sediments in a core from the eastern basin had DDT, DDE and DDD concentrations of 1 ppb, 2 ppb and 8 ppb, respectively. The highest concentrations of total DDT was 23 ppb at a depth of 15 cm. Beneath this depth, concentrations fell to 15 ppb total DDT at 35 cm depth. The high sedimentation rates in Lake Erie allow for good resolution of trends of inputs of dioxin and furans. In two cores, the maximum input of PCDDs and PCDFs was in the mid 1970S (Czuczwa and Hites, 1986). Following the mid 1970s, inputs decreased (Figure 10). Extrapolation to deeper layers and times of sediment deposition indicated that initial inputs of PCDDs and PCDFs to Lake Erie probably occurred in the mid to late 1930s.

In 1971, PCBs were in sediment deposited during 1954-1956 in a core from the Toledo area. The upper layers had progressively rapidly increasing PCB concentrations of up to 340 ppb for the layers being deposited in 1971 (Frank *et al.*, 1977). In 1982, the surface 3 cm of sediment for the western, central and eastern basins of Lake Erie had PCB concentrations of 300 ppb (range of 140-660 ppb), 131 ppb (range 38-190 ppb), and 91 ppb (range 37-140 ppb) (Oliver and Bourbonniere, 1982). These values can be compared with the mean concentrations of 252 ppb in 1971 in the surficial sediment (3 cm) from the western basin (Frank *et al.*, 1977). The reasons for this may be that the surficial sediments of the western basin are thoroughly mixed (Eadie and Robbins 1987) or the inputs of PCBs have not decreased significantly.

2.6 NIAGARA RIVER

The Niagara River connects Lake Erie to Lake Ontario. It is a short connecting channel of approximately 60 km with a very high discharge rate. The river is divided into upper and lower reaches by Niagara Falls. The main sources of contamination to the river are point source discharges from steel and petrochemical industries and municipal wastewater treatment plants (Figure 11). These treatment plants receive effluents discharged from industries. The large petrochemical industries on the U.S. side of the river have produced a variety of chlorinated industrial organic chemicals and pesticides. Most of the wastes from these industries have been buried in waste landfills such as Hyde Park and Love Canal. These sites now produce leachate which enters the Niagara River.

Data on the contamination of Niagara River and downstream Lake Ontario were published in a special volume of the Journal of Great Lakes Research (Allan *et al.*, 1983). Numerous papers and reports have since been published on this subject. The Niagara River was the subject of the bi-national Niagara River Toxics Committee Study (NRTC, 1984) which described the contamination of the river in great detail. The NRTC (1984) identified 261 synthetic chemicals in the ecosystem and reported that 1400 kg per day of pollutants were discharged to the river from municipal and industrial point sources and that 89% of the total came from U.S. sources. It also reported that 61 U.S. hazardous waste disposal sites and 5 Canadian landfills had the potential to contaminate the river (and downstream and that 28 of these contribute contaminants to the river and that groundwater contamination covers a large area along the U.S. side of the river. Since the release of this report, Canada and the U.S. have agreed to a plan which has a goal of 50% reduction of selected persistent toxic chemicals from both point and non-point sources by 1996.

In general, the longer term monitoring data on suspended solids and the more recent data on water quality are the best long term (1979 for metals) (1980 for organics) water quality data on toxic chemicals in the Great Lakes. The data indicate that concentrations of many contaminants have decreased. This decrease can also be seen in the bottom sediments of Lake Ontario and is discussed later.

Between 1981/2 and 1986/7, the point source loadings to the Canadian side were estimated to have decreased by 60% (MOE, 1987). On the U.S. side, an 80% reduction in total organic and inorganic priority pollutants from point sources was estimated to have taken place between 1981/82 and 1985/86 (NYDEC, 1987). A significant proportion of these decreases were related to plant closures or process shut-downs (NYDEC, 1987). In 1984, no assessment could be made of the loadings of toxic chemicals from groundwater from 215 hazardous waste sites (NRTC, 1984).

Further study concluded that 61 of the 164 sites within 5 km of the river have the potential to contaminate it (NRTC, 1984). Of the 17 landfill sites on the Canadian side, 5 have the potential to contaminate the Niagara River (Koszalka *et al.*, 1985). Although estimates of inputs have been made, there are large uncertainties involved and more sampling and modelling is needed to calculate loadings accurately. The existing calculations are based on 70 sites on the U.S. side of the river and estimate that a total of 180 kg/day of organic compounds are discharged. Thus, there is a possibility that the contribution from non-point groundwater sources of chemicals could be as high as that from point sources. The four major superfund sites of 102nd Street, Love Canal, S-area and Hyde Park contain a total of 304,000 tonnes of chemical wastes. They are hydraulically connected to the river and have been associated with off-site migration of chemicals (Brooksbank, 1987). Several of the small tributaries to the Niagara River have bottom sediments with high concentrations of toxic contaminants and these could be long term sources of contaminants to the river.

Contamination of the Niagara River has been studied very intensively. This is because the Niagara River was the first area in which there was a major chemical crisis (1980), that of Love Canal. In the late 1970s, monitoring for concentrations of metals in suspended solids was initiated in Canada. By the early 1980s, this had been extended to organic chemicals in suspended solids at the mouth of the Niagara River. Later, in the mid 1980s, more sophisticated aqueous phase analyses were performed. These developments required new sampling and analytical techniques which have since been extended throughout the Great Lakes.

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

Between 1984 and 1987, Environment Canada collected data on water and suspended solids concentrations at NOTL and Fort Erie. The objective was to assess the differential loads of toxic organic chemicals added along the course of the Niagara River. Two reports have been released, the first for Dec. 1984 to March 1986 and the second for April 1986 to March 1987. Collectively, the data in these reports on organic chemicals concentrations in the water and suspended solids at NOTL and Fort Erie represent the most comprehensive data base of its type anywhere in the world. Suspended solids were sampled by high speed centrifugation. Concentrations in the aqueous fraction are based on a continuous extraction system over a 24 hour period. A value for recombined water (RWW) was calculated from the aqueous concentrations and the suspended solids concentrations based on the suspended solid content of the water. Using these values for RWW, 21 of the organic chemicals exceeded the strictest water quality criteria at least once, 15 at both NOTL and Fort Erie, 3 at Fort Erie only.

