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Occurrence, Distribution, and Loads of Selected Pesticides in Streams in the Lake Erie-Lake St. Clair Basin, 1996–98

By Jeffrey W. Frey

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<URL:http://water.usgs.gov/nawqa>

Foreword

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

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

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

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

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

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

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Conversion Factors, Vertical Datum, and Abbreviations

Multiply	By	To obtain
inch (in.)	25.4	millimeter
inch per year (in/yr)	25.4	millimeter per year
foot (ft)	0.3048	meter
square foot (ft^2)	0.09290	square meter
mile (mi)	1.609	kilometer
square mile (mi^2)	2.590	square kilometer
gallon (gal)	3.785	liter
cubic foot per second (ft^3/s)	0.02832	cubic meter per second
pound per day (lb/d)	0.4536	kilogram per day

Temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) as follows:

$$°F = 1.8 \times °C + 32$$

Vertical Datum: In this report, “sea level” refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

The following abbreviations and acronyms are used in this report:

a.i.	active ingredient
K_{oc}	organic-carbon-normalized adsorption coefficient
ESA	ethane sulfonic acid
GC/MS	gas chromatography/mass spectrometry
HA-L	health advisory lifetime value
HPLC	high performance liquid chromatography
IBI	Index of Biological Integrity
IJC	International Joint Commission
LC/MS	liquid chromatography/mass spectrometry
MCL	Maximum Contaminant Level
MCPP	2-(4-chloro-2-methylphenoxy)-propanoic acid, potassium salt
MDL	method detection limit
MRLC	Multi-Resolution Land Characteristics
MS	mass spectrometry
NAWQA	National Water-Quality Assessment Program
NWQL	National Water Quality Laboratory
QHEI	Qualitative Habitat Evaluation Index
RSD	risk-specific dosage
SPE	solid phase extraction
STATSGO	State Soil Geographic Data Base
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
L	liter
mL	milliliter
mg/L	milligram per liter
µg/L	microgram per liter
mm	millimeter

Occurrence, Distribution, and Loads of Selected Pesticides in Streams in the Lake Erie-Lake St. Clair Basin, 1996–98

By Jeffrey W. Frey

Abstract

Thirty pesticides or their degradates were detected in 315 samples collected from 10 streams in the Lake Erie-Lake St. Clair Basin between March 1996 and February 1998 as part of the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program. Atrazine was detected in every sample, and deethylatrazine, metolachlor, and simazine were detected in more than 90 percent of all samples. Atrazine and metolachlor, the most heavily applied pesticides in the Basin, had the highest detected concentrations (85 and 78 micrograms per liter, respectively). No annual average concentrations exceeded the U.S. Environmental Protection Agency Maximum Contaminant Level or health advisory level at any of the surface-water-sampling sites. Seasonally elevated pesticide concentrations, however, have economic consequences on water-treatment facilities required to remove pesticides in water to meet drinking-water standards. From May through July, when most pesticides are transported by runoff into streams, time-weighted average concentrations of atrazine exceeded the Maximum Contaminant Level at five row-crop sites, and time-weighted average concentrations of atrazine and cyanazine frequently exceeded lifetime adult health advisories at these same sites. For some heavily used herbicides such as atrazine, metolachlor, cyanazine, and acetochlor, elevated concentrations persisted 4 to 6 weeks after the initial maximum concentration in the row-crop streams was measured.

Land use and physical processes can affect the occurrence and distribution of pesticides. Pesticides were detected at greater frequency and at higher concentrations in samples from streams in basins dominated by row-crop agriculture than in samples from streams in urban or pasture/forest areas. Maximum measured concentrations were higher in 1997 than in 1996 and probably were related to greater precipitation in 1997. Generally, the number of pesticides detected in a basin increased with basin size. Pesticide concentrations showed strong seasonal trends related to the timing and amount of pesticide application. Row-crop herbicides applied in the spring, such as atrazine, had maximum measured concentrations in the spring; pesticides typically applied in late summer and early fall, such as diazinon, had maximum measured concentrations then. The increased number of detections and maximum measured concentrations of acetochlor and the corresponding decrease in the number of detections and concentrations of alachlor reflected changes in the amount of pesticides applied during the sampling period. The percentage of the applied atrazine that was detected in streams, in general, increased when the percentage of impermeable soils within each basin increased.

Loads and yields of selected pesticides were calculated. The highest loads calculated were those for atrazine and metolachlor in the Maumee River at Waterville, Ohio, with 47,000 and 44,000 pounds per year, respectively. Of the row-crop basins, either the St. Joseph River near Newville, Ind., or the Auglaize River near Fort Jennings, Ohio, had the highest yields for the herbicides acetochlor, alachlor, atrazine, cyanazine, metolachlor, and simazine. The Cuyahoga River at Cleveland, Ohio, had the highest yields for diazinon and prometon—pesticides that typically are applied heavily in urban areas. The percentage of the applied atrazine that was calculated in the stream was determined for each basin in 1997. The export of atrazine ranged from 0.10 percent at the River Raisin near Manchester, Mich., to 10.6 percent at the St. Joseph River near Newville, Ind.

Introduction

The Lake Erie-Lake St. Clair Basin is one of 59 basins and aquifer studies (known as “Study Units”) in the National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey (USGS) (Hirsch and others, 1988; Leahy and others, 1990). These 59 Study Units, which are distributed throughout the Nation, account for 60 to 70 percent of the Nation’s water use and population served by public water supplies (Leahy and Wilbur, 1991). The overall goals of the NAWQA Program are to describe the status of and trends in the quality of ground and surface waters of the United States and to improve our understanding of natural and human factors that affect these resources on local, regional, and national scales.

Study-Unit investigations and national synthesis are the major design features of the NAWQA Program that allow water-quality information collected at local and regional scales to be integrated into a national description of water quality. USGS investigators in the 59 Study Units collect and analyze water-quality data, following national protocols for the surface-water, ground-water, and ecological components of the program design. These data then are used with other information from the Study Units to assess water quality at regional and national scales.

The major components of the Study-Unit investigations are (1) retrospective analysis of existing water-quality data, (2) assessment of the geographic and seasonal distribution of evaluated contaminants, (3) long-term monitoring to determine water-quality trends, and (4) case studies of selected contaminants in local areas and specific hydrologic processes or environmental effects.

Pesticides, nutrients, volatile organic compounds, and suspended sediment are the primary topics for retrospective analysis and national synthesis in the NAWQA Program. The objectives of the study described in this report were to describe the occurrence, distribution, and loads of selected pesticides and degradates in the streams of the Lake Erie-Lake St. Clair Basin. Data were collected from March 1996 to February 1998 at 10 surface-water-sampling sites and additionally from March 1996 to February 1999 at 2 of the 10 sites—the St. Joseph River near Newville, Ind., and the Maumee River at Waterville, Ohio.

Purpose and Scope

This report describes (1) the occurrence, distribution, and temporal variation of pesticide concentrations in selected streams in the Lake Erie-Lake St. Clair Basin; (2) the relation between pesticides in surface water in the Basin and land use, current and historical pesticide use, other environmental factors, and chemical properties of the pesticides; (3) the occurrence and temporal variation of concentrations of degradates of selected pesticides at one stream site in the Basin; and (4) pesticide loads and yields for selected streams within the Basin. These analyses are based upon water samples collected at 10 surface-water-sampling sites.

Acknowledgments

The following USGS employees contributed to this report: Charles G. Crawford assisted with the computations and interpretation of the pesticide loads and reviewed several early drafts; Jeffrey D. Martin reviewed the quality-assurance section; Daniel T. Button assisted with map production and processed the land-use information; Donna N. Myers, Sandra Y. Panshin, and Dale M. Robertson provided technical reviews; Martha L. Erwin provided editorial review; and Patricia H. Long assisted with production of the text.

Description of the Lake Erie-Lake St. Clair Basin

Location and Hydrologic Setting

Lake Erie is the smallest (by volume) of the Great Lakes. About 78.5 percent of the water supplied to Lake Erie comes from the upper Great Lakes by way of the St. Clair and Detroit Rivers. The Lake Erie-Lake St. Clair Basin Study Unit encompasses approximately 22,300 mi^2 in parts of five states: Michigan, Indiana, Ohio, Pennsylvania, and New York (fig. 1). Lake Erie also drains 8,900 mi^2 in Canada. For the purposes of this study, the Lake Erie-Lake St. Clair Basin encompasses that part of the drainage basin to Lake Erie within the United States and excludes the area drained by the upper Great Lakes; it is hereafter referred to as “the Lake Erie Basin” or the “Basin.” Only the streams on the U.S. side of the Basin were sampled for this study. A more complete description of the Study Unit is given by Casey and others (1997).

The Maumee River, the largest river in the Basin, drains 6,609 mi^2 and discharges nearly 24 percent of the streamflow into Lake Erie. Eight streams—the Clinton, Huron, and Raisin Rivers in Michigan; the Maumee River in Indiana and Ohio; the Sandusky, Cuyahoga, and Grand Rivers in Ohio; and Cattaraugus Creek in New York—drain approximately 54 percent of the land area of the Basin.

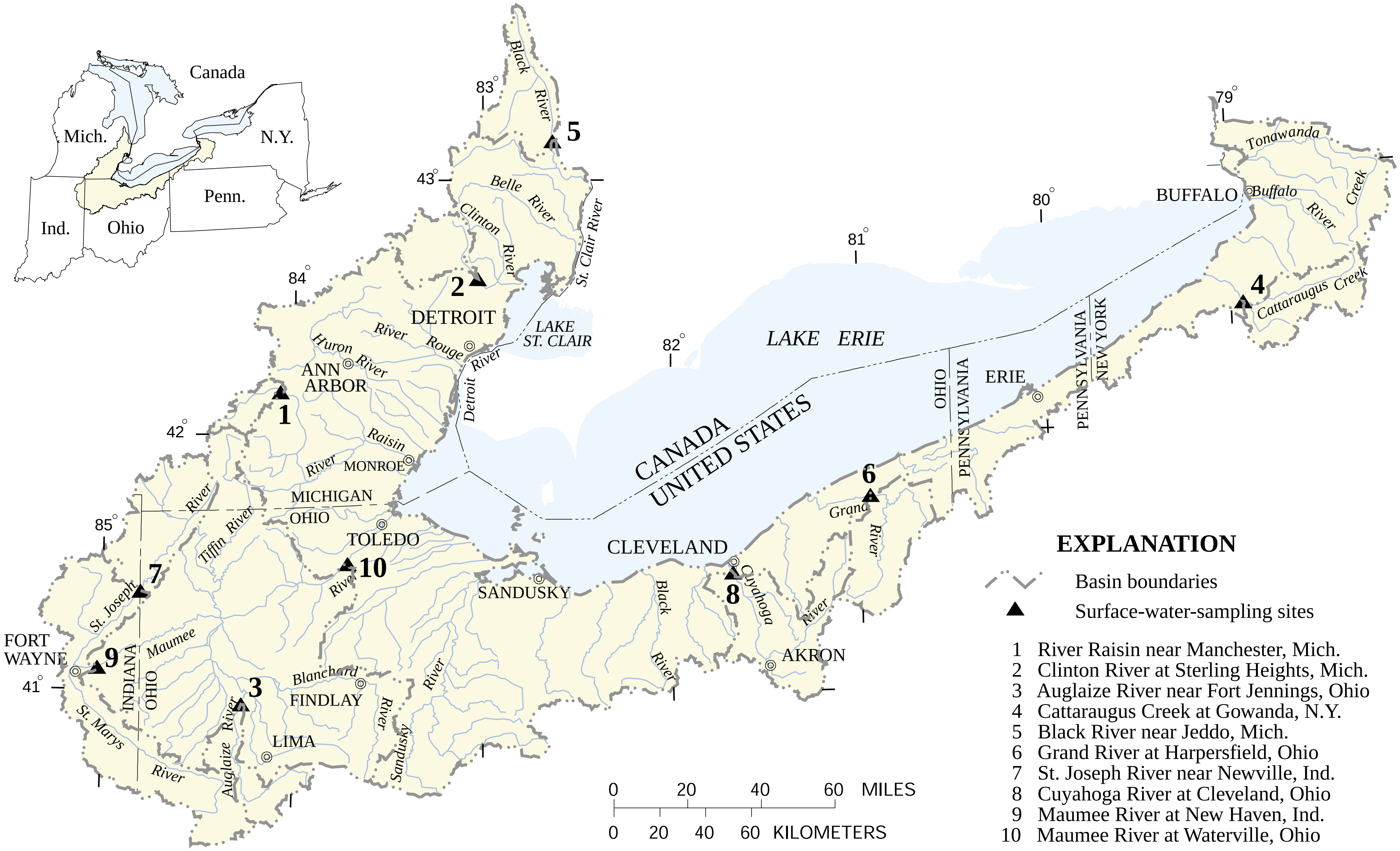
Physiography

The Lake Erie Basin spans two physiographic provinces, the Central Lowland Province and the Appalachian Plateaus Province (Casey and others, 1997). The Central Lowland Province encompasses nearly 19,000 mi^2 in the western and central areas of the Basin. The Appalachian Plateaus Province covers the remaining area in the eastern part of the Basin. The Central Lowland Province contains two distinct physiographic sections, the Eastern Lake Section and the Till Plains Section. The Eastern Lake Section encompasses 14,300 mi^2 of the Basin in Michigan, northeastern Indiana, and northwestern Ohio; it is dominated by recessional moraines and beach ridges, lacustrine plains, and outwash plains. The Till Plains Section encompasses approximately 4,700 mi^2 in the southern parts of the Basin in Indiana and Ohio. The till plains are characterized by flat topography and thick glacial deposits.

Geology and Soils

In general, the bedrock in the Lake Erie Basin varies from west to east; sandstone shale in the western part changes to shale in the eastern part of the Basin as it approaches the Appalachian Plateaus (Casey and others, 1997). Bedrock is predominantly carbonate in the center of the Basin, which includes the northwestern corner of Ohio, the northeastern corner of Indiana, and the southeastern corner of Michigan (including the Maumee River Basin). The bedrock throughout the Basin is overlain by predominantly unconsolidated Pleistocene deposits that range in thickness from a few feet to more than 600 ft in parts of the Cuyahoga Basin.

Two major soil types are found in the Basin—the Alfisols (74 percent) and Inseptisols (18 percent) (Casey and others, 1997). These relatively young soils are derived from lacustrine deposits that have high clay content and are unsorted and



Base from U.S. Geological Survey digital data 1:250,000 1983
Albers Equal-Area Conic projection
Standard parallels 29°30' and 45°30' central meridian -83°00

Figure 1. Location and surface-water-sampling sites of the Lake Erie-Lake St. Clair Basin.

unconsolidated. Subgroups of the two major types include the Hapludalfs, the Ochraqualfs, and the Dystrocrepts. The coarse, moderately well-drained Hapludalfs (an Alfisol) are found in western Michigan, specifically the River Raisin Basin. The Ochraqualfs (also an Alfisol) are poorly drained soils that encompass the area formerly known as the Black Swamp in the region near or in the Auglaize River Basin. The Dystrocrepts (which are Inseptisols) are thin, infertile soils found in the eastern regions in or near the Cattaraugus Creek Basin. A gradient of poorly drained Ochraqualf soils, which contain mostly fine clays, extends from the Auglaize River Basin in the south-central part of the Lake Erie Basin and surrounding area to the River Raisin Basin, which contains moderately well-drained, coarse Hapludalf soils (fig. 2, p. 6). This gradient has a pronounced effect on pesticide transport from cropland.

Climate and Hydrologic Conditions

Precipitation in the Lake Erie Basin during the study period was about 120 percent of the mean monthly or “normal” (based on the 1961–90 average computed from data for the precipitation stations listed in table 1). Precipitation generally was above normal in the eastern and the western parts of the Basin during 1996 and 1997 (fig. 3, p. 7). This precipitation resulted in above-normal streamflows during much of the study period, especially in the western part of the Basin. Streamflows were above normal in 16 of the 24 months during which samples were collected (fig. 3). Heavy rains in spring 1996 in the western part of the Basin resulted in record or near-record streamflows and unusually high runoff, especially in the northwestern part of the Basin but also throughout Michigan, Indiana, and Ohio. The highest streamflow of record (1947–98) occurred in the St. Joseph River near Newville, Ind., during May 1996.

Table 1. National Weather Service precipitation stations used to compute 30-year (1961–90) normals[a] for four surface-water-sampling sites in the Lake Erie-Lake St. Clair Basin

Station name[b]	Station number
Black River near Jeddo, Mich.	
Lapeer, Mich.	204655
Port_Huron_Sewage_Plant	206680
St. Joseph River near Newville, Ind.	
Fort_Wayne_WSO_AP	123037
Defiance, Ohio	332098
Auglaize River near Fort Jennings, Ohio	
Lima_WWTP	334551
Van_Wert	338609
Cattaraugus Creek at Gowanda, N.Y.	
Fredonia, N.Y.	303033

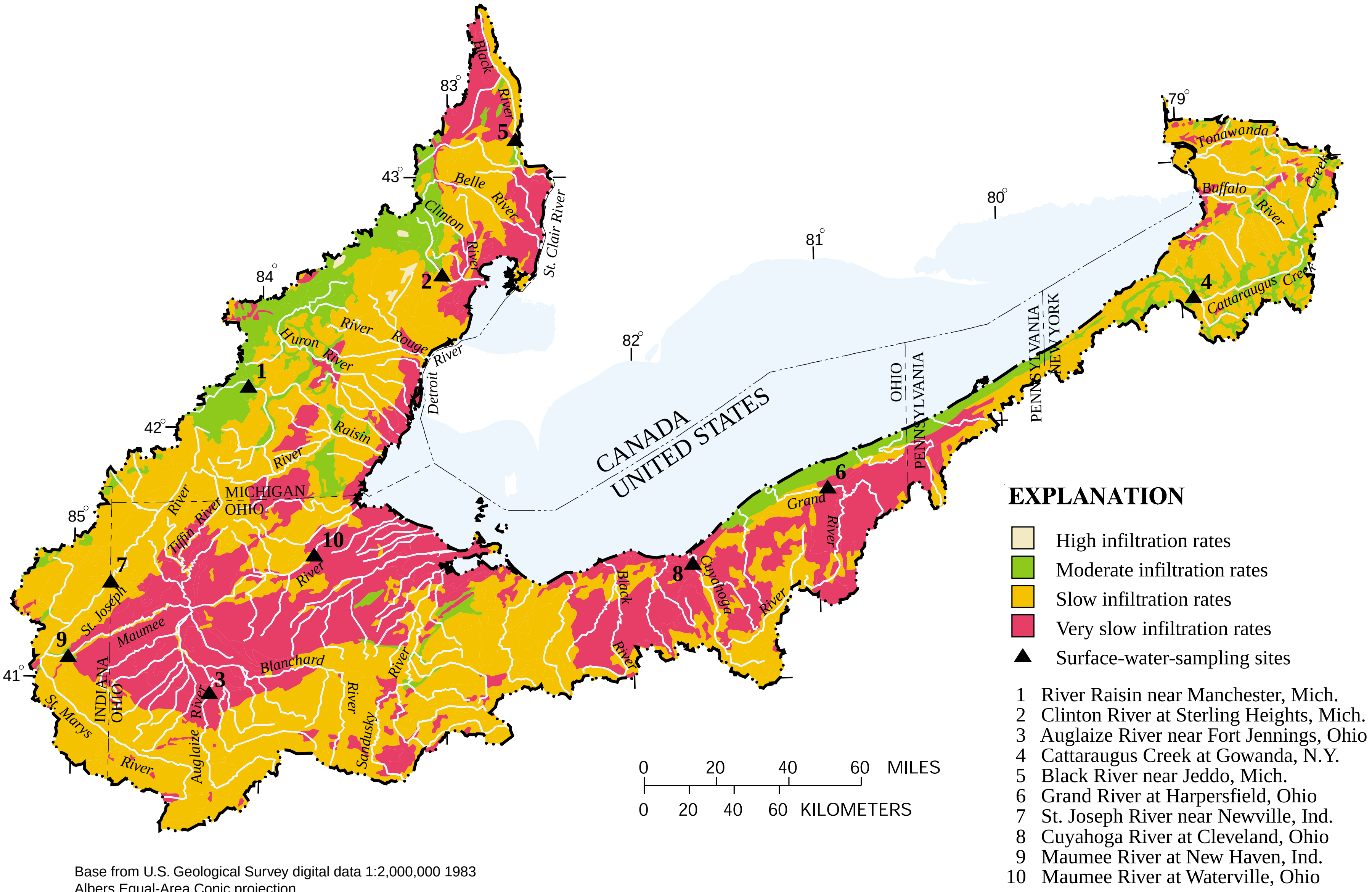
[a] The 30-year normals for precipitation were calculated, when possible, by averaging the monthly precipitation data from 1961 through 1990 from two rain gages near the surface-water-sampling sites.

