

## Lake Erie Lakewide Management Plan (LaMP) Technical Report Series

**Characterization of Data and Data Collection Programs for Assessing Pollutants of Concern to Lake Erie** 

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Lake Erie LaMP Technical Report

## Note to the Reader

This technical report was prepared as part of Stage 1, or the problem definition stage, of the Lake Erie Lakewide Management Plan. The report provides detailed technical and background information that characterizes pollutant sources, water quality data, and water quality data-collection programs. These data were evaluated for their potential use in characterizing concentrations and loads of pollutants that impair beneficial uses in the Lake Erie basin.

## Contents

List of Figures	iv
List of Tables	v
Conversion Factors and Abbreviations	vi
Acronyms	vii
Acknowledgments	viii
Summary	ix
Introduction	1
Characterization of Sources and Source Data	5
Point Sources Discharging to Surface Water	5
Domestic Wastewater	5
Industrial Wastewater	8
Stormwater and Sewer Overflows	13
Point Source Discharge or Release Data	15
Toxics Emission Data	18
Nonpoint Sources	25
Agriculture	26
Abandoned Solid Waste and Hazardous Waste Landfills	29
Water Quality and Ancillary Data	31
Water Quality Data for Lake Erie, the Connecting Channels, and Tributaries	31
Aquatic Sediments	39
Fish Tissue	43
Precipitation and Dry Deposition	43
Pathways	44
Suitability of Available Data	47
Conclusions and Future Direction	49
References	53
Appendix A. Endocrine-Disrupting Chemicals	57
Appendix B. Data Screening Procedure and Selection Criteria	59

## List of Figures

Figure 1.	Lake Erie and its watershed, United States and Canada	2
Figure 2.	Location and range of average flows of sewage treatment plants in the Lake Erie Basin	6
Figure 3.	Locations of primary metal, fabricated metal, and transportation facilities in the Lake Erie Basin	9
Figure 4.	Locations of petroleum and chemical facilities in the Lake Erie Basin	10
Figure 5.	Locations of paper facilities in the Lake Erie Basin	11
Figure 6.	Locations of electric, gas, and sanitary service facilities in the Lake Erie Basin	12
Figure 7.	Suspected endocrine-disrupting chemical releases, from the 1996 TRI and NPRI	13
Figure 8.	Locations of facilities that have regulated discharges in the Lake Erie Basin	16
Figure 9.	Facilities that monitor for benzo(a)pyrene in the Lake Erie Basin	20
Figure 10.	Facilities that monitor for mercury in the Lake Erie Basin	21
Figure 11.	Facilities that monitor for PCBs in the Lake Erie Basin	22
Figure 12.	Facilities that monitor for total phosphorus in the Lake Erie Basin	23
Figure 13.	1993 atrazine use in Great Lakes Region	27
Figure 14.	Atrazine concentrations in the lower lakes: 1992-1993	27
Figure 15.	Suspected endocrine-disrupting chemicals used in agriculture in 1993	28
Figure 16.	Frequency of observations of benzo(a)pyrene in surface waters of the Lake Erie basin, United States: 1986-1996	35
Figure 17.	Frequency of observations of mercury in surface waters of the Lake Erie basin, United States: 1986-1996	36
Figure 18.	Geometric mean concentrations of total phosphorus in the Lake Erie basin compared to selected guidelines established for streams and Lake Erie: 1986-1996	37
Figure 19.	Geometric mean nitrate-nitrogen concentrations in surface waters of the Lake Erie basin, Canada and the United States: 1986-1996	38
Figure 20.	Single-sample concentrations of total PCBs in aquatic sediments of the Lake Erie basin in relation to the Probable Effect Level of 0.277 mg/kg: 1990-1997	41
Figure 21.	Single-sample concentrations of mercury in aquatic sediments of the Lake Erie basin in relation to the Probable Effect Level of 0.486 mg/kg: 1990-1997	42

## **List of Tables**

Table 1.	Beneficial use impairments in the Lake Erie basin	3
Table 2.	Pollutants identified for analysis of sources and loads in the Lake Erie LaMP	4
Table 3.	Reported concentration ranges of selected Lake Erie pollutants of concern in sewage effluent and sludge	8
Table 4.	Concentration ranges of selected Lake Erie pollutants of concern in storm water	14
Table 5.	Required minimum analytical detection limits reported in SRDS and PCS databases	17
Table 6.	Pollutant class, pollutant, number of reporting facilities, number of observations, and percent of samples reported above the detection limit, Lake Erie basin in the United States: 1986-1997	18
Table 7.	Pollutant class, pollutant, number of reporting facilities, number of observations, and percent of samples reported above the detection limit, Lake Erie basin in Ontario: 1995	19
Table 8.	Lake Erie LaMP pollutants of concern reported in the TRI and NPRI inventories, 1996	24
Table 9.	Total releases of chemicals in eight Great Lakes states and Ontario, from the 1996 TRI and NPRI databases	24
Table 10.	Top 25 chemicals released into the environment in 1996 reported in TRI (total for eight Great Lakes states)	25
Table 11.	The top 25 chemicals released into the environment in 1996 reported in NPRI (total for Ontario)	25
Table 12.	Pollutants of concern regulated by RCRA for the Lake Erie basin	29
Table 13.	Number of municipal solid waste landfills; RCRA Treatment, Storage and Disposal sites; CERCLA sites; and National Priority List sites in five Great Lake states	30
Table 14.	Quantity of selected Lake Erie pollutants of concern transferred to landfills, 1996	30
Table 15.	Pollutant class, pollutant, percentage of samples with detected concentrations, number of samples, number of sites, and number of sites within indicated range of samples per site, Lake Erie basin tributaries in the United States: 1986-1996	33
Table 16.	Pollutant class, pollutant, percentage of samples with detected concentrations, number of samples, number of sites, and number of sites within indicated range of samples per site, Lake Erie basin tributaries in Ontario: 1986-1996	34
Table 17.	Dissolved- and particulate-phase pollutants, number of samples, percentage of samples with detected concentrations, detection limits, and number of samples per site; St. Clair River and Niagara River at Fort Erie sampling sites: 1990-1996	34
Table 18.	Number of samples and detection frequency of selected pollutants of concern in near surface sediments: Lake Erie basin in the United States: 1990-1997	40
Table 19.	Summary of National Sediment Inventory data for selected pollutants in fish tissue by pollutant class, pollutant, number of tissue samples, and median concentration: 1980-1993	43
Table 20.	Summary of available IADN data by pollutant and phase, Lake Erie at Sturgeon Point, New York: 1993	45

## **Conversion Factors and Abbreviations**

Multiply	By	To Obtain
Inch (in)	25.4	Millimeter (mm)
Foot (ft)	0.3048	Meter (m)
Mile (mi)	1.609	Kilometer (km)
Square foot (ft2)	0.0929	Square meter (m2)
Square mile (mi2)	2.59	Square kilometer (km2)
Acre	0.4047	Square hectometer (hectare)
Pound (lb)	0.000454	Metric ton
Ton	0.9072	Metric ton
Acre-foot (acre-ft)	1,234.3	Cubic meter (m3)
Cubic feet per second (cfs)	0.02832	Cubic meters per second
Gallons per minute (gal/min)	3.785	Liters per minute
Million gallons per day (Mgal/d)	3,743.06	Cubic meters per day

Temperatures are given in degrees Fahrenheit (°F), which can be converted to degrees Celsius (°C) by use of the following equation:  $^{\circ}C = (^{\circ}F - 32)/1.8$ 

Water temperatures are given in degrees Celsius.

#### **Abbreviated Environmental Concentrations**

Chemical concentrations are given in metric units. The units commonly used are milligrams (one-thousandth gram) per liter (mg/L), micrograms (one-millionth gram) per liter (mg/L), nanograms (one-billionth gram) per liter (ng/L), milligrams per kilogram (mg/kg), micrograms per kilogram (mg/kg), and picograms (one-trillionth gram) per cubic meter (pg/m3). These units express the concentration of chemical constituents as weight (milligrams, micrograms, nanograms, or picograms) of constituent per unit volume of water or air (liter or cubic meter) or per unit mass of sediment or biological tissue (kilogram).

## Acronyms

AOC	Area of Concern
BCC	Bioaccumulative Chemical of Concern
BOD	Biochemical oxygen demand
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COA	Canada-Ontario Agreement
COD	Chemical oxygen demand
CSO	Combined sewer overflow
DDT	1,1,1-trichloro-2,2-bis(p-chlorophenyl ethane)
DMR	Discharge Monitoring Report
EDC	Endocrine-Disrupting Chemical
EDS	Effluent Data Statistics
ENVIRODAT	Connecting channel database
EPA	Environmental Protection Agency
FIELDS	Fully Integrated Environmental Locational Decision Support System
GLWQA	Great Lakes Water Quality Agreement
IADN	Integrated Atmospheric Deposition Network
IJC	International Joint Commission
LaMP	Lakewide Management Plan
MDN	Mercury Deposition Network
MISA	Municipal-Industrial Strategy for Abatement
MOE	Ontario Ministry of Environment
MSWLF	Municipal solid waste landfill
NADP/NTN	National Atmospheric Deposition Program/National Trends Network
NOAA	National Oceanic and Atmospheric Administration
NPDES	National Pollutant Discharge Elimination System
NPL	National Priorities List
NPRI	National Pollutant Release Inventory
NSI	National Sediment Inventory
OSI	Ohio Sediment Inventory
PAH	Polynuclear aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PCS	Permit Compliance System
PWQMN	Provincial Water Quality Monitoring Network
RAP	Remedial Action Plan
RAPIDS	Regional Air Pollution Inventory Database System
RCRA	Resource Conservation and Recovery Act
SIC	Standard Industrial Classification
SRDS	Sample Results Data Store
SSO	Sanitary sewer overflow
STAR	Storage and Retrieval System-Environment Canada
STORET	Storage and Retrieval System-EPA
STP	Sewage treatment plant
TRI	Toxics Release Inventory
USACE	United States Army Corps of Engineers
USGS	United States Geological Survey
WWTP	Wastewater treatment plant

## Acknowledgments

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## Summary

Many pollutants arising from past and present agricultural, industrial, and municipal sources are impairing or could impair the beneficial uses of Lake Erie. This report focuses on concentration and loadings information for selected pollutants that are or might be affecting fish, other aquatic life, human health, and ecosystem function. Particular emphasis was placed on analyzing data for polychlorinated biphenyls (PCBs) and mercury. These two pollutants are associated with widespread fish consumption advisories in the basin. Fish consumption advisories are issued to protect human health from the risks associated with ingesting pollutants in fish tissue. The advisories represent an impairment of a beneficial use of the water resources of Lake Erie. Because of widespread fish consumption advisories, mercury and PCBs have been designated as critical pollutants in the Lake Erie Lakewide Management Plan (LaMP).

The information presented in this report includes the physical location of municipal, industrial, and agricultural activities and estimated chemical releases and emissions from these sources. The report also provides data on the concentrations of selected pollutants in tributaries, connecting channels, Lake Erie, aquatic sediments, fish tissue, and atmospheric deposition. A thorough examination of environmental data for point and nonpoint sources, streams, connecting channels, Lake Erie, aquatic sediments, fish, and the atmosphere will provide an understanding of useful data, data gaps, and data limitations for assessing concentrations or loadings.

This report lays the groundwork for establishing the relationship between sources and environmental concentrations and loadings. Concentrations in the environment often reflect proximity to sources, particularly for those pollutants for which local sources are significant relative to long-range transport. Data examined for this report suggest that environmental sources and environmental concentrations of PCBs, mercury, polynuclear aromatic

hydrocarbons, selected pesticides, and nutrients (atrazine, nitrate-nitrogen, and total phosphorus) are closely related geographically. These pollutants are detected in concentrations that are elevated above recommended levels in various parts of the aquatic system-in water, in aquatic sediment, in fish, and in the atmosphere. The data further point to the conclusion that the Lake Erie basin as a whole, and in particular the western portion, is a stressed environment. Concentrations of mercury and PCBs in aquatic sediments in the western portion of the basin are frequently found at levels associated with probable adverse effects on aquatic life.

Of all the Great Lakes, Lake Erie receives the greatest amount of domestic wastewater, totaling more than 7,355,000 cubic meters per day. That amount is equivalent to the amount received by several of the lake's major tributaries. Sewage treatment plants (STPs) are the source of most of the domestic wastewater and represent a potentially important source of pollutants. Typical concentrations of PCBs reported in effluents from STPs across North America range from 0.005 to 0.055 µg/L. Although equivalent data are lacking for the Lake Erie basin, suspected endocrine-disrupting chemicals (EDCs) and pharmaceuticals have been reported in municipal effluents from STPs elsewhere. But STPs also represent a significant line of defense against the discharge of pollutants to the environment. The larger STPs are designed to remove about 90 percent or more of the phosphorus, as required by the Great Lakes Water Quality Agreement. From studies elsewhere in North America, PCB removal efficiencies of STPs can be as high as 97 percent. The industrial pretreatment program in the United States and the municipal sewer-use bylaws in Ontario contribute significantly to minimizing the inputs of pollutants to STPs and the outputs from STPs to receiving waters.

Air emissions are an important source of certain critical pollutants, such as PCBs and mercury, that are delivered to Lake Erie through atmospheric deposition. Because of long-range transport by the atmosphere, there is a need to consider areas beyond the Lake Erie basin as possible source areas. In 1996 most of the mercury and PCB releases in the Lake Erie basin reported by the United States through the Toxics Release Inventory (TRI) database and the mercury releases reported by Canada through the National Pollutant Release Inventory (NPRI) database were to the atmosphere.

As a percentage of total land use, agricultural and urban land uses within the Lake Erie basin are the highest in the Great Lakes basin. Most fertilizers, sediment, and pesticides are discharged to surface waters from nonpoint sources associated with urban and agricultural land use and chemical use. Atrazine and metolachlor are the pesticides used in greatest quantities in the basin, and surface water concentrations reflect their application to row crops. Some agricultural pesticides are suspected EDCs. Several of these suspected EDCs are used in agriculture in the basin, in the upper Midwest, and in areas adjacent to and upwind from Lake Erie.

Available environmental emissions data from point sources and ambient data from tributaries, Lake Erie, connecting channels, sediments, fish tissue, and the atmosphere were obtained and aggregated from databases of monitoring programs designed to describe concentrations and loads. Fourteen major environmental databases representing contributions from 10 national, 10 state and provincial, four binational, and two nongovernmental monitoring programs were examined. Databases evaluated for the United States were STORET, PCS, TRI, OSI, FIELDS, NSI, and USGS. Databases evaluated for Canada were STAR, ENVIRODAT, PWQMN, SRDS, and NPRI. Binational networks evaluated were IADN and MDN.