2.6.1 Water and Suspended Solids

Between 1975 and 1979 less than 10% of the samples analyzed at the mouth of the Niagara River exceeded the 1978 Water Quality Agreement (GLWQA) objectives, yet the river was a source of toxic metals and organic chemicals to Lake Ontario (DOE and MOE, 1981). The main contaminants were DDT, PCBs, mirex and mercury. Most organic chemicals were present at concentrations below the minimum detection level in water, which are usually less than the GLWQA objectives. In 1980, PCBs, alpha-BHC and lindane; and alpha and gamma-chlordane, HCB, dieldrin, heptachlor epoxide, and p,p'-DDE were observed in 80% of samples of ambient waters collected over a 10 day period from the mouth of the Niagara River (Kuntz, 1983).

The partitioning of organic chemicals between aqueous and particulate fractions varies considerably with the location in the river and with time. Most of the organic chemicals are in the aqueous phase and the river has a low concentration of suspended solids (5 to 10 mg/L). The collection and analyses of suspended solids from the mouth of the Niagara have been important in establishing long term concentration trends. However, Kuntz and Warry (1983) found that only 40% of the loadings of p,p'-DDE, mirex and PCBs (all extremely hydrophobic organic chemicals) were in the particulate phase. The proportions of other toxic organics were significantly less.

The general pattern of toxic chemical concentrations in the Niagara River above Niagara Falls results primarily from sources on the U.S. side of the River (IJC, 1987b). The presence of compounds such as dioxins and furans, which are known to be present in waste disposal sites, implies that active leaching is occurring to the Niagara River. This conclusion was reached by the NRTC (1984) and from results showing that specific compounds associated with specific waste disposal sites can be found in Lake Ontario sediments (Kaminsky *et al.*, 1983).

Between 1984 and 1987, Environment Canada collected whole water samples from NOTL and Fort Erie for metal analyses. The mean concentrations and ranges for lead, cadmium and arsenic are shown in Table 13. In 1981, the highest levels of lead in water were 2, 3 and 5 ppb (Kuntz, 1984b). These were found just downstream of Buffalo. Between 1975 and 1983, the 12-month moving average of total lead concentrations decreased and is equivalent to loading reductions of from some 430 tonnes/annum in 1975 down to some 200 tonnes/annum in 1983 (Kuntz, 1988b). Between 1979 and 1980, Kauss (1983) reported that mean mercury concentration in the Tonawanda Channel was 100 ppt, compared to 60 ppt in the Chippawa Channel. Mercury concentrations (MOE and DOE, 1981) varied from 60 to 110 ppt in waters of the upper Niagara River. In 1986, mercury was not detected at NOTL or at Fort Erie. In 1982 to 1983, the analytical detection limit for cadmium was 10 ppb which is above the GLWQA objective of 2 ppb (Kuntz, 1984a). In 1985, the cadmium concentrations at NOTL and Fort Erie were less than the minimum detection level of 2 ppb at 1.5 m depths. During 1980, arsenic concentrations in the upper Niagara River were 1 ppb or less but 1 ppb was the minimum detection level.

The database on organic chemicals in water from the Niagara River is extensive because of the focus on the river is a source of contaminants to Lake Ontario. Concentrations of organic chemicals in the Niagara River are shown in Table 12. The 1978 GLWQA objectives have been exceeded in less than 10% of the water sample for total DDT endrin heptachlor/heptachlor epoxide, and endosulphan (DOE and MOE, 1981). Most concentrations were less than 1 or 5 ppt depending on the minimum detection level of the chemical. Most PCB concentrations were less than the minimum detection level of 20 ppt. In 1979, the highest values recorded were 80 ppt for total PCBs; 20 ppt for dieldrin, 7 ppt for alpha-BHC, 1 ppt for lindane, 5 ppt for total DDT and 15 ppt for HCB (MOE and DOE, 1980). Most of these concentrations were from the U.S. side of the upper Niagara River.

Kuntz (1984b) found that between 1975 and 1982 concentrations of total DDT were 1-2 times greater at NOTL than at Fort Erie. El-Shaarawi *et al.* (1985) reported there was a significant difference in mean concentrations between Fort Erie and at NOTL for sixteen toxic chemicals. These chemicals included PCBs, alpha-BHC, mirex, and some chlorobenzenes, including HCB, in whole water. Concentrations of lindane and p,p'-DDE in the aqueous phase and mercury in the suspended phase also increased. McCrea *et al.* (1985) found that alpha-BHC, lindane and dieldrin, and to a lesser extent p,p'-TDE, were mainly in the aqueous phases.

Between 1981 and 1983, weekly water samples from Niagara-on-the-Lake were analyzed by Oliver and Nicol (1984) for several organic compounds and isomers. The distribution of the concentrations of alpha-BHC, total PCBs, 1,2,3,4-tetrachlorobenzene, and HCB, show that maximum concentrations occurred as short-lived (one sample) peaks (Figure 12). The peak concentrations were as follows: 50 ppt alpha-BHC, 34 ppt total PCBs, 36 ppt 1,2,3,4-Tetrachlorobenzene and 30 ppt HCB, but these occurred only on rare occasions. Normally, the concentrations were far less. Concentrations of alpha-BHC and total PCBs varied seasonally more than those for HCB and 1,2,3,4-tetrachlorobenzene. Oliver and Nicol (1984) attributed this to the influence of non-point sources rather than point sources. This problem of short term fluctuations in chemical concentrations in the Niagara River has recently been resolved by installing a continuous extraction system. Oliver and Nicol (1982) found that HCB concentrations in the water above Niagara Falls were near or below the minimum detection level of 0.02 ppt. They found higher concentrations of 1 ppt and 17 ppt near a chemical outfall and a waste disposal site, respectively. In 1982, chlorobenzenes, alpha-BHC and lindane were detected in the plume from the Niagara River in Lake Ontario (Fox and Carey, 1986). In 1979-80, Kauss (1983) found higher concentrations of alpha-BHC and lindane in the Tonawanda Channel than in the rest of the river. In 1986, Stevens and Neilson (in press) found that concentrations of chlorobenzenes, (except for HCB) increased between the outlet of Lake Erie and the Niagara River plume.

Between 1975 and 1982, mirex was observed at levels of 0.0005-0.0075 ppt in the aqueous fraction of 6 of 22 samples (Kuntz, 1984b). El-Shaarawi *et al.* (1985) stated that between 1978 and 1984 there was a significant difference between concentrations of mirex in the combined suspended sediment and aqueous phases at NOTL and Fort Erie. Waste dumps on the U.S. side of the Niagara River could contain large amounts of dioxins produced as by-products of chemical manufacturing (Hallett, 1985). In 200 litre samples taken in tandem 6 m offshore, upstream, opposite and downstream of the 'S' area landfill (Figure 11), isomers of penta-, hexa-, hepta-, and octa-chlorodioxins and dibenzofurans, including isomers of 2,3,7,8,9-pentachlorodioxin and dibenzofuran were detected at concentrations in the order of 0.01 ppt (Hallett, 1985). Residues of 2,3,7,8-TCDD and 2,4,5-trichlorophenol were not detected.