[b] Sites taken from Midwest Regional Climate Center, 1999.

Land and Water Use

Agriculture is the predominant land use in the Lake Erie Basin (fig. 4, p. 8); it accounts for 65 percent of the total area of the Basin (table 2, p. 9). Of the agricultural lands, row crops (mostly corn and soybeans) account for 48 percent and pasture for 17 percent. In 1995, 6 million acres in the Basin were planted with crops (Brody and others, 1998). Soybeans and corn accounted for more than 73 percent of total planted acres (41 and 32.5 percent, respectively). Other significant crops include wheat, hay, and oats.

The second most common land use is urban. Although urban land accounts for only 10 percent of the Basin, there are several large urban areas—including Detroit, Mich.; Fort Wayne, Ind.; Cleveland, Toledo, and Akron, Ohio; and Buffalo, New York. In 1990, the population in the Basin was



Base from U.S. Geological Survey digital data 1:2,000,000 1983
Albers Equal-Area Conic projection
Standard parallels 29°30' and 45°30' central meridian -83°00

Figure 2. Infiltration rates of soils in the Lake Erie-Lake St. Clair Basin.

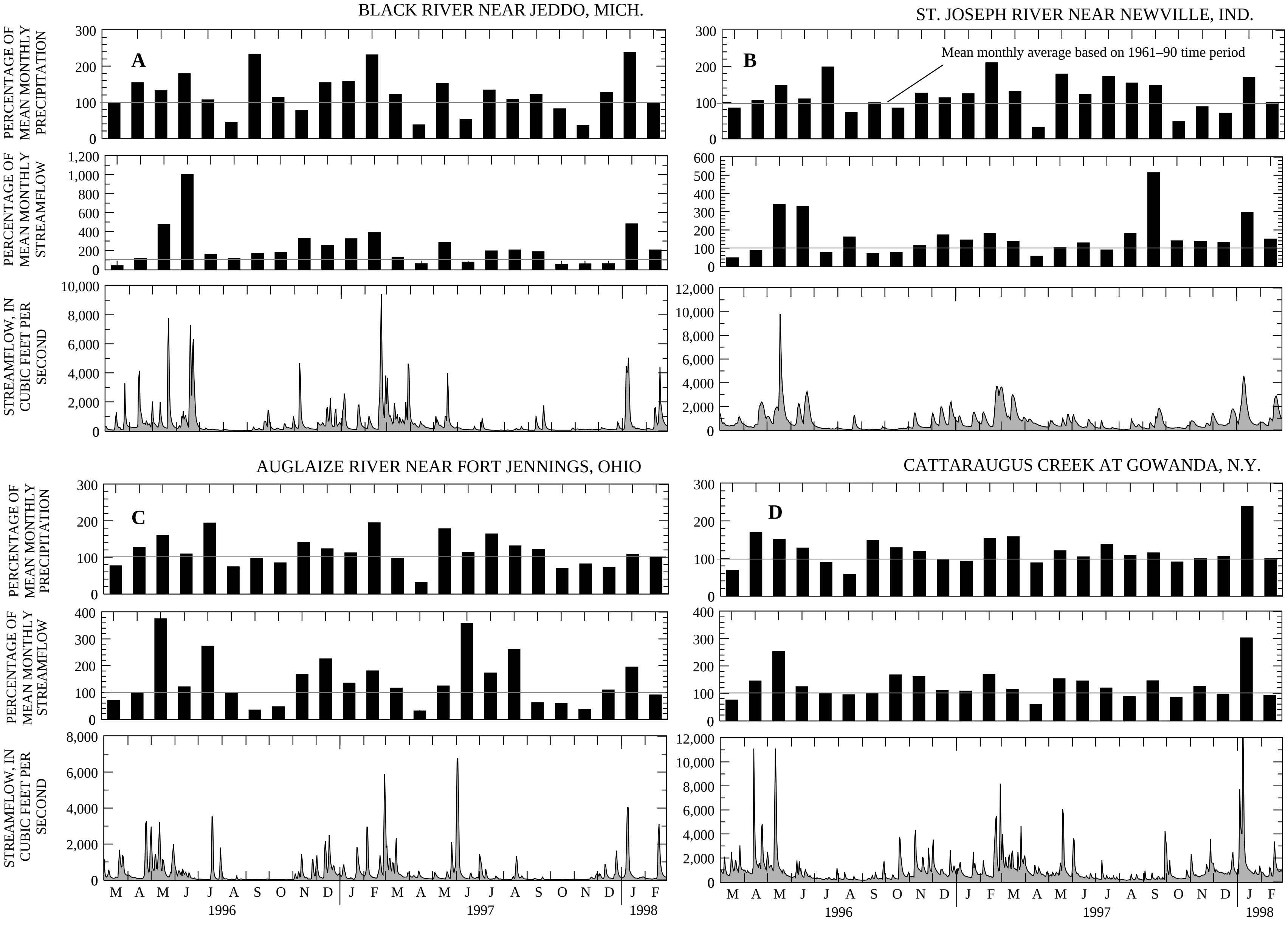
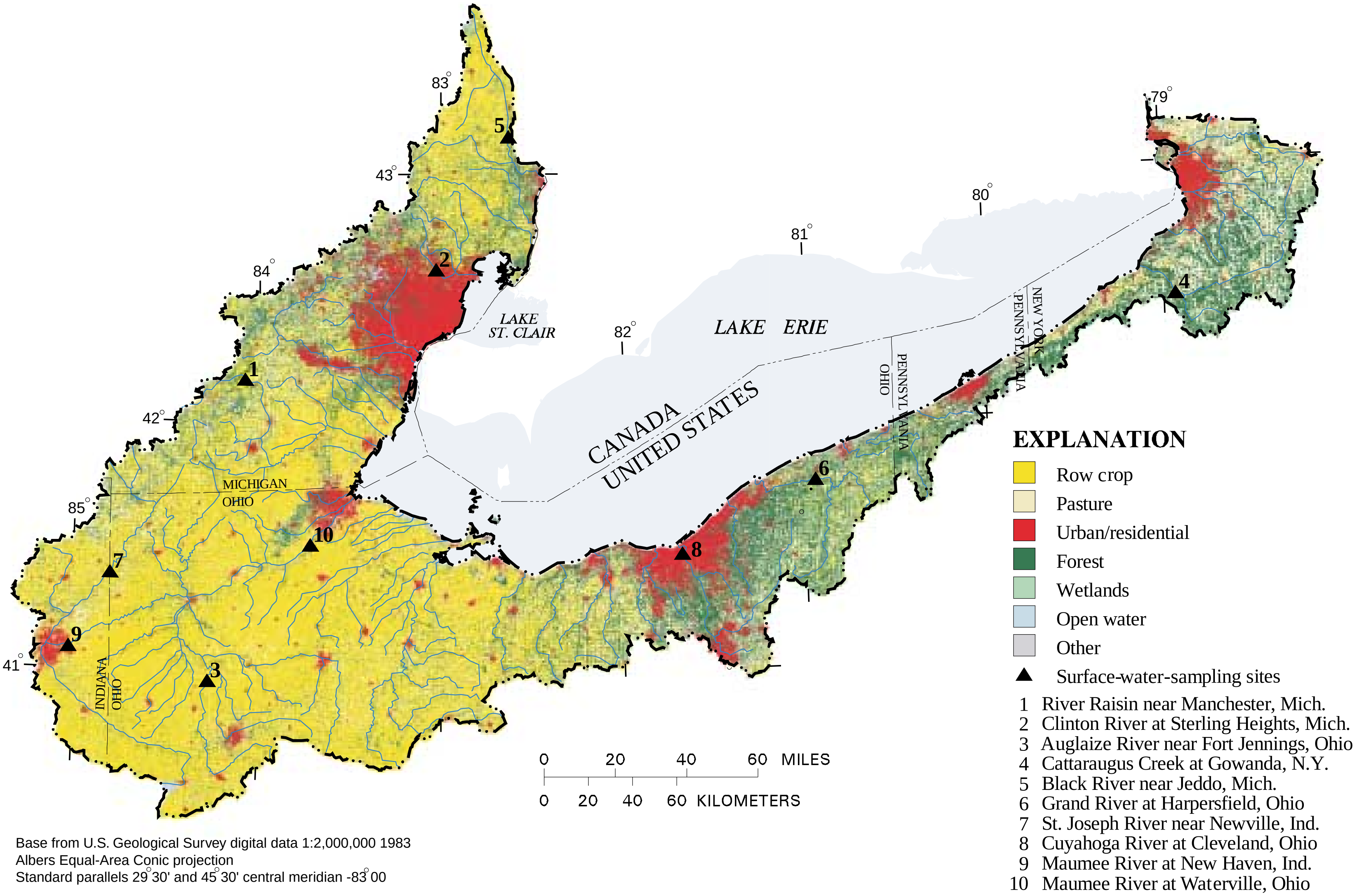


Figure 3. Percentage of mean monthly precipitation, percentage of mean monthly streamflow, and streamflow from March 1996 to February 1998 at three surface-water-sampling sites in the western part of the Lake Erie Basin-Lake St. Clair Basin—(A) Black River near Jeddo, Mich., (B) St. Joseph River near Newville, Ind., (C) Auglaize River near Fort Jennings, Ohio—and one site in the eastern part of the Basin, (D) Cattaraugus Creek at Gowanda, N.Y.



Base from U.S. Geological Survey digital data 1:2,000,000 1983
Albers Equal-Area Conic projection
Standard parallels 29°30' and 45°30' central meridian -83°00

Figure 4. Land use in the Lake Erie-Lake St. Clair Basin.

Table 2. Drainage area, land use, percent permeable soils, and base-flow index for surface-water-sampling sites in the Lake Erie-Lake St. Clair Basin

[Values taken from the Multi-Resolution Land Characteristics coverage (Vogelmann, Sohl, and others, 1998; Vogelmann, Sohl, and Howard, 1998) based upon Anderson land-use classifications (Anderson and others, 1976) (minor uses are not included in the table); mi^2, square miles; nd, no data; na, not applicable]

			Percent land use in Basin					
			Agriculture		Forest[a]	Urban[b]		
Site number and name	Drainage area (mi^2)	Primary land use	Row crop	Pasture			Percent permeable soils[c]	Base-flow index[d]
1. River Raisin near Manchester, Mich.	132	Row crop	44	13	36	2	58	90
2. Clinton River at Sterling Heights, Mich.	309	Urban	19	8	40	25	67	78
3. Auglaize River near Fort Jennings, Ohio	332	Row crop	76	13	8	2	2	30
4. Cattaraugus Creek at Gowanda, N.Y.	436	Pasture	6	35	58	1	27	57
5. Black River near Jeddo, Mich.	464	Row crop	72	12	14	1	20	37
6. Grand River at Harpersfield, Ohio	552	Pasture	20	22	54	1	2	33
7. St. Joseph River near Newville, Ind.	610	Row crop	54	24	20	1	22	62
8. Cuyahoga River at Cleveland, Ohio	788	Urban	8	19	44	25	67	66
9. Maumee River at New Haven, Ind.	1,967	Row crop	66	16	12	4	11	51
10. Maumee River at Waterville, Ohio	6,330	Row crop	74	13	9	3	28	33
Lake Erie-Lake St. Clair Basin	22,300	Row crop	48	17	9	10	nd	na

[a] Includes Anderson classes: mixed forest, deciduous forest, evergreen forest, woody wetlands.

[b] Includes Anderson classes: low-intensity residential, high-intensity residential, commercial/industrial/transportation, quarries/strip mines/gravel pits, and grasses.

[c] Based on the Natural Resources Conservation's State Soil Geographic Data Base (STATSGO) values for hydrologic soils groups A and B, the most permeable soil types.

[d] Based on the ratio of ground-water discharge to surface-water discharge (Rutledge, 1998).

10.4 million; the Detroit, Cleveland, and Buffalo Metropolitan Areas accounted for 62 percent of the total population.

About 98 percent of the total amount of water use in the Lake Erie Basin comes from surface water (Casey and others, 1997). Power generation accounts for about 77 percent of the total water use, followed by industrial, domestic, public, and agricultural uses. Most drinking-water supplies, which are included in the public- and domestic-use groups, are provided by surface-water sources (91.8 and 85.2 percent, respectively); the remainder comes from ground water.

Pesticide Use

Pesticides are used widely in the extensive row-crop agricultural areas in the Basin. No pesticide-use data, however, are collected by states for 16 of the 44 pesticides evaluated in this report. Also, some of the most heavily used pesticides in the Basin, such as glyphosate, were not evaluated in this study. Regardless of the missing data, herbicides are applied more heavily than insecticides (fig. 5); approximately 8.1 million pounds of herbicides and more than 28,100 pounds of insecticides were applied to agricultural areas in the Basin in 1995 (Brody and others, 1998). Herbicides are applied during spring planting to nearly all corn and soybean fields. Metolachlor (an acetanilide herbicide used on soybeans and corn) and atrazine (a triazine herbicide used primarily on corn) were the most heavily used pesticides in the Basin during 1995 (Brody and others, 1998; table 3, p. 12). More than 2.0 and 1.7 million pounds of metolachlor and atrazine, respectively, were applied. More than 100,000 pounds of active ingredient of cyanazine, acetochlor, alachlor, glyphosate, 2,4-D, pendimethalin, dicamba, metribuzin, and dimethenamid also were applied. Insecticides occasionally are applied to corn in the summer but usually are not applied to soybeans. Chlorpyrifos, carbaryl, and ethoprop were the most heavily used insecticides in the Basin.

Use of pesticides in urban and other nonagricultural areas in the Lake Erie Basin is not as well documented as that in agricultural areas. Insecticides usually represent a larger percentage of the total amount of pesticides used in urban areas than in row-crop agricultural areas. The herbicide 2,4-D is the most heavily applied pesticide in urban and other nonagricultural areas of the U.S.; an estimated 17 to 22 million pounds of active ingredient were used in 1994 (Aspelin, 1997). The insecticides chlorpyrifos, diazinon, and malathion, and the herbicides glyphosate, dicamba, and MCPP also commonly are used in urban areas.

The total amount of pesticides applied cannot be determined accurately with existing data because most states require that statistics be kept for only the most heavily used pesticides. For example, according to Brody and others (1998), no data have been systematically collected on the application of simazine in the Lake Erie Basin. Simazine was detected in 93.4 percent of the samples collected in this study. Data also are not reported or rarely are reported for pesticides used in urban and other areas (such as highway medians). For example, prometon (a nonselective triazine herbicide) commonly is applied for “total vegetation control on industrial sites and under asphalt roads” (Capel and others, 1999). Prometon was detected in 75.7 percent of the samples, which indicates this pesticide was used in the study area. The quantity and quality of pesticide-use data collected by states vary, making Basin-wide estimates difficult. For example, Brody and others (1998) note that pesticide usage in the Lake Erie Basin probably is underestimated because New York State does not keep statistics on pesticide use. Data from Brody and others (1998) are used in this report, however, because they provide the best available estimate of agricultural pesticide use in the Lake Erie Basin during this study.

Sampling-Site Locations

Water quality in streams is affected by a complex combination of natural and human factors. To contrast these influences, NAWQA Study Units are stratified into smaller areas that have relatively

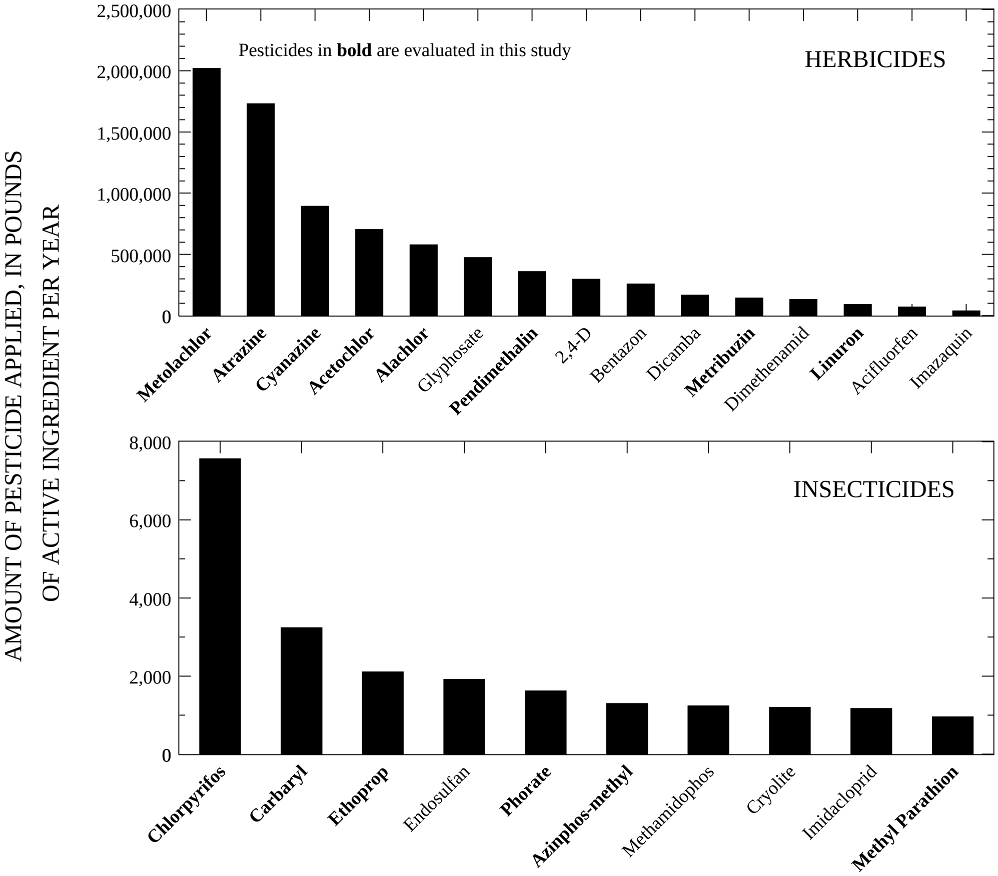


Figure 5. Amount of agricultural-use herbicides and insecticides applied in 1995 in the Lake Erie-Lake St. Clair Basin (from Brody and others, 1998).

homogenous combinations of land use and physical characteristics (Gilliom and others, 1995). For this study, 10 surface-water-sampling sites were selected that represent typical streams in the Basin and contrast the major surficial and bedrock geology and land-use types (table 2). Surface-water-sampling sites were selected for purposes of comparison as being either (1) small and relatively homogenous or (2) large and heterogenous to represent the integrated effects of many upstream factors. The smaller sampling sites were as large as possible yet still representative of a single, major land use. The three land-use classes that differentiate the basins are row-crop agriculture, urban, and pasture/forest. Because there are no streams of sufficient size (50 percent or more of the land area in the basin) that flow entirely through urban or pasture/forest areas in the Basin, sampling sites were selected in streams that drain significant amounts of land in urban or pasture/forest use. Sampling sites also were selected to represent a gradient from poorly drained to well-drained soils. Soil types were differentiated, based on the National Resources Conservation Service's State Soil Geographic Data Base (STATSGO) (Wolock, 1997).