The results of the analysis of these data collected from 1986 to 1997 indicate that available concentration data for PCBs, organochlorine pesticides, mercury, and polynuclear aromatic hydrocarbon compounds in effluents and surface waters might not be suitable to describe the occurrence and distribution of concentrations or to compute loads. One reason is that the detection limits for concentrations of PCBs, organochlorine pesticides, polynuclear aromatic hydrocarbons, and mercury reported by monitoring programs in the United States and Ontario often are too high to measure the relatively low concentrations of these pollutants found in discharges and in surface waters. PCB concentrations were monitored and reported at 15 facilities in the United States, but only 5 percent of the nearly 1,000 observations were reported above the detection limit. Mercury concentrations were monitored and reported at 21 facilities in Ontario in 1995, but like PCBs, the percentage of observations above the detection limit was too low to assess concentrations and loads. In the United States, 170 point sources reported mercury concentrations, but only 23 percent of the reported observations were above detection limits. Likewise, data for organochlorine compounds, polynuclear aromatic hydrocarbon compounds, and mercury reported by monitoring programs for tributaries in the United States and Ontario-in particular, for mercury and PCBs-did not meet the minimum criteria to characterize concentrations and loads to Lake Erie. Only the atmospheric data from the Integrated Atmospheric Deposition Network were sufficient to estimate loads for trace organics, including PCBs. Data from 1995 to 1998 that are suitable for the computation of mercury deposition from the atmosphere are available from the Mercury Deposition Network (MDN).

Conversely, a large number of samples were collected, analyzed, and reported from many point sources, tributaries, connecting channels, and Lake Erie for total phosphorus, nitrate-nitrogen, and total nonfilterable residue or suspended sediment. Data reported from greater than 90 percent of these samples were well above the detection limits. Basinwide characterizations of concentrations of nitrate-nitrogen, total phosphorus, and total nonfilterable residue in effluents, tributaries, connecting channels, and Lake Erie appear to be possible. Nutrient data for surface waters are potentially suitable to characterize loads.

Although environmental data from point sources and surface waters for most trace organic substances were not suitable for characterizing concentrations or computing loads, other available data may be used in their place for some types of analyses. Near-surface streambed and lakebed sediments can indicate the recent deposition or resuspension of pollutants to the aquatic environment. Fish tissue can help integrate the bioaccumulation of pollutants by aquatic life and the potential for human health impacts. The detection frequency of organochlorine and trace metal pollutants in aquatic sediments is markedly higher than in water or effluents. Pollutants such as PCBs, organochlorine pesticides, polynuclear aromatic hydrocarbons, and mercury that are reported with few or no detections in point source effluents and surface waters are reported at concentrations above detection limits at frequencies of 25 percent or more in aquatic sediments. Bed sediment concentration data examined from 1990 to1997 for the United States and for 1997 by Environment Canada suggest that at many sites in the basin, concentrations of PCBs and mercury in aquatic sediments exceed guidelines associated with potential adverse effects on aquatic life.

The next step is to further characterize and track sources. With source-tracking information, a scientific basis for sound management decisions to reduce or eliminate these sources can be formulated. Many point sources can be identified from the data compiled for this report. Maps of discharge locations, pesticide use, agricultural areas, abandoned landfill sites, and other land uses will be compared to tributary, connecting channel, and lake concentrations, fish tissue concentrations, and aquatic sediment concentrations to identify major source areas and the most highly contaminated areas in the basin. Whether the most contaminated areas and major sources already have been targeted for priority action may be assessed by identifying and crossreferencing implementation and remediation actions already under way. The Lake Erie Areas of Concern have been previously identified as priority areas for source control and remediation. Analyses done to compare the magnitude and extent of contamination in Remedial Action Plan (RAP) areas, can also point out where further action or attention may be needed, whether it be monitoring, additional research, or remediation.

Several efforts independent of the Lake Erie LaMP that may contribute to further identification and remediation of sources are under way. The Binational USEPA/Environment Canada Toxics Reduction Strategy is investigating sources of pollutants of concern to the Great Lakes both within and outside the basin. Several contaminated sediment and landfill remediation projects recently were completed or are under way in the River Raisin, Ashtabula River, and Ottawa River/Maumee Areas of Concern. Another ongoing project of the LaMP is the review of the status of government agency programs for pollution prevention and reduction activities throughout the Lake Erie basin, particularly for mercury and PCBs.

Lake Erie is continuously changing as a result of declines in phosphorus loads, management of toxic pollutants, and the introduction and establishment of exotic species. To better understand pathways of critical pollutants, additional research is needed on changes in food web dynamics and the linkages in energy and flow between the lake bottom and the water column. For example, concentrations in fish have fluctuated over the years, even as loads from the land surface and from point source discharges appear to have decreased. This finding demonstrates that it is important to understand what is happening to the pollutants already in the lake. An analysis must be done of the ambient concentrations of critical pollutants in all media compared to the objectives of Annex 1 of the Great Lakes Water Quality Agreement. Such an analysis would include an assessment of the potential of certain pollutants to cause impairment and would ensure a thorough evaluation of the links between sources of pollutants and the response of the Lake Erie system to these pollutants. Selected data examined for this report could be used for these purposes and to identify the areas in greatest need of restoration.

## Introduction

From the perspective of reducing the presence of persistent toxic substances in Lake Erie, the Great Lakes Water Quality Agreement (GLWQA) suggests that the Problem Definition stage analysis of the Lakewide Management Plan (LaMP) should include the following:

- A definition of the threat posed by critical pollutants to human health or aquatic life, singly or in synergistic or additive combinations with other substances, including their contribution to the impairment of beneficial uses.
- An evaluation of information available on concentrations, sources, and pathways of the critical pollutants in the Great Lakes system, including all information on loadings of the critical pollutants from all sources and an estimation of total loadings of the critical pollutants by modeling or other identified methods.
- Development of information necessary to determine the schedule of load reductions of critical pollutants that would result in meeting Agreement objectives, pursuant to Article VI of the Agreement and including steps to develop the necessary standard approaches and agreed procedures.

As a preliminary step to meeting these requirements, the Sources and Loads Subcommittee (Subcommittee) of the Lake Erie LaMP Work Group was charged with the following:

- Describe the status and trends in concentrations and loads of pollutants that are causing, or have the potential to cause, beneficial use impairments in Lake Erie.
- Identify the major sources and the relative contribution of those sources to the beneficial use impairments.
- Provide a scientific basis for sound management decisions for reducing, removing, and eliminating the pollutants from the Lake Erie system.

• Identify gaps in the information needed to identify the sources and loads, and recommend the monitoring needed to fill the gaps.

This report presents a summary of the data available to address the above charge and provides an assessment of data suitable for developing loading estimates. The potential sources are categorized as either point or nonpoint, and generic descriptions of size, location, and available data by sector are presented. Ambient environmental data, such as concentrations of pollutants in sediment and fish tissue, are briefly described and will be evaluated more fully in the next phase of this project. This assessment covers the entire Lake Erie basin (Figure 1).

The initial list of chemicals selected for review was identified in the beneficial use impairment assessment reports. The chemicals are presented in Table 1 with a summary of conclusions describing impairment in Lake Erie. Of these chemicals, the Lake Erie LaMP Management Committee has designated mercury and PCBs as critical pollutants for priority action.

The Subcommittee developed a list of pollutants and their degradation products designated by a variety of agency programs as being pollutants of concern throughout the Lake Erie basin (Table 2). These pollutants include those listed in Table 1, as well as those with the potential to impair beneficial uses in Lake Erie. This expanded list allows the Subcommittee to begin evaluating information on all pollutants of concern in Lake Erie and to determine the suitability of the data for estimating loads. This report also identifies whether the available data represent a pollutant source or pathway to the Lake Erie ecosystem.

This report presents a detailed analysis of the information available in various databases. It provides an overall view of the Lake Erie basin, highlighting areas where most of the sources are located. It also provides a starting point for the next phase of the process–tracking down the sources.



Figure 1. Lake Erie and its watershed, United States and Canada.

BUI	Causes of Impairment	Impairment Conclusions <sup>a</sup>
Fish and Wildlife Consumption	<i>Fish-</i> PCBs, mercury, lead, chlordane, and dioxins	Impaired for fish
Restrictions	<i>Wildlife-</i> PCBs, chlordane, DDE, DDT, and mirex	Inconclusive for wildlife
Restrictions on Dredging Activities	PCBs and heavy metals	Impaired
Eutrophication or Undesirable Algae	Phosphorus	Impaired in Maumee Bay and lake-effect zones of the Maumee and Ottawa Rivers in Ohio
		<b>Potentially Impaired</b> in lake-effect zones of the Toussaint, Portage, and Sandusky rivers and Turtle and Muddy creeks in Ohio
		<b>Potentially Impaired</b> in lake-effect zones of Old Woman Creek and Vermillion, Rocky Huron, Black, Chagrin, and Cuyahoga rivers in Ohio
		Rondeau Bay, Ontario, 1998-1999 sampling results are expected to provide data for conclusive determination of impairment in the nearshore and river mouths in Ontario.
Recreational Water Quality Impairment	Violations of PAHs, <sup>♭</sup> <i>Escherichia coli,</i> or fecal coliform standards	Impaired

Table 1.	Beneficial	use impairme	ents in the	Lake Erie	basin.
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<sup>a</sup>When a beneficial use impairment is noted for a particular basin, the impairment is occurring somewhere within that basin, not necessarily throughout the entire basin. Details about the location and extent of impairment, where known, are provided in the technical reports (available on request) that support this summary.

<sup>10</sup>PAHs are the basis for a human contact advisory in the Black River, Ohio, Area of Concern but are not the basis for a fish consumption advisory. The human contact advisory issued by the Ohio Department of Health indicates that it is not safe to go into the water in this area.

#### Table 2. Pollutants identified for analysis of sources and loads in the Lake Erie LaMP.

Pollutant(s)	Common Source(s)
Organochlorine insecticides and biocides	
DDT <sup>b,c,d,e,t,h</sup>	Historical use on crops, trace in dicofol.
• DDD, DDE	
Chiordane weblerdene eie neneebler	Historical use on crops and for termite and ant control.
• $\alpha$ -chiordane, $\gamma$ -chiordane, cis-nonachior, trans popachlor	
Dieldrin <sup>b,d,e,f,h</sup>	Historical use on crops, termite and moth control.
Toxaphene <sup>c,d,e,f,h</sup>	Historical use on crops, topical insecticide.
<i>Mirex</i> <sup>c,d,e,t, h</sup>	
Photomirex	Historical use for fire ant control and flame retardant.
α-hexachlorocyclohexane <sup>c,d,e</sup>	Agricultural and topical insecticides.
β-hexachlorocyclohexane <sup>co,e</sup>	
δ-hexachlorocyclohexane <sup>c,u,e</sup>	
γ-nexachlorocyclonexane <sup>-135</sup>	
Industrial organochlorine compounds or by-prod	lucts
PCBs <sup>u,c,u,e,i,ii</sup>	I ransformers, hydraulic fluids, capacitors, heat transfer fluids,
$Diaxin (2.3.7.8-TCDD)^{d,e,f,h}$	Inks, casting waxes.
	preservative, other chlorophenols and derivatives, including
	herbicides.
1,4-dichlorobenzene <sup>d, e</sup>	Mothballs, household deodorants, other biocides.
Pentachlorobenzene <sup>d,e</sup>	Chemical synthesis.
1,2,3,4-tetrachlorobenzene <sup>d,e</sup>	
1,2,3,5-Tetrachiorobenzene	Chloroalkali plante, wood procervatives
Hexachlorobenzene <sup>de,h</sup>	Byproduct of chemical manufacturing historical wood
	preservative and fungicide.
3,3'- Dichlorobenzidine <sup>d,e</sup>	Plastic manufacturing, glues and adhesives, dyes and pigments
	for printing inks.
4,4'-Methylenebis(2-chloroaniline) <sup>0,0</sup>	Plastics, adhesives.
Polynuclear aromatic hydrocarbons (PAHs) <sup>de</sup>	
Anthracene, Benz(a)anthracene	Coal, oil, gas, and coking byproducts, waste incineration, wood
Benzo(a)pyrene, Benzo(b)fluoranthene	and tobacco smoke, and forest fires, engine exhaust, asphalt
Chrysene Eluoranthene Phenanthrene	tars and tar products.
Indeno(123-cd)pvrene	
Trace Metals	
Alkyl lead <sup>d,e,f</sup>	Leaded gasoline.
Cadmium <sup>d,e</sup>	Batteries, pigments, metal coatings, plastics, mining, coal
	burning, metal alloys, rubber, dye, steel production.
Copper	Same as cadmium, plus plumbing and wiring.
Lead	Same as cadmium, plus solder.
ZINC Mercun <sup>c,d,e,f</sup>	Same as caumium, plus roomy. Batteries, coal burning, chloroalkali plants, paints, switches
Mercury	light bulbs, dental material, medical equipment, ore refining.
Tributyl tin <sup>d,e</sup>	Antifouling paint, biocide, plastic stabilizer.
Current-use berbicides <sup>9</sup>	
Atrazine, Cyanazine, Alachlor, Metolachlor	Agricultural herbicides.
Other Pollutante	č
Total phosphorus. Nitrate-nitrogen	Fertilizers and sewage.
Fecal coliform, <i>Escherichia coli</i>	Sewage and animal waste.
Total suspended sediments	Soil erosion.
Dioxin (2,3,7,8-TCDD) <sup>d.e.t.h</sup> 1,4-dichlorobenzene <sup>d.e</sup> Pentachlorobenzene <sup>d.e</sup> 1,2,3,4-tetrachlorobenzene <sup>d.e</sup> 1,2,3,5-tetrachlorobenzene <sup>d.e</sup> Pentachlorophenol <sup>d.e</sup> Hexachlorobenzene <sup>d.e.h</sup> 3,3'- Dichlorobenzidine <sup>d.e</sup> 4,4'-Methylenebis(2-chloroaniline) <sup>d.e</sup> <b>Polynuclear aromatic hydrocarbons (PAHs)</b> <sup>d.e</sup> Anthracene, Benz(a)anthracene Benzo(a)pyrene, Benzo(b)fluoranthene Benzo(k)fluoranthene, Benzo(g,h,i)perylene Chrysene, Fluoranthene, Phenanthrene Indeno(123-cd)pyrene <b>Trace Metals</b> Alkyl lead <sup>d.e.f</sup> Cadmium <sup>d.e</sup> Copper <sup>f</sup> Lead Zinc <sup>f</sup> Mercury <sup>c.d.e.f</sup> Tributyl tin <sup>d.e</sup> <b>Current-use herbicides</b> <sup>g</sup> Atrazine, Cyanazine, Alachlor, Metolachlor <b>Other Pollutants</b> Total phosphorus, Nitrate-nitrogen Fecal coliform, Escherichia coli Total suspended sediments	Combustion byproducts, in pentachlorophenol wood preservative, other chlorophenols and derivatives, including herbicides. Mothballs, household deodorants, other biocides. Chemical synthesis. Chloroalkali plants, wood preservatives. Byproduct of chemical manufacturing, historical wood preservative and fungicide. Plastic manufacturing, glues and adhesives, dyes and pigments for printing inks. Plastics, adhesives. Coal, oil, gas, and coking byproducts, waste incineration, wood and tobacco smoke, and forest fires, engine exhaust, asphalt tars and tar products. Leaded gasoline. Batteries, pigments, metal coatings, plastics, mining, coal burning, metal alloys, rubber, dye, steel production. Same as cadmium, plus plumbing and wiring. Same as cadmium, plus roofing. Batteries, coal burning, chloroalkali plants, paints, switches, light bulbs, dental material, medical equipment, ore refining. Antifouling paint, biocide, plastic stabilizer. Agricultural herbicides. Fertilizers and sewage. Sewage and animal waste. Soil erosion.