In the late 1970s, suspended solids collected at the mouth of the Niagara River were analyzed to determine trends in loadings of toxic metals to Lake Ontario. In the 1980s, these particulates were also analyzed for toxic organic chemicals. A summary of the chemical concentrations in suspended sediments is shown in Tables 12 and 13. In 1981, a comparison of chemical analyses of suspended sediments from NOTL and from Thunder Bay in Lake Erie showed that many of the chemicals detected at NOTL were not detected in samples from Thunder Bay (DOE and MOE, 1980). However, the process of calculating mean values and loadings is difficult. Wind generated resuspension in Lake Erie can alter the suspended load of the Niagara River by 100%. This has major effects on the partitioning of chemicals between suspended solids and the aqueous phase. McCrea *et al.* (1985) noted that PCB concentrations in suspended solids were lower when the concentrations of suspended solids were higher because of sediment input from Lake Erie. Thus, the partitioning between aqueous and suspended solids phases varies for different organic chemicals and at different locations (NRTC, 1984).

In the late 1970s, lead concentrations were somewhat higher in the upper river perhaps because the method of sampling was intended to detect sources (DOE and MOE, 1981). Mercury concentrations in suspended solids were consistently 3 to 4 times higher in the lower Niagara River compared to the upper Niagara River (Kuntz, 1984b). The distribution of mercury and arsenic in the suspended solids in the river showed that the former increases downstream in concentration, whereas arsenic appears to be relatively evenly distributed (Kuntz, 1984b). The highest concentration of mercury in 1981 was 450 ppb (ng/g) and for arsenic it was 15 ppm (mg/kg).

In 1981, the distributions of toxic organic chemicals in suspended solids showed two patterns (Figure 13) (Kuntz, 1984b). DDT and dieldrin had relatively constant concentrations throughout the river. However, concentrations of PCBs, mirex and HCB were higher in the lower river than in the upper river. The maximum concentration for total DDT, dieldrin, HCB, mirex and total PCBs in suspended solids were 60 ppb, 175 ppb, 3 ppb and 800 ppb, respectively. There are considerable variations with location and time. In 1980, Oliver and Nicol (1982) detected chlorobenzene congeners in suspended sediments at NOTL. The mean concentrations (n = 28) were as follows: 1,2-di 148 ppb, 1,4-di 180 ppb, 1,3-di 95 ppb, 1,3,5,-tri 20 ppb, 1,2,4-tri 61 ppb, 1,2,3-tri 19 ppb, 1,2,4,5-tetra 28 ppb, 1,2,3,4-tetra 71 ppb, penta 58 ppb, hexa 94 ppb. The source of the particulate-associated mirex detected in samples from 1979 and 1980 was considered to be leakage or overflow from storage facilities downstream of Grand Island (Warry and Chan, 1981). Both PCDDs and PCDFs are strongly associated with suspended solids. The higher chlorinated congeners predominated.

Concentrations of organic chemicals in suspended solids collected from the mouth of the Niagara River did not show any distinct trends over the period of measurement (DOE and MOE, 1981; Kuntz, 1983). Lake Erie is not the major source of PCBs, chlorobenzenes and mirex to Lake Ontario because concentrations of these chemicals in Lake Erie bottom sediments are ten times less for PCBs, undetectable for mirex and twenty times lower for hchlorobenzenes than the suspended solids concentrations at Niagara-on-the-Lake (Kuntz and Warry, 1983). Fox *et al.* (1983) reached similar conclusions for these chemicals and HCBD.

2.6.2 Bottom Sediments

The Niagara River has an extremely high discharge rate, about 6,000 m^3/s.

Above the falls there are some areas of nearshore sediment accumulation, at least on a temporary basis. The bottom of the river is either scoured glaciolacustrine sediments or bedrock with very little deposition of unconsolidated recent sediments (NRTC, 1984). Most of the data that follow are based on sampling conducted very close to the shore or near the mouths of tributaries. Thus, although they are sediment data, they do not represent a bottom sediment survey of the type discussed for the depositional basins of the open Great Lakes. The concentrations are more representative of the relative sources to each side of the river. Some of these nearshore samples are highly contaminated. Concentrations of pesticides were generally the highest in samples from the Black Rock Canal, the Wheatfield-Upper River segment, the Buffalo River and the Tonawanda-North Tonawanda and lower river segments (NRTC, 1984). There are considerable variations in the concentrations of individual chemicals, but overall there are higher concentrations in the Buffalo River, Tonawanda-North Tonawanda and Wheatfield-Upper River segments; medium levels in the Lake Erie, Black Rock Canal and Lower River segments; low levels in the Bird Island-Riverside, Fort Erie and Chippawa segments. Cores analyzed by Czuczwa and Hites (1986) indicated that there has been a considerable increase in inputs of total PCDDs and PCDFs since approximately 1940 (Figure 6).

2.7 LAKE ONTARIO

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

Lake Ontario has been contaminated for many years by industrial, agricultural and municipal sources. The highest contaminant levels are in industrialized harbours and embayments. Some of the main contaminants that have been investigated in Lake Ontario are mercury, mirex, PCBs, and chlorobenzenes. Lake Ontario is the receiving water for the largest volume of persistent toxic substances is urban runoff in Canada (Marsalek and Schroeter, 1984). The main industrial centres are Toronto, Hamilton, and Rochester and other important ports are Kingston and Oswego. Seven areas, four in Canada, and the Niagara River, have been designated as Areas of Concern by the International Joint Commission.

2.7.1 Water and Suspended Solids

Metal concentrations in Lake Ontario water (Table 15) are less than those in Lakes Erie and Michigan, but higher than those in Lakes Huron and Superior (Rossmann and Barres 1988). Concentrations of lead in the waters of Lake Ontario are low and uniform although there is a small zone with higher concentrations at the extreme west end of the lake (Schmidt and Andren 1984; Neilson 1983). Lake Ontario has significantly less total and dissolved lead than Lake Erie and significantly less dissolved lead than Lake Michigan (Rossmann and Barres, 1988). Mercury levels in Lake Ontario water are low (Table 15). Levels of total mercury in Lake Ontario were significantly less than those in Lakes Erie and Michigan, while levels of dissolved mercury were significantly less than those in Lake Michigan (Rossmann and Barres, 1988). In the late 1960s, Lake Ontario had the highest arsenic concentrations of all the Great Lakes with a maximum value of 1,200 ppt (Traversy *et al.*, 1975) (Table 15). Arsenic concentrations in the dissolved phase were at least 60% of the total concentration (Rossmann and Barres, 1988).