The River Raisin, the smallest stream in the study, drains 132 mi^2 near Manchester, Mich. This basin lies within the Eastern Lake section of

Table 3. Characteristics of compounds analyzed and their use in the Lake Erie-Lake St. Clair Basin study area in 1995

[Method: Pesticide degradates in **bold** were sampled only at the St. Joseph River near Newville, Ind.; MDL, method detection limit; a.i., active ingredient; μg/L, microgram per liter; ESA, ethane sulfonic acid; OA, oxanilic acid; GC/MS, gas chromatography/mass spectrometry; HPLC, high-performance liquid chromatography; nd, no data; na, not applicable (degradate). Family: AM, amide; TR, triazine; OP, organophosphate; DI, dinitroanaline; CA, carbamate; OC, organochlorine; UR, urea; PY, pyrethroid; MI, miscellaneous; UL, uracil. Type: H, herbicide; I, insecticide; d-H, herbicide degradate product; d-I, insecticide degradate product]

Compound	Trade or common name(s)[a]	Family	Type	Method of analysis	MDL (μg/L)	Runoff potential[b]	Estimated agricultural use[c] in 1995 (in 1,000 pounds of a.i.)
Acetochlor	Harness, Surpass	AM	H	GC/MS	0.002	medium	703.5
Acetochlor ESA	None	AM	d-H	HPLC	.20	nd	na
Acetochlor OA	None	AM	d-H	HPLC	.20	nd	na
Alachlor	Lasso	AM	H	GC/MS	.002	medium	577.0
Alachlor ESA	None	AM	d-H	HPLC	.20	nd	na
Alachlor OA	None	AM	d-H	HPLC	.20	nd	na
Atrazine	AAtrex	TR	H	GC/MS	.001	large	1,729.5
Atrazine, deethyl	None	TR	d-H	GC/MS	.002	nd	na
Atrazine, deisopropyl	None	TR	d-H	GC/MS	.05	nd	na
Atrazine, hydroxy	None	TR	d-H	HPLC	.20	nd	na
Azinphos, methyl	Azinos, Gusathion A	OP	I	GC/MS	.001	medium	nd
Benfluralin	Ballin, Benefin	DI	H	GC/MS	.002	medium	nd
Butylate	Sutan +, Genate Plus	CA	H	GC/MS	.002	large	nd
Carbaryl	Sevin, Savit, Slam	CA	I	GC/MS	.003	medium	3.2
Carbofuran	Furadan, Terrafuran	CA	I	GC/MS	.003	large	.1
Chlorpyrifos	Lorsban, Scout	OP	I	GC/MS	.004	small	7.6
Cyanazine	Bladex	TR	H	GC/MS	.004	medium	893.1
Cyanazine amide	None	TR	d-H	GC/MS	.05	nd	na
DCPA	Dacthal	OC	H	GC/MS	.002	medium	.07
DDE, *p,p'*	None	OC	d-I	GC/MS	.006	medium	0
Diazinon	Spectracide, Sarolex	OP	I	GC/MS	.002	large	.1
Dieldrin	Panoram-D-31	OC	I	GC/MS	.001	medium	nd
Diethylanaline-2,6	None	AM	d-H	GC/MS	.003	nd	na
Disulfoton	Di-Syston	OP	I	GC/MS	.017	large	.01
EPTC	Eptam, Eradicane	CA	H	GC/MS	.002	medium	.11
Ethalfluralin	Sonalan, Curbit	DI	H	GC/MS	.004	medium	.2
Ethoprop	Mocap	OP	I	GC/MS	.003	medium	2.1
Fonofos	Dyfonate, Cudgel	OP	I	GC/MS	.003	large	.6

Table 3. Characteristics of compounds analyzed and their use in the Lake Erie-Lake St. Clair Basin study area in 1995—Continued

Compound	Trade or common name(s)[a]	Family	Type	Method of analysis	MDL (μg/L)	Runoff potential[b]	Estimated agricultural use[c] in 1995 (in 1,000 pounds of a.i.)
HCH, alpha	None	OC	I	GC/MS	0.002	nd	nd
HCH, gamma	Lindane	OC	I	GC/MS	.004	large	na
Linuron	Lorax, Linex	UR	H	GC/MS	.002	large	91.0
Malathion	Cythion, Acimal	OP	I	GC/MS	.005	small	.4
Metolachlor	Dual, Pennant	AM	H	GC/MS	.002	large	2,018.8
Metolachlor ESA	None	AM	d-H	HPLC	.20	nd	na
Metolachlor OA	None	AM	d-H	HPLC	.20	nd	na
Metribuzin	Lexone, Sencor	TR	H	GC/MS	.004	large	143.1
Molinate	Ordram	CA	H	GC/MS	.004	medium	nd
Napropamide	Devrinol	AM	H	GC/MS	.003	large	1.2
Parathion	Orthophos, Panthion	OP	I	GC/MS	.004	medium	nd
Parathion, methyl	Penncap-M, Prompt	OP	I	GC/MS	.006	medium	1.0
Pebulate	Tillam	CA	H	GC/MS	.004	medium	1.5
Pendimethalin	Prowl, Stomp	DI	H	GC/MS	.004	medium	359.3
Permethrin, cis	Ambush, Pounce	PY	I	GC/MS	.005	small	.4
Phorate	Thimet, Rampart	OP	I	GC/MS	.002	large	1.6
Prometon	Pramitol	TR	H	GC/MS	.003	large	nd
Pronamide	Kerb	AM	H	GC/MS	.003	large	nd
Propachlor	Ramrod	AM	H	GC/MS	.007	medium	nd
Propanil	Stampede	AM	H	GC/MS	.004	medium	nd
Propargite	Comite, Omite	MI	I	GC/MS	.013	medium	nd
Simazine	Aquazine, Princep	TR	H	GC/MS	.005	large	nd
Tebuthiuron	Spike	UR	H	GC/MS	.010	large	nd
Terbacil	Sinbar	UL	H	GC/MS	.007	large	.02
Terbufos	Counter	OP	I	GC/MS	.013	medium	.3
Thiobencarb	Bolero, Saturn	CA	H	GC/MS	.002	medium	nd
Triallate	Far-Go	CA	H	GC/MS	.001	large	nd
Trifluralin	Treflan, Trilin	DI	H	GC/MS	.002	medium	11.3

[a] From Sine (1995).

[b] From Goss (1992).

[c] From Brody and others (1998).

the Central Lowland Province. The bedrock—a combination of shales, siltstone, and imbedded sandstone—is overlain by moderately well-drained soils. In the gradient of poorly drained to well-drained soils for the agricultural basins, the River Raisin has the most well-drained soils. Nearly 90 percent of the streamflow is derived from ground water (table 2). Row-crop agriculture is the predominant land use (44 percent), but a significant amount (36 percent) is forested.

The Clinton River drains 309 mi^2 at Sterling Heights, Mich. This basin lies within the Eastern Lake Section of the Central Lowland Province. The sandstone-shale bedrock is overlain by moderately well-drained till and coarse soils. Approximately 78 percent of the streamflow is derived from ground water. The Clinton River Basin was selected to represent urban land use, which accounts for 25 percent of the land in this basin. Forty percent of this basin is forested; 19 percent is planted in row crops, mostly in the headwaters region.

The Auglaize River drains 332 mi^2 near Fort Jennings, Ohio. This basin lies within the Till Plains Section of the Central Lowland Province. The bedrock is predominantly carbonate. The Auglaize River Basin, which drains the former Black Swamp, contains very poorly drained soils that have a large clay content and that require tile drains and ditches to make them suitable for farming. In the gradient of poorly drained to well-drained soils, this basin has the most poorly drained soils. Approximately 30 percent of streamflow comes from ground water. The primary land use in this basin is row-crop agriculture. It is the most heavily farmed basin of the basins studied, with 76 percent in row crops. The Auglaize River is the source of drinking water for several small communities.

Cattaraugus Creek drains 436 mi^2 at Gowanda, N.Y., and is the easternmost site in the Basin. It flows through the Appalachian Plateaus Province. The shale bedrock is overlain by moderately well-drained to poorly drained soils. Approximately 57 percent of the streamflow comes from ground water. This basin was selected to represent pasture/forest land use because of the large amount (35 percent) used for pasture. This basin also has the most forested areas (58 percent) of all the basins in the study area. The hilly terrain of the Appalachian Plateaus Province makes farming difficult; thus, this basin has the smallest amount of row-crop agriculture acreage (6 percent) in the study area.

The Black River near Jeddo, Mich., drains 464 mi^2 and is the northernmost basin in the study. This basin lies within the Eastern Lake Section of the Central Lowland Province. The sandstone and shale bedrock is overlain by poorly drained till and fine soils. Approximately 37 percent of the streamflow is derived from ground water. Row-crop agriculture is the primary land use and accounts for 72 percent of the land.

The Grand River drains 552 mi^2 at Harpersfield, Ohio, and flows through the Appalachian Plateaus Province. The shale and sand/shale bedrock underlies mostly till soils that are moderately drained to very poorly drained. Ground water contributes about 33 percent of the streamflow. This basin was selected to represent pasture/forest land use; about 22 percent is used as pasture, and 54 percent is forested. The Grand River supports the most diverse biological communities of the 10 surface-water-sampling sites in this study area (Stephen Rheaume, U.S. Geological Survey, oral commun., 1999).

The St. Joseph River drains 610 mi^2 near Newville, Ind. Parts of this basin are within either the Till Plains or Eastern Lake Sections of the Central Lowland Province. The poorly drained soils are mostly till that have high clay content and overlay sandstone and shale bedrock; these soils require tile drains for farm use. About 62 percent of the streamflow comes from ground water. Row-crop agriculture, primarily corn and soybeans, is the primary land use (54 percent). The St. Joseph River is the source of drinking water for the city of Fort Wayne, Ind.

The Cuyahoga River drains 788 mi^2 at Cleveland, Ohio, and flows through the Appalachian Plateaus Province. The sandstone-shale bedrock is overlain by till and coarse soils that are moderately well-drained to poorly drained. Ground water contributes about 66 percent of the streamflow. This basin was selected to represent urban land use;

about 25 percent of the basin is urban land, mostly the Cleveland Metropolitan Area. About 44 percent of this basin is forested, mainly in the headwaters, and 8 percent of the basin is planted in row crops.

The Maumee River at New Haven, Ind., drains 1,967 mi^2 near Fort Wayne, Ind. Parts of this basin are within either the Till Plains or Eastern Lake Sections of the Central Lowland Province. The poorly drained till soils overlay a sandstone-shale/carbonate bedrock and require tile drains for farm use. Ground water accounts for 51 percent of the streamflow. This basin was selected to represent multiple land uses, but about 66 percent is used for row-crop agriculture. The St. Joseph River Basin lies within the Maumee River Basin.

The Maumee River at Waterville, Ohio, drains 6,330 mi^2 and is the largest stream in the Lake Erie Basin. It flows through the Till Plains and Eastern Lake Sections of the Central Lowland Province. This basin has moderately well-drained to poorly drained soils over predominantly carbonate and sandstone/shale bedrock. Approximately 33 percent of the streamflow is derived from ground water. This basin was selected to represent the effects of multiple land uses, but row-crop agriculture is the primary land use, with 74 percent of the basin in row crops. The St. Joseph River, Auglaize River, and Maumee River at New Haven lie within this basin. The Maumee River is the source of drinking water for the cities of Defiance, Napoleon, Grand Rapids, and Maumee, Ohio.

Analytical and Sampling Methods

The NAWQA Program evaluates pesticides for analysis that (1) are among the most heavily used pesticides in the U.S., (2) have potentially adverse human-health or environmental effects, and (3) are amenable to analysis by gas chromatography/mass spectroscopy (GC/MS). Forty-four pesticides and three degradates are compared among all surface-water-sampling sites in this report. Of these, 26 are herbicides, 18 insecticides, 2 herbicide degradates, and 1 insecticide degradate (table 3). These pesticides (except for acetochlor) accounted for about 72 and 66 percent, respectively, of the estimated annual application of herbicides and insecticides in the United States between 1990 and 1993 (Larson and others, 1999).

Additionally, 10 samples from the St. Joseph River near Newville, Ind., were analyzed for nine selected degradates of the heavily used herbicides atrazine, metolachlor, alachlor, acetochlor, and cyanazine (table 3). All the degradates in these 10 samples were analyzed, using high-performance liquid chromatography (HPLC); exceptions were deisopropylatrazine and cyanazine amide, which were analyzed using GC/MS. In total, 56 pesticides or degradates will be discussed in this report.

Field Methods

Water samples were collected at equal-width increments across the stream in 1- or 3-liter Teflon bottles placed into a USGS D-77 sampler. The D-77 sampler is designed to collect equal amounts of streamwater at all depths (depth-integrated). Samples were composited by pouring the water through a Teflon conesplitter into stainless-steel or Teflon containers. Approximately 900 mL of sample were filtered to remove sediment and organic debris by passing the water through a 0.7-mm glass-fiber filter into a 1-L baked-glass bottle. Pesticides were extracted by pumping these samples through C-18 solid-phase extraction (SPE) cartridges. Detailed descriptions of equipment and procedures used to decontaminate the sampling equipment and to collect, process, and extract the samples, using the SPE method, are in Shelton (1994). Samples were packed on ice and shipped to the USGS National Water Quality Laboratory (NWQL) in Arvada, Colo., for analysis. For the 10 additional samples collected for degradate analyses from the St. Joseph River near Newville, Ind., another aliquot was taken and filtered through a 0.7-mm glass-fiber filter. Two 125-mL standard brown glass bottles were filled with the filtered water, packed on ice, and shipped to the Organic Geochemistry Research Laboratory in Lawrence, Kans., for analysis.

The transport of pesticides into streams or surface-water bodies is affected by the timing of pesticide application and subsequent runoff. Consequently, samples were collected more frequently during the growing season after many pesticides have been applied. Samples were collected at six surface-water-sampling sites at least monthly between March and April 1996 until February 1998 and twice monthly during the growing season (May–August) in 1997. Samples were collected at another four surface-water sites at least monthly throughout the same time frame and more frequently during the growing season; samples were collected at least monthly in 1996, three to four times per month during the growing season in 1997, and twice monthly in 1998. When possible, samples also were collected to coincide with rising, peak, and falling stages of the streamflow hydrograph at a higher frequency and still adhere to the weekly, bimonthly, or monthly sampling schedule. Approximately 52 percent of the samples were collected on the rising (12.8 percent), peak (7.5 percent), and falling (31.5 percent) stages of the streamflow hydrograph (fig. 6).

Overall, 315 samples were collected and analyzed for pesticides at the 10 surface-water-sampling sites in the Lake Erie Basin between March 1996 and February 1998. At the six less-intensively sampled sites (River Raisin, Cattaraugus Creek, Black River, Grand River, Cuyahoga River, and the Maumee River at New Haven), from 24 to 29 samples were collected. At the more-intensively sampled sites (Clinton River, Auglaize River, St. Joseph River, and the Maumee River at Waterville), from 33 to 36 samples were collected. Additionally, 10 samples were collected at the St. Joseph River near Newville, Ind., between May 1997 and March 1998 as part of a national USGS study at selected NAWQA surface-water-sampling sites to evaluate the occurrence of some degradates of heavily used herbicides acetochlor, alachlor, atrazine, cyanazine, and metolachlor.

Laboratory Methods

The SPE cartridges were eluted at the NWQL and then analyzed by GC/MS for separation and analysis of the pesticides (Zaugg and others, 1995). Pesticides were identified and quantified, using a mass selective detector operating in the selective ion monitoring mode. Each compound has a method detection limit (MDL), which is the minimum concentration at which a substance can be identified with 99 percent confidence that the concentration is greater than zero (Martin and others, 1999). Concentrations near the method detection

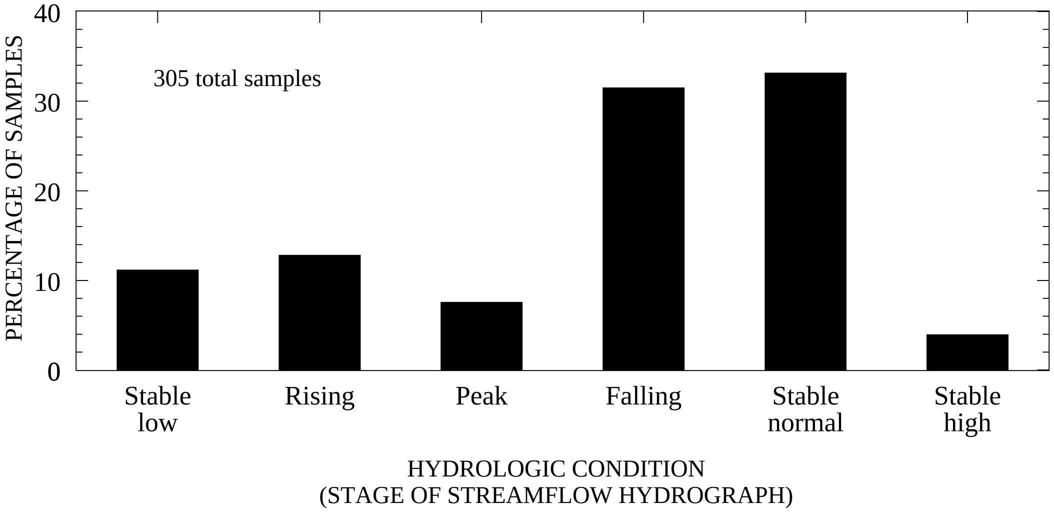


Figure 6. Percentage of samples collected for each hydrologic condition at 10 surface-water-sampling sites, Lake Erie-Lake St. Clair Basin, 1996–98.

limit were not censored; instead, compounds detected below the MDL were remarked as “E” (estimated) in the analytical results reported by the NWQL.