<sup>a</sup>Pollutants indented are degradation products; those shown in italics have been identified as chemicals of concern. <sup>b</sup>Lake Erie Chemicals of Concern identified by Lake Erie LaMP in 1994. <sup>c</sup>Great Lakes Initiative Bioaccumulative Chemical of Concern (BCC). <sup>d</sup>COA-Tier 1 or tier 2. <sup>e</sup>Binational Toxics Strategy. <sup>f</sup>Identified by the IJC or in Remedial Action Plans. <sup>e</sup>USEPA. <sup>b</sup>Canadian Toxic Substance Management Policy-Track 1.

## **Characterization of Sources and Source Data**

Many pollutant sources threaten or potentially threaten aquatic resources and human health in the Lake Erie basin. A description of what is known about point and nonpoint sources within the basin is needed. By focusing on broad categories of pollutant sources as the first step of the process, a better understanding of available data, data gaps, and data limitations can be developed. The remainder of this section describes the pollutant sources and the data that might be used to characterize concentrations and to compute loads for the pollutants responsible for beneficial use impairments.

Not all the pollutants of concern (Table 2) are discussed in this section or in other sections of the report. The pollutants inventoried herein were selected for data characterization because they are typical of their chemical classes with regard to the number of results reported, collection locations, collection and analysis methods, detection and reporting limits, frequency of sampling, and period of record of sampling. PCBs, DDT and its degradates, chlordane, and mirex were selected to represent toxic and bioaccumulative organochlorine compounds. Benzo(a)pyrene was selected to represent a persistent, toxic, and carcinogenic polynuclear aromatic hydrocarbon (PAH) compound. Mercury and lead were selected to represent toxic and persistent trace metals. Total phosphorus and nitrate-nitrogen were selected to represent nutrients and fertilizers. Atrazine was selected to represent the classes of commonly used herbicides. Suspended sediment represents land and/or stream habitat disturbance. Total nonfilterable residue represents particulate materials discharged from sewage that can exert an oxygen demand on receiving waters. Fecal coliform bacteria and Escherichia coli are intestinal bacteria that represent the microbiological pollutants in wastes from humans and warm-blooded animals. Loads are not usually

computed for fecal bacteria because concentrations are more appropriate.

# Point Sources Discharging to Surface Water

In this document, point sources are defined as sources where pollutants are discharged from a pipe or at a point. These sources are regulated to control the concentrations and loads discharged to surface waters and include

- Municipal wastewater
- Industrial wastewater
- Combined storm water and sewer overflows

#### Domestic Wastewater

Of all the Great Lakes, Lake Erie has the highest discharge volume of domestic wastewater (Figure 2). Sewage treatment plants (STPs) receive human sewage, industrial effluents, and in some cases storm water combined with sewage. STPs remove approximately 90 percent of conventional pollutants such as phosphorus, suspended solids, and biochemical oxygen demand (BOD). By removing suspended solids, the treatment process also removes toxic pollutants that have an affinity for particles. For example, the larger STPs precipitate phosphorus using metal salts, as required under the Great Lakes Water Quality Agreement. This practice enhances the precipitation of solids and fine colloidal particles and benefits water quality by increasing removal efficiencies for absorbed

Sewage Treatment Discharge Volumes (m³/day)		
Indiana		
Michigan		
New York		
Ohio		
Pennsylvania		
Ontario		
Total	7,355,000	



Figure 2. Location and range of average flows of sewage treatment plants in the Lake Erie basin.

pollutants (Daigger and Buttz, 1992; Monteith, 1987). Nevertheless, STPs do not remove 100 percent of the pollutants.

Although STPs represent a potentially significant source of pollutants, they also represent a significant line of defense against the discharge of pollutants to the environment from domestic and industrial wastewater. For example, in Ontario approximately 12,000 industries discharge to STPs, but only 400 industries discharge their treated wastewater directly to surface waters (Monteith, 1987). Industrial discharges are not the only source of trace pollutants in waste streams received by STPs. Society's use and disposal of chemicals results in pollutants in urban waste streams, even from unlikely places. Dioxins, for example, have been found in laundry wastewater and consequently have been observed in STP effluents. A study of household sewage found dioxin concentrations of 0.014 µg/L (Horstmann and McLachlan, 1995). Dioxins have not been reported in STP effluents in the Lake Erie basin (Tam and Diamond, in press), and it is not suggested that laundry wastewater or even STPs are a significant source of dioxin. This finding simply illustrates that urban waste streams are complex and require a number of different strategies to optimize their treatment to protect the Great Lakes. Municipal/industrial programs such as industrial pretreatment and municipal sewer use by laws contribute significantly to minimizing the input of pollutants to municipal wastewater plants. In Ontario, "optimization" of the treatment process has resulted in improved treatment efficiency without modification of the existing facilities and at reduced operating costs.

The presence of PCBs, a Lake Erie critical pollutant, is of particular concern. Monteith (1987) reported PCB concentrations in sewage effluent ranging from  $0.005 \,\mu$ g/L to  $0.030 \,\mu$ g/L. That range has been confirmed by more recent studies in New York, New Jersey, and Delaware, where the reported concentration was 0.010 to 0.055  $\mu$ g/L (Durell and Lizotte, 1998; Fikslin and

Greene, 1998). Reductions in PCB concentrations at STPs from influent to effluent were as high as 97 percent, with an influent concentration range of 0.050 to  $1.5 \mu g/L$ . STPs are not the original sources of PCBs or dioxins–rather, they act as conduits for PCBs or dioxins inadvertently or deliberately introduced into sewage collection systems.

Monteith (1987) summarized the trace concentrations in sewage effluents from various Canadian and U.S. sources (Table 3). Table 3 also illustrates the range of reported concentrations found in sewage sludge (note the difference in concentration units). The implications of the higher concentrations in the sludge are twofold. First, they are an indication of the higher concentration of the pollutants in the influent and removal effected by treatment. Second, the sludge must be discarded and therefore is another possible source from domestic wastewater.

Endocrine-disrupting chemicals (EDCs) and pharmaceutical chemicals in the environment and wastewater have recently attracted worldwide attention. STPs receive and ultimately discharge many of these chemicals. For example, sewage treatment discharge impact zones have been identified using vitamin E acetate as a tracer (Eganhouse, R.P. and I.R. Kaplan, 1985). Caffeine has also been used as an indicator of contamination by wastewaters (Barber et al., 1995). Studies downstream of sewage treatment plants have detected EDC effects in fish populations (Folmar et al., 1996). Nonylphenol, a reported EDC, and its metabolites have been observed in sewage effluent at concentrations ranging from 1 to 15 µg/L (Lee and Peart, 1995) and from 3 to  $700 \,\mu\text{g/L}$  (Lee et al., 1998), respectively. Although data are not available to address these concerns in the Lake Erie basin, broad scans have detected 30 to 60 pharmaceuticals in both treated water and rivers in Germany (Ternes, in press). These are but a few examples to illustrate that wastewater can contain chemicals such as drugs and EDCs.

	Effluent Concentration	Sludge Concentration
Pollutant	(μg/L or ppb)	(mg/kg or ppm)
$\alpha$ -hexachlorocyclohexane	nd-0.092	nd
$\gamma$ -hexachlorocyclohexane	nd–0.23	0.05–27
p,p <sup>1</sup> -DDE	nd–0.03	nd
PCBs	0.005–0.030	0.11–844
Dieldrin	nd-0.02	0.05–0.81
Naphthalene	nd-47	0.06–159
Fluorene	nd-1.0	0.009–98
Phenanthrene	nd–3	0.1–593
Anthracene	0.5–1.2	0.1–114
Fluoranthene	nd–0.61	0.35–232
Pyrene	nd–0.8	0.33–171
Benz(a)anthracene	nd-1.0	0.79–33
Chrysene	nd-1.0	0.25–39
Benzo(k)fluoranthene	nd-3.0	0.63–43
Benzo(b)fluoranthene	nd-3.0	Not reported
Benzo(a)pyrene	nd–0.62	nd–28
Cadmium	0.0004–20	0.5–320
Copper	10–340	60–5200
Mercury	nd-0.9	0.037–130
Lead	nd–180	11–1440
Zinc	23–1775	22-13000

Table 3.	Reported concentration ranges of selected Lake Erie pollutants of concern in sewage effluent
	and sludge.

Note: nd, not detected.

#### Industrial Wastewater

The industrial sector, drawn to the region by the abundant water supply in the lakes, has concentrated in steel production, food processing, petroleum refining, chemicals and allied products, and paper. Figures 3 to 6 illustrate the extent of the industries in the basin, showing the locations of facilities in primary metal, fabricated metal, and transportation equipment; petroleum refining and chemicals; paper; and electric, gas, and sanitary services, respectively.

Figure 7 illustrates the releases of EDCs to the environment from the industrial sector in the eight Great Lake states and the province of Ontario, using data reported in the 1996 U.S. Toxics Release Inventory (TRI) and Canadian National Pollutant Release Inventory (NPRI) databases. The EDCs included in Figure 7 are presented in Appendix A. Significant quantities of suspected EDCs are released into the environment in and upwind of the basin. Most of the industrial releases are air emissions, which are discussed in a later section. It is interesting to note that 40 percent of the EDCs are also Lake Erie Sources and Loads chemicals of concern (Table 2).

Industrial discharges include a broad range of wastewater produced by various industries (e.g., chemical manufacturers, pulp and paper mills, steam-electric power plants, iron and steel manufacturing facilities), which usually use treatment processes designed specifically for their wastewater.



Figure 3. Locations of primary metal, fabricated metal, and transportation facilities in the Lake Erie Basin.



Figure 4. Locations of petroleum and chemical facilities in the Lake Erie Basin.



Figure 5. Locations of paper facilities in the Lake Erie Basin.



Figure 6. Locations of electric, gas, and sanitary service facilities in the Lake Erie Basin.



Figure 7. Suspected endocrine-disrupting chemical releases, from the 1996 TRI and NPRI. (The chemicals included are listed in Appendix A.)

Industrial wastewater treatment may be similar to that used in municipal systems or may consist of a wide variety of other treatment technologies.

#### Stormwater and Sewer Overflows

As various activities alter the watershed landscape, adverse impacts on receiving waters may result from changes in the quantity and quality of storm water runoff. The magnitude and types of pollutants associated with storm water runoff are based largely on land use characteristics, as well as atmospheric transport, and they vary with the duration and intensity of rainfall events and their antecedent dry weather periods. Table 4 illustrates the range of reported concentrations of pollutants in storm water from various studies throughout North America (Makepeace et al., 1995). Besides chemical pollutants, other characteristics of storm water causing environmental concerns include high runoff flows (hydraulic loading), suspended solids (which cause physical impacts and interfere with water quality processes), fecal bacteria (which affect recreational waters), and heat collected on impervious surfaces. In the United States, current Phase I regulations under Section 402 of the Clean Water Act require National Pollutant Discharge Elimination System (NPDES) storm water permits for the following categories:

- Storm water discharges associated with industrial activity.
- Storm water discharges from construction sites that disturb 5 acres or more.
- Discharges from municipal separate storm sewers from cities with populations of more than 100,000.

Additional regulations currently under development will be issued in 1999. The Phase II NPDES storm water program will focus on separate storm sewer systems in smaller municipalities and construction activities on 1 to 5 acres.

In Ontario, discharges to storm water sewers also have allowable limits defined in the Provincial Model Sewer Use Bylaw. Discharges to storm water sewers may not include PCBs or pesticides. The limit for mercury discharges to storm water sewers is  $1 \mu g/L$ .

A combined sewer overflow (CSO), by design and by function, carries both sanitary sewage and storm water. During dry weather, these systems should carry all sanitary flows to the STP for treatment as specified in the NPDES permit. Discharges of CSOs during dry weather are prohibited. During periods of rainfall or snowmelt, the sewer carrying capacity can be exceeded, causing an overflow at relief points in the sewer system. These relief points are often designed into the sewer system to prevent basement flooding or overloading of the wastewater treatment facilities. CSOs should not be confused with sanitary sewer overflows (SSOs), which occur

Table 4. Concentration ranges of selected Lake Erie pollutants of concern in storm water.

Pollutant	Concentration (µg/L)
Naphthalene	0.036-2.3
Fluorene	0.096-1.0
Phenanthrene	0.045-10.0
Anthracene	0.009–10.0
Fluoranthene	0.03–56.0
Pyrene	0.045-10.0
Benzo(a)anthracene	0.0003-10.0
Chrysene	0.0038-10.0
Benzo(b)fluoranthene	0.0012-10.0
Benzo(a)pyrene	0.0025-10.0
$\alpha$ - hexachlorocyclohexane	0.0027-0.1
γ- hexachlorocyclohexane	0.052–11.0
p,p'-DDE	nd–0.015
Dieldrin	0.005–0.1
Cadmium	0.05-13,730
Copper	0.06-1,410
Mercury	0.05-67.0
Lead	0.57-26,000
Zinc	0.7–22,000
PCBs	0.03–11

Note: nd, not detected.

when sanitary sewage is diluted by storm water infiltrating into sanitary sewers during heavy rains. Though CSOs are not subject to secondary treatment requirements at the end of the pipe, they must not cause a violation in water quality-based standards in receiving waters. The quality of CSO discharge water can vary significantly depending on the area drained and rainstorm characteristics. Pollutants commonly found in CSO discharges include suspended solids, BOD, chemical oxygen demand (COD), nutrients (including ammonia), fecal bacteria, metals, hydrocarbons, PAHs, and other toxic pollutants.

#### Point Source Discharge or Release Data

Municipal and industrial point source dischargers to surface waters (Figure 8) may be required to report selected specific chemical loadings, and these data are subsequently entered into the Permit Compliance System (PCS) in the United States and the Sample Results Data Store (SRDS) in Ontario. Estimated emissions for various chemicals are reported in TRI in the United States and NPRI in Ontario. Air emissions of some toxics are also reported in the Regional Air Pollution Inventory Database System (RAPIDS).

The NPDES program in the United States and the Municipal-Industrial Strategy for Abatement (MISA) program in Ontario regulate the discharges from the municipal and industrial sectors. Data from NPDES reports submitted to EPA or the states by dischargers are stored in PCS. Data from MISA reports submitted to the Ontario Ministry of Environment (MOE) are stored in SRDS. The NPDES and MISA programs establish discharge limits and monitoring requirements intended to control the magnitude of discharges to water bodies. Whether a facility is required to obtain an NPDES permit depends on where the facility discharges. In general, if the facility discharges into the waters of the United States, it requires an NPDES permit. If the discharge enters a municipal sanitary sewer

system, it might not require an NPDES permit, but if the discharge is into a municipal storm sewer system, the plant might need a permit, depending on what it discharges.

The permits issued under the NPDES and MISA programs establish monitoring and reporting requirements for concentrations and/or loads of pollutants for each permitted discharge point. The major dischargers, defined by EPA as those that discharge more than 1 million gallons per day or that have a significant environmental impact, are required to monitor more frequently than smaller dischargers. For most facilities, information on the analytical detection limits for the monitored pollutants is not included in PCS. However, maximum detection limits are specified in Method 625 as required in 40 CFR Part 136 and MOE's MISA requirements (Table 5). In the United States, detection limits are modified as permits are reviewed, making it difficult to characterize the available information. As the Great Lakes Initiative (GLI) program is implemented, detection limits will become much lower. For example, New York currently uses  $0.065 \,\mu\text{g/L}$  as the detection limit for PCBs, and according to Foran (1991), both Ohio's and Michigan's detection limit for PCBs was 0.1 µg/L at the time of that report. All dischargers in the United States must follow EPA methods for sample collection and analysis, and all dischargers in Ontario must follow MISA requirements, which specify certain detection limits. Specific detection or reporting limit information is available only through review of each facility's discharge monitoring reports. These reports were not reviewed because the magnitude of such an effort is beyond the scope of this document.