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

In 1981, all of the dieldrin in Lake Ontario was in the aqueous phase and the concentration was just less than 0.04 ppt (McCrea *et al.*, 1985). In 1983, Biberhofer and Stevens (1987) reported that the highest levels of dieldrin were in the mid-lake area rather than at nearshore stations. The average concentration of dieldrin in 1986 was similar to that in Lakes Erie, Huron and Superior and indicated that the inputs were historical, atmospheric or from resuspension of contaminated sediments (Stevens and Neilson, in press). In 1981, McCrea *et al.* (1985) found alpha-BHC and lindane completely in the aqueous phase at concentrations of 9 and 8 ppt, respectively. In 1986, the mean concentration of alpha-BHC was similar to that in Lake Erie, but lower than concentrations in Lakes Huron and Superior (Figure 14). Lindane concentrations were similar throughout the lakes (Stevens and Neilson, in press). The mean concentration of HCB in 1986 was lower than that in Lake Erie and higher than in Lakes Huron and Superior (Stevens and Neilson, in press). Mirex is extremely insoluble and was not detected in the aqueous phase in 1977, 1981 and 1983 (Strachan and Edwards, 1984; McCrea *et al.*, 1985; Biberhofer and Stevens, 1987) or in whole water samples in 1986 (Stevens and Neilson, in press). Mirex was detected in 1982 in water from Oswego Harbour (Mudambi *et al.*, 1983) where concentrations in the dissolved phase ranged from less than the minimum detection level (0.005 ppt) to 0.130 ppt. Strachan and Eisenreich (1988) calculated the whole water concentration of mirex in Lake Ontario to be 0.060 ppt. The mean toxaphene concentration of 0.6 ppt in Lake Ontario was the same as the average for all the Great Lakes for that year (Sullivan and Armstrong, 1985). Strachan and Edwards (1984) reported that there are no data for dioxins in the waters of Lake Ontario. Strachan and Eisenreich (1988) used a value of 3 ppt total water B[a]P concentration for their mass balance calculations. In 1981, the concentration of PCBs in the aqueous phase of Lake Ontario was 0.5 ppt (McCrea *et al.*, 1985). Ninety-one percent of the total PCBs were in the aqueous phase (McCrea *et al.*, 1985). In 1983, the highest total PCB concentration (Table 15) was detected adjacent to Hamilton Harbour (Biberhofer and Stevens, 1987). Concentrations of PCBs in Lakes Ontario and Erie were significantly higher than those in Lakes Huron and Superior. Locations identified as having high PCB concentrations in 1983 were Black River Bay (1.9 ppt) and the Niagara River plume (1.1 ppt) (Biberhofer and Stevens, 1987). In 1986, the central area of the lake had PCB concentrations of 1.5 to 2.5 ppt, higher than values nearer the north and south shores (Stevens and Neilson, in press). In 1986, concentrations of chlorinated benzenes were higher in Lake Ontario waters than in the other Great Lakes. In particular, there were major differences in concentrations of di, tri, and tetra chlorobenzenes between Lake Erie at its inflow to the Niagara River and Lake Ontario to the east of the mouth of the Niagara River (Figure 14)(Steven and Neilson, in press).

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

Data on particulate metal concentrations are shown in Table 15. In 1978 and 1985, most of the lead in Lake Ontario water (approximately two-thirds) was in the particulate fraction (Nriagu *et al.*, 1980; Rossmann and Barres, 1988). In 1981, Sandilands and Mudroch (1983) found that the suspended particulate concentrations of mercury were less than the surface sediment concentrations at the same locations. Nriagu *et al.* (1980) reported higher particulate concentrations of cadmium in nearshore, than offshore waters. When metal levels in each of the Great Lakes were compared (Rossmann and Barres, 1988), Lake Ontario was found to have significantly higher particulate cadmium concentrations than Lakes Superior, Michigan and Huron. Generally, the concentration of particulate cadmium in Lake Ontario decreases from west to east because of sedimentation (Lum, 1987).

In 1981, Sandilands and Mudroch (1983) found that the concentrations of arsenic in suspended solids were less than the surface sediment concentrations at the same locations.

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

2.7.2 Bottom Sediments

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

Concentrations of toxic chemicals in Lake Ontario bottom sediments are summarised in Table 16. Background levels of lead in Lake Ontario bottom sediments are between 18 and 32 ppm. (Mudroch *et al.*, 1985). In 1968, surface sediments were enriched with lead approximately six times above background levels (Thomas and Mudroch, 1979). High concentrations of over 150 ppm conformed to the depositional basins indicating diffuse, rather than point sources (Thomas *et al.*, 1988). Levels of lead in the bottom sediments of the depositional basins of Lake Ontario were significantly higher than those in Lakes Huron and Superior, and higher than those in Lakes Erie (Hodson *et al.*, 1984). In a review of 1974-84 data, Mudroch *et al.* (1988) calculated that the range of lead concentrations reported for the depositional zones in Lakes Ontario and Erie were almost identical. Also, the range of concentrations completely enclosed (with much higher maximum values) those of Lakes Huron, Michigan and Superior. However, they noted that comparisons of concentrations should be treated cautiously because different sampling techniques were used. Background levels of mercury in sediments in depositional zones of Lake Ontario are 30-90 ppb (IJC, 1987b). Background concentrations in the Niagara and Rochester Basins are more than twice those in the Mississauga Basin (IJC, 1987b). The major anthropogenic source of mercury to Lake Ontario is the Niagara River (Thomas, 1972). Because of the effect of the lake currents on the Niagara River plume, the highest concentrations of mercury were found in sediments along the south shore and in an area to the northwest of the river mouth (Figure 3). Eadie *et al.* (1983) suggested that these may be significant local sources of mercury as well as the Niagara River. The range of background levels of cadmium in Lake Ontario is 0.9-3.7 ppm (Mudroch *et al.*, 1985). Concentrations of cadmium in bottom sediments have increased. In 1968, there were many areas with concentrations greater than 6 ppm cadmium in bottom sediments from both depositional and non-depositional areas (Thomas and Mudroch, 1979). In 1970 and 1971, cadmium levels were still increasing in the depositional basin sediments (Kemp and Thomas, 1976a). Lake Ontario has the highest concentrations of cadmium in sediments in the Great Lakes (Lum, 1987), approximately twice those in Lakes Michigan and Erie. Generally, cadmium concentrations are higher in non-depositional zones and embayments (maximum levels of 18.6, 20.6 and 22.0 ppm, respectively) than in the depositional zones (maximum level of 6.2 ppm) (Mudroch *et al.*, 1985). Background levels of arsenic in Lake Ontario are not available. Mudroch *et al.* (1985) reported that surface sediment levels in depositional and non-depositional zones from the late 1960s and the early 1980s were 0.2-17.0 and 0.2-24.0 ppm, respectively.

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

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

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

In 1970 and 1971 sediment cores from all five stations in Lake Ontario showed surface enrichment with anthropogenic mercury, lead, zinc, cadmium and copper (Kemp and Thomas, 1976a). In 1981, two cores taken from the eastern end of the lake were shown to have subsurface maximum concentrations of mercury (Figure 16) and lead. However, surface levels (120-150 ppm) were still considerably higher than background concentrations (Eadie *et al.*, 1983). The cores indicated that the average lead flux to Lake Ontario increased by 680% from the early 1800s to the time of maximum lead usage in the mid 1970s (Eadie *et al.*, 1983). Concentrations of lead in surface sediment were still high in the early 1980s: they were between 100 and 200 ppm near the Niagara River mouth (Mudroch, 1983). Changes in concentrations of mercury are the most dramatic of any in metal levels (Mudroch, 1983; Mudroch *et al.*, 1988). Mercury concentrations increased rapidly in a core taken in 1970 between the turn of the century and the early 1940s. Between then and 1970, concentrations increased at a slower rate and were in the range of 1-1.5 ppm (Thomas, 1972). Similar increases were seen in cores sampled in 1970 and 1971 from the depositional basins. Higher surface concentrations were reported for the Niagara and Rochester Basins than for the Mississauga Basin. The surface sediment concentration range for the three basins was 2.6-3.9 ppm (Kemp *et al.*, 1974). Cores taken in 1981, from both ends of the lake showed a reversal of this trend (Eadie *et al.*, 1983; Mudroch, 1983) (Figure 16). Immediately adjacent to the mouth of the Niagara River, maximum subsurface mercury concentrations ranged from 4 to 7 ppm. Surface levels were approximately 1 ppm. Ranges in the eastern cores were slightly lower. This site now has surface sediment concentrations less than those of surficial sediments farther out in the lake although it used to have the highest surficial concentration. The more contaminated sediments are still within mixing depths for benthic organism, whereas the previous highest concentrations near the Niagara River mouth are now below this (Allan, 1986).

In 1976, the highest concentrations of total DDT in cores were in the surface sediments. DDT first appeared in sediments in the late 1950s (Frank *et al.*, 1979a). In a 1982 core, peak levels of total DDT were seen in the late 1950s to the early 1960s. This agrees with DDT patterns (Oliver *et al.*, 1987).

Oliver and Nicol's (1982) core showed that concentrations of chlorobenzenes in sediment began to increase in the early 1940s and began to decrease in the late 1960s (Figure 16). This corresponds to the use of chlorobenzenes in the production of phenols. There was little, if any, change in the proportions of the various chlorobenzenes in this core. Cores analyzed by Onuska *et al.*, (1983) also showed that there may have been a decrease in chlorobenzene loading from the Niagara River during the 1970s. HCBD and OCS concentrations in cores also peaked (160 ppb and 550 ppb, respectively) in the 1960s and 1970s, respectively. Concentrations of HCBD were low prior to the late 1950s and after the early 1970s, but there were high concentrations during the 1960s (Durham and Oliver, 1983). Concentrations of mirex in sediment cores reflected its production in the Niagara River area (Durham and Oliver, 1983; Eadie *et al.*, 1983) (Figure 16). Because concentrations continued to increase and the area affected got larger after production ceased (in 1976), remobilization of contaminated sediments from the Niagara River has been suspected (Thomas *et al.*, 1988). Durham and Oliver (1983) found the highest concentrations of PCBs were at sediment depths corresponding to the early 1960s (Figure 16). Concentrations of PAHs in sediment cores were 100 times higher in surface layers than in deeper sediments, indicating extensive loading in the late 1970s.

2.8 ST. LAWRENCE RIVER

The St. Lawrence River drains Lake Ontario and the Great Lakes. It discharges to the Atlantic Ocean. Its discharge rate is approximately 7,700 m^3/s. The mean concentration of suspended solids in the river at its source in Lake Ontario is 1.3 mg/L (mean of four years of data). The international section of the river included in the Great Lakes Water Quality Agreement stretches from Lake Ontario to the Province of Quebec and thus does not include Lake St. Francis. Major industries are located on the Canadian and shores of the river, just upstream from Quebec. They include a major foundry, automobile plant and two large aluminium plants. In the Cornwall area, a chlor-alkali plant used to discharge mercury and this resulted in high levels of mercury in downstream bottom sediments. A former tetraethyl lead plant located near Maitland used to be a source of alkyl leads to the river.

2.8.1 Water and Suspended Solids

In 1977, the mean concentrations of the metals discussed here were 0.50 to 1.01 ppb for lead; ND - 0.004 ppb for mercury; less than the minimum detection level for cadmium; and 0.55 - 0.73 ppb for arsenic between Kingston and Cornwall (Chan, 1980). These results were based on unfiltered water. Between 1977 and 1983, water samples from the St. Lawrence outflow from Lake Ontario were routinely analyzed for inorganic chemicals (Sylvestre *et al.*, 1987). When means were calculated, values less than the minimum detection level were taken as equal to it. Between 1977 and 1983, the mean concentration of lead was 1.2 ppb (n= 341). There were no data on mercury, cadmium or arsenic. Between 1979 and 1982, filtered water samples showed that mercury concentrations at Cornwall - Massena were less than 0.2 ppb. Lum and Kaiser (1986) reported dissolved cadmium concentrations of between 3 and 23 ppt (mean = 10pp: n=11).

In 1977, lindane and alpha-BHC, were detected in water from the St. Lawrence River between Kingston and Cornwall at concentrations from 3 to 7 ppt and 3 to 8 ppt respectively (Chan, 1980). In 1982, water and suspended sediments collected from the source of the St. Lawrence River near Wolfe Island began to be analyzed routinely for toxic organic chemicals (Sylvestre, 1987). Samples were analyzed for PCBs, PAHs, chlorobenzenes and organochlorine pesticides. In whole water, only 3 of the 18 organochlorine pesticides measured were detected in more than 40% of the samples. Between 1982 and 1984, mean concentrations were 5.8 ppt alpha-BHC, 1.0 ppt lindane, and 0.4 ppt dieldrin (Sylvestre, 1987). The results for <40% detection were not considered meaningful to calculate means using the minimum detection level as the lower value. When larger volume samples (200 L versus 2 L) were extracted in 1983, other chemicals were detected above the more sensitive minimum detection level. The results from this 1983 study were 4.8 ppt alpha-BHC, 1.2 ppt lindane, 0.54 ppt dieldrin (all similar to the above), 0.17 ppt total DDT and 0.43 ppt total PCBs. Concentrations of mirex were less than the minimum detection level. The concentration of p,p'-DDT was 0.065 ppt in the aqueous phase and 0.02 ppt in the suspended solids, while PCBs were present at 2.0 ppt in the aqueous phase and at less than 0.1 ppt in suspended solids. In 1977, PCBs were detected in water at the mouth of the Grass River at concentrations of 60 and 180 ppt.

PCBs concentrations of 20 to 70 ppt in water and up to 660 ppb in suspended solids were measured at the mouth of the Grass River between 1979 and 1982 (MOE, 1988a).

Lum and Kaiser (1986) reported particulate cadmium concentrations of 1.0 to 3.8 ppm (mean = 2.1 ppm; n = 12) for 1985. Between Cornwall and Massena, suspended solids had mercury concentrations of up to 2.4 ppt in 1979-82. Merriman (1987) reported concentration ranges in suspended solids of <1-2 ppb alpha-BHC, <1 ppb for lindane, <1-14 ppb for dieldrin, <1-16 ppb for p,p'-DDT, 7-18 ppb for p,p'-DDE, 11-34 ppb for total DDT, <1 to 6 ppb for mirex, 1-27 ppb for HCB, and 30 to 126 ppb for total chlorobenzenes between Kingston and Cornwall in 1981. The spatial distributions of total DDT, total PCBs and mirex are shown in Figure 17. Between 1982 and 1984, concentrations of lindane were less than the minimum detection level of 4 ppb, while alpha-BHC and dieldrin were detected in more than 40% of the samples at mean concentrations of 6 ppb and 9 ppb, respectively, in suspended solids collected from Wolfe Island (Sylvestre, 1987). PCBs were detected in 93% of the samples, at a mean value of 162 ppb. Total DDT was found in 90% of the samples at a mean concentration of 18 ppb. Mirex was detected in 33% of the samples and concentrations ranged from less than the minimum detection level of 4 ppb to a maximum of 27 ppb. A mean concentration could not be calculated for mirex because the frequency of detection was only 33%, however, the mean of the concentrations above the minimum detection level was 9.8 ppb (n= 26). In 1981, mirex concentrations ranged from less than the minimum detection level to 6 ppb (Figure 17). The occurrence of some chlorinated benzene congeners in suspended solids was >50%. The mean concentrations (maximum values are in brackets,) were 32 ppb (131) 1, 2, 4-tri, 14 ppb (95) 1, 2, 3, 4-tetra, 11 ppb (56) penta, and 13 ppb (54) hexa chlorobenzene (Sylvestre, 1987). Most PAHs were not detected in the suspended solids at a minimum detection level of 50 ppb. The few exceptions could be the result of interference in the analyses.

2.8.2 Bottom Sediments

In 1975, Kuntz (1988a) collected bottom sediments between Kingston and Cornwall and Cape Vincent and Massena on the Canadian and U.S.

sides of the St. Lawrence River. Lead concentrations ranged from less than the minimum detection level of 50 ppm up to 190 ppm. Mercury concentrations were usually well below 0.3 ppm, except for a site immediately downstream of Cornwall where the concentration was 4.9 ppm. Concentrations of cadmium were generally less than minimum level of 10 ppm. Five of fifty-six samples contained detectable concentrations of cadmium and the maximum was 14 ppm. This was from a site just downstream of the Grass River. Concentrations of arsenic ranged up to 7.6 ppm on the Canadian side and 8.0 ppm on the U.S. side of the river.

In 1975, p,p'-DDT was not detected in any of the 57 samples analyzed (Kuntz, 1988a). Several samples contained p,p'-TDE at concentrations above the minimum detection level. These were in the range of 3 to 11 ppb, and were in samples from the Gananoque-Rockport area. Concentrations of p,p'-DDE were usually less than the minimum detection limit of 1 ppb and the maximum concentration was 90 ppb. In 1981, the highest concentration of total DDT was 56 ppb. This was in a sample collected from just off Kingston (Merriman, 1987) (Figure 17). The maximum HCB concentration detected in 1981 was 13 ppb for the seven sites sampled (Merriman, 1987) and occurred in a sample in the DuPont outfall zone near Maitland (MOE, 1988b). The bottom sediment survey of 1975 did not detect mirex in any of the samples at a minimum detection level of 1 ppb (Kuntz, 1988a). In 1981, Merriman (1987) detected mirex at only one site near Kingston at 9 ppb.

In 1975, Kuntz (1988a) found levels of PCBs above 50 ppb at 10 of 57 stations. The highest value was 1.5 ppm downstream of the Grass River. In 1981, the highest bottom sediment PCB concentration was 8.74 ppm at the mouth of the Grass River (Merriman, 1987). Total chlorobenzenes were found at low concentrations of 8-9 ppb in bottom sediments (Merriman, 1987). The maximum concentration was 50 ppb.

3. CONCLUSIONS

The most heavily contaminated of the Great Lakes are Lakes Ontario, Michigan and Erie, based on an assessment as concentrations of contaminants in abiotic aquatic media. Lake Superior is the least contaminated. Lake Huron is relatively uncontaminated, except for some local areas. Generally, the concentrations of toxic chemicals in the Great Lakes are decreasing. Concentrations of some chemicals are still increasing especially along the St. Clair-Detroit River corridor and in the Niagara River.

There are higher concentrations of contaminants in the water of the nearshore areas and there are higher concentrations in sediments in the depositional basins, harbours and deltas. In the connecting channels, higher concentrations of contaminants are usually found along the shore downstream from sources. There are also unique patterns in each lake and channel. In Lake Superior, concentrations of organics are higher in the northern part of lake than in the southern part. High levels of lead, mercury and cadmium have been reported in some of the bays and harbours. All of Rossmann's metal concentrations in Lake Superior were below the GLWQA objectives. The highest levels of toxic chemicals in the St. Marys River were generally found along the Canadian shore. In Lake Michigan, concentrations of toxic organic chemicals are usually higher in the southern section of the lake and Green Bay. PCB concentrations are highest in the sediments of the southwest part of the lake. Saginaw and Georgian Bays are major sources of toxic chemicals to Lake Huron. In the St. Clair River, high concentrations of toxic chemical are confined primarily to a 100 metre wide area along the Ontario shore near Sarnia's chemical industrial area, for example, PCBs, volatile hydrocarbons, lead and mercury. Spills are an important problem. Increasing water and/or sediment concentrations have been reported for lead, mercury, HCB, HCBD, OCS, OCB and PAHs over the course of the river. Levels above the GLWQA objectives have been found for lead, HCB and HCBD, and above dredging guidelines for OCS, PAHs and PCBs. In Lake St. Clair, the highest concentrations of PCBs have been reported on the western side. High levels of contaminants have been found in sediments from the central depositional basin and at the outlet. In the Detroit River the majority of sources are along the U.S. shore and along the Rouge River. Chemical concentrations of cadmium, PCBs, chlorobenzenes, lindane, industrial volatile halocarbon and PAHs in water and/or sediment have been reported to increase along the river. Levels of lead, mercury, cadmium, arsenic, PCBs, PAHs, alpha-BHC and lindane have been reported to be above dredging guidelines. The western basin of Lake Erie is the most affected by toxic chemicals mainly because of inputs from the Detroit River; for example, PCBs and industrial halocarbons in water; PCBs, HCB, HCBD, and PAHs in sediments; and DDT and metabolites, mercury and cadmium in sediments in the 1970s. The main sources of toxic chemicals to the Niagara River are along the U.S. shore. Concentrations of many contaminants are higher in the water and sediments from the Tonawanda Channel than in the Chippawa Channel. Since there is extensive mixing at Niagara Falls, there is no plume. Increases along the course of the river were observed in the late 1970s-1980s for PCBs, alpha-BHC, lindane, chlorobenzenes (sometimes including HCB), HCBD, mirex, p,p'-DDE, mercury, cadmium, arsenic, PAHs and B[a]P. Sources of dioxins and furans have also been found. Concentrations of mercury, arsenic, PCBs, mirex, HCB and HCBD are much lower in the sediments of Lake Erie than in Lake Ontario. Concentrations of DDT and its metabolites have decreased recently between Fort Erie and Niagara-on-the-Lake. The Niagara River has historically been the main source of toxic chemicals to Lake Ontario. These chemicals initially collect in the sediments in a pattern which reflects lake circulation. Eventually, they move into the depositional basins. Along with other dioxins and furans, 2,3,7,8-TCDD has been detected in the sediments offshore from the mouth of the Niagara River.

Temporal trends in concentrations of contaminants have been determined for each of the lakes and channels. In Lake Superior, historic data for concentrations of lead, mercury and cadmium could not be used to determine trends in the water. Arsenic concentrations in whole water have decreased since the 1970s. There has been a dramatic reduction in PCB concentrations in the waters and sediments of Lake Superior since the early and mid 1970s. Lead in sediments had a higher anthropogenic enrichment factor than mercury, cadmium and arsenic. Concentrations of lead and mercury are now decreasing in the surface sediments. Historic data on concentrations of lead, mercury and cadmium in Lake Michigan can not be used to determine trends in the water. Arsenic concentrations in whole water have decreased since the 1970s. Concentrations of lead have decreased in the sediments from high levels in the 1950s and 1960s. Concentrations of cadmium have also decreased from the peak levels in the 1940s and 1960s. Levels of PCBs have decreased from peak levels in the 1960s and 1970s. In Lake Huron, historic data on mercury, cadmium and arsenic in water can not be used to determine trends. Dissolved lead concentrations have decreased in Lake Huron. There are indications that levels of lead, cadmium and DDT in the water of Saginaw Bay have decreased since the 1970s. In cores taken before 1980, there was surface enrichment of lead, mercury, cadmium and arsenic. Mercury levels in bottom sediments have decreased in most parts of the St-Clair River, however, levels are often still above the dredging guideline. Concentrations of HCB, HCBD and PAHs in sediments show that concentrations have decreased slightly over time. For Lake St. Clair, concentrations of PCBs, mercury and DDT decreased in bottom sediments following the restrictions on its use imposed in the early 1970s. The concentrations of HCB and HCBD in the sediments of Lake St. Clair are still increasing or at least not dropping significantly. Generally, levels of mercury have decreased in the bottom sediments of the Detroit River, however, levels are often still above the dredging guideline. In Lake Erie, historic lead data can not be used to determine trends in the water but concentrations of mercury, cadmium and arsenic are decreasing. Concentrations of PCBs may be decreasing in the water of Lake Erie. Cores collected in the early 1970s showed that concentrations of lead, mercury and PCBs from anthropogenic sources increased. More recent cores show that concentrations of lead, arsenic, DDT and its metabolites, dioxins and furans have decreased at the surface. Levels of PCBs may not be decreasing in the sediments. During the 1980s, point source loadings to the Niagara River decreased by over 60% on both sides of the river. Because of changes in analytical methods, water samples from the early 1980s cannot be compared to those of the mid 1980s. Between the mid 1970s and the 1980s, lead loadings from the Niagara River to Lake Ontario fell by half. Peak levels of mercury in the sediments of the delta occurred in the early 1950s. By the end of the 1970s, mercury levels were back to pre 1940 levels. From the late 1960s to the early 1980s, concentrations of mirex and PCBs in surface sediments of Lake Ontario increased; however, this may have been done to improved analytical and sampling techniques because analyses of cores refute this trend. Analyses of cores showed enrichment of lead, mercury, cadmium, DDT, chlorobenzenes, HCBD, OCS, mirex, PCBs and PAHs from anthropogenic sources in bottom sediments, but concentrations are now decreasing or levelling off. In the St. Lawrence River, lead and mercury concentrations in sediments have decreased following the closure of source industries.

The sources of toxic chemicals and the physical characteristics of the lakes and channels influence the relative concentrations of contaminants in each area. The atmosphere is a more important source of most of the critical toxic chemicals to the upper Great Lakes than the lower lakes. The major contributing factors are the large surface areas and drainage basins of the upper lakes. Conversely, the lower lakes receive greater inputs from their main tributaries, industries, municipalities and agriculture than the upper lakes. Concentrations of contaminants, such as dieldrin and toxaphene tend to be similar throughout the Great Lakes. The major sources of these chemicals are atmospheric and/or sediment resuspension. Total suspended matter concentrations in the lake are (from highest to lowest) Lakes Erie, Ontario, Huron and Michigan and Lake Superior. Sedimentation rates are highest in Lake Erie, followed by Lakes Ontario and Michigan, followed by Lakes Huron and Superior. Higher total suspended matter and sedimentation rates reduce bioaccumulation of contaminants and accelerate natural self cleansing of the lakes. Lakes Michigan and Superior have long water residence times so that most of the chemicals introduced into these lakes are not quickly translocated downstream.