Parent compounds and several degradates of triazine herbicides were separated from the water samples, using C-18 SPE; they were analyzed, using GC/MS. Degradates for all acetanilide herbicides and one atrazine compound were isolated from the samples, using C-18 SPE; they were identified and quantified, using HPLC coupled with mass spectroscopy (MS) by means of electrospray ionization and negative ion detection. Liquid chromatography/mass spectrometry (LC/MS) is necessary for analysis because, using the GC/MS method, the ionic characteristics of the degradates make recovery difficult. Evaluated pesticides and degradates were extracted in the laboratory by passing 100 mL of sample through a C-18 SPE cartridge. For further details on methods, see Ferrer and others (1997) and Zimmerman and Thurman (1999).

Quality-Assurance Procedures

Field blanks, field spikes, and split replicates were used to estimate sample contamination and matrix effects and to determine variability affecting the pesticide concentrations, following the quality-control design of the NAWQA Program (Mueller and others, 1997). Blanks and spikes were used to estimate bias. Replicates were used to determine variability. The precision and bias associated with the pesticide samples were estimated, using 7 field blanks, 15 field spikes, and 10 split replicates. Of the seven pesticides detected in the blanks, only metolachlor was detected in more than two samples—but it was detected at such low concentrations (median of 0.003 μg/L and maximum of 0.007 μg/L) that the interpretation of the data was not affected. In the 15 field spikes, 26 of the pesticides were within 10 percent of 100-percent recovery. For 40 of the 47 pesticides analyzed in the spikes by the GC/MS method, the mean percent recovery ranged from 71 to 130 percent. Of the seven pesticides outside this range, deethylatrazine, disulfuton, phorate, and *p,p'*-DDE were biased low; carbaryl, carbofuran, and tebuthiuron were biased high. Further discussion of quality-assurance procedures followed in this study is provided in appendix A.

Computation of Pesticide Loads

The load of a chemical in a stream is defined as the mass of the chemical passing by a fixed measuring point in a specified period of time. Average annual loads of pesticides for this study were estimated, using the rating-curve method (Cohn and others, 1989, 1992; Crawford, 1991, 1996). This method allows an estimate of daily loads to be made from relatively few samples when daily streamflow data are available. Loads can be calculated by multiplying the concentration of the chemical in the sample by the streamflow in the stream at the time of sample collection and an appropriate unit’s conversion factor.

Concentrations of pesticides detected in this study showed a strong seasonal pattern related to the timing of application of the pesticides and their subsequent runoff from the land surface. Consequently, a rating curve incorporating two seasonal periods was used

$$\ln L = b0 + b1\,period + b2 \ln Q + b3 \ln (Q * period),$$

where,

ln indicates the natural logarithm of the quantity,

L is pesticide load,

$b0$, $b1$, $b2$, and $b3$ are rating-curve parameters,

Q is daily value streamflow, and

$period$ is a variable equal to 1 if an observation falls within a selected month and 0 otherwise.

For pesticides commonly applied during spring, such as the agricultural herbicides atrazine and metolachlor, the seasonal periods used were May through July and August through April. For pesticides commonly applied in mid to late summer, such as chlorpyrifos or diazinon, the seasonal periods used were July through September and October through June. An example of the seasonal relation between load of a pesticide (atrazine) and streamflow is shown in figure 7.

Because some of the concentrations reported were below the detection limit, rating-curve parameters were estimated by the linear attribution method (Chatterjee and McLeash, 1986) rather than the linear least squares method. A correction for transformation bias was made, using Duan's (1983) method when converting model predictions in logarithmic units to arithmetic units (Miller, 1984). This was done because model parameters were estimated, using a model in which the response variable (load) is log transformed.

Given a time series of streamflow data, such as that available from a USGS streamflow-gaging station, the average pesticide load, $\bar{L}$, can be estimated by:

$$\bar{L} = \sum_{i=1}^{N} \frac{\hat{L}_i}{N} ,$$

where,

$\hat{L}_i$ is the estimated load obtained from the rating curve for the *ith* value of streamflow in the time series, and

N is the total number of streamflow values.

The accuracy of this estimate is a function of the accuracy with which the rating curve describes the relation between pesticide load and streamflow and the interval between streamflow observations in the time series. For small streams in which flow is highly responsive to runoff, a short interval between streamflow values in the time series may be required. For larger, less responsive streams, a daily or longer interval may be sufficient. A time series of daily mean streamflow values

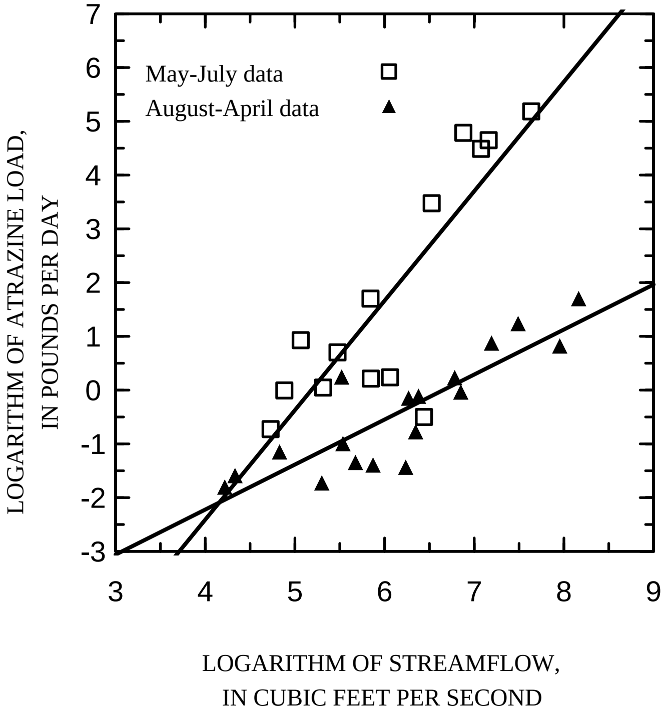


Figure 7. Seasonal relation of atrazine load to streamflow, St. Joseph River near Newville, Ind., 1996-98.

usually is used to compute average loads because these values readily are available. Because some of the streams sampled for this study are small, however, the use of daily mean flows and hourly flows for computing average loads was compared at a subset of the surface-water-sampling sites for a few pesticides. The average annual loads were similar between the two sets of estimates, computed as the percent difference defined as:

$$[y - x/(y+x)/2] * 100,$$

where,

y is load obtained, using the daily mean streamflow, and

x is load obtained, using the hourly streamflow.

Most of the load estimates had relative differences of 0 to 4 percent; loads of acetochlor had the greatest relative difference of less than 7 percent. Consequently, daily mean streamflows were used to compute all average loads in this report.

The degree of uncertainty in the loads was estimated, using the jackknife method (Efron, 1982). (Crawford, 1996, presents a more-detailed description of the methods used to compute pesticide loads in this report.) Yields were calculated by dividing loads by the drainage area of each basin.

Occurrence, Distribution, and Loads of Selected Pesticides

Pesticide Detections and Concentrations

Of the 44 pesticides and three degradates evaluated in this study, 30 were detected at least once (table 4). In general, more pesticides were detected as basin size increased (fig. 8). In the River Raisin near Manchester, Mich. (the smallest basin sampled at 132 mi^2), 14 pesticides were detected at least once; 27 pesticides were detected at the Maumee River at Waterville, Ohio (the largest basin at 6,330 mi^2). Exceptions to this trend were observed at the pasture/forest sites, Cattaraugus Creek and Grand River—basins in which fewer numbers and smaller quantities of pesticides are applied than in the row-crop basins in the study. Atrazine (an herbicide used primarily on corn) was detected in every sample, including samples from the basins with relatively small amounts of row crops (less than 10 percent) such as the Cattaraugus Creek and Cuyahoga River Basins. Concentrations of atrazine were much greater, however, in the row-crop basins than in other basins. The atrazine degradate deethylatrazine and the herbicide metolachlor were detected in 99 percent of the samples. Eight of the

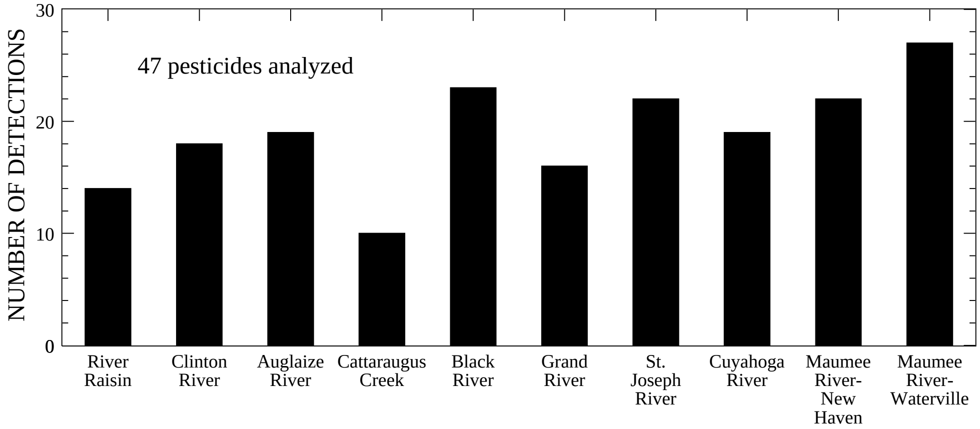


Figure 8. Number of pesticides detected in the Lake Erie-Lake St. Clair Basin, 1996–98. Surface-water-sampling sites listed in order of increasing basin size.

Table 4. Frequency of detection and summary of pesticide concentrations for evaluated pesticides in the Lake Erie-Lake St. Clair Basin, 1996–98

[Pesticide degradates in **bold** were sampled only at the St. Joseph River near Newville, Ind.; µg/L, micrograms per liter; ESA, ethane sulfonic acid; OA, oxanilic acid; E, pesticide detected and concentration estimated; nd, no detections; ld, less than detection limit; --, insufficient number of samples to calculate value]

Compound	Method detection limit (µg/L)	Number of samples analyzed	Frequency of detection (percent)	Median (µg/L)	95th percentile (µg/L)	Maximum (µg/L)
Acetochlor	0.002	305	58.0	0.009	2.57	11
Acetochlor ESA	.20	10	90.0	.585	--	4.50
Acetochlor OA	.20	10	70.0	.475	--	6.76
Alachlor	.002	305	63.9	.011	1.28	6.70
Alachlor ESA	.20	10	100	.665	--	2.29
Alachlor OA	.20	10	70.0	.250	--	1.96
Atrazine	.001	305	100	.134	14.0	E 85
Atrazine, deethyl	.002	305	99.0	E .024	E .433	E 1.51
Atrazine, deisopropyl	.05	10	80.0	.160	--	.910
Atrazine, hydroxy	.20	10	80.0	.580	--	2.02
Azinphos, methyl	.001	302	0	nd	nd	nd
Benfluralin	.002	305	1.6	ld	ld	E .004
Butylate	.002	305	1.6	ld	ld	.021
Carbaryl	.003	305	16.4	ld	E .027	E .432
Carbofuran	.003	305	3.6	ld	ld	E .247
Chlorpyrifos	.004	301	21.6	ld	.020	E .211
Cyanazine	.004	305	70.5	.023	3.36	9.97
Cyanazine amide	.05	10	60.0	.235	--	4.82
DCPA	.002	302	11.9	ld	.002	.006
DDE, *p,p'*	.006	305	1.3	ld	ld	E .003
Diazinon	.002	305	43.0	ld	.063	.290
Dieldrin	.001	305	1.0	ld	ld	.009
Diethylanaline-2,6	.003	305	1.0	ld	ld	E .002
Disulfoton	.017	305	0	nd	nd	nd
EPTC	.002	305	7.5	ld	.003	.177
Ethalfluralin	.004	305	0	nd	nd	nd

Table 4. Frequency of detection and summary of pesticide concentrations for evaluated pesticides in the Lake Erie-Lake St. Clair Basin, 1996–98—Continued

Compound	Method detection limit (µg/L)	Number of samples analyzed	Frequency of detection (percent)	Median (µg/L)	95th percentile (µg/L)	Maximum (µg/L)
Ethoprop	0.003	305	0	nd	nd	nd
Fonofos	.003	305	1.3	ld	ld	.021
HCH, alpha	.002	305	.3	ld	ld	E .004
HCH, gamma	.004	305	0	nd	nd	nd
Linuron	.002	305	11.1	ld	.049	.438
Malathion	.005	305	4.3	ld	ld	.026
Metolachlor	.002	305	99.3	.120	9.95	E 78
Metolachlor ESA	.20	10	100	1.63	--	4.20
Metolachlor OA	.20	10	100	.660	--	3.24
Metribuzin	.004	305	49.5	ld	1.25	5.36
Molinate	.004	305	0	nd	nd	nd
Napropamide	.003	305	0	nd	nd	nd
Parathion	.004	305	0	nd	nd	nd
Parathion, methyl	.006	305	.3	ld	ld	.008
Pebulate	.004	305	0	nd	nd	nd
Pendimethalin	.004	305	8.5	ld	.021	.152
Permethrin, cis	.005	305	0	nd	nd	nd
Phorate	.002	305	0	nd	nd	nd
Prometon	.003	305	75.7	.013	.120	.248
Pronamide	.003	305	0	nd	nd	nd
Propachlor	.007	305	.3	ld	ld	.008
Propanil	.004	305	0	nd	nd	nd
Propargite	.013	305	0	nd	nd	nd
Simazine	.005	305	93.4	.026	.864	3.05
Tebuthiuron	.010	305	25.9	ld	.023	.155
Terbacil	.007	305	2.0	ld	ld	E .021
Terbufos	.013	305	0	nd	nd	nd
Thiobencarb	.002	305	0	nd	nd	nd
Triallate	.001	305	0	nd	nd	nd
Trifluralin	.002	305	9.2	ld	.003	.009

47 pesticides and degradates were detected in at least 50 percent of the samples (table 4). All eight of these are herbicides used on row crops, except for prometon which is used primarily in urban areas. Of the 15 most commonly used agricultural pesticides evaluated in this study, all were detected in at least 8.5 percent of the samples. Diazinon and chlorpyrifos were the most frequently detected insecticides—detected in 43 and 21.6 percent of the samples, respectively. Additional data on detection frequencies and other statistics for each of the basins sampled are included in appendix B.

Seventeen of the 47 evaluated pesticides and degradates were not detected (table 4). Of these, nine had no reported agricultural use in the Basin. Of the 17 evaluated insecticides, 9 were not detected. The most heavily applied agricultural pesticide not detected was the insecticide ethoprop (2,100 pounds applied annually).

Atrazine and metolachlor had the highest detected concentrations in the Basin at 85 and 78 µg/L, respectively. All seven pesticides that had the highest measured concentrations are row-crop herbicides (either triazines or amides) and, except for simazine, also are the seven most heavily applied pesticides. As was noted previously, however, use of simazine probably is underreported in the individual state statistics.

Spatial Distribution

The spatial distribution of pesticides in streams coincides with the types and amounts of land uses in basins. Many herbicides, such as atrazine, are used exclusively or predominantly on row crops while other pesticides, such as the herbicide prometon and the insecticide diazinon, usually are used in urban areas. Most row-crop agriculture is in the western section of the Lake Erie Basin, while land use in easternmost section is primarily pasture and forest. Only 17 pesticides were detected in these eastern basins. At row-crop sites in western Ohio, northeastern Indiana, and southeastern Michigan, 30 pesticides were detected—the same 30 pesticides that were detected in the entire Basin. In the urban streams, 20 pesticides were detected.

The frequency of detections for certain pesticides also reflects the predominant land uses in basins. Pesticides used primarily in urban areas, such as diazinon or carbaryl, were detected up to four times more frequently in urban basins than in row-crop or pasture/forest basins (fig. 9). Prometon, a non-selective herbicide, is used for total vegetation control mostly in urban areas, but it also is used in agricultural areas (Capel and others, 1999). It was detected in almost 75 percent of the samples in row-crop basins and in 90 percent of the samples in urban basins. Herbicides used primarily on row crops—such as acetochlor, alachlor, linuron, and metribuzin—were detected up to seven times more often in row-crop basins than in urban basins.

A comparison of atrazine and diazinon reflects the relation between land use in a basin and the frequency of detection and concentration of pesticides in streams (fig. 10). Atrazine had higher concentrations in the row-crop basins than in the urban or pasture/forest basins. Diazinon had higher concentrations in the urban basins than in the row-crop or pasture/forest basins.

Although atrazine and metolachlor were detected in 99 to 100 percent of all samples, maximum measured and median concentrations were higher in the row-crop basins. Likewise, concentrations of cyanazine and diazinon in an urban basin (Clinton River) and a row-crop basin (Auglaize River) reflect the differences between the land uses in these basins. At the Auglaize River site, maximum measured concentrations of 7 µg/L of cyanazine (an herbicide used primarily on corn) occurred in May and June (fig. 11, p. 24). At the Clinton River, a peak occurred in May and June, with a maximum measured concentration of 0.410 µg/L. The median concentration of cyanazine was higher in the Auglaize River at 0.095 µg/L than in the Clinton River at 0.022 µg/L. Diazinon, an insecticide used mostly in urban and residential areas, had a higher maximum measured concentration in the Clinton River at 0.197 µg/L than in the Auglaize River at 0.048 µg/L (fig. 11). Maximum measured concentrations of diazinon occurred following application in late July to September at both sites.

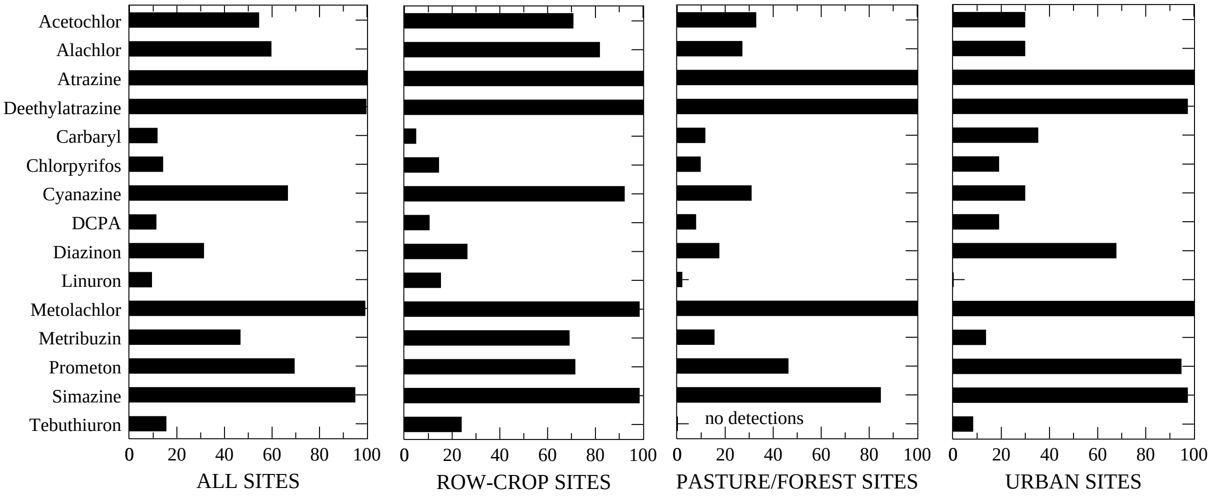


Figure 9. Relation of frequency of detections for selected pesticides to primary land use in the Lake Erie-Lake St. Clair Basin, 1996–98.

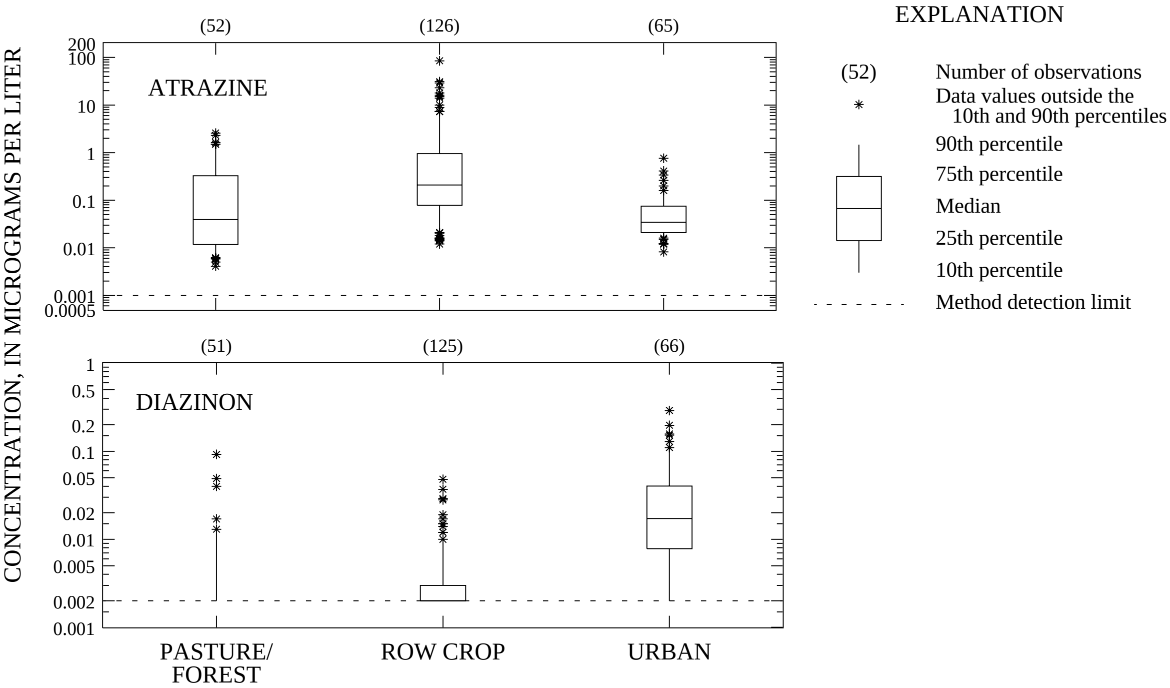


Figure 10. Concentrations of atrazine and diazinon in streams in pasture/forest, row-crop, and urban areas, Lake Erie-Lake St. Clair Basin, 1996–98.

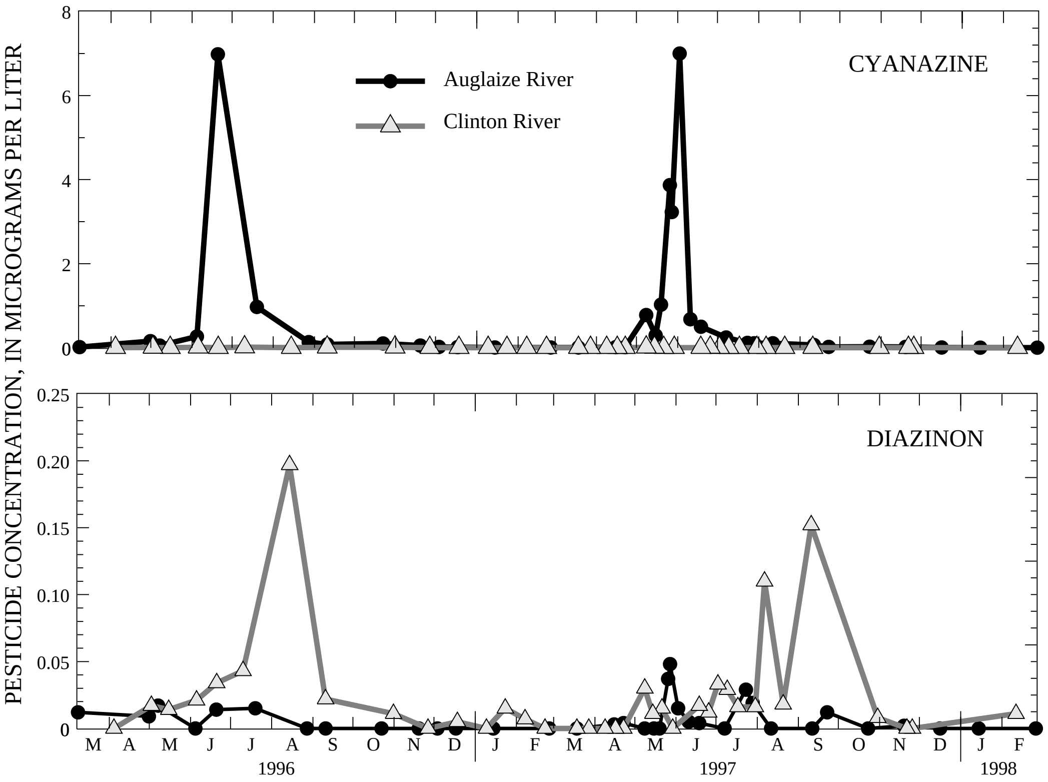


Figure 11. Relation of cyanazine and diazinon concentrations to time for samples collected in streams in an urban area (the Clinton River at Sterling Heights, Mich.) and in a row-crop area (the Auglaize River near Fort Jennings, Ohio).

The spatial distribution of atrazine concentrations among the 10 surface-water-sampling sites is similar to that of the most commonly used row-crop herbicides. As shown in figure 12, in general, atrazine concentrations are lower at the urban sites (Clinton and Cuyahoga Rivers) and at the pasture/forest sites (Grand River and Cattaraugus Creek) than at the row-crop sites. Most row-crop basins (Auglaize, St. Joseph, and both Maumee River sites) have higher concentrations of atrazine. The River Raisin, the one exception, has lower atrazine concentrations than all other row-crop sites. The relatively low concentrations of atrazine in the River Raisin probably are because of (1) a lower percentage of row crops than in the other row-crop basins (table 2); (2) less surface runoff (90 percent of streamflow comes from ground water, which allows for more adsorption of the pesticides to soils); (3) fewer tile drains; and (4) more riparian buffer zones that hinder pesticide transport by overland runoff into streams.

Some pesticides were detected locally in certain parts of the Basin. EPTC, a thiocarbamate herbicide used on corn and beans, was detected in 23 of the 315 samples; 65 percent of the detections were in the Black River near Manchester, Mich. Even though DDT was banned from use in the United States in 1973 because of human-health and environmental concerns, a DDT degradate (*p,p'*-DDE) was detected in four samples at low concentrations; three detections were in the Black River and all four detections occurred in Michigan. Although reliable usage data are not available for either pesticide, EPTC detections probably are caused by recent use; *p,p'*-DDE detections probably are the result of historical use of DDT, its

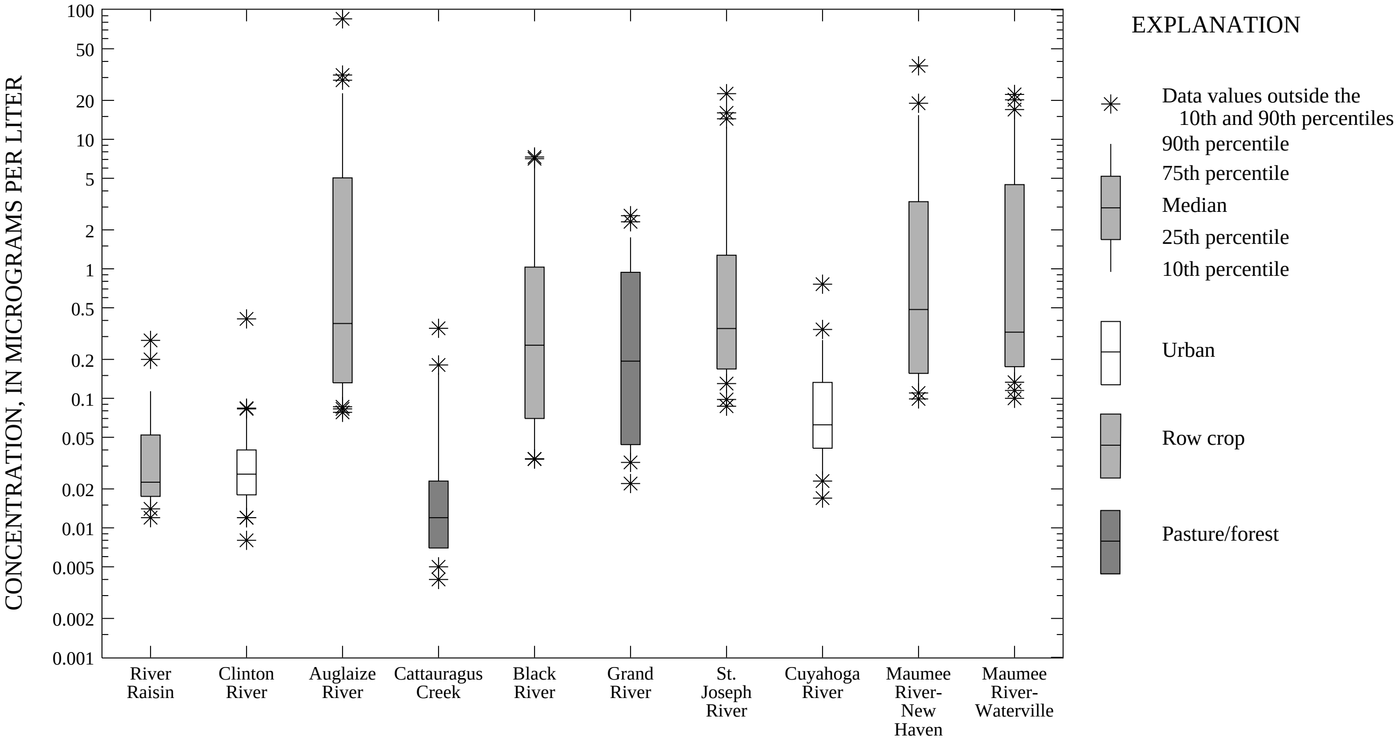


Figure 12. Atrazine concentrations in the Lake Erie-Lake St. Clair Basin, 1996–98. Surface-water-sampling sites listed in order of increasing basin size.

sorption to sediments, and resuspension into the streamwater. One blank also had a detection of *p,p'*-DDE (discussed in appendix A, p. 55).

Temporal Variations

It has been well documented that highest concentrations of pesticides in streams occur when precipitation causes surface-water runoff and tile drains to transport recently applied pesticides into streams (Richards and Baker, 1993; Fenelon and Moore, 1998; Crawford, 1995; Larson and others, 1997). Most agricultural herbicides are applied either as pre-emergent or early post-emergent in the spring, and the corresponding highest concentrations in streams occur soon after application.

In the Lake Erie Basin, highest herbicide concentrations typically coincided with the first runoff after application and then steadily decreased to pre-application values. For some heavily used herbicides such as atrazine, metolachlor, cyanazine, and acetochlor, elevated concentrations persisted for 4 to 6 weeks after the initial maximum measured concentration in the streams in row-crop basins. A typical seasonal pattern for agricultural herbicides applied in the spring is shown in a graph of atrazine concentrations in the St. Joseph River near Newville, Ind. (fig. 13A). Maximum measured concentrations of prometon occurred in late summer (fig. 13B); some herbicides that primarily are used in urban areas, such as prometon, commonly are applied in late summer or early fall. Some insecticides primarily used in urban areas, such as diazinon, are applied over a longer period that can extend from late spring to late summer. A typical seasonal pattern for insecticides commonly used in urban areas is shown in a graph of diazinon concentrations in the Clinton River at Sterling Heights, Mich. (fig. 13C).

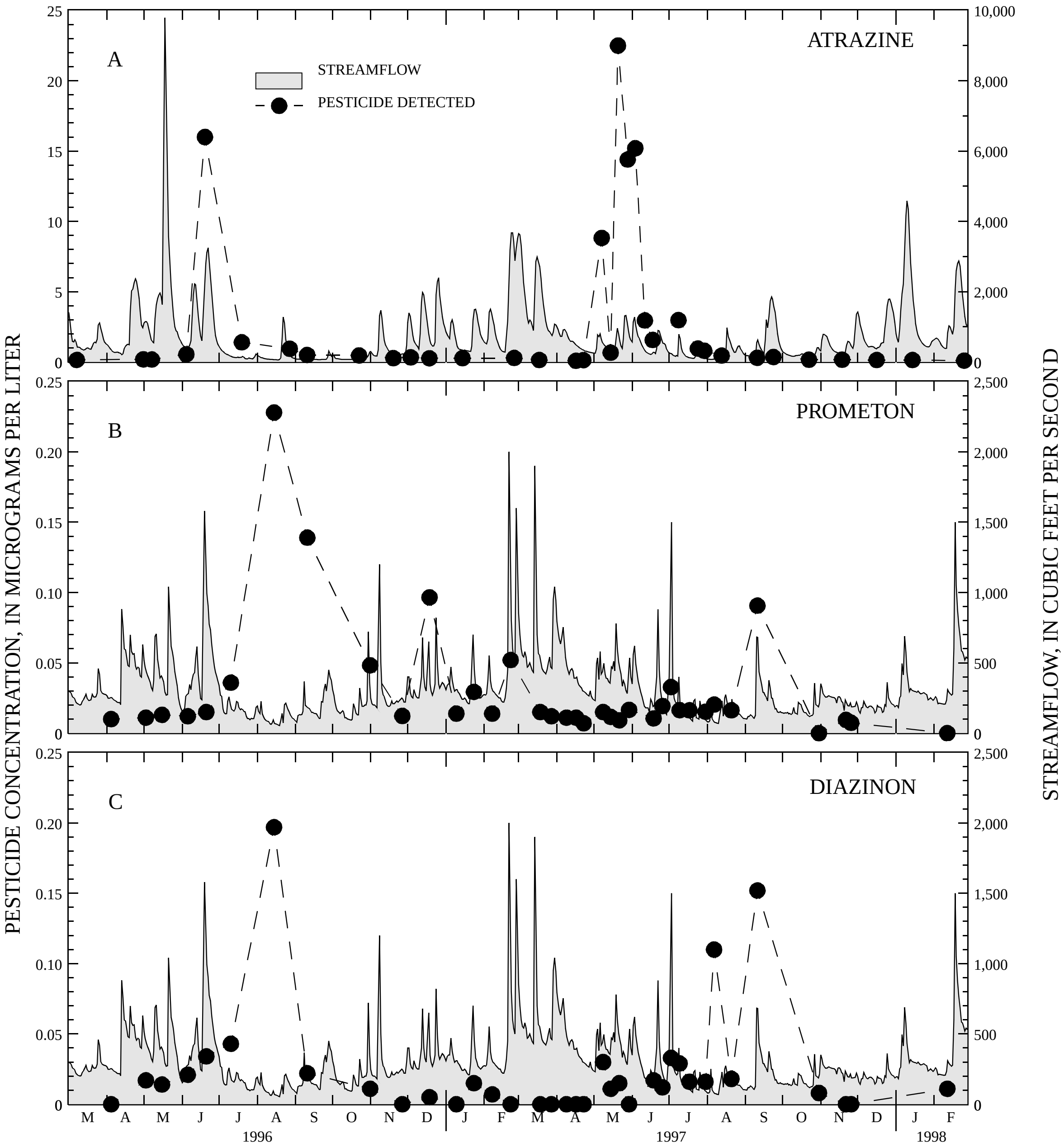


Figure 13. Relation of selected pesticide concentrations and streamflow to time, (A) atrazine in the St. Joseph River near Newville, Ind.; (B) prometon in the Clinton River at Sterling Heights, Mich.; and (C) diazinon in the Clinton River at Sterling Heights, Mich.

Degradates of Selected Herbicides

Typically, only 0.01 to 10 percent of the mass of pesticide compounds applied to fields is detected in streams (Larson and others, 1999). The remaining 90 to 99 percent of pesticides adsorb to soil, percolate into ground water, or volatilize (Larson and others, 1997). The major degradates of the most heavily used herbicides found in surface water have not been studied widely. It is believed, however, that some degradates are as toxic or more toxic than the parent compound (Day, 1991).

Many physical properties of pesticides affect the amount transported to streams but, in general, acetanilide herbicides are more soluble in water and thus more mobile than the triazines (Crawford, 2001). The solubility of sulfonated degradates of acetanilides (ethane sulfonic acid—ESA), can be 10 times the solubility of the parent (Thurman and others, 1996). The greater mobility of the degradates of the acetanilides (amide family) can explain their greater frequency of detection and concentrations when compared to the triazines in the 10 samples from the St. Joseph River site. The frequency of detection of degradates ranged from 60 percent (6 of 10 samples) for cyanazine amide to 100 percent (10 of 10 samples) for metolachlor degradates (table 4). Acetochlor ESA, acetochlor oxanilic acid, and cyanazine amide had maximum measured concentrations greater than 4 µg/L; acetochlor oxanilic acid had the highest maximum measured concentration of 6.76 µg/L.

Concentrations of the triazine and acetanilide degradates had seasonal trends similar to their parent compounds (fig. 14). The greatest concentrations of the degradates detected in the 10 samples from the St. Joseph River were in the samples collected in the spring after the first rains following application of pesticides. The maximum measured concentrations of the degradates, however, were in samples collected from 1 to 2 weeks after the maximum measured concentration of the parent compound. After the maximum concentration was measured, degradate and parent compound concentrations steadily decreased to detection levels for the triazines. For the acetanilides, the degradate concentrations also decreased with time. Concentrations of acetanilide degradates, however, were higher than that of the parent compound for most of the year (except immediately after application). Acetanilide degradates constituted a much larger fraction of the total acetanilide herbicides washing off fields than triazine degradates did for triazine herbicides. These limited data suggest that degradates (especially of acetanilide herbicides) can contribute a significant proportion of the pesticide load to Lake Erie. This pattern is similar to results found in Iowa (Kalkhoff and others, 1998).

Relation to Drinking-Water Standards or Guidelines and Aquatic-Life Guidelines

Although the use of pesticides has increased agricultural productivity significantly and has helped to limit disease transmission by insects, many pesticides can have carcinogenic, mutagenic, or other toxic effects on humans and aquatic life. Recently, for example, some pesticides were linked to endocrine disruption in some species (Goodbred and others, 1997; Smith, 1998).

To protect the health of human and aquatic life, enforceable standards and advisory guidelines have been set by several agencies, including the U.S. Environmental Protection Agency (USEPA), Environment Canada, and the International Joint Commission (IJC). In this report, observed and time-weighted average concentrations are compared to USEPA standards and guidelines if they exist, or to Canadian or IJC values. The USGS NAWQA Program is designed to assess the quality of the Nation’s water resources; it is not designed to monitor drinking-water quality. Comparisons made in this report to drinking-water standards and guidelines are made in the context of the available untreated (raw) resource (U.S. Geological Survey, 1999).

In the United States, the USEPA sets the primary drinking-water regulations to protect human health (U.S. Environmental Protection Agency, 2000). Maximum Contaminant Levels (MCL’s) are the maximum permissible concentration of a contaminant in water that is delivered to any user of public water systems; they are established on the basis, among other factors, of health effects, feasibility and cost of water treatment, and analytical

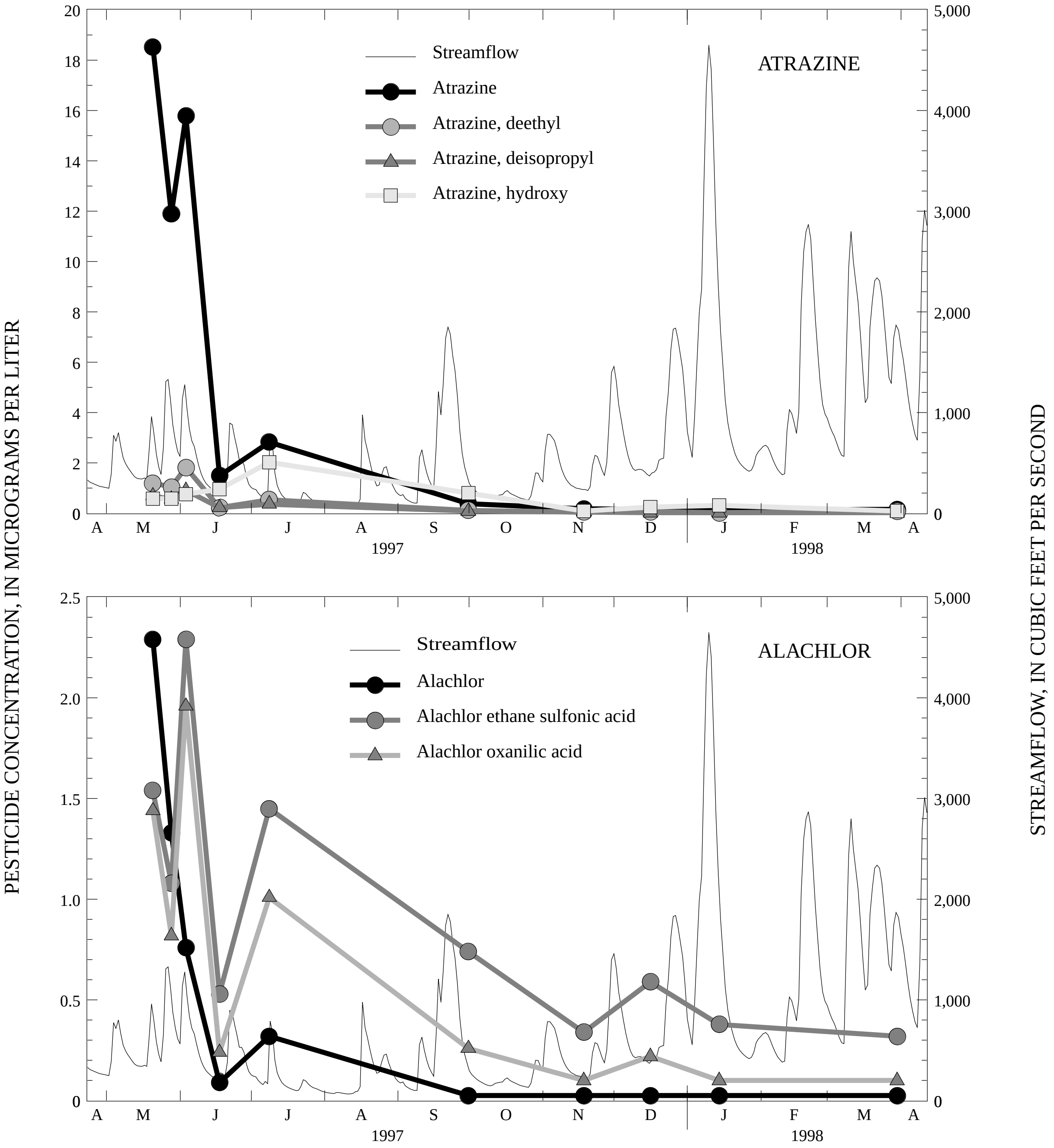


Figure 14. Relation of the triazine compound atrazine, the acetanilide alachlor, and selected degradate concentrations and streamflow to time in the St. Joseph River near Newville, Ind.

detection limits (Nowell and Resek, 1994). MCL's are enforceable standards, and a water-treatment facility's compliance with these standards is based on an average concentration of four quarterly samples of treated (finished) drinking water. Of the 47 pesticides and degradates evaluated in this study, MCL's have been set for five: alachlor, atrazine, carbofuran, lindane, and simazine (table 5). No MCL has been established for acetochlor, but an annual time-weighted average benchmark of 2.0 µg/L has been suggested as part of a conditional registration ("REG" in table 5).

For some pesticides, the USEPA also sets nonenforceable drinking-water health advisories. These guidelines represent concentrations that are expected to result in no adverse noncarcinogenic acute (1- and 10-day, child), longer-term (7-year, child and adult), and lifetime (70-year, adult) human-health effects. For health advisories to be exceeded, a child would need to drink 1 L per day or an adult would need to drink 2 L per day of water at the guideline concentration for the length of the specific time period (1 day, 10 days, 7 years, or 70 years). Drinking-water health advisories—but no MCL's—have been set for 20 of the pesticides evaluated in this study (table 5).

For some pesticides, the USEPA also sets nonenforceable risk-specific dose (RSD) guidelines that are associated with some degree of cancer risk. For example, an RSD5 represents a risk of 1 in 100,000 for a concentration in drinking water equal to the RSD. In other words, the lifetime consumption of drinking water with a concentration equal to the RSD would result in an upper-bound excess cancer risk of 1 in 100,000. Of the 47 pesticides and degradates monitored, RSD guidelines have been set for 5: alachlor, alpha-HCH, *p,p'*-DDE, dieldrin, and trifluralin.

For some pesticides, nonenforceable guidelines have been set to prevent long- and short-term effects on aquatic life. The USEPA aquatic-life guidelines are based upon 4-day average concentrations, are intended to protect 95 percent of the aquatic species, and are not to be exceeded more than once in 3 years. Canadian and IJC aquatic-life guidelines, which are more stringent than those of the USEPA, indicate a single maximum measured concentration that should never be exceeded. Of the 47 pesticides or degradates analyzed, aquatic-life guidelines for 18 have been set by either the USEPA, Environment Canada, or the IJC.

Several researchers have noted the limitations of available standards and guidelines as a basis for evaluating the potential effects of pesticides in surface water (Nowell and Resek, 1994; Larson and others, 1999). These limitations include

(1) Standards and guidelines have not been set for many pesticides. Of the 47 pesticides evaluated, only 5 MCL's, 25 drinking-water health advisories, and 18 aquatic-life guidelines have been set.

(2) Few standards and guidelines have been set for pesticide degradates. Degradates, especially of the acetanilides such as metolachlor and alachlor were detected frequently and at greater concentrations than the parent compound.

(3) Standards and guidelines are established on the basis on toxicity tests that are conducted on a single pesticide and that do not evaluate the possible additive or synergistic effects of multiple pesticides. Of the 47 pesticides and degradates monitored in this study, 27 were detected in the Maumee River at Waterville, Ohio, at least once, and up to 19 pesticides were detected in a single sample.

(4) Aquatic-life guidelines do not account for the effects of multiple stressors in concert with pesticides such as suspended sediment, low dissolved oxygen, or inorganic contaminants.

(5) Standards and guidelines do not address possible effects of pesticides on the endocrine systems of humans (Colborn and others, 1993) and aquatic organisms (Goodbred and others, 1997).

Table 5. Human-health and aquatic-life benchmarks established for evaluated compounds

(RSD5, risk-specific dose associated with an excess cancer risk of 1 in 100,000 for a concentration in drinking water equal to the RSD; µg/L, microgram per liter; REG, Conditional registration with the U.S. Environmental Protection Agency; MCL, U.S. Environmental Protection Agency–established Maximum Contaminant Level for drinking water; --, no standard or guideline established; CAN, Canadian guideline for protection of aquatic life; USEPA, U.S. Environmental Protection Agency; CAN-INT, Canadian interim guideline for protection of aquatic life; IJC, Great Lakes water-quality objective from the International Joint Commission]

		Human-health standards and guidelines[a]							Aquatic-life guidelines[a]	
		Primary drinking-water standard		Drinking-water health advisories					Chronic freshwater	
Compound	Number of samples	Value (µg/L)	Source	1 and 10 day, child value (µg/L)	Longer term, child value[b] (µg/L)	Longer term, adult value (µg/L)	Lifetime, adult value (µg/L)	RSD5 at 1 in 10^5 cancer risk (µg/L)	Value (µg/L)	Source
Acetochlor	305	2.0	REG	8.0	--	--	--	--	--	--
Alachlor	305	2.0	MCL	100	--	--	--	4.0	--	--
Atrazine	305	3.0	MCL	100	50	200	3.0	--	1.8	CAN
Atrazine, deethyl	305	--	--	--	--	--	--	--	--	--
Azinphos, methyl	302	--	--	--	--	--	--	--	.01	USEPA
Benfluralin	305	--	--	--	--	--	--	--	--	--
Butylate	305	--	--	2,000	1,000	4,000	350	--	--	--
Carbaryl	305	--	--	1,000	1,000	1,000	700	--	.2	CAN
Carbofuran	305	40	MCL	50	50	200	40	--	1.8	CAN
Chlorpyrifos	301	--	--	30	30	100	20	--	.041	USEPA
Cyanazine	305	--	--	100	20	70	1.0	--	2.0	CAN-INT
DCPA	302	--	--	80,000	5,000	20,000	--	--	--	--
DDE, *p,p'*	305	--	--	--	--	--	--	1.0	--	--
Diazinon	305	--	--	20	5	20	.6	--	.08	IJC
Dieldrin	305	--	--	.5	.5	2	--	.02	.056	USEPA
Diethylaniline -2,6	305	--	--	--	--	--	--	--	--	--
Disulfoton	305	--	--	10	3	9	.3	--	--	--
EPTC	305	--	--	--	--	--	--	--	--	--
Ethalfluralin	305	--	--	--	--	--	--	--	--	--
Ethoprop	305	--	--	--	--	--	--	--	--	--
Fonofos	305	--	--	20	20	70	10	--	--	--

Table 5. Human-health and aquatic-life benchmarks established for target compounds—Continued

		Human-health standards and guidelines[a]							Aquatic-life guidelines[a]	
		Primary drinking-water standard		Drinking-water health advisories					Chronic freshwater	
Compound	**Number of samples**	**Value (μg/L)**	**Source**	**1 and 10 day, child value (μg/L)**	**Longer term, child value[b] (μg/L)**	**Longer term, adult value (μg/L)**	**Lifetime, adult value (μg/L)**	**RSD5 at 1 in 10^5 cancer risk (μg/L)**	**Value (μg/L)**	**Source**
HCH, alpha	305	--	--	--	--	--	--	0.06	--	--
HCH, gamma	305	.2	MCL	1,000	30	100	.2	--	.08	IJC
Linuron	305	--	--	--	--	--	--	--	7.0	CAN-INT
Malathion	305	--	--	200	200	800	200	--	.1	USEPA
Methyl parathion	305	--	--	300	30	100	2.0	--	--	--
Metolachlor	305	--	--	2,000	2,000	5,000	70	--	7.8	CAN-INT
Metribuzin	305	--	--	5,000	300	500	100	--	1.0	CAN-INT
Molinate	305	--	--	--	--	--	--	--	--	--
Napropamide	305	--	--	--	--	--	--	--	--	--
Parathion	305	--	--	--	--	--	--	--	.013	USEPA
Pebulate	305	--	--	--	--	--	--	--	--	--
Pendimethalin	305	--	--	--	--	--	--	--	--	--
Permethrin, cis	305	--	--	--	--	--	--	--	--	--
Phorate	305	--	--	--	--	--	--	--	--	--
Prometon	305	--	--	200	200	500	100	--	--	--
Pronamide	305	--	--	800	800	3,000	50	--	--	--
Propachlor	305	--	--	500	100	500	90	--	--	--
Propanil	305	--	--	--	--	--	--	--	--	--
Propargite	305	--	--	--	--	--	--	--	--	--
Simazine	305	4.0	MCL	70	70	70	4.0	--	10	CAN
Tebuthiuron	305	--	--	3,000	700	2,000	500	--	1.6	CAN-INT
Terbacil	305	--	--	300	300	900	90	--	--	--
Terbufos	305	--	--	5	1	5	.9	--	--	--
Thiobencarb	305	--	--	--	--	--	--	--	--	--
Triallate	305	--	--	--	--	--	--	--	.24	CAN-INT
Trifluralin	305	--	--	80	80	300	5.0	50	.2	CAN

[a] Values taken from http://infotrek.er.usgs.gov/wdbctx/nawqa_www/NWQ_MNG.STDS_REPORT.html on August 30, 2000.

[b] Intended to represent 10 percent of a lifetime or 7 years.

An Ohio Environmental Protection Agency report noted that at no drinking-water-treatment facility in Ohio did annual average pesticide concentrations exceed the primary drinking-water standards (MCL's) from 1995 to 1999 (Kelleher, 1999). Four of the surface-water-sampling sites in this study are either near drinking-water intakes or in a stream used as a source of drinking water: the Auglaize River near Fort Jennings, Ohio; St. Joseph River near Newville, Ind.; Maumee River at New Haven, Ind.; and the Maumee River at Waterville, Ohio. MCL's apply to treated water. Although the data collected in this study are from stream samples, they provide temporal and spatial information on pesticide concentrations in raw water used for public supply in the Lake Erie Basin.

The elevated concentrations of pesticides observed during spring runoff has economic as well as health consequences for areas that use surface water as a source for drinking water. Many larger water-treatment facilities that use surface water (other than Lake Erie) use activated carbon during the spring to meet drinking-water standards. In areas where pesticides are applied heavily, some facilities use activated carbon all year to remove pesticides. The annual cost of this treatment is approximately $210,000; about 40 percent of this cost is incurred during April to July (Doug Pooler, Fort Wayne Water Filtration Plant, oral commun., 1999). Moreover, despite carbon treatment, some individual samples collected by the treatment facilities during the spring exceeded the MCL for atrazine, although the annual average concentrations did not exceed the MCL.

Annual time-weighted average concentrations and time-weighted average concentrations of selected pesticides for May through July were calculated at all surface-water-sampling sites, using data collected from March 1, 1996, to February 28, 1998 (table 6). No annual time-weighted average concentrations exceeded the MCL for pesticides with established MCL's. During May through July, however, when pesticide runoff into streams is greatest, time-weighted average concentrations would meet or exceed the MCL for atrazine of 3.00 μg/L at five row-crop sites: Maumee River at New Haven (10 μg/L), Maumee River at Waterville (9.26 μg/L), Auglaize River (8.87 μg/L), St. Joseph River (5.45 μg/L), and Black River (3.00 μg/L). No other time-weighted average concentrations for pesticides with an established MCL were exceeded May through July.

No annual time-weighted average concentrations exceeded the acute, longer-term, or lifetime health advisories (table 6). The time-weighted average concentrations of atrazine and cyanazine, however, frequently exceeded lifetime adult health advisories (HA-L) during May through July.

Chronic aquatic-life guidelines were exceeded for atrazine, metolachlor, cyanazine, metribuzin, diazinon, chlorpyrifos, and carbaryl. The heavily used row-crop herbicides atrazine, metolachlor, cyanazine, and metribuzin had the largest number of exceedences of these guidelines; diazinon had the highest number of exceedences of any insecticide. One or more aquatic-life guidelines were exceeded at least once in every stream except the River Raisin and Cattaraugus Creek. The number of exceedences did not increase with stream size; instead, the type of land use in the basin was more of a factor in determining the number of exceedences. Samples from the row-crop basins had the highest number of exceedences of aquatic-life guidelines: the Auglaize River had the highest at 27 exceedences, followed by the Maumee River at Waterville, the St. Joseph River, the Maumee River at New Haven, and the Black River (fig. 15, p. 34). Most of the exceedences at these sites were because of high concentrations of row-crop herbicides, while exceedences of aquatic-life guidelines in urban basins were mostly because of high concentrations of diazinon and chlorpyrifos.

Exceedences of aquatic-life guidelines may impact fish communities in the Lake Erie Basin. One component of the NAWQA Program is the collection of biological samples to help determine water quality; the fish community and instream and riparian habitat at the sampled sites were studied. Most of the surface-water-sampling sites in this study have good to excellent fish habitat based upon Qualitative Habitat Evaluation Index (QHEI) scores (Ohio Environmental Protection Agency, 1989). The fish communities, however,

Table 6. Two-year time-weighted average concentrations and time-weighted May through July average concentrations for selected pesticides at 10 surface-water-sampling sites in the Lake Erie-Lake St. Clair Basin, 1996–98

[Concentrations in **bold** exceeded a human-health or aquatic-life benchmark; mi^2, square mile; µg/L, microgram per liter]

Site name	Drainage area (mi^2)	Acetochlor		Alachlor		Atrazine		Cyanazine		Metolachlor	
		Time-weighted average (µg/L)[a]	Time-weighted average May–July (µg/L)	Time-weighted average (µg/L)	Time-weighted average May–July (µg/L)	Time-weighted average (µg/L)	Time-weighted average May–July (µg/L)	Time-weighted average (µg/L)	Time-weighted average May–July (µg/L)	Time-weighted average (µg/L	Time-weighted average May–July (µg/L)
River Raisin near Manchester, Mich.	132	0.006	0.019	0.004	0.012	0.037	0.090	0.010	0.024	0.013	0.030
Clinton River at Sterling Heights, Mich.	309	.012	.040	.005	.015	.038	.084	.007	.010	.020	.050
Auglaize River near Fort Jennings, Ohio	332	.205	.759	.268	.997	2.41	**8.87**	.458	**1.68**	2.95	**10**
Cattaraugus Creek at Gowanda, N.Y.	436	.002	.002	.004	.010	.036	.111	.005	.009	.025	.087
Black River near Jeddo, Mich.	464	.190	.709	.097	.327	.905	**3.00**	.232	**.791**	1.68	5.68
Grand River at Harpersfield, Ohio	552	.038	.106	.012	.041	.527	1.29	.022	.029	.248	.678
St. Joseph River near Newville, Ind.	610	.331	1.28	.247	.912	1.58	**5.45**	.358	**1.25**	1.05	3.53
Cuyahoga River at Cleveland, Ohio	788	.015	.048	.005	.010	.098	.243	.016	.039	.040	.106
Maumee River at New Haven, Ind.	1,967	.470	1.83	.254	.928	2.75	**10**	.511	**1.84**	2.21	**7.82**
Maumee River at Waterville, Ohio	6,330	.500	1.93	.349	1.31	2.57	**9.26**	.747	**2.73**	2.22	8.00

Site name	Drainage area (mi^2)	Simazine		Chlorpyrifos		Diazinon		Prometon	
		Time-weighted average (µg/L)	Time-weighted average May–July (µg/L)	Time-weighted average (µg/L)	Time-weighted average May–July (µg/L)	Time-weighted average (µg/L)	Time-weighted average May–July (µg/L)	Time-weighted average (µg/L)	Time-weighted average May–July (µg/L)
River Raisin near Manchester, Mich.	132	0.101	0.220	0.004	0.004	0.003	0.004	0.015	0.016
Clinton River at Sterling Heights, Mich.	309	.019	.030	.005	.005	.029	.024	.040	.019
Auglaize River near Fort Jennings, Ohio	332	.180	.617	.007	.013	.006	.013	.050	.067
Cattaraugus Creek at Gowanda, N.Y.	436	.013	.040	.004	.004	.002	.002	.016	.011
Black River near Jeddo, Mich.	464	.017	.036	.005	.005	.004	.003	.014	.014
Grand River at Harpersfield, Ohio	552	.033	.086	.007	.015	.010	.007	.018	.021
St. Joseph River near Newville, Ind.	610	.131	.220	.012	.034	.002	.003	.028	.069
Cuyahoga River at Cleveland, Ohio	788	.019	.041	.009	.017	.045	**.081**	.043	.066
Maumee River at New Haven, Ind.	1,967	.191	.654	.017	**.046**	.023	.028	.064	.110
Maumee River at Waterville, Ohio	6,330	.194	.677	.013	.024	.007	.014	.037	.048

[a] Calculated using 2 years of data from March 1, 1996, to February 28, 1998.

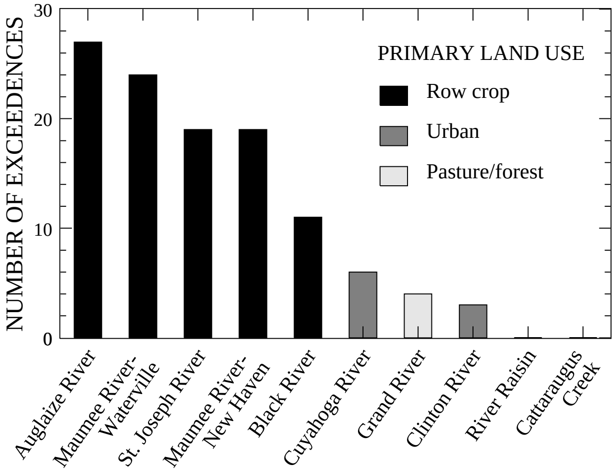


Figure 15. Number of times U.S. Environmental Protection Agency aquatic-life guidelines were exceeded, by site, in the Lake Erie-Lake St. Clair Basin, 1996-98. (There were no exceedences for River Raisin, which is primarily row crop, and Cattaraugus Creek, which is primarily pasture/forest.)

have only poor to good Index of Biological Integrity (IBI) values (Ohio Environmental Protection Agency, 1987). Two sites that had low numbers of exceedences of aquatic-life guidelines (Grand River and the River Raisin) also had IBI values that ranked “good,” whereas the four sites with the highest number of exceedences (Auglaize River, St. Joseph River, and both Maumee River sites) had IBI values that ranked “poor” (Stephen Rheaume, U.S. Geological Survey, oral commun., 1999). Similar results were found in the White River Basin in Indiana (Frey and others, 1996).

The USEPA aquatic-life guidelines specify a recurrence interval of 3 years, which implies that an aquatic ecosystem can recover if the contaminant concentration does not exceed the guideline more than once in 3 years (Larson and others, 1999). This study found that concentrations of pesticides commonly associated with a specific land use in the Lake Erie Basin exceeded the aquatic-life guidelines at least once from 1996 to 1998. In the row-crop basins, guidelines were exceeded by atrazine, cyanazine, metolachlor, and metribuzin; in the urban basins by diazinon and chlorpyrifos.

Drinking-water standards, human-health advisories, or aquatic-life guidelines have not been established for acetochlor. As a requirement of conditional registration in 1994, however, restrictions regarding concentration levels of acetochlor in drinking water were established by the USEPA (U.S. Environmental Protection Agency, 1994). Those restrictions apply if the annual time-weighted average concentration of acetochlor exceeds 2.00 µg/L in one or more community water supplies that derive water primarily from surface water. These restrictions range from prohibiting the use of acetochlor in the affected watershed to cancellation of the registration if the exceedences are widespread. For example, a single measured concentration of 8.0 µg/L in a community water supply deriving its water primarily from surface water would result in a requirement for additional monitoring.

The annual time-weighted average concentrations of acetochlor in the four surface-water-sampling sites in this study that are near a public water intake or are used as a public water supply did not exceed 2.00 µg/L. The highest calculated annual time-weighted average acetochlor concentration was 0.500 µg/L for the Maumee River at Waterville, Ohio. Individual concentrations of acetochlor in samples exceeded 8.00 µg/L twice—once in the Maumee River at New Haven, Ind., (8.88 µg/L) and once in the Maumee River at Waterville, Ohio (11.0 µg/L). Both exceedences occurred in May 1997.

Loads and Yields of Selected Pesticides in Streams of Lake Erie

Public officials and water-resource managers often need to know the amount of a contaminant transported in a stream to determine the stream's condition and how it has changed over time. Loads and yields of the contaminants are common measures for these assessments. Loads and yields were calculated for selected pesticides for each basin on the basis of 2 years of data collected from March 1996 to February 1998 (table 7). Application estimates were based on county-level data for pesticides applied to corn and soybeans collected as part of the Census of Agriculture in 1997 (National Agricultural Statistics Service, 1999). Sufficient data were available for estimating application of pesticides used primarily on corn or soybeans (or both), such as alachlor, acetochlor, atrazine, and metolachlor. For other pesticides, use estimates were unreliable (chlorpyrifos) or unavailable (diazinon and prometon).

Atrazine and metolachlor had the highest estimated use and the highest estimated loads. Loads were less for insecticides and herbicides that have primarily nonagricultural uses. For example, the loads of chlorpyrifos and prometon in the Maumee River at Waterville were only 0.3 and 0.6 percent, respectively, of the atrazine load.

Estimated annual loads of commonly used agricultural herbicides in the Maumee River at Waterville for the study period were about 3 to 7 percent of that applied in the basin. Smaller basins tended to have a higher percentage of the amount of applied pesticide exported from the basin than did larger basins. For example, 10.6 percent of the atrazine applied in the St. Joseph River near Newville was exported, compared to 7.1 percent in the Maumee River at New Haven and 4.4 percent in the Maumee River at Waterville (table 8, p. 39). Relatively high percentages also were found in other small, predominantly row-crop basins (the Auglaize River and the Black River). A notable exception was the River Raisin Basin, where less than 0.1 percent of the amount of atrazine applied to cropland in that basin was detected. This may be because of (1) the high percentage of permeable soils in the basin and (2) streamflow contribution by ground water (90 percent).

Pesticide loads in streams as a percentage of the applied amount reported in this study are higher than those found in earlier studies in the Lake Erie Basin and in other basins in the United States. Richards and others (1996) reported 0.1 to 4.0 percent loads for streams tributary to Lake Erie in 1983 through 1993. Goolsby and Pereira (1995) reported that loads of pesticides in major tributaries to the Mississippi River in the early 1990's were generally less than 3 percent of the amount applied to cropland. Crawford (1995) reported that loads of alachlor, atrazine, cyanazine, and metolachlor in the 11,305-mi^2 White River Basin in Indiana were 0.2 to 1.3 percent of the amount applied in 1992 through 1994. Percentages in this Lake Erie study ranged from 0.1 to 10.6. It is not known if the higher percentages found in this Lake Erie study are because of regional differences in soils, geology, or other natural factors or because of differences in rainfall or other factors that vary temporarily.

Annual pesticide loads reported for the Maumee River at Waterville, Ohio, by Richards and others (1996) are less than those estimated in this study. For example, the loads of atrazine and metolachlor for 1983 through 1993 reported by Richards and others (1996) were 78 and 54 percent, respectively, of those found in this study. As noted previously, however, precipitation and streamflow during the study period were above normal. The higher runoff during the period of this study is the likely cause of the increased pesticide loads. Unusually high runoff was probably also the cause for the high pesticide loads detected in the White River in Indiana in 1996 and 1997 (Charles G. Crawford, U.S. Geological Survey, written commun., 1999). Annual loads for atrazine in the

Table 7. Estimated pesticide application in 1997 and summary of loads and yields calculated March 1996 to February 1998 per drainage area of selected pesticides in Lake Erie-Lake St. Clair Basin surface-water-sampling sites

[mi^2, square mile; lb/yr, pound per year; lb/mi^2/yr, pound per square mile per year; -- , insufficient number of detections to determine loads and yields; nd, no data]

		Acetochlor				Alachlor				Atrazine			
Site name	**Drainage area (mi^2)**	**Estimated amount of pesticide applied to corn and soybeans in 1997[a] (pounds)**	**Load (lb/yr)**	**Standard deviation of load (lb/yr)**	**Yield per drainage area[b] (lb/mi^2/yr)**	**Estimated amount of pesticide applied to corn and soybeans in 1997[a] (pounds)**	**Load (lb/yr)**	**Standard deviation of load (lb/yr)**	**Yield per drainage area[b] (lb/mi^2/yr)**	**Estimated amount of pesticide applied to corn and soybeans in 1997[a] (pounds)**	**Load (lb/yr)**	**Standard deviation of load (lb/yr)**	**Yield per drainage area[b] (lb/mi^2/yr)**
River Raisin near Manchester, Mich.	132	5,200	2.0	0.66	0.02	400	1.5	0.40	0.01	10,000	8.4	1.6	0.06
Clinton River at Sterling Heights, Mich.	309	1,200	13	7.7	.04	100	5.1	1.6	.02	2,500	22	5.5	.07
Auglaize River near Fort Jennings, Ohio	332	22,000	660	550	2.0	6,600	620	510	1.9	57,000	4,700	2,900	14
Cattaraugus Creek at Gowanda, N.Y.	436	nd	--	--	--	nd	--	--	--	nd	100	13	.23
Black River near Jeddo, Mich.	464	12,000	260	260	.55	800	110	88	.24	23,000	1,200	950	2.5
Grand River at Harpersfield, Ohio	552	7,600	84	73	.15	1,400	27	14	.05	19,000	440	260	.79
St. Joseph River near Newville, Ind.	610	34,000	11,000	14,000	17	6,200	1,600	1,400	2.6	79,000	8,400	5,800	14
Cuyahoga River at Cleveland, Ohio	788	7,000	140	950	.18	1,500	37	15	.05	18,000	260	66	.33
Maumee River at New Haven, Ind.	1,967	120,000	6,600	5,500	3.3	26,000	2,900	2,200	1.5	310,000	22,000	15,000	11
Maumee River at Waterville, Ohio	6,330	420,000	12,000	6,600	1.9	110,000	8,000	4,000	1.3	1,100,000	47,000	21,000	7.5

Table 7. Estimated pesticide application in 1997 and summary of loads and yields calculated March 1996 to February 1998 per drainage area of selected pesticides in Lake Erie-Lake St. Clair Basin surface-water-sampling sites—Continued

		Cyanazine				Metolachlor				Simazine			
Site name	Drainage area (mi^2)	Estimated amount of pesticide applied to corn and soybeans in 1997[a] (pounds)	Load (lb/yr)	Standard deviation of load (lb/yr)	Yield per drainage area[b] ($lb/mi^2/yr$)	Estimated amount of pesticide applied to corn and soybeans in 1997[a] (pounds)	Load (lb/yr)	Standard deviation of load (lb/yr)	Yield per drainage area[b] ($lb/mi^2/yr$)	Estimated amount of pesticide applied to corn and soybeans in 1997[a] (pounds)	Load (lb/yr)	Standard deviation of load (lb/yr)	Yield per drainage area[b] ($lb/mi^2/yr$)
River Raisin near Manchester, Mich.	132	1,900	3.0	0.91	0.02	12,000	2.7	0.37	0.02	nd	16	3.7	0.12
Clinton River at Sterling Heights, Mich.	309	500	6.6	.99	.02	2,900	11	3.4	.03	nd	12	1.4	.04
Auglaize River near Fort Jennings, Ohio	332	26,000	730	510	2.2	71,000	5,500	2,900	16	5,600	400	160	1.2
Cattaraugus Creek at Gowanda, N.Y.	436	nd	--	--	--	nd	--	--	--	nd	15	18	.04
Black River near Jeddo, Mich.	464	4,300	240	180	.53	30,000	2,200	1,800	4.7	nd	19	7.3	.04
Grand River at Harpersfield, Ohio	552	8,800	27	13	.05	18,000	220	130	.39	1,900	47	20	.09
St. Joseph River near Newville, Ind.	610	25,000	2,200	1,500	3.6	92,000	7,300	6,200	12	3,200	580	310	1.0
Cuyahoga River at Cleveland, Ohio	788	8,100	77	26	1.0	18,000	110	62	.13	1,700	58	12	.07
Maumee River at New Haven, Ind.	1,967	100,000	4,400	2,600	2.2	330,000	24,000	11,000	12	11,000	1,800	910	.91
Maumee River at Waterville, Ohio	6,330	440,000	15,000	7,700	2.4	1,300,000	44,000	15,000	6.9	79,000	4,700	1,500	.75

Table 7. Estimated pesticide application in 1997 and summary of loads and yields calculated March 1996 to February 1998 per drainage area of selected pesticides in Lake Erie-Lake St. Clair Basin surface-water-sampling sites—Continued

		Chlorpyrifos				**Diazinon**				**Prometon**			
Site name	**Drainage area (mi^2)**	**Estimated amount of pesticide applied to corn and soybeans in 1997[a] (pounds)**	**Load (lb/yr)**	**Standard deviation of load (lb/yr)**	**Yield per drainage area[b] (lb/mi^2/yr)**	**Estimated amount of pesticide applied to corn and soybeans in 1997[a] (pounds)**	**Load (lb/yr)**	**Standard deviation of load (lb/yr)**	**Yield per drainage area[b] (lb/mi^2/yr)**	**Estimated amount of pesticide applied to corn and soybeans in 1997[a] (pounds)**	**Load (lb/yr)**	**Standard deviation of load (lb/yr)**	**Yield per drainage area[b] (lb/mi^2/yr)**
River Raisin near Manchester, Mich.	132	700	--	--	--	nd	1.1	0.15	0.01	nd	2.0	0.37	0.02
Clinton River at Sterling Heights, Mich.	309	200	3.5	.73	.01	nd	13	3.5	.04	nd	19	4.8	.06
Auglaize River near Fort Jennings, Ohio	332	5,600	12	4.4	.04	nd	14	3.7	.04	nd	25	4.4	.07
Cattaraugus Creek at Gowanda, N.Y.	436	nd	--	--	--	nd	--	--	--	nd	--	--	--
Black River near Jeddo, Mich.	464	1,500	--	--	--	nd	-	--	--	nd	9.5	2.9	.02
Grand River at Harpersfield, Ohio	552	1,900	--	--	--	nd	30	19	.05	nd	17	2.7	.03
St. Joseph River near Newville, Ind.	610	5,800	40	25	.07	nd	--	--	--	nd	31	5.8	.05
Cuyahoga River at Cleveland, Ohio	788	1,700	40	6.6	.05	nd	200	95	.26	nd	120	18	.16
Maumee River at New Haven, Ind.	1,967	20,000	110	55	.06	nd	320	300	.16	nd	240	51	.12
Maumee River at Waterville, Ohio	6,330	91,000	160	37	.02	nd	120	23	.02	nd	290	33	.05

[a] From National Agricultural Statistics Service, 1999.

[b] Calculated using square miles of drainage area.

Table 8. Drainage area, estimated atrazine application in 1997, atrazine load, and percentage of applied atrazine exported at Lake Erie-Lake St. Clair Basin surface-water-sampling sites, 1996–98

[mi^2, square mile; nd, no data]

Site name	Drainage area (mi^2)	Atrazine, estimated application[a] in 1997 (pounds of active ingredient)	Atrazine, load (pounds/year)	Percentage of applied atrazine detected in stream
River Raisin near Manchester, Mich.	132	10,400	8.4	0.10
Clinton River at Sterling Heights, Mich.	309	2,500	22	.90
Auglaize River near Fort Jennings, Ohio	332	56,900	4,700	8.3
Cattaraugus Creek at Gowanda, N.Y.	436	nd	nd	nd
Black River near Jeddo, Mich.	464	22,900	1,200	5.1
Grand River at Harpersfield, Ohio	552	19,400	440	2.3
St. Joseph River near Newville, Ind.	610	73,900	8,400	10.6
Cuyahoga River at Cleveland, Ohio	788	17,800	260	1.5
Maumee River at New Haven, Ind.	1,967	309,000	22,000	7.1
Maumee River at Waterville, Ohio	6,330	1,070,000	47,000	4.4

[a] Estimated from county level data collected by National Agricultural Statistics Service, 1999.

White River in 1996 through 1997 were as much as 600 percent higher than the smallest load that occurred during 1992 through 1998. As in the Lake Erie Basin, precipitation and streamflow were above normal in the White River Basin during 1996 through 1997.

Yields are loads normalized to a unit area; for this report, loads are normalized by the amount of drainage area. Because yields minimize the influence of differences in streamflow, they are useful measures for identifying streams that export more pesticides. The St. Joseph and Auglaize Rivers had the highest yields of commonly used row-crop herbicides (acetochlor, alachlor, atrazine, cyanazine, metolachlor, and simazine). Atrazine yields were 14 lb/mi^2/yr for both of these streams (table 7); metolachlor yields were 12 and 16 lb/mi^2/yr, respectively. The Cuyahoga River, an urban site, had the highest yields of the pesticides that more typically are used in urban areas (diazinon and prometon). Of these, diazinon had the highest yield (0.26 lb/mi^2/yr).

Relation of Pesticide Occurrence to Pesticide Properties, Pesticide Use, and Environmental Factors

Pesticide Properties

The chemical and physical properties of pesticides affect their behavior in the environment. Panshin and others (1998) investigated the influence of some of these properties on the occurrence and distribution of pesticides in the San Joaquin Basin in California. Two variables associated with the physical and chemical properties of pesticides—runoff potential and pesticide family—also are analyzed in this report. These properties are identified in the plots of pesticides applied versus the frequency of detection to compare general tendencies of these pesticides (table 3). A pesticide's runoff potential is based on its solubility in water, soil half-life, and the normalized organic-carbon adsorption coefficient (K_{oc}) and indicates the likelihood the pesticide will be transported to surface water (Goss, 1992).

In general, the frequency of detection of pesticides in samples collected from streams in the Lake Erie Basin increased as the amount of pesticides used in those stream basins increased (fig. 16A). Pendimethalin is an exception; although more than 300,000 lb of this herbicide were applied in 1995 in the Basin, it rarely was detected. Application data were available only for pesticides used in agricultural areas; as a result, pesticides with significant nonagricultural use (such as chlorpyrifos, diazinon, prometon, simazine, and tebuthiuron) will be underestimated (Aspelin, 1997).

There was also a trend of increasing frequency of detection with increasing runoff potential. Pesticides with medium or small runoff potential could be detected at a higher frequency if greater amounts of pesticide are applied—as reflected by detections of cyanazine, alachlor, and acetochlor. Linuron (large runoff potential) and pendimethalin (medium runoff potential) plot much lower than other pesticides with large or medium runoff potential and are exceptions to this trend.

Because families of pesticides have similar chemical structure and physical properties, similar frequency of detections would be expected when families of pesticides are analyzed (fig. 16B). In general, the families of pesticides detected more than 10 percent of the time can be categorized in decreasing order of detection frequency: triazines, amides, organophosphates, ureas, carbamates, organochlorines, and dinitroanalines. Linuron and tebuthiuron, both members of the urea family, have large runoff potential yet the lowest frequency of detection of all of the compounds that have a large runoff potential. This may be a factor of the amount of pesticide applied, the timing of application, or method of application that hinders runoff. Pendimethalin, the sixth most-applied pesticide in the Basin, has a much lower frequency of detection than the other heavily used pesticides with medium runoff potential (alachlor, acetochlor, and cyanazine). This lower frequency is more likely a function of pendimethalin having a lower water solubility and higher K_{oc} value than the other herbicides with higher frequencies of detection (Panshin and others, 1998).

Pesticide Use

Pesticide concentrations in streams are related to pesticide use, as illustrated by the application and concentrations of atrazine (fig. 17, p. 42). The maximum measured and median concentrations of atrazine detected in streams tended to increase with increasing application amounts. An exception to this trend was observed at the Maumee River at Waterville site, which is in the largest of the basins sampled (6,330 mi^2). Degradation of atrazine and dilution by the larger volume of water may account for this exception. Another exception was observed at the Auglaize River site, where the maximum (85 μg/L) and 95th percentile (40 μg/L) measured concentrations were much higher than at the other sites (table 4). These higher concentrations may be explained by the very poorly drained soils in the Auglaize River Basin, which necessitate tile drains for agriculture. Even though the highest measured concentrations were detected at the Auglaize River near Fort Jennings, Ohio, site, median concentration of atrazine was highest at the Maumee River at New Haven, Ind., site, probably because this basin is six times larger than the Auglaize River Basin.

Changes in pesticide use over time can be seen in the concentrations of alachlor and acetochlor in the St. Joseph River (fig. 18, p. 43). Acetochlor was conditionally registered for use by the USEPA in 1994 (U.S. Environmental Protection Agency, 1994). Between 1991 and 1993, alachlor was one of the most heavily used herbicides on corn and soybeans in the Lake Erie Basin; nearly 10 to 12.5 million pounds were applied to corn and soybeans in Ohio, Indiana, and Michigan. After use of acetochlor began in 1994, use of alachlor in the Basin dropped every year. Only about 800,000 pounds of alachlor were applied in these states in 1997. Acetochlor usage increased from 1.1 million pounds in 1994 to about 5.4 million pounds in 1996 and 1997. In 1996, the highest concentration of alachlor in a sample collected in this study was greater than the highest measured concentration of acetochlor; by 1997, the highest measured acetochlor concentration was almost double the highest concentration of alachlor, and it

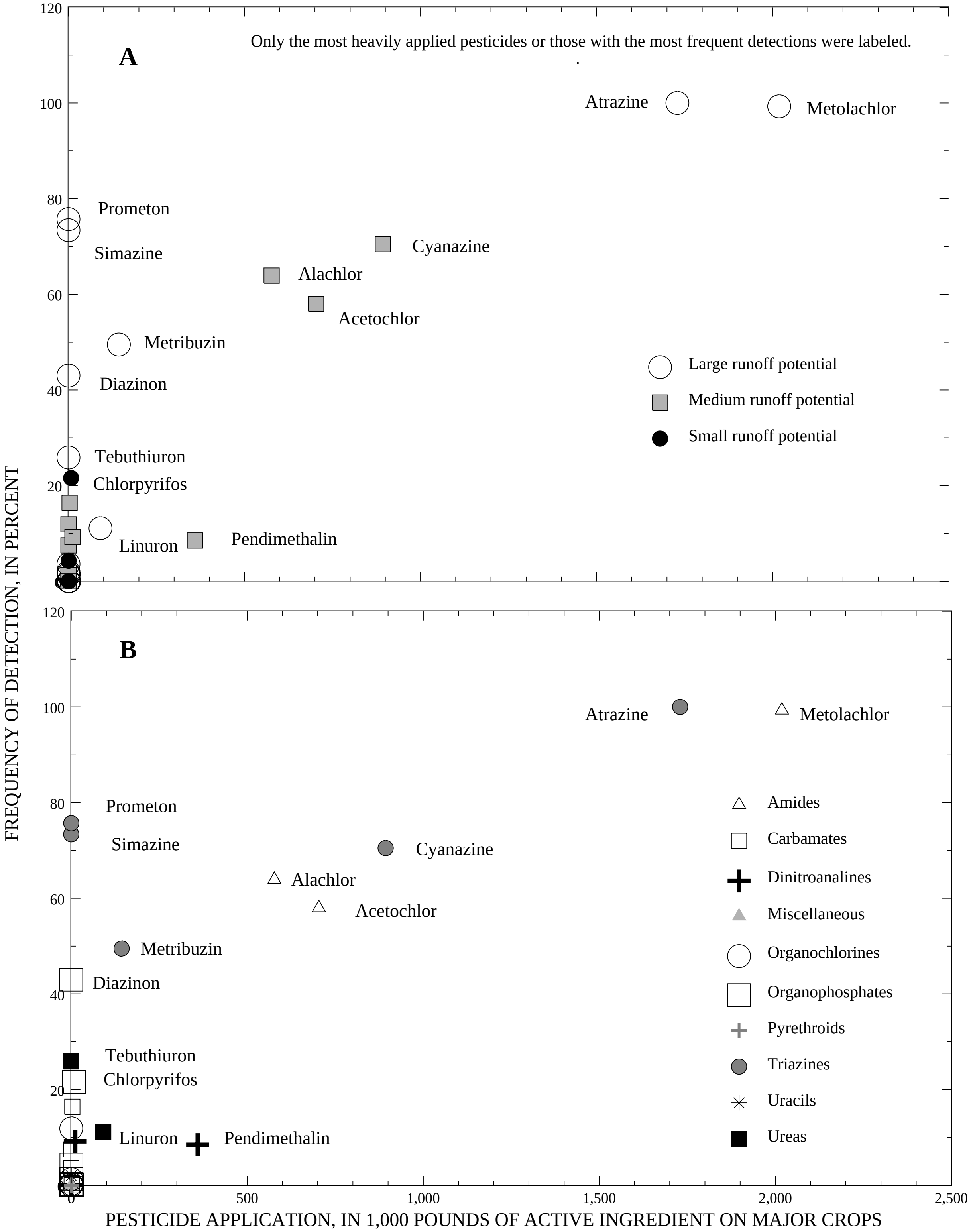


Figure 16. Relation of frequency of pesticide detection to pesticide application for all surface-water-sampling sites by (A) runoff potential and (B) pesticide family, Lake Erie-Lake St. Clair Basin, 1996–98. (Pesticide-application data from Brody and others, 1998.)

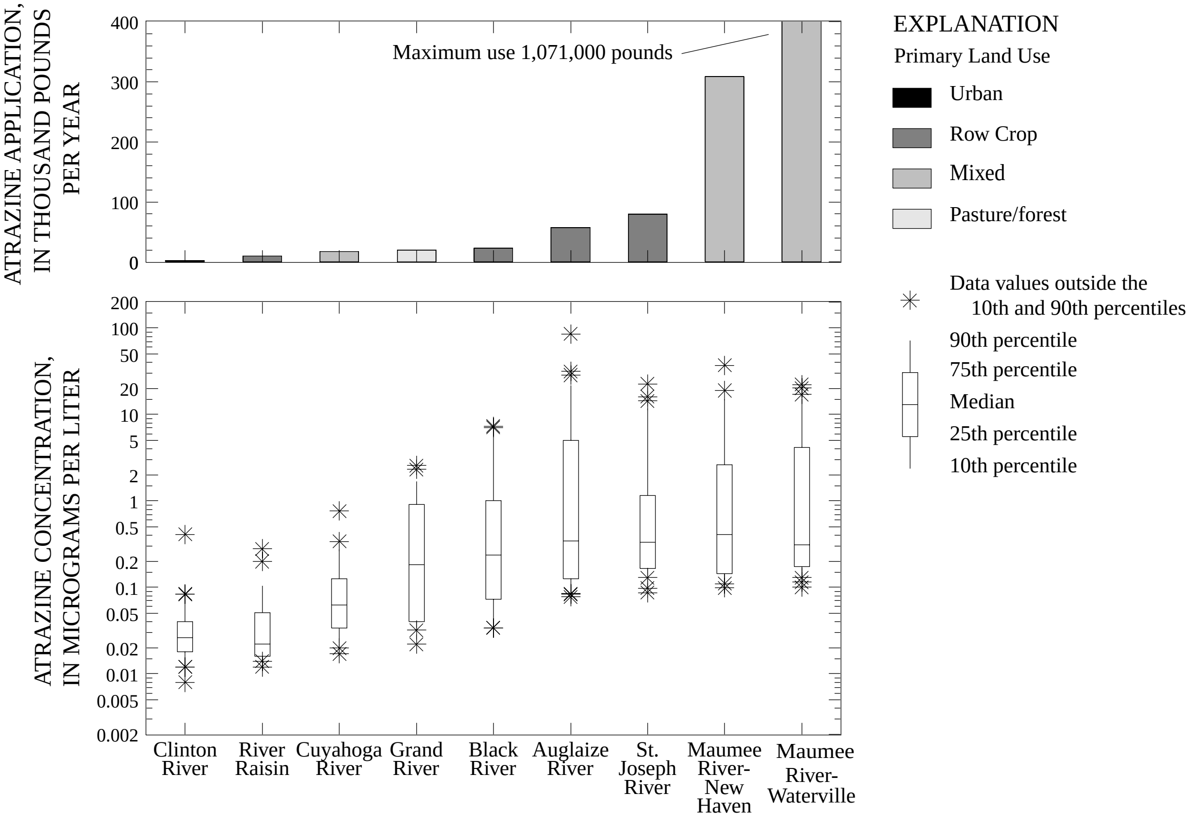


Figure 17. Atrazine application in 1997 and concentrations, by site. Lake Erie-Lake St. Clair River Basin surface-water-sampling sites listed in of order increasing application of atrazine. (Application data from National Agricultural Statistics Service, 1999.)

was nearly 10 times greater in 1998. Similar patterns for these herbicides were found in the White River in Indiana (Crawford, 1997).

Environmental Factors

The amount and timing of rainfall after pesticide application affect pesticide concentrations in surface water. A conceptual model of pesticide interaction with soils and water shows these variations. After application, some of a pesticide is taken up by the plants, some adsorbs to soils, some volatilizes, and some goes into solution in the soil water. In the soil, some of the pesticide breaks down into degradates through biological or physical processes. When rain falls, some pesticides percolate into soil until the soil becomes saturated. Once the soil is saturated or the infiltration rate is exceeded, rainfall flows over the land surface as runoff. More rain results in more runoff. Years with long, intense rainfall on fields with relatively moist soils shortly after pesticide application will result in the transport of more pesticides into streams than years in which the rain occurs a long time after application. These differences in wet and dry years and timing of rainfall can be seen in the concentrations of atrazine in the St. Joseph River from 1996 through 1998 (fig. 19, p. 44). In May and June 1996, streamflow was 330 to 340 percent of the normal May–June flow; in 1997, streamflow was 103 to 129 percent of the normal May–June flow; and in 1998, streamflow was 36 to 78 percent of the normal May–June flow. The median atrazine concentration detected in the stream was 0.40 µg/L in 1996, 0.45 µg/L in 1997, and 0.14 µg/L in 1998[1].

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[1] When the medians were calculated from the same number of samples per month from March to December in 1996, 1997, and 1998, the medians were 0.47 µg/L, 0.30 µg/L, and 0.13 µg/L, respectively.

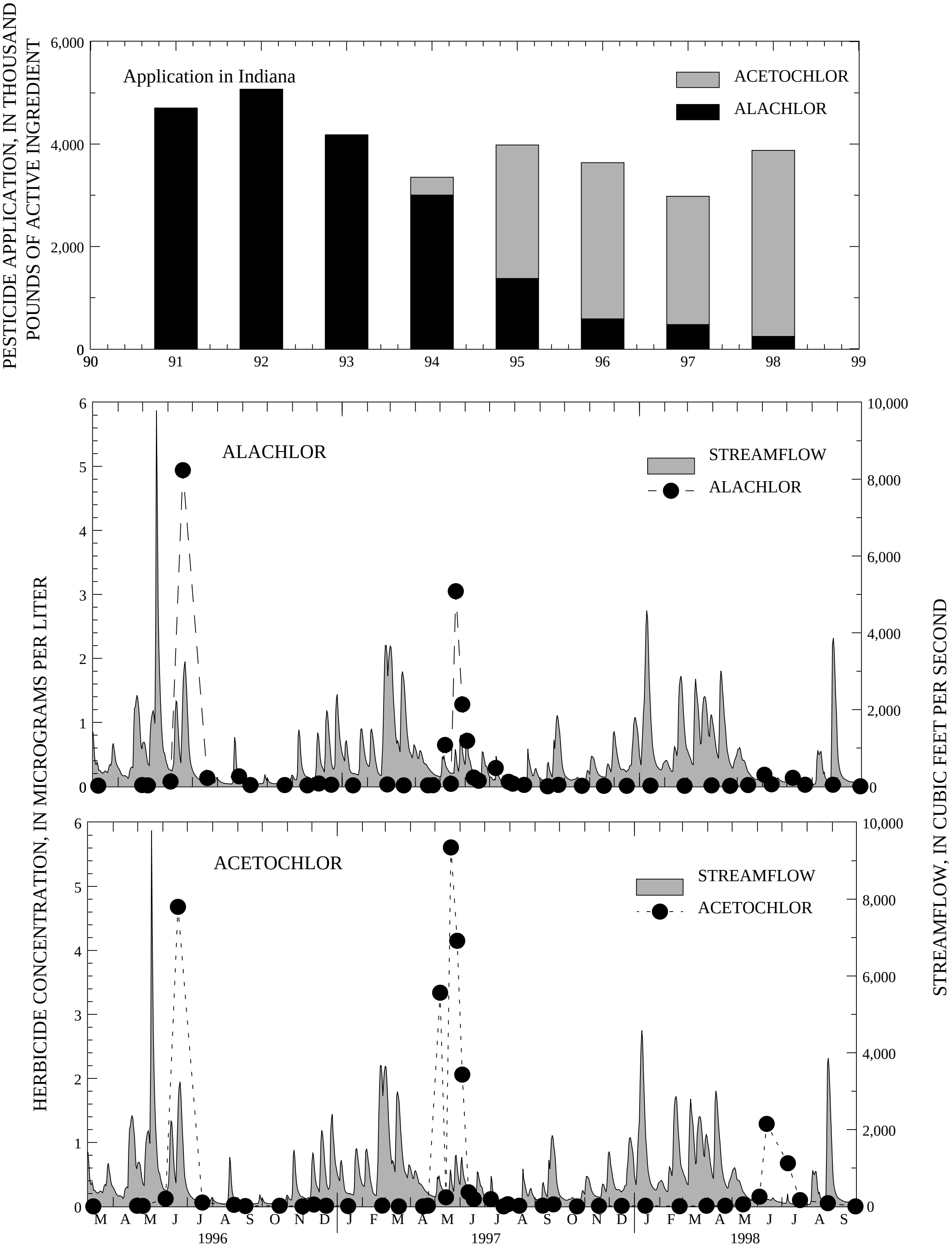

Figure 18. Relation of alachlor and acetochlor concentrations and streamflow to time in the St. Joseph River near Newville, Ind., and alachlor and acetochlor application in Indiana 1991–98. (Application data from National Agricultural Statistics Service, 1999.)

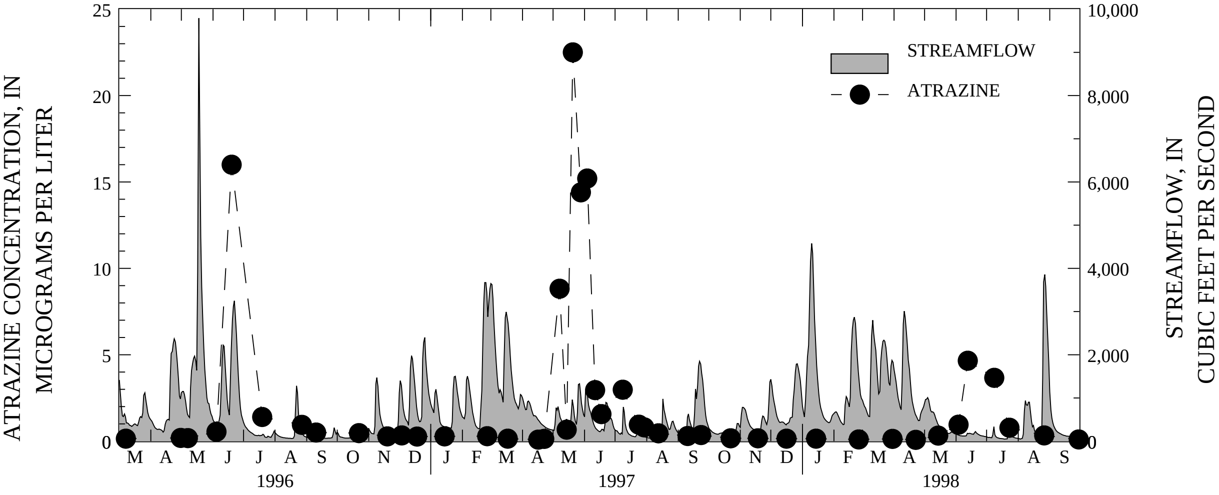

Figure 19. Relation of atrazine concentrations and streamflow to time in the St. Joseph River near Newville, Ind., March 1996-September 1998.

The maximum measured atrazine concentration detected in the stream was 16 µg/L in 1996, 23 µg/L in 1997, and 4.7 µg/L in 1998. Differences in the timing of rainfall between 1996 and 1998 also influenced when maximum measured concentrations of pesticides occurred. Above-average rainfall led to the highest recorded streamflow in May 1996 in the St. Joseph River between 1947 and 1998 and delayed planting. Peak concentrations of rainfall occurred 2 to 4 weeks later in 1996 than in 1997.

Another factor that appears to influence pesticide concentrations in streams is soil permeability. Well-drained soils (hydrologic soil type A and B soils in the State Soil Geographic Data Base in Wolock, 1997) allow water to percolate to ground water. As water percolates through soil, some pesticides are filtered by the soil and broken down to degradates by bacteria. In areas with impermeable soils, more water enters streams as surface runoff. Such areas also require tile drains to make the land arable. Because tile drains lessen the underground filtration of the soils, they can transport elevated concentrations of pesticides (Fenelon, 1998; Zucker and Brown, 1998). This may account for the elevated pesticide concentrations in the Auglaize River. In four row-crop basins in which the percentage of permeable soils ranges from 2 percent (Auglaize River Basin) to 58 percent (River Raisin Basin), comparisons of the percentage of atrazine exported in streams to the amount applied in the basin illustrate the generally increasing amount of atrazine exported in basins with more impermeable soils (fig. 20). This trend corresponds to the more frequent detections and higher concentrations of pesticides and degradates in ground water in areas with more permeable soils than in areas with more impermeable soils (M.A. Thomas, U.S. Geological Survey, oral commun., 2000). Apparently, at least one factor is unaccounted for because the St. Joseph and Black Rivers, which have similar percentages of permeable soils (22 and 20 percent, respectively) have different amