

Water Quality in the Lake Erie-Lake Saint Clair Drainages

Michigan, Ohio, Indiana, New York, and Pennsylvania, 1996-98



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Front cover: Marblehead Lighthouse, a symbol of Lake Erie, located on the Marblehead Peninsula, near Sandusky, Ohio. (Photograph from Ohio Lake Erie Commission, Toledo, Ohio).

Back cover: left, waterways such as the harbor of the Ashtabula River, Ohio, are used for industry, commerce, and recreation; right, country roads and small farms are still common in some areas.

Water Quality in the Lake Erie-Lake Saint Clair Drainages

Michigan, Ohio, Indiana, New York, and Pennsylvania, 1996-98

By Donna N. Myers, Mary Ann Thomas, Jeffrey W. Frey, Stephen J. Rheaume, and Daniel T. Button

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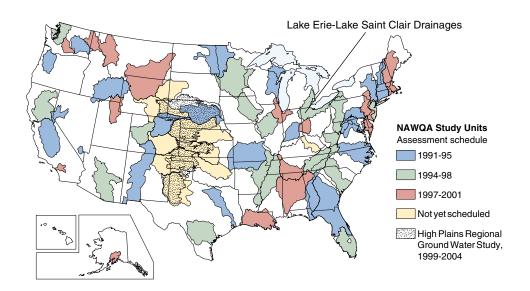
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THIS REPORT summarizes major findings about water quality in the Lake Erie-Lake Saint Clair Drainages that emerged from an assessment conducted between 1996 and 1998 by the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program. Water quality is discussed in terms of local and regional issues and compared to conditions found in all 36 NAWQA study areas, called Study Units, assessed to date. Findings are also explained in the context of selected national benchmarks, such as those for drinking-water quality and the protection of aquatic organisms. The NAWQA Program was not intended to assess the quality of the Nation's drinking water, such as by monitoring water from household taps. Rather, the assessments focus on the quality of the resource itself, thereby complementing many ongoing Federal, State, and local drinking-water monitoring programs. The comparisons made in this report to drinking-water standards and guidelines are only in the context of the available untreated resource. Finally, this report includes information about the status of aquatic communities and the condition of instream habitats as elements of a complete water-quality assessment.

Many topics covered in this report reflect the concerns of officials of State and Federal agencies, water-resource managers, and members of stakeholder groups who provided advice and input during the Lake Erie-Lake Saint Clair Drainages assessment. Residents who wish to know more about water quality where they live will find this report informative as well.



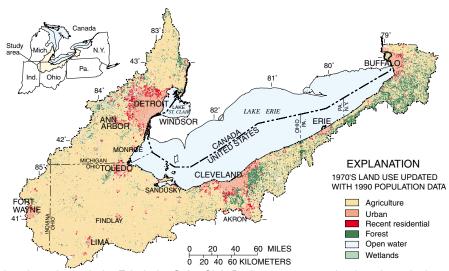
THE NAWQA PROGRAM seeks to improve scientific and public understanding of water quality in the Nation's major river basins and ground-water systems. Better understanding facilitates effective resource management, accurate identification of water-quality priorities, and successful development of strategies that protect and restore water quality. Guided by a nationally consistent study design and shaped by ongoing communication with local, State, and Federal agencies, NAWQA assessments support the investigation of local issues and trends while providing a firm foundation for understanding water quality at regional and national scales. The ability to integrate local and national scales of data collection and analysis is a unique feature of the USGS NAWQA Program.

The Lake Erie-Lake Saint Clair Drainages is one of 51 water-quality assessments initiated since 1991, when the U.S. Congress appropriated funds for the USGS to begin the NAWQA Program. As indicated on the map, 36 assessments have been completed, and 15 more assessments will conclude in 2001. Collectively, these assessments cover about one-half of the land area of the United States and include water resources that are available to more than 60 percent of the U.S. population.

Stream and River Highlights

Water quality in the Lake Erie-Lake Saint Clair Drainages is greatly influenced by land use and human activities. A major pathway for contaminant transfer from the land surface to streams is storm runoff from urban and agricultural areas.

As a result of herbicides in runoff. concentrations in streams were in the top 25 percent of streams nationwide and many public-water supplies must treat stream water to reduce herbicide concentrations. As a result of nutrients in runoff, concentrations of total phosphorus and nitrate in some small streams in agricultural areas and in



Land use in the Lake Erie-Lake Saint Clair Drainages was predominantly agricultural and urban. This level of human activity has had substantial effects on water quality in the region.

Indicators of Stream Quality

	;	Small strean	Major rivers	
	Urban	Row crop	Pasture/ forest	Mixed
Pesticides ¹				
Total phosphorus ²				o c
Nitrate ³				T a
Arsenic ⁴				
Other trace elements ⁴				
Polycyclic aromatic hydrocarbons ⁵				
Polychlorinated biphenyls ⁵				

Percentage of samples with concentrations equal to or greater than a health-related national guideline for drinking water, aquatic life, or above a national goal for preventing excess algal growth (a Percentage is 1 or less and may not be clearly visible.)

Percentage of samples with concentrations less than a health-related national guideline for drinking water, aquatic life, or below a national goal for preventing excess algal growth (^b Percentage is 1 or less and may not be clearly

Percentage of samples with no detection (C Percentage is 1 or less and may not be clearly

- ¹ Insecticides, herbicides, and pesticide metabolites, sampled in water.
- ² Total phosphorus, sampled in water.
- ³ Nitrate (as nitrogen), sampled in water
- ⁴ Arsenic, cadmium, copper, lead, mercury, and zinc, sampled in sediment.
- ⁵ Industrial chemicals, combustion byproducts, and polychlorinated biphenyls sampled in sediment

major rivers were in the top 25 percent of streams nationwide. Concentrations of nitrate, although elevated relative to many other streams in the Nation, were infrequently greater than the drinking-water standard of 10 milligrams per liter.

Contamination of the bed sediments of small streams and major rivers by persistent and bioaccumulative contaminants was prevalent. The highest concentrations of PCBs (polychlorinated biphenyls) and mercury were detected in streams draining highly populated urban and mixed land-use areas. Detections of contaminants in fish tissues indicate bioaccumulation; in fact, bioaccumulation of PCBs and DDT in some fish species presents a health risk to fish-eating wildlife.

- · The pesticides detected most frequently were among those applied in the greatest quantities to agricultural and mixed land-use areas. The herbicides atrazine, acetochlor, cyanazine, metolachlor, and simazine were detected in 50 to 100 percent of samples. (p. 6)
- · Several heavily used herbicides and insecticides were detected in spring and summer at or above a standard for drinking water or a guideline for aguatic life. Elevated pesticide concentrations in streams persisted for 4 to 6 weeks after applications in agricultural and mixed-land-use areas. (p. 8)
- · Annual average concentrations of total phosphorus were greater than the U.S. Environmental Protection Agency recommended level for control of nutrient enrichment at 8 of 10 sites sampled in small streams and major rivers draining agricultural and mixed-use land. Streams draining row-crops and mixed-use land are major pathways of phosphorus to Lake Erie. (p. 10)

- Contaminants detected most often in the bed sediments of small streams and major rivers were arsenic, cadmium, copper, lead, mercury, zinc, PCBs, and PAHs (polycyclic aromatic hydrocarbons). The concentrations of arsenic, mercury, PCBs, and PAHs were equal to or greater than sediment guidelines, indicating probable adverse effects on aquatic life, in about 11 to 30 percent of samples. (p. 13)
- The most frequently detected contaminants in fish were highly persistent contaminants—DDT, chlordane, dieldrin, PCBs, and mercury. Except for mercury, use of these compounds in industry and agriculture in the United States was discontinued 15 to 25 years ago. (p. 14)
- Agricultural land use appears to be affecting fish communities in streams draining areas of row-crops. As the amount of row-crops increased relative to forested land, the number of pollution-intolerant fish species decreased. It appears that pollution-intolerant fish can live where agriculture is the primary land use when streams are protected by natural cover. (p. 17)

Major Influences on Surface-Water Quality and Aquatic Biota

- · Storm runoff
- · Land use and chemical releases
- · Bioaccumulative and persistent contaminants

Trends in Surface-Water Quality

Suspended-sediment discharges from the Maumee River Basin decreased by 11.2 percent over the period 1970–98 and corresponded to increased use of conservation tillage to control soil erosion.

Ground Water Highlights

The glacial aquifer is the major source of drinking water in the northwestern part of the study area. In this area, ground-water quality is affected by a combination of human and natural factors. Land use determines which chemicals are used; how readily these chemicals are transported to the ground water is affected by geology.

- In residential areas underlain by sand and gravel, more than 75 percent of ground water recharged since 1953 shows evidence of human activities in the form of nitrate, chloride, or volatile organic compounds (VOCs). Probable sources are (1) septic systems containing human waste and household chemicals, (2) road salt and gasoline residue from paved surfaces, (3) waste from water softeners, or (4) lawn fertilizer. Pesticides were rarely detected. (p. 18)
- In the agricultural study area, which is underlain by till, nitrate and herbicides were detected less frequently than in

most other agricultural areas of the Nation. This observation partially supports the belief that till or tile drains protect the aquifer from contamination. Nevertheless, the ground water is still vulnerable to contamination; almost 60 percent of shallow ground water contained herbicides or elevated concentrations of nitrate. Herbicides were predominantly detected as breakdown products. (p. 20)

• In residential and agricultural areas, samples from domestic wells met health-related drinking-water standards. However, ground water affected by human activities was detected at depths below 25 feet, the minimum required depth for wells in Ohio and Michigan. (p. 19)

Major Influences on Ground-Water Quality

- · Septic systems, roads, and lawns in residential areas
- · Herbicides and fertilizer in agricultural areas
- · Geology, especially deposits at land surface
- · Well depth and ground-water age

Trends in Ground-Water Quality

A significant change in ground-water quality is linked to recent residential development near Detroit. Ground water recharged before 1953 (which predates suburbanization) has concentrations of chemical constituents typical of natural water. In contrast, ground water recharged after 1953 has significantly higher concentrations of constituents derived from human activities

	Shallov	ground water	Domestic-supply wells	
	Urban	Agricultural		
Pesticid	es ¹			
Nitrate ²				
Volatile organic	3 T	_		
— 。		i an a health-relat	oncentrations equal to ted national guideline for	
	Percentage of samples with concentrations less than health-related national guideline for drinking water.			
P	ercentage o	of samples with n	o detection.	
— N	ot assesse	d.		
_ N	ot assesse cides, herb	d.	cide metabolites, sar	

³ Solvents, refrigerants, fumigants, and gasoline compounds,

² Nitrate (as nitrogen), sampled in water.

sampled in water.

INTRODUCTION TO THE LAKE ERIE-LAKE SAINT CLAIR DRAINAGES

Major water-quality issues

Streams and aquifers in the Lake Erie-Lake Saint Clair Drainages study area provide water for 10.6 million people. The major water-quality issues in the study area are similar to those facing the rest of the Nation. Natural-resource managers are interested in the effects of urban and agricultural land use on the quality of surface water and ground water, specifically:

- pesticide and nutrient contamination of stream water used for public supply
- nutrient enrichment and sedimentation in streams and subsequent effects on aquatic biota
- impairment of aquatic life from bioaccumulation of organochlorine compounds and mercury
- consumption advisories for certain fish due to bioaccumulation of PCBs and mercury
- degradation of ground water used for domestic supply in areas of new residential development and areas of row-crops

Environmental setting and hydrologic conditions

Lake Erie is the 11th-largest freshwater lake in the world. About two-thirds of the Lake Erie watershed is in the United States, and is referred to as the Lake Erie-Lake Saint Clair Drainages. (For simplicity, this area will be referred to as the "basin.") This 22,300square-mile area includes sections of Michigan, Indiana, Ohio, Pennsylvania, and New York. The land surface is gently rolling to nearly flat lying. Eight major rivers, all with drainage areas greater than 500 square miles, flow into the system.

Land use

In the Lake Erie-Lake Saint Clair Drainages, about 75 percent of the

land area is in agriculture, 11 percent is urban land, 11 percent is forest, and 3 percent is open water or wetlands. (See land-use map in summary section.)

Corn, soybeans, and wheat are grown predominantly in the western part of the basin (fig. 1). Other agricultural land uses include pasture and forage crops, grown predominantly in the eastern part of the basin (fig. 2). Orchards and vineyards, located mainly along the shores of Lake Erie and in parts of Michigan, is the least widespread type of agricultural land use.

Urban land is an important component of land use in the basin (fig. 3). Detroit and Pontiac, Mich.; Akron, Cleveland, Lima, and Toledo, Ohio; Fort Wayne, Ind.;

Erie, Pa.; and Buffalo, N.Y., were historically significant contributors to industrial America through the production of automobiles, rubber, steel, petroleum, and chemicals. These cities remain important industrial and manufacturing centers. Major urban centers rely on abundant supplies of water for shipping, electric power generation, industry, domestic consumption, and waste assimilation.

Forest and wetlands, once common throughout the basin, have been greatly reduced since the mid-1800s. The greatest percentage of forested land today is in Pennsylvania and New York. Metropolitan parks also support substantial urban forests. Wetlands lie primarily along Lake Erie and Lake Saint



Figure 1. Agriculture is a major industry in the western part of the basin, where corn and soybeans are grown. (Photograph from Natural Resources Conservation Service.)

Figure 2. Pasture and forage crops are found in the eastern part of the basin.





Figure 3. The port of Toledo, Ohio, on the Maumee River exports large amounts of grain from Midwestern farms. Toledo is an industrial center for automobile manufacturing. (Photograph from Ohio Lake Erie Commission.)

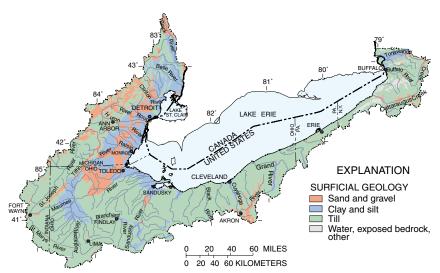


Figure 4. Glacial deposits throughout the basin influence the quality and flow of surface water and ground water.

Clair from Detroit, Mich., to Sandusky, Ohio.

Geology

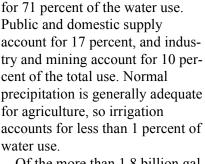
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A layer of glacial deposits from 20 to 200 feet thick mantles the entire basin and overlies limestone, sandstone, or shale bedrock. The glacial sediments consist of sand and gravel, till, and fine-grained sediments composed of fine sands, silts, and clay (fig. 4). Sand and gravel are present as discontinuous deposits in river valleys and in the western part of the basin. The most widespread deposit is till, a mixture

of grain sizes. Tills in the Lake Erie-Lake Saint Clair Drainages contain a high content of clay, which slows infiltration of rainfall into the ground.

Water use

More than 10.6 billion gallons of water is used each day in the basin (fig. 5). Cooling during power generation accounts



Of the more than 1.8 billion gallons per day used for public and domestic supply, about 88 percent is from surface-water sources. Most of the major cities are near Lake Erie and Lake Saint Clair and therefore derive their water from the lakes or their connecting channels (fig. 6). Major rivers are an important source of drinking water for inland cities such as Fort

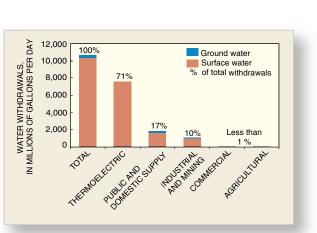


Figure 5. Water withdrawals in the basin are dominated by thermoelectric power production.

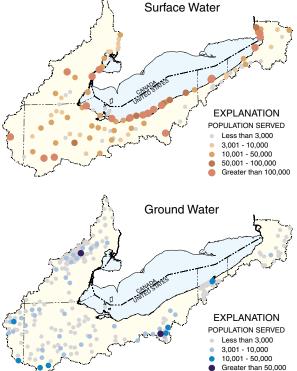


Figure 6. Many public-water supplies with surface-water sources are near Lake Erie or major rivers, whereas public-water supplies with ground-water sources generally are some distance from the lake and major rivers.

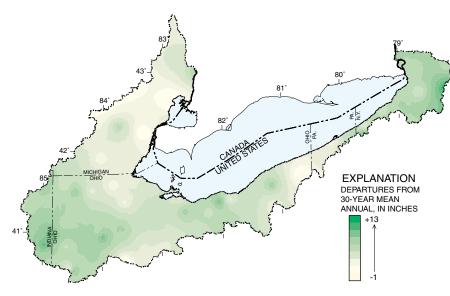


Figure 7. Departures from 30-year mean annual precipitation patterns for water years 1996–98, based on data from 133 weather stations.

Wayne, Ind., and Akron and Lima, Ohio.

About 12 percent of water for human consumption comes from ground water. The cities that use ground water as their major source of drinking water are generally inland (fig. 6). The most productive aquifers are in glacial deposits and limestone and sandstone bedrock.

Hydrologic conditions

Average annual precipitation across the basin ranges from 28 to 47 inches. Precipitation is highest in the northeast because of lake effect, whereby cool, dry air picks up moisture as it travels over warmer lake water and then produces rain or snow as it reaches land. The lowest amounts of precipitation are in the northwestern part of the basin in Michigan. During the study, annual precipitation was 4 to 5 inches above the 30-year mean annual. Some areas received 13 inches of precipitation above the mean, and a few isolated areas

received slightly less than the mean (fig. 7).

The highest streamflows are typically in February, March, and April, as a result of increased precipitation, cold temperatures and little vegetative growth. The lowest streamflows are in August, September, and October (Casey and

others, 1997). During low streamflow, ground water typically contributes most of the flow.

Mean monthly streamflows for the Maumee River at Waterville. Ohio, at the west end of the basin, exceeded the long-term averages by a factor of 2 or more for some months in 1997–98 (fig. 8). Overall, the mean annual streamflow in the Maumee River was 25 percent above average during the sampling period. For Cattaraugus Creek at Gowanda, N.Y., at the east end of the basin, mean monthly streamflow during 1996-98 closely followed the long-term average (fig. 8). In most areas of the basin, higher than average streamflows were observed in water years 1996-98.

Increased streamflow tends to carry higher concentrations of materials associated with land-surface runoff. Low streamflow conditions tend to increase concentrations of materials associated with industrial and municipal discharges or ground water.

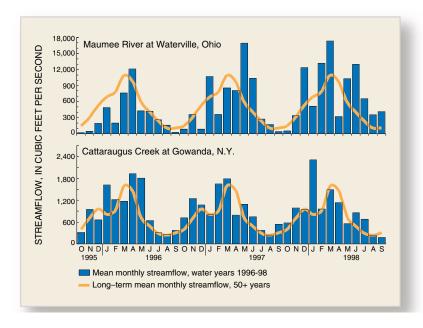


Figure 8. Mean monthly streamflows during water years 1996–98 greatly exceeded long-term averages in some months.

The quality of streams and ground water in the Lake Erie-Lake Saint Clair Drainages is affected by a complex combination of natural factors (precipitation, streamflow, geology) and human factors (land use, chemical use, population density). Specific parts of the basin were targeted for investigation because they have particular combinations of natural and human factors. (See Appendix for details.) A primary factor that was found to influence water quality was land use, and this factor is emphasized throughout the report.

Pesticides were detected in every stream sample

Between March 1996 and February 1998, 305 samples were collected from 10 streams in the basin. Every sample contained at least one pesticide, and most contained mixtures of several pesticides. Some samples contained a mixture of 18 pesticide compounds, which is among the highest number of pesticides detected in a sample nationally.

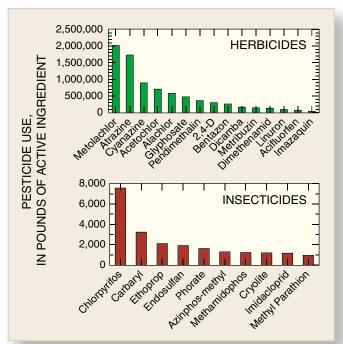


Figure 9. A total of nearly 8.3 million pounds of pesticides was applied in the agricultural areas of the Lake Erie-Lake Saint Clair Drainages during 1994–95. (Data from Brody and others, 1997.)

More pesticides were detected in large streams than small streams. Overall, 30 different pesticides were detected within the basin. The number of pesticides detected was greater in large streams and rivers that drain areas of mixed land use (urban and agricultural) than in smaller streams that drain basins dominated by a single land use.

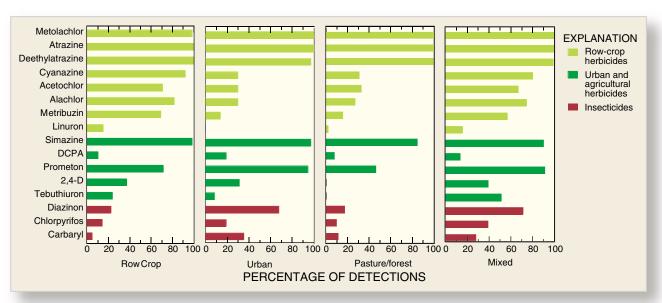


Figure 10. Metolachlor, atrazine, deethylatrazine, cyanazine, and simazine were the most frequently detected herbicides. Diazinon, chlorpyrifos, and carbaryl were the most frequently detected insecticides.

The pesticides most frequently detected in streams were generally those most heavily applied

Pesticide applications to crops in the Lake Erie-Lake Saint Clair Drainages are among the highest nationwide. The five most heavily applied agricultural pesticides—metolachlor, atrazine, cvanazine, acetochlor, and alachlor—were also among the most frequently detected (figs. 9 and 10). Atrazine was detected in every stream-water sample collected during 1996-98 (fig. 10). Metolachlor was detected in 99 percent of samples, and simazine was detected in greater than 80 percent of samples, regardless of land use (fig. 10). Two pesticides that are heavily used in the basin were not analyzed for in this study: (1) glyphosate, an herbicide used in agricultural and urban areas, and (2) endosulfan, an organochlorine insecticide, which was analyzed for in streambed sediment but not in water.

Pesticides detected more frequently in urban than in agricultural areas include the herbicide prometon and the insecticides diazinon and chlorpyrifos (figs. 10 and 11). Chlorpyrifos (Dursban), which was detected in 22 percent of the samples, was recently restricted for residential and commercial use by the U.S. Environmental Protection Agency (USEPA).

Historical-use pesticides are seldom detected in water. Aldrin and DDT are organochlorine insecticides banned in the mid-1970s. Their metabolites (dieldrin and DDE) were each detected in about 1 percent of stream samples. In contrast, total DDT was detected in

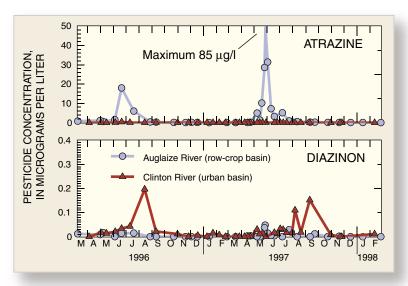


Figure 11. The concentration of atrazine was higher in streams draining row-crops, whereas the concentration of diazinon was higher in streams draining urban-land use.

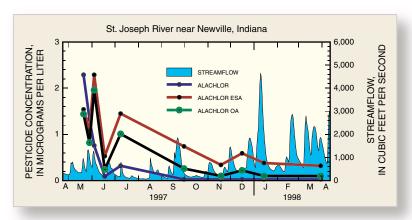


Figure 12. Metabolite concentrations for alachlor, as well as acetochlor and metolachlor (not shown), were greater than parent compounds for much of the year.

nearly 35 percent of all streambed sediment samples (fig. 19, p. 13).

Pesticide metabolites were frequently detected

Little is known about pesticide metabolites (breakdown products) on a watershed level. After application, most pesticides adsorb to soil, infiltrate to ground water, volatilize, or break down to a metabolite (Larson and others, 1999). Deethylatrazine, a metabolite of atrazine, was detected in every sample collected during 1996–98. Additional

triazine and acetanilide herbicides and their metabolites were intensively sampled for at one site, the St. Joseph River near Newville, Ind. Here, the metabolites of triazine compounds, like atrazine, showed the same seasonal pattern and relative concentrations as parent compounds. In contrast, concentrations of the acetanilide parent compounds—alachlor, acetochlor, and metolachlor—were lower than those of their metabolites for most of the year (fig. 12).

No benchmarks for metabolites have been set to protect human health or aquatic life, but some metabolites are believed to be as toxic as parent compounds (Day, 1991). Because metabolites may account for a significant amount of the total pesticides in the environment, they are considered a waterquality concern.

Pesticide concentrations in streams are related to land use, rainfall, runoff, and season

Herbicide concentrations were highest in streams draining rowcrops followed by streams draining mixed-use and urban land, and were lowest in streams draining pasture/forested land. Atrazine was detected at the highest concentrations, as high as 85 µg/L (micrograms per liter), in streams draining row crops and at much lower concentrations in streams draining urban land (fig. 11).

Rainfall and runoff affected the concentrations of atrazine in the wet years of 1996–97 compared to the dry year of 1998 in the St. Joseph River near Newville, Ind. (fig. 13). In 1996, streamflow was 330 to 340 percent above average in May and June; in 1997, streamflow was 103 to 129 percent above average in May and June; and in 1998, streamflow was only 36 to 78 percent of the average. The median atrazine concentration detected in the stream was 0.40 μ g/L in 1996, 0.45 μ g/L in 1997, and $0.14 \mu g/L$ in 1998.

Herbicide concentrations in streams are typically highest after application and steadily decrease thereafter. Elevated concentrations of the most heavily used herbicides—metolachlor. atrazine, cyanazine, and ace-

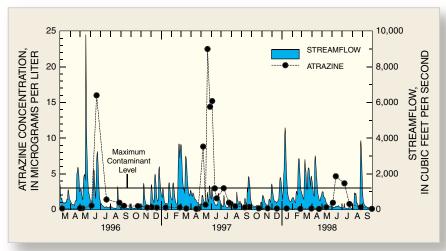


Figure 13. Pesticides such as atrazine show a seasonal trend with streamflow, as shown for the St. Joseph River near Newville, Ind. Differences in the amount and timing of precipitation affect the concentrations, as illustrated by the differences between the wet years of 1996-97 and the dry year of 1998.

tochlor-were detected for 4 to 6 weeks after rainfall and runoff in the spring and early summer (fig. 13, table 1). Pesticides used mostly in urban areas, such as prometon and diazinon, are typically applied in late summer, and this is when the highest concentrations were detected in streams (fig. 11).

Pesticide concentrations in streams have publichealth and economic consequences

When concentrations of a contaminant in stream water are greater than a Maximum Contaminant Level (MCL), treatment might be needed to reduce the concentration (Box 1).

The time-weighted average annual concentrations of atrazine were not greater than the drinking-water standard, or MCL, of 3 μg/L at any of the 10

Table 1. Annual and seasonal time-weighted average concentrations of atrazine at 10 stream sites in the Lake Erie-Lake Saint Clair Drainages, 1996-98

	Concentrations of atrazine			
Site and primary land use	Annual average (μg/L)	May - July average (μg/L)		
ROW-CRO	P LAND US	SE.		
River Raisin, Mich.	0.04	0.09		
Auglaize River, Ohio ¹	2.4	8.9		
Black River, Mich.	0.91	3.0		
St. Joseph River, Indl	1.6	5.5		
PASTURE/FOF	REST LAND	USE		
Cattaraugus Creek, N.Y.	0.04	0.11		
Grand River, Ohio	0.53	1.3		
URBAN L	AND USE			
Clinton River, Mich.	0.04	0.08		
MIXED L	AND USE			
Cuyahoga River, Ohio	0.10	0.24		
Maumee River, Ind.	2.8	10.1		
Maumee River, Ohio ¹	2.6	9.3		

¹Stream is used as a source of drinking water

Box 1—What concentrations of pesticides are considered safe in drinking water?

The USEPA sets drinking-water standards, or Maximum Contaminant Levels (MCLs), and health advisory—lifetime quide-lines (HALs) for drinking water, to protect human health. The MCL is the maximum permissible concentration of a contaminant in water delivered to any user of public water systems. MCLs are enforceable standards and are based on an average annual concentration taken from quarterly samples of finished drinking water. HA (Health Advisories) are nonenforceable, risk-based guidelines. Health advisories indicate contaminant exposures below which no short- or long-term adverse human-health effects are expected, based on drinking a specific amount of water for a specific period of time. Risk of illness increases with exposure time and concentration. This report lists only HALs, which are based on a lifetime of 70 years. Standards and guidelines to evaluate the potential adverse effects of pesticides have limitations: (1) Few standards and guidelines have been set for pesticides; of the 88 pesticides analyzed in this study, only 14 MCLs and 38 HALs have been established. (2) Drinking-water standards are based on toxicity tests on a single pesticide and do not evaluate the additive or synergistic effects of multiple pesticides. (3) The standards and guidelines do not address possible effects of pesticides on endocrine systems of humans (Nowell and Resek, 1994; Larson and others, 1999).

stream sites sampled during 1996–98 (table 1). The values from May–July, however, were greater than the MCL at five stream sites (table 1), indicating a need for sourcewater treatment during that period to remove the pesticides.

Many large water-treatment facilities that withdraw surface water (other than Lake Erie) use activated-carbon filtration during the spring to meet drinking-water standards. In areas of heavy pesticide use, specialized treatment may be necessary year round. For example, the Fort Wayne Water-Filtration Plant uses activated carbon all vear. The annual cost of the treatment chemicals at Fort Wayne is approximately \$210,000, about 40 percent of this amount being spent from April to July (Doug Pooler, Fort Wayne Water Filtration Plant, oral commun., 1999). Even with carbon treatment, some treated drinking-water samples tested for atrazine were in excess of the MCL

during 1996–98 (Kelleher, 1999).

Another consequence of heavy pesticide use is the potential effect on aquatic life

Of the 10 streams sampled, 8 had pesticide concentrations, in single samples, in excess of one or more aquatic-life guidelines (fig. 14) (Frey, in press). Concentrations in excess of aquatic-life guidelines were detected for the herbicides atrazine, metolachlor, cyanazine, and metribuzin, and for the insecticides chlorpyrifos, carbaryl, and diazinon. Heavily used compounds—metolachlor, atrazine, cyanazine, and metribuzin-were the compounds with concentrations

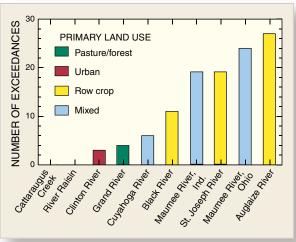


Figure 14. The greatest number of concentrations of pesticides affecting aquatic life were detected in streams draining row crops and mixed-use land.

most frequently greater than guidelines. The time-weighted average concentration of atrazine, for example, was in excess of the 1.8µg/L guideline at 3 of 10 sites annually and at 5 of 10 sites during May–July (table 1).

Box 2—What concentrations of pesticides are considered safe for aquatic life?

Several agencies, including the USEPA, Environment Canada, and the IJC (International Joint Commission), have set guidelines to protect aquatic life. These guidelines are designed to prevent adverse short-term (acute) and long-term (chronic) effects on aquatic life. The aquatic-life guidelines or benchmarks developed by USEPA are based on 4-day average concentrations, are intended to protect 95 percent of the aquatic species, and should not be exceeded more than once in 3 years. The Canadian and IJC aquatic-life guidelines, which are more stringent than those of the USEPA, indicate a single maximum concentration that should never be exceeded. Aquatic-life guidelines have been developed for only 18 pesticides.



Concentrations of nutrients and herbicides in certain streams are among the highest in the Nation

Because the amounts of fertilizers and herbicides applied to agricultural areas are among the highest in the Nation, concentrations of nutrients and herbicides in stream water also are comparatively high at 8 of 10 streams sampled during 1996–98. In eight streams draining agricultural and mixed-use land, average annual concentrations of total phosphorus were in excess of the 0.1-mg/L (milligram per liter) guideline recommended by USEPA to reduce stream eutrophication (fig. 15). In four streams, phosphorus concentrations were in the upper 25 percent of all streams sampled nationwide by NAWQA, as were nitrate concentrations in six streams. In two streams that serve as source waters for public supply, nitrate concentrations in a few samples were detected in excess of the drinking-water standard. Although total phosphorus concentrations appear to be relatively high, the work of other investigators has shown that concentrations of total phosphorus were 40 percent lower in 1995 than in 1976 (Baker and others, 1998). In two of the streams where nutrient concentrations were in the upper 25 percent range on a national basis, average annual concentrations of herbicides were in the upper 25 percent as well. Mixtures of pesticide compounds were found in every stream sample and a total of 30 different pesticides were detected. In one sample, 18 different pesticides were detected. This sample contained more pesticide compounds than 98.5 percent of all the samples collected at 343 sites across the Nation during 1993–98.

Runoff from agricultural land to streams is an important pathway of phosphorus to Lake Erie

In the 1960s, Lake Erie was considered "dead" from the excessive growth and decay of algae and the oxygen-depleting effects of this

decay on the bottom water of the lake (Herdendorf, 1986). By 1971, it was well known that the major sources of phosphorus to the lake were sewage, laundry detergents, and fertilizers. The Great Lakes Water-Quality Agreement (International Joint Commission, 1994) set goals for United States and Canada

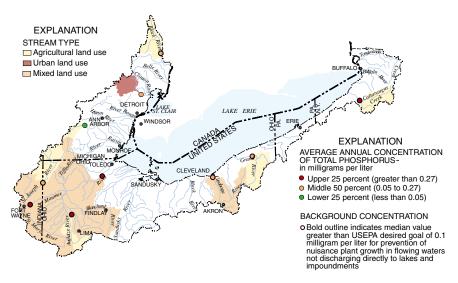


Figure 15. Median concentrations of total phosphorus at 8 of 10 sites in the Lake Erie–Lake Saint Clair Drainages were in excess of 0.1 milligram per liter, the USEPA guideline to control eutrophication in streams.

to reduce phosphorus inputs to the lake. Actions taken to reduce phosphorus included a limit on the phosphorus content of detergents, a limit of 1.0 mg/L in discharges from sewage-treatment plants, and a total load limit for Lake Erie of 11,000 metric tons per year (International Joint Commission, 1994). Having achieved the point-source reductions over the period 1968–92 (Litke, 1999), the focus shifted to reducing nonpoint sources of phosphorus.

A sustained focus on reducing nonpoint sources of phosphorus to Lake Erie has continued because oxygen depletion in the bottom water in some areas occurs intermittently (Bertram, 1993; Litke, 1999). One reason may be that in years with above-average runoff, annual phosphorus loads to the lake exceed 11,000 metric tons (Dolan, 1993). The excess phosphorus in wet years is thought to come from nonpoint sources (Dolan, 1993).

Fertilizers appear to be the major nonpoint sources of phosphorus to Lake Erie. Greater amounts of phosphorus were applied as fertilizers to each square kilometer of agricultural and mixed-use land than to urban-residential land in 1996–98 (fig. 16). Phosphorus yields, or the amount of phosphorus discharged from a stream per unit area of its basin, ranged from 8.2 to 293 kg/km² (kilograms per square kilometer). The phosphorus yield from only 1 of 10 streams sampled during 1996–98 was in the lower range of yields typical of streams flowing through undeveloped land (Clark and others, 2000). Phosphorus yields in eight streams were similar to or slightly higher than the yields typical of streams flowing through agricultural and mixed-use lands (Gibson and others, 2000).

Phosphorus concentrations were highest in the same streams where vields were highest. Therefore, streams receiving runoff from agricultural and mixed-use lands contributed greater concentrations and amounts of phosphorus to Lake Erie than did streams receiving runoff from urban-residential land

(fig. 16). A conclusion is that agricultural runoff is an important nonpoint source of phosphorus to small streams and major rivers and that major rivers. like the Maumee River, provide a direct pathway to Lake Erie. During 1996–98, the Maumee River contributed an average of 24 percent per year to the 11.000-metric-ton limit

In the last few years, phosphorus concentrations in Lake Erie appear to be increasing above levels recommended in the Great Lakes Water-Quality Agree-

ment (Scott Painter, Environment Canada, written commun., Oct. 2000). Continued emphasis on managing levels of phosphorus in

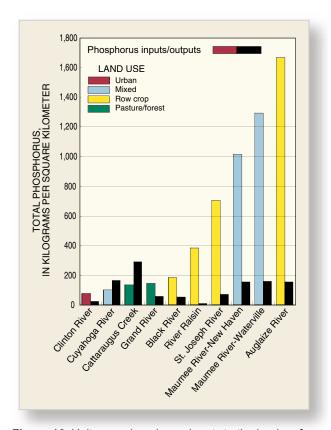


Figure 16. Unit-area phosphorus inputs to the land surface from fertilizer and manure and unit-area phosphorus outputs from 10 streams in the Lake Erie-Lake Saint Clair Drainages, 1996-98.

Lake Erie appears to be warranted (Box 3).

Box 3—Recent changes in the food web of Lake Erie-the role of phosphorus and zebra mussels

Concerns about recent declines in some important fish species and the proliferation of zebra mussels, an exotic species, have prompted a renewed interest in the role of phosphorus in Lake Erie. Zebra mussels (shown in the photograph) were introduced into Lake Saint Clair in the mid-1980s and quickly became established in Lake Erie. Because of their filter-feeding behavior, zebra mussels may be affecting fish production in Lake Erie by consuming large amounts of small invertebrates and algae, or plankton, that are the food for small fish, which in turn are the food of larger game fish like yellow perch and walleye. Recent

decreases in sport- and commercial-fish harvests, proliferation of zebra mussels, and reductions in phosphorus concentrations in Lake Erie have prompted a renewed interest in how factors such as phosphorus and zebra mussels may be affecting sustainable fish harvests. Adding more phosphorus to the lake to stimulate algal productivity has been suggested, but this could result in increased eutrophication of tributary streams and a return to excessive oxygen depletion in the bottom water of the lake. Furthermore, uncertainties about the response of the lake to phosphorus additions in light of its changing food web have held back plans to apply such a solution. One thing about which everyone can agree is the remarkable ability of exotic species to cause unexpected consequences in ecosystems (U.S. Environmental Protection Agency and Environ-Photograph from Ohio Lake Erie Commission ment Canada, 2000).



Decreases in the amounts of suspended sediment carried by rivers correspond to increases in farmers' use of conservation tillage

Cropland in the Maumee River Basin is the largest contributor to soil erosion and sediment in the Maumee River (U.S. Department of Agriculture, 1998), and the river is the largest tributary source of suspended sediments to Lake Erie (Myers and others, 2000). Excessive amounts of sediment discharged from the Maumee River to Lake Erie diminishes the aquatic habitats of fish and other organisms. Maintenance of navigation requires the dredging of approximately 800,000 tons of sediment each year from the Maumee River and Lake Erie at an average annual cost of about \$2.2 million. In response to these problems, the Ohio Lake Erie Commission has set a goal of reducing suspended sediment in Lake Erie tributaries by 67 percent (Ohio Lake Erie Commission, 1998), and the U.S. Army Corps of Engineers has set a



Figure 17. Conservation tillage protects the soil. (Photograph by Steven Davis, Natural Resources Conservation Service).

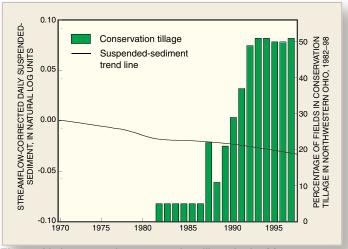


Figure 18. Increases in conservation tillage in the Maumee River Basin and elsewhere in northwestern Ohio correspond to decreases in the amount of suspended-sediment carried by the Maumee River at Waterville, Ohio.

goal of reducing the amount of sediment dredged from the lower river and its harbor by 15 percent.

Conservation tillage (fig. 17) is a reduced-cultivation method that is being used to decrease soil erosion and thereby the amount of suspended sediment carried by the Maumee River and its tributaries. By maintaining a layer of crop residue from the past year's crop on 30 percent or more of the soil surface. conservation tillage protects the soil from the forces of water erosion. During 1993–98, about 53 percent of all crop fields in the Maumee River Basin and about 50 percent of the crop fields in northwestern Ohio were planted using conservation tillage methods (fig. 18).

Significant decreases in the amounts of suspended sediment carried by the Maumee and Auglaize Rivers over time correspond to increases in conservation tillage. Data from previous studies and new data collected at two sites in the Maumee River Basin during 1996–98 support this conclusion (Myers and others, 2000). An 11.2-percent decrease in

the amount of suspended sediment carried by the Maumee River was detected at Waterville, Ohio, near the mouth (fig. 18), and a 49.8-percent decrease was detected in the amount carried by the Auglaize River near Fort Jennings, Ohio, a tributary stream (Myers and others, 2000). During 1970–98, no trends in streamflow at these two sites were detected. If conditions leading to the downward trends remain the same, then the estimated time necessary to achieve the 15 and 67 percent reduction goals are 30.1 and 205 years, respectively, from the reference condition in 1992.

One reason for the smaller downward trend in the Maumee River compared to that found in its tributary may be related to drainage-basin size. In the large drainage basin of the Maumee River, sediment is deposited in small drainage ditches and streams. These stored sediments are available for resuspension and transport in subsequent storms. This process, as described by Trimble (1975, 1999), creates a lag in the response of rivers to conservation tillage on the land.

Contamination of bed sediments may be causing adverse effects on aquatic life

Bed sediments of small streams and major rivers provide habitat for many aquatic organisms but also serve as a repository for persistent and toxic chemical contaminants that have been released into the environment or that occur naturally. Sediments, once contaminated, can provide a pathway for bioaccumulation. Activities such as dredging of sediments can release contaminants to the surrounding water.

Evidence from laboratory tests shows that contaminated bed sediments can be toxic to aquatic invertebrates (worms, clams, and insect larvae) that are of recreational, commercial, or ecological importance. Contaminated sediments also can affect the food supply required to sustain fish populations (U.S. Environmental Protection Agency, 1997).

Data collected by the U.S. Geological Survey (USGS) and other public-sector agencies at more than 800 locations from 1990 to 1997 were aggregated and analyzed to assess bed-sediment contamination. These data show that zinc, lead, copper, arsenic, cadmium, mercury, PAHs (polycyclic aromatic hydrocarbons), PCBs (total polychlorinated biphenyls), DDT, and its breakdown products are prevalent in bed sediments, being detected in 30 to 100 percent of samples (Rheaume and others, in press) (fig. 19).

Concentrations of mercury and PCBs (figs. 20 and 21) exceeded Probable Effect Levels (PELs) in 11.8 and 22.4 percent of samples, respectively. PELs are the guide-

Box 4—How are contaminated sediments evaluated?

Effect levels are screening values used to indicate when contaminant concentrations in the bed sediments are likely to be associated with adverse effects on aquatic life. The Threshold Effect Level (TEL) is an estimate of the concentration of a contaminant in bed sediment below which adverse biological effects rarely occur and, if so, only in very sensitive species. The Probable Effect Level (PEL) is an estimate of the concentration of a contaminant in bed sediment above which adverse biological effects frequently occur. These guidelines were developed for the Great Lakes sediments and are used for national assessment in this report. For anthracene and total PAHs, no guideline was available from Smith and others (1996), so guidelines developed by Ingersoll and others (1996) for the Great Lakes were used.

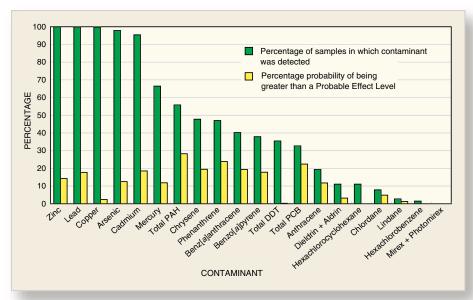


Figure 19. Percentage detection and percentage probability of sample concentrations being greater than a Probable Effect Level in bed sediments of small streams, major rivers, and lakes, Lake Erie-Lake Saint Clair Drainages, 1990–97.

lines established for the protection of aquatic life (Box 4). Contamination of bed sediments with mercury and PCBs was greatest in nearshore areas of Lake Erie, in Lake Saint Clair, and in major rivers that flow through urban areas with industry and populations over 100,000.

Concentrations of arsenic, DDT, and chlordane also exceeded PELs

in the bed sediments of some smaller streams. Samples with detection limits higher than Threshold Effect Levels (TELs) (open circles, figs. 20 and 21) were not useful for assessment purposes. Lower detection limits would have made these data more useful.

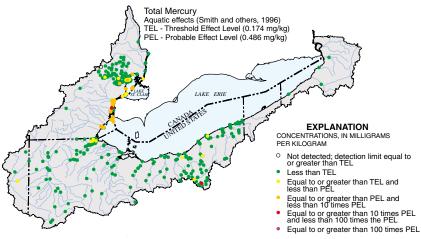


Figure 20. Concentrations of total mercury in recently deposited lakebed and streambed sediments (Data from 1990–97).

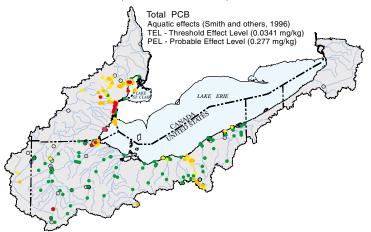


Figure 21. Concentrations of total PCB in recently deposited lakebed and streambed sediments (Data from 1990–97).

Land use and chemical use contribute to contamination of sediments and fish

Most organochlorine pesticides and PCBs have not been manufactured or used in the United States for at least 10–25 years; however, because of their chemical stability (persistence), they were detected in bed sediments and fish collected in 1996–98. Aldrin, DDT, and chlordane were the organochlorine insecticides used in the greatest quantities in the Corn Belt and Great Lakes States in the 1970s. Similarly, historical use of PCBs in industry contributed to their occur-

rence in urban and mixed-use areas.

The highest concentrations of DDT, chlordane, dieldrin, and their breakdown products were detected in bed sediments and fish collected from small streams and major rivers flowing through row-crop, urban, and mixed-use lands. The highest concentrations of PCBs, DDT, and chlordane were detected in bed sediments and fish from streams flowing through urban and mixed-use lands where historical use was greatest. Organochlorine contamination was the lowest in fish and sediments collected from streams in pasture/forest settings.

Unlike organochlorine compounds, mercury has more than 2,000 uses in industry, medicine, agriculture, and commerce. Mercury also is released to the atmosphere as a by-product of coal combustion and waste incineration (Irwin and others, 1997). In 1996-97, mercury was detected in all 15 bed-sediment samples and in all 11 fish-liver samples collected from streams, independent of land-use type. The highest concentrations of mercury, however, were detected in bed sediments and fish collected from small streams and major rivers that flow through urban and mixed-use lands. The magnitude of mercury contamination in bed sediments and fish appears to follow patterns of use in commerce and industry. Mercury was detected in several different fish species that have different feeding habits and that occupy different positions in the food web. Mercury was detected in carp, which are bottomfeeders, in northern hog suckers, which eat insects, and in rock bass, which eat smaller fish (fig. 22).



Figure 22. Total chlordane, total DDT, dieldrin, heptachlor epoxide, mercury, and total PCBs were detected in the tissues of carp, rock bass, and northern hog suckers collected in 1996–97.

Bioaccumulative contaminants in fish may pose a risk to fish-eating wildlife

Where PCBs were detected in fish, they frequently posed a threat to fish-eating wildlife because of their high concentrations. PCBs were found in fish at 8 of 11 sites. and concentrations in fish from 6 sites exceeded the New York State guideline for the protection of fisheating wildlife (table 2). The maximum concentration of PCBs found in fish was 25 times higher than the guideline set by the New York State Department of Environmental Conservation (NYSDEC) for the protection of fish-eating wildlife (Newell and others, 1987). These fish were collected from the Cuyahoga River at Cleveland, Ohio, a major river that flows through mixed-use land.

DDT was present in fish at 10 of 11 sites but concentrations in fish from only 2 sites exceeded the NYSDEC guideline. The highest concentrations of DDT were in whole fish in streams flowing through urban and mixed-use land—the Clinton River at Sterling Heights, Mich., and the Cuyahoga River at Cleveland, Ohio. Although mercury is a concern, no wildlife consumption guidelines have been established.

Fish-consumption restrictions for humans are based on contaminant concentrations in edible fish fillets, which are typically lower than those in whole fish. The contaminants of most concern in the Lake Erie Basin for human consumption of fish are mercury, PCBs, DDT, chlordane, and dieldrin. These are the same contaminants that are a concern for wildlife consumption (fig. 23). Because of

Table 2. Summary of contaminant concentrations in fish tissue in relation to guidelines for the protection of fish-eating wildlife [μ g/kg, micrograms per kilogram; NYSDEC, New York State Department of Environmental Conservation]

Compound found in fish tissue	Number of sites with detections (11 sites sampled)	Maximium detected concentra- tion (μg/kg)	NYSDEC whole-fish quideline for the protection of fish- eating wildlife (μg/kg)	Number of sites with contamin- ation in excess of NYSDEC criteria
Chlordane, total	6	157	500	0
DDT, total	10	450	200	2
Dieldrin	5	32.0	120	0
Heptachlor epoxide	2	10.0	100	0
PCBs, total	8	3,200	130	6

widespread human consumption advisories for fish in the Lake Erie Basin, mercury and PCBs have been identified as critical pollutants and targeted by the USEPA and Environment Canada for cleanup and elimination (Daher, 1999).

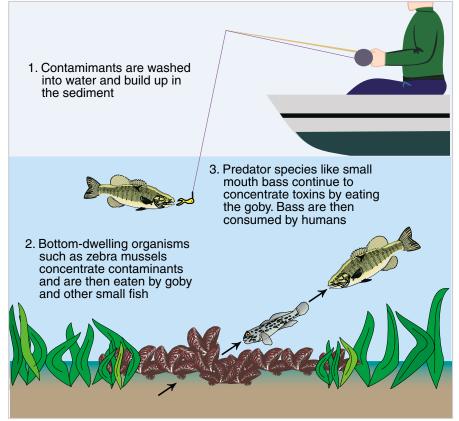


Figure 23. Contaminants can bioaccumulate upward through the food web and may affect the health of human and animal consumers of fish.

Land use appears to affect fish-community composition

Contaminants and nutrients in water and bed sediments appear to affect aquatic life, but human disturbance of physical stream habitat also is thought to be one of the most important causes of declines in certain fish species (Ohio Environmental Protection Agency, 1995). To differentiate the effects on fish of human disturbance from those of contaminants, sites considered to represent good to excellent stream habitat, as rated by the Qualitative Habitat Evaluation Index (QHEI) (Box 5) were selected for assessment of fish. Fish communities were assessed by means of the Index of Biotic Integrity (Box 5).

In 1996–98, stream habitats were rated good to excellent at 11 of 13 sites (fig. 24A), but fish communities were rated good to excellent at only 5 sites (fig. 24B). This may be an indication that the contaminants detected in water and bed sediments

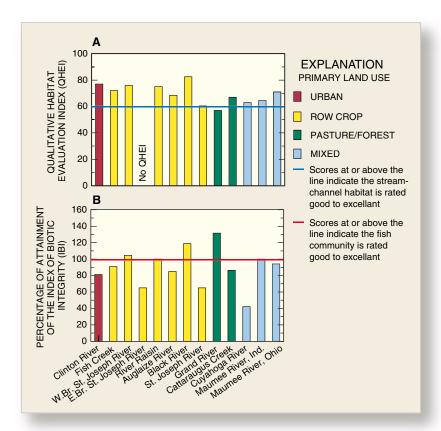


Figure 24. Although most stream sites were rated good to excellent for habitat as measured by the Qualitative Habitat Evaluation Index (A), only five sites were rated good to excellent for fish community composition as measured by the Index of Biotic Integrity (B).

Box 5—Index of Biotic Integrity and Qualitative Habitat Evaluation Index

Aquatic biological communities are sensitive indicators of stream quality. The biological condition of streams is evaluated within water-quality assessment programs by comparing the type, number, and abundance of fish species to those of streams known to be "least impacted" by human activities. The Index of Biotic Integrity (IBI), used by the Ohio Environmental Protection Agency (Ohio Environmental Protection Agency, 1989), also was used in this study to assess fish-community composition. IBI scores are derived by summing 12 individual metric scores from separate factors that describe fish communities. Examples of such metrics are the number of taxa, the number of insect-eating or omnivorous species, the number of pollution-tolerant and pollution-intolerant species, and the relative abundance of fish in each of these categories. Scores for the IBI range from 12 to 60; with ratings of poor, fair, good, and excellent quality assigned to numerical ranges. Higher scores indicate better overall fish-community diversity and abundance. Because the minimum IBI score required for a "good" rating differs somewhat from one ecological region to another, and there are five such regions in this study, each IBI score was reported as a percentage attainment of a "good" rating. A comparison of IBI scores computed independently for the same sites in the same years by the Ohio Environmental Protection Agency and USGS show that results are comparable between the two agencies as long as fish-collection methods are appropriate for the stream size (Covert, in press). A Qualitative Habitat Evaluation Index (QHEI), also developed by the Ohio Environmental Protection Agency (1989), was applied to data collected by USGS at the same stream sites where fish were assessed. The QHEI is composed of seven metrics that describe the physical habitat of streams: width, depth, pools, riffles, grain size of streambed substrates, and vegetation type and width along stream banks. Scores for the QHEI range from 0 to 100, with scores of 60 or better indicating excellent stream-channel habitat.

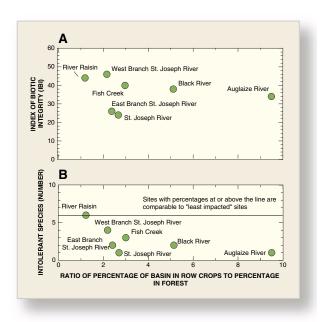


Figure 25. As the percentage of row-crop land use increased in a stream basin (A) scores for the Index of Biotic Integrity decreased and (B) the number of pollution-intolerant fish decreased.

are affecting fish-community composition.

For example, agricultural runoff appears to be affecting fish communities in streams draining row crops. Agricultural practices can heavily stress fish communities because of runoff of pesticides, nutrients, and sediments (figs.14-16, 18–19). As the amount of row-crop agriculture increased, IBI scores at stream sites tended to decrease, although not proportionately (fig. 25A). In contrast, as the amount of forested land in a basin increased, IBI scores tended to increase. Forested lands, especially along the banks of streams, have been shown to be effective in removing sedi-

ment, pesticides, and nutrients that otherwise drain into streams with runoff from the land surface (Sweeney, 1992; Lowrance and others, 1997).

Clear differences can be seen in fish-community composition

among streams draining row-crops that may be related to the relative amount of row crops compared to woodlands and forests. As the amount of row-crops increased, the number of pollution-tolerant fish species in streams also increased (fig. 25B). In contrast, more pollution-intolerant fish species were found in streams draining areas with lower percentages of row crops and higher percentages of forested land in their basins, especially when the forests were along streams.

Although only a few sites were examined, it appears that pollution-intolerant fish can live in streams where agriculture is the primary land use under certain conditions. This information corroborates the findings of others on the water-quality benefits provided by undisturbed natural stream habitats and wooded riparian areas (figs. 26 and 27).



Figure 26. High-quality stream habitat supports a variety of pollution-intolerant fish species along the West Branch of the St. Joseph River.



Figure 27. Poor-quality stream habitat supports pollution-tolerant fish along the East Branch of the St. Joseph River.

Recent residential development has had a widespread effect on groundwater quality

Two studies were done to assess ground-water quality in areas west of Detroit, where recent suburban development overlies sand-and-gravel deposits (Thomas, 2000a). Recent suburban development typically consists of homes on large residential/rural lots or in uppermiddle-class subdivisions (fig. 28). Most homes have private wells, septic systems, and water softeners.

Samples of shallow and deep ground water were collected from co-located wells (fig. 29). Shallow ground water was sampled from 30 monitor wells (median depth of 25 feet). Deeper ground water was sampled from 28 domestic wells (median depth of 93 feet). In most places, clay till of varied thickness separates the shallow and deep sand-and-gravel deposits (fig. 29).

Tritium concentrations were used to distinguish ground waters recharged before 1953 ("old waters") from those recharged after



Figure 28. Much of the recent development west of Detroit in the residential study area consists of low- to medium-density subdivisions. Most homes have private wells, septic systems, and water softeners.

1953 ("young waters") (Plummer and others, 1993). Water in about one-third of domestic-wells was recharged before 1953, which is prior to widespread residential development in the study area. Old waters show no evidence of human activities. All nitrate concentrations were less than the estimated background value of 2 mg/L (U.S. Geological Survey, 1999), and all

chloride concentrations were less than 25 mg/L, the estimated background concentration based on a historical data set from the same area (Mozola, 1953).

In contrast, more than 75 percent of young waters show evidence of human influence:

- Seventy-six percent of young waters had chloride concentrations greater than background (fig. 30). Probable sources of elevated chloride concentrations are road salt, septic systems, and backwash from water softeners.
- Twenty-six percent of young waters contained nitrate concentrations greater than background (fig. 30). Probable sources of elevated nitrate concentrations in residential areas are septic systems, lawn fertilizer, and pet waste.
- Trace concentrations of VOCs were detected in 29 of the 30 samples from monitor wells. The most frequently detected VOCs were BTEX compounds, which are components of fuels and solvents.

Samples that contained nitrate or VOCs also contained elevated

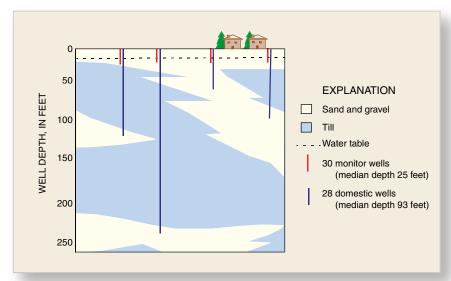


Figure 29. Ground-water samples were collected from pairs of shallow monitor wells and deeper domestic wells. Sand-and-gravel deposits are at land surface and at varied depths in the subsurface.

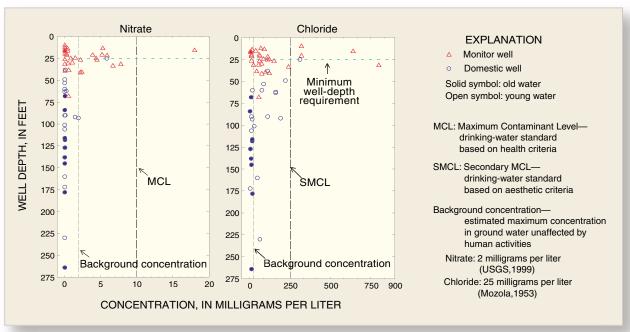


Figure 30. In the residential study area, concentrations of nitrate and chloride greater than background concentrations are the result of human activities. Elevated concentrations of chloride were detected far below 25 feet, the minimum well depth required by State regulations.

chloride concentrations. The cooccurrence of these compounds suggests that ground water is affected by a mixture of sources, such as (1) septic systems containing domestic waste (nitrate and chloride), watersoftener backwash (chloride), and/or household solvents such as drain cleaners (VOCs), (2) infiltration of runoff from roads containing road salt (chloride) and fuel residue (VOCs), and/or (3) fertilizer or pet waste (nitrate) from lawns.

Pesticides were detected infrequently. Trace concentrations of herbicides were detected in 2 of 30 (7 percent) monitor-well samples. This value is low compared to similar studies in 25 other urban/residential areas, where the median detection frequency of herbicides in shallow ground water was 44 percent (Kolpin, 2000). In the study area, most of the pesticides commonly used on lawns and roadways were analyzed for but were not detected in the shallow ground water.

One monitor-well sample had a nitrate concentration exceeding health-related standards (fig. 30). The sample was from a well too shallow to be used as a source of drinking water, but shallow ground water can migrate to deeper parts of ground-water system or discharge to streams, lakes, and wetlands.

No health-related drinking-water standards were exceeded in samples from domestic wells; however, standards do not exist for all compounds or for mixtures of compounds. Also, all possible constituents were not tested; for example, septic systems can contain bacteria, viruses, or pharmaceuticals.

In Michigan, the minimum depth required for domestic wells is 25 feet. In the study area, the effects of human activities were detected far below this depth (fig. 30). A proposal to increase the required depth for private wells in subdivisions is under consideration by the Michigan Department of Environmental Quality.

Box 6—Chloride/bromide ratios verify that elevated chloride concentrations are due to human activities.

In parts of eastern Michigan, elevated chloride concentrations in shallow ground water have been attributed to upward movement of brine from deep bedrock formations (Mozola, 1953; Long and others, 1988). In the study area, however, Cl/Br ratios indicate that elevated chloride concentrations were not derived from brine, but from halite (rock salt) (Davis and others, 1998). Natural sources of halite are not present in near-surface bedrock or sediments. However, halite is commonly used as road salt, table salt, and as a water-softener additive. The conclusion that elevated chloride concentrations are due to recent human activities is consistent with the observations that (1) chloride concentrations are highest in young, shallow waters, and (2) all old waters have concentrations that are less than background values.



Figure 31. In the agricultural study area, the predominant crops are corn, soybeans, and small grains. (Photograph from Ohio Department of Natural Resources.)

Ground water is vulnerable to contamination in agricultural areas underlain by till

Ground-water quality was assessed in agricultural areas in the northwestern part of the Lake Erie-Lake Saint Clair Drainages (Thomas, 2000b) (fig. 31). In this

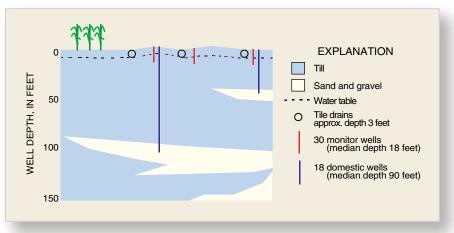


Figure 32. In the agricultural study area, clay-rich till occurs at land surface. Shallow tile drains are installed in low spots of farm fields to improve drainage.

region, clay-rich till is at the land surface, and the rate of water infiltration is generally less than in the residential study area, where sand and gravel are at the surface (compare figs. 29 and 32).

Samples of shallow ground water were collected from 30 monitor wells installed in the till at a

median depth of 18 feet. Deeper ground water, from the glacial sand-and-gravel aquifer, was collected from 18 domestic wells with a median depth of 90 feet (fig. 32).

Samples were analyzed for pesticides in the form of parent compounds (the original active ingredient) and metabolites (break-

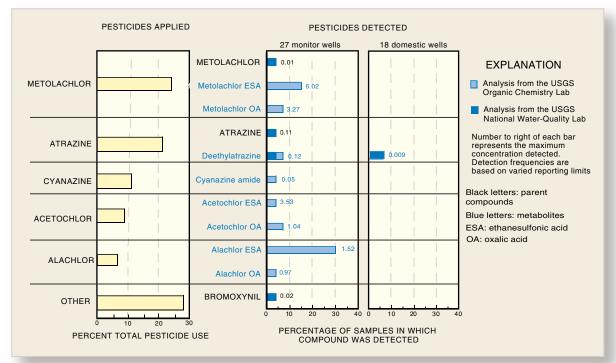


Figure 33. Pesticides detected in the shallow ground water closely correspond to those most heavily applied in the Lake Erie—Lake Saint Clair Drainages (data from Brody and others, 1997). All are herbicides used on corn and soybeans. Metabolites were detected more frequently, and at higher concentrations, than parent compounds.

down products). Pesticides were detected in 41 percent of monitor-well samples. The six compounds detected closely correspond to those most heavily applied in the basin—herbicides used on corn and soybeans (fig. 33). Metabolites were detected three times more frequently, and at higher concentrations, than were parent compounds. Concentrations did not exceed drinking-water standards, but standards do not exist for 9 of the 11 compounds detected. In addition, many samples contained more than one herbicide, and the health effect of mixtures is unknown.

Nitrate concentrations indicative of human influence were detected in 37 percent of monitor-well samples. Probable sources

are nitrogen fertilizers (which are heavily used in the study area), manure, or septic systems. Nitrate concentrations exceeded health-related drinking-water standards in two shallow monitor wells (fig. 34).

Pesticides and nitrate were detected much less frequently in domestic wells than in monitor wells (fig. 34). About 6 percent (1 of 18) of samples from domestic wells contained a trace concentration of a pesticide metabolite, and 6 percent contained a nitrate concentration approximately equal to the background concentration of 2 mg/L.

A common belief is that till protects the ground water from contamination. There appears to

be some truth to this idea because detections of nitrate and herbicides are low relative to other agricultural areas with similarly high application rates. At the same time, this belief is a simplification that may be misleading because ground water is still vulnerable to contamination, especially at shallow depths.

Fifty-nine percent of monitorwell samples showed evidence of human activity—either an herbicide or an elevated nitrate concentration. Moreover, 83 percent of waters from monitor wells were recharged after 1953. These observations indicate that till does not prevent water at the land surface from moving to the shallow ground water. In the study area,

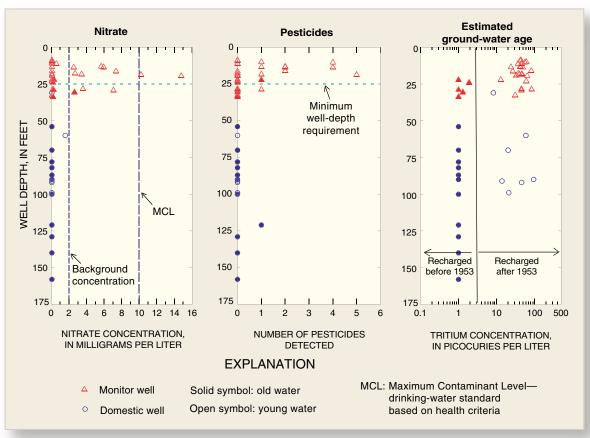


Figure 34. Detections of nitrate or pesticides are relatively infrequent at depths greater than 35 feet; however, deeper ground water is not completely isolated from the land surface because almost half of the waters between depths of 35 and 100 feet were recharged after 1953.

till contains vertical fractures and numerous stringers of sand and gravel that are potential pathways for movement of water from the surface. In areas with similar geology to that in the agricultural study area, active ground-water flow occurs to depths of 35 feet, and sometimes much deeper (Keller and others, 1991).

Similarly, till does not completely prevent water at the land surface from entering the deeper ground water. Eleven percent of domestic-well samples contained either a pesticide or elevated nitrate concentration. Moreover, almost half of the waters from domestic wells between depths of 35 to 100 feet were recharged after 1953 (fig. 34).

Naturally occurring **geochemi**cal processes may be partly responsible for the relatively low

detection frequencies of agrochemicals in the ground water. Till and till soils are generally rich in clay and organic matter and therefore are conducive to the sorption or breakdown of pesticides. Most of the pesticides detected were metabolites that had already been partially broken down (fig. 33).

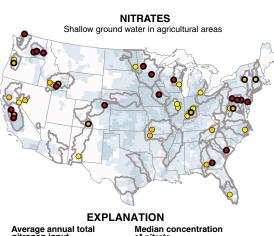
Nitrate also can be transformed in the subsurface. In the presence of organic matter, low dissolvedoxygen concentrations are conducive to denitrification. Groundwater samples from 100 percent of the domestic wells and 50 percent of the monitor wells had dissolvedoxygen concentrations less than 1 mg/L. In addition, the till contains numerous fragments of black shale rich in pyrite, a mineral that can also lead to denitrification (Robertson and others, 1996).

Within the study area, the thickness and composition of the till are variable and not well defined in all locations. Therefore, the degree to which the till protects the ground water—by physical or geochemical means—is probably also variable and difficult to predict.

Low detections of agrochemicals in ground water may be partly due to tile drains, which can divert contaminants from the shallow ground water to streams (Nolan and Stoner, 2000), but tile drains do not completely prevent contaminants from reaching shallow ground water. Nitrate and pesticides were detected in monitor wells 10 to 34 feet deep, whereas tile drains are typically about 3 feet deep. Vertical fractures in the till can provide a direct pathway from the land surface to the water table.



Nitrate and herbicides in ground water in agricultural areas



Average annual total nitrogen input--in pounds per acre, by county, for 1995-98. Inputs are from fertilizer, manure, and the atmosphere

- Greater than 25
- ☐ 6 to 25 Less than 6

- of nitrate-in milligrams per liter. Each circle
 represents a ground-water study
- Highest (greater than 5.1)Medium (.48 to 5.1)
- O Lowest (less than .48)

Background concentration

 Bold outline indicates median values greater than background concentration (2 milligrams per liter)

In general, agrochemicals are most frequently detected where they are most heavily used; but exceptions to this pattern have been found (U.S. Geological Survey, 1999). For example, in the agricultural study area, detections of nitrate and herbicides in shallow ground water are among the lowest in the Nation even though nitrogen inputs and herbicide use are among the highest. In deeper ground water, nitrate and herbicide detections are also low relative to the Nation as a whole.

A similar phenomenon has been noted elsewhere. In parts of the Midwest, the proposed explanations for low detections of nitrate in ground water are that (1) till impedes movement of contaminants from land surface, or (2) tile drains divert contaminants to streams (Fenelon, 1998; Nolan and Stoner, 2000). In an area of the Southeast Coastal Plain, biogeochemical processes are the proposed cause of the low detections (Nolan and Stoner, 2000). In the study area, low detections of nitrate (and herbicides) are probably due to a combination of physical and geochemical processes.

Stream Chemistry

A network of 10 stream sites was sampled for various chemical constituents and physical properties from March 1996 through February 1998 (fig. 35, table 3). Sampling was done over a range of streamflows. Sites were sampled 18–32 times per year; intensive sites were sampled more frequently than basic sites (table 3).

Assessments of contaminants in streambed sediments and fish tissue were made at the 10 fixed streams sites and at one to five

additional sites. Sediment samples were collected and sieved in the field. Whole fish were collected and analyzed for concentrations of organochlorine compounds. Fish livers were analyzed for trace-element concentrations.

Stream Ecology

Sampling was done at least once at 10 sites where water samples were collected. Multiple-year and multiple-reach sampling was done at three sites (table 3). Stream

reaches ranged from 200 to 500 meters in length.

Fish surveys involved electrofishing and seining. Macroinvertebrates and algae were sampled from natural substrates. Habitats were assessed by identifying and mapping riparian vegetation and measuring geomorphic features of stream channels. Samples of bed and bank materials were collected and analyzed for grain size.

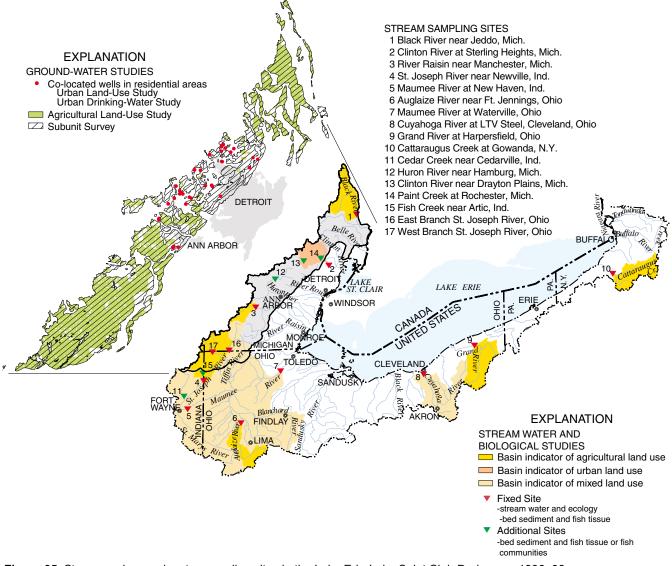


Figure 35. Stream and ground-water sampling sites in the Lake Erie-Lake Saint Clair Drainages, 1996–98.

TABLE 3. SUMMARY OF DATA COLLECTION IN THE LAKE ERIE-LAKE SAINT CLAIR DRAINAGES, 1996-98

Study component	What data were collected and why	Types of sites sampled	Number of sites	Sampling frequency and period			
Stream Chemistry							
Contaminants in stream- water— basic sites	Streamflow, pH, specific conductance, temperature and concentrations of nitrogen and phosphorus compounds, major ions, organic carbon, suspended sediment, herbicides, and <i>E. coli</i> were measured to determine occurrence and distribution of contaminants and other constituents	Streams draining areas ranging in size from 132 square miles to 1,230 square miles reflecting agricultural, urban, and mixed land uses.	6	Monthly, plus storms and low flows from March 1996 to February 1998			
Contaminants in stream- water— intensive sites	Physical properties and chemical and microbiological constituents mentioned above plus insecticides and VOCs.	Streams draining areas ranging from 310 square miles to 6,330 square miles reflecting agricultural, urban, and mixed land uses.	4	Weekly to monthly, plus storms and low flows from October 1996 to September 1997, bracketed by monthly plus storms from March 1996 to Febru- ary 1998			
Contaminants in streambed sediment	Concentrations as dry weight of trace elements, semivolatile organic compounds, organochlorine compounds, and percent organic content. Determined to assess occurrence and distribution of contaminants.	reach at all 10 sites sampled for stream- water chemistry and at 5 additional sites	15	One to three times in June–October, 1996– 98			
Contaminants in fish tissue	Concentrations of trace elements in fish liver and orga- nochlorine compounds, such as PCBs and organochlo- rine pesticides, in fish tissue were analyzed to determine occurrence and distribution.	Resident fish such as carp, rock bass, and hog suckers at all sites sampled for stream-water chemistry and at one additional site	15	One to three times in June–October, 1996– 98			
		am Ecology					
Aquatic biota at stream sites	Community composition of aquatic macroinvertebrates, algae, fish and stream habitat were surveyed to determine effects of water quality on aquatic biota.	Sites co-located with basic and intensive stream-water chemistry sites and at three additional sites	10	One to three times in June–October in 1996– 98			
	Ground-	Water Chemistry					
Subunit survey	Water level, pH, specific conductance, temperature and con- centrations of nitrogen and phosphorus compounds, major ions, VOCs, organic carbon, insecticides, herbi- cides, herbicide degradates, radon, and tritium were mea- sured to determine the quality of an aquifer that is an important source of drinking water.	Domestic wells in the northwestern part of the Study Unit. Eighteen of the wells are co-located with monitor wells of the	28	Once, June–August 1998			
Agricultural land-use study	Above measurements and compounds (except VOCs and radon) to determine the effects of agricultural land use on shallow ground water.	Monitor wells in agricultural areas in northwestern part of Study Unit.	30	Once, June–August, 1998			
Urban land-use study	Above compounds (plus VOCs and radon) to determine effects of recent residential development on shallow ground water.	Monitor wells in new residential areas near Detroit, Mich.	30	Once, September– December 1996			
		ecial Study					
Urban drink- ing-water study	Same as for Subunit survey	Domestic wells co-located with urban land- use wells in new residential areas near Detroit.	28	Once, May–July 1997			

Ground-Water Chemistry

Four ground-water studies were done in the northwestern part of the basin (fig. 35), where glacial deposits greater than 100 feet thick serve as the major source of drinking water.

Two of the studies were done on the far outskirts of Detroit, where recent residential developments overlie sand and gravel. An urban land-use study was done by installing and sampling 30 shallow monitor wells (table 3). A second study involved sampling 28 domestic-supply wells, each of which was co-located with a monitor well.

The agricultural land-use study was done in areas where corn and soybean row crops overlie clayrich till. Thirty shallow monitor wells were installed in the till and sampled for a various constituents, including pesticide metabolites.

The subunit survey involved sampling 28 domestic wells that produce water from the glacial aquifer in areas where it is overlain by till. Of the 28 wells, 18 were colocated with monitor wells in the agricultural land-use study area (fig. 35).

- **Anthropogenic** A condition or occurrence that is the result of, or is influenced by, human activity.
- **Aquifer** A water-bearing layer of soil, sand, gravel, or rock that will yield usable quantities of water to a well.
- **Background concentration** A concentration of a substance in a particular environment that is indicative of minimal influence by human (anthropogenic) sources.
- **Base flow** Sustained, low flow in a stream; ground-water discharge is the source of base flow in most places.
- **Bed sediment** The material that temporarily is stationary in the bottom of a stream or other watercourse.
- **Benthic** Refers to plants or animals that live on the bottom of lakes, streams, or oceans.
- Bioaccumulation The biological sequestering of a substance at a higher concentration than that at which it occurs in the surrounding environment or medium.

 Also, the process whereby a substance enters organisms through the gills, epithelial tissues, dietary, or other sources.
- **Biota** Living organisms.
- **Breakdown product** A compound derived by chemical, biological, or physical action upon a pesticide. The breakdown is a natural process which may result in a more toxic or a less toxic compound and a more persistent or less persistent compound.
- **BTEX** Benzene, toluene, ethylbenzene, and xylene; volatile organic compounds found in gasoline and solvents.
- **Chlordane** Octachloro-4,7-methanotetrahydroindane. An organochlorine insecticide no longer registered for use in the U.S. Technical chlordane is a mixture in which the primary components are *cis* and *trans*-chlordane, *cis* and *trans*-nonachlor, and heptachlor.
- **Community** In ecology, the species that interact in a common area.
- **Concentration** The amount or mass of a substance present in a given volume or mass of sample. Usually expressed as microgram per liter (water sample) or micrograms per kilogram (sediment or tissue sample).
- **Denitrification** A process by which oxidized forms of nitrogen such as nitrate (NO₃⁻) are reduced to form nitrites, nitrogen oxides, ammonia, or free nitrogen: commonly brought about by the action of denitrifying bacteria and usually resulting in the escape of nitrogen to the air.
- **Detect** To determine the presence of a compound.
- **DDT** Dichloro-diphenyl-trichloroethane. An organochlorine insecticide no longer registered for use in the United States.
- **Dieldrin** An organochlorine insecticide no longer registered for use in the United States. Also a degradation product of the insecticide aldrin.
- **Discharge** Rate of fluid flow passing a given point at a given moment in time, expressed as volume per unit of time.

- **Domestic well** A private home well, or a well that serves less than 15 households or 25 individuals.
- **Endocrine system -** The collection of glands in animals that secrete hormones, which influence growth, gender and sexual maturity.
- **Eutrophication** The process by which water becomes enriched with plant nutrients, most commonly phosphorus and nitrogen.
- **Ground water** In general, any water that exists beneath the land surface, but more commonly applied to water in fully saturated soils and geologic formations.
- **Herbicide** A chemical or other agent applied for the purpose of killing undesirable plants. See also Pesticide.
- **Insecticide** A substance or mixture of substances intended to destroy or repel insects.
- Intolerant organisms Organisms that are not adaptable to human alterations to the environment and thus decline in numbers where human alterations occur. See also Tolerant species.
- Invertebrate An animal having no backbone or spinal col-
- MCL (Maximum Contaminant Level) Maximum permissible level of a contaminant in water that is delivered to any user of a public water system. MCLs are enforceable standards established by the U.S. Environmental Protection Agency.
- **Median** The middle or central value in a distribution of data ranked in order of magnitude. The median is also known as the 50th percentile.
- Metabolite See breakdown product.
- **Monitor well** A well designed for measuring water levels and testing ground-water quality.
- **Nitrate** An ion consisting of nitrogen and oxygen (NO₃⁻). Nitrate is a plant nutrient and is very mobile in soils. In this report, the term "nitrate" is used as shorthand for "nitrate plus nitrite, reported as nitrogen."
- **Nutrient** Element or compound essential for animal and plant growth. Common nutrients in fertilizer include nitrogen, phosphorus, and potassium.
- Organochlorine compound Synthetic organic compound containing chlorine. As generally used, term refers to compounds containing mostly or exclusively carbon, hydrogen, and chlorine. Examples include organochlorine insecticides, polychlorinated biphenyls, and some solvents containing chlorine.
- **Pesticide** A chemical applied to crops, rights of way, lawns, or residences to control weeds, insects, fungi, nematodes, rodents or other "pests."
- **Phosphorus** A nutrient essential for growth that can play a key role in stimulating aquatic growth in lakes and streams.
- **Polychlorinated biphenyls (PCBs)** A mixture of chlorinated derivatives of biphenyl, marketed under the trade name Aroclor with a number designating the chlorine

- content (such as Aroclor 1260). PCBs were used in transformers and capacitors for insulating purposes and in gas pipeline systems as a lubricant. Further sale for new use was banned by law in 1979.
- Polycyclic aromatic hydrocarbon (PAH) A class of organic compounds with a fused-ring aromatic structure. PAHs result from incomplete combustion of organic carbon (including wood), municipal solid waste, and fossil fuels, as well as from natural or anthropogenic introduction of uncombusted coal and oil. PAHs include benzo[a]pyrene, fluoranthene, and pyrene.
- **Recharge** Water that infiltrates the ground and reaches the saturated zone.
- **Runoff** Excess rainwater or snowmelt that is transported to streams by overland flow, tile drains, or ground water.
- SMCL (Secondary maximum contaminant level) Nonenforceable drinking-water standards established by the U.S. Environmental Protection Agency for contaminants that may adversely affect the odor or appearance of drinking water.
- **Sediment** Particles, derived from rocks or biological materials, that have been transported by a fluid or other natural process, suspended or settled in water.
- Semivolatile organic compound (SVOC) Operationally defined as a group of synthetic organic compounds that are solvent-extractable and can be determined by gas chromatography/mass spectrometry. SVOCs include phenols, phthalates, and polycyclic aromatic hydrocarbons (PAHs).
- **Streamflow** A type of channel flow, applied to that part of surface runoff in a stream whether or not it is affected by diversion or regulation.
- **Suspended sediment** Particles of rock, sand, soil, and organic detritus carried in suspension in the water column, in contrast to sediment that moves on or near the streambed.
- **Taxon (plural taxa)** Any identifiable group of taxonomically related organisms.
- **Tile drain** A buried perforated pipe designed to remove excess water from soils.
- Till An unsorted glacial deposit characterized by low permeability.
- **Triazine herbicide** A class of herbicides containing a symmetrical triazine ring (a nitrogen-heterocyclic ring composed of three nitrogens and three carbons in an alternating sequence). Examples include atrazine, propazine, and simazine.
- Volatile organic compounds (VOCs) Organic chemicals that have a high vapor pressure relative to their water solubility. VOCs include components of gasoline, fuel oils, and lubricants, as well as organic solvents, fumigants, some inert ingredients in pesticides, and some by-products of chlorine disinfection.

- Water table The point below the land surface where ground water is first encountered and below which the earth is saturated. Depth to the water table varies widely across the country.
- Water year The continuous 12-month period, October 1 through September 30, in U.S. Geological Survey reports dealing with the surface-water supply. The water year is designated by the calendar year in which it ends and which includes 9 of the 12 months. Thus, the year ending September 30, 1980, is referred to as water year 1980.

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APPENDIX—WATER-QUALITY DATA FROM THE LAKE ERIE-LAKE SAINT CLAIR DRAINAGES IN A NATIONAL CONTEXT

For a complete view of Lake Erie-Lake Saint Clair Drainages data and for additional information about specific benchmarks used, visit our Web site at http://water.usgs.gov/nawqa/. Also visit the NAWQA Data Warehouse for access to NAWQA data sets at http://water.usgs.gov/nawqa/data.

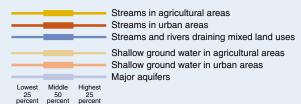
This appendix is a summary of chemical concentrations and biological indicators assessed in the Lake Erie-Lake Saint Clair Drainages. Selected results for this Study Unit are graphically compared to results from as many as 36 NAWQA Study Units investigated from 1991 to 1998 and to national water-quality benchmarks for human health, aquatic life, or fish-eating wildlife. The chemical and biological indicators shown were selected on the basis of frequent detection, detection at concentrations above a national benchmark, or regulatory or scientific importance. The graphs illustrate how conditions associated with each land use sampled in the Lake Erie-Lake Saint Clair Drainages compare to results from across the Nation, and how conditions compare among the several land uses. Graphs for chemicals show only detected concentrations and, thus, care must be taken to evaluate detection frequencies in addition to concentrations when comparing study-unit and national results. For example, in the Lake Erie-Lake Saint Clair Drainages acetochlor concentrations in agricultural streams were similar to the national distribution, but the detection frequency was much higher (61 percent compared to 33 percent).

CHEMICALS IN WATER

Concentrations and detection frequencies, Lake Erie-Lake Saint Clair Drainages, 1996–98—Detection sensitivity varies among chemicals and, thus, frequencies are not directly comparable among chemicals

- ◆ Detected concentration in Study Unit
- 66 38 Frequencies of detection, in percent. Detection frequencies were not censored at any common reporting limit. The lefthand column is the study-unit frequency and the right-hand column is the national frequency
 - -- Not measured or sample size less than two
 - 12 Study-unit sample size. For ground water, the number of samples is equal to the number of wells sampled

National ranges of detected concentrations, by land use, in 36 NAWQA Study Units, 1991–98—Ranges include only samples in which a chemical was detected

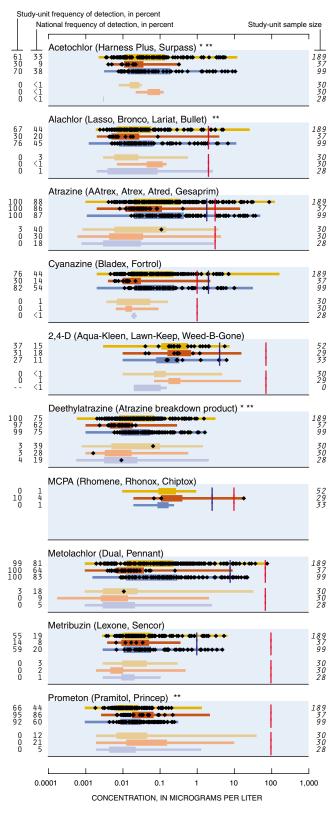


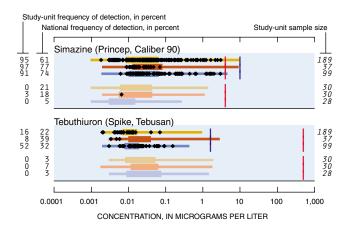
National water-quality benchmarks

National benchmarks include standards and guidelines related to drinking-water quality, criteria for protecting the health of aquatic life, and a goal for preventing stream eutrophication due to phosphorus. Sources include the U.S. Environmental Protection Agency and the Canadian Council of Ministers of the Environment

- Drinking-water quality (applies to ground water and surface water)
- Protection of aquatic life (applies to surface water only)
- Prevention of eutrophication in streams not flowing directly into lakes or impoundments
- No benchmark for drinking-water quality
- ** No benchmark for protection of aquatic life

Pesticides in water—Herbicides





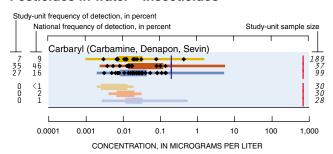
Other herbicides detected

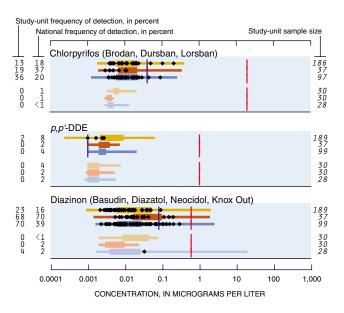
Acifluorfen (Blazer, Tackle 2S) ** Benfluralin (Balan, Benefin, Bonalan) * ** Bentazon (Basagran, Bentazone) Bromoxynil (Buctril, Brominal) Butylate (Sutan +, Genate Plus, Butilate) ** DCPA (Dacthal, chlorthal-dimethyl) * Dicamba (Banvel, Dianat, Scotts Proturf) 2,6-Diethylaniline (Alachlor breakdown product) * ** Diuron (Crisuron, Karmex, Diurex) EPTC (Eptam, Farmarox, Alirox) ' Fenuron (Fenulon, Fenidim) * Linuron (Lorox, Linex, Sarclex, Linurex, Afalon) * MCPB (Thistrol) * Pendimethalin (Pre-M, Prowl, Stomp) * ** Picloram (Grazon, Tordon) Propachlor (Ramrod, Satecid) ** Terbacil (Sinbar) 3 Triclopyr (Garlon, Grandstand, Redeem, Remedy) * ** Trifluralin (Treflan, Gowan, Tri-4, Trific)

Herbicides not detected

Bromacil (Hyvar X, Urox B, Bromax) Chloramben (Amiben, Amilon-WP, Vegiben) ** Clopyralid (Stinger, Lontrel, Transline) 2,4-DB (Butyrac, Butoxone, Embutox Plus, Embutone) * ** Dacthal mono-acid (Dacthal breakdown product) * Dichlorprop (2,4-DP, Seritox 50, Lentemul) * ** Dinoseb (Dinosebe) Ethalfluralin (Sonalan, Curbit) * ** Fluometuron (Flo-Met, Cotoran) ** Molinate (Ordram) * * Napropamide (Devrinol) * ** Neburon (Neburea, Neburyl, Noruben) * **
Norflurazon (Evital, Predict, Solicam, Zorial) * **
Oryzalin (Surflan, Dirimal) * ** Oryzalin (Surflan, Dirimal) Pebulate (Tillam, PEBC) ' Pronamide (Kerb, Propyzamid) ** Propanil (Stam, Stampede, Wham) * **
Propham (Tuberite) ** 2,4,5-T 2,4,5-TP (Silvex, Fenoprop) ** Thiobencarb (Bolero, Saturn, Benthiocarb) * **

Pesticides in water—Insecticides





Other insecticides detected

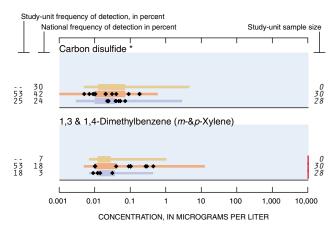
Carbofuran (Furadan, Curaterr, Yaltox)
Dieldrin (Panoram D-31, Octalox, Compound 497)
Fonofos (Dyfonate, Capfos, Cudgel, Tycap) **
alpha-HCH (alpha-BHC, alpha-lindane) **
Malathion (Malathion)
Methyl parathion (Penncap-M, Folidol-M) **

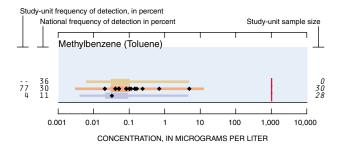
Insecticides not detected

Aldicarb (Temik, Ambush, Pounce) Aldicarb sulfone (Standak, aldoxycarb) Aldicarb sulfoxide (Aldicarb breakdown product) Azinphos-methyl (Guthion, Gusathion M) Disulfoton (Disyston, Di-Syston) ** Ethoprop (Mocap, Ethoprophos) * ** gamma-HCH (Lindane, gamma-BHC) 3-Hydroxycarbofuran (Carbofuran breakdown product) * ** Methiocarb (Slug-Geta, Grandslam, Mesurol) Methomyl (Lanox, Lannate, Acinate) Oxamyl (Vydate L, Pratt) ** Parathion (Roethyl-P, Alkron, Panthion, Phoskil) * cis-Permethrin (Ambush, Astro, Pounce) * * Phorate (Thimet, Granutox, Geomet, Rampart) * ** Propargite (Comite, Omite, Ornamite) Propoxur (Baygon, Blattanex, Unden, Proprotox) * ** Terbufos (Contraven, Counter, Pilarfox)

Volatile organic compounds (VOCs) in ground water

These graphs represent data from 16 Study Units, sampled from 1996 to 1998





Other VOCs detected

Benzene

Bromodichloromethane (Dichlorobromomethane)

2-Butanone (Methyl ethyl ketone (MEK)) '

Chlorodibromomethane (Dibromochloromethane)

1,4-Dichlorobenzene (p-Dichlorobenzene)

Dichlorodifluoromethane (CFC 12, Freon 12)

Dichloromethane (Methylene chloride)

1.2-Dimethylbenzene (o-Xylene)

1-4-Epoxy butane (Tetrahydrofuran, Diethylene oxide) *

Ethenylbenzene (Styrene) Ethylbenzene (Phenylethane)

Iodomethane (Methyl iodide)

2-Propanone (Acetone)

Tetrachloroethene (Perchloroethene)

1,1,1-Trichloroethane (Methylchloroform)

Trichloromethane (Chloroform)

1,2,4-Trimethylbenzene (Pseudocumene) *

VOCs not detected

tert-Amylmethylether (tert-amyl methyl ether (TAME)) *

Bromobenzene (Phenyl bromide)

Bromochloromethane (Methylene chlorobromide)

Bromoethene (Vinyl bromide) *

Bromomethane (Methyl bromide)

n-Butylbenzene (1-Phenylbutane) *

sec-Butylbenzene *

tert-Butylbenzene '

3-Chloro-1-propene (3-Chloropropene) *

1-Chloro-2-methylbenzene (o-Chlorotoluene)

1-Chloro-4-methylbenzene (p-Chlorotoluene)

Chlorobenzene (Monochlorobenzene)

Chloroethane (Ethyl chloride)

Chloroethene (Vinyl chloride)

Chloromethane (Methyl chloride)

1,2-Dibromo-3-chloropropane (DBCP, Nemagon)

1,2-Dibromoethane (Ethylene dibromide, EDB)

Dibromomethane (Methylene dibromide)

trans-1,4-Dichloro-2-butene ((Z)-1,4-Dichloro-2-butene) *

1,2-Dichlorobenzene (o-Dichlorobenzene)

1.3-Dichlorobenzene (m-Dichlorobenzene)

1,2-Dichloroethane (Ethylene dichloride)

1,1-Dichloroethane (Ethylidene dichloride)

1,1-Dichloroethene (Vinylidene chloride)

trans-1,2-Dichloroethene ((E)-1,2-Dichlorothene)

cis-1,2-Dichloroethene ((Z)-1,2-Dichloroethene)

1,2-Dichloropropane (Propylene dichloride)

2,2-Dichloropropane

1,3-Dichloropropane (Trimethylene dichloride) *

trans-1,3-Dichloropropene ((E)-1,3-Dichloropropene)

cis-1,3-Dichloropropene ((Z)-1,3-Dichloropropene)

1,1-Dichloropropene

Diethyl ether (Ethyl ether) *

Diisopropyl ether (Diisopropylether (DIPE)) *

Ethyl methacrylate *

Ethyl tert-butyl ether (Ethyl-t-butyl ether (ETBE)) *

1-Ethyl-2-methylbenzene (2-Ethyltoluene) *

Hexachlorobutadiene

1,1,1,2,2,2-Hexachloroethane (Hexachloroethane)

2-Hexanone (Methyl butyl ketone (MBK)) *

Isopropylbenzene (Cumene) *

p-Isopropyltoluene (p-Cymene) *

Methyl acrylonitrile *

Methyl tert-butyl ether (MTBE)

Methyl-2-methacrylate (Methyl methacrylate) *

4-Methyl-2-pentanone (Methyl isobutyl ketone (MIBK)) *

Methyl-2-propenoate (Methyl acrylate) *

Naphthalene

2-Propenenitrile (Acrylonitrile)

n-Propylbenzene (Isocumene)

1,1,2,2-Tetrachloroethane *

1,1,1,2-Tetrachloroethane Tetrachloromethane (Carbon tetrachloride)

1,2,3,4-Tetramethylbenzene (Prehnitene)

1,2,3,5-Tetramethylbenzene (Isodurene) Tribromomethane (Bromoform)

1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113) *

1,2,4-Trichlorobenzene

1,2,3-Trichlorobenzene '

1,1,2-Trichloroethane (Vinyl trichloride)

Trichloroethene (TCE)

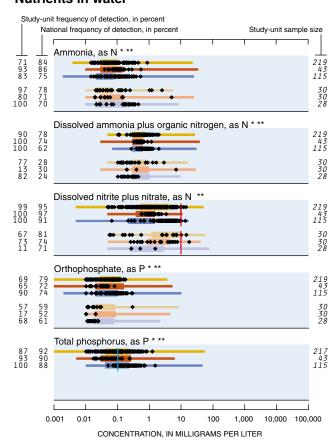
Trichlorofluoromethane (CFC 11, Freon 11)

1,2,3-Trichloropropane (Allyl trichloride)

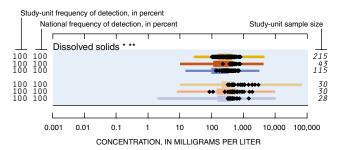
1,2,3-Trimethylbenzene (Hemimellitene)

1,3,5-Trimethylbenzene (Mesitylene) '

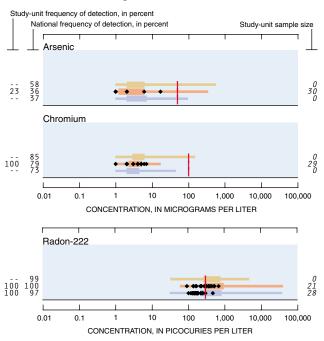
Nutrients in water



Dissolved solids in water



Trace elements in ground water



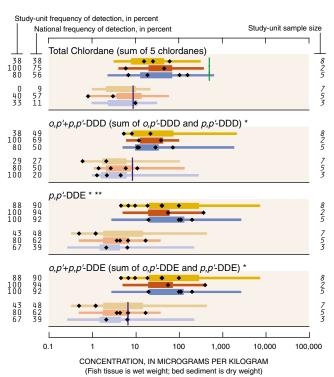
Other trace elements detected

Lead Selenium Uranium Zinc

Trace elements not detected

Cadmium

Organochlorines in fish tissue (whole body) and bed sediment

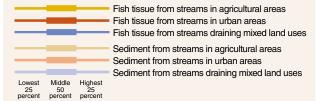


CHEMICALS IN FISH TISSUE AND BED SEDIMENT

Concentrations and detection frequencies, Lake Erie-Lake Saint Clair Drainages, 1996–98—Detection sensitivity varies among chemicals and, thus, frequencies are not directly comparable among chemicals. Study-unit frequencies of detection are based on small sample sizes; the applicable sample size is specified in each graph

- ◆ Detected concentration in Study Unit
- 66 38 Frequencies of detection, in percent. Detection frequencies were not censored at any common reporting limit. The lefthand column is the study-unit frequency and the right-hand column is the national frequency
 - -- Not measured or sample size less than two
 - 12 Study-unit sample size

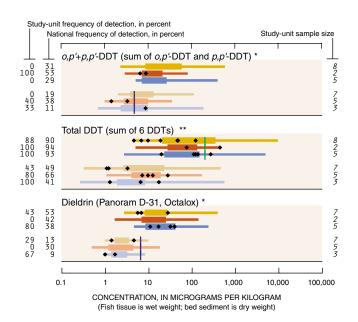
National ranges of concentrations detected, by land use, in 36 NAWQA Study Units, 1991–98—Ranges include only samples in which a chemical was detected

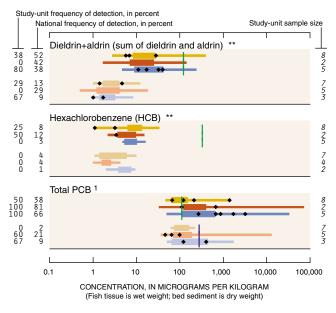


National benchmarks for fish tissue and bed sediment

National benchmarks include standards and guidelines related to criteria for protection of the health of fish-eating wildlife and aquatic organisms. Sources include the U.S. Environmental Protection Agency, other Federal and State agencies, and the Canadian Council of Ministers of the Environment

- Protection of fish-eating wildlife (applies to fish tissue)
- Protection of aquatic life (applies to bed sediment)
- No benchmark for protection of fish-eating wildlife
- ** No benchmark for protection of aquatic life





¹ The national detection frequencies for total PCB in sediment are biased low because about 30 percent of samples nationally had elevated detection levels compared to this Study Unit. See http://water.usgs.gov/nawqa/ for additional information.

Other organochlorines detected

Heptachlor epoxide (Heptachlor breakdown product) * Heptachlor+heptachlor epoxide (sum of heptachlor and heptachlor epoxide) **Pentachloroanisole (PCA) * **

Organochlorines not detected

Chloroneb (Chloronebe, Demosan) * **
DCPA (Dacthal, chlorthal-dimethyl) * **

Endosulfan I (alpha-Endosulfan, Thiodan) * **

Endrin (Endrine)

gamma-HCH (Lindane, gamma-BHC, Gammexane) *

Total-HCH (sum of alpha-HCH, beta-HCH, gamma-HCH, and delta-HCH) $\,^{**}$ Isodrin (Isodrine, Compound 711) * **

p,p'-Methoxychlor (Marlate, methoxychlore) * **

o,p'-Methoxychlor * **

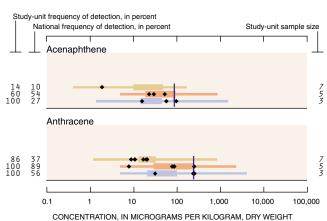
Mirex (Dechlorane) **

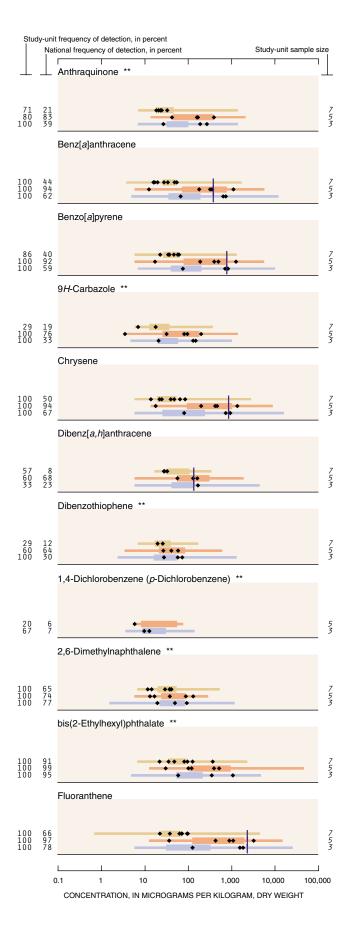
cis-Permethrin (Ambush, Astro, Pounce) * **

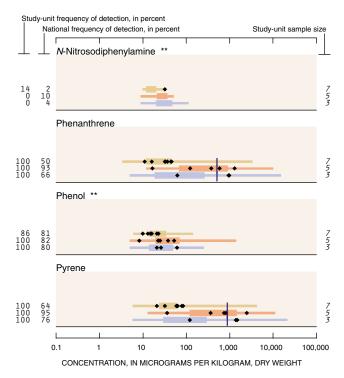
trans-Permethrin (Ambush, Astro, Pounce) * **

Toxaphene (Camphechlor, Hercules 3956) * **

Semivolatile organic compounds (SVOCs) in bed sediment







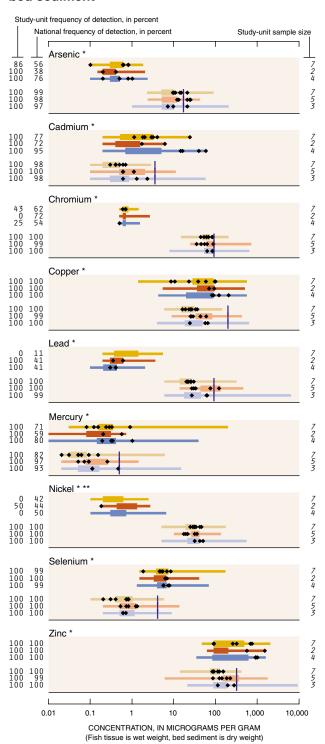
Other SVOCs detected

Acenaphthylene Acridine ** Benzo[b]fluoranthene ** Benzo[c]cinnoline Benzo[ghi]perylene ** Benzo[k]fluoranthene ** 2,2-Biquinoline Butylbenzylphthalate ** p-Cresol ** Di-n-butylphthalate ** Di-n-octylphthalate ** Diethylphthalate ' 1,2-Dimethylnaphthalene ** 1,6-Dimethylnaphthalene **
3,5-Dimethylphenol ** Dimethylphthalate ** 2-Ethylnaphthalene ** 9H-Fluorene (Fluorene) Indeno[1,2,3-cd]pyrene **
Isophorone ** Isoquinoline ** 1-Methyl-9*H*-fluorene ** 2-Methylanthracene ** 4,5-Methylenephenanthrene ** 1-Methylphenanthrene * 1-Methylpyrene ** Naphthalene Phenanthridine **

2,3,6-Trimethylnaphthalene **

SVOCs not detected C8-Alkylphenol Azobenzene ** 4-Bromophenyl-phenylether ** 4-Chloro-3-methylphenol ** bis(2-Chloroethoxy)methane ** 2-Chloronaphthalene 2-Chlorophenol ' 4-Chlorophenyl-phenylether ** 1,2-Dichlorobenzene (o-Dichlorobenzene) ** 1,3-Dichlorobenzene (m-Dichlorobenzene) ** 2,4-Dinitrotoluene ' Nitrobenzene ** N-Nitrosodi-n-propylamine ** Pentachloronitrobenzene Quinoline ** 1,2,4-Trichlorobenzene **

Trace elements in fish tissue (livers) and bed sediment



BIOLOGICAL INDICATORS

Higher national scores suggest habitat disturbance, water-quality degradation, or naturally harsh conditions. The status of algae, invertebrates (insects, worms, and clams), and fish provide a record of water-quality and stream conditions that water-chemistry indicators may not reveal. **Algal status** focuses on the changes in the percentage of certain algae in response to increasing siltation, and it often correlates with higher nutrient concentrations in some regions. **Invertebrate status** averages 11 metrics that summarize changes in richness, tolerance, trophic conditions, and dominance associated with water-quality degradation. **Fish status** sums the scores of four fish metrics (percent tolerant, omnivorous, non-native individuals, and percent individuals with external anomalies) that increase in association with water-quality degradation

Biological indicator value, Lake Erie - Lake Saint Clair Drainages, by land use, 1996–98

♦ Biological status assessed at a site

National ranges of biological indicators, in 16 NAWQA Study Units, 1994–98

Streams in undeveloped areas

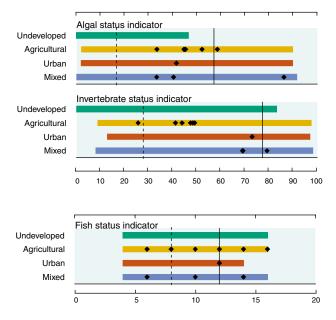
Streams in agricultural areas

Streams in urban areas

Streams in mixed-land-use areas

- 75th percentile

- - 25th percentile



A COORDINATED EFFORT

Coordination with agencies and organizations in the Lake Erie-Lake Saint Clair Drainages was integral to the success of this water-quality assessment. We thank those who served as members of our liaison committee.

Federal Agencies

U.S. Environmental Protection Agency

U.S. Army Corps of Engineers

U.S. Department of Agriculture

Environment Canada, Great Lakes Division

State Agencies

Ohio Environmental Protection Agency
Ohio Department of Natural Resources
Ohio Lake Erie Commission
Michigan Department of Agriculture
Michigan Department of Environmental Quality
Indiana Department of Natural Resources
New York Department of Environmental Conservation

Local Agencies

City of Fort Wayne
City of Toledo
Southeast Michigan Council of Governments
Washtenaw County, Michigan, Health Department
Oakland County, Michigan, Health Department
Allen County, Indiana, Soil and Water Conservation
District

Other public and private organizations

Rouge River Program Office, Michigan The Nature Conservancy Great Lakes Commission International Association of Great Lakes Researchers Michigan State University University of Michigan, Dearborn

We thank the following individuals for contributing to this effort.

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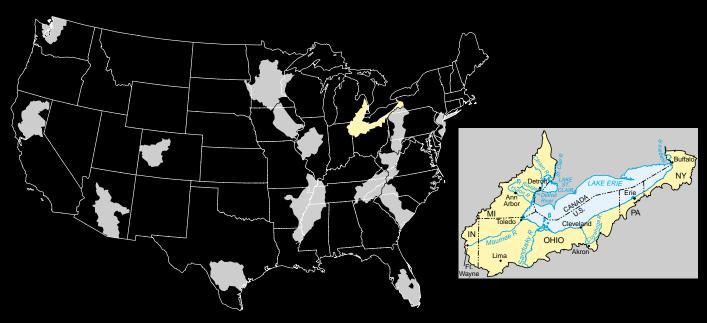
Special thanks to U.S. Geological Survey employees for their contributions:

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NAVQA

National Water-Quality Assessment (NAWQA) Program Lake Erie-Lake Saint Clair Drainages





rs and others—Water Quality in the Lake Erie-Lake Saint Clair Drainages U.S. Geological Survey Circular 1203