The basis for the selection criteria used to screen data from PCS and SRDS is included in Appendix B. These criteria recommend that the minimum number of observations needed to characterize concentrations of pollutants discharged from point sources is 10. However, if data are censored (reported below detection), 25 to 50 percent or more of the observations should be



Figure 8. Locations of facilities that have regulated discharges in the Lake Erie Basin.

	All values in micrograms per liter		
Pollutant	SRDS <sup>a</sup>	PCS <sup>▶</sup>	
Acenaphthene	1.3	1.9	
Acenaphthylene	1.4	3.5	
Anthracene	1.2	1.9	
Benz(a)anthracene	0.5	7.8	
Benzo(a)pyrene	0.6	2.5	
Benzo(b)fluoranthene	0.7	4.8	
Benzo(g,h,i)perylene	0.7	4.1	
Benzo(k)fluoranthene	0.7	2.5	
Chrysene	0.3	2.5	
Dibenzo(a,h)anthracene	1.3	2.5	
Fluoranthene	0.4	2.2	
Fluorene	1.7	1.9	
Indeno(1,2,3-cd)pyrene	1.3	3.7	
Naphthalene	1.6	1.6	
Phenanthrene	0.4	5.4	
Pyrene	0.4	1.9	
PCBs	0.1	30-36°	
Chlordane	nr <sup>e</sup>	0.014 <sup>d</sup>	
p,p' DDT	nr <sup>e</sup>	4.7	
p,p' DDE	nr <sup>e</sup>	5.6	
p,p' DDD	nr <sup>e</sup>	2.8	
Dieldrin	nr <sup>e</sup>	2.5	
Mirex	nr <sup>e</sup>	nr <sup>e</sup>	
Dioxin (2,3,7,8-TCCD)	0.0039	0.002	
Mercury	0.1	0.2 <sup>e</sup>	
Lead	30	100 <sup>f</sup>	

Table 5. Rec	uired minimum ana	vtical detection limits rep	ported in SRDS and PCS databases
	4		

<sup>a</sup>1998 Ontario MISA municipal regulations.

<sup>b</sup> Federal Register, 1984, Guidelines establishing test procedures for the analysis of pollutants under the Clean Water Act; final rule and interim final rule and proposed rule: Part VIII, 40 CFR Part 136.

<sup>°</sup>Ohio's and Michigan's detection limit for PCBs was 0.1µg/L in 1991 (Foran, 1991). New York's detection limit for PCBs is 0.065 µg/L.

<sup>4</sup>Ämerican Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1985, pp. 538-549.

°nr, none reported.

<sup>1</sup>USEPA, 1979, pp. 239.1 and 245.1.

reported above the detection limit. The minimum criteria established to compute loads discharged from point sources were at least 25 percent of the observations above the detection limit. Dischargers are required to report discharge volume along with concentrations so this criterion was met for major dischargers that reported data (Figures 2 and 8).

In reviewing the detection limits used in PCS and MISA, it is worth noting that some of the detection limits are similar, but in general the provincial detection limits are lower. Unfortunately, PCB detection limits are too high in either database to characterize concentrations or to measure the PCB load from sewage treatment plants. The effluents from sewage treatment plants typically contain PCB concentrations from 0.005 to  $0.03 \mu g/L$ . Note that the detection limits required in PCS were established almost 20 years ago. With advances in analytical chemistry, lower detection limits are possible.

PCS data reported by dischargers in the United States from 1986 to 1997 are summarized in Table 6. For Ontario, data included in the 1995 SRDS are summarized in Table 7. The United States regulated mercury at 170 facilities from 1986 to 1997; no detections were found at 77 percent of 7,664 observations (Table 6). An examination of the mercury concentration data reported for Ontario in 1995 shows that only 18 of the 143 observations, or 12.6 percent, were above detection, not sufficient to characterize concentrations or to compute loads (Table 7). These data could be used for source track-down because 12 of the 18 observations above detection came from one facility. For PCBs, the number of observations above the detection limit ranged from 0 to 5 percent for Ontario and the United States, respectively. Similar patterns were observed for other pollutants representing classes of organochlorine compounds and for PAHs. Conversely, concentration data reported in PCS and SRDS for lead, total phosphorus, nitrate-nitrogen, and total nonfilterable residue appeared to be suitable for preliminary

assessment of concentrations and loads to Lake Erie. Data for fecal coliform bacteria and E. coli in PCS appear to be suitable to characterize concentrations, and because they are reported for many locations they are suitable for further assessment. Figures 9 through 12 present the point source discharge locations for facilities regulated to report discharges of benzo(a)pyrene, mercury, PCBs, and total phosphorus. Of the three pollutants, only total phosphorus is widely reported across the basin.

#### **Toxics Emission Data**

Two databases provide most of the data used to report releases of hazardous and toxic chemicals. The TRI contains information on toxic chemicals

Pollutant class	Pollutant	Number of Facilities	Number of Observations	Percent Above Reporting Limit
Organochlorine	DDT	3	127	2
Compounds	Mirex	0	0	0
	Dioxin	1	94	0
	Chlordane	0	0	0
	PCBs	15	926	5
Polynuclear Aromatic	Anthracene	0	0	0
Hydrocarbons	Benz(a)anthracene	2	18	0
	Benzo(a)pyrene	5	59	7
	Benzo(b)fluoranthene	0	0	0
	Benzo(k)fluoranthene	0	0	0
	Benzo(g,h,i)perylene	0	0	0
	Chrysene	2	18	0
	Indeno(123-cd)pyrene	0	0	0
	Fluoranthene	3	260	0
Trace Metals	Mercury	170	7,664	23
	Lead	214	11,522	40
Other Pollutants	Total phosphorus	591	47,609	74
	Nitrate-nitrogen	153	9,883	92
	Fecal coliform bacteria	388	17,234	72
	Escherichia coli	93	1,994	75
	Total nonfilterable residue	945	98,523	70

 Table 6.
 Pollutant class, pollutant, number of reporting facilities, number of observations, and percent of samples reported above the detection limit, Lake Erie basin in the United States; 1986-1997.

		Number of	Number of	Percent Above
Pollutant Class	Pollutant	Facilities	Observations	Limit
Organochlorine	DDT	0	0	0
Compounds	Mirex	0	0	0
	Dioxin	17	62	1.6
	Chlordane	0	0	0
	PCBs	15	37	0
Polynuclear aromatic	Anthracene	19	43	0
hydrocarbons	Benz(a)anthracene	13	35	0
	Benzo(a)pyrene	19	69	0
	Benzo(b)fluoranthene	13	35	0
	Benzo(k)fluoranthene	13	35	0
	Benzo(g,h,i)perylene	19	43	0
	Chrysene	19	43	0
	Indeno(123-cd)pyrene	19	43	0
	Fluoranthene	19	43	0
Trace Metals	Mercury and its compounds	21	143	12.6
	Lead and its compounds	17	1,514	73.2
Other Pollutants	Total phosphorus	31	1,530	83
	Nitrate-nitrogen (in solution, $pH \ge 6.0$ )	13	41	73
	Fecal coliform bacteria	1	8	25
	Escherichia coli	1	30	47
	Total nonfilterable residue	40	7,372	83.9

 Table 7.
 Pollutant class, pollutant, number of reporting facilities, number of observations, and percent of samples reported above the detection limit, Lake Erie basin in Ontario, 1995.

that are being used, manufactured, treated, transported, or released into the environment. Section 313 of the Emergency Planning and Community Right-To-Know Act and Section 6607 of the Pollution Prevention Act mandate that this information be publicly accessible. The data contained in TRI include more than 600 chemicals and can illustrate the locations of potential sources of pollutants. Any facility listed in Standard Industrial Classification (SIC) code 20 to 39 with more than 10 full-time employees that manufactures or uses 25,000 lb/yr or more or otherwise uses 10,000 lb/yr or more of any one TRI chemical is required to participate in the system. The TRI data represent estimated releases rather than measured concentrations or loads. Because TRI data include direct and indirect releases, the same facilities sometimes report to both TRI and PCS. All of the data reported in PCS, however, represent measured values.

NPRI provides information on the on-site Canadian releases to air, water, and land; transfers off-site in wastes; and recovery, reuse, and recycling (3Rs) of 176 listed substances. The NPRI is the only legislated, nationwide, publicly accessible inventory of releases and transfers in Canada. Facilities that manufacture, process, and/or use any of the NPRI-listed substances in quantities of 10,000 kg (22,000 lb) or more per year in a concentration equal to or greater than 1 percent and that employ 10 or more



Figure 9. Facilities that monitor for benzo(a)pyrene in the Lake Erie Basin.



Figure 10. Facilities that monitor for mercury in the Lake Erie Basin.



Figure 11. Facilities that monitor for PCBs in the Lake Erie Basin.



Figure 12. Facilities that monitor for total phosphorus in the Lake Erie Basin.

people per year will meet all NPRI reporting criteria and must report any releases or transfers in wastes of those substances to Environment Canada. The TRI and NPRI databases were queried for releases for the 1996 reporting year. Table 8 illustrates whether the pollutants of concern are included in TRI and NPRI. Table 9 summarizes reported releases in 1996 for all chemicals to water, air, and land from the eight Great Lake states and the province of Ontario. The top 25 chemicals released into the environment from major industries in the Great Lakes states as reported in the 1996 TRI and in Ontario as reported in the 1996 NPRI are presented in Tables 10 and 11, respectively. The TRI and NPRI programs only partially cover the chemicals of interest to the

LaMP. Mercury is included in both programs, but PCBs are included only in TRI.

The significant releases to air justify the need to be aware of sources outside the Lake Erie watershed specifically. The emissions from the eight Great Lakes states and the province have been obtained and analyzed at this time. Subsequent analysis may extend to a broader geographical area. Other programs such as the Great Lakes Binational Toxics Strategy and the North American Regional Action Plan developed by the North American Commission for Environmental Cooperation are dealing with emissions from outside as well as within the Great Lakes basin. The Lake Erie LaMP Sources and Loadings activities will need to reflect these other programs.

Pollutant	TRI	NPRI
DDT, Chlordane, Dieldrin, Mirex	No	No
$\alpha$ -hexachlorocyclohexane	Yes	No
γ-hexachlorocyclohexane (Lindane)	Yes	No
Polychlorinated biphenyls	Yes	No
Dioxin	No	No
Hexachlorobenzene	Yes	No
Octachlorostyrene	No	No
Anthracene	Yes	Yes
Other PAHs <sup>a</sup>	Yes	No
Phenanthrene	Yes	No
Cadmium (and its compounds)	Yes	Yes
Copper (and its compounds)	Yes	Yes
Lead (and its compounds)	Yes	Yes
Mercury (and its compounds)	Yes	Yes
Zinc (and its compounds)	Yes	Yes
Total phosphorus, nitrate (in solution at $pH \ge 6.0$ )	Yes	Yes
Fecal coliform, <i>Escherichia coli</i>	No	No
Suspended solids	No	No
Atrazine, Cyanazine	Yes	No
Metolachlor, Alachlor	No	No

Table 8. Lake Erie LaMP pollutants of concern reported in the TRI and NPRI inventories, 1996.

<sup>a</sup>Other PAHs include benz(a)anthracene, benzo(a)pyrene, benzo(k)fluoranthene, benzo(g,h,i)perylene, chrysene, dibenzo(a,h)anthracene, fluoranthene, and indeno(1,2,3-cd)pyrene.

Table 9.	Fotal releases of chemicals in eight Great Lakes states and Ontario, from the 1996 TRI and NPR
	databases.

	Releases to Water (kg)	Releases to Air (kg)	Releases to Landfills (kg)
TRI	20 X 10 <sup>6</sup>	160 X 10 <sup>6</sup>	31 X 10 <sup>6</sup>
NPRI	4.4 X 10 <sup>6</sup>	48 X 10 <sup>6</sup>	3.8 X 10 <sup>6</sup>
# Table 10. Top 25 chemicals released into the<br/>environment in 1996 reported in TRI<br/>(total for eight Great Lakes states)

	Released
Chemical	(kg)
Toluene	18,994,350
Nitrate (in solution at pH > 6.0)	17,437,917
Ammonia (total)	16,190,209
Zinc (and its compounds)	16,075,928
Xylene (mixed isomers)	14,661,397
Methanol	12,841,244
Manganese (and its compounds)	11,881,982
Hydrochloric acid aerosols	9,990,413
n-Hexane	9,046,862
Dichloromethane	8,802,883
Methyl ethyl ketone	8,357,169
Glycol ethers	7,916,449
Styrene	6,285,163
Trichloroethylene	5,189,565
Carbon disulfide	4,355,631
n-butyl alcohol	3,706,122
Methyl isobutyl ketone	3,625,136
Carbonyl sulfide	3,004,472
Sulfuric acid aerosols	2,368,900
Phenol	1,849,658
Ethylene	1,586,130
Chromium	1,574,211
Ethylbenzene	1,517,932
Tetrachloroethylene	1,331,188
Formaldehyde	1,265,953

In 1996 the Great Lakes states reported releases of 1,472 kg of mercury from 15 facilities and 116 kg of PCBs from three facilities, virtually all released to the air. In 1996 the NPRI reported releases of 1,206 kg of mercury from two facilities, most released to the atmosphere. Only 4 pollutants of concern in Lake Erie rank among the top 25 pollutants released to the environment in the Great Lakes region. In the 1996 TRI, nitrate ranked 2nd and zinc ranked 4th (Table 10); in the 1996 NPRI, nitrate ranked 9th, zinc ranked 14th, copper ranked 22nd, and nickel ranked 25th (Table 11).

# Table 11. The top 25 chemicals released into the<br/>environment in 1996 reported in NPRI<br/>(total for Ontario)

	Released
Chemical	(kg)
Ammonia (total)	7,579,616
Xylene (mixed isomers)	5,127,102
Sulfuric acid	4,622,876
Hydrochloric acid	4,296,318
Toluene	4,256,816
Methanol	3,729,681
Methyl ethyl ketone	3,677,901
Cyclohexane	2,842,599
Nitrate (in solution at pH > 6.0)	1,637,687
Dichloromethane	1,611,506
Isopropyl alcohol	1,500,468
Benzene	1,409,562
Ethylene glycol	1,304,933
Zinc (and its compounds)	1,164,354
Acetone	1,105,827
n-Butyl alcohol	981,436
Ethylene	966,673
Trichloroethylene	778,310
Manganese (and its compounds)	710,330
Methyl isobutyl ketone	679,642
Chloromethane	648,505
Copper (and its compounds)	539,104
Propylene	496,793
Ethylbenzene	474,899
Nickel (and its compounds)	383,564

#### **Nonpoint Sources**

Nonpoint sources, as defined in this document, are those sources for which the discharge of a pollutant into the environment is diffuse and therefore difficult to quantify and control. The NPS pollutants of concern for the Sources and Loadings Subcommittee are nitrogen, phosphorus, sediment, atrazine, cyanazine, alachlor, and metolachlor. The nonpoint sources described in this document include agriculture and abandoned solid waste and hazardous waste landfills.