There is considerable variation in the concentrations of contaminants in the waters of the Great Lakes. The total concentrations of metals in water are (from highest to lowest) Lakes Michigan, Erie, Ontario, Huron and Superior. Concentrations of metals in Lake Superior are lower than in the other lakes, except for dissolved arsenic in Lake Huron and particulate cadmium in Lake Michigan. Concentrations of metals in Lake Huron are also consistently less than in the other lakes. In the mid 1970s, PCB concentrations in suspended solids of the Detroit River and the Niagara River were the highest in the Great Lakes. In the mid 1980s, Lake Ontario had higher concentrations of toxic organic chemicals in whole water than Lakes Superior, Huron and Erie. The mean concentrations of chlorobenzenes and lindane ranked highest in Lake Ontario. Concentrations of PCBs, p,p'-DDE, chlorobenzenes and alpha-BHC were higher in Lakes Ontario and Erie than in Lakes Superior and Huron. Whole water concentrations of chlorobenzenes, dieldrin and PCBs were similar in Lakes Superior and Huron. Dieldrin, lindane and toxaphene were found to be ubiquitous. Mirex is generally not detected in the waters of the Niagara River and Oswego Harbour (Lake Ontario).

There were also variations in sediment concentrations. In the sediment survey of the late 1960s and early 1970s, concentrations of lead, mercury and cadmium in the lower lakes were higher over greater areas of the lake bottom than in the three upper Great Lakes. Lead enrichment in Lake Superior is less than in the other Great Lakes. Information on arsenic concentrations in Great Lakes sediments is scarce. In 1980, levels of HCB in the sediments were much higher in Lake Ontario than in Lakes Superior, Huron and Erie. PAH concentrations in sediments are about 10 times lower in Lake Superior than the other Great Lakes, reflecting both its remote location and that the atmosphere is the primary source. There has been a recent decrease in the level of B[a]P in Lake Superior and the St. Marys River. Lake Michigan has high concentrations of PAH in the sediments. The main sources of dioxins and furans to the Great Lakes sediments are municipal and industrial combustion of waste containing chlorinated organic chemicals. OCDD and HpCDF predominated. The highest concentrations of OCDD were in Lake Ontario, followed by Lake Erie and Lakes Michigan and Huron. Lake Ontario also had high levels of OCDF, indicating a local source.

The high concentrations of metals in water documented in the past are now thought to reflect sample contamination. The use of special sampling and clean laboratory techniques is now suggesting that dissolved concentrations of lead, cadmium and other metals are much less (in the low ppt range) than previously thought (in the low ppb range). Likewise recent sampling techniques using large volume aqueous phase or continuous flow extraction systems have allowed extremely low concentrations (< 1 ppt) of organic chemicals to be detected in water samples. Historical data on concentrations of organic chemicals in water included a lot of non-detected concentrations or high concentrations which now must be interpreted cautiously.

The data on concentration of toxic chemicals in the water of each of the lakes shows that different contaminants are found in the different lakes. The historical data on metals and organic chemicals indicate that concentrations have decreased over time. However, this conclusion should be viewed in the context of the above comments on data reliability. If the historical values are taken at face value, then concentrations of some chemicals such as lead, cadmium and PCBs have decreased dramatically in some of the lakes. Decreases in concentrations measured in the last few years are probably more accurate. The most recent data on metals and organic chemicals are the most reliable and show that ambient concentrations are much lower than those determined in the past.

Data on contaminants in nearshore areas are scarce. There are data on the connecting channels and the concentrations of chemicals in water in these channels can vary considerably over short periods of time. The same is probably true for nearshore sites, if they are affected by tributaries or effluents from industry or municipalities. More data on the nearshore areas of Canada are being generated for the Remedial Action Plans (RAPs) and for the Ontario Municipal and Industrial Strategy for Abatement (MISA) There is no simple relationship between concentrations of contaminants in raw water and those in drinking water from the Great Lakes. Drinking water intakes are located nearshore, often within a kilometre or less of the shoreline. Wave action or storms can resuspend nearshore sediments, cause an upwelling of deeper lake water or can cause increased sediment loads in small creeks which discharge to the nearshore zone. Each intake is unique because the environmental conditions at each one are different. Drinking water treatment plants are designed to take account of these local factors by filtering the raw water and by removing suspended and colloidal material by flocculation. Thus, human exposure is best assessed by analyses of treated drinking water.

The open water data are a good measure of the total lake contamination and can be used for comparison with information on contaminant level in open lake fish. However, the relationship between the concentrations of chemicals in water and sediments and the concentrations in biota in the lakes is not simple. It is possible that the majority of contaminants are taken up directly by fish from the water and bioconcentrated. However, an alternative hypothesis is that contaminants are primarily bioaccumulated in the food web. The sediments or water surrounding them may be a major source of chemicals for biota which inhabit contaminated sediments or for fish which eat organisms living in such sediments. For some fish it may well be all three, i.e., water, sediments and other biota. The mix will be different for different organisms, at different trophic levels, with different diets and dependent on local contamination.

Until recently, analyses of bottom sediments, and in particular cores of bottom sediments, have been used to detect trends in chemical inputs and concentrations in water in the lakes. Temporal trends for many contaminants indicate that concentrations have decreased, compared to concentrations 10 and 15 years ago. The data suggest that the major influx of contaminants to the Great Lakes aquatic ecosystem took place in the 1960s and 1970s. Dated cores show similar trends for most of the contaminants discussed in this report. Some of these decreases have been dramatic and followed the bans and restrictions on the manufacture and use of contaminants, such as PCB and mirex. Often, the periods of peak input of contaminants occurred several years before they were first detected in lake media. Thus, the overall evidence from the abiotic data is that the maximum inputs of most of these contaminants occurred in the past and that the inputs of such chemicals have decreased.

The purpose of this report was to give an overview of concentrations of contaminants in water and sediments of the Great Lakes over time. However, problems with the historical data on concentrations of contaminants in water make this difficult. There are better data available on sediments because there are many maps of the distribution of contaminants in sediments and there are sediment core data. There are more data on water because concentrations, particularly in the connecting channels, can change rapidly with time.

No new ubiquitous, highly toxic and persistent contaminants have been detected in any of the Great Lakes since 1982. Future control actions will have to take into account non-point sources of the contaminants, especially atmospheric sources, chemicals recycled from contaminated sediments, agricultural, forestry and urban sources, and contaminated groundwater. The sequencing of control actions and remedial programs will rely heavily on accurate assessments of relative source loadings and mass balances for the connecting channels and whole lakes. The next major steps in the continued