

Areal Distribution and Concentrations of Contaminants of Concern in Surficial Streambed and Lakebed Sediments, Lake Erie-Lake Saint Clair Drainages, 1990–97

Water-Resources Investigations Report 00-4200



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U.S. Geological Survey, Columbus, Ohio.

U.S. Department of the Interior
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Areal Distribution and Concentrations of Contaminants of Concern in Surficial Streambed and Lakebed Sediments, Lake Erie-Lake Saint Clair Drainages, 1990–97

By S.J. Rheame, D.T. Button, D.N. Myers, and D.L. Hubbell

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FOREWORD

The U.S. Geological Survey (USGS) is committed to serve the Nation with accurate and timely scientific information that helps enhance and protect the overall quality of life, and facilitates effective management of water, biological, energy, and mineral resources. (<http://www.usgs.gov/>). Information on the quality of the Nation's water resources is of critical interest to the USGS because it is so integrally linked to the long-term availability of water that is clean and safe for drinking and recreation and that is suitable for industry, irrigation, and habitat for fish and wildlife. Escalating population growth and increasing demands for the multiple water uses make water availability, now measured in terms of quantity *and* quality, even more critical to the long-term sustainability of our communities and ecosystems.

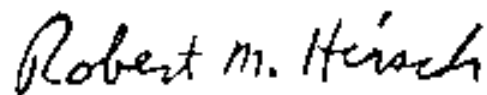
The USGS implemented the National Water-Quality Assessment (NAWQA) Program to support national, regional, and local information needs and decisions related to water-quality management and policy. (<http://water.usgs.gov/nawqa>). Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are the conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities. NAWQA results can contribute to informed decisions that result in practical and effective water-resource management and strategies that protect and restore water quality.

Since 1991, the NAWQA Program has implemented interdisciplinary assessments in more than 50 of the Nation's most important river basins and aquifers, referred to as Study Units. (<http://water.usgs.gov/nawqa/nawqamap.html>). Collectively, these Study Units account for more than 60 percent of the overall water use and population served by public water supply, and are representative of the Nation's major hydrologic landscapes, priority ecological resources, and agricultural, urban, and natural sources of contamination.

Each assessment is guided by a nationally consistent study design and methods of sampling and analysis. The assessments thereby build local knowledge about water-quality issues and trends in a particular stream or aquifer while providing an understanding of how and why water quality varies regionally and nationally. The consistent, multi-scale approach helps to determine if certain types of water-quality issues are isolated or pervasive, and allows direct comparisons of how human activities and natural processes affect water quality and ecological health in the Nation's diverse geographic and environmental settings. Comprehensive assessments on pesticides, nutrients, volatile organic compounds, trace metals, and aquatic ecology are developed at the national scale through comparative analysis of the Study-Unit findings. (<http://water.usgs.gov/nawqa/natsyn.html>).

The USGS places high value on the communication and dissemination of credible, timely, and relevant science so that the most recent and available knowledge about water resources can be applied in management and policy decisions. We hope this NAWQA publication will provide you the needed insights and information to meet your needs, and thereby foster increased awareness and involvement in the protection and restoration of our Nation's waters.

The NAWQA Program recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for a fully integrated understanding of watersheds and for cost-effective management, regulation, and conservation of our Nation's water resources. The Program, therefore, depends extensively on the advice, cooperation, and information from other Federal, State, interstate, Tribal, and local agencies, non-government organizations, industry, academia, and other stakeholder groups. The assistance and suggestions of all are greatly appreciated.



Robert M. Hirsch
Associate Director for Water

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CONVERSION FACTORS AND ABBREVIATIONS

	Multiply	By	To obtain
<u>Length</u>	mile (mi)	1.609	kilometer
<u>Area</u>	square mile (mi ²)	2.590	square kilometer
<u>Weight</u>	milligram (mg)	0.00003527	ounce, avoirdupois
	kilogram (kg)	2.205	pound, avoirdupois

Abbreviated water-quality units used in this report: Chemical concentrations for bed sediment are given in milligrams per kilogram (mg/kg), a unit expressing the concentration of chemical constituents in bed sediment (dry weight) for synthetic organic compounds and trace elements. Numerical values expressed as milligrams per kilogram are the same as concentrations in parts per million (ppm).

MISCELLANEOUS ABBREVIATIONS

NAWQA	<u>N</u> ational <u>W</u> ater- <u>Q</u> uality <u>A</u> ssessment
LERI	<u>L</u> ake <u>E</u> rie- <u>L</u> ake Saint Clair Drainages study unit
IJC	<u>I</u> nternational <u>J</u> oint <u>C</u> ommission
LaMP	<u>L</u> akewide <u>M</u> anagement <u>P</u> lan
RAP	<u>R</u> emedial <u>A</u> ction <u>P</u> lan
PCB	<u>P</u> olychlorinated biphenyl
PAH	<u>P</u> olycyclic aromatic hydrocarbon
SVOC	<u>S</u> emi-volatile <u>o</u> rganic compound
NSI	<u>N</u> ational <u>S</u> ediment <u>I</u> nventory
OSI	<u>O</u> hio <u>S</u> ediment <u>I</u> nventory
FIELDS	<u>F</u> ully <u>I</u> ntegrated <u>E</u> nvironmental <u>L</u> ocal <u>D</u> ecision <u>S</u> upport system
AOC	<u>A</u> reas <u>O</u> f <u>C</u> oncern (Identified by the International Joint Commission)
GLWQA	<u>G</u> reat <u>L</u> akes <u>W</u> ater <u>Q</u> uality <u>A</u> greement
USEPA	<u>U</u> . <u>S</u> . <u>E</u> nvironmental <u>P</u> rotection <u>A</u> gency
OME	<u>O</u> ntario <u>M</u> inistry of <u>E</u> nvironment
Ohio EPA	<u>O</u> hio <u>E</u> nvironmental <u>P</u> rotection <u>A</u> gency
MDNR	<u>M</u> ichigan <u>D</u> epartment of <u>N</u> atural <u>R</u> esources
USGS	<u>U</u> . <u>S</u> . <u>G</u> eological <u>S</u> urvey
TOC	<u>T</u> otal <u>O</u> rganic <u>C</u> arbon
STORET	<u>S</u> torage and <u>R</u> etrieval (U.S. Environmental Protection Agency data system)
USACE	<u>U</u> . <u>S</u> . <u>A</u> rmy <u>C</u> orps of <u>E</u> ngineers
EMAP	<u>E</u> nvironmental <u>M</u> onitoring and <u>A</u> ssessment <u>P</u> rogram
SED BIO	<u>S</u> ediment data <u>B</u> iological (data collected by Ohio Environmental Protection Agency)
BHC	Hexachlorocyclohexane
TEL	<u>T</u> hreshold <u>E</u> ffect <u>L</u> evel
PEL	<u>P</u> robable <u>E</u> ffect <u>L</u> evel
LEL	<u>L</u> owest <u>E</u> ffect <u>L</u> evel
SEL	<u>S</u> evere <u>E</u> ffect <u>L</u> evel

Areal Distribution and Concentrations of Contaminants of Concern in Surficial Streambed and Lakebed Sediments, Lake Erie–Lake Saint Clair Drainages, 1990–97

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Abstract

Concerns about elevated concentrations of contaminants such as polychlorinated biphenyls and mercury in aquatic bed sediments throughout the Great Lakes Basin have resulted in a need for better understanding of the scope and severity of the problem. Various organochlorine pesticides, polychlorinated biphenyls, trace metals, and polycyclic aromatic hydrocarbons are a concern because of their ability to persist and accumulate in aquatic sediments and their association with adverse aquatic biological effects. The areal distribution and concentrations in surficial bed sediments of 20 contaminants of concern with established bed-sediment-toxicity guidelines were examined in relation to their potential effects on freshwater aquatic biota. Contaminants at more than 800 sampling locations are characterized in this report. Surficial bed-sediment-quality data collected from 1990 to 1997 in the Lake Erie–Lake Saint Clair Drainages were evaluated to reflect recent conditions. In descending order, concentrations of total polycyclic aromatic hydrocarbons, phenanthrene, total polychlorinated biphenyls, chrysene, benz[*a*]anthracene, benzo[*a*]pyrene, cadmium, lead, zinc, arsenic, and mercury were the contaminants that most commonly exceeded levels associated with probable adverse effects on aquatic benthic organisms. The highest concentrations of most of these contami-

nants in aquatic bed sediments are confined to the 12 specific geographic Areas of Concern identified in the 1987 Revisions to the Great Lakes Water Quality Agreement of 1972. An exception is arsenic, which was detected at concentrations exceeding threshold effect levels at many locations outside Areas of Concern.

Introduction

The Lake Erie–Lake Saint Clair Drainages (fig. 1) covers approximately 22,300 mi² in parts of Indiana, Michigan, Ohio, Pennsylvania, and New York. This area is one of a select set of hydrologic systems (referred to as study units) throughout the Nation that were studied between 1991 and 2000 as part of the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program. The program was established to (1) provide a nationally consistent description of recent water-quality conditions for a large part of the Nation's freshwater streams and aquifers, (2) define long-term trends in water quality, and (3) identify, describe, and explain, where possible, the major natural and anthropogenic factors that affect water-quality conditions and trends (Hirsch and others, 1988).

Anthropogenic contaminants (those resulting from human activity) are deposited from the atmosphere and discharged from point sources such as sanitary, combined, and storm sewers and from industrial facilities. Contaminants also originate as runoff from nonpoint sources such as urban, suburban, agricul-

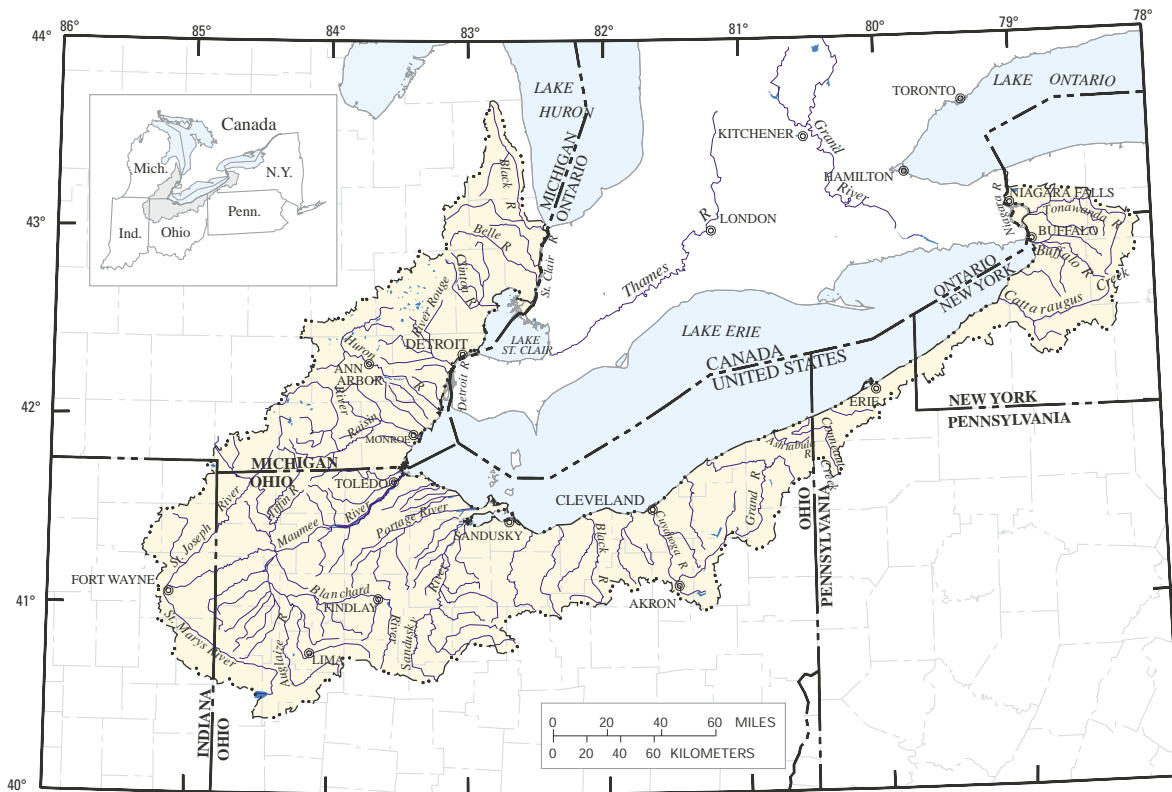


Figure 1. Location of Lake Erie-Lake Saint Clair Drainages study unit, principal streams, and major cities.

tural, and silvicultural areas. Areal distribution, concentrations, and bioavailability of contaminants in streambed and lakebed sediments are key issues in the Lake Erie–Lake Saint Clair Drainages. Although numerous studies of contaminants in aquatic sediments have been done in the Lake Erie–Lake Saint Clair Drainages, few studies have assessed how these contaminants vary from place to place and under different environmental conditions.

Streambed and lakebed sediments of the Lake Erie–Lake Saint Clair Drainages provide habitat for many aquatic organisms, but they also serve as a major repository for persistent and toxic chemicals that have been released into the environment or occur naturally. Since the early 1970's, people have been concerned about elevated concentrations of various synthetic organic compounds and trace metals in these streambed and lakebed sediments. Evidence from laboratory tests shows that contaminated aquatic sediments can reduce or eliminate benthic (bottom-dwelling) species of recreational, commercial, or ecological importance or affect the food supply required to sustain fish populations (U.S. Environmental Protection Agency, 1997a). Furthermore, bed-sediment contami-

nants can accumulate in the tissue of benthic organisms, causing health risks to predatory fish, wildlife, and human consumers as the contaminants move through the food chain.

The Great Lakes Water Quality Agreement (GLWQA) calls for governments throughout the Great Lakes Basin to reduce and eliminate persistent bioaccumulative and toxic substances. The Lake Erie Lake-wide Management Plan (LaMP) and 11 other Remedial Action Plans (RAP's) are programs that Canada and the United States are undertaking as part of an ongoing commitment to carry out the GLWQA (Daher, 1998). The committees of citizens and natural-resource managers comprising the LaMP's and RAP's have been charged with identifying, remediating, and restoring beneficial uses of the lake where impairments to these uses have been identified. Key findings from the study of the Lake Erie–Lake Saint Clair Drainages will provide needed information to these and other water-resources-management programs.

Fourteen highly desirable human uses of aquatic resources in the Great Lakes Basin, termed "beneficial uses," were identified by the International Joint Commission (IJC). As many as 9 of the 14 beneficial uses

are potentially impaired by sediment contamination in the Lake Erie–Lake Saint Clair Drainages. The possible consequences of these impairments are degraded fish populations, loss of fish habitat, fish tumors or other deformities, bird or animal deformities or reproductive problems, degradation of bottom-dwelling invertebrates (benthos), fish- and wildlife-consumption restrictions, tainting of fish and wildlife flavor, and restrictions on dredging activities. The impairment potential of populations of benthos is specifically addressed by this report.

A total of 37 bed-sediment contaminants of concern have been identified in the Lake Erie Basin (table

1). The list is inclusive of most contaminants identified by Federal, state, provincial, binational, and other organizations who are involved in water-quality programs in the Great Lakes Basin. For example, the list (table 1) includes the LaMP “critical pollutants,” PCB’s (polychlorinated biphenyls), mercury, U.S. Environmental Protection Agency (USEPA) “bioaccumulative” chemicals of concern, the Canada-Ontario Agreement Tier 1 and Tier 2 chemicals, and three additional trace metals (zinc, copper, and lead) identified by the Detroit River RAP. Of the 37 bed-sediment contaminants identified in table 1, available data for only 20 were sufficient for analysis.

Table 1. Organic compounds and trace metals in bed sediment identified by the Lake Erie Lakewide Management Plan (LaMP) as chemical contaminants of concern in the Lake Erie Basin, United States and Canada.

[Contaminants with a* are degradation products; those shown in italics have been identified as “critical pollutants” by the Lake Erie LaMP or have been shown to impair beneficial uses of Lake Erie]

Contaminant(s)	Common sources or uses
Organochlorine insecticides or biocides	
<i>Chlordane total</i> ^{1,3,4,5}	Historical use for control of mosquitoes, ants, cockroaches, and termites. Chlordane was used on agricultural crops, such as corn, potatoes, and tomatoes, as well as on home gardens, to control soil insects (Shelton, 1990). Canceled in 1988.
<i>γ chlordane</i>	
<i>α chlordane</i>	
* <i>Cis nonachlor</i>	
* <i>Trans nonachlor</i>	
DDT total ^{1,2,3,4,5}	Widespread use as a contact insecticide. Canceled in 1972 (Gessner and Griswold, 1978).
* <i>DDD</i>	
* <i>DDE</i>	
<i>Dieldrin</i> ^{1,3,4,5}	Used to control insect pests on corn and citrus fruits. Canceled in 1989 (Binational Toxic Strategy, 1998).
Toxaphene ^{2,3,4,5}	Turpentine, fish control, row crops. canceled in 1982.
<i>Mirex</i> ^{2,3,4,5}	Historical use for fire ants and as a flame retardant. Canceled in 1977. May still be used as a color-enhancing agent in fireworks (Binational Toxic Strategy, 1998).
* <i>Photomirex</i>	
Hexachlorocyclohexane, total ³	Agricultural and topical insecticides used in the United States to control flies, cockroaches, aphids, and boll weevils. Lindane (the gamma isomer of hexachlorocyclohexane) is registered for commercial and home use. Lindane is an active ingredient in several head-lice shampoos and is used to treat seeds.
<i>α</i> -Hexachlorocyclohexane	
<i>β</i> -Hexachlorocyclohexane	
<i>δ</i> -Hexachlorocyclohexane	
<i>γ</i> -Hexachlorocyclohexane (Lindane) ^{3,5}	
Hexachlorobenzene ^{3,4}	Wood preservatives, fluorocarbons, tetrachloroethylene.
Industrial organochlorine compounds or byproducts	
<i>PCB and congeners</i> ^{1,2,3,4,5}	Transformers, lubricants, hydraulic fluids. Restricted in 1979.
<i>Dioxin (2,3,7,8 TCDD)</i> ^{3,4,5}	Paper production; waste, coal, and automobile combustion.

Table 1. Organic compounds and trace metals in bed sediment identified by the Lake Erie Lakewide Management Plan (LaMP) as chemical contaminants of concern in the Lake Erie Basin, United States and Canada.—*Continued*

Contaminant(s)	Common sources or uses
Polycyclic aromatic hydrocarbons^{3,4}	
PAH's, total (expressed as a sum of 16 compounds)	
Anthracene	From incomplete combustion of coal, oil, gas, and coking byproducts, waste incineration, wood and tobacco smoke, forest fires, automotive exhaust, tars and tar products. PAH's are usually found in smoke and soot. PAH's are produced in petroleum refining and kerosene processing. PAH's are found in runoff containing greases and oils, and are a potential roadbed and asphalt leachate (Verschueren, 1977).
Benz[<i>a</i>]anthracene	
Benzo[<i>a</i>]pyrene	
Benzo[<i>b</i>]fluoranthene	
Benzo[<i>k</i>]fluoranthene	
Chrysene	
Dinitropyrene	
Perylene	
Phenanthrene	
Trace metals	
Arsenic ⁵	Orchard and forest sprays, natural occurring in some areas.
Cadmium ^{3,4}	Batteries, ceramics, metal coatings, sludge disposal.
Copper ⁵	Electrical industry, plumbing, fungicides and algal control.
Lead ^{3,4,5}	Leaded gasoline, batteries, plumbing, pigments in paint.
Mercury ^{1,2,3,4,5}	Coal and waste combustion, batteries, paint, industrial uses.
Tributyl tin ^{3,4}	Antifouling paint.
Zinc ⁵	Galvanizing, dyes, paints, pesticides, and fertilizers.

¹ Lake Erie critical pollutant identified by Lake Erie LaMP in 1994.

² Great Lakes Initiative Bioaccumulative Chemical of Concern (BCC).

³ Canada-Ontario Agreement (COA) tier 1 or tier 2 contaminant.

⁴ Binational Toxics Strategy contaminant.

⁵ Contaminant identified by the International Joint Commission or in Remedial Action Plans (RAP's)

Purpose and Scope

The purposes of this report are to (1) describe the areal distribution and concentrations of contaminants of concern in streambed and selected lakebed sediments in the Lake Erie–Lake Saint Clair Drainages, (2) compare these bed-sediment contaminant concentrations to guidelines that indicate concentrations either acutely or chronically toxic to aquatic macroinvertebrates, and (3) compare the extent and magnitude of contamination within Areas of Concern (AOC's) to other areas. AOC's are defined as the 12 specific geographic areas in the Lake Erie–Lake Saint Clair Drainages that have been identified as Areas of Concern by the International Joint Commission in the 1987 Revisions to GLWQA of 1972 (International Joint Commission, 1987; see fig. 25).

Accomplishing these objectives required the merging of four large databases that covered parts of the Lake Erie–Lake Saint Clair Drainages: the National Sediment Inventory (NSI), Ohio Sediment Data Inventory (OSI), USEPA Fully Integrated Environmental Locational Decision Support system (FIELDS) database, and the USGS-NAWQA sediment data. Only those bed-sediment samples collected from 1990 to 1997 (in the top 5 in. of sediment) in the United States part of the Lake Erie–Lake Saint Clair Drainages were evaluated to reflect recent U.S. conditions. The location and concentration range of selected contaminants of concern are mapped, and each contaminant is discussed with regard to its toxicity to aquatic macro-invertebrates according to three regional bed-sediment-quality guidelines (Persaud and

others, 1993; Ingersoll and others, 1996; Smith and others, 1996).

Background

The Lake Erie–Lake Saint Clair Drainages (fig. 1) is a 22,300-mi² area in the United States, approximately two-thirds of the total 30,140-mi² area of the Lake Erie Basin in the United States and Canada. From west to east, this includes parts of northeastern Indiana (6 percent), southeastern Michigan (27 percent), northern Ohio (62 percent), and areas in northwestern Pennsylvania and western New York (5 percent). Drainage for the study unit begins at the outflow of Lake Huron and includes all the tributaries draining to the St. Clair River, Lake Saint Clair, the Detroit River, and Lake Erie, the 11th-largest freshwater lake in the world. The study unit ends at the Niagara River, the outflow of Lake Erie. Principal rivers in the study unit are the Black, Belle, Clinton, River Rouge, Huron, and River Raisin in Michigan; the Maumee River and its tributaries (St. Joseph, St. Marys, Tiffin, Auglaize, Ottawa, and Blanchard) in Ohio, Michigan, and Indiana; the Portage, Sandusky, Black, Cuyahoga, Grand, and Ash-tabula Rivers in Ohio; Conneaut Creek in Ohio and Pennsylvania; and Cattaraugus Creek, the Buffalo River, and Tonawanda Creek in western New York.

Population density and growth in the Lake Erie–Lake Saint Clair Drainages are among the highest in the Great Lakes area. About 40 percent of the total population of the Great Lakes Basin lives in the Lake Erie–Lake Saint Clair Drainages. The U.S. population in 1990 was 9.76 million: 3.93 million in Ohio, 4.64 million in Michigan, 0.34 million in Indiana, 0.23 million in Pennsylvania, and 0.62 million in New York (Casey and others, 1997). Land use is a mix of agriculture, urban, and forest areas (Casey and others, 1997; fig. 2). Agriculture makes up 74.8 percent of the total Basin area, with croplands and pasture as the predominant types. Orchards and vineyards are located along the Lake Erie shoreline in Ohio, Pennsylvania, and New York because of the moderating effect of the lake on the local climate. Urban land use accounts for 11.2 percent of the Basin area, with residential (6.7 percent) predominating and commercial (1.5 percent), transportation (0.9 percent), industrial (0.8 percent) and other mixed urban land (1.3 percent) making up the remainder. The largest cities are near the Lake. Forested areas

constitute 10.5 percent of the Basin area, whereas water, wetlands, and barren land constitute less than 4.0 percent of the Basin area (Casey and others, 1997). Detailed information on the environmental and hydro-logic setting of the Lake Erie–Lake Saint Clair Basin is given in Casey and others (1997).

Study Design

Surficial bed-sediment data from streams across the Lake Erie–Lake Saint Clair Drainages and selected sites in Lakes St. Clair and Erie have been evaluated for this report in an effort to provide a better understanding of recent U.S. conditions and to identify areas where new or additional aquatic bed-sediment data are needed. The classes of compounds investigated in this report were organochlorine pesticides, total polychlorinated biphenyls (PCB's), polycyclic aromatic hydrocarbons (PAH's), and trace metals.

Throughout the Lake Erie Basin, aquatic bed-sediment samples have been collected and analyzed, and the data have been stored in several large databases. Data have been collected by many public-sector agencies; the USEPA, U.S. Army Corps of Engineers (USACE), U.S. Fish and Wildlife Service (USFWS), USGS, Ontario Ministry of the Environment (OME), Ohio EPA, Michigan Department of Natural Resources (MDNR), more recently named Michigan Department of Environmental Quality (MDEQ), and universities, and their consultants (Fox, 1994). Most of these data were found in four national and regional databases, the NSI, OSI, USEPA-FIELDS, and NAWQA. These databases include chemical and physical data for aquatic bed-sediment samples from tributaries, connecting channels, harbors, and Lake Erie and Lake Saint Clair (proper) collected in the United States and Canada. Data consist of information on sampling location, sampling method, analytical method, concentration, sample weight, core depth, grain-size information, and percent total organic carbon (TOC) for a large list of contaminants in samples collected from the early 1970's to 1997. For this report, only recent data (1990-97) collected from the United States part of the Lake Erie Basin were analyzed (fig. 3). Only contaminants of concern with both sufficient data for analysis and existing bed-sediment quality guidelines were included in the report.

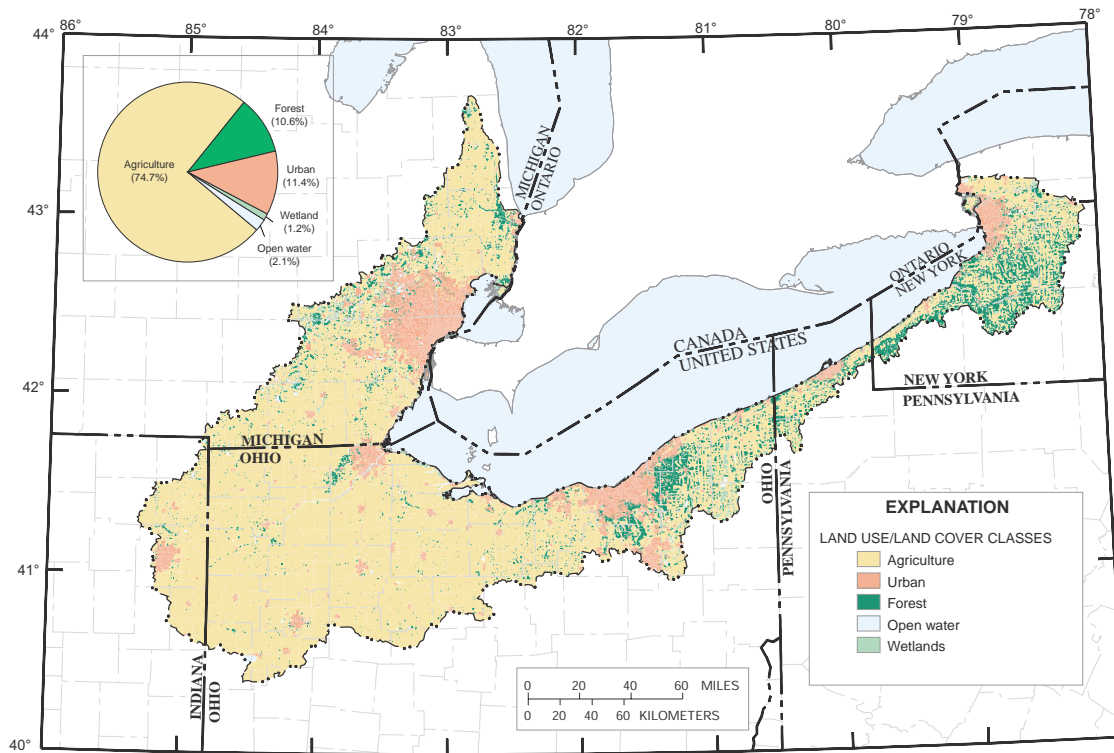


Figure 2. Landuse/land cover in the Lake Erie-Lake Saint Clair Drainages, 1992.

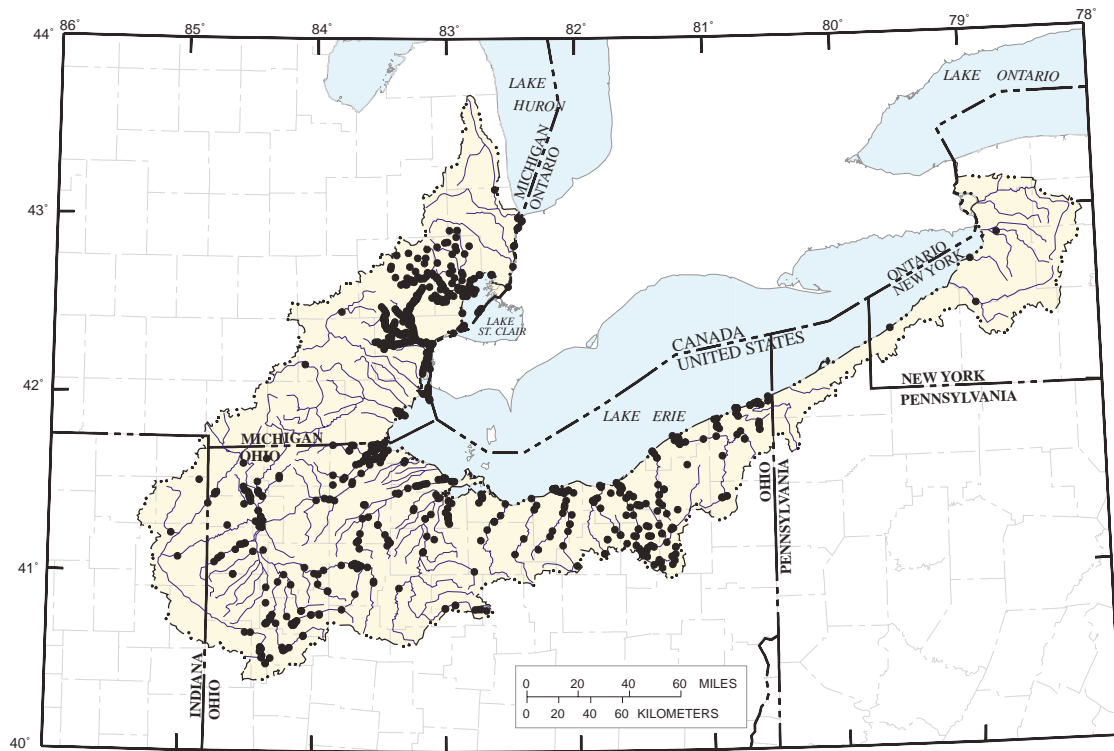


Figure 3. Location of bed-sediment samples analyzed for potential contaminants in the Lake Erie-Lake Saint Clair Drainages, 1990-97.

National Sediment Inventory (NSI). In 1993, the USEPA began developing the NSI. The scope of the NSI database was to review readily available sediment-chemistry data and evaluate the extent and severity of bed-sediment contamination throughout the United States. Data incorporated into the NSI database from the Great Lakes area include contributions from the USEPA's Storage and Retrieval System (STORET), USACE, USGS, USEPA National Bioaccumulation Study, USEPA Great Lakes Sediment Inventory, USEPA Environmental Monitoring and Assessment Program (EMAP), state resource agencies, universities, and consultants. Approximately two-thirds of the sampling stations in NSI were obtained from STORET.

Ohio Sediment Inventory (OSI). The Ohio EPA's Division of Surface Water maintains two sediment databases: the OSI database and the SED BIO database. The OSI is the larger of the two, and it currently (2000) contains organic and trace-element data collected from 1972 to 1997 by Ohio EPA or their contractors from more than 1,000 sites throughout Ohio.

The SED BIO database contains Ohio EPA bed-sediment data for trace metals collected by the Ohio EPA's Ecological Assessment Unit. Both databases include fields for database sample number, project station, sample date, time of sample, sampling organization, collection device, site name, river code, river mile, and latitude and longitude.

Fully Integrated Environmental Locational Decision Support system (FIELDS). The USEPA FIELDS database contains data from (1) USACE reports for the Detroit River, Clinton River, River Rouge, Huron River, and River Raisin for the period 1970–93, (2) USACE sediment sampling digital files for the River Rouge, (3) MDNR Surface Water Quality Division's digital sediment data for the Detroit River, and (4) Ontario Ministry of Environment (OME) Detroit River Study digital bed-sediment data collected in 1991.

FIELDS is no longer housed and maintained by USEPA-Region 5. The FIELDS program has shifted focus from database aggregates to GIS visualization and interpretation models. The database currently contains data from approximately 2,380 sites, most of which are in southeastern Michigan.

National Water-Quality Assessment Program (NAWQA). The NAWQA bed-sediment database includes information on contaminants in aquatic bed sediment at 15 environmentally representative sites on

major streams in the Lake Erie–Lake Saint Clair Drainages. Digital data includes information on grain size, percent total organic carbon, and concentrations of total PCB's, 30 organochlorine pesticides, 16 polycyclic aromatic hydrocarbons, 48 semivolatile organic compounds, and 44 elements.

Study Methods

Screening procedures applied to the data before analysis are described in this section. Further details about the screening criteria used to evaluate whether the data were suitable to include in the analyses made for this report (methods and reporting limits) are contained in Appendix A.

Data from each of the four databases were combined into a single data set for statistical analysis. Screening criteria were applied in an attempt to provide the degree of consistency necessary to combine, analyze, and interpret these data. Although these data were collected for different purposes by different agencies, the overall purpose of the studies from which these data arise was to assess aquatic bed-sediment contamination for toxic, persistent, and bioaccumulative contaminants. Because of that common objective, most of the data were collected and analyzed by use of accepted and published methods for soils and (or) streambed sediments. Sample analytical results were produced under the guidelines contained in each project's QA/QC (quality assurance and quality control) Plans. Only those project data meeting the screening criteria were accepted for further statistical analysis and interpretation.

Sampling Agencies and Analyzing Laboratories

A total of seven public agencies collected and provided the data used in this report. The seven agencies included three Federal, one regional, and three state agencies. The Federal agencies were the USEPA Region 5, the USGS, and the USACE. The state agencies were the Ohio EPA, the MDNR, and the New York State Department of Environmental Conservation (DEC). The regional (multicounty) agency was the Rouge Program Office (RPO).

A total of 15 laboratories analyzed and reported sample results, 5 in the public sector and 10 in the private sector. Of the five public-sector laboratories, two were Federal and three were state laboratories. The public-sector laboratories were the USGS National

Water Quality Laboratory and the USACE Ohio River Division Laboratory. The three state laboratories were the Ohio EPA Division of Environmental Services Laboratory, the MDNR State Water Laboratory, and the New York State Laboratory of Health. Private-sector laboratories included Ecology and Environment, Inc., National Environmental Testing, Inc., Betz Laboratories, Aquatec Laboratories, Metcalf and Eddy, Inc., Thermo Analytical Inc., Ross Laboratory, Inc., Heidelberg College Water Quality Laboratory, and three other laboratories identified as “Other” by the Ohio EPA.

Other Screening Criteria

In all, data from 823 sample sites were selected for analysis from the 2,938 Lake Erie–Lake Saint Clair Drainages sites listed in the USEPA NSI, Ohio EPA’s OSI, FIELDS, and NAWQA sediment databases (fig. 3). Data were selected or eliminated on the basis of sample location, date, depth, and replication for each of the databases, as follows:

Location. Data analysis was limited to the U.S. side of the Lake Erie–Lake Saint Clair Drainages. Samples collected at contaminated sites such as landfills or known hazardous-waste disposal sites were excluded in an effort to characterize only ambient stream or lake conditions. Sediment data from sites in lagoons, ponds, reservoirs, or inland lakes were not used in the analysis. The vast majority of sites are stream sites, but several sites on the margin or within Lakes St. Clair and Erie met the location criteria (fig. 3).

Date. In an effort to characterize recently deposited sediments, only samples collected from calendar year 1990 through 1997 were included for analyses. At a few locations, a site may have been revisited over the 8-year period. In these instances, the most recent sample was used in the analysis, and the previous sample results were excluded.

Depth. In order to characterize recently deposited sediments, only the top 5 in. of surficial bed sediments of streams were included in the analysis. Common methods for sampling sediment usually involve either core or grab samples. Core samples include material (sediment) from a wide range of depths, whereas grab samples usually represent the top 5 in. or less of material.

Replication. Field duplicate and field replicate samples were not included in the data set. These additional samples are used primarily for quality control or quality assurance of field or laboratory methods of sample collection, handling, and analysis. They might include

additional samples collected at the same location and time (replicates) or subsamples split from the original (duplicates). The NSI contained sediment information for 955 sites in the Lake Erie–Lake Saint Clair Drainages. After screening against the data-selection criteria, only 0.5 percent of the data in NSI were used in the analysis. The most limiting factor for NSI site selection was the year of sampling; only 3 percent of the samples were collected during or after 1990. NSI data in this report include only three sites in the New York part of the Lake Erie–Lake Saint Clair Drainages.

The Ohio EPA’s OSI database contained sediment information for 666 sites in the Lake Erie–Lake Saint Clair Drainages. After screening, only 347 sites in OSI database were used in the analysis. Approximately 50 percent of the data met the criteria for being sampled between 1990 and 1997. A few sites represented samples collected in lagoons, ponds, or small lakes, and these sites were excluded from the analysis. Multiple samples collected from the same location on the same date were excluded. These additional samples were assumed to be replicates.

The FIELDS database contained sediment information for 1,302 sites in the Lake Erie–Lake Saint Clair Drainages. After screening, only 455 sites in FIELDS were used in the analysis. As much as 55 percent of FIELDS data were excluded because samples had been collected before 1990. Any samples with qualifiers or comments indicating that they were extraction replicates were excluded. Also, in any case where a sample was collected at the same location on the same day, only data from the first occurrence was selected. Some sampling projects within FIELDS used grab samples, whereas others used core samples. Only samples meeting the requirements of being collected from the top 5 in. of the surficial sediments were used in the analysis. If a depth was not specified for a core sample, data from that sample were not used in the analysis. If a grab-sample depth was not recorded, the sample was assumed to be only a few inches deep and was used in the analysis. Because of the uncertainty of sample depth, limitation based on depth was the most restrictive requirement in selecting data from FIELDS.

The NAWQA data set contained sediment information for 15 sites in the Lake Erie–Lake Saint Clair Drainages. The NAWQA samples were collected in 1996 and 1997. Sediment samples collected by NAWQA investigators were obtained with a hand-held grab sampler in wadeable areas. Each sample was col-

lected from the top 2 to 3 inches of the sediment deposit. Replicates of field samples were not included in the data set. All 15 sample results were used in this analysis.

Sediment-Quality Guidelines Selected for Comparison With Site Data

Because of the many complex factors involved in bioaccumulation, contaminant concentrations in streambed sediments cannot be used as direct measures of the potential for contaminants to cause adverse effects on human health. It is possible, however, to relate sediment-contaminant concentrations to the potential for adverse effects on the health of aquatic organisms that live in or on these sediments. Although much still needs to be understood with respect to the behavior, bioavailability, and toxicity of contaminants in the aquatic bed sediments of the Lake Erie–Lake Saint Clair Drainages, recent progress in developing bed-sediment-quality guidelines for aquatic life has greatly helped environmental managers to make regulatory and cleanup decisions that are based on the best scientific information available.

Numerical sediment-quality guidelines are useful tools for assessing sediment quality. Such guidelines have been developed by various jurisdictions around North America using many approaches (U.S. Environmental Protection Agency, 1997a). Many of the studies resulting in guidelines deal with the concentrations of individual contaminants in sediments at which toxicity is rarely and (or) frequently observed; however, most deal with marine and estuarine sediments (Long and Morgan, 1991). Only a few studies have been published on Great Lakes (freshwater) sediments (Persaud and others, 1993; Ingersoll and others, 1996; Smith and others, 1996).

This study compares the concentrations of contaminants of concern detected in bed-sediment samples to three freshwater bed-sediment-quality guidelines used in the Great Lakes area (table 2). These are (1) Ontario Ministry of Environment (OME) guidelines for the protection and management of Canadian freshwater sediments, (2) USEPA guidelines for Great Lakes sediments, and (3) Environment Canada and the Great Lakes (EC&GL) guidelines for ecosystems throughout Canada and the Great Lakes Drainages (Graphical comparisons, referred to later in this report, are in Appendix B. Information on the development of the Canadian and U.S. guidelines is given in Appendix C.). These guidelines can serve

only as screening tools for streambed sediments in freshwater streams, and they do not replace the need for toxicity testing or aquatic-community assessments to determine specific adverse effects on aquatic organisms endemic to a particular site. Evaluation of fish and benthic communities at a site provides an indication of the effect of contaminant biomagnification up the food chain and of the subtle effects of contaminants on reproduction, growth, and behavior. Numerical sediment-quality assessment values used for comparisons in this report are listed in table 2.

Guidelines Selected

For this report, the Threshold Effect Levels (TEL's) and Probable Effect Levels (PEL's) developed by Smith and others (1996) for Environment Canada and the Great Lakes (EC&GL) were most frequently used to assess the possible effects of contaminants in surficial bed sediments on populations of aquatic macroinvertebrates. These sediment quality criteria were selected over the other two available guidelines (table 2) because they contained guidelines for more organochlorine insecticides, PCB's, PAH's, and trace metals than the other two. In addition, Smith and others' criteria (1996) are considered to be the most sensitive of the three sets of guidelines; therefore, using them represents the most conservative approach to protecting sediment quality.

If bed-sediment-quality guidelines indicating the adverse biological effects of contaminants of concern were not available from Smith and others (1996), TEL's and PEL's from Ingersoll and others (1996) were used. These two sets of guidelines were in greater agreement about the concentrations of contaminants likely to cause various degrees of adverse effects in benthic communities than either set was in comparison to Persaud and others (1993). In addition, the sediment-quality guideline concentrations proposed by Ingersoll and others (1996) and Smith and others (1996) were almost always lower than those proposed by Persaud and others (1993).

Lowest Effect Levels (LEL's) and Severe Effect Levels (SEL's) from Persaud and others (1993) were used only if guidelines for a constituent of concern were not available from either of the other two references. However, for SEL nonpolar organic compound values listed in table 2, the conservative approach, as suggested by Smith and others (1996), was taken (which assumed a 1 percent total organic carbon (TOC) sample value). This approach seemed appropri-

Table 2. Selected guidelines for chemical concentrations in freshwater bed sediment that have been observed or predicted to be associated with adverse effects on aquatic biota

[Sediment concentrations are in milligrams per kilogram dry weight; --, no guidelines available; (), guideline used in contaminant maps--figures 4-23 of this report.]

Chemical constituent	Ontario Ministry of the Environment		U. S. Environmental Protection Agency		Environment Canada and Great Lakes	
	Provincial Sediment Quality Guidelines ¹		Great Lakes Sediment Effect Concentrations ²		Sediment Quality Assessment Values ³	
	Lowest Effect Level	Severe Effect Level ⁴	Threshold Effect Level	Probable Effect Level	Threshold Effect Level	Probable Effect Level
Organochlorine insecticides or biocides						
Chlordane, total	0.007	0.06	--	--	(0.0045)	(0.0089)
DDT, total	.007	.12	--	--	(.0070)	(4.45)
Dieldrin plus aldrin	.002	.910	--	--	(.00285)	(0.00667)
Hexachlorobenzene	(.02)	(.24)	--	--	--	--
Hexachlorocyclohexane, total	(.003)	(.12)	--	--	--	--
Lindane	--	--	--	--	(.00094)	(.00138)
Mirex, total	(.007)	(1.30)	--	--	--	--
Industrial organochlorine compounds						
PCB's, total	0.07	5.3	0.032	0.24	(0.0341)	(0.277)
Polycyclic aromatic hydrocarbons						
Anthracene	0.22	3.70	(0.010)	(0.17)	--	--
Benz[a]anthracene	.32	14.8	.016	.28	(0.0317)	(.385)
Benzo[a]pyrene	.37	14.4	.032	.32	(.0319)	(.782)
Chrysene	.34	4.6	.027	.41	(.0571)	(.862)
Phenanthrene	.56	9.5	.019	.41	(.0419)	(.515)
PAH's (total)	4.0	100.0	(.260)	(3.4)	--	--
Trace metals						
Arsenic	6	33	11	48	(5.9)	(17)
Cadmium	0.6	10	0.58	3.2	(.596)	(3.53)
Copper	16	110	28	100	(35.7)	(197)
Lead	31	250	37	82	(35)	(91.3)
Mercury	.2	2	--	--	(.174)	(.486)
Zinc	120	820	98	540	(123)	(315)

¹ Persaud and others, 1993.

² Ingersoll and others, 1996.

³ Smith and others, 1996.

⁴ Severe Effect Level values for nonpolar organic compounds are based on an assumed 1 percent total organic carbon in the sample.

ate for the Lake Erie– Lake Saint Clair Drainages, where TOC values averaged between 1-2 percent.

Statistical and Graphical Methods

Areal-distribution maps are used to illustrate the range of concentrations of contaminants reported for bottom sediments of streams, rivers, harbors, and shorelines in the Lake Erie–Lake Saint Clair Drain-

ages. The ranges shown on the maps were selected to compare sediment concentrations relative to detection limits and to sediment-quality guidelines reported by Persaud and others (1993), Ingersoll and others (1996), and Smith and others (1996). Areal-distribution maps were generated for each contaminant of concern (figs. 4–23). Each map shows the location at which that specific contaminant was reported and its

concentration relative to bed-sediment guidelines. Maps were created by use of a geographic information system (GIS) plotting program linked with the data sets selected for the study.

Probability plots, which are plots of the probability of a sample concentration being greater than a given value, were constructed for each contaminant (Appendix B). A probability plot is a type of quantile plot that uses a plotting position. The plotting position is subsequently multiplied by 100 and displayed as a percentile on the x-axis of the graph while the concentration is displayed on the y-axis. This method is a robust procedure and is recommended for analyzing and displaying data sets that are characterized by multiple detection limits (Helsel and Hirsch, 1995, p. 362-364). Data analyzed for this report are characterized by multiple detection limits. By use of probability plots, the data can be displayed as the percent probability of occurrence (Helsel and Hirsch, 1995, p. 29). The probability plots show samples with no detected concentrations, samples with detected concentrations, concentration ranges, and contaminant guidelines. The percent frequency of detection was computed as the fraction of total samples reported with results above the detection limit times 100.

Star diagrams (figs. 26-27) were used to display and summarize contaminant-concentration data on multiple axes. One observation, either the 75th- or 90th-percentile concentration, was represented by a point on an axis of the multiple-axis star, and these points are connected by line segments. Star diagrams used for this report are six-pointed, so that data for six contaminants can be shown on one star. Unusual observations will stand out as a noticeable difference in the shape from other stars (Helsel and Hirsch, 1995, p. 53).

Areal Distribution and Concentrations of Contaminants of Concern in Surficial Bed Sediments

Twenty contaminants of concern found in surficial bed sediments of surface waters in the Lake Erie–Lake Saint Clair Drainages are discussed in this section. These 20 contaminants are those for which sufficient data were available for analysis and for which bed-sediment-quality guidelines also are available. They are among four chemical classes: organochlorine pesticides, PCB's, PAH's, and trace metals. The number of samples collected for analysis of each chemical constituent, the number of samples with detections,

and the range of the detected concentrations used in this report, are listed in table 3. Maps showing the spatial distribution and concentration range for each of the 20 contaminants of concern are included in the discussion of the four chemical classes (figs. 4-23), and contaminant probability-distribution plots are shown in Appendix B.

Stream reaches for which data are inadequate or unavailable include the following:

Michigan--main stems of the Black River, Bell River, Huron River, and upper River Raisin;

Indiana--lower St. Mary's River and most of the St. Joseph River;

Ohio--upper Sandusky River, and upper Grand River; and

New York--Cattaraugus Creek, the Buffalo River and its tributaries, and Tonawanda Creek. For the most part, recent bed-sediment data were not electronically available for Pennsylvania and New York.

Organochlorine Compounds

Organochlorine compounds analyzed for this report are organochlorine pesticides and polychlorinated biphenyls. Many organochlorine pesticides are no longer manufactured or sold for use in the United States or Canada because of environmental and human-health concerns. An exception is lindane. Organochlorine pesticides and PCB's are still manufactured and used in certain parts of the world. Organochlorine compounds generally are characterized by their great persistence in the environment and are considered highly toxic to fishes and lower aquatic organisms. These compounds have a high affinity for lipids (fatty tissue), resulting in their biomagnification within organisms. Chlorinated organic compounds are hydrophobic; they tend to absorb to organic carbon and other fine particles in suspended and bed sediments. Because of this behavior, these compounds can be present in sediments in concentrations that are orders of magnitude greater than those in water. Therefore, sediments can provide a mechanism by which environmentally persistent organochlorine compounds remain in a surface-water system many years after their initial input (Smith and others, 1988).

Total chlordane (sum of chlordane, oxychlordane, cis-nonachlor, and trans-nonachlor). Chlordane is a wide-spectrum insecticide that was introduced in 1947 for urban and agricultural uses. Chlordane consists of gamma and alpha isomers and technical chlordane. Its degradates are oxychlordane, cis-nonachlor,

and trans-nonachlor. Chlordane has been used for the control of mosquitoes, cockroaches, ants, and termites. Until April 1976, chlordane was used on agricultural crops such as corn, potatoes, and tomatoes, as well as home garden crops, to control soil insects (Shelton, 1990). USEPA restricted its agricultural use in 1976 and the canceled virtually all other uses in April 1988.

Of the 371 bed-sediment samples analyzed for total chlordane, only 29 samples (7.82 percent) showed detectable concentrations. Of the 29 samples with chlordane detections, 4 sample concentrations ranged from the TEL to less than the PEL, 16 samples were from 1 to less than 10 times the PEL, and 2 sample concentrations ranged from 10 to less than 100 times the PEL (figs. 4 and B1, table 3). Of the 342 samples with no detections of chlordane, detection limits for less than half, 36 and 155 samples, were less than the TEL and PEL, respectively; thus, these samples were used for assessment purposes. Lower detection limits would have made the data more useful.

The highest concentrations of chlordane in bed sediments were found in samples collected from 1994–95 in Michigan in the Clinton River near the mouth and in Lake Saint Clair (fig. 4). At these locations, concentrations ranged from 0.10 to 0.12 mg/kg. These concentrations were 11.7 to 13.5 times the PEL. Other locations where concentrations of chlordane exceeded the PEL (listed in order of decreasing concentration) were as follows: the mouth of the Maumee River, Ohio; a tributary to the Ottawa River at Toledo, Ohio; a tributary to the Little Cuyahoga River near Akron, Ohio; tributaries to the lower Cuyahoga River near Cleveland, Ohio; the main stem of the Little Cuyahoga River, Ohio; the mouth of the Vermilion River, Ohio; and the mouth of the Ashtabula River, Ohio.

Total DDT (sum of isomers of DDT, DDD, DDE). DDT degrades to DDE and DDD, which also are toxic and highly resistant to further chemical decomposition. DDT and its isomers are the most permanent and durable of all contact insecticides because of their insolubility in water, their low vapor pressure, and their resistance to destruction by light and oxidation (Gessner, 1978). Widespread use of DDT began in 1939, peaked in the 1960's, continued until about 1970, and greatly declined when use of DDT was canceled in 1972.

Of the 409 bed-sediment samples analyzed for total DDT, 145 samples (35.4 percent) contained detectable concentrations. Of the 145 samples with

detectable concentrations, 109 sample concentrations ranged from the TEL to less than the PEL, and 1 sample concentration was greater than the PEL (figs. 5 and B2, table 3). Of the 264 samples with no detections of total DDT, detection limits for 127 and 261 sample concentrations were less than the TEL and PEL, respectively; thus, these samples were used for assessment purposes.

The highest concentration of total DDT was found in bed sediment at the mouth of the Clinton River, Michigan, in 1994 (fig. 5). At this location, the detected concentration was 22 mg/kg. This exceeded the PEL by 4.9 times. Other locations with elevated concentrations of total DDT were the Ottawa River and its tributaries at Toledo, Ohio and a small tributary near the mouth of the Maumee River, Ohio, Lake Saint Clair, and the main stem of the Clinton River, in Michigan.

Total dieldrin (sum of dieldrin plus aldrin). Aldrin, which quickly transforms into dieldrin, is metabolically converted to dieldrin by aquatic organisms. Both chemicals were used primarily in agricultural areas to control insect pests, originally on corn and later on citrus fruits (U.S. Environmental Protection Agency, 1993c). These substances also were used in urban areas for control of termites, cockroaches, and fire ants into the 1980's. Dieldrin and aldrin were two of the most widely used chlorinated hydrocarbon pesticides prior to their cancellation for surface use in 1974. Most remaining aldrin products were canceled by 1987, the last product being canceled in 1991 (Binational Toxic Strategy, 1998).

Of the 407 bed-sediment samples analyzed for dieldrin plus aldrin, 45 samples (11.1 percent) showed detectable concentrations. Of the 45 samples with detectable concentrations, 7 sample concentrations ranged from the TEL to less than the PEL, 12 sample concentrations were from 1 to less than 10 times the PEL, and 1 sample concentration was from 10 to less than 100 times the PEL (figs. 6 and B3, table 3). Of the 362 samples with no detections of dieldrin plus aldrin, detection limits in 25 and 228 samples were less than the TEL and the PEL, respectively; thus, these samples were used for assessment purposes.

The highest concentration of total dieldrin in aquatic bed sediment was found in a tributary to the Ottawa River at Toledo, Ohio, in 1993 (fig. 6). At this location, the detected dieldrin concentration was 0.102 mg/kg. This concentration was 15.2 times the PEL. Other locations where concentrations of dieldrin

Table 3. Number of bed-sediment samples reported, number with detected values, and the number detected in relation to sediment-quality guidelines, Lake Erie–Lake Saint Clair Drainages, 1990–97
 [TEL, Threshold Effect Level; PEL, Probable Effect Level; LEL, Lowest Effect Level; SEL, Severe Effect Level. Values and references for all effect levels are listed in table 2]

Contaminant	Total	Number of samples in category					
		With detected values	Less than the TEL	Equal to or greater than the TEL but less than the PEL	Equal to or greater than the PEL but less than 10 times the PEL	Equal to or greater than 10 times PEL but less than 100 times the PEL	Equal to or greater than 100 times the PEL
Chlordane, total	371	29	7	16	4	2	0
DDT, total	409	145	36	108	1	0	0
Dieldrin plus aldrin	407	45	25	7	12	1	0
Lindane ¹	404	11	4	2	4	1	0
PCB, total	683	223	3	67	91	35	27
PAH, total	414	231	36	78	83	30	4
Anthracene	392	76	4	26	30	13	3
Benz[<i>a</i>]anthracene	393	158	17	65	55	20	1
Benzo[<i>a</i>]pyrene	388	147	15	63	59	9	1
Chrysene	396	189	26	86	65	11	1
Phenanthrene	398	187	26	66	74	19	2
Arsenic	480	470	141	269	58	2	0
Cadmium	616	588	276	198	114	0	0
Copper	587	586	363	209	14	0	0
Lead	615	614	349	156	109	0	0
Mercury	465	309	195	59	51	4	0
Zinc	575	575	326	167	82	0	0
			Less than LEL	Equal to or greater than the LEL but less than the SEL	Equal to or greater than the LEL but less than 10 times the SEL	Equal to or greater than 10 times SEL but less than 100 times the SEL	Equal to or greater than 100 times the SEL
Hexachlorobenzene	411	6	1	3	2	0	0
Hexachlorocyclohexane, total	407	45	21	24	0	0	0
Mirex, total	199	0	0	0	0	0	0

¹, γ -hexachlorocyclohexane.

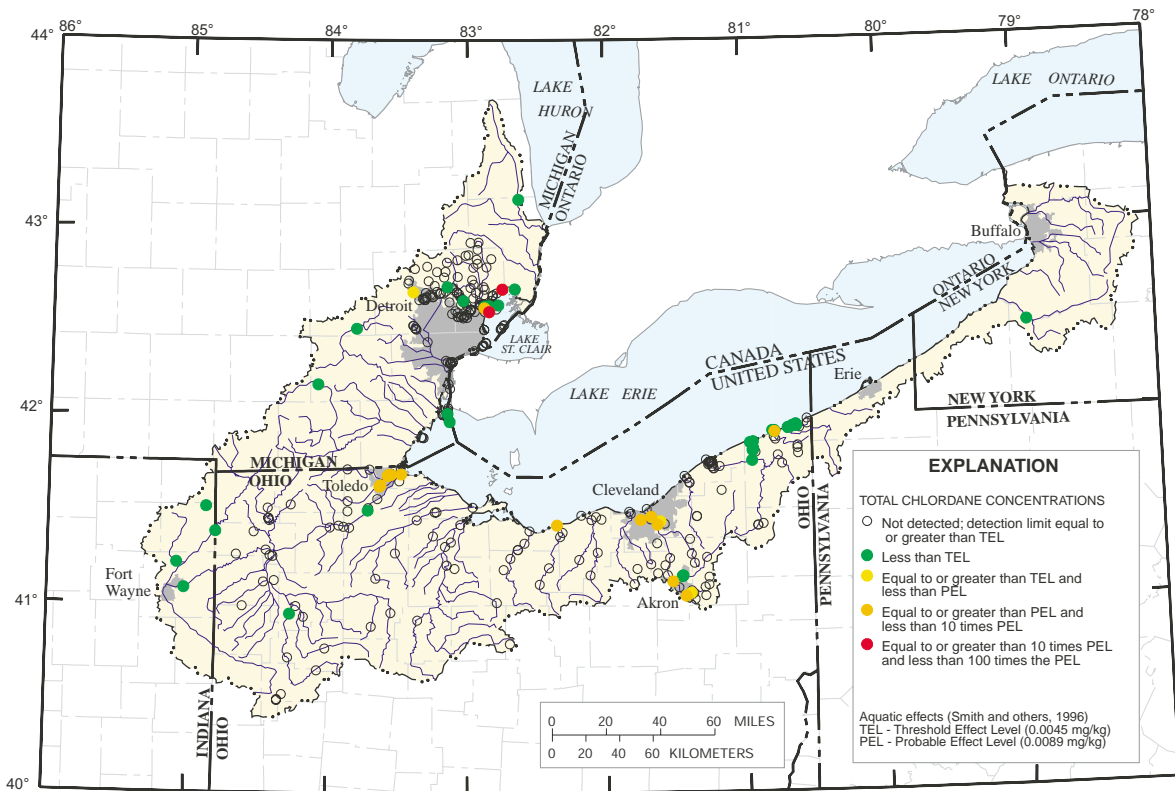


Figure 4. Total chlordane concentrations in streambed and lakebed sediments, Lake Erie–Lake Saint Clair Drainages, 1990–97.

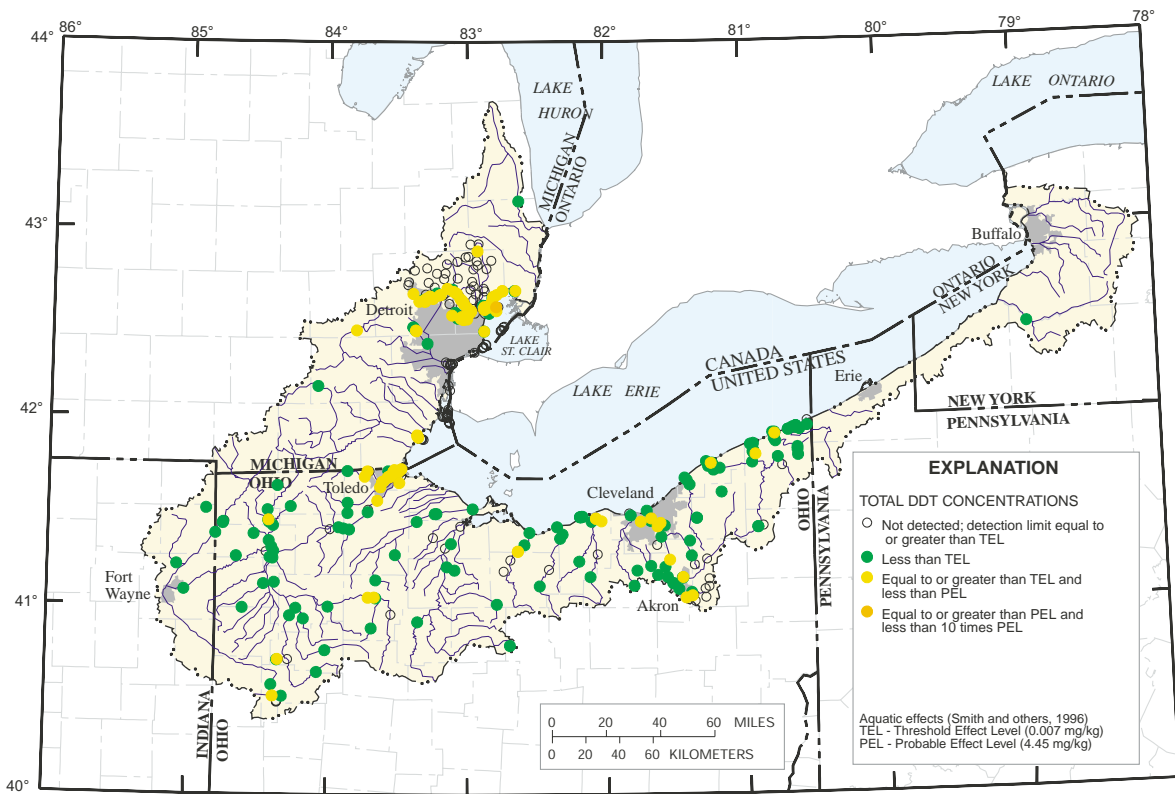


Figure 5. Total DDT concentrations in streambed and lakebed sediments, Lake Erie–Lake Saint Clair Drainages, 1990–97.

exceeded the PEL (listed in order of decreasing concentration) were the main stem of the Ottawa River at Toledo, Ohio; a tributary to the mouth of the Cuyahoga River, Ohio; and the lower main stem of the Huron River, Ohio.

Hexachlorobenzene. Hexachlorobenzene is used as a wood preservative, is used in production of aromatic fluorocarbons, and is a byproduct in the manufacturing of tetrachloroethylene (Verschuere, 1977).

Of the 411 bed-sediment samples analyzed for hexachlorobenzene, 6 samples (1.46 percent) showed detectable concentrations. Only Persaud (1993) provides sediment-quality guidelines for hexachlorobenzene. Of the six samples with detectable hexachlorobenzene, the concentration in three samples ranged from the LEL to less than the SEL, none were in the range from 1 to less than 10 times the SEL, and 2 sample concentrations ranged from 10 to less than 100 times greater than the SEL (figs. 7 and B4, table 3). Of the 405 samples with no detections of hexachlorobenzene, detection limits for 185 and 248 samples were less than the LEL the SEL, respectively; thus, these samples were used for assessment purposes.

The highest concentrations of hexachlorobenzene ranged from 4.9 to 5.9 mg/kg in bed sediment sampled at two sites in the lower Ashtabula River, Ohio, in 1993 (fig. 7). Concentrations were 20.4 to 24.6 times the SEL of 0.24 mg/kg

Total hexachlorocyclohexane (sum of α , β , δ , and γ isomers). Hexachlorocyclohexane and its isomers are agricultural and topical insecticides (Parker, 1984). There are four forms of hexachlorocyclohexane: alpha, beta, delta, and gamma (α , β , δ , and γ isomers).

Of the 407 bed-sediment samples analyzed for total hexachlorocyclohexane, 45 samples (11.1 percent) showed detectable concentrations. Only Persaud (1993) provides sediment-quality guidelines for total hexachlorocyclohexane. Of the 45 samples with detectable total hexachlorocyclohexane, 24 sample concentrations ranged from the LEL to less than the SEL (figs. 8 and B5, table 3). Of the 362 samples with no detections of hexachlorocyclohexane, detection limits for 60 and 296 samples were less than the LEL and the SEL, respectively; thus, these samples were used for assessment purposes.

The highest concentration of hexachlorocyclohexane, 0.04 mg/kg, was found in a headwater tributary to the Clinton River, Michigan, in 1994 (fig. 8). This concentration was about 17 times the LEL. Other locations where concentrations exceeded the LEL

(listed in order of decreasing concentration) were the lower Clinton River, near Detroit, Michigan; the Ottawa River at Toledo, Ohio; the upper Maumee River, Ohio; a headwater tributary to the Auglaize River, Ohio; a headwater tributary to the Tiffin River, Ohio; a headwater tributary to the River Rouge, Michigan; the main stem of the Blanchard River, Ohio; and the headwaters of the St. Marys River, Ohio.

Lindane (γ -hexachlorocyclohexane). Lindane (the gamma isomer of hexachlorocyclohexane) is an organochlorine insecticide registered for commercial and home use. It is an active ingredient in several prescription shampoos used for the elimination of head lice (Shelton, 1990).

Of the 404 bed-sediment samples analyzed for lindane, only 11 samples (2.72 percent) showed detectable concentrations. Of the 11 samples with detections of lindane, 2 sample concentrations ranged from the TEL to less than the PEL, 4 sample concentrations ranged from the PEL to less than 10 times the PEL, and 1 sample concentration was from 10 to less than 100 times the PEL (figs. 9 and B6, table 3). Of the 393 samples with no detections of lindane, the detection limits for 32 and 64 samples were less than the TEL and PEL; thus, these samples were used for assessment purposes. Lower detection limits could have made most of the data more useful.

The highest concentration of lindane, 0.04 mg/kg, was found in the sediments of a headwater tributary to the Clinton River, Michigan, in 1994 (fig. 9). This concentration was more than 25 times the PEL. Other locations where concentrations of lindane exceeded the PEL (listed in order of decreasing concentration) were the upper Maumee River, Ohio; a headwater tributary to the Tiffin River, Ohio; a headwater tributary to the Auglaize River, Ohio; and the Ottawa River at Toledo, Ohio.

Total mirex (sum of mirex plus photomirex). The degradation product of mirex is photomirex. Mirex was used in the Great Lakes area in the 1960's and 1970's, primarily as a fire-retardant additive under the trade name Dechlorane. Mirex may still be used as a color-enhancing agent in fireworks (Binational Toxic Strategy, 1998). Mirex was used extensively in the southeastern United States to control fire ants. All pesticide uses of mirex were canceled in 1977.

Of the 199 bed-sediment samples analyzed for mirex, no detections were reported (figs. 10 and B7, table 3). Only Persaud (1993) provides a sediment-quality guidelines for mirex. Detection limits for a relatively large percentage, 139 and 199 samples, showed

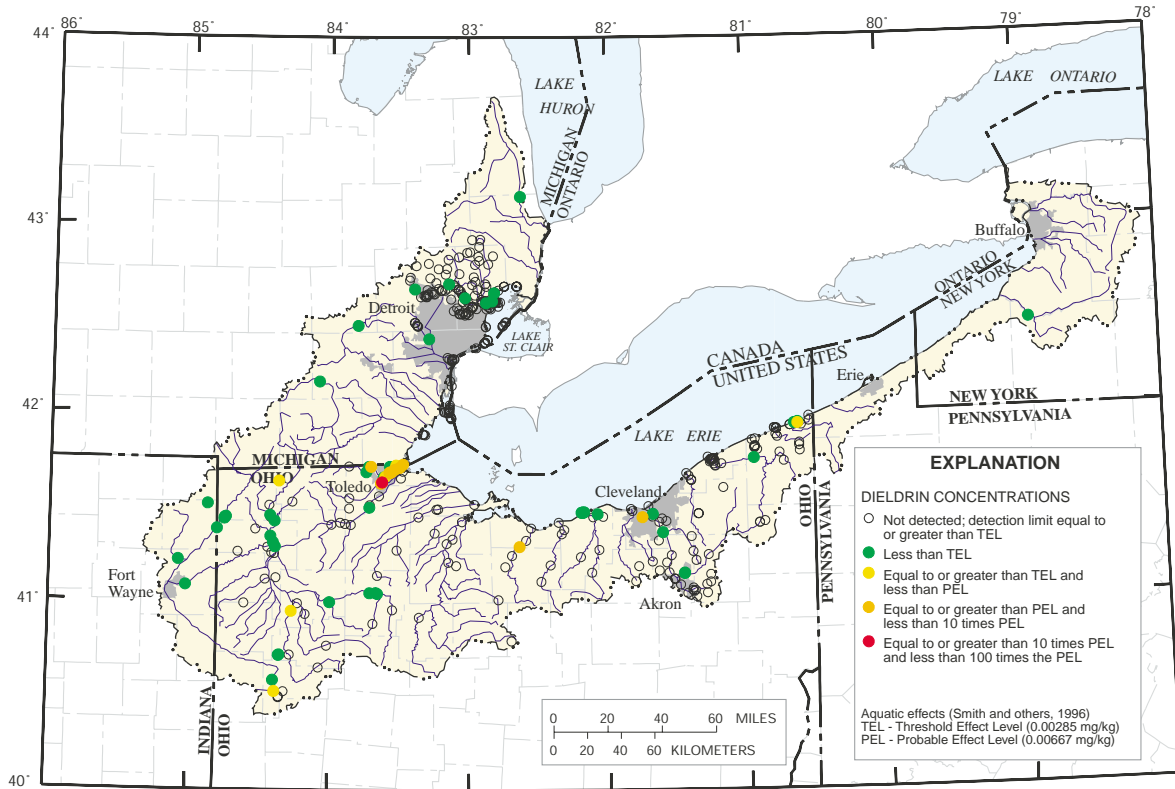


Figure 6. Total dieldrin concentrations in streambed and lakebed sediments, Lake Erie–Lake Saint Clair Drainages, 1990–97.

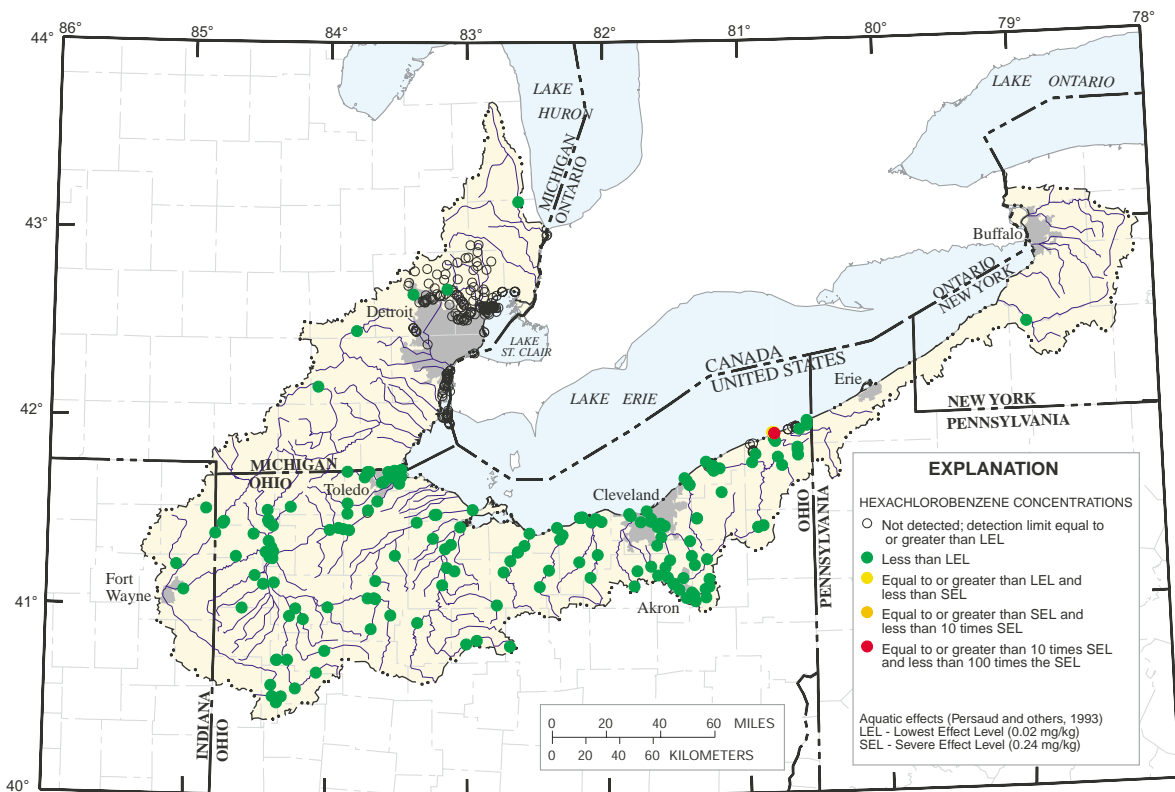


Figure 7. Hexachlorobenzene concentrations in streambed and lakebed sediments, Lake Erie–Lake Saint Clair Drainages, 1990–97.

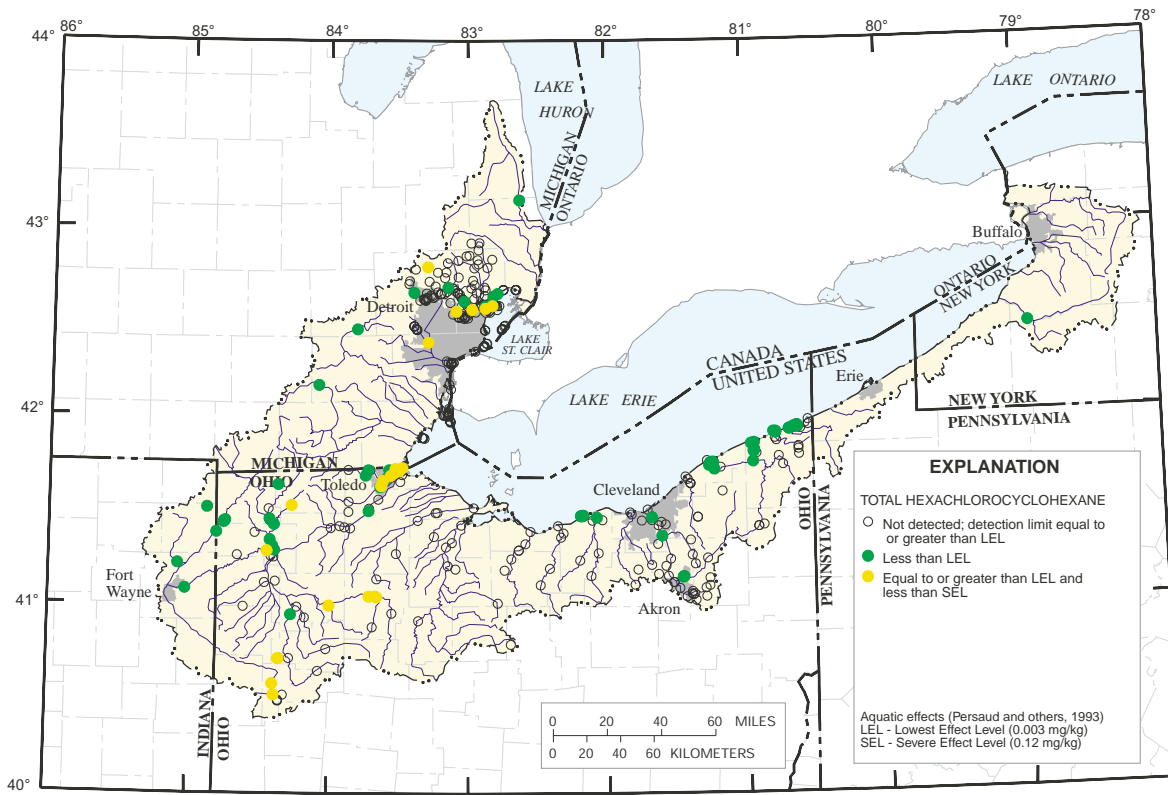


Figure 8. Total hexachlorocyclohexane concentrations in streambed and lakebed sediments, Lake Erie–Lake Saint Clair Drainages, 1990–97.

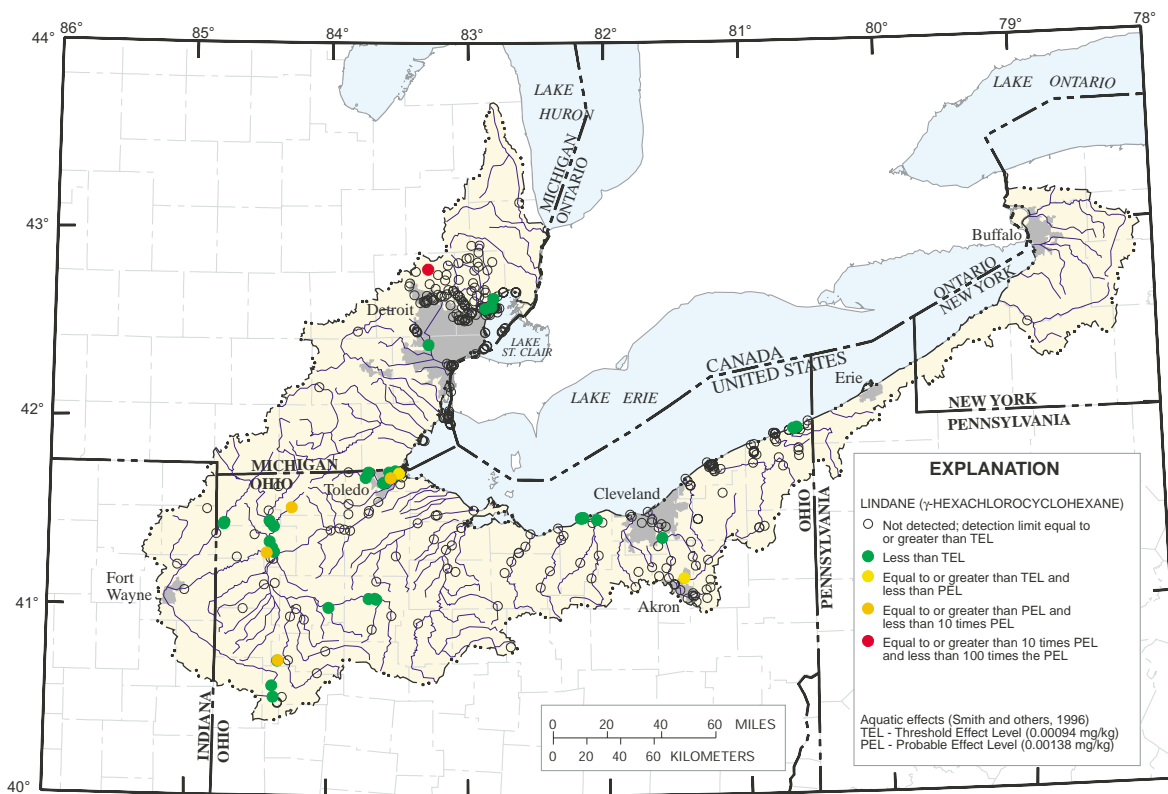


Figure 9. Lindane (γ -hexachlorocyclohexane) concentrations in streambed and lakebed sediments, Lake Erie–Lake Saint Clair Drainages, 1990–97.

no detections but at detection limits that were less than the LEL and SEL, respectively; thus, these samples were used for assessment purposes. Spatial distribution of sites where mirex was sampled for is shown in figure 10.

Total PCB (sum of congeners 1016, 1221, 1232, 1242, 1248, 1254, and 1260 or as total PCB's). Polychlorinated biphenyls are complex mixtures containing 1 to 8 chlorine atoms in 210 possible structural configurations (congeners). PCB's are constituents of various industrial products such as hydraulic fluids and electrical transformers. Other past uses consisted of diverse applications such as in carbonless-copy papers, plasticizers, epoxy compounds, synthetic resins, machine and high-vacuum oils, compressor oils, textile dyes, putties, waxes, and pesticides (International Joint Commission, 1993). In 1979, manufacture and import of PCB's were prohibited in the United States (International Joint Commission, 1993). PCB's remaining in use are almost exclusively found in closed systems. Spills and leaks, however, result in releases to the environment. Of the 683 bed-sediment samples analyzed for PCB's, 223 samples (32.7 percent) contained detectable PCB concentrations. Of the 223 samples with PCB detections, 67 sample concentrations ranged from the TEL to less than the PEL, 91 sample concentrations were from 1 to less than 10 times the PEL, 35 sample concentrations were from 10 to less than 100 times the PEL, and 27 sample concentrations were greater than 100 times the PEL (figs. 11 and B8, table 3). Of the 460 samples with no PCB detections, detection limits for 100 and 360 samples were less than the TEL and PEL, respectively; thus, these samples were used for assessment purposes.

The highest concentrations of PCB's in bed sediment were found at the mouth of the River Raisin near Monroe, Michigan, in 1991 and 1993 (fig. 11). At this location, concentrations ranged from 53 to 40,000 mg/kg. These concentrations were 191 to 145,000 times the PEL. Other locations with PCB concentrations at least 10 times the PEL (listed in order of decreasing concentration) were in the Detroit River, Michigan; the main stem of the River Rouge, Michigan; the lower Clinton River, Michigan; Lake Saint Clair, Michigan; the Ottawa River at Toledo, Ohio; and a tributary to the Auglaize River, Ohio.

Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAH's) are considered to be the most acutely toxic component of petroleum products, and they are also associated with chronic and carcinogenic effects (Irwin and others, 1997). Acute toxicity is rarely reported in humans, fish, or wildlife, as a result of exposure to low concentrations of a single PAH compound. PAH's in general are more frequently associated with long-term chronic toxicity (Irwin and others, 1997). Exposure to PAH's in bed sediment has resulted in liver and skin tumors in fish such as brown bullheads and white suckers and disruption of cellular or subcellular processes within organs or tissue of other organisms (Baumann and others, 1982; International Joint Commission, 1993; Smith and others, 1994)

Total PAH (sum of acenaphthene, acenaphthylene, anthracene, benzo[*a*]anthracene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*ghi*]perylene, benzo[*k*]fluoranthene, chrysene, dibenz[*a,h*]anthracene, fluoranthene, fluorene, indeno[1,2,3-*cd*]pyrene, naphthalene, phenanthrene, pyrene). PAH's result from the incomplete combustion of organic carbon such as wood, municipal solid waste, tobacco, and fossil fuels such as coal, gasoline, and fuel oil. However, even natural occurrences such as forest fires introduce some PAH's into bed sediments (National Research Council, 1983).

Of the 414 bed-sediment samples analyzed for total PAH's, 231 samples (55.8 percent) contained detectable concentrations. Of the 231 samples with total PAH detections, 77 sample concentrations ranged from the TEL to less than the PEL, 84 sample concentrations were from 1 to less than 10 times the PEL, 30 sample concentrations ranged from 10 to less than 100 times the PEL, and 4 sample concentrations were greater than 100 times the PEL (figs. 12 and B9, table 3). Of the 183 samples with no detections of total PAH's, detection limits in 53 and 151 samples were less than the TEL and the PEL, respectively; thus, these samples were used for assessment purposes.

The highest concentrations of total PAH's in bed sediment were found in a tributary to the Ottawa River at Toledo, Ohio in 1993, and the upper Clinton River, Michigan, in 1995 (fig. 12). At these locations, detected concentrations ranged from 470 to 2,657 mg/kg. These concentrations were 138 to 781 times the PEL. Other sampling locations with concentrations greater than 10 times the PEL (listed in order of decreasing concentration) were the mouth of the River

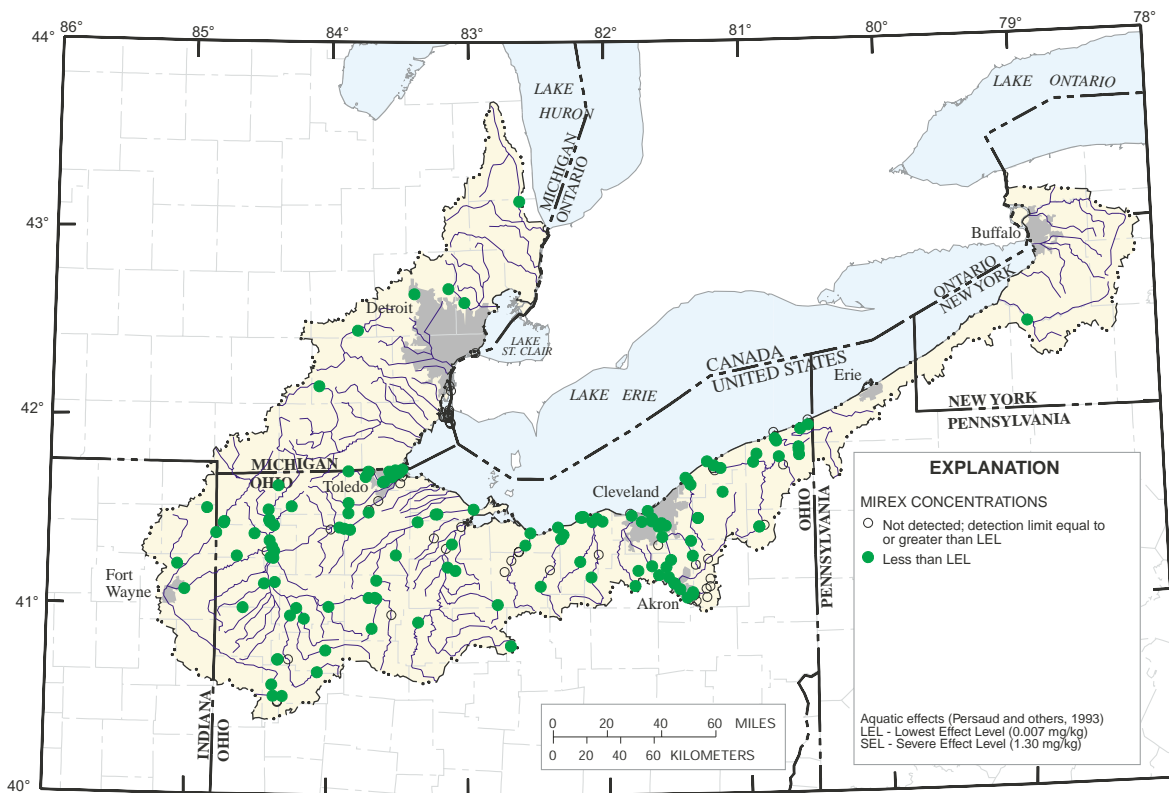


Figure 10. Total mirex concentrations in streambed and lakebed sediments, Lake Erie–Lake Saint Clair Drainages, 1990–97.

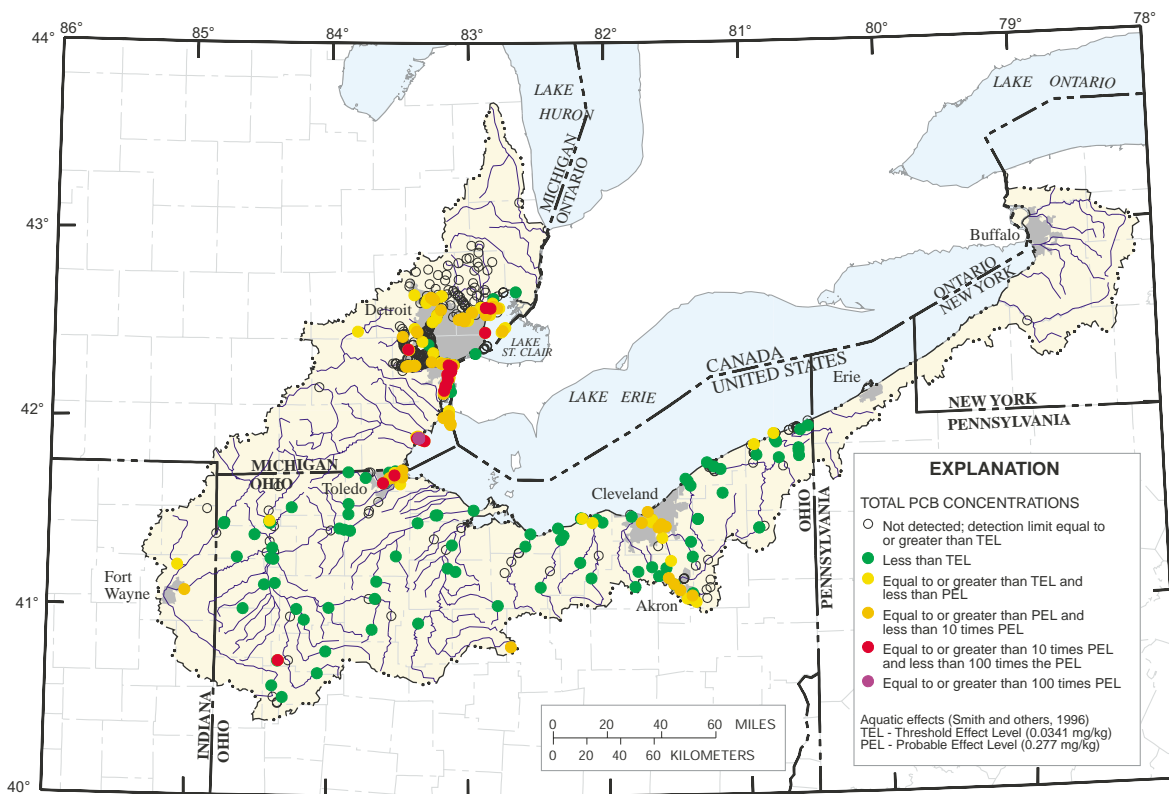


Figure 11. Total PCB concentrations in streambed and lakebed sediments, Lake Erie–Lake Saint Clair Drainages, 1990–97.

Rouge, the Detroit River, and the main stem of the Clinton River, in Michigan; and the upper Cuyahoga River near Akron, the lower Cuyahoga River near Cleveland; and at the mouth of the Maumee River in Toledo, in Ohio.

Anthracene. Anthracene is a low-molecular-weight, 3-ring PAH. Anthracene is used in industry as a source of dyestuffs and in coating applications (Parker, 1984).

Of the 392 bed-sediment samples analyzed for anthracene, 76 samples (19.4 percent) contained detectable concentrations. Of the 76 samples with anthracene detections, 26 sample concentrations were ranged from the TEL to less than the PEL, 30 sample concentrations were from 1 to less than 10 times the PEL, 13 sample concentrations were from 10 to less than 100 times the PEL, and 3 sample concentrations were greater than 100 times the PEL (figs. 13 and B10, table 3). Of the 316 samples with no detections of anthracene, detection limits in 27 and 40 samples were less than the TEL and PEL, respectively; thus, these samples were used for assessment purposes. Lower detection limits could have made the data more useful.

The highest concentrations of anthracene in bed sediments were found in a tributary to the Ottawa River at Toledo, Ohio, in 1993; the Detroit River, Michigan, in 1996; and the lower River Rouge, Michigan, in 1993 (fig. 13). At these locations, anthracene concentrations ranged from 25 to 51 mg/kg, or 147 to 300 times the PEL. Other locations where concentrations of anthracene exceeded the PEL (listed in order of decreasing concentration) were the main stem of the Clinton River, Michigan; the mouth of the Ashtabula River, Ohio; a tributary to the upper Cuyahoga River, Ohio; two tributaries to the lower Cuyahoga River, at Cleveland, Ohio; Lake Saint Clair, Michigan; and the upper and lower Maumee River, Indiana and Ohio.

Benz[*a*]anthracene. Benz[*a*]anthracene is a high-molecular-weight, 4-ring PAH (Parker, 1984). Because it is formed when gasoline, garbage, or any animal or plant materials are burned, it is usually found in smoke and soot. Benz[*a*]anthracene is also found in creosote (Irwin and others, 1997). The sources of benz[*a*]anthracene are mainly urban and industrial.

Of the 393 bed-sediment samples analyzed for benz[*a*]anthracene, 158 samples (40.2 percent) contained detectable concentrations. Of the 158 samples with benz[*a*]anthracene detections, 65 sample concentrations ranged from the TEL to less than the PEL, 55

sample concentrations were from 1 to less than 10 times the PEL, 20 sample concentrations ranged from 10 to less than 100 times the PEL, and 1 sample concentration was greater than 100 times the PEL (figs. 14 and B11, table 3). Of the 235 samples with no detections of benz[*a*]anthracene, detection limits in 33 and 84 samples were less than the TEL and PEL, respectively; thus, these samples were used for assessment purposes. Lower detection limits could have made the data more useful.

The highest concentration of benz[*a*]anthracene in bed sediment was found in a tributary to the Ottawa River at Toledo, Ohio, in 1993 (fig. 14). At this location, the benz[*a*]anthracene concentration was 160 mg/kg or 416 times the PEL. Other locations where concentrations of benz[*a*]anthracene exceeded the PEL (listed in order of decreasing concentration) were the headwaters and main stem of the Clinton River, Michigan; the mouth of the River Rouge, Michigan; the Detroit River, Michigan; the Ottawa River at Toledo, Ohio; a tributary to and the lower main stem of the Cuyahoga River, at Cleveland, Ohio; a tributary to and the main stem of the Little Cuyahoga River at Akron, Ohio; the upper and lower main stem of the Maumee River, Ohio; the mouth of the Ashtabula River, Ohio; the middle main stem of the Cuyahoga River at Akron, Ohio; the mouth of the River Raisin, Michigan; Lake Saint Clair, Michigan; and the mouth of the Chagrin River, Ohio.

Benzo[*a*]pyrene. Benzo[*a*]pyrene is a high-molecular-weight, 5-ring PAH. The release of benzo[*a*]pyrene to the environment is widespread because it is a ubiquitous product of incomplete combustion (Irwin and others, 1997). Its sources are mainly industrial; coal-tar processing, petroleum refining, shale refining, coal and coke processing, kerosene processing, heat and power generation, combustion of tobacco, and combustion of fuels. Benzo[*a*]pyrene is found in runoff containing greases and oils, and it is a potential roadbed and asphalt leachate (Verschueren, 1977).

Of the 388 bed-sediment samples analyzed for benzo[*a*]pyrene, 147 samples (37.9 percent) contained detectable concentrations. Of the 147 samples with benzo[*a*]pyrene detections, 63 sample concentrations ranged from the TEL to less than the PEL, 59 sample concentrations were from 1 to less than 10 times the PEL, 9 sample concentrations were from 10 to less than 100 times the PEL, and 1 sample concentration was greater than 100 times the PEL (figs. 15 and B12,

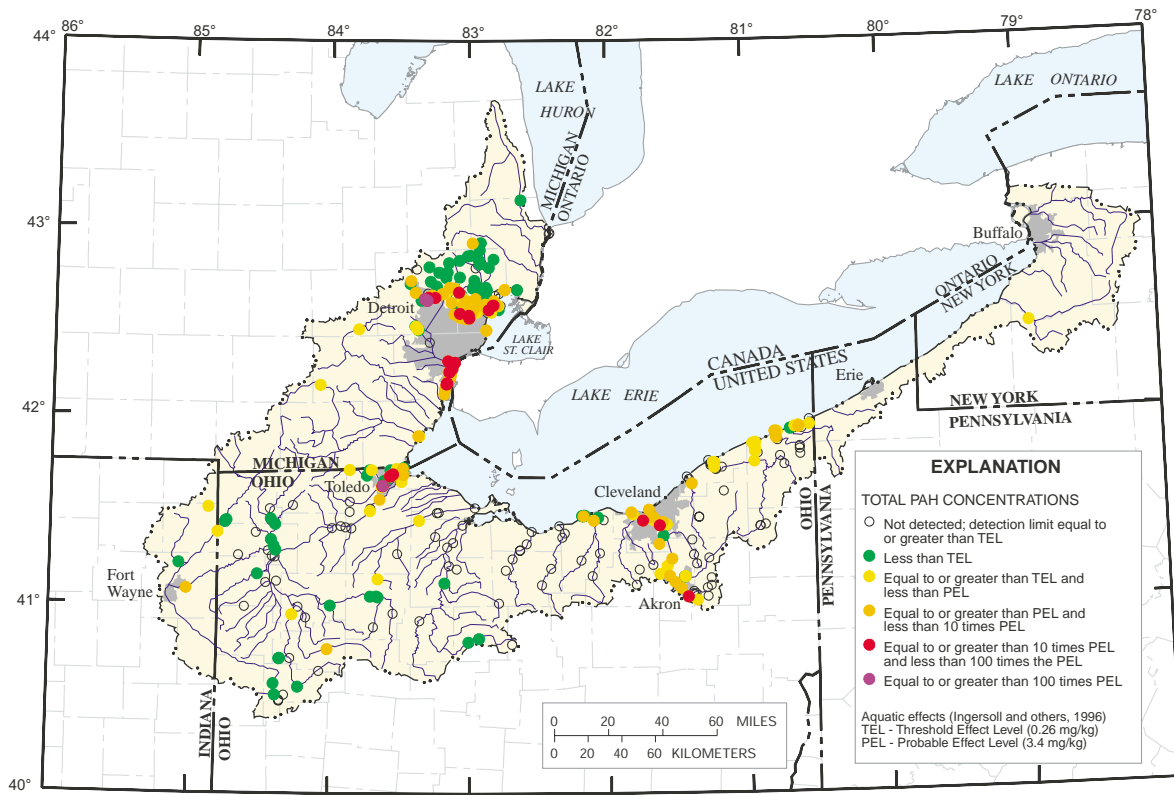


Figure 12. Total PAH concentrations in streambed and lakebed sediments, Lake Erie–Lake Saint Clair Drainages, 1990–97.

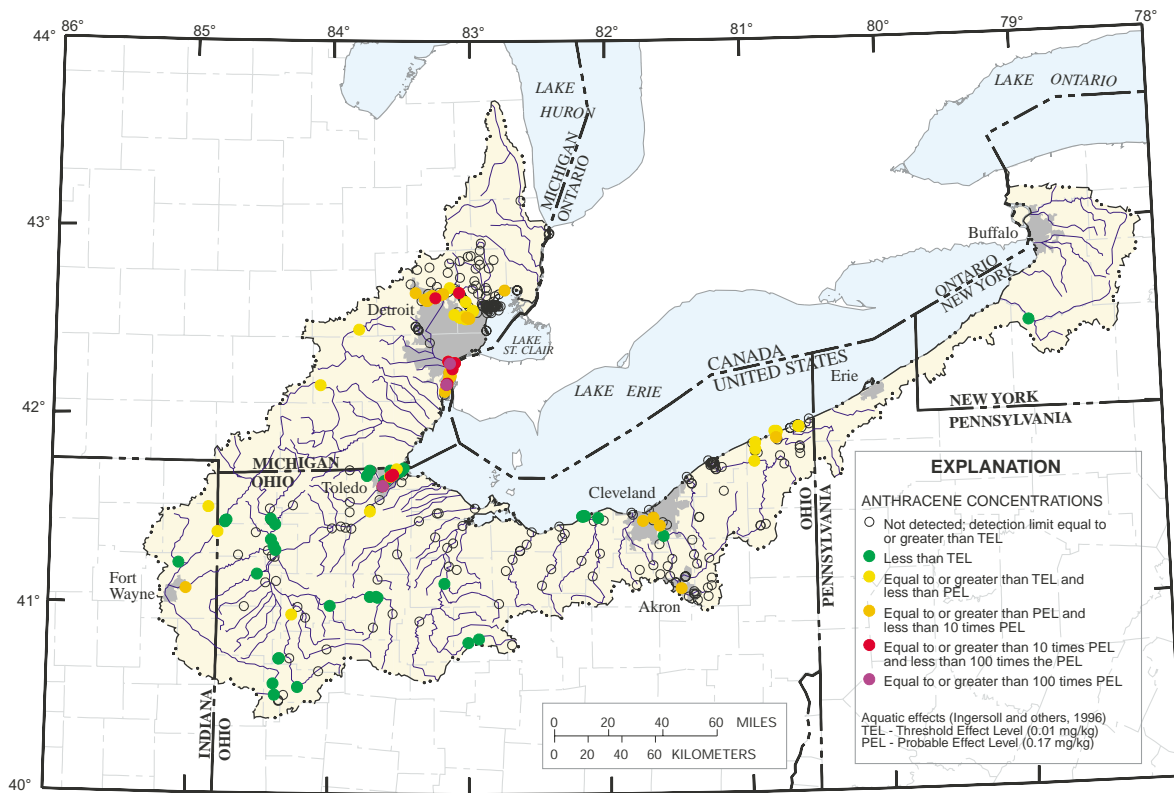


Figure 13. Anthracene concentrations in streambed and lakebed sediments, Lake Erie–Lake Saint Clair Drainages, 1990–97.

table 3). Of the 241 samples with no detections of benzo[a]pyrene, detection limits for 31 and 241 samples were less than the TEL and PEL, respectively; thus, these samples were used for assessment purposes.

The highest concentrations of benzo[a]pyrene in bed sediment were found in tributaries to the Ottawa River near Toledo, Ohio, in 1992 and 1993; the entire main stem of the Clinton River, Michigan, in 1994 and 1995; the mouth of the River Rouge, Michigan, in 1993; and the Detroit River, Michigan, in 1996 (fig. 15). At these locations, detected concentrations ranged from 9.3 to 110 mg/kg or 11.9 to 141 times the PEL. Other locations where concentrations of benzo[a]pyrene exceeded the PEL (listed in order of decreasing concentration) were the Cuyahoga River main stem and lower tributaries, Ohio; the Little Cuyahoga River, near Akron, Ohio; the mouth of the Ashtabula River, Ohio; the lower Maumee River, Ohio; the mouth of the River Raisin, Michigan; and Lake Saint Clair, Michigan.

Chrysene. Chrysene, a 4-ring PAH, is a component in coal tar and is present in exhaust from gasoline engines (Verschuere, 1977). Chrysene is usually found in smoke and soot, coal tar, coke oven emissions, and cigarette smoke (U.S. Environmental Protection Agency, 1997b).

Of the 396 bed-sediment samples analyzed for chrysene, 189 samples (47.7 percent) showed detectable concentrations. Of the 189 samples with chrysene detections, 86 sample concentrations ranged from the TEL to less than the PEL, 65 sample concentrations were from 1 to less than 10 times the PEL, 11 sample concentrations were from 10 to less than 100 times the PEL, and 1 sample concentration was greater than 100 times the PEL (figs. 16 and B13, table 3). Of the 207 samples with no detections of chrysene, detection limits for 35 and 179 samples were less than the TEL and PEL, respectively; thus, these samples were used for assessment purposes.

The highest concentrations of chrysene in bed sediment were found in tributaries to the Ottawa River, near Toledo, Ohio, in 1992 and 1993; the main stem of the Clinton River, Michigan, in 1994 and 1995; the mouth of the River Rouge, Michigan, in 1993; and the Detroit River, Michigan, in 1996 (fig. 16). At these locations, detected concentrations ranged from 8.7 to 180 mg/kg. These concentrations were 10.1 to 209 times the PEL. Other locations where concentrations of chrysene in bed sediment exceeded the PEL (listed

in order of decreasing concentration) were the tributaries to and the lower main stem of the Cuyahoga River, Ohio; the lower Maumee River, Ohio; the mouth of the Ashtabula River, Ohio; the Little Cuyahoga River, near Akron, Ohio; the mouth of the River Raisin, Michigan; Lake Saint Clair, Michigan; and the mouth of the Chagrin River, Ohio.

Phenanthrene. Phenanthrene, a low-molecular-weight 3-ring PAH. It is naturally present in coal and petroleum and is used in industry and in the synthesis of dyes and drugs (Parker, 1984). Phenanthrene is a high-temperature combustion product of coal and petroleum (U.S. Environmental Protection Agency, 1993d).

Of the 398 bed-sediment samples analyzed for phenanthrene, 187 samples (47.0 percent) showed detectable concentrations. Of the 187 samples with phenanthrene detections, 66 sample concentrations ranged from the TEL to less than the PEL, 74 sample concentrations were from 1 to less than 10 times the PEL, 19 sample concentrations were from 10 to less than 100 times the PEL, and 2 sample concentrations were more than 100 times the PEL (figs. 17 and B14, table 3). Of the 211 samples with no detections of phenanthrene, detection limits for 30 and 112 samples were less than the TEL and PEL, respectively; thus, these samples were used for assessment purposes. Lower detection limits could have made the data more useful.

The highest concentrations of phenanthrene in bed sediment were found in tributaries to the Ottawa River near Toledo, Ohio, in 1992 and 1993; the lower River Rouge, Michigan, in 1993; along the main stem of the Clinton River, Michigan, in 1994 and 1995; the Detroit River, Michigan, in 1996; and the mouth of the Ashtabula River, Ohio, in 1996 (fig. 17). At these locations, detected concentrations ranged from 5.2 to 600 mg/kg. These concentrations were 10.1 to 1,165 times the PEL. Other locations where concentrations of phenanthrene in bed sediment exceeded the PEL (listed in order of decreasing concentration) were the tributaries to and the lower main stem of the Cuyahoga River, Ohio; the Little Cuyahoga River, near Akron, Ohio; the mouth of Rocky River, Ohio; the lower Maumee River, Ohio; Lake Saint Clair, Michigan; the lower Chagrin River, Ohio; the upper Maumee River, Indiana; the mouth of the Black River, Ohio; the Ottawa River at Lima, Ohio; and the mouth of the River Raisin, Michigan.

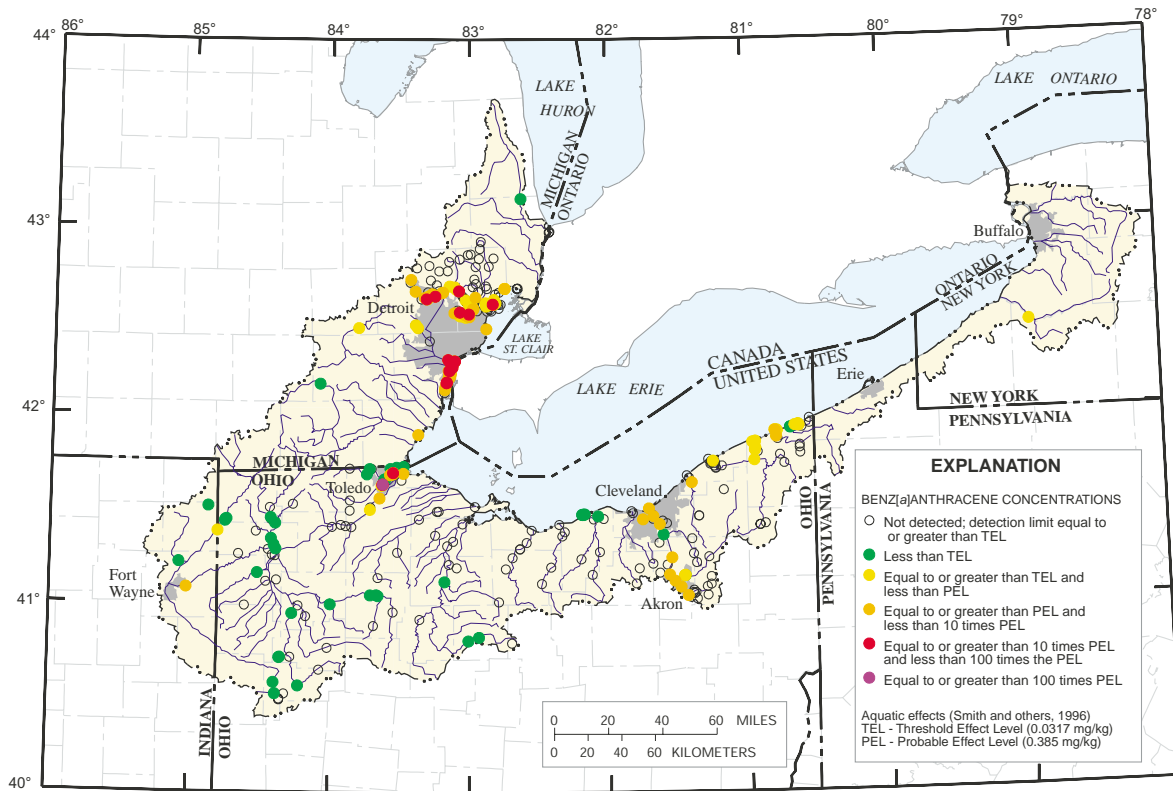


Figure 14. Benz[a]anthracene concentrations in streambed and lakebed sediments, Lake Erie–Lake Saint Clair Drainages, 1990–97.

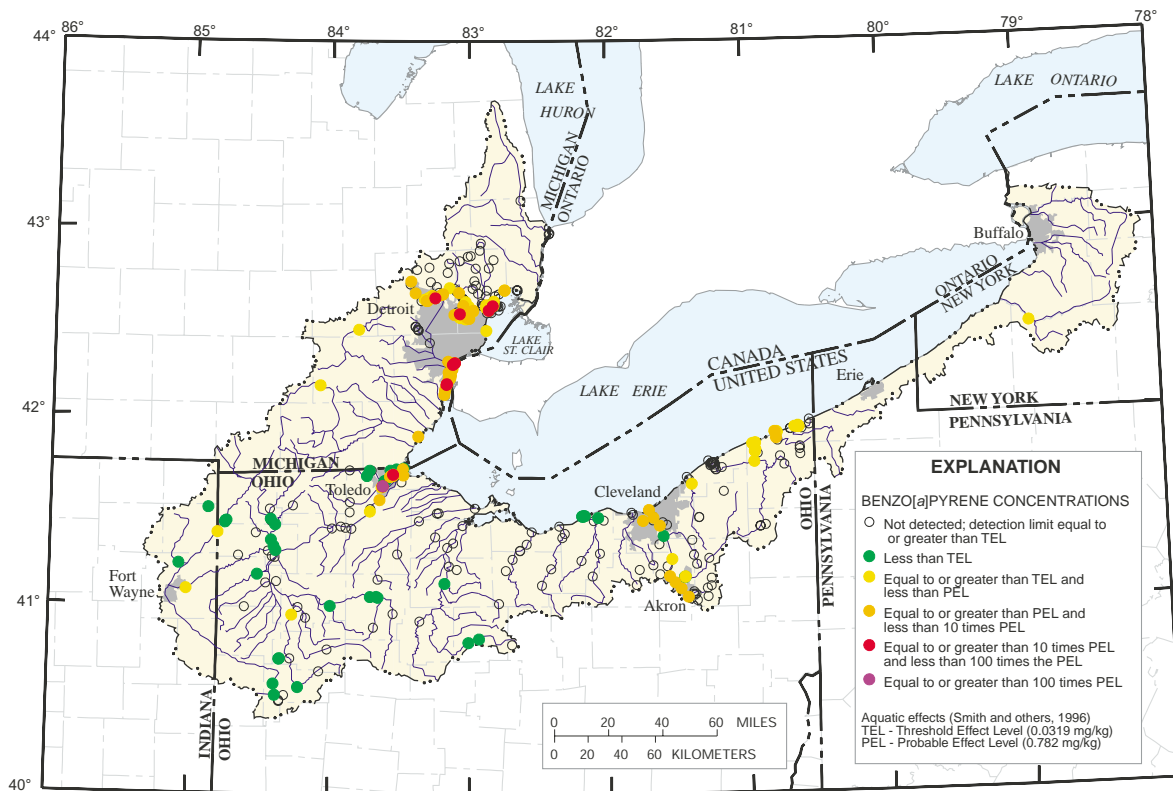


Figure 15. Benzo[a]pyrene concentrations in streambed and lakebed sediments, Lake Erie–Lake Saint Clair Drainages, 1990–97.

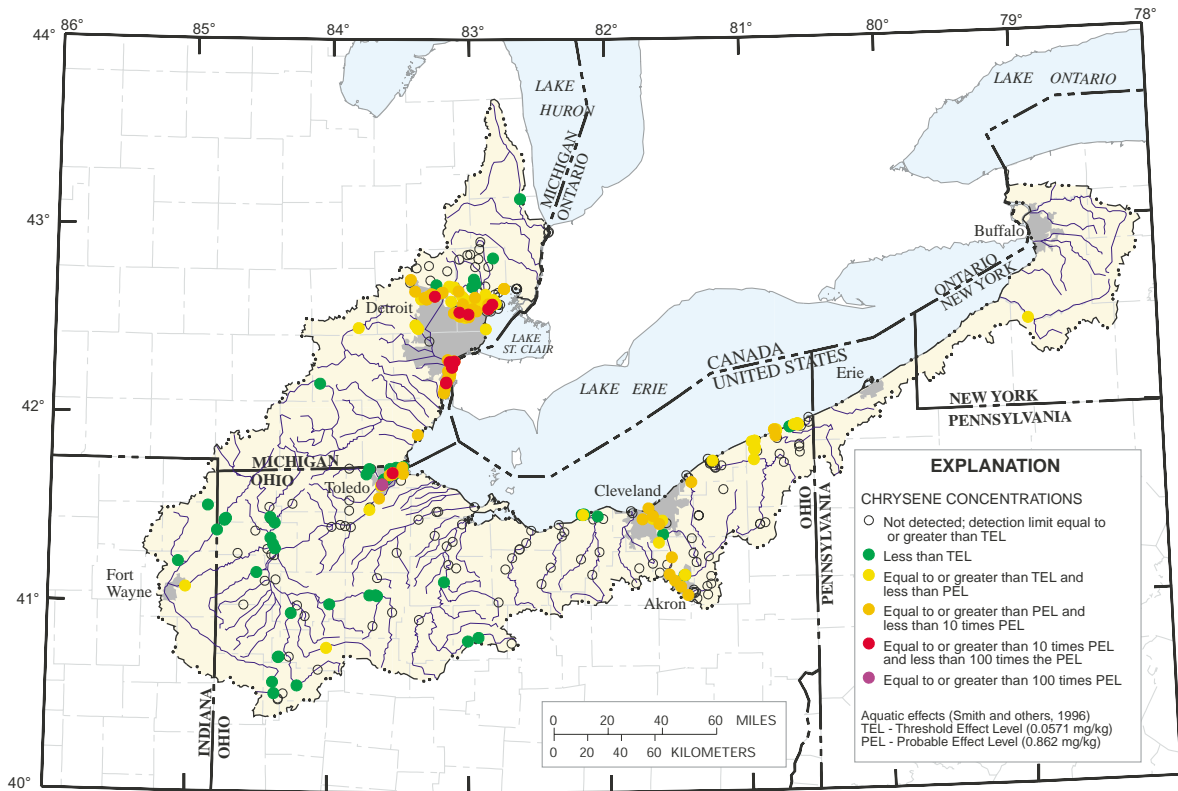


Figure 16. Chrysenes concentrations in streambed and lakebed sediments, Lake Erie–Lake Saint Clair Drainages, 1990–97.

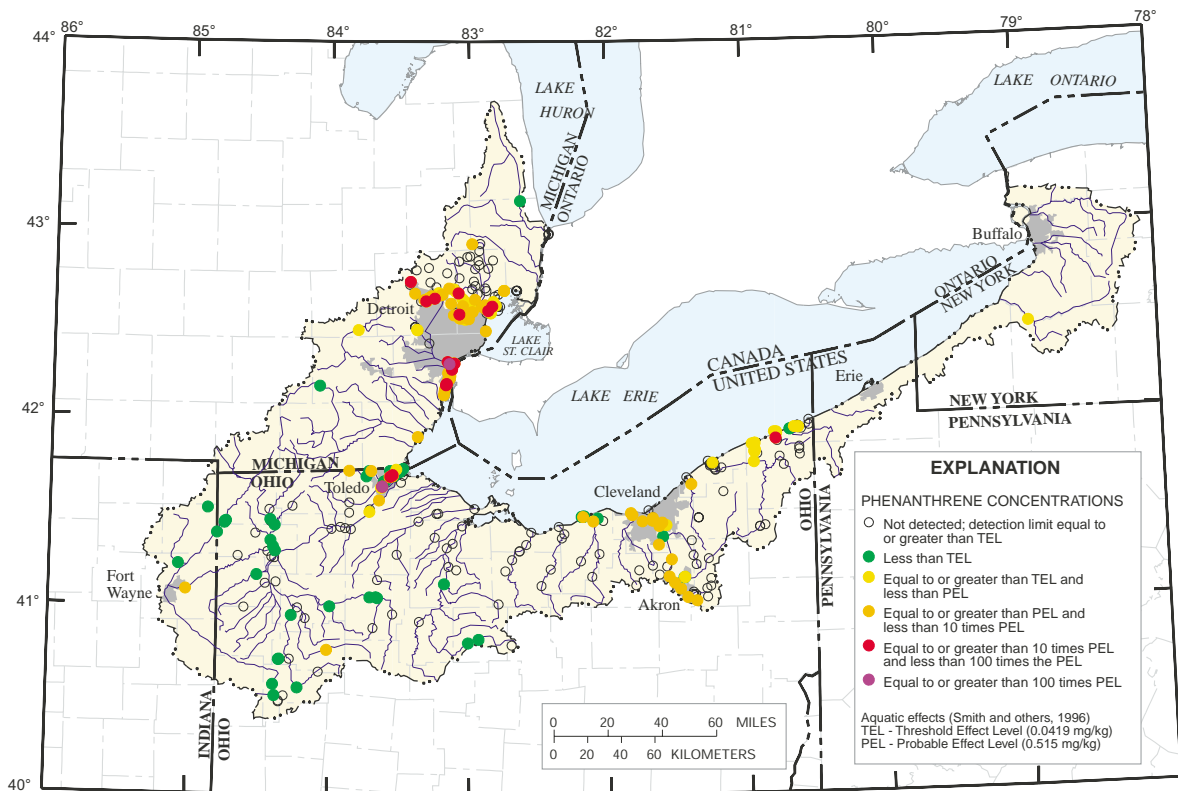


Figure 17. Phenanthrene concentrations in streambed and lakebed sediments, Lake Erie–Lake Saint Clair Drainages, 1990–97.

Trace Metals

Trace metals in bed sediment are derived from a variety of sources including weathering of rocks and soils and input from anthropogenic sources. Trace metals at naturally occurring concentrations generally are not harmful to aquatic life; however, the high end of the natural concentration range typically falls in the lower range of the various sediment-quality criteria, an overlap that can seriously confound interpretation. Of all the contaminants discussed in this report, trace metals were those detected most frequently in streambed and lakebed sediments. Elevated concentrations in bed sediment are of particular interest because some trace metals may be toxic to and accumulate in aquatic organisms. Avenues by which trace metals are introduced into bed sediments include atmospheric deposition, industrial emissions (especially from activities such as plating, smelting, and refining), wastewater discharges, landfills, stormwater runoff, and automobile exhaust. The extensive use of trace metals in industry often results in concentrations far greater than natural levels (Armitage, 1995). Certain trace metals are known to be highly toxic and bioaccumulative in food chains, but little is known about the occurrence and biological significance of others.

Arsenic (semi-metallic element). Sources of arsenic include wood preservatives, herbicides, and insecticides; however, arsenic compounds are present naturally in some waters. Lead arsenate and calcium arsenate have been applied extensively as miticides and pesticides on orchard crops. Additional uses include metal-ore processing, glassware, ceramics, leather tanning, chemical industries, pigmentation in paints, and additives in medical treatments (Michigan Water Resources Commission, 1972).

Of the 480 bed-sediment samples analyzed, arsenic was detected in 470 samples (97.9 percent). Of the 470 samples with arsenic detections, 269 sample concentrations ranged from the TEL to less than the PEL, 58 sample concentrations were from 1 to less than 10 times the PEL, and 2 sample concentrations were from 10 to less than 100 times the PEL (figs. 18 and B15, table 3). Of the 10 samples with no detections of arsenic, detection limits in 1 and 10 samples were less than the TEL and the PEL, respectively; thus, all samples were used for assessment purposes.

The highest concentrations of arsenic in bed sediment were found in a small tributary to Lake Erie, near North Kingsville, Ohio, in 1993 and 1995; a tributary to the main stem of the Cuyahoga River, Ohio, in

1991; the lower Rocky River, Ohio, in 1992; and the mouth of the River Raisin, Michigan, in 1993 (fig. 18). At these locations, detected concentrations ranged from 33 to 649 mg/kg. These concentrations were from 1.9 to 38.2 times the PEL. Other locations with elevated concentrations of arsenic greater than the PEL (listed in order of decreasing concentration) were the Blanchard River near Findlay, Ohio; Ottawa River at Toledo, Ohio; a tributary to the main stem of the Auglaize River, Ohio; Ottawa River near Lima, Ohio; the upper Clinton River, Michigan; Cuyahoga River near Akron, Ohio; the mouth of the Ashtabula River, Ohio; the upper Huron River, Michigan; the upper River Raisin, Michigan; the mouth of the Cuyahoga River, Ohio; the Detroit River, Michigan; and the upper St. Marys River, Ohio.

Cadmium. Industrial use of cadmium has been in metallurgy to alloy with copper, lead, silver, aluminum, and nickel. Cadmium also is used in electroplating, ceramics, pigmentation, photography, and nuclear reactors. Cadmium salts are sometimes employed as insecticides and antihelminthics (Michigan Water Resources Commission, 1972). Other sources of cadmium emissions are releases to the environment from fossil-fuel use, fertilizer applications, and sewage-sludge disposal (Shelton, 1990). Trace amounts of cadmium occur naturally, chiefly as a sulfide salt. Cadmium is found in very low concentrations in most rocks, in coal and petroleum, and often in combination with zinc.

Of the 616 bed-sediment samples analyzed for cadmium, 588 samples (95.5 percent) showed detectable concentrations. Of the 588 samples with cadmium detections, 198 sample concentrations ranged from the TEL to less than the PEL, and 114 sample concentrations were from 1 to less than 10 times the PEL (figs. 19 and B16, table 3). Of the 28 samples with no detections of cadmium, detection limits for 1 and 27 samples were less than the TEL and the PEL, respectively; thus, all samples were used for assessment purposes.

The highest concentrations of cadmium in bed sediment were found in the main stem of the Clinton River, Michigan, in 1994 and 1995; the mouth of the Cuyahoga River, Ohio, in 1993; the Detroit River, Michigan, in 1996; the main stem of the Black River, Ohio, in 1992; and the main stem of the River Rouge, Michigan, in 1993 (fig. 19). At these locations, detected cadmium concentrations ranged from 10.0 to 28 mg/kg. These concentrations were 2.8 to 7.9 times

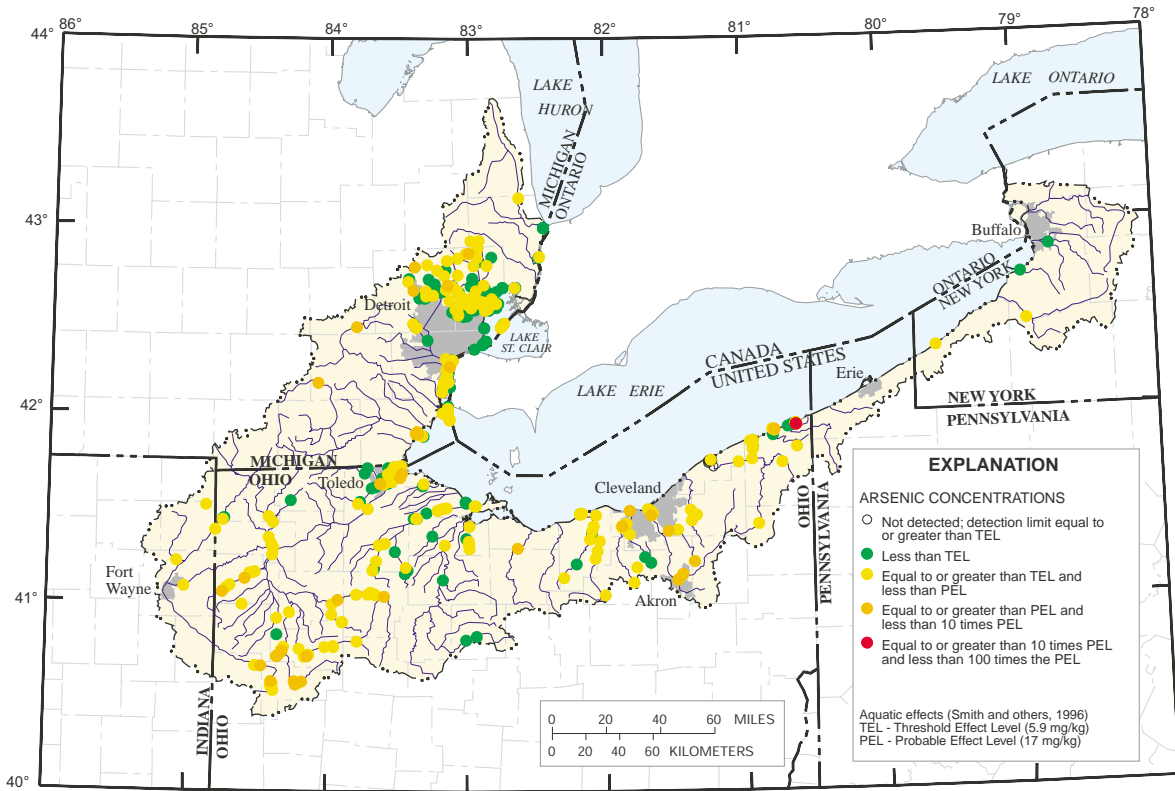


Figure 18. Arsenic concentrations in streambed and lakebed sediments, Lake Erie–Lake Saint Clair Drainages, 1990–97.

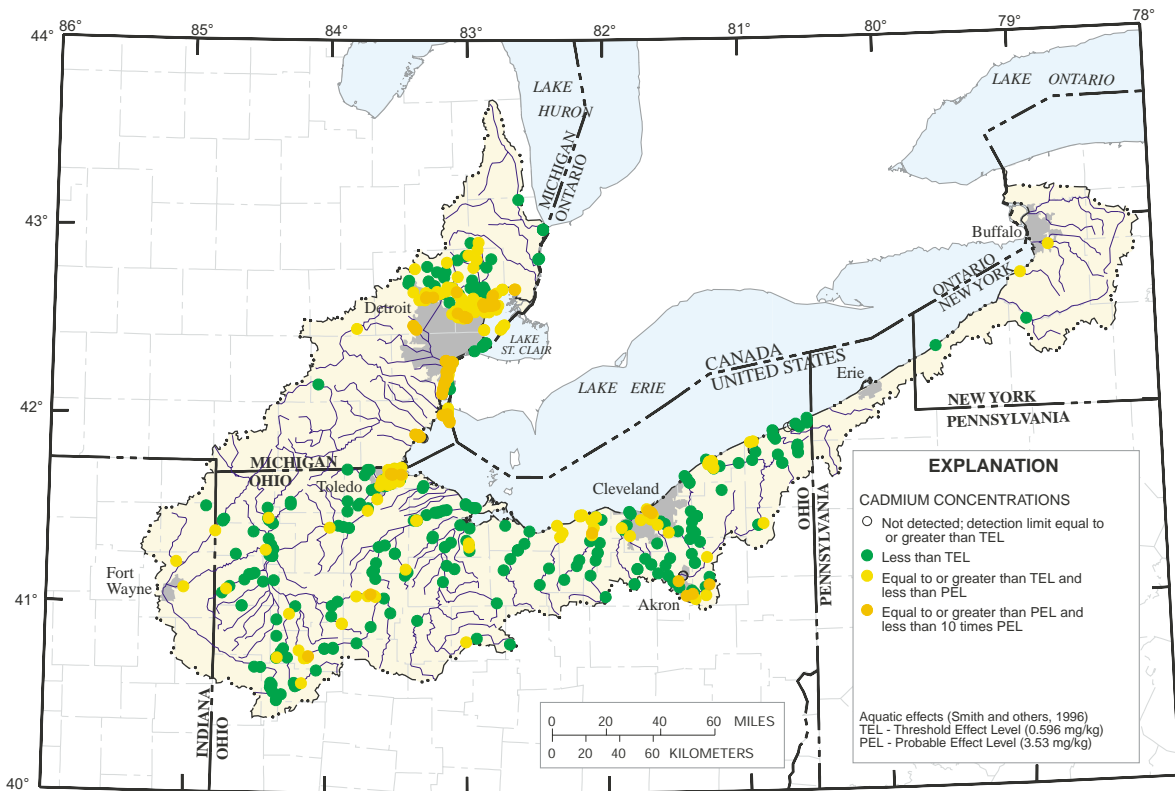


Figure 19. Cadmium concentrations in streambed and lakebed sediments, Lake Erie–Lake S Clair Drainages, 1990–97.

the PEL. Other locations where concentrations of cadmium in bed sediments exceeded the PEL (listed in order of decreasing concentration) were the upper Cuyahoga River near Akron, Ohio; Ottawa River at Toledo, Ohio; upper Blanchard River near Findlay, Ohio; the mouth of the River Raisin, Michigan; Lake Saint Clair, Michigan; Ottawa River near Lima, Ohio; and the lower Maumee River, Ohio.

Copper. Metallic copper is used extensively in the electrical industry, in many alloys for cooking utensils, and for water pipes and roofing. Copper salts are used in textile processes, pigmentation, tanning, photography, engraving, electroplating, insecticides, fungicides, control of algae and other aquatic growths, and many other industrial processes. Copper is a known contaminant in urban stormwater runoff (Michigan Water Resources Commission, 1972).

Of the 587 bed-sediment samples analyzed for copper, 586 samples (99.8 percent) showed detectable concentrations. Of the 586 samples with copper detections, 209 sample concentrations ranged from the TEL to less than the PEL, and 14 sample concentrations were from 1 to less than 10 times the PEL (figs. 20 and B17, table 3). All samples were used for assessment purposes.

The highest concentrations of copper in bed sediment were found in the main stem and East Branch of the Portage River, Ohio, in 1994; the Ottawa River near Toledo, Ohio, in 1996; the Detroit River, Michigan, in 1996; the mouth of the Cuyahoga River, Ohio, in 1996; the mouth of Black River, Ohio, in 1996; the mouth of the River Raisin, Michigan, in 1992; and the River Rouge, Michigan, in 1993 (fig. 20). At these locations, detected concentrations ranged from 200 to 649 mg/kg and were 1 to 3.2 times the PEL.

Lead. In the past, a major use of lead was the antiknock agent tetraethyl lead in gasoline. Other uses include leaded glass, storage batteries, plumbing, and lead oxides and pigments in paint. Lead is released as a waste byproduct from coal and oil combustion, metal refining and fabrication, cement manufacture, and waste incineration. Lead is a known contaminant in urban stormwater runoff and in landfill leachate (Michigan Water Resources Commission, 1972).

Of the 615 bed-sediment samples analyzed for lead, 614 samples (99.8 percent) showed detectable concentrations. Of the 614 samples with detectable lead, 156 sample concentrations ranged from the TEL to less than the PEL, and 109 sample concentrations were from 1 to less than 10 times the PEL (figs. 21 and

B18, table 3). All samples were used for assessment purposes.

The highest concentrations of lead in bed sediment were found in a tributary to and the mainstem of the Ottawa River near Toledo, Ohio, in 1992; the mouth of the River Rouge, Michigan, in 1993; the lower Cuyahoga River near Cleveland, Ohio, in 1990; the mouth and the main stem of the Clinton River, Michigan, in 1995; the Detroit River, Michigan, in 1996; and the Ottawa River near Lima, Ohio, in 1991 (fig. 21). At these locations, lead concentrations ranged from 260 to 589 mg/kg and were 2.8 to 6.4 times greater than the PEL. Other locations where concentrations of lead in bed sediments exceeded the PEL (listed in order of decreasing concentration) were the mouth of the River Raisin, Michigan; Lake Saint Clair, Michigan; the lower Maumee River, Ohio; the upper Cuyahoga River, near Akron, Ohio; the headwaters of the Clinton River, Michigan; the main stem of the Chagrin River, Ohio; and the Little Cuyahoga River near Akron, Ohio.

Mercury. Mercury is a volatile metal that can exist in metallic, elemental, inorganic salt, and organic compound forms. Methyl mercury is an example of the latter. These various forms have different properties and toxicities. Mercury is widely used within the industrial, medical, agricultural, and consumer sectors; more than 2,000 applications have been identified. Coal combustion and municipal and medical waste incineration are the major anthropogenic sources to the atmosphere (Irwin and others, 1997). Most biocidal and fungicidal uses and use in paints have now been canceled. Mercury is released as a waste byproduct in metal smelting and battery manufacturing, waste incineration, and disposal of batteries and other consumer goods. Implementation of pollution controls and closures of chlorine and caustic soda manufacturing plants have reduced releases of mercury to the environment (International Joint Commission, 1993). Global atmospheric transport of mercury through rainfall is a common source.

Of the 465 bed-sediment samples analyzed for mercury, 309 samples (66.4 percent) showed detectable concentrations. Of the 309 mercury detections, 59 sample concentrations ranged from the TEL to less than the PEL, 51 sample concentrations were from 1 to less than 10 times the PEL, and 4 sample concentrations were from 10 to less than 100 times the PEL (figs. 22 and B19, table 3). Of the 156 samples with no

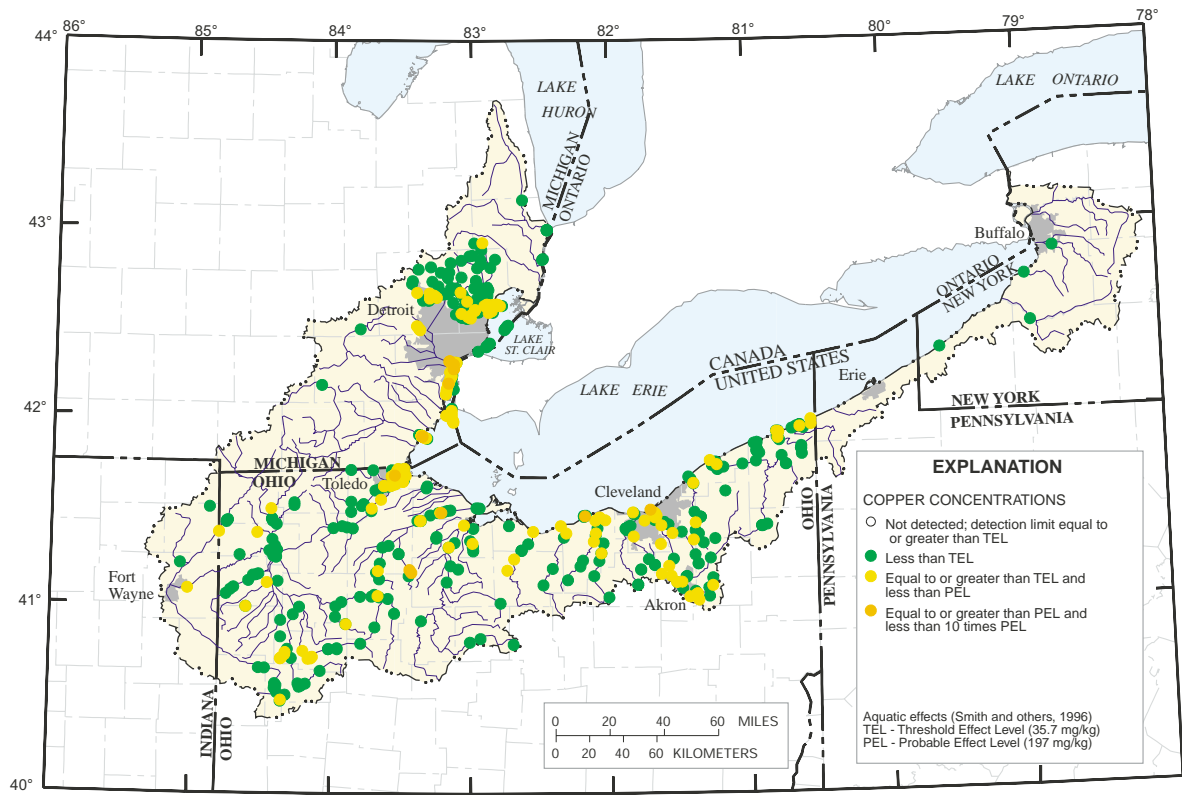


Figure 20. Copper concentrations in streambed and lakebed sediments, Lake Erie–Lake Saint Clair Drainages, 1990–97.

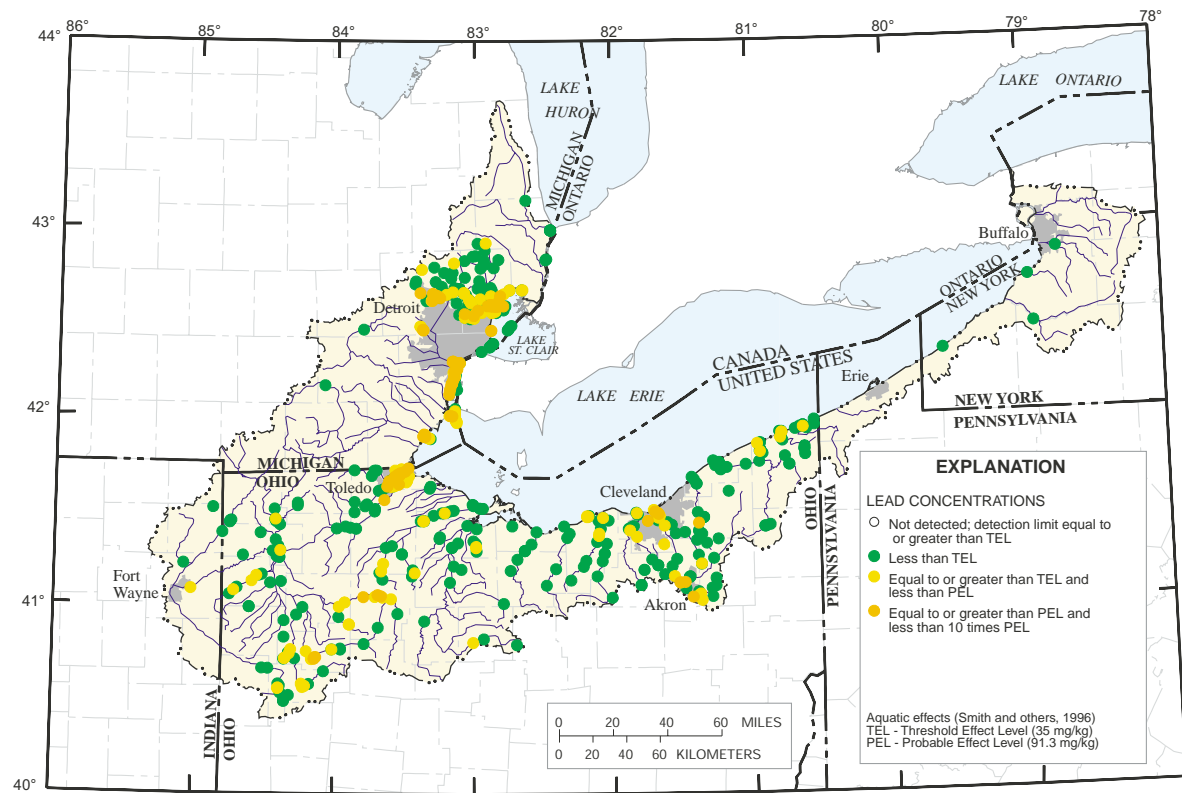


Figure 21. Lead concentrations in streambed and lakebed sediments, Lake Erie–Lake Saint Clair Drainages, 1990–97.

detections of mercury, detection limits in 152 and 155 samples were less than the TEL and the PEL, respectively. All samples were used for assessment purposes.

The highest concentrations of mercury in bed sediment were found in 1996 in the Detroit River, Michigan, and the Little Cuyahoga River near Akron, Ohio (fig. 22). At these locations, detected concentrations ranged from 6.06 to 16.0 mg/kg and were 12.5 to 32.8 times the PEL. Other locations where concentrations of mercury in bed sediments exceeded the PEL (listed in order of decreasing concentration) were the mouth of River Raisin, Michigan; Lake Saint Clair, Michigan; the Monroe Harbor, in Lake Erie; the mouth of the River Rouge, Michigan; and the mouth of the Clinton River, Michigan.

Zinc. Elemental zinc has been used extensively for galvanizing, alloys, electrical purposes, printing plates, dye manufacture, dyeing processes, and many other industrial processes. Zinc is a known contaminant in urban stormwater runoff and in landfill leachate, and it is leachable from galvanized pipes used as culverts. Zinc salts are used in paint pigments, cosmetics, pharmaceuticals, dyes, and pesticides and fertilizers. Industrial wastes sometimes contain high concentrations of zinc (Michigan Water Resources Commission, 1972).

Of the 575 bed-sediment samples analyzed for zinc, 100 percent showed detectable concentrations. 167 sample concentrations ranged from the TEL to less than the PEL, and 82 sample concentrations were from 1 to less than 10 times the PEL (figs. 23 and B20, table 3). The highest concentrations of zinc in bed sediments were found in the Detroit River, Michigan, in 1996; the mouth of the Maumee River, Ohio, in 1996; the mouth of the River Rouge, Michigan, in 1993; the mouth of the Cuyahoga River, Ohio, in 1996; and the mouth of the Clinton River, Michigan, in 1995 (fig. 23). At these locations, detected concentrations ranged from 830 to 2,300 mg/kg. These concentrations were 2.6 to 7.3 times the PEL.

Other locations where concentrations of zinc in bed sediments exceeded the PEL (listed in order of decreasing concentration) were the mouth of the Black River, Ohio; the headwaters of the Portage River, Ohio; the main stem of the Ottawa River, at Toledo, Ohio; the lower River Raisin, Michigan; the main stem of the Clinton River, Michigan; the Ottawa River near Lima, Ohio; the mouth of the Rocky River, Ohio; the Little Cuyahoga River at Akron, Ohio; and the mouth of the Ashtabula River, Ohio.

Sediment Contamination and Potential Impairments of Aquatic Life

The extent to which contaminant concentrations are in excess of sediment-quality guidelines indicates the potential for impairment of aquatic life (table 4, fig. 24). The link between the organisms most at risk for impairment and exposure to surficial sediments is strong because benthic macroinvertebrates and fish live in or forage near the surface of these sediments. Information presented in this section compares sediment contamination in AOC's to sediment contamination outside of AOC's. AOC's represent some of the most highly contaminated bed-sediment areas in the Lake Erie–Lake Saint Clair Drainages. Additional analysis ranked areas where multiple contaminants exceed PEL's and SEL's to show the most severe sediment contamination.

Occurrence and Magnitude of Potential Impairments

Trace-elements were the most frequently detected contaminants of the 20 contaminants investigated for this report; yet the potential for impairment of aquatic organisms in the Lake Erie–Lake Saint Clair Drainages was most often indicated by the concentrations of PAH's, DDT, and PCB's (table 4; fig. 24). Zinc was detected in 100 percent of surficial bed-sediment samples, and lead, copper, arsenic, and cadmium were detected in more than 95 percent of the samples. Of the trace-metals group, mercury was detected at the lowest frequency, in 67 percent of the samples. Of the six trace metals, cadmium and lead were the most likely to exceed a PEL, whereas copper was the least likely to exceed a PEL (Smith and others, 1996).

Compared to trace metals, the next most frequently detected group of contaminants in aquatic sediments were the PAH's. Concentrations of total PAH, chrysene, phenanthrene, benz[*a*]anthracene, and benzo[*a*]pyrene were detected in 37.9 to 55.8 percent of surficial bed-sediment samples. Anthracene concentrations were the exception, being detected in only 19.4 percent of samples. Concentrations of total DDT and total PCB were detected in surficial bed sediments at similar frequencies (35.4 percent for total DDT and 37.6 percent for PCB's). The remaining organochlorine compounds of concern (total chlordane, dieldrin plus aldrin, hexachlorobenzene, total hexachlorocyclohexane, lindane, and total mirex) were detected at much lower frequencies than trace metals, PAH's, total PCB's, and total DDT. The percentage of sample val-

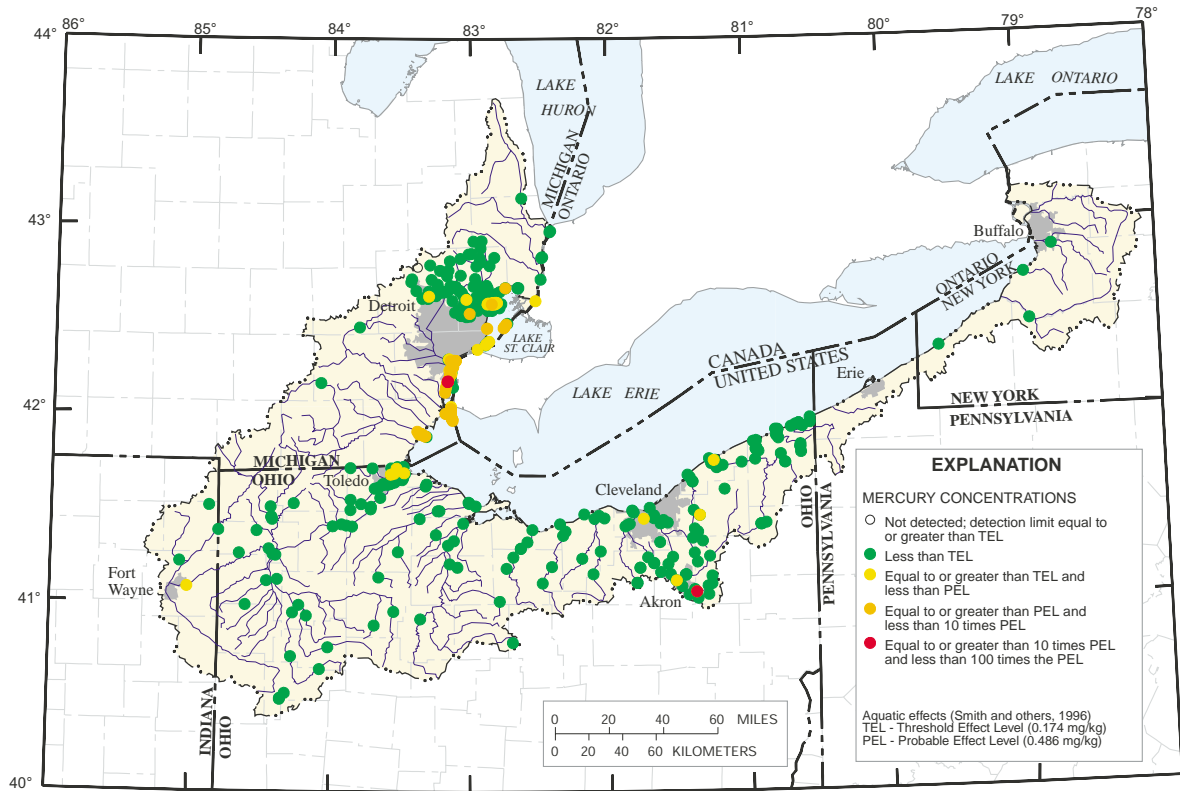


Figure 22. Mercury concentrations in streambed and lakebed sediments, Lake Erie–Lake Saint Clair Drainages, 1990–97.

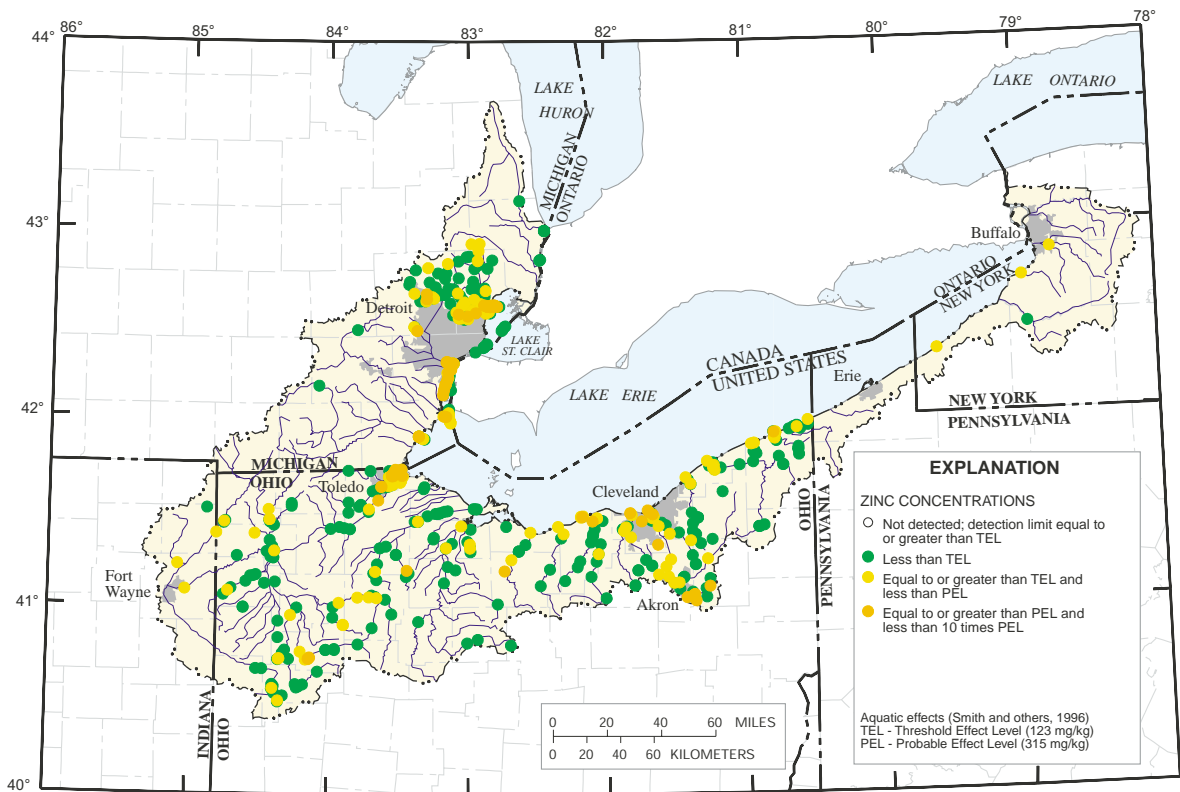


Figure 23. Zinc concentrations in streambed and lakebed sediments, Lake Erie–Lake Saint Clair Drainages, 1990–97.

ues exceeding a PEL (Smith and others, 1996; Ingersoll and others, 1996) was greater for individual PAH's than for trace metals or total PCB's. The percentage of sample values exceeding a SEL (Persaud and others, 1993) was greater for total DDT, copper, total PCB's, and total PAH's than for any other contaminants of concern listed in this report. The number of observations, frequency of detection, and the percentage probability of sample concentrations to exceed a sediment-quality guideline are listed in table 4.

Contamination within and outside of Areas of Concern

In 1987, the International Joint Commission (IJC) identified 12 Areas of Concern (AOC's) in the Lake Erie–Lake Saint Clair Drainages (fig. 25) where aquatic health has been harmed. These geographic areas are mostly represented by river mouths, harbors, and connecting channels. In some cases, an entire sub basin is designated as an AOC. In most cases, the primary reason AOC's were designated was the documented contamination of sediments and its potential impact on aquatic health and habitat.

AOC's within the Lake Erie–Lake Saint Clair Drainages typically comprise river segments in the most heavily industrialized centers. They include the following:

Michigan—Clinton River, River Rouge, the mouth of the River Raisin at Monroe Harbor, and the Detroit River and Saint Clair River connecting channels including their tributaries;

Ohio—The downstream segments of the Maumee River and Ottawa River and their adjacent Lake Erie shoreline tributaries, the Black River, the lower Cuyahoga River and adjacent Lake Erie shoreline, and the mouth of the Ashtabula River;

Pennsylvania—Presque Isle Bay;

New York—the mouth of the Buffalo River and the Niagara River connecting channel. These last two AOC's were not evaluated because data were not available in digital form.

The star diagrams (figs. 26 and 27), referred to in the following sections of the report, represent the 75th- and 90th-percentile concentrations of selected trace metals and organic compounds in relation to sediment-quality guidelines within and outside of AOC's in the United States. The 75th- and 90th-percentile concentrations are the concentrations that are exceeded in 25 and 10 percent of all samples, respectively. For all contaminants shown in figures 26 and 27, concentrations associated with the 75th and 90th

percentiles were measured values because detection frequencies for those contaminants were greater than 25 percent.

Trace metals. Except for arsenic, selected trace metals were detected somewhat more frequently and at slightly greater concentrations within AOC's than outside AOC's (fig. 26). Within AOC's, detection frequencies for copper, lead, and zinc were 100 percent and were greater than those for arsenic (78 percent), cadmium (97 percent), and mercury (69 percent). Outside AOC's, detection frequencies for copper, lead, and zinc were 100 percent and were greater than those for arsenic (96 percent), cadmium (94 percent), and mercury (63 percent). Within AOC's, the top 25 percent of selected trace-metal concentrations were greater than their corresponding TEL's. Outside AOC's, the top 25 percent of trace-metal concentrations, except for mercury, were greater than their TEL's. Within AOC's, the top 10 percent of trace-metal concentrations, except for copper, were greater than their respective PEL's (fig. 26). Outside AOC's, the top 10 percent of selected trace-metal concentrations, except for copper and mercury, were greater than their PEL's.

Organic compounds. Organic compounds were detected much more frequently and at much greater concentrations within AOC's than outside AOC's. In AOC's, total PAH's were detected at the greatest frequency (71 percent), followed by phenanthrene (62 percent), benz[a]anthracene (52 percent), benzo[a]pyrene (51 percent), total DDT (42 percent), and total PCB (39 percent) (fig. 27). Outside AOC's, total PAH's were detected at the greatest frequency (39 percent), followed by phenanthrene (31 percent), benz[a]anthracene (28 percent), benzo[a]pyrene (24 percent), total DDT (29 percent), and total PCB (19 percent) (fig. 27). In AOC's, the top 25 percent of selected organic-compound concentrations were far greater than their TEL's, and except for total DDT, were also somewhat greater than their PEL's (fig. 27). Outside AOC's, the top 25 percent of all selected organic-compound concentrations were somewhat greater than their TEL's and except for total PCB and total DDT, were equal to or slightly greater than their PEL's (fig. 27). Within AOC's, the top 10 percent of selected organic-compound concentrations, except total DDT, were more than 10 times greater than their PEL's. Outside AOC's, the top 10 percent of selected

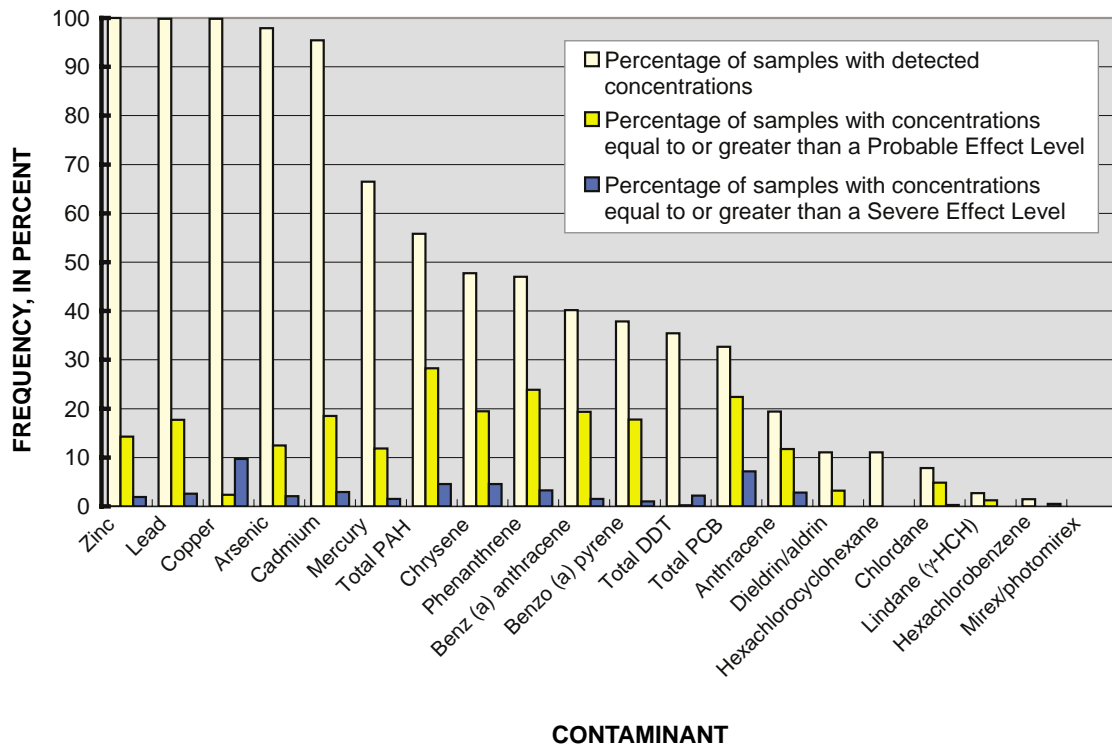


Figure 24. Frequency of detection and percentage of sample concentrations exceeding a sediment-quality guideline; Lake Erie–Lake Saint Clair Drainages, 1990–97.

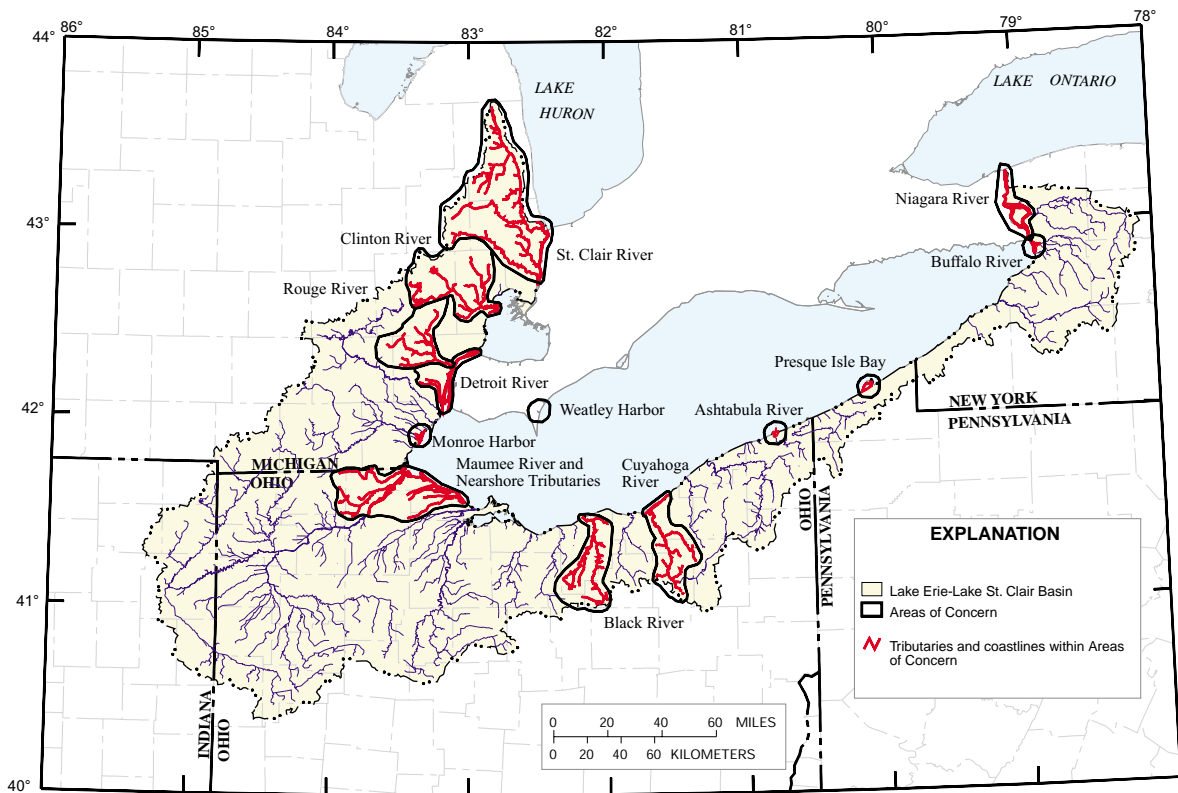


Figure 25. Areas of Concern (in red) in the Lake Erie–Lake Saint Clair Drainages (International Joint Commission, 1987).

Table 4. Probability of sample concentrations being equal to or greater than a sediment-quality guideline, Lake Erie–Lake Saint Clair Drainages, 1990–97

[N, number of samples; LEL, Lowest Effect Level; SEL, Severe Effect Level; USEPA, U.S. Environmental Protection Agency; TEL, Threshold Effect Level; PEL, Probable Effect Level; --, no guideline; i.d., insufficient data to compute exceedance percentage (less than 25 percent of the samples had detected values); **bold type**, data used in figure 24; values represent detected concentrations or nondetected concentrations greater than guidelines]

Contaminant	N ^a (percent of N with detected val- ues)	Probability of sample concentrations being equal to or greater than a guideline (in percent)					
		Ontario– Provincial Sedi- ment Quality Guidelines ^b		USEPA–Great Lakes Sediment Effect Concentrations ^c		Environment Canada– Great Lakes Guidelines ^d	
		LEL	SEL	TEL	PEL	TEL	PEL
Organochlorine compounds							
Chlordane, total	371 (7.82)	i.d.	i.d.	--	--	i.d.	i.d.
DDT, total	409 (35.4)	59.8	40.7	--	--	59.8	0.20
Dieldrin plus aldrin	407 (11.0)	i.d.	i.d.	--	--	i.d.	i.d.
Hexachlorobenzene	411 (1.46)	i.d.	i.d.	--	--	--	--
Hexachlorocyclohexane, total	407 (11.0)	i.d.	i.d.	--	--	--	--
Lindane	404 (2.72)	--	--	--	--	i.d.	i.d.
Mirex, total	199 (0.00)	i.d.	i.d.	--	--	--	--
PCB, total	683 (37.6)	66.0	7.8	87.2	25.4	84.8	23.8
Polycyclic aromatic hydrocarbon compounds							
PAH, total	414 (55.8)	30.7	4.73	78.6	36.1	--	--
Anthracene	392 (19.4)	i.d.	i.d.	i.d.	i.d.	--	--
Benz[<i>a</i>]anthracene	393 (40.2)	64.0	1.45	88.9	66.8	87.3	57.7
Benzo[<i>a</i>]pyrene	388 (37.9)	62.1	1.20	88.2	66.0	88.2	30.0
Chrysene	396 (47.7)	61.9	4.30	87.5	59.2	89.5	26.4
Phenanthrene	398 (47.0)	47.9	3.39	87.1	59.7	85.8	48.8
Trace metals							
Arsenic	480 (97.9)	68.6	1.17	29.3	0.84	69.7	11.8
Cadmium	616 (95.4)	53.2	2.37	55.4	22.5	33.2	18.3
Copper	587 (99.8)	69.6	9.13	47.4	11.2	37.7	1.32
Lead	615 (99.8)	46.4	2.54	41.7	19.9	42.8	17.6
Mercury	465 (66.4)	23.7	1.33	--	--	25.4	12.1
Zinc	575 (100)	44.4	1.89	53.8	5.12	43.3	14.1

^a If detection rate was less than 25 percent of N, exceedance percentage was not computed.

^b Persaud and others, 1993.

^c Ingersoll and others, 1996.

^d Smith and others, 1996.

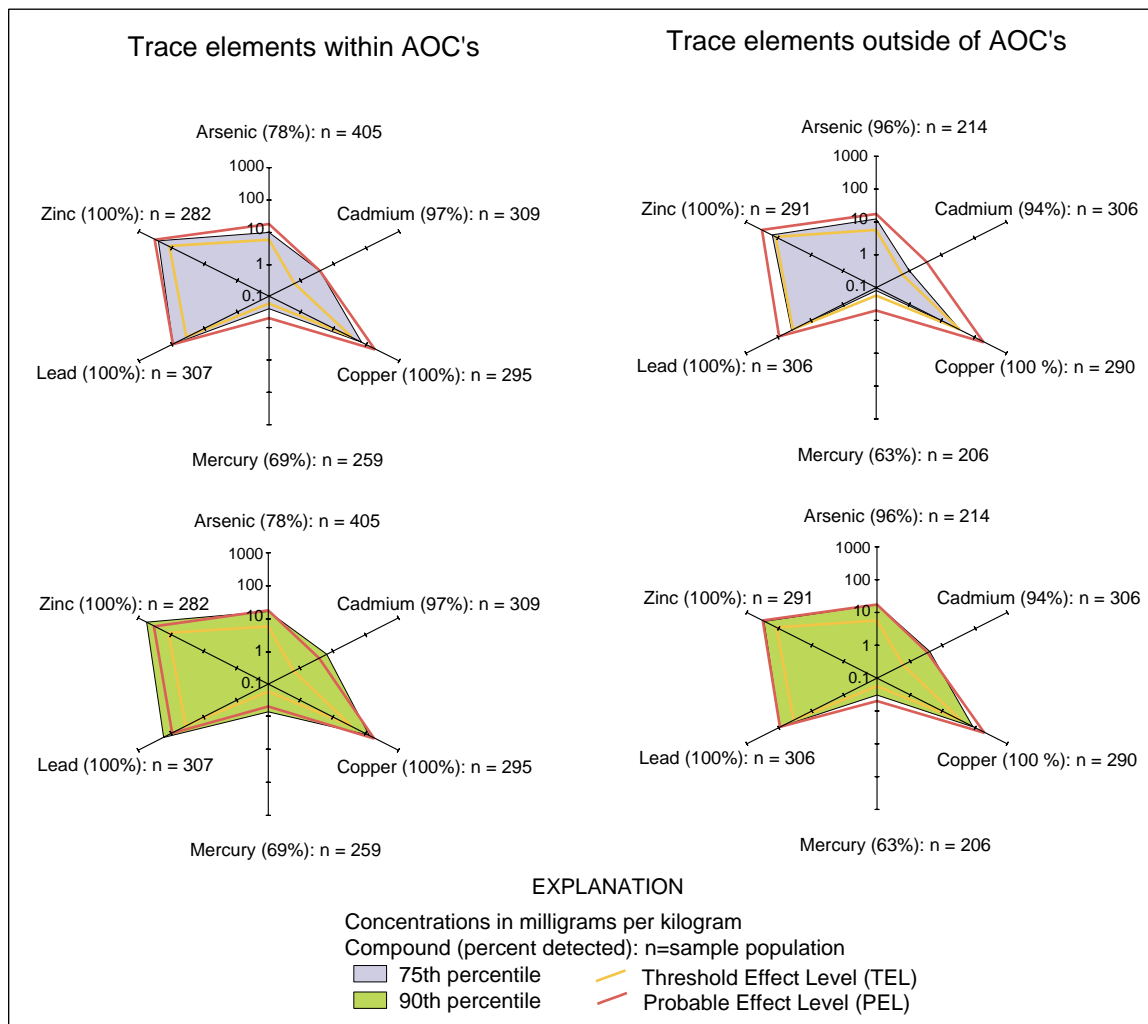


Figure 26. Star diagrams showing 75th- and 90th-percentile concentrations of selected trace element contaminants in relation to sediment-quality guidelines within and outside of Areas of Concern, Lake Erie–Lake Saint Clair Drainages, 1990–97.

organic-compound concentrations, except for DDT, were only equal to or slightly greater than their PEL's.

Comparative Ranks by Location

Compared to the area as a whole, the highest detection frequencies and highest concentrations of total PCB's and total PAH's in the Lake Erie–Lake Saint Clair Drainages were in AOC's. Because the AOC's are in the largest urban areas (those with populations greater than 100,000), contamination is usually considered to be related to major cities and urban land use. The highest concentrations of anthracene, total PAH, phenanthrene, benz[a]anthracene, total PCB, chrysene, benzo[a]pyrene, and total chlordane in bed sediment were in AOC's along the following large rivers: Clin-

ton River, Detroit River, River Raisin, and River Rouge, in Michigan; and the Maumee River and Cuyahoga River in Ohio. Total DDT, total dieldrin, hexachlorocyclohexane, and lindane, at concentrations greater than their PEL's or SEL's, were reported in streams draining urban and agricultural areas throughout the Lake Erie–Lake Saint Clair Drainages, an indication that sources are present in both types of land use. Mirex and hexachlorobenzene were not found to any great extent in samples; however, lower detection limits for hexachlorobenzene would improve confidence in this assessment.

The highest detection frequencies and concentrations of most trace metals were not dramatically greater in AOC's than in other areas of the Drainages.

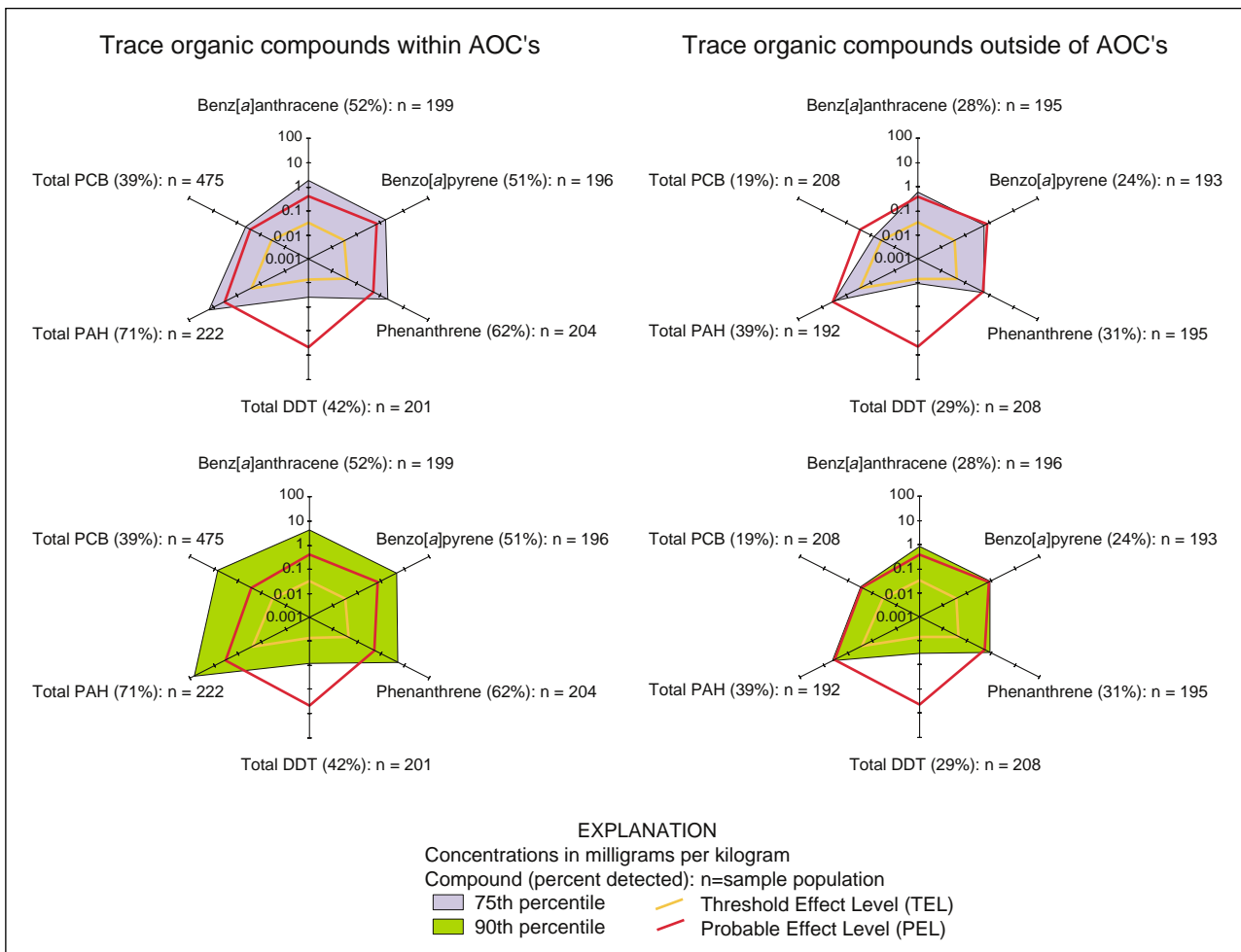


Figure 27. Star diagrams showing 75th- and 90th-percentile concentrations of selected organic compound contaminants in relation to sediment-quality guidelines within and outside of Areas of Concern, Lake Erie–Lake Saint Clair Drainages, 1990-97.

The dominant factor that may be influencing the concentrations of cadmium, copper, lead, and mercury in the bed sediment appears to be the presence of urban land in drainage areas of receiving streams. Trace-metal concentrations in many principal streams in Lake Erie–Lake Saint Clair Drainages were frequently greater than sediment-quality guidelines. Because the concentrations of some trace metals in soils vary naturally (depending on the type of surficial and bedrock materials from which they are derived), distinguishing the primary sources of arsenic and zinc may be complicated.

A ranking of the 10 most heavily contaminated rivers in the Lake Erie–Lake Saint Clair Drainages was based on the frequency of exceeding one or more PEL's (table 5). The Ottawa River at Toledo, Ohio, ranked first, with six contaminants of concern detected

at concentrations greater than 100 times their PEL's; the Ashtabula River, in Ohio, ranked tenth, with the concentration of only one contaminant of concern greater than 10 times the PEL (table 5). Maximum concentrations of contaminants ranged from 4.9 times the PEL for total DDT at the mouth of the Clinton River, in Michigan, to 145,000 times the PEL for total PCB's at the mouth of the River Raisin, in Michigan. In the Ottawa River Drainages at Toledo, Ohio, maximum concentrations of 15 contaminants were greater than their PEL's. Maximum concentrations of anthracene, total PAH, phenanthrene, benz[a]anthracene, chrysene, and benzo[a]pyrene ranged from 141 to 1,165 times their respective PEL's. Maximum concentrations of total PCB's and dieldrin plus aldrin ranged from 10 to less than 100 times their PEL's. Maximum concentrations of total chlordane,

arsenic, lindane, zinc, cadmium, lead, and copper ranged from 1 to less than 10 times their PEL's. Most of the elevated concentrations of PAH's were reported in Williams Ditch, a tributary to the Ottawa River, but elevated PAH's were also found in the main stem.

In the River Rouge in Michigan, maximum concentrations of 12 contaminants were greater than their PEL's. Maximum concentrations of anthracene and phenanthrene were 115 and 147 times their PEL's, respectively. Maximum concentrations of total PAH's, benz[a]anthracene, total PCB, chrysene, and benzo[a]pyrene ranged from 10 to less than 100 times their PEL's. Maximum concentrations of mercury, zinc, cadmium, lead, and copper ranged from 1 to less than 10 times their PEL's. Elevated total PCB, mercury, zinc, cadmium, lead, and copper were a problem throughout the area, but most of the contamination

was noted in the lower reach near the mouth of the River Rouge.

In the Clinton River in Michigan, maximum concentrations of 15 contaminants were greater than their PEL's. The highest concentrations of total PAH's were 138 to 722 times the PEL. The maximum concentrations of anthracene, phenanthrene, benz[a]anthracene, total PCB's, chrysene, benzo[a]pyrene, total chlordane, and lindane ranged from 10 to less than 100 times their PEL's. The maximum concentrations of mercury, arsenic, zinc, cadmium, lead, and total DDT ranged from 1 to less than 10 times their PEL's. The worst bed-sediment contamination from total PAH's was in the headwaters of the Clinton River. The 14 other contaminants of concern with concentrations that exceeded PEL's were elevated throughout the study area; however, maximum con-

Table 5. Ten river basins with highest level and frequencies of bed-sediment contamination in the Lake Erie-Lake Saint Clair Drainages, 1990–97

[Rankings based on the degree and frequency that bed-sediment samples exceed Probable Effect Level (PEL) guidelines; ● = concentration in at least one sample exceeded 100 times the contaminant's PEL; ● = concentration in at least one sample exceeded 10 times the contaminant's PEL; ● = concentration in at least one sample exceeded the contaminant's PEL; ● = concentrations in all samples were below the contaminant's PEL]

River basin names listed in degree of exceedance of PEL's	Contaminants of Concern listed in frequency of exceedance of PEL's																
	Anthracene	Total PAH	Phenanthrene	Total PCB	Benz[a]anthracene	Chrysene	Benzo[a]pyrene	Total Chlordane	Mercury	Lindane	Dieldrin/aldrin	Lead	Zinc	Cadmium	Arsenic	Copper	Total DDT
Ottawa River at Toledo, Ohio	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
River Rouge, Mich.	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Clinton River, Mich	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Detroit River, Mich.	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
River Raisin, Mich.	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Lake St. Clair, Mich.	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Cuyahoga River, Ohio	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Maumee River, Ohio	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Little Cuyahoga River, Ohio	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
Ashtabula River, Ohio	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●

centrations were most frequently found in the lower reach and near the mouth of the Clinton River.

In the Detroit River in Michigan, maximum concentrations of 13 contaminants were greater than their PEL's. The maximum concentration of anthracene was 147 times the PEL, and the maximum concentrations of total PAH, phenanthrene, benz[*a*]anthracene, total PCB, chrysene, benzo[*a*]pyrene, and mercury ranged from 10 to less than 100 times their PEL's. The maximum concentrations of arsenic, zinc, cadmium, lead, and copper ranged from 1 to less than 10 times their PEL's. The highest bed-sediment contamination was found in the downstream reach of the Detroit River, known as the Trenton Channel.

In the River Raisin in Michigan, maximum concentrations of 12 bed-sediment contaminants were greater than their PEL's. The highest concentrations of total PCB's ranged from 191 to 145,000 times the PEL, and the maximum concentrations of total PAH, phenanthrene, benz[*a*]anthracene, chrysene, benzo[*a*]pyrene, mercury, arsenic, zinc, cadmium, lead, and copper ranged from 1 to less than 10 times their PEL's. The worst bed-sediment contamination was from total PCB's, near the mouth of the River Raisin. The 11 other contaminants of concern were found mostly in the lower reach near the mouth of the River Raisin. The exception was arsenic, which was found at concentrations greater than the PEL in the headwater area of the River Raisin.

In Lake Saint Clair in Michigan, maximum concentrations of 12 contaminants were greater than their PEL's. The maximum concentrations of total PCB's and total chlordane ranged from 11.7 to 27.3 times their PEL's, and maximum concentrations of anthracene, phenanthrene, benz[*a*]anthracene, chrysene, benzo[*a*]pyrene, mercury, cadmium, and lead ranged from 1 to less than 10 times their PEL's. The worst contamination was found in bed sediments along the western shoreline of Lake Saint Clair.

In the Cuyahoga River in Ohio, maximum concentrations of 14 contaminants were greater than their PEL's. The highest concentrations of total PAH's ranged from 10 to 11.1 times the PEL and the maximum concentration of mercury was 12.5 times the PEL. Maximum concentrations of anthracene, phenanthrene, benz[*a*]anthracene, total PCB, chrysene, benzo[*a*]pyrene, total chlordane, arsenic, dieldrin plus aldrin, zinc, cadmium, lead, and copper ranged from 1 to less than 10 times their PEL's. The worst bed-sedi-

ment contamination was from total PAH, found in some of the tributaries to the main stem near Cleveland and at Akron, Ohio. The 13 other contaminants of concern that exceeded their PEL's were found at many locations throughout the Cuyahoga River from Akron to Cleveland, Ohio. In the Little Cuyahoga River near Akron, Ohio, concentrations of mercury, phenanthrene, benz[*a*]anthracene, chrysene, benzo[*a*]pyrene, total chlordane, zinc, and lead were greater than their PEL's.

In the Maumee River, which drains parts of Michigan, Indiana, and Ohio, maximum concentrations of 13 contaminants were greater than their PEL's. The maximum concentration of total PAH was 10.6 times the PEL. Maximum concentrations of anthracene, phenanthrene, benz[*a*]anthracene, total PCB, chrysene, benzo[*a*]pyrene, total chlordane, arsenic, lindane, zinc, cadmium, and lead ranged from 1 to less than 10 times their PEL's. Most of the organic contaminants were found in the lower reach near the mouth at Toledo, Ohio, and downstream from Fort Wayne, Indiana. Trace-metal contamination appears to be widespread downstream from many of the urban centers of various sizes throughout the study area.

In the Ashtabula River, the maximum concentrations of eight contaminants were greater than their PEL's. The maximum concentration of phenanthrene was 10.1 times the PEL, and maximum concentrations of anthracene, benz[*a*]anthracene, chrysene, benzo[*a*]pyrene, total chlordane, arsenic, and zinc ranged from 1 to less than 10 times their PEL's. All the bed-sediment contaminants were found near or at the mouth of the Ashtabula River.

Summary

This report describes the occurrence and distribution of contaminants of concern in streambed sediments in the Lake Erie–Lake Saint Clair Drainages, compares these bed-sediment contaminant concentrations to guidelines that indicate concentrations either acutely or chronically toxic to aquatic macroinvertebrates, and discusses the extent and magnitude of contamination within Areas of Concern (AOC's) relative to other areas. The study that produced this report used four large databases that cover parts of the Lake Erie–Lake Saint Clair Drainages: the National Sediment Inventory (NSI), Ohio Sediment data Inventory (OSI), USEPA-Fully Integrated Environmental Locational Decision Support system (FIELDS) database, and the

USGS-National Water-Quality Assessment Program (NAWQA) sediment data. Only bed-sediment samples collected during 1990–1997 (in the top 5 inches of sediment) in the United States part of the Lake Erie–Lake Saint Clair Drainages were evaluated to reflect recent U.S. conditions.

The data are compared to three freshwater bed-sediment-quality guidelines used in the Great Lakes area: Ontario Ministry of Environment guidelines for the protection and management of Canadian freshwater sediments; USEPA guidelines for Great Lakes sediments; and Environment Canada and the Great Lakes guidelines for ecosystems throughout Canada and the Great Lakes Basin. The location and concentration range of selected contaminants of concern are mapped in this report, and each compound is discussed as to its toxicity to biota according to these regional bed-sediment guidelines.

The larger the stream, the more likely it was to be contaminated by one or more organic-chemical compounds or trace metals. This study showed that surficial bed sediments in streams within “Areas of Concern” (AOC’s), previously identified by the International Joint Commission, contained the highest percentage of detections of the organic compounds chlordane, total PCB, and various PAH’s and were most likely to have contaminant concentrations greater than Probable Effect Level (PEL) and Severe Effect Level (SEL) guidelines. The highest concentrations of anthracene, total PAH, phenanthrene, benz[*a*]anthracene, total PCB, chrysene, benzo[*a*]pyrene, and (or) chlordane in bed sediment were in the Clinton River, Detroit River, River Raisin, and River Rouge AOC’s, in Michigan; and in the Maumee River and Cuyahoga River AOC’s, in Ohio. The dominant factor influencing bed-sediment trace-metal concentrations of cadmium, copper, lead, and mercury appeared to be urban land use in the basin of the receiving stream. The study indicated a fairly high probability that trace-metal concentrations will exceed the PEL and SEL guidelines in many principal streams or tributaries to Lake Saint Clair and Lake Erie that pass through major urban centers.

Exceedance of PEL’s and SEL’s for total DDT, dieldrin, hexachlorocyclohexane, and lindane concentrations were found in streams draining urban and agricultural areas throughout the Lake Erie–Lake Saint Clair Drainages; indicating the influence of both types of land use. Mirex and hexachlorobenzene were not found to be a significant problem in the basin; how-

ever, lower detection limits would improve confidence in the assessment of hexachlorobenzene. Because the concentrations of some trace-metals in soil vary naturally, depending on the type of surficial and bedrock materials they are derived from, distinguishing the primary sources of arsenic and zinc may be complicated.

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Appendix A

Methods of sample collection, analysis, quality assurance, and quality control

Table A1. Chemical class, number of agencies providing databases, and number of analyzing laboratories contributing sediment-quality data, 1990–97

Table A2. Summary of sample-collection methods

Table A3. Summary of sample preparation and analysis methods

Table A4. Summary of quality-assurance programs and quality-control procedures

Methods of sample collection, analysis, quality assurance, and quality control

Seven public agencies collected and provided the data used in this report, and 15 laboratories analyzed and reported sample results. (see section on “Sampling Agencies and Analyzing Laboratories.”) A summary of data classes collected and reported by these entities is given in table A1. Aquatic sediment-collection methods varied with the depth, location, and texture of sediments (table A2). Shallow areas in streams were sampled with stainless steel spoons or scoops, Petit Ponar or Ponar dredges, or hand corers. Deeper samples were collected with Ponar dredges or with core samplers. All samples for subsequent analysis of organic contaminants were handled with cleaned stainless steel or Teflon-coated utensils and stored in pre-cleaned glass jars with Teflon lid liners. Samples for trace metals were collected and processed with polypropylene sieves and stored in plastic jars.

Most protocols stipulated that samples be sieved or otherwise processed in the field to eliminate coarse material and debris. After removal of coarse material, samples were subsequently homogenized by thoroughly mixing or stirring with a clean utensil or with a blender. After collection and processing, all samples were chilled or frozen until analysis. For organic compounds, if samples were chilled, analysis was completed within 2 to 40 days. If samples were frozen, analysis for organic compounds was completed within 1 year. For trace metals, analysis was completed within 1 to 6 months. In the case of mercury, samples were analyzed within 30 days.

All contaminant concentrations in bed sediments are reported as dry weight, in milligrams per kilogram. Analysis of trace metals followed methods published by the U.S. Environmental Protection Agency (1979, 1993a, 1998); Foreman and others (1995); Furlong and others (1996); or the American Public Health Association and others (1995) for analysis of aquatic bed sediments or solid-waste materials (table A3). Subsamples were dried and weighed to determine percent moisture. Trace-element samples were digested prior to analysis with a strong acid, either nitric acid or hydrochloric acid, or a combination of both. Results obtained from acid-digested samples are considered “total recoverable trace metals.”

For trace-element samples analyzed by XRF (X-ray fluorescence spectroscopy), no digestion was done. For USGS samples, acid digestion was done with hydrofluoric acid followed by AAS (Atomic

Absorption Spectroscopy), ICP (Inductively Coupled Plasma Emission Spectroscopy), or ICP-MS (mass spectroscopy). Results obtained by XRF or following hydrofluoric acid digestion are considered “total trace metals” (Smith and others, 1995) and represent a more complete measure of trace-element composition of sediments than those for sediments digested with nitric or nitric and hydrochloric acid. Results obtained using XRF are approved for use by USEPA in the SW-846 (Solid Waste Methods, U.S. Environmental Protection Agency, 1998) along with the more commonly used AAS and ICP methods. Only mercury samples analyzed by the cold vapor-AAS method were used for this report.

Analysis of organochlorine and semivolatile compounds was done after solid phase/solvent or soxhlet extraction and sample cleanup to remove sample-matrix interferences. Instrumental analysis for determination of organochlorine compounds was done by dual capillary column GC (gas chromatography) or by GC/MS (gas chromatography/mass spectrometry). Instrumental analysis of PAH's and other semivolatile compounds was done by GC with FID (flame ionization detector) or GC/MS. One laboratory used immunoassay methods for PCB's and PAH's. Although not commonly used, these methods are approved and documented for analysis of soils and sediments by USEPA as part of SW-846 (U.S. Environmental Protection Agency, 1998). Samples may have been analyzed for concentrations of total organic carbon as well as trace organic contaminants. Samples for this report were not normalized against individual results for concentrations of total organic carbon.

Quality-assurance/quality-control (QA/QC) methods were used by each collecting agency and analyzing laboratory (table A4). The elements of a quality-assurance and quality-control program deemed to be the most important to this interpretive report are (1) the documentation and use of a QA/QC plan, (2) documentation of methods of collection, field preparation, transport, and analysis, and (3) evaluation of precision, bias, and overall accuracy through the use of various quality-control procedures. All data accepted for inclusion in this report came from programs or projects that had QA/QC plans in place and used quality-control procedures to evaluate data quality, as indicated in tables A3-A4.

Table A1. Chemical class, number of agencies providing databases, and number of analyzing laboratories contributing sediment-quality data, 1990–97

Class of chemical compound	Number of collecting and reporting agencies	Number of analyzing laboratories
Organochlorine pesticides	4	8
Polycyclic aromatic hydrocarbons	5	9
Polychlorinated biphenyls	6	11
Trace metals	6	12
Total	7	15

Table A2. Summary of sample-collection methods

[USEPA, U.S. Environmental Protection Agency; USGS, U.S. Geological Survey; USACE, U.S. Army Corps of Engineers; MDNR, Michigan Department of Natural Resources; NYSDEC, New York State Department of Environmental Conservation; Ohio EPA, Ohio Environmental Protection Agency; RPO, Rouge Program Office]

Collection methods	Collecting agency					
	USEPA ¹	USGS ²	USACE/ MDNR ³	NYS DEC ⁴	Ohio EPA ⁵	RPO ⁶
Grab sample(s)	X		X		X	X
Composite sample		X		X		
Petit ponar			X			
Ponar			X			X
Hand core			X			
Vibracore	X		X			
Van Veen			X			

¹ U.S. Environmental Protection Agency, 1993a.

² Shelton and Capel, 1994.

³ Nielson and Sanders, 1983.

⁴ Myers and others, 1994.

⁵ Ohio Environmental Protection Agency, 1995, 1997.

⁶ Smith and others, 1995.

Table A3. Summary of sample preparation and analysis methods

[n/a, not applicable; P, sample preparation; A, sample analysis; D-nh, digestion with nitric and hydrochloric acids; D-f, digestion with hydrofluoric acid; Ex, Extraction; SE, solvent extraction; SoE, soxhlet extraction; C, cleanup procedure; F, fluorosil cleanup; S, elemental sulfur cleanup; Me-NaS, methanol-sodium sulfate extraction; SG, silica gel cleanup; ICP, inductively coupled plasma emission spectroscopy; ICP/MS, inductively coupled plasma emission spectroscopy-mass spectrometry; GP, gel permeation chromatography; GC-ECD, gas chromatography-electron capture detection; GC/FID, gas chromatography-flame ionization detection; GC-MS, gas chromatography-mass spectrometry; XRF, X-ray fluorescence spectrometry; I, immunoassay; U.S. Environmental Protection Agency, 1993a; USEPA, U.S. Environmental Protection Agency; USGS, U.S. Geological Survey; USACE, U.S. Army Corps of Engineers; MDNR, Michigan Department of Natural Resources; NYSDEC, New York State Department of Environmental Conservation; Ohio EPA, Ohio Environmental Protection Agency; RPO, Rouge Program Office]

Organization	Methods of sample preparation and analysis									
	Trace elements		Mercury		PCB's and organochlorine pesticides			Semivolatile compounds		
	P	A	P	A	Ex	C	A	Ex	C	A
USEPA ^{1,2,3}	D-nh	ICP	D	AA-CV	SoE	F,S	GC-ECD	SoE	SG	GC/FID
USGS ^{4,5,6}	D-f	ICP/MS	D	AA-CV	SoE	GP	GC-ECD	SE	GP	GC/MS
USACE/ MDNR ^{1,2,7}	D	AAS	D	AA-CV	SoE	GP	GC-MS	SoE	GP	GC/MS
NYSDEC ^{1,2,3,10}	D-nh	AAS	D-nh	AA-CV	n/a	n/a	n/a	n/a	n/a	n/a
Ohio EPA ^{2,3,8,9}	D	ICP	D	AA-CV	SE	F,S	GC-MS	SE	SG	GC/MS
RPO ^{1,2,11}	n/a	XRF ¹²	n/a	n/a	n/a	n/a	I ¹	Me-NaS	n/a	I ¹

¹ U.S. Environmental Protection Agency, 1994.

² U.S. Environmental Protection Agency, 1998.

³ U.S. Environmental Protection Agency, 1979.

⁴ Arbogast, 1990.

⁵ Foreman and others, 1995.

⁶ Furlong and others, 1996.

⁷ U.S. Environmental Protection Agency, 1993b.

⁸ Ohio Environmental Protection Agency, 1995.

⁹ American Public Health Association and others, 1995.

¹⁰ Myers and others, 1994.

¹¹ Rouge Program Office, 1995.

¹² Nielson and Sanders, 1983.

Table A4. Summary of quality-assurance programs and quality-control procedures

[Y, yes; QA, quality assurance; CRM, Certified Reference Material; SRM, Standard Reference Material; USGS, U.S. Geological Survey; USACE, U.S. Army Corps of Engineers; MDNR, Michigan Department of Natural Resources; NYSDEC, New York State Department of Environmental Conservation; Ohio EPA, Ohio Environmental Protection Agency; RPO, Rouge Program Office]

Organization	Quality-assurance plans and quality-control procedures				
	QA plan	Analysis frequency of replicate samples (percent)	Analysis frequency of laboratory blanks (percent)	Analysis frequency of laboratory matrix or surrogate spike samples	Other quality-control checks
USEPA ¹	Y	20	Daily	5	SRM CRM
USGS ^{2,3}	Y	10	5	10	SRM
USACE/MDNR ^{1,4}	Y	15	Daily	5	SRM, CRM
NYSDEC ⁵	Y	7	10-15	7	SRM
Ohio EPA ^{6,7}	Y	5-10	Daily	1-5	SRM
RPO ⁸	Y	5	5	5	SRM

¹ Schumaker, 1994.

² Arbogast, 1990.

³ Jones, 1987.

⁴ Michigan Department of Natural Resources, 1994.

⁵ Myers and others, 1994.

⁶ Ohio Environmental Protection Agency, 1995.

⁷ Ohio Environmental Protection Agency, 1997.

⁸ Rouge Program Office, 1994.

Appendix B

Figures B1-B20—Graphs showing probability distributions of concentrations and detection limits for streambed and lakebed sediments in relation to sediment-quality guidelines, Lake Erie–Lake Saint Clair Drainages, 1990–97.

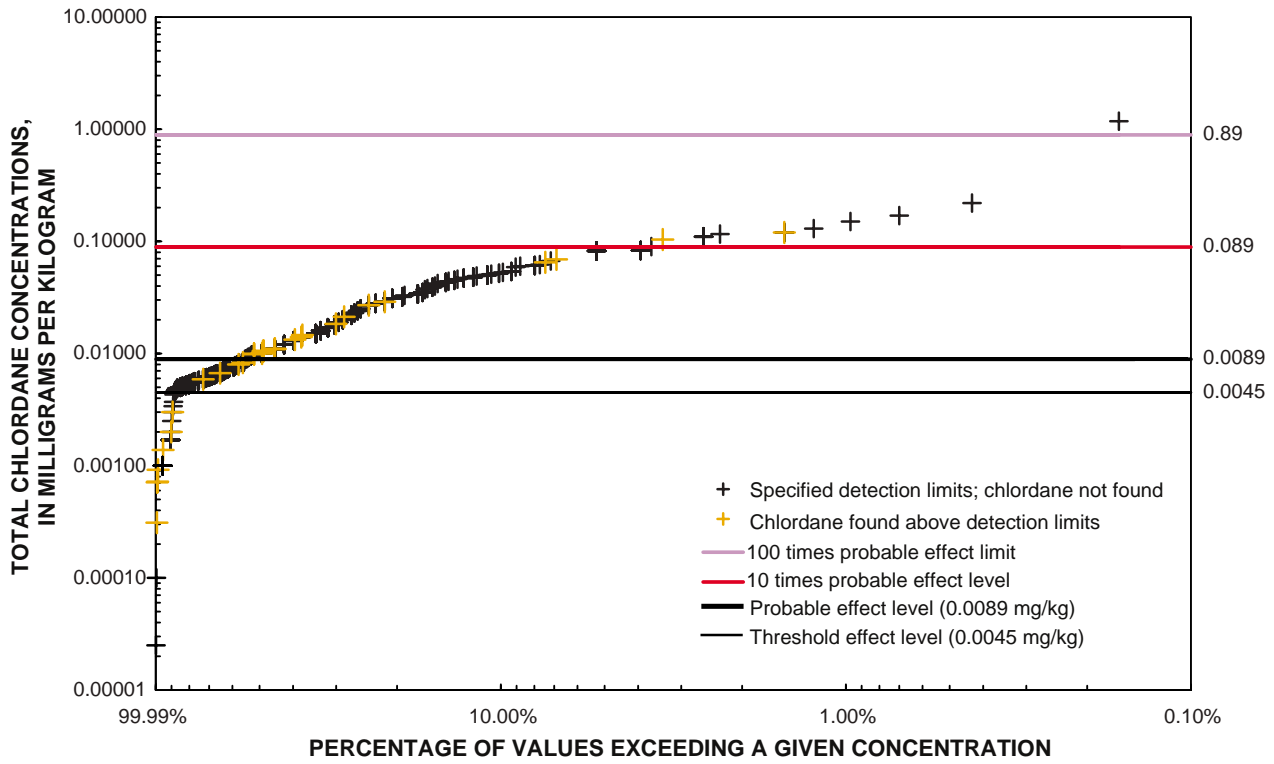


Figure B1. Probability distribution of total chlordane concentrations and detection limits for streambed and lakebed sediments in relation to aquatic-life criteria, Lake Erie–Lake Saint Clair Drainages, 1990–97.

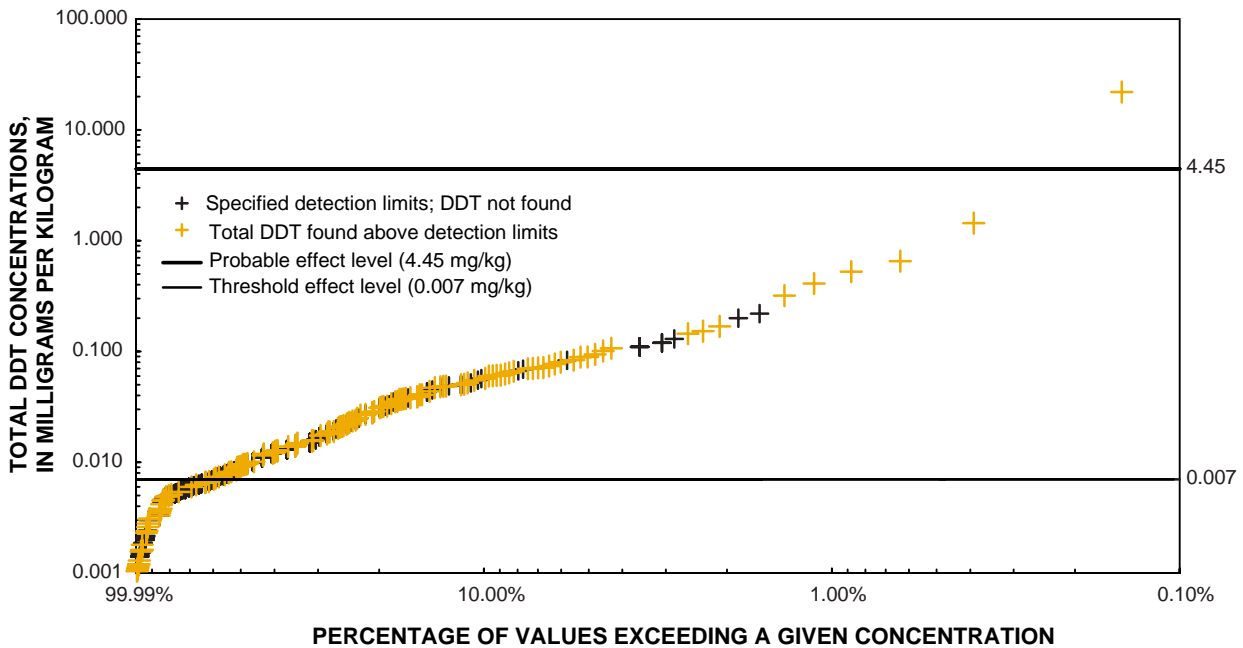


Figure B2. Probability distribution of total DDT concentrations and detection limits for streambed and lakebed sediments in relation to aquatic-life criteria, Lake Erie–Lake Saint Clair Drainages, 1990–97.

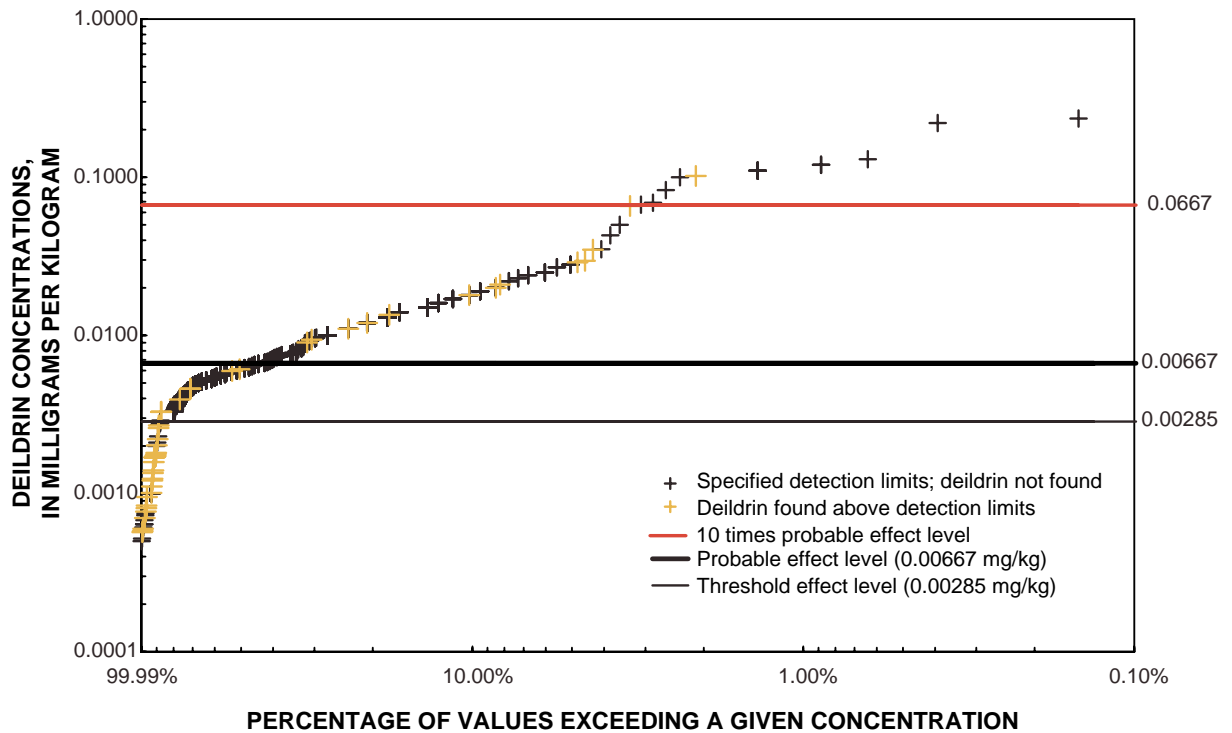


Figure B3. Probability distribution of dieldrin concentrations and detections limits for streambed and lakebed sediments in relation to aquatic-life criteria, Lake Erie–Lake Saint Clair Drainages, 1990–97.

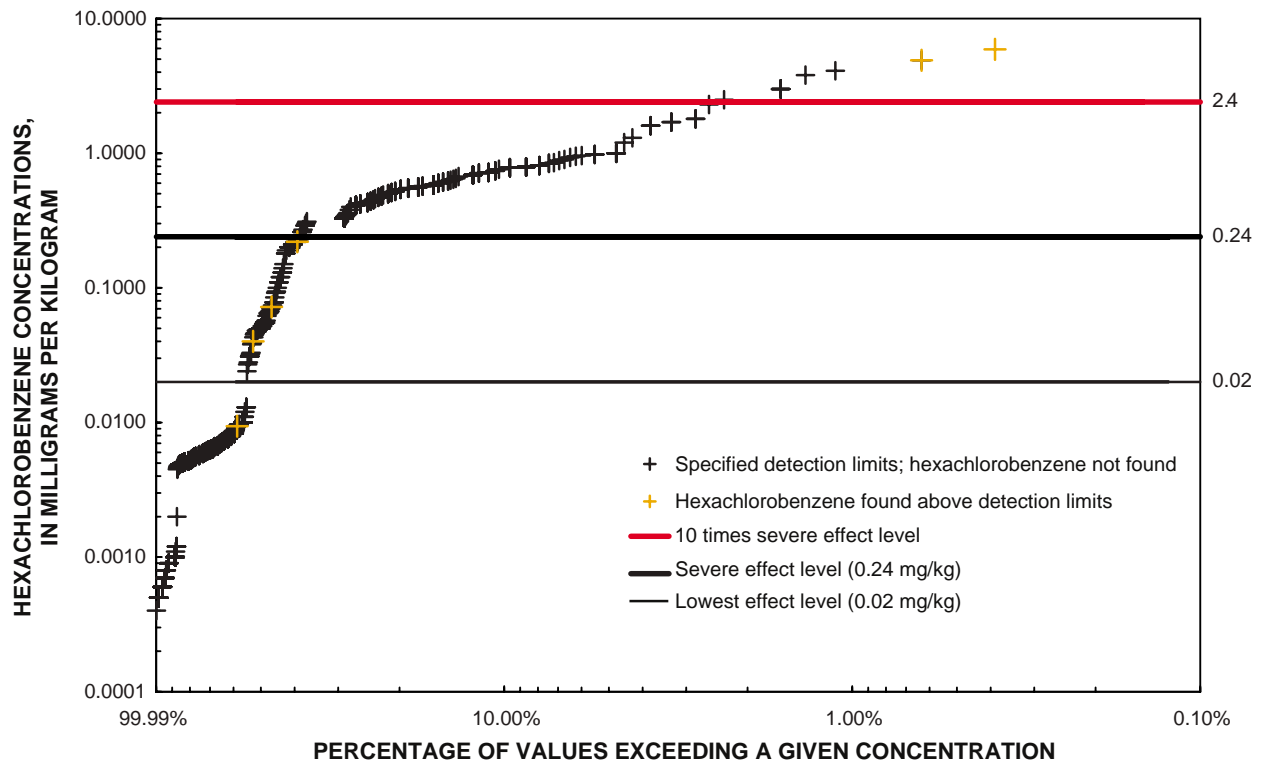


Figure B4. Probability distribution of hexachlorobenzene concentrations and detection limits for streambed and lakebed sediments in relation to aquatic-life criteria, Lake Erie–Lake Saint Clair Drainages, 1990–97.

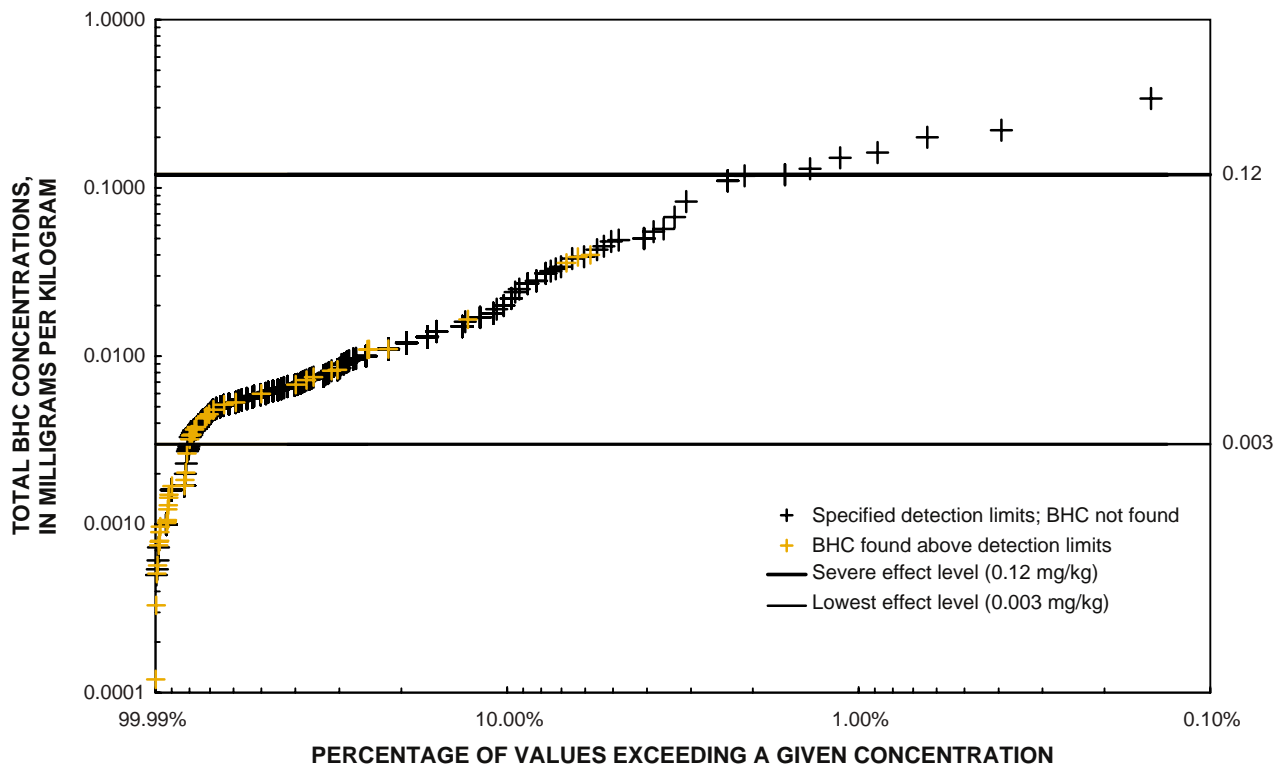


Figure B5. Probability distribution of total hexachlorocyclohexane (BHC) concentrations and detection limits for streambed and lakebed sediments in relation to aquatic-life criteria, Lake Erie–Lake Saint Clair Drainages, 1990–97.

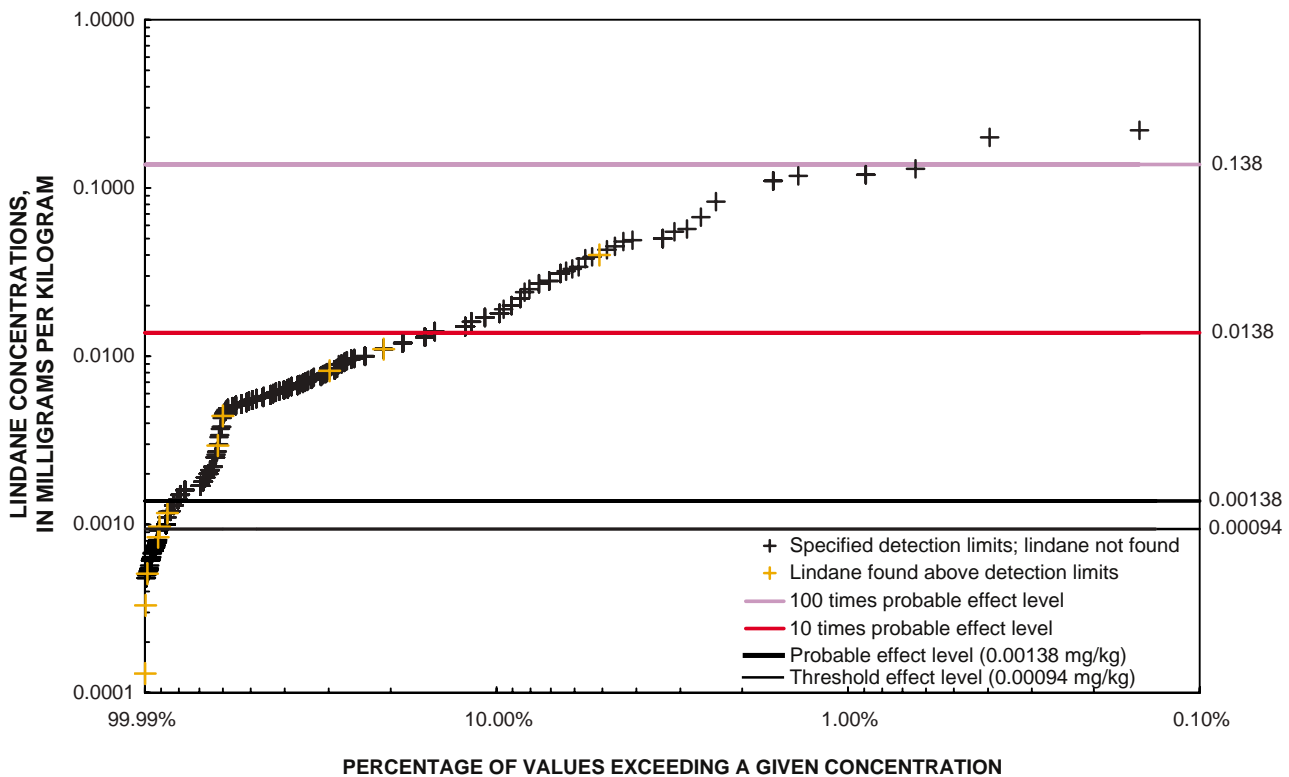


Figure B6. Probability distribution of lindane (γ -hexachlorocyclohexane) concentrations and detection limits for streambed and lakebed sediments in relation to aquatic-life criteria, Lake Erie–Lake Saint Clair Drainages, 1990–97.

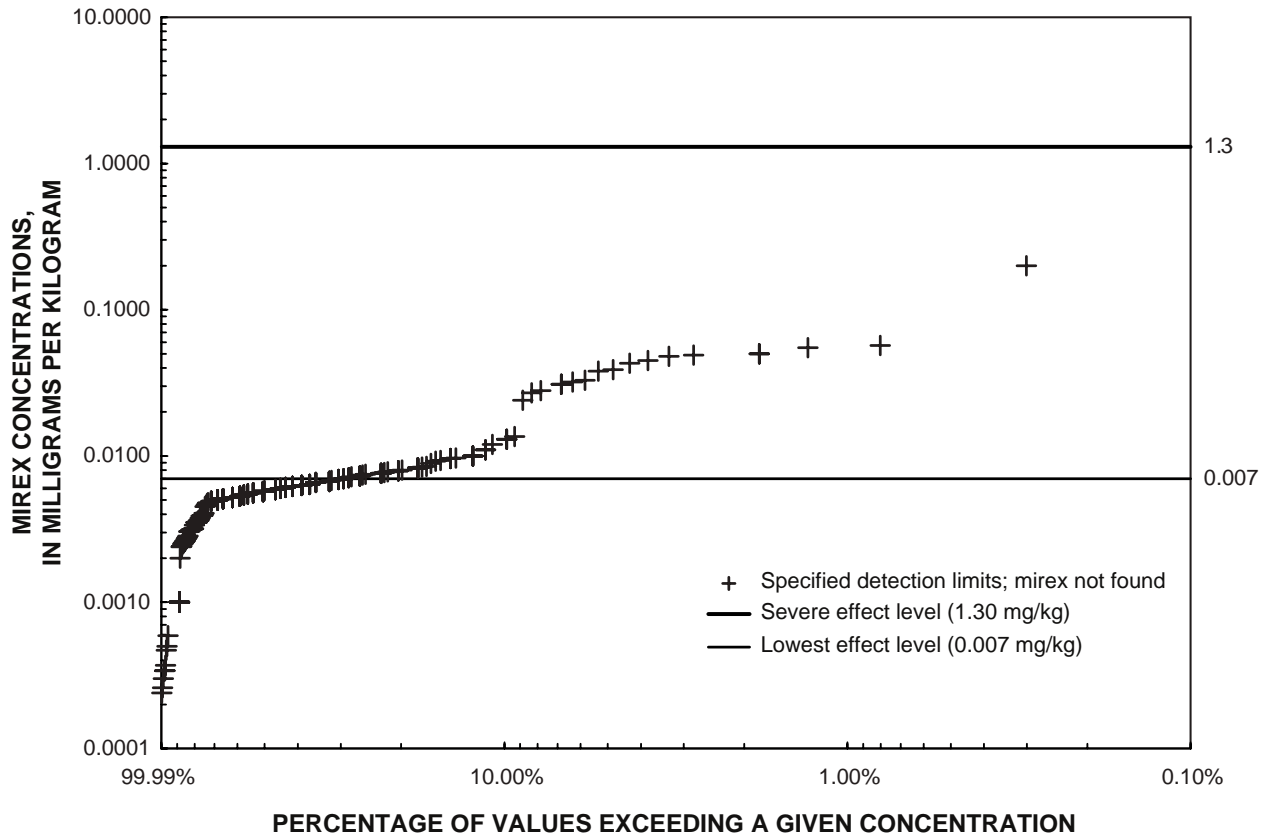


Figure B7. Probability distribution of total mirex concentrations and detection limits for streambed and lakebed sediments in relation to aquatic-life criteria, Lake Erie–Lake Saint Clair Drainages, 1990-97.

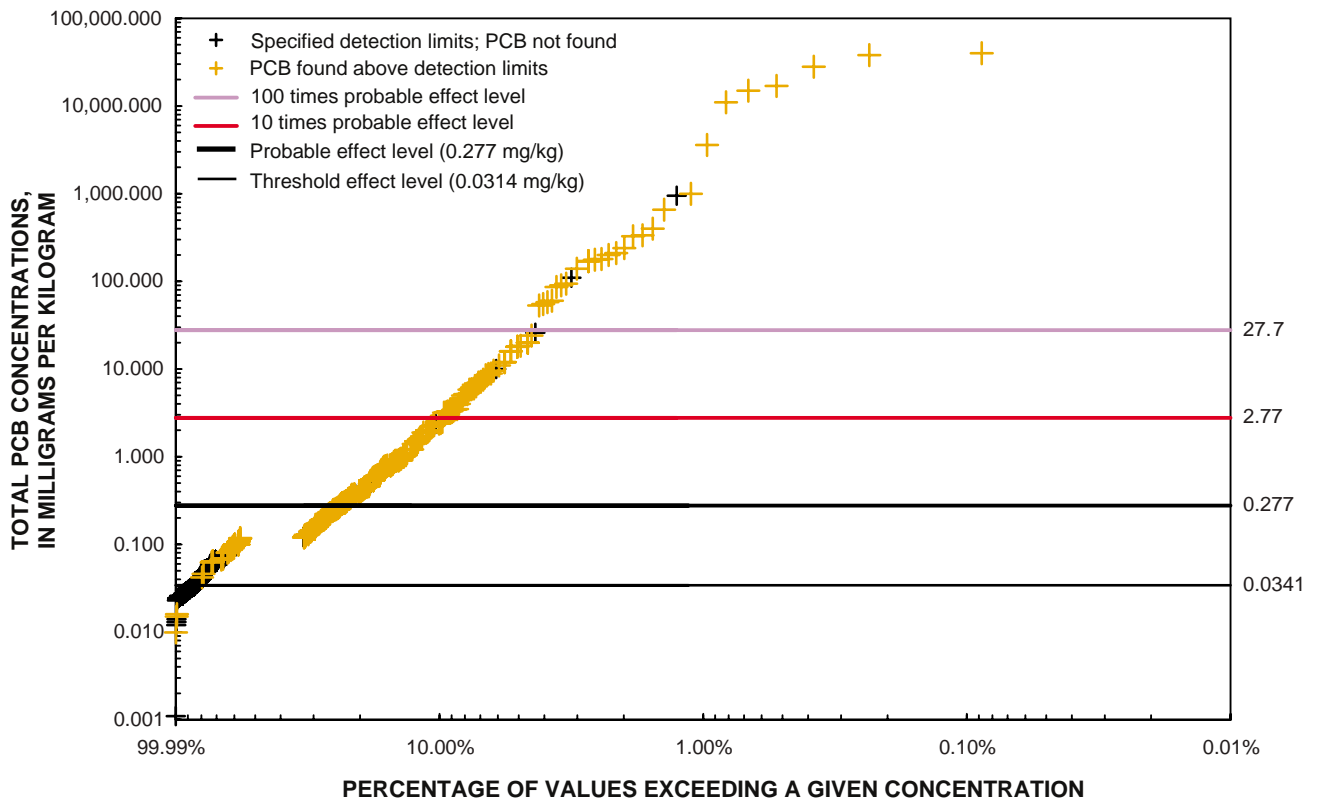


Figure B8. Probability distribution of total PCB concentrations and detection limits for streambed and lakebed sediments in relation to aquatic-life criteria, Lake Erie–Lake Saint Clair Drainages, 1990-97.

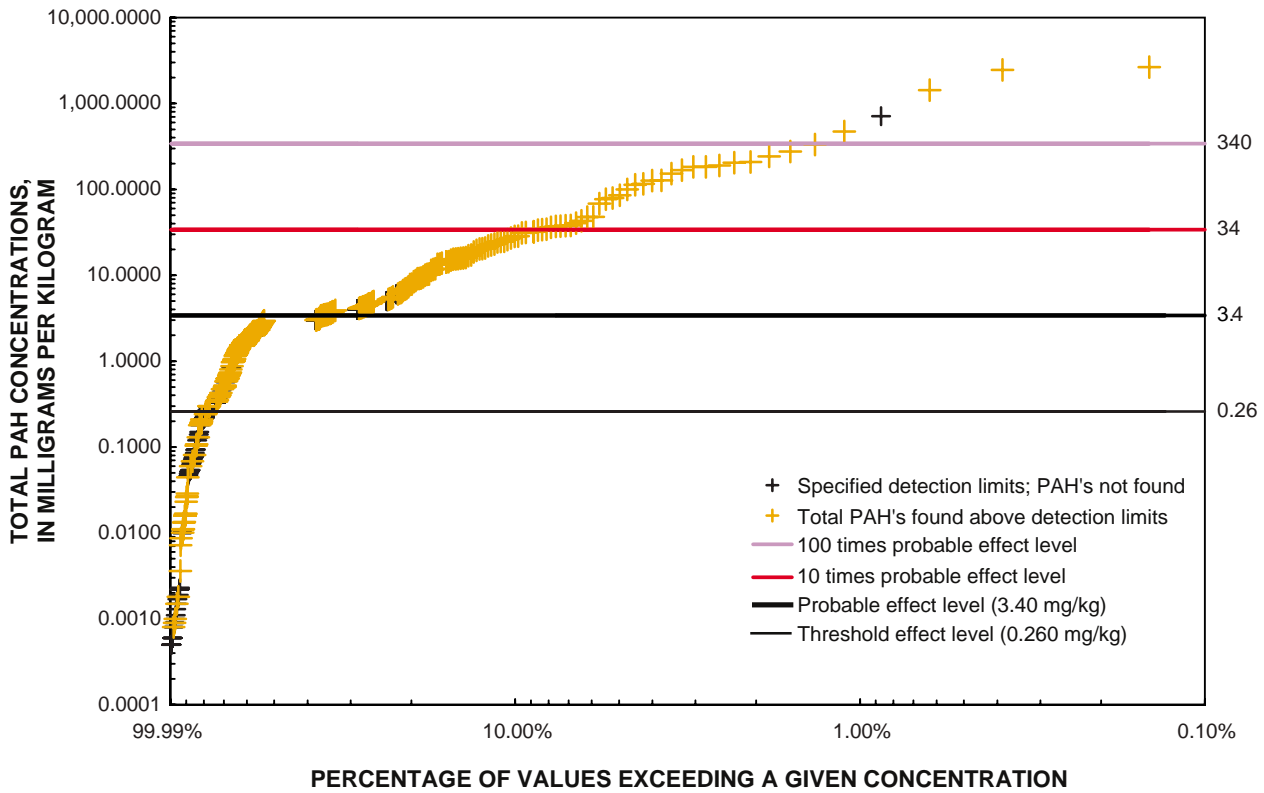


Figure B9. Probability distribution of total PAH concentrations and detection limits for streambed and lakebed sediments in relation to aquatic-life criteria, Lake Erie–Lake Saint Clair Drainages, 1990–97.

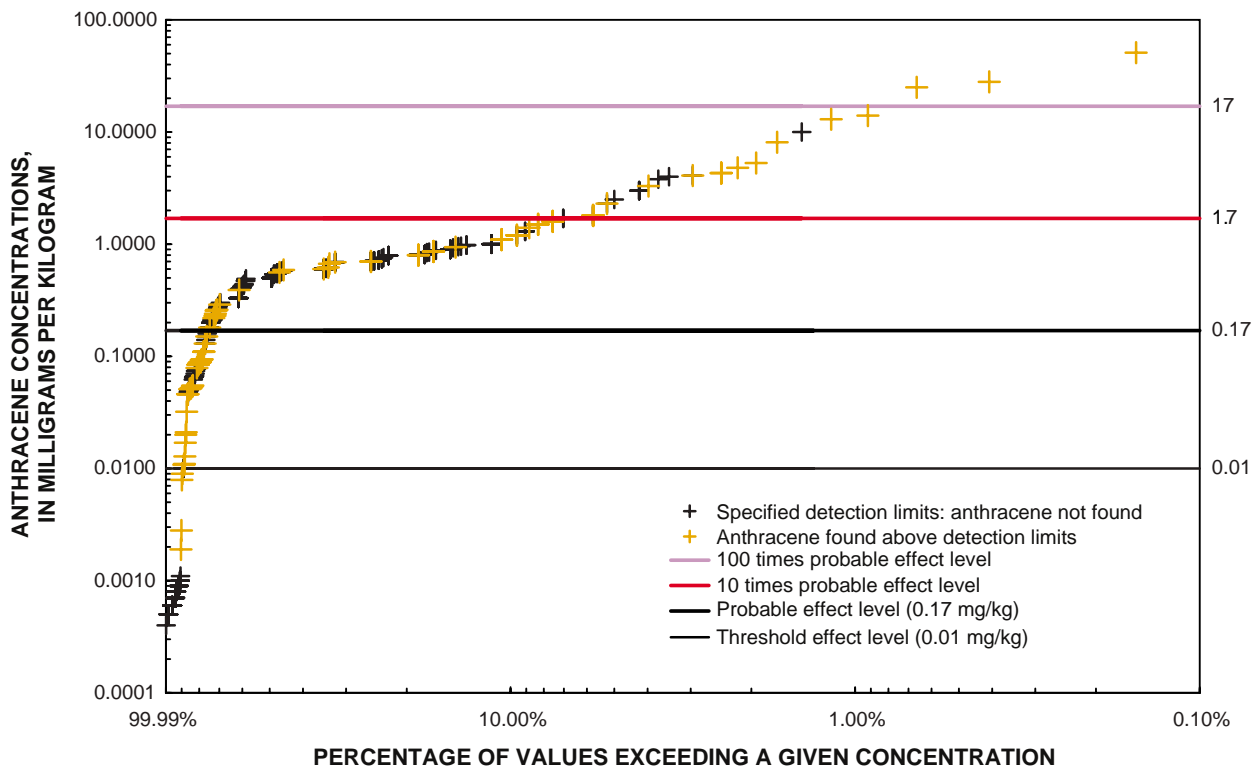


Figure B10. Probability distribution of anthracene concentrations and detection limits for streambed and lakebed sediments in relation to aquatic-life criteria, Lake Erie–Lake Saint Clair Drainages, 1990–97.

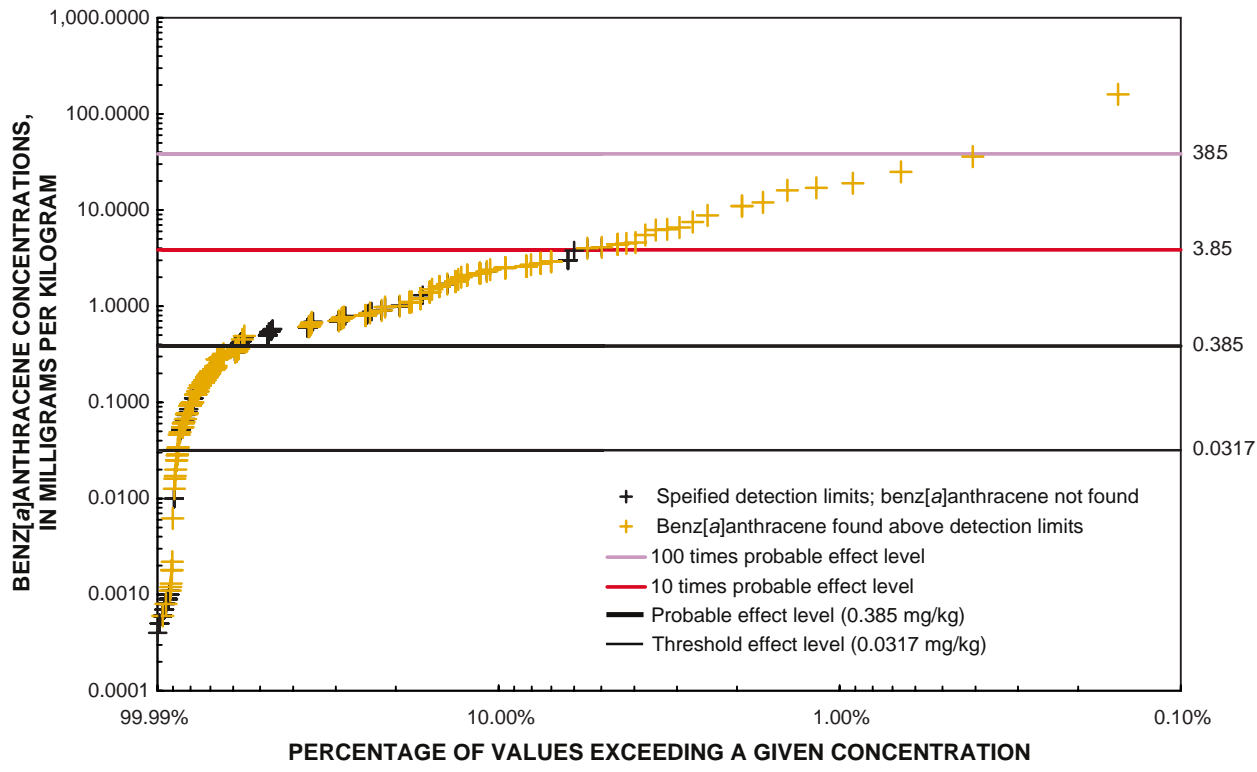


Figure B11. Probability distribution of benz[a]anthracene concentrations and detection limits for streambed and lakebed sediments in relation to aquatic-life criteria, Lake Erie–Lake Saint Clair Drainages, 1990–97.

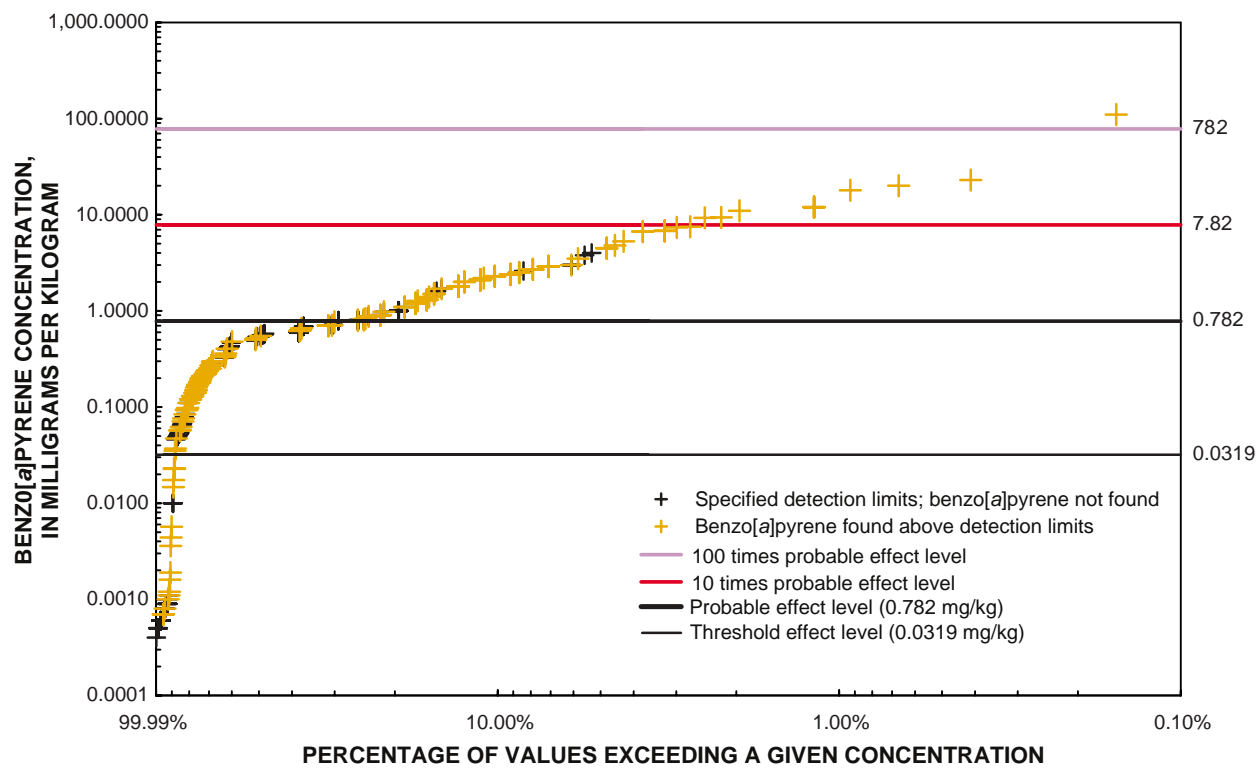


Figure B12. Probability distribution of benzo[a]pyrene concentrations and detection limits in streambed and lakebed sediments in relation to aquatic-life criteria, Lake Erie–Lake Saint Clair Drainages, 1990–97.

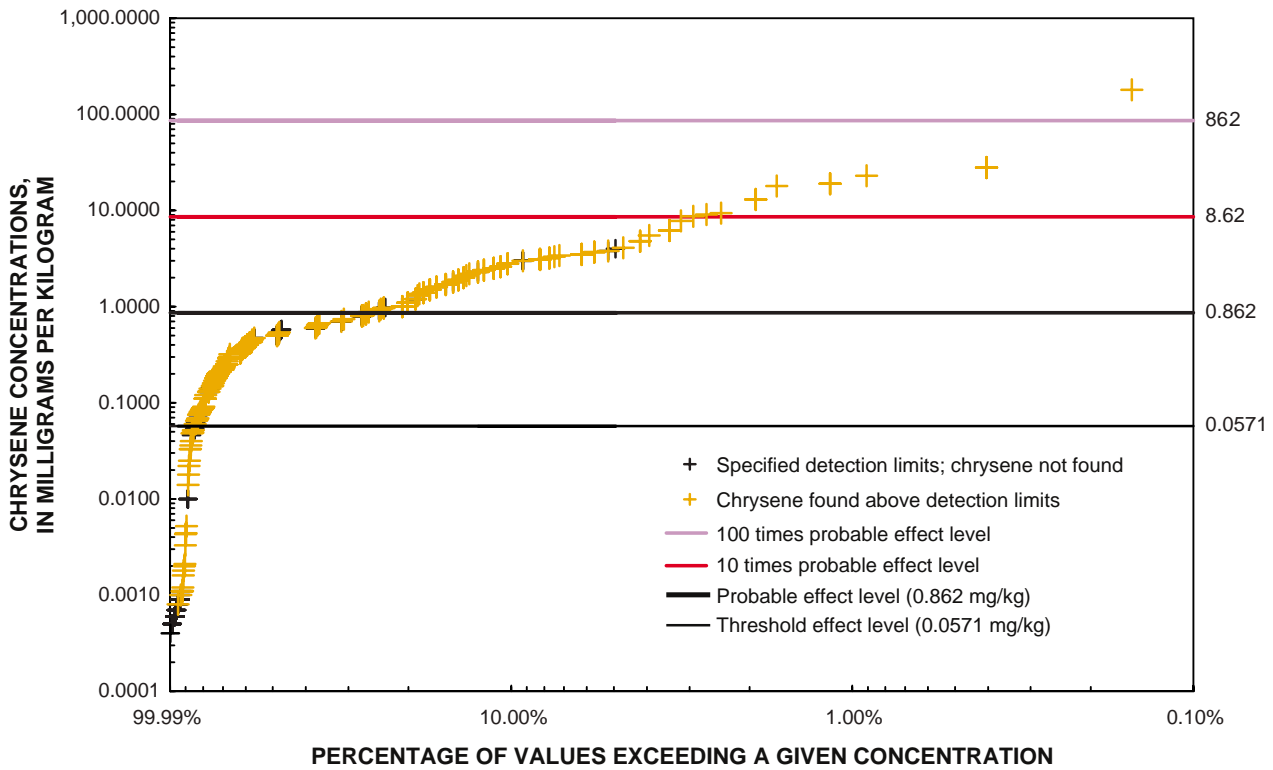


Figure B13. Probability distribution of chrysene concentrations and detection limits for streambed and lakebed sediments in relation to aquatic-life criteria, Lake Erie–Lake Saint Clair Drainages, 1990–97.

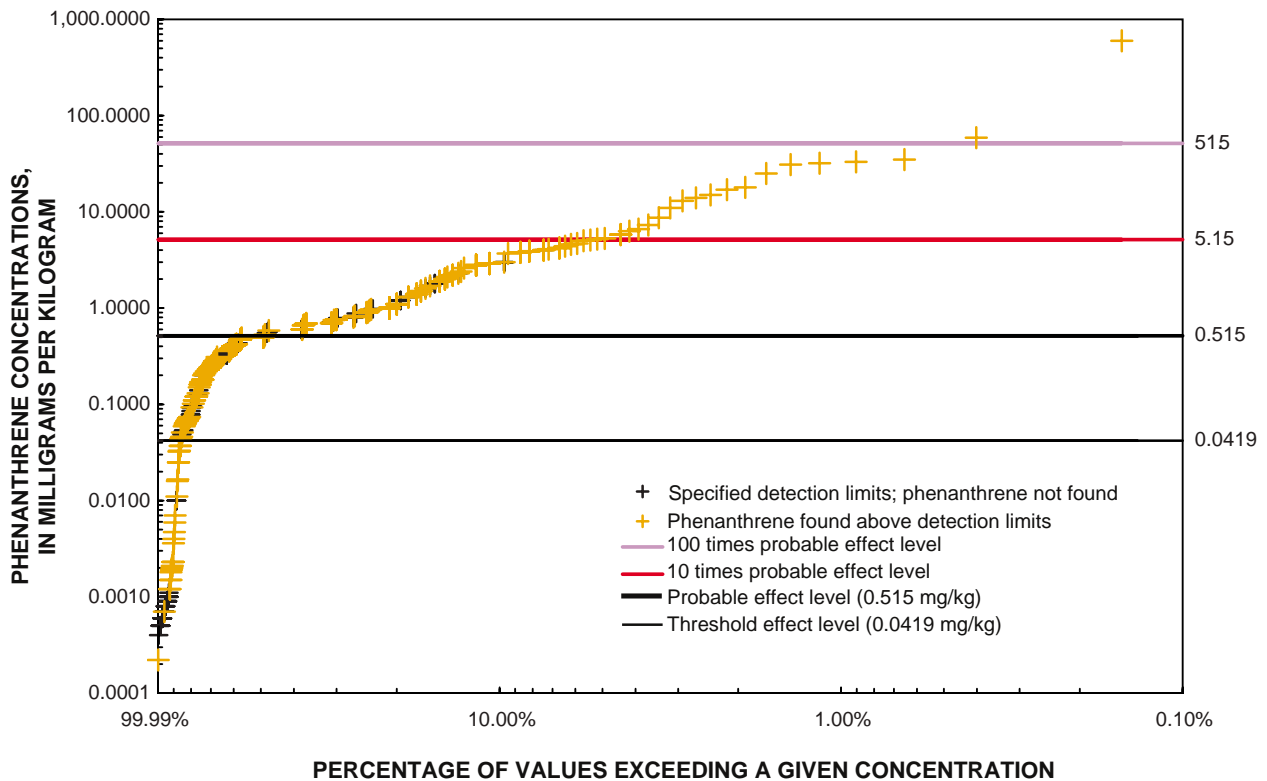


Figure B14. Probability distribution of phenanthrene concentrations and detection limits for streambed and lakebed sediments in relation to aquatic-life criteria, Lake Erie–Lake Saint Clair Drainages, 1990–97.

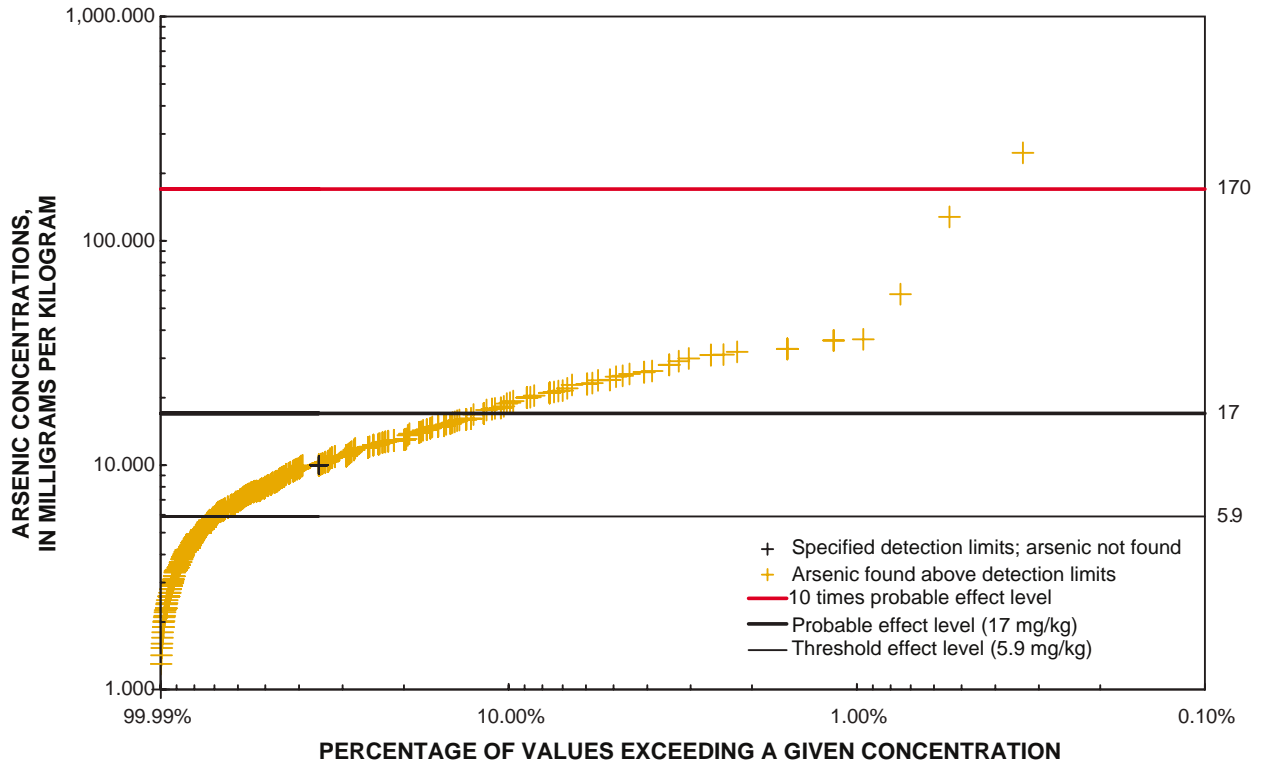


Figure B15. Probability distribution of arsenic concentrations and detection limits for streambed and lakebed sediments in relation to aquatic-life criteria, Lake Erie–Lake Saint Clair Drainages, 1990–97.

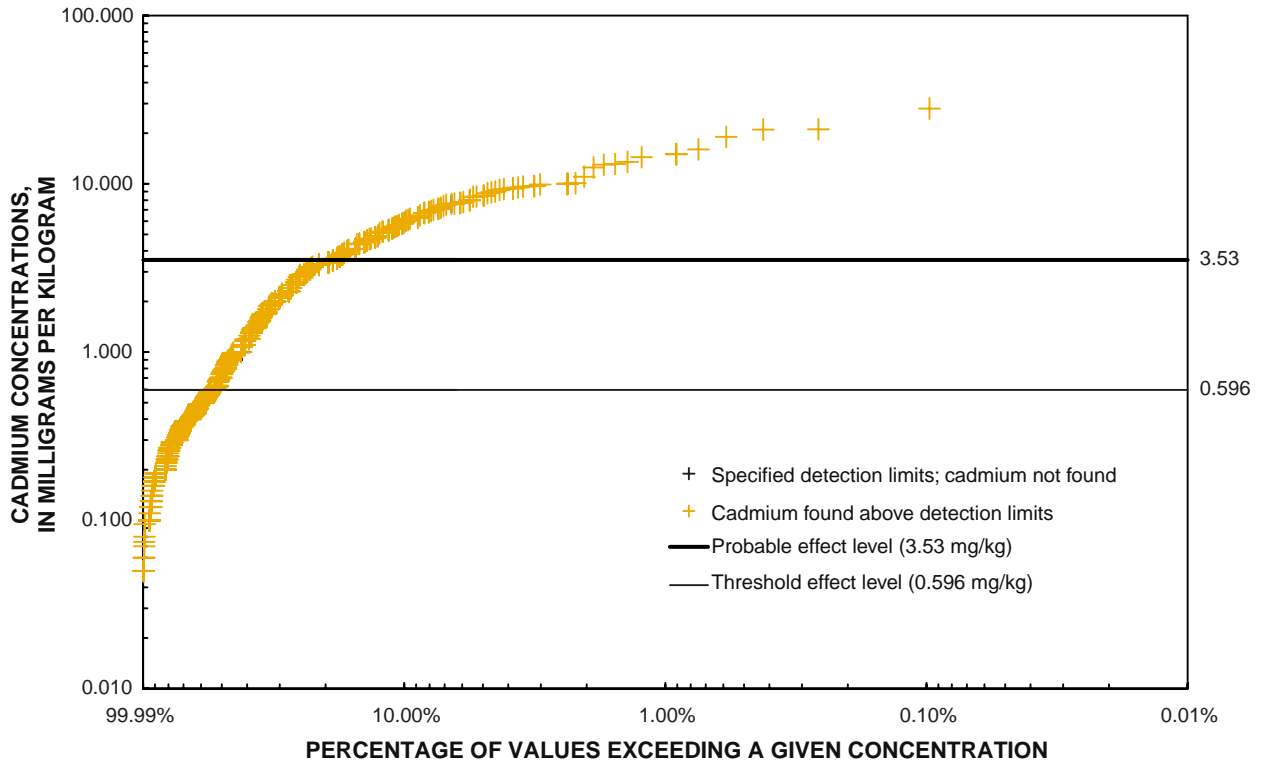


Figure B16. Probability distribution of cadmium concentrations and detection limits for streambed and lakebed sediments in relation to aquatic-life criteria, Lake Erie–Lake Saint Clair Drainages, 1990–97.

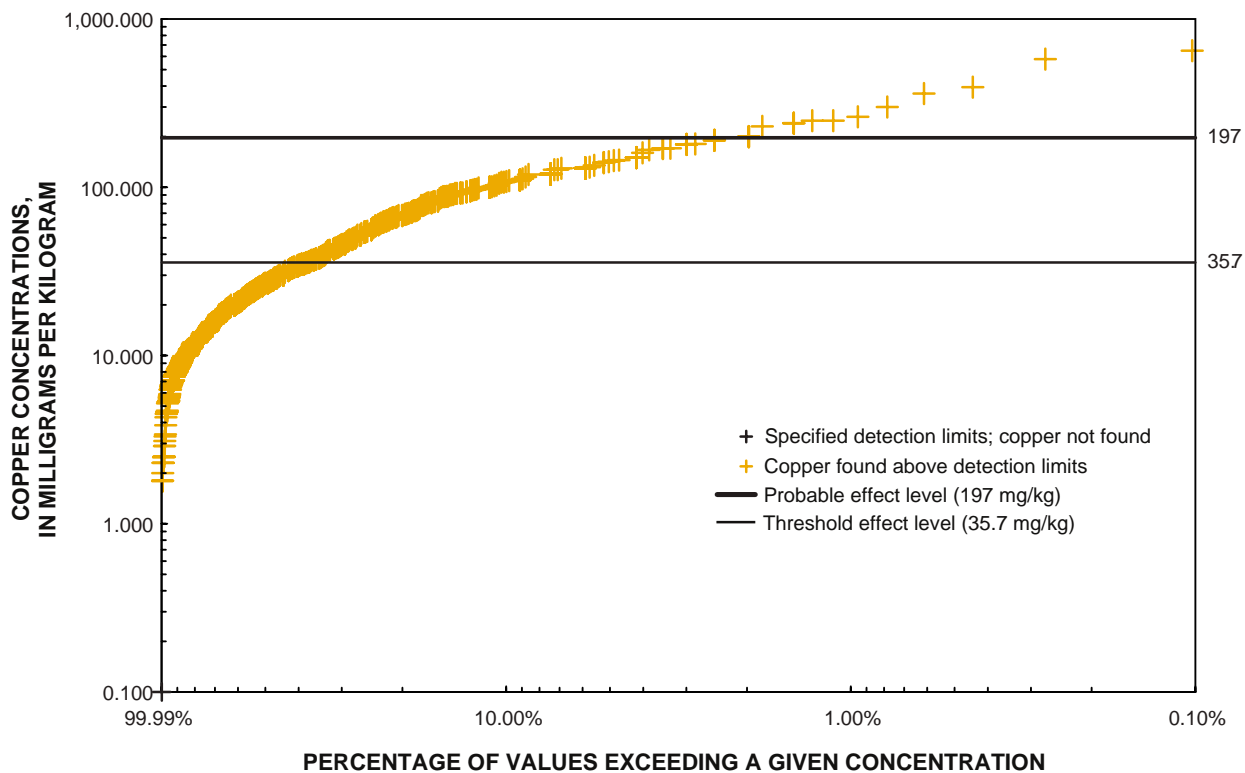


Figure B17. Probability distribution of copper concentrations and detection limits for streambed and lakebed sediments in relation to aquatic-life criteria, Lake Erie–Lake Saint Clair Drainages, 1990–97.

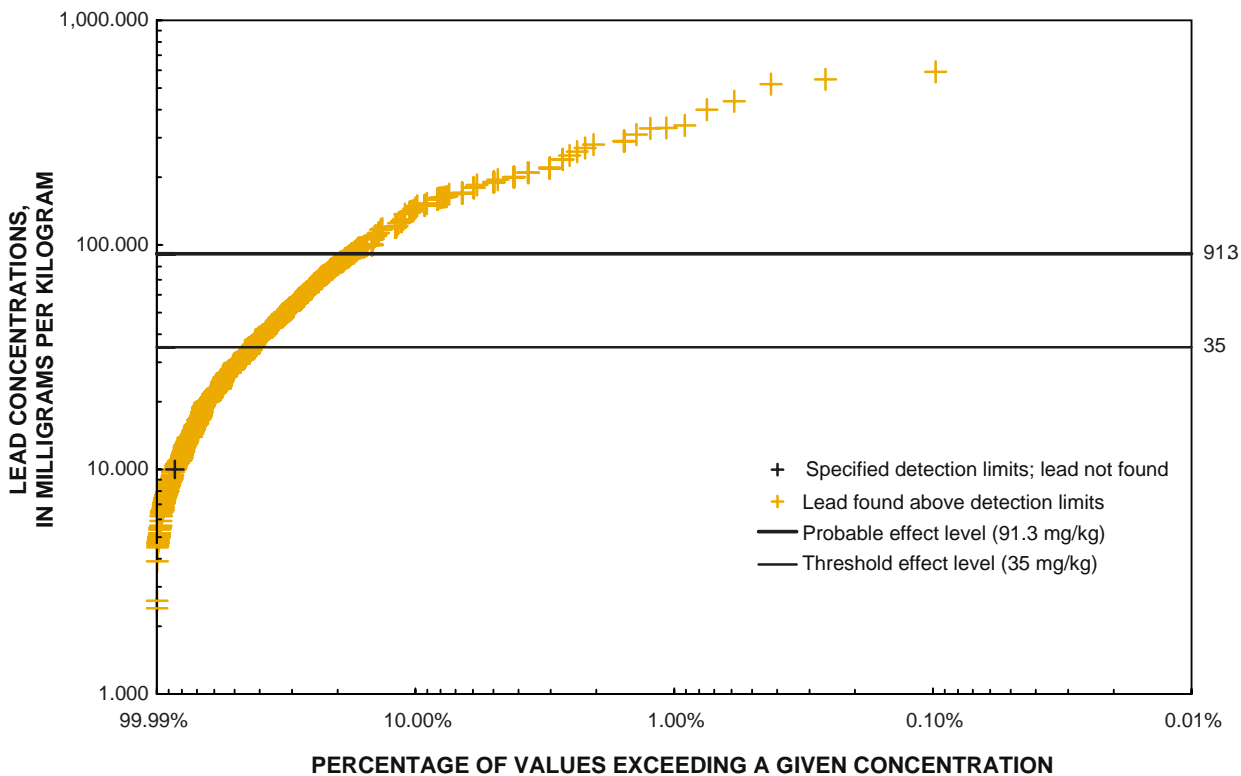


Figure B18. Probability distribution of lead concentrations and detection limits for streambed and lakebed sediments in relation to aquatic-life criteria, Lake Erie–Lake Saint Clair Drainages, 1990–97.

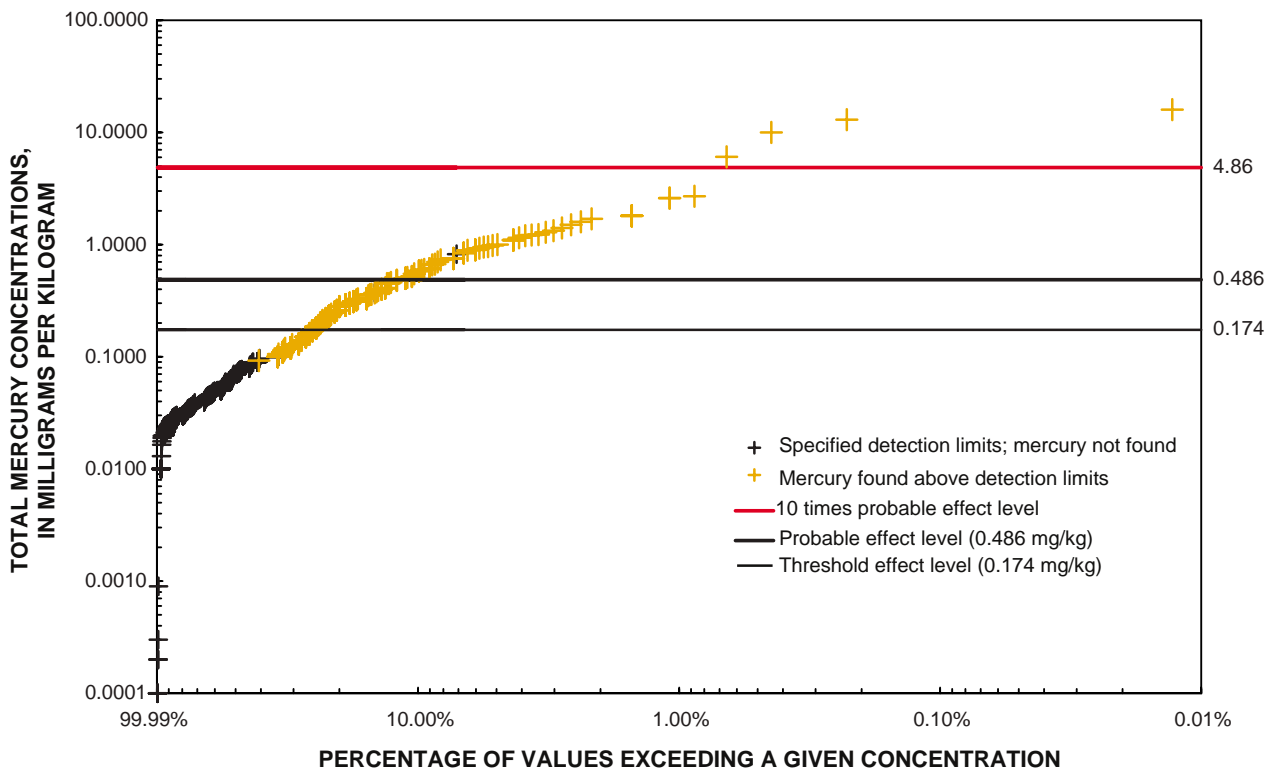


Figure B19. Probability distribution of mercury concentrations and detection limits for streambed and lakebed sediments in relation to aquatic-life criteria, Lake Erie–Lake Saint Clair Drainages, 1990–97.

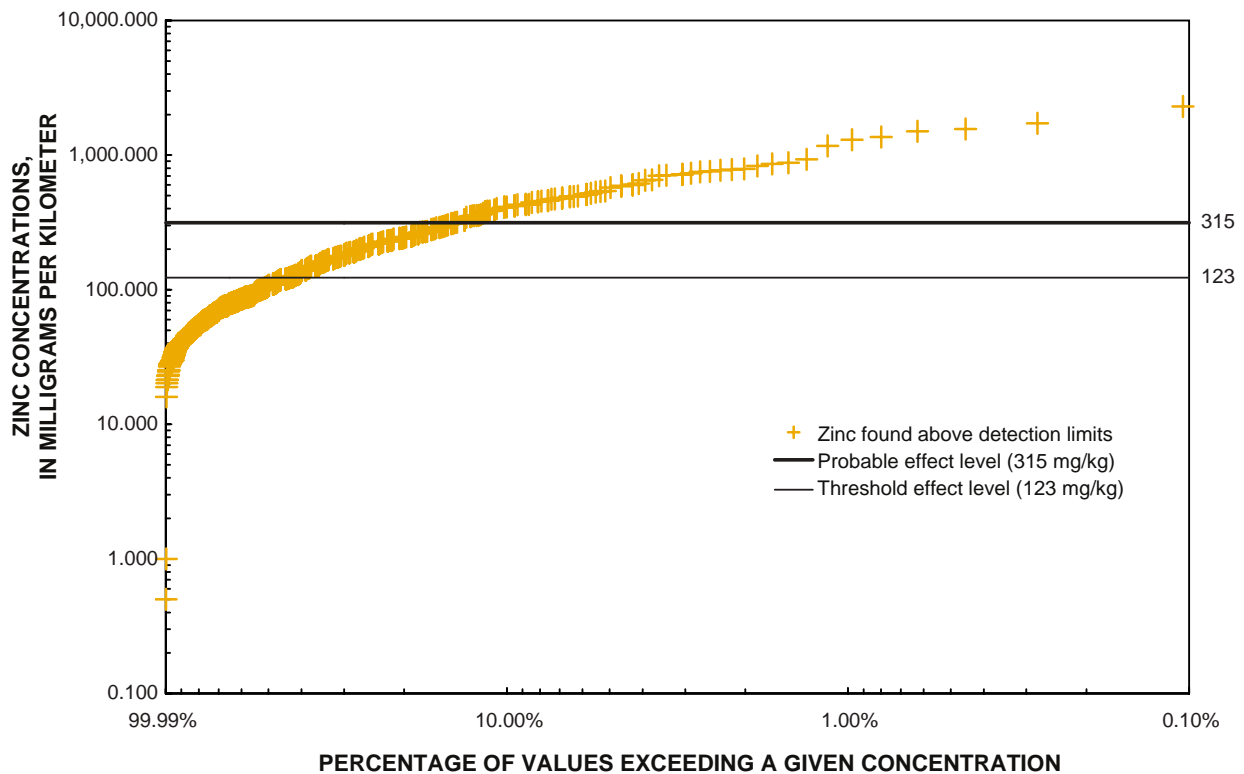


Figure B20. Probability distribution of zinc concentrations and detection limits for streambed and lakebed sediments in relation to aquatic-life criteria, Lake Erie–Lake Saint Clair Drainages, 1990–97.

Appendix C

Development of bed-sediment-quality guidelines in Canada and the United States
Sediment Effect Concentrations—Classifying Toxicity of United States Great Lakes Sediment
Sediment Quality Assessment Values for Ecosystems in Canada and the Great Lakes

Development of Bed-Sediment-Quality Guidelines In Canada and the United States

In 1992, the Ontario Ministry of Environment developed guidelines for evaluating sediments throughout Ontario (Persaud and others, 1993) that replaced the Open Water Disposal Guidelines (published by the Ministry in 1976). The PSQG (Provincial Sediment Quality Guidelines) are intended to provide guidance during decision making in relation to sediment issues, ranging from prevention to remedial action (Persaud and others, 1993). The PSQG's were developed for the protection of aquatic biological resources, particularly organisms that are directly effected by contaminated sediments; namely the sediment-dwelling (benthic) species.

These guidelines are designed to help environmental managers determine (1) when sediments may be considered clean, (2) what concentrations of contamination are acceptable for short periods of time while the source of the contamination is being controlled and cleanup plans are being developed, and (3) what concentrations of contamination are severe enough to consider the possibility of either removing the sediment or capping it with a layer of cleaner sediment.

The Ontario guidelines define three levels of ecotoxic effects and are based on the chronic, long-term effects of contaminants on benthic organisms. These levels are (1) NEL (No Effect Level) at which no toxic effects have been observed on aquatic organisms, (2) LEL (Lowest Effect Level) indicating a level of sediment contamination that can be tolerated by the majority of benthic organisms, and (3) SEL (Severe Effected Level) indicating the level at which pronounced disturbance of the sediment-dwelling community can be expected.

The NEL guidelines were developed by use of the partitioning approach, by which existing criteria such as a water quality or tissue residue criteria can be considered as virtual no-effect values. The approach is limited by its assumption of a single route of exposure for aquatic organisms and its restriction to the nonpolar organics. The NEL guidelines cannot be calculated for trace metals and polar organic compounds.

The LEL (Lowest Effect Level) is the concentration at which actual ecotoxic effects become apparent. It is derived using field-based data on the co-occurrence of sediment concentrations and benthic species. The LEL is calculated by means of a two-step

screening-level concentration method. The first step is to calculate the screening-level concentration of each chemical for a large number of species (at least 10 for each chemical) and then plot the frequency distribution of the contaminant concentrations over all sites where the species is present (at least 10 sites). The 90th percentile of this distribution is then taken as the species screening-level concentration. In the second step, the species screening-level concentrations for each species are plotted as a frequency distribution, and the 5th percentile is interpolated from this distribution. This 5th percentile concentration represents the LEL concentration that 95 percent of the species can tolerate (table 2 in the main text).

The SEL (Severe Effect Level) represents contaminant concentrations in bed sediment that could potentially eliminate most of the benthic organisms. It is obtained by calculating the 95th percentile of the screening-level concentration as described for LEL's (the concentration below which 95 percent of all species screening-level concentrations fall). This concentration value represents the SEL concentration that 95 percent of the species cannot tolerate.

Persaud and others (1993) published the LEL and SEL guideline concentrations for trace metals, nutrients, and polar organics in parts per million dry weight. For nonpolar organics; however, many compounds tend to adsorb to organic carbon in suspended and bed sediments, reducing bioavailability (Scudder and others, 1997). Persaud and others (1993) suggested that their SEL concentration guideline for nonpolar organics be converted to bulk sediment values by multiplying by the actual total organic carbon (TOC) concentration of the sediments (to a maximum of 10 percent). For this report, we took the conservative approach suggested by Smith and others (1996) and assumed 1 percent TOC to determine SEL guideline values. If however, the percentage of TOC in the sample is known to be greater than 1 percent, then nonpolar organic SEL guideline values should be adjusted upward accordingly.

Sediment Effect Concentrations—Classifying Toxicity of United States Great Lakes Sediment

In 1992, the USEPA proposed a national strategy to manage the problems of contaminated bed sediments at numerous sites throughout much of the United States (Ingersoll and others, 1996). In the Great Lakes area, the concern was that these sediments pose a health risk to humans and the ecosystem as a whole.

Yet, much uncertainty remained about the concentrations and spatial distribution of these contaminants in aquatic sediments, especially in harbors and other disturbed areas. The need to map contaminant deposits accurately and to characterize them became apparent to the USEPA, which established the ARCS (Assessment and Remediation of Contaminated Sediments) program to help address the contaminated sediment problem at the 42 Great Lakes AOC's (Ross and others, 1992). The program was administered out of the USEPA Great Lakes National Program Office in Chicago, Illinois.

As part of the ARCS program (Ross and others, 1992; and Fox and Tuchman, 1996), whole-sediment toxicity tests were done by several contracted researchers during 1993-96 (Ingersoll and others, 1996) using the amphipod *Hyaella azteca* and the midge *Chironomus riparius* in sediments collected from various Great Lakes AOC's and additional sites across the United States in order to make the database as robust as possible. Ingersoll and others (1996) described the procedures for calculating and evaluating SEC (sediment effect concentrations) with this data set.

SEC's were determined by classifying chemicals measured in each sample in terms of their association with the observed toxicity. Each of the chemicals in the toxic samples was classified as an "effect" or "no concordance," depending on whether the ratio of the concentration in the sample to the mean concentration in the nontoxic samples was > 1 or ≤ 1 . Concentrations of chemicals in nontoxic samples were designated as "no effects." Samples designated with the no concordance descriptor were also included with no-effect samples for calculation of SEC's.

Three types of SEC's were calculated by Ingersoll and others (1996) using the greater than mentioned data: (1) ERL (Effect Range Low) and ERM (Effect Range Median), (2) TEL (Threshold Effect Level) and PEL (Probable Effect Level), and (3) NEC (No Effect Concentration). They were able to calculate 23 SEC's primarily for total trace metals, simultaneously extracted metals, PCB's, and PAH's (table 2 in main text). The ranges of concentrations in their sediment database were too narrow to adequately evaluate SEC's for butyltins, methyl mercury, polychlorinated dioxins and furans, or chlorinated pesticides.

ERL's and ERM's were determined from concentrations observed or predicted by different methods to be associated with effects, sorted in ascending

order, and the lower 15th percentile (or ERL) and 50th percentile (or ERM) effect concentrations were then calculated. An ERL was defined as the concentration of a chemical in sediment below which adverse effects were rarely observed or predicted among sensitive species. An ERM was defined as the concentration of a chemical in sediment greater than which effects are frequently or always observed or predicted among most species.

In addition, the 50th-percentile concentration (or NERM, No Effect Range Median) and the 85th-percentile concentrations (or NERH, No Effect Range High) of the "no-effects" data set were calculated. The TEL's were calculated as the geometric mean of the ERL and NERM, whereas the PEL's were calculated as the geometric mean of the ERM and NERH. The geometric mean was used rather than the arithmetic mean because the two data sets are not normally distributed. The NEC (No Effect Concentration) was calculated as the maximum concentration of a chemical in a sediment that did not significantly adversely affect the particular response (for example, survival, growth, or maturation) compared to the control.

The work by Ingersoll and others (1996) also showed that their calculated ERL's and ERM's are generally as reliable as paired calculated TEL's and PEL's at classifying toxic and nontoxic samples. In addition, they determined that SEC's calculated from sediment concentrations normalized to TOC (total organic carbon) concentrations did not improve the reliability compared to SEC's calculated from dry-weight concentrations. Therefore, all values of Ingersoll and others (1996) have been reported as dry-weight concentrations.

Sediment Quality Assessment Values for Ecosystems in Canada and the Great Lakes

In 1992, the freshwater bed-sediment information in the National Oceanic and Atmospheric Administration database (Long and Morgan, 1991) was expanded by Environment Canada to incorporate additional information available on the toxicity of chemicals in freshwater sediments (Smith and others, 1996). Many large data sets, including the screening-level concentration data collected and evaluated in Ontario (Persaud and others, 1993) and data sets generated through the ARCS program (Ingersoll and others, 1996) were integrated into the BEDS (freshwater biological effects database for sediments). Other relevant studies available in the published literature also were included.

Overall, 56 publications met all of Smith and others screening criteria, (1996) and were used in the development of the freshwater BEDS. Of these, roughly 35 percent were studies done in the Great Lakes Basin. The expanded freshwater database now supports the calculation of numerical sediment-quality assessment values for a range of chemical substances and will continue to form an important part of the Canadian sediment-quality guidelines in the future.

The BEDS sediment quality assessment values (Smith and others, 1996) were developed by means of a weight-of-evidence approach in which matching biological and chemical data from numerous modeling, laboratory, and field studies of freshwater sediments were compiled and analyzed. Two assessment values, a TEL and a PEL, were derived for 23 substances (eight trace metals, six PAH's, total PCB's, and eight organochlorine pesticides). The two values define three ranges of chemical concentrations: those that were (1) rarely, (2) occasionally, and (3) frequently associated with adverse biological effects. This method is being used as a basis for developing national sediment-quality guidelines for freshwater systems in Canada and sediment-effect concentrations as part of the ARCS program in the Great Lakes.

The TEL's and PEL's were calculated for those chemicals having at least 20 data entries in both the effect and the no-effect data sets. The TEL was derived by calculating the geometric mean of the 15th percentile of the effect data set and the 50th percentile of the no-effect data set. This value was intended to estimate the concentration of a chemical below which adverse biological effects only rarely occurred. The PEL was derived by calculating the geometric mean of the 50th percentile of the effect data set and the 85th percentile of the no-effect data set. The PEL was intended to estimate the concentration of a chemical greater than which adverse biological effects frequently occurred. Sediment-quality assessment values could not be calculated for a number of individual PAH's and other chemicals for which information was included in BEDS but for which fewer than 20 effect data entries were available. Future expansions of BEDS are expected to result in sufficient information to calculate assessment values for additional substances, including silver, individual PAH's and classes of PAH's, individual PCB congeners and formulations, pesticides, dioxins, and furans.