#### Agriculture

Unlike pollutants from municipal and industrial facilities that discharge directly to surface waters, agricultural chemicals applied to the land surface normally do not pose a significant or an immediate threat to surface waters unless they are washed off during storm events. Once agricultural chemicals have been applied to the land surface, their ultimate environmental fate is decided by several factors, including the method of application, the time elapsed from application, the physical and chemical properties of the chemicals, and the physical characteristics of the land on which the chemicals were applied.

The Lake Erie basin in the United States includes parts of 64 different counties in Indiana, Michigan, New York, Pennsylvania, and Ohio. Excluding New York, 3.3 million hectares (8.2 million acres) of crops were planted. Most of the agricultural land use is in the western part of the basin. In 1995, 41 percent of the acreage was planted in soybeans and 32.5 percent in field corn. Other significant crops included wheat (14.9 percent), hay (9 percent), and oats (1.3 percent). In the Ontario portion of the Lake Erie watershed, Statistics Canada reported that agricultural crops were cultivated on 1,397,020 hectares (3,446,448 acres) of land in 1991 (from a 1994 report, Human Activities and the Environment). Of that land, 791,690 hectares (1,953,099 acres) were wide-row monoculture crops like corn, soybeans, vegetables, and tobacco, which require more pesticides and fertilizers and, depending on the tillage regime, are subject to higher rates of erosion than close-row crops like wheat.

# Ontario Municipal Discharges of Phosphorus (kg) Compared to Agricultural Application<sup>a</sup>

	<u>Municipal</u>	<u>Agricultural</u>
Phosphorus	215,000	70,316,000
Nitrogen	3,225,000	136,000,000

<sup>a</sup>Total nitrogen discharges based on a 15:1 ratio between nitrogen and phosphorus in sewage effluent.

Pesticide use in the U.S. portion of the Lake Erie basin for 1992 totaled 3.75 million kg (8,280,250 lb), which is very high compared to the rest of the Great Lakes basin (Gianessi and Anderson, 1995a-h). According to a pesticide use survey conducted every 5 years by the Ontario Ministry of Agriculture, Food, and Rural Affairs, 3.80 million kg (8.36 million lb) of pesticides were used in the Ontario portion of the watershed in 1993 (OMAFRA, 1993).

Atrazine use by county is presented in Figure 13. The concentrations of atrazine in the Great Lakes reflect their proximity to application (Figure 14). Many agricultural pesticides are suspected EDCs. Figure 15 illustrates the application of suspected EDCs within the Great Lakes states and the province of Ontario in 1993. As with the TRI and NPRI EDC release distribution, many suspected EDCs are used in and upwind of the Lake Erie basin.

Agricultural nonpoint sources also can generate large bacterial loads during individual runoffproducing events. For agricultural lands, the most significant sources of bacteria are animal operations, where large quantities of fecal matter are generated, stored, and land-applied.

The major pollutants associated with agriculture are nutrients (primarily nitrogen and phosphorus), sediment, pesticides, and when animals are present, bacteria or other pathogens. From 0.1 percent to 10 percent of agricultural pesticides enter the aqueous environment after application (Larson et al., 1997). For streams, nitrogen yields in agricultural areas were less than or equal to about half of the total nonpoint inputs of nitrogen from the atmosphere, commercial fertilizer, and manure. Phosphorus yields were less than or equal to about one-sixth of the total phosphorus inputs from commercial fertilizer and manure (Fuhrer et al., 1999).

In general, the agricultural chemicals identified as pollutants of concern in the Lake Erie LaMP enter surface waters as a result of runoff-producing storms that occur after application in the spring and



Figure 13. 1993 atrazine use in Great Lakes Region





Canadian Atrazine Guideline for Protection of Aquatic Life = 2000 ng/L; and for Drinking Water = 5000 ng/L.

WTP data from 1993 MOEE DWS Program. MOEE tributary data from 1992 (Thames) and 1993 (Grand & Saugeen) MOEE PWQMN Program.

Niagara River average of Environment Canada 1992 and 1993 data. Open lake surveillance data from Environment Canada (Erie) and Schottler and Eisenreich (1994) (Huron, Erie and Ontario).

US tributary data from Richards and Baker (1993).

#### Figure 14. Atrazine concentrations in the lower lakes: 1992-1993.



Figure 15. Suspected endocrine-disrupting chemicals used in agriculture in 1993.

summer or from improper application or disposal. Of the agricultural chemicals included in the LaMP, nitrogen and phosphorus are most commonly used in the basin. The pesticide DDT and its derivatives, mirex, and chlordane are no longer used, and the effects associated with these pollutants can be classified as "legacy" effects; that is, the impairments observed today are the results of past practices. The chemicals have accumulated in bed sediments and wildlife to a degree that is difficult to characterize or mitigate.

Conservation tillage is an agricultural best management practice that reduces erosion from row crops like corn and soybeans. Erosion takes place when raindrops strike cultivated, bare soil and dislodge soil particles, which are subsequently carried by overland runoff to streams and lakes. Conservation

tillage maintains 30 percent or greater ground cover on current-year fields using the residue from the previous year's crop. Tillage is greatly reduced or not practiced in this form of cultivation. In northwestern Ohio from 1988 to 1997, conservation tillage increased on corn and soybean fields from about 10 percent to 54 percent as a result of intensive efforts by state and federal resource management agencies (U.S. Department of Agriculture, 1998). Trends in suspended sediment loads appear to have decreased about 17.5 percent (Baker et al., 1998) in the Maumee River at Waterville, Ohio, as a result of the high rate of implementation of conservation tillage. Maintaining and increasing participation in conservation tillage by farmers is an important goal for the agricultural sector in the Lake Erie basin.

#### Abandoned Solid Waste and Hazardous Waste Landfills

Wastes generally fall into two categories-hazardous waste and solid (nonhazardous) waste. To make waste management more effective, governments are promoting recycling and source reduction to decrease the toxicity and quantity of waste and are providing safer disposal capacity by improving the design and management of incinerators and landfills. Historically, landfills have been associated with some significant problems, including groundwater contamination. In the United States, the Resource Conservation and Recovery Act (RCRA) regulates the management of municipal solid waste and hazardous waste.

A comparison of LaMP pollutants to the constituents of hazardous wastes regulated by RCRA is presented in Table 12. From this information, it might be possible to map RCRA hazardous waste generators and handlers by ZIP code to determine the location and quantity of hazardous wastes within the watershed.

Municipal solid waste is managed in accordance with state requirements that meet federal municipal waste standards. In the United States, 27 percent of municipal solid waste is recycled, 16 percent is incinerated, and 57 percent is disposed of in landfills. The Municipal Solid Waste Landfill regulations, established in 1993, apply to all municipal solid waste landfills (MSWLF) receiving waste after October 9, 1993; however, landfills closed before October 9, 1991, need not comply. An MSWLF can accept household solid waste, commercial solid waste, nonhazardous sludge, small quantity generator waste, and industrial solid waste. The MSWLF criteria do not apply to landfills that accept only industrial nonhazardous waste.

# Simplified Description of RCRA Waste Stream Regulated and RCRA Waste CodePCBsAs constituents present in chlorobenzene production by-products K085ChlordaneAs a constituent in chlordane production by-products, as a discarded pesticide, and as a<br/>constituent in solid waste K097, U036, and D020DDTAs discarded products or chemical intermediates U061and U060MercuryAs a constituent present in waste from the production of iron and steel, inorganic chemicals,<br/>and veterinary pharmaceuticals; as a discarded product or chemical intermediate; and as a<br/>constituent in solid wastes K061, K071, K101, K106, P065, P092, U151, and D009

#### Table 12. Pollutants of concern regulated by RCRA for the Lake Erie Basin.

Dioxin	As a constituent in wastes from production of certain chlorobenzenes or chlorophenols, and
	their treatment residues and wastewaters F020, F021, F022, F023, F026, F027, F028, F032,
	K043, and K099
PAHs	As a constituent in wood preserving process wastes; as a constituent in petroleum refining

PAHs	As a constituent in wood preserving process wastes; as a constituent in petroleum refining
	wastes; as a constituent in leachate; as a constituent in wastes from the production of organic
	chemicals, pesticides, refined petroleum, and coke; and as discarded products or chemical
	intermediates F032. F034, F037, F038, F039, K001, K015, K022, K035, K048, K049, K050,
	K052, K060, K087, K141, K142, K143, K144, K145, K147, K148, U018, U022, U050, U063,
	and U137

State	MSWLF	RCRA TSD	CERCLA	NPL (final)
Indiana	32	126	175	29
Michigan	54	96	239	69
New York	42	114	533	85
Ohio	63	237	232	32
Pennsylvania	47	126	545	98

Table 13. Number of municipal solid waste landfills; RCRA Treatment, Storage and Disposal sites; CERCLA sites; and National Priority List sites in five Great Lakes States.

MSWLFs must conduct groundwater monitoring and must be operated to ensure they do not release pollutants at levels that violate the Clean Water Act. Table 13 presents the total number of active municipal landfills in each of five Great Lakes states.

Past practices were not as stringent as they are today. The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), known as "Superfund," provides EPA the authority to respond to releases or potential releases of toxic and hazardous substances that may endanger human health or the environment from abandoned hazardous waste sites. CERCLA requires EPA to maintain a National Priorities List (NPL) of all sites that require remedial action because of imminent danger to the public or the environment. The Great Lakes Binational Toxics Strategy Pesticide Report (USEPA, 1998) presents information on the presence of the pesticides aldrin, dieldrin, chlordane, DDT, mirex, and toxaphene at hazardous waste sites in the Great Lakes region. The number of CERCLA and NPL sites in each state is presented in Table 13.

In Ontario, the generation, handling, and disposal of waste materials are regulated extensively by both provincial and federal regulations. Regulation 347 of the Ontario Environmental Protection Act establishes three categories of waste that dictate the responsibilities of generators, operators, and transporters. Waste is categorized as (1) hazardous, liquid industrial waste that does not meet the criteria of a hazardous waste; (2) registerable waste that produces a leachate of intermediate toxicity but less than the criteria for hazardous waste; and (3) nonregisterable waste.

In the Ontario portion of the Lake Erie watershed, 87 landfills are active and 464 are closed. Of the active sites, only four accept hazardous waste. Under the Canada-Ontario Agreement (COA) Respecting the Great Lakes Basin Ecosystem, the Ontario MOE has assessed 377 closed sites throughout the province that were considered to have the greatest potential for adverse environmental effects and has identified no significant impacts.

As mentioned above, transfers to landfills are reported in both the TRI and NPRI inventories. The quantities of PCBs, PAHs, and mercury transferred to landfills as reported in the 1996 TRI and NPRI are presented in Table 14.

Pollutants of Concern	TRI Transfer to Landfills (kg)	NPRI Transfer to Landfills (kg)
PCBs	0	Not included in inventory
PAHs	15,600	15,014
Mercury (and its compounds)	0	186

#### Table 14. Quantity of selected Lake Erie pollutants of concern transferred to landfills, 1996.

## Water Quality and Ancillary Data

The data used in this report were gathered mainly from public sector environmental and water-quality monitoring programs that are binational, federal, state, and provincial. Data sources not in the public sector were private academic institutions and water-research laboratories. Data obtained from these organizations do not represent the full range of available information. The data described in this report are restricted to those available in digital formats. The pollutants, screening procedures, and data-selection criteria are the same as those described in the preceding section on point sources and are detailed in Appendix B.

The digital data sources evaluated in this section include those describing pollutant concentrations in

- Lake Erie, its tributaries, and its connecting channels
- Aquatic sediments
- Fish
- The atmosphere

In addition to data on chemical contaminants from water and other media, ancillary data on streamflow and/or lake level are needed to compute contaminant loads. Because concentrations are frequently related to streamflows and lake levels, these hydrologic data are needed to establish how well contaminant concentrations represent the possible range of hydrologic conditions. The primary agency responsible for the collection and analysis of streamflow data in the United States is the U.S. Geological Survey (USGS). Streamflow gaging stations are present near the outflows of most principal Lake Erie tributaries in the United States. Information from the USGS on the relative contribution of streamflow to Lake Erie from its principal tributaries in the United States is available in a water quality assessment report by Casey and others (1997). Both historical and near real-time values for streamflows are available at USGS state office links from the URL http://water.usgs.gov. The agency responsible for streamflow data in Canada is the Water Survey of Canada. In the United States, the U.S. Army Corps of Engineers (USACE) and National Oceanic and Atmospheric Administration (NOAA) operate a system of water-level gages on the connecting channels and on Lake Erie.

# Water Quality Data for Lake Erie, the Connecting Channels, and Tributaries

Water-quality data are reported as chemical concentrations in milligrams (mg), micrograms ( $\mu$ g), or nanograms (ng) per liter, which are generally equivalent to parts per million, billion, or trillion, respectively. Loads are the product of concentration and streamflow and are reported as grams or kilograms per unit of time (day, month, season, or year).

Concentration data can be used to identify and track sources of pollutants in the environment. Concentration data can be used to evaluate pollutants in relation to standards, criteria, or guidelines for the protection of water quality, aquatic life, and human health. Loading data can be used to compare the mass of a contaminant that is delivered to or from streams, point sources, and the atmosphere. Identification of the contaminant loading sources to Lake Erie can provide information on when, where, and how quantities of pollutants enter Lake Erie.

In the United States, STORET is the primary database containing information on chemical quality (concentrations), physical characteristics, and ancillary data for surface water and groundwater. STORET contains information submitted by federal, state, and interstate agencies, universities, contractors, and water-research laboratories. In Canada, ENVIRODAT and PWQMN are the primary databases containing information on the chemical quality and physical characteristics of streams and lakes. The STORET, PWQMN, and ENVIRODAT databases contain identifying information on collecting agency, site name, site number, location by latitude and longitude, sampling date and time, sample medium, sample type, units of measure, and remark codes to indicate detection limits and other data qualifiers.

Data of defined quality are needed to provide confidence in results and interpretations of data analyses. Appendix B provides an explanation of the rationale for data-selection procedures and selection criteria used in this report to determine which data are of sufficient quality and quantity to be suitable for the objectives of this report. To use these data with confidence requires that the reported sample concentrations or loads be representative of the location from which samples were taken and that the samples be collected at an appropriate frequency to describe the range of concentrations, loads, and streamflow or lake level at a particular site.

The next logical step once data have been identified for further analysis is to review sample-collection and analysis methods. Although important, examination of specific collection and analysis methods and quality control procedures and programs was beyond the scope of this report. Because of the need to further screen the data for methods comparability, the data in the tables and figures in this section are considered to be potentially useful for the intended purpose of characterizing concentrations and loads of pollutants of concern to Lake Erie.

For purposes of this report, concentration data sets from Lake Erie, its tributaries, and connecting channels with at least 10 samples per site and for which all sample results are reported as detected are considered suitable for the description of contaminant concentrations. Data sets with censored data also were judged to be suitable for the computation of statistical summaries if the detection frequency was at least 50 percent for sample sizes of 25 to 49 and at least 25 percent for sample sizes of 50 or more. Data sets considered potentially suitable for the computation of tributary loads should be represented by at least 50 samples per site and detection limits should be low enough that at least 25 percent of the samples are reported above the detection limits. Samples applicable to the computation of loads must be collected at or near a daily streamflow gage. The samples also must be collected over a range of low to high streamflows representative of the stream at the sample-collection site.

The results of the initial data screening are presented in the remainder of this section. Summary tables of the number of observations, the number of sites, and the percentage of samples above the detection limit for selected pollutants of concern in surface waters of the United States and Canada are provided (Tables 15 through 17).

At tributary sites (Tables 15 and 16), detection frequencies for concentrations of total PCBs, total DDT, total chlordane, dieldrin, mirex, benzo(a)pyrene, and mercury were less than the minimum of 50 percent and the number of samples per site was often less than 10, indicating insufficient data to characterize concentrations. Maps of the location of sampling sites and the number of observations reported per site show the limited extent of monitoring programs for these pollutants. Examples are given for two selected pollutants, benzo(a)pyrene (Figure 16) and mercury (Figure 17). In both countries, there were fewer than 10 tributary sites where 10 or more samples were collected for analysis of concentrations of organochlorine pollutants and benzo(a)pyrene. In the United States, there were 74 sites with 10 or more samples reported for mercury, but there were few detections.

Concentrations of atrazine, total phosphorus, nitrate-nitrogen, and suspended sediment (or total nonfilterable residue) were detected at frequencies from 76.9 to 99.8 percent in samples collected from tributaries and Lake Erie in both countries.

 Table 15. Pollutant class, pollutant, percentage of samples with detected concentrations, number of samples, number of sites, and number of sites within indicated range of samples per site, Lake Erie basin tributaries in the United States: 1986-1996.

		Percent Greater		No	No. Rai	of Site	s With Sample	in Indica es per Si	i <b>ted</b> ite <sup>ª</sup>
Pollutant Class	Pollutant (STORET pcode)	Detection Limit	No. of Samples <sup>ª</sup>	of Sites	1–9	10– 49	50– 99	100– 500	> 500
Organochlorine compounds	DDT (39300, 39310, 39320,39360, 39365, 39370)	11.2	596	93	88	4	0	1	0
	Mirex (39500)	0.0	141	77	73	4	0	0	0
	Chlordane (39350)	0.0	117	9	4	4	1	0	0
	Dieldrin (39380)	23.6	199	93	88	4	1	0	0
	PCBs (39488-39516, 34671, 81648, 81649)	0.1	1,112	89	79	5	1	4	0
PAHs	Benzo(a)pyrene (34247)	0.0	196	120	116	4	0	0	0
Trace metals	Mercury (71900)	17.4	3,197	312	228	74	2	8	0
	Lead (01051)	46.2	10,433	1,141	972	120	30	19	0
Other pollutants	Atrazine (39632, 39033)	85.6	938	11	4	2	0	5	0
	Nitrate-N (00630, 00631)	94.6	32,607	1,417	1,181	153	32	38	13
	Total phosphorus (00665)	95.5	35,078	1,435	1,175	162	44	41	13
	<i>Escherichia coli</i> (31633, 31648 <i>)</i>	99.8	1,503	35	9	16	7	3	0
	Suspended sediment or total nonfilterable residue (00530, 70300, 80154)	89.8	29,477	1,418	970	336	46	59	7

Note: STORET, Storage and Retrieval system for environmental data in the United States; pcode, parameter code, a numeric label that identifies a specific chemical compound, physical property, characteristic, or biological property and indicates how it was analyzed; >, greater than; no., number.

Includes all observations reported as less than detected or with remark codes indicating the same.

Data are from the STORET database.

Basinwide, the number of sites with 10 or more samples per site ranged from 263 for nitrate-N to 475 for suspended sediment. The number of sites with 50 or more samples ranged from 107 for nitrate-N to 136 for suspended sediment. Basinwide, 58 sites showed 10 or more samples of E. coli. Figure 18 shows geometric mean concentrations of total phosphorus in relation to criteria developed by the International Joint Commission (IJC), state of Ohio, and Ontario as eutrophication benchmarks (Figure 18). Figure 19 shows geometric mean concentrations of nitrate-nitrogen. Geometric mean concentrations of total phosphorus at many sites (Figure 18) are above respective guidelines in agricultural and urban areas. Geometric mean concentrations of nitrate-N (Figure 19) are above 10 mg/L at several sites on streams that

serve as source waters for public supply. The USEPA's Maximum Contaminant Level for drinking water is 10 mg/L. Source waters containing concentrations of nitrate-N in excess of 10 mg/L should be treated to reduce nitrates, or warnings should be issued to consumers. Maps such as these can be used to examine the spatial gradients and geographic patterns in the occurrence and distribution of these compounds across the Lake Erie basin.

Table 17 presents data from samples collected by Environment Canada from 1990 to 1996 at two sites in the connecting channels-at the head of the St. Clair River and at the outflow of Lake Erie at Fort Erie, Ontario. The data for the dissolved and particulate phases show that the frequency of detection of these data varies from 0 to 100 percent (Table 17).

 Table 16.
 Pollutant class, pollutants, percentage of samples with detected concentrations, number of samples, number of sites, and number of sites within indicated range of samples per site, Lake Erie Basin tributaries in Ontario: 1986-1996.

		Percent Greater Than			Number of Sites Within Indicate Range of Samples per Site*			icated lite <sup>®</sup>	
Pollutant Class	Pollutant	Detection Limit	No. samples	No. sites		10– 49	5– 99	100– 500	>500
Organochloine	DDT	0.07	2,673	5	0	1	1	2	1
compounds	Mirex	0.0	850	5	1	1	1	1	1
	Chlordane	0.0	976	5	0	2	0	2	1
	Dieldrin	0.0	850	5	1	1	1	1	1
	PCBs	0.2	899	5	0	2	1	1	1
PAHs	Benzo(a)pyrene	0.0	0	0	0	0	0	0	0
Trace metals	Mercury	15.2	1,253	4	0	0	1	3	0
	Lead	14.6	2,334	19	2	2	9	6	0
Other	Atrazine	70.3	791	3	0	1	0	1	1
pollutants	Nitrate-N	97.6	3,534	29	2	3	11	12	1
	Total phosphorus	99.8	3,408	29	2	3	11	13	0
	Escherichia coli	76.9	338	27	5	22	0	0	0
	Suspended sediment or total nonfilterable residue	98.0	3,383	29	1	4	12	12	0

Note: No., number; numbers of samples shown are for those sites located at downstream terminus of stream basin; >, greater than. <sup>a</sup>Includes all observations reported as less than detected or with remark codes indicating the same. Data are from Ontario's Provincial Water-Quality Monitoring Network (PWQMN).

# Table 17. Dissolved- and particulate-phase pollutants, number of samples, percentage of samples with detected concentrations, detection limits, and number of samples per site; St. Clair River and Niagara River at Fort Erie sampling sites: 1990-1996.

St. Clair River Dissolved Phase (Particulate Phase)			Niagara River at Fort Erie Dissolved Phase (Particulate Phase)			
Contaminant <sup>1</sup>	Number of samples	Percent > detection limit	Detection limits ng/L (ng/g) <sup>ª</sup>	Number of samples	Percent > detection limit	Detection limits ng/L (ng/g) <sup>a</sup>
PCBs	nd (78)	0 (27)	nd (77)	278 (287)	65 (11)	0.81 (89)
DDE	86 (78)	0 (56)	0.08 (5.6)	276 (291)	3 (24)	0.06 (6.4)
Mirex	86 (78)	0 (0)	0.05 (4.3)	279 (287)	0 (0)	0.05 (4.4)
α-Chlordane	86 (78)	0 (0)	0.09 (2.3)	279 (287)	5 (5)	0.06 (2.9)
Benzo(a)pyrene	86 (78)	0 (0)	0.17 (30)	276 (287)	21 (38)	0.24 (161)
Mercury	36 (12)	11 (100)	5 (10)	126 (136)	34 (99)	5 (10)
Lead	99 (nd)	17 (nd)	200 (nd)	126 (nd)	41 (nd)	200 (nd)

Note: nd, no data.

Pollutants monitored but not shown in the table include dieldrin, anthracene, benz(a)anthracene,

benzofluoranthene, benzo(g,h,i)perylene, and fluoranthene.

\*nanograms per liter are equivalent to parts per trillion; nanograms per gram are equivalent to parts per billion.

Data are from Environment Canada's ENVIRODAT database.



Figure 16. Frequency of observations of benzo(a)pyrene in surface waters of the Lake Erie Basin, United States: 1986-1996.



Figure 17. Frequency of observations of mercury in surface waters of the Lake Erie Basin, United States: 1986-1996.



Figure 18. Geometric mean concentrations of total phosphorus in the Lake Erie basin compared to selected guidelines established for streams and Lake Erie: 1986-1996.



Figure 19. Geometric mean nitrate-nitrogen concentrations in surface waters of the Lake Erie basin, Canada and the United States: 1986-1996.

Detection frequencies in the dissolved phase usually were lower than those in the particulate phase. For some pollutants, the ENVIRODAT database for the connecting channels (Table 17) provided more suitable data for computing concentration summary statistics and for computing loads than did the STORET and PWQMN databases (Tables 15 and 16). The ENVIRODAT database, however, contained data for only two sites in the Lake Erie basin and contained data for fewer pollutants than did the STORET or PWOMN databases. A comparison of the data from the St. Clair River and Lake Erie at Fort Erie (inflow compared to outflow) indicates that selected pollutants of concern are detected more frequently at the outflow station than at the inflow station.

For lakewide assessment purposes data must be available from sites that are well distributed throughout the basin. Concentration data for total phosphorus and nitrate-N appear to meet this criterion. The IJC has used extensive areal and temporal total phosphorus data sets to compute status and trends in total phosphorus loads to Lake Erie and to evaluate the relative contribution from point sources, the atmosphere, and tributaries (Dolan, 1993). Data used by the IJC to compute a total phosphorus budget were obtained from the same sources as the data described in Tables 5, 6, 15, and 16 and in Figures 2 and 18.

Because of a discontinuation of tributary monitoring for phosphorus at many sites between 1993 and 1996, the IJC identified the highest-priority tributaries for monitoring annual total phosphorus loads (Heidtke, 1999). The highest-priority tributaries were identified as those with the largest or the most variable annual loads. In Canada, the highestpriority tributaries for monitoring total phosphorus loads are the Grand, Sydenham, and Thames Rivers. In the United States, the highest-priority tributaries are the River Rouge in Michigan; the Maumee, Sandusky, Cuyahoga, and Grand rivers in Ohio; and the Cattaraugus Creek in New York (Heidtke, 1999). Today, tributary monitoring for total phosphorus is not being done at several of the highest-priority tributaries in the Lake Erie basin. Therefore, the quality of the total phosphorus load estimates for Lake Erie after 1994 might not be as reliable as the quality of estimates in the past.

#### **Aquatic Sediments**

Aquatic sediment quality is a useful indicator of water quality for several reasons. First, aquatic sediment concentrations of PCBs, organochlorine pesticides, PAHs, and concentrations of trace metals elevated above natural background levels are a direct result of the presence of these pollutants at some point in time in the overlying water. Near-surface aquatic sediments, in particular, may indicate the recent history of contaminant loadings at a site. Further, the presence of pollutants in near-surface sediments can indicate a repository of pollutants available for resuspension and transport to Lake Erie.

The second reason aquatic sediments are a good indicator of water quality is that sediment concentration data are less susceptible to problems associated with method detection limits than are surface-water-quality data. Because aquatic sediments adsorb several types of pollutants on their surfaces, contaminant concentration or accumulation on sediments is common where a source is releasing pollutants to the aquatic environment. The detection frequencies of organochlorine compounds, PAHs, and trace metal pollutants in aquatic sediments (Table 18) are markedly higher than those in surface water (Tables 15-17). Pollutants such as PCBs, PAHs, and mercury, which are reported with few or no detections in surface water, are reported at concentrations well above detection limits at frequencies of 25 percent or more in aquatic sediments (Table 18).

The third reason for the importance of sediment data is that over the period 1990 to 1997, there were a larger number of sites with detections of pollutants in aquatic sediments than in water (Table 18). Fourth, sediment-quality assessment values such as threshold effect levels (TELs) and probable effect levels (PELs) are available for the evaluation of sediment concentrations in relation to potential adverse effects on aquatic life (Smith et al, 1996). The TEL and PEL values developed by Smith et al. (1996) define three ranges of chemical concentrations: those that were (1) rarely, (2) occasionally, or (3) frequently associated with adverse biological effects. These guidelines were developed using a weight of evidence approach in which matching biological and chemical data from numerous modeling, laboratory, and field studies performed on freshwater sediments were compiled and analyzed. A TEL and a PEL were derived for 23 substances, including eight trace elements, six PAHs, total PCBs, and eight organochlorine pesticides. This method is being used as a basis for developing national sediment-quality guidelines for freshwater systems in Canada. It is also being used as part of USEPA's Assessment and Remediation of Contaminated Sediments (ARCS) program in the Great Lakes.

Sediment concentrations are reported in milligrams per kilogram (mg/kg), an equivalent to parts per million, or in micrograms per kilogram ( $\mu$ g/kg), an equivalent to parts per billion.

In 1997 Environment Canada conducted a survey of near-surface sediment contamination in Lake

Erie. USGS analyzed the near-surface sediment contaminant data collected from 1990 to 1997 for the U.S. portion of the basin (Rheaume et al., 2000). Results of these studies were compared to Canadian sediment quality guidelines (Smith et al., 1996). Maps of these data for PCBs (Figure 20) and mercury (Figure 21) show relative concentration ranges, areal distribution, and extent of contamination. The data show that concentrations of total PCBs in sediments collected from many tributary and connecting channels sites are greater than the PEL of 0.277 mg/kg. There are several areas where concentrations of mercury in sediments are greater than the PEL of 0.486 mg/kg. The data also show that concentrations of PCBs and mercury are lower in Lake Erie sediments compared to connecting channel and tributary sediments, suggesting sources within the basin. Compared to PCBs, there appear to be fewer hotspots of mercury-contaminated sediments in tributary and connecting channels. The observed pattern suggests connecting channel sources of mercury might be important. Although the data can be useful for source tracking, contaminant concentrations in aquatic sediment cannot be converted readily into contaminant loads because the major pathways are unknown. Although most of the data in the National Sediment Inventory (NSI; USEPA, 1997a) were collected before 1994, the NSI is an additional source of data on sediment quality.

Table 18.	Number of samples and detection frequency of selected pollutants of concern in near surface
	sediments: Lake Erie basin in the United States: 1990-1997.

Pollutant Class	Pollutants <sup>ª</sup>	Number of Samples	Frequency of detection
Organochlorine compounds and	DDT	409	35.5
pesticides	Chlordane	371	7.81
	Total PCBs	683	32.7
Polynuclear aromatic hydrocarbons	Benzo(a)pyrene	388	32.7
Trace metals	Lead	615	99.8
	Mercury	465	66.4

<sup>a</sup>All data for bioaccumulative and persistent pollutants identified in Table 2 were included in the original analysis. Nitrate-nitrogen, total phosphorus, atrazine, and *Escherichia coli* are not contained in the aquatic sediment databases. Compiled from Region 5 FIELDS database. OSI, National Sediment Inventory, and USGS National Water Quality Assessment

Compiled from Region 5 FIELDS database, OSI, National Sediment Inventory, and USGS National Water Quality Assessment Program.



Figure 20. Single-sample concentrations of total PCBs in aquatic sediments of the Lake Erie basin in relation to the Probable Effect Level of 0.277 mg/kg: 1990-1997.



Figure 21. Single-sample concentrations of mercury in aquatic sediments of the Lake Erie basin in relation to the Probable Effect Level of 0.486 mg/kg; 1990-1997.

#### **FishTissue**

EPA developed the NSI (USEPA, 1997a) to identify the national extent and severity of sediment and fish-tissue contamination. The minimum data requirements for including data in the NSI were location information, sampling date, and measured units. NSI reports contain results relevant to the Lake Erie basin from samples collected from 1980 to 1993 and retrieved from STORET and the databases of USACE, USGS, EPA, NOAA, and states bordering Lake Erie. Table 19 shows fish-tissue pollutants in the Lake Erie basin at approximately 479 sampling sites from the most contaminated areas (USEPA, 1997b) in relation to guidelines for wildlife consumption (NAS/NAE, 1973). The fish species from which tissue samples were obtained for subsequent analysis were not reported. Data are shown for five selected pollutants of concern. Contaminant concentrations in fish tissue are reported in micrograms per kilogram.

#### **Precipitation and Dry Deposition**

Atmospheric deposition has been identified as a significant source of many pollutants, including

nutrients and bioaccumulative and persistent pollutants banned or restricted in the United States and Canada. The control of these atmospheric sources is complicated by the difficulty in identifying and tracking the original sources and estimating the magnitude of the deposition. Atmospheric deposition is computed by multiplying pollutant concentrations by rainfall and dryfall amounts.

Deposition of PCBs appears to be uniform across the Great Lakes basin. However, the relative importance of the atmosphere as a source for PCBs differs from lake to lake based on the ratio of lake surface area to drainage area. EPA has estimated that as much as 90 percent of PCB loadings to Lake Superior result from atmospheric deposition (USEPA, 1997c). Comparatively, PCB inputs from the atmosphere were estimated to be only 7 percent of the total input to Lake Erie (Strachan and Eisenreich, 1988). Both wet and dry deposits contain trace elements such as arsenic, cadmium, lead, and selenium, and the PAHs benzo(k)fluoranthene and benzo(a)pyrene. An increasing trend in wet deposition of PAHs from Lake Superior to Lake Ontario mirrors the gradient of human population density. Among the Great Lakes, Lake Erie is thought to receive the highest

Pollutant Class	Pollutant (STORET pcode)	No. of Tissue Samples	Median Concentration (µg/kg)	NAS/NAE Recommended Maximum Whole-Fish Concentration for the Protection of Fish-Eating Wildlife (µg/kg)
Organochlorine pesticides	Chlordane: cis isomer (39063, 79005)	101	20	100
	DDD, DDE, DDT (81896, 81897, 39290)	162	98	1,000
Organochlorine Compounds	PCBs (19136, 19141, 19153, 19157, 19160, 19165, 19170, 39525)	163	2,480	500
Trace metals	Lead (71934)	16	203	na
	Mercury (71933)	37	52	500

 Table 19.
 Summary of National Sediment Inventory data for selected pollutants in fish tissue by pollutant class, pollutant, number of tissue samples, and median concentration: 1980-1993.

Notes: STORET, data storage and retrieval system for environmental data in the United States; pcode, parameter code, a numeric label that identifies a specific chemical compound, physical property or characteristic, or biological property and indicates how it was analyzed; µg/kg, micrograms per kilogram; na, not applicable; No., number NAS/NAE, National Academy of Science/National Academy of Engineering, 1973

deposition of PAHs, lead, arsenic, and selenium through dry deposition.

The gas transfer component is a significant proportion of the total loading of pollutants to the Great Lakes. The concentrations of certain chemicals in the atmosphere are in equilibrium with lake concentrations. At equilibrium, annual losses from volatilization equal annual gains from deposition. For example, in 1993-1994, volatilization from the Great Lakes was estimated to exceed deposition, resulting in a net loss of chemicals to the atmosphere (USEPA, 1997c).

Through the Integrated Atmospheric Deposition Network (IADN), concentrations in rainfall, vapor phase, and dryfall (particulate) are collected in the United States and Canada. IADN monitors organochlorine compounds and other selected organic pollutants. The IADN program has one master station, near Buffalo, and four Canadian satellite stations in the Lake Erie basin. The IADN reports wet and dry deposition of many organic pollutants of concern to the Lake Erie basin, and their gas transfer components.

The Mercury Deposition Network (MDN) monitors mercury in rainfall at more than 25 sites in the United States and at 5 sites in Canada. The MDN is part of the U.S. National Atmospheric Deposition Program (NADP). The MDN began in 1995 with 13 sites; by 1998 it had expanded to more than 30 sites, including one at Sturgeon Point, New York, in the Lake Erie basin. The objective of the MDN is to develop a national database of weekly concentrations of total mercury in precipitation and the seasonal and annual flux of total mercury in wet deposition. The data are available at the URL http://nadp.sws.uiuc.edu. The IADN and MDN are joint ventures between the United States and Canada.

The latest atmospheric deposition results from the IADN, described by Hoff and others (1996), include recent mercury deposition results. Of the available databases inventoried for this report, only

the IADN's and MDN's database were designed to measure contaminant loads. Table 20 presents a summary of the available IADN data from the Sturgeon Point master station. Both the number and the percentage of samples greater than the detection limit are described for the particulate phase, vapor phase, and precipitation for a number of pollutants of concern.

Loading estimates of both atmospheric deposition to and volatilization from Lake Erie of pollutants of concern have shown the lake is very sensitive to atmospheric concentrations. IADN data indicate that many pollutants of concern might come from outside the Great Lakes basin, while some other anthropogenic substances of concern, such as PAHs and trace elements, come from sources in the basin. For example, the Great Lakes Binational Toxics Strategy Pesticide Report (USEPA, 1998) contains information on the potential for longterm transport and deposition of toxaphene and p,p'-DDT.

#### Pathways

Pathways are environmental processes that link contaminant sources to receptors like sediment or biota. Hydroclimatic pathways include atmospheric deposition. Fluvial pathways include transport of pollutants from streams and connecting channels to Lake Erie. Aquatic sediment pathways include physical reactions such as adsorption, desorption, deposition, and resuspension. The relative magnitude and importance of selected pathways cannot be assessed without adequate environmental and ancillary data to characterize contaminant concentrations and loads and ancillary data on processes, rates, constants, and pollutant kinetics.

Information on pathways is useful it because provides information about where, when, how, and why a contaminant reaches the level of being identified as a critical pollutant in Lake Erie. It is apparent that sediment and fish tissue concentrations of PCBs and mercury are higher than surface-

	Particulate Phase		Vapor Phase			Precipitation			
Pollutant <sup>a</sup>	DL pg/m <sup>3</sup>	No. of Samples	% > DL	DL pg/m <sup>3</sup>	No. of Samples	% > DL	DL ng/L	No. of samples	% > DL
PCBs	7.5	11	45	96.8	29	90	0.38	13	92
γ-Chlordane	0.4	11	55	1.8	31	100	0.03	13	92
α-Chlordane	0.1	11	18	2.1	31	94	0.02	13	38
Mirex	0.5	11	9	0.4	31	26	0.07	13	0
DDT	0.6	11	82	2.4	31	87	0.08	13	77
DDD	0.005	11	73	0.8	31	71	0.14	13	8
DDE	0.3	11	55	1.0	31	100	0.02	13	100
Dieldrin	2.1	11	73	2.7	31	97	0.01	13	85
α-HCH	1.8	11	18	2.2	31	100	0.14	13	92
γ-HCH	0.9	11	27	2.0	31	100	0.02	13	69
Hexachlorobenzene	6.2	11	0	5.7	31	100	0.25	13	0
Acenaphthene	8.5	11	0	38.7	30	97	0.7	12	8
Acenaphthylene	8.0	11	0	28.5	30	63	1.6	12	8
Anthracene	4.0	11	45	8.8	30	50	0.8	12	42
Benz(a)anthracene	2.7	11	100	1.2	30	20	0.2	12	100
Benzo(b)fluoranthene	7.8	11	100	1.2	30	10	0.2	12	100
Benzo(k)fluoranthene	2.0	11	100	3.7	30	0	0.4	12	100
Benzo(g,h,i)perylene	2.8	11	100	1.2	30	0	0.4	12	83
Benzo(a)pyrene	1.8	11	100	13.5	30	0	0.3	12	100
Chrysene	10.7	11	100	3.7	30	77	0.7	12	100
Dibenzo(a,h)anthracene	3.5	11	64	3.7	30	0	0.7	12	25
Fluoranthene	30.9	11	100	31.4	30	97	0.4	12	100
Fluorene	15.6	11	9	24.8	30	100	0.8	12	83
Indeno(123-cd)pyrene	3.5	11	100	2.4	30	0	0.3	12	92
Phenanthrene	15.7	11	100	70.1	30	97	0.5	12	100
Pyrene	19.1	11	100	20.1	30	97	0.3	12	100

Table 20.	Summary of available	IADN data by pollutan	t and phase, Lake Erie	at Sturgeon Point, New	York; 1993.
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Notes: DL, detection limit; %, percent; No., number; pg/m<sup>3</sup>, picogram per cubic meter; ng/L, nanogram per liter.

Nanograms per liter and picograms per cubic meter are both equivalent to parts per trillion.

<sup>a</sup>Pollutants monitored but not included in table are lead, cadmium, and arsenic.

Data from integrated Atmospheric Deposition Network (IADN) database.

water concentrations. Selected data shown in Figures 20 and 21 suggest that aquatic sediments in tributaries and connecting channels may be a repository for mercury and PCBs. These nearsurface sediments appear to be available for transport to Lake Erie from tributaries and connecting channels with uptake indicated in fish (Table 19). Sufficient data exist to identify aquatic sediments as a potentially important pollutant source to the Lake Erie system. Resuspension of pollutants from aquatic sediments, subsequent transport to the lake, and uptake by biota appear to be important pathways.

## Suitability of Available Data

The suitability of the available data for characterizing concentrations and for estimating loads of pollutants to Lake Erie varies widely. Tributary and point source data for pollutants representing classes of organochlorine compounds, polynuclear aromatic compounds, and trace metals were almost always reported below detection in surface water at rates of 50 percent or greater. Additionally, the detection levels widely used are well above those considered environmentally relevant to the water medium. As a result, few sample concentrations were reported above detection for the trace metals, organochlorine, and polynuclear aromatic hydrocarbon compounds investigated for this report.

When pollutants were detected in sufficient numbers of samples, there were usually an insufficient number of locations to characterize concentrations or to estimate loads for lakewide assessment purposes. Atmospheric loading data for organochlorine compounds, PAHs , and trace metals are the only data readily available and consistently collected for the purpose of computing deposition or loading from the atmosphere.

The available water quality data for atrazine, nitrate-nitrogen, total phosphorus, and suspended sediment can be used to characterize concentrations and may be suitable to compute loads to Lake Erie from tributaries. Nutrient data (nitrogen and phosphorus) are available from almost all data sources inventoried for this report. These data are available in sufficient amounts, the pollutants are commonly detected at environmentally relevant concentrations, and the studies are characterized by sampling sites covering a wide geographic area. These data may be suitable for constructing a loading model or for evaluating environmental concentrations in relation to existing water quality standards and criteria or criteria under development. Frequently, these data are accompanied by the necessary ancillary data for streamflow or discharge volume necessary for the computation of a load. Before computing concentration summary statistics or loads, the sample-collection and analysis methods should to be reviewed to further establish data comparability. This step was beyond the scope of this report.

The deficiency in quality and quantity of data for point source and surface-water contaminant concentrations for organochlorine compounds, PAHs, and trace metals can be attributed to several factors. The first factor is the past use of methods that do not meet current quality assurance and quality control specifications for sampling in the part per billion and part per trillion concentration ranges. The second factor is that the methods of collection and analysis used from 1986 to 1996 were not sufficiently sensitive for measuring the range of low-level concentrations now currently known to persist in the water environment. The third factor is that the cost of analyzing these pollutants is high compared to the cost of analyzing the more commonly detected pollutants like nitrate-N and total phosphorus. Because of the high cost of analysis, a relatively small number of samples for organochlorine compounds, PAHs, and trace elements have been collected and analyzed over the past 20 years in the Lake Erie basin. Data sets containing virtually no detections or a small number of samples are of limited use for characterizing concentrations and loads.

Implementation of the GLI in the United States will require that the technology for monitoring be improved so that pollutants such as PCBs and mercury will be analyzed in effluents and water at environmentally relevant concentrations. Widespread improvements in monitoring will take years to implement as changes to permit reporting requirements are updated periodically, after every 5 years or more. While programs to reduce concentrations and loads of toxic and persistent substances from point source discharges are being undertaken, better information on the response of the Lake Erie system to these management actions will be useful for measuring success. However, the ability to measure this success is difficult to document under current monitoring programs, which lack the resources to be effective for characterizing sources and loads.

Aquatic sediments and biota tend to concentrate pollutants so that the data derived from samples analyzed in the mid to late 1980s might be comparable to data collected in the 1990s. The methods used 10 to 15 years ago might be sufficiently sensitive by current standards to meet data quality objectives for detecting environmental concentrations present in aquatic sediments and biota. The aquatic sediment concentration data for pollutants are likely to meet current data quality objectives for evaluating exposure effects on aquatic life, and the fish residue data are useful for evaluating the exposure and risk to human and wildlife health from consumption. Both of these data sources can be used to evaluate the extent and magnitude of beneficial use impairments. These data also can be used to compare the extent and magnitude of contamination in Areas of Concern. These comparisons can be used to make management decisions about the areas most in need of remediation. In addition, these data can be used with contaminant release data from TRI, NPRI, PCS, and SRDS to formulate weight of evidence approaches to identifying and characterizing major sources. Specifically, location data for point sources and contaminant releases are valuable as an indicator of where to look for a signature of environmental contamination. Data for concentrations of pollutants in aquatic sediments, biota, and pollutant releases can serve as a guide for source track-down and pollution prevention when used together and interpreted as multiple lines of evidence.

Data to characterize the most important pollutant pathways must meet or exceed the criteria established to characterize concentrations and loads from point sources, the atmosphere, tributaries, connecting channels, and aquatic sediments and to address the subsequent effects on aquatic life and human health. Use of inappropriate or incomplete data can result in flawed decisions based on incomplete or incorrect information. A long-term goal might be to determine the relative importance of pathways and sources to virtually eliminate certain pollutants. Given the inadequacy of data for characterizing concentrations and loads for bioaccumulative and persistent pollutants, however, most pathways cannot now be determined with any confidence. The lack of supporting data to indicate the relative importance of the major pathways suggests a major effort will be needed to fill this data gap.

## **Conclusions and Future Direction**

This document characterizes the information available from the public sector and research laboratories in digital databases and the suitability of these data for identifying sources and characterizing pollutant concentrations and loads. The data search included all the Lake Erie chemicals of concern listed in Table 2, with a particular emphasis on analyzing and presenting the data for PCBs and mercury, the two chemicals designated as Lake Erie critical pollutants.

In the databases reviewed for information from the reporting period 1986 to 1996, data characteristics examined included contributing agency, media code, parameter code, location by latitude and longitude, sampling and analysis frequencies, period of record, detection limits, number of observations, number of observations above the detection limits, concentration, units of measure, and availability of flow or other ancillary data. Fourteen major environmental databases representing contributions from 10 national, 10 state and provincial, four binational, and two nongovernmental monitoring programs were examined. Databases evaluated for the United States were STORET, PCS, TRI, OSI, FIELDS, NSI, and USGS. Databases evaluated for Canada were STAR, ENVIRODAT, PWQMN, SRDS, and NPRI. Binational networks evaluated were IADN and MDN.

This report draws the following conclusions from an analysis of these databases and data:

1. The data obtained from 11 of the 14 major databases in the Lake Erie basin were, in part, considered to be either of insufficient quality and quantity or not applicable to characterize concentrations and loads for tributary, lake, or point source concentrations or annual loads to Lake Erie within acceptable levels of uncertainty. These results apply for DDT and its degradates, chlordane and its degradates, aldrin, dieldrin, PCBs, dioxin, PAHs, arsenic, copper, mercury, and zinc.

- 2. Data from the IADN and MDN were found to be of sufficient quality and quantity to estimate summary statistics for concentrations and to compute annual deposition to Lake Erie for organochlorine compounds, mercury, and PAHs. These two networks represent only the atmospheric contribution of these pollutants.
- 3. Concentration data for nitrate-nitrogen, total phosphorus, suspended sediment, and atrazine from all applicable databases might be adequate for characterizing tributary and point source concentrations and loads to Lake Erie. Data for Escherichia coli can be used to characterize summary statistics for concentrations in selected tributary and nearshore areas. Another use of these data is to compare ambient concentrations to water quality criteria, standards, and guidelines. This approach would provide an estimate of the potential exposure of aquatic life and humans to these pollutants and the resulting effects. However, none of these chemicals are bioaccumulative and most are not as persistent in the environment as organochlorine pesticides, PCBs, PAHs, and trace metals.
- 4. Concentration data for aquatic bed sediments and fish tissue were less susceptible to the limitations of quality and quantity than data reported for surface water. Although not suitable for computing loads, these data could provide a strong indication of the extent and severity of contamination in the Lake Erie basin. Those areas with the highest sediment concentrations can be identified and used to evaluate the potential for adverse effects on aquatic life and

human health by comparison to both sediment and fish consumption advisory guidelines.

- 5. The existing concentration data for bed sediments, fish tissue, point sources, the lake, connecting channels, and tributaries, coupled with location data, can be used to indicate areas of both historical contamination and potential sources or source areas. This information can be useful to managers to prioritize remedial actions to reduce or eliminate loads.
- 6. Because the decision to seek virtual elimination of persistent toxic substances already has been made, and given the relative inadequacy of existing data to compute loads for these pollutants, it might be more productive to pursue other methods to identify the major sources and pathways of critical pollutants in Lake Erie.
- 7. Past and present agricultural, industrial, and municipal activities are sources of pollutants in Lake Erie. The weight of evidence from the physical location of these activities, their potential chemical impacts, and the known chemical impacts in the water and sediments as determined by comparison to guidelines suggests the basin as a whole, and in particular the western portion, is a stressed environment.

The next step is to identify sources and provide a scientific basis for sound management decisions. Known point sources can be identified from the data compiled for this report. Maps of discharge locations, pesticide use, agricultural areas, abandoned landfill sites, and other land uses will be compared to ambient water column concentrations, aquatic biota tissue concentrations, and sediment concentrations to identify major source areas and the most highly contaminated areas in the lake. An assessment of whether the most contaminated areas and major sources already have been targeted for priority action may be accomplished by identifying and cross-referencing implementation and remediation actions already under way. The Lake Erie Areas of Concern RAP sites have already been identified as priority areas for source control and remediation. This exercise not only will further confirm the RAP sites as priority areas, but also will point out additional areas where further action or attention might be needed, whether it be monitoring, additional research, or remediation.

Several efforts independent of the Lake Erie LaMP are under way and may contribute to tracking down sources. The Binational USEPA/ Environment Canada Toxics Reduction Strategy is investigating sources of pollutants of concern to the Great Lakes both within and outside the basin. This strategy is designed to further identify sources and develop and implement the actions needed to move closer to the goal of virtual elimination of persistent toxic substances from the Great Lakes. Several contaminated sediment and landfill remediation projects recently were completed or are under way in the River Raisin, Ashtabula River, and Ottawa River/Maumee Areas of Concern. Another project under way by the Sources and Loads Subcommittee is the review of these programs and other individual government agency programs to create a report documenting the status of pollution prevention and reduction activities throughout the Lake Erie basin, particularly for mercury and PCBs.

The ambient concentrations of critical pollutants in all media must be analyzed compared to the GLWQA specific objectives listed in Annex 1, and possibly other more recent objectives (i.e., Great Lakes Initiative). This analysis must assess the potential of certain chemicals to cause impairment and ensure a thorough evaluation of sources and potential critical pollutants. Selected data examined for this report could be used for these purposes. Other steps related to the completion of Stage 1 could be completed if desired, but it is unlikely these additional data would result in muchimproved basinwide assessment conclusions. The resulting load estimates for selected bioaccumulative and persistent pollutants still would be highly uncertain because of the many assumptions that would be needed to compute loads. A partial literature review conducted by the Sources and Loads Subcommittee suggests that Lake Erie studies conducted for purposes other than calculating loads might provide useful information for only a small number of pollutants or for a limited number of source areas.

There is no question that Lake Erie is in flux. To better understand pathways of critical pollutants, additional research is needed on changes in food web dynamics and the linkages in energy and flow between the lake bottom and the water column. For example, concentrations in fish have fluctuated over the years, even as point and nonpoint source loads appear to have decreased. Is this a reflection of food web changes, impact from exotic species, climate change, or something else? Although it might be possible to further decrease loads into the lake, it is also important to understand what is happening to the pollutants already in the lake. Once the major sources of pollutants and the most seriously contaminated areas have been identified, it is recommended that resources and remedial actions be focused on those areas immediately rather than spent on further attempts to estimate total loads.

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## **Appendix A. Endocrine-Disrupting Chemicals**

(Chemicals in boldface are also Lake Erie LaMP Sources and Loads chemicals of concern; see Table 2)

#### **Pesticides**

Mirex

Parathion

Toxaphene

Transnonachlor

Oxychlordane

Synthetic pyretrhoids

Herbicides	Nematocides				
2,4,-D	Aldicarb				
2,4,5-T	DBCP				
Alachlor	Industrial Chamicala				
Amitrole					
Atrazine					
Metribuzin	<b>Dioxin</b> (2,3,7,8-TCDD)				
Nitrofen	Lead Mercury				
Trifluralin					
Fundicides	PBBs				
Benomyl	PCBs				
Hoveehlorehonzone	Pentachlorophenol (PCP)				
Manaozah	Penta- to nonylphenols				
Mancozeo	Phthalates				
Matine complex	Styrene				
meuram-complex					
Tributyl tin					
Zineb					
Ziram					
Insecticides					
β-ΗCΗ					
Carbaryl					
Chlordane					
Dicofol					
Dieldrin					
DDT and metabolites					
Endosulfan					
Heptachlor and H-epoxide					
Lindane					
Methomyl					
Methoxychlor					

## Appendix B. Data Screening Procedure and Selection Criteria

The first purpose of this appendix is to identify data that can be used to characterize contaminant concentrations. The second purpose of this appendix is to identify data that can be used for the computation of loads.

#### Minimum Criteria for Estimating Concentrations and Loads

The objectives of this report are to characterize concentrations and loads. Available data with which to achieve these objectives were collected by many agencies for various purposes, but not necessarily for purposes similar to those of this report. Screening procedures based on dataselection criteria were used to determine which data were suitable to characterize contaminant concentrations and loads. The basis for the dataselection criteria was a review of published literature on techniques to statistically analyze water quality data for concentrations and techniques to estimate constituent loads. The objective of screening criteria is to extract as much suitable data as possible from the available data sets in order to characterize concentrations and loads with some degree of confidence.

Minimizing errors and maximizing confidence in the information presented in this report is a primary goal because management actions might arise from conclusions drawn from the data. There can be many sources of error in any reported data. Variability in an estimate of a concentration or load is dependent on the sampling errors and nonsampling errors in the data. Nonsampling errors can be random or nonrandom. Random nonsampling errors tend to cancel each other out in large data sets (Iman and Conover, 1983) and therefore are not considered a serious problem for the data sets discussed in this report.

Biases (nonrandom errors) in the data might not cancel each other out, and elimination of bias improves data quality. Biases can be minimized

by the use of selection criteria that provide the analyst with only data applicable to the purposes of the data analysis. Sampling error is the other type of error that is an important consideration. Sampling theory dictates that the magnitude of the error in any data is inversely proportional to the square root of the number of samples (Richards, 1999, in press). To reduce this error by one-half requires that four times as many samples be collected. This knowledge translates into certain minimum sample sizes for data sets intended to be used to characterize contaminant concentrations and compute loads. The questions to be answered are (1) How many samples are enough? and (2) How much confidence in the sample estimates is desired or needed?

#### Selection Criteria

One consideration is how well the samples represent the environment from which they were obtained, such as point sources, the lake, connecting channels, tributaries, sediments, fish, or atmosphere. Even for simple descriptions of concentration and loading data, it is important that the samples collected represent the range of environmental conditions. For example, the concentrations of pollutants that are primarily delivered during runoff and high streamflows will be underestimated when samples are collected only during low or moderate streamflows. In much the same way, contaminant concentration in rain is dependent on rainfall volume. Samples collected from streams, lakes, and the atmosphere at daily, weekly, monthly, or seasonal frequencies were deemed suitable and were included in data analysis for this report. Only where data are reported for a representative number of locations across the range of environmental conditions were they deemed suitable for lakewide assessment purposes.

Another consideration is the period of record of data collection. Only water quality samples

collected from October 1, 1985, to September 30, 1996, were inventoried for selected pollutants. The distribution of data sites is also a consideration.

For aquatic sediments, single surficial sediment samples were deemed to be most representative of recently deposited or redeposited sediments and associated pollutants. The period of record for analysis of aquatic sediments was 1990 to 1997. For fish tissue, single samples were deemed to be most representative of collection sites. The period of record for analysis of fish tissue was 1983 to 1993.

#### Minimum Criteria for Concentrations

The distribution of contaminant concentrations in surface water can be highly variable. Estimates of the mean, median, and range of concentrations cannot be described adequately with very small sample sizes (Helsel and Hirsch, 1995). Summary statistics used for this report are used to describe the center of the data (median or mean), the variability of the data (variance and standard deviation), the symmetry of the data distribution (kurtosis), and the data quantiles and extremes (minimum, maximum, or some large or small percentiles) (Helsel and Hirsch, 1995). For purposes of this report, concentration data sets with a sample size of at least 10 in which no sample results are reported below the limits of detection are deemed suitable for the description of contaminant concentrations. A sample size of 10 provides sufficient information for computation of median, mean, estimates of variability, and percentiles of the distribution. In addition, these samples should represent a range of streamflows representative of the sample-collection site.

A further complication is that the concentrations of certain pollutants are often reported as being censored or "below the detection or reporting limit." Censored data can present an interpretation problem. For example, censored data might be of limited use for evaluating the presence or absence of a contaminant if the reporting limit is higher than an environmentally relevant concentration. Concentration and/or loading data can be used for evaluating a discharge or permit limit. Concentration data also can be used for evaluating compliance with a standard or criteria for the protection of aquatic life or human health. Data censoring is considered severe at the level of 50 percent or more (Helsel and Hirsch, 1995). At censoring levels greater than 50 percent, the median concentration, for example, might have to be estimated because it is not a detected value.

Statistical techniques that substitute values for censored data can be used to overcome the detection limit problem. The Maximum Likelihood Estimate (MLE; Cohen, 1959) is one technique that substitutes values for censored data based on what is known about the distribution of the data reported above the detection limit and the percentage of data below the detection limit. The MLE is a favored method for computing the median and other percentiles of a data set because it is less biased compared to simpler techniques that substitute zero, onehalf, or the detection limit value for censored data (Helsel and Hirsch, 1995). The MLE works best with sample sizes greater than 25 (Helsel and Hirsch, 1995). If the MLE is used with lognormally distributed data, estimates of the mean and standard deviation may require some adjustment when retransformed into the original units (Gilliom and Helsel, 1986). For purposes of this report, the MLE is the desired method for addressing censored data.

Data sets with censored data were judged to be suitable for the computation of statistical summaries if the detection frequency is at least 50 percent for sample sizes of 25 to 49, and at least 25 percent for sample sizes of 50 or more (Gleit, 1985). Sample sizes of 50 can produce biases of 50 to 100 percent in the estimated mean and standard deviation when there are low percentages of detected values (Helsel and Hirsch, 1995).
The minimum criteria to characterize contaminant concentrations from point sources can differ somewhat from those for tributaries. Tributaries are predominately influenced by wide ranges of flows and concentrations, hence the need for more stringent screening criteria to avoid bias. Point sources, on the other hand, are process-based and are therefore characterized by relatively constant flows and concentrations. The minimum number of observations needed to characterize concentrations of pollutants discharged from point sources remains at 10. If data are censored (reported below detection), however, 25 to 50 percent or more of the observations should be reported above the detection limit. With small data sets, the computation of the MLE can produce unexpected results. Therefore, an MLE based on 50 percent or more observations above the detection limit would still be preferable.

## Minimum Criteria for Loads

Contaminant loads are computed using two types of data: (1) concentration data and (2) streamflow, effluent discharge, rainfall, or dryfall. A load is a measure of the rate of transport of a known mass of a contaminant expressed in kilograms or tons per unit of time. The most desirable situation for computing annual loads is if samples and measurements are taken concurrently each day. Daily loads are computed and summed for the year. The availability of daily concentrations for computation of annual loads is uncommon because of funding constraints on monitoring programs. Daily streamflow values are typically collected at gaging stations. In the absence of daily concentrations from which to compute daily loads, statistical techniques are available that can make up for limited data. Load estimators (loadestimating equations) based on statistical regressions are techniques commonly used to estimate daily loads from water samples collected at lessthan-daily frequencies where daily streamflow

data are available (Cohn, 1988; 1994; Cohn et al., 1992; Richards, in press).

Load estimators for tributaries and connecting channels require that sample data be collected at sufficient frequencies with regard to streamflow and season (Cohn, 1994; Richards, in press). Most load estimators in use today can accommodate some degree of censored values. The Minimum Variance Unbiased Estimator (MVUE; Cohn et al., 1992; Cohn, 1994) can be used to compute tributary load estimates when at least 25 percent of the sample data are above the detection limit and when there are 50 or more samples with at least 25 samples collected per year. The Adjusted Maximum Likelihood Estimator (AMLE; Cohn and others, 1992; Cohn, 1994) requires the same sampling frequency with at least 20 samples above the detection limit. Realistically, an estimator technique may perform quite well with anywhere from as few as 30 to as many as 75 or more samples. Many samples are more desirable than few samples. For smaller sample sizes, the percentage of censored data must be kept to a minimum of 50 percent.

For purposes of this report, data sets suitable for the computation of contaminant loads from tributaries were best represented by a sample size of at least 50. In addition, concentrations of pollutants should be detected in at least 25 percent of the samples. Samples applicable to the computation of loads should be collected at or near a daily streamflow gage. The samples also must be collected over a range of low to high streamflows representative of the stream at the sample-collection site.

Referring to the prior discussion on point sources, the minimum number of reported observations needed to compute loads from point sources remains 10. The minimum criteria established to compute loads discharged from point sources is at least 25 percent of the observations above the detection limit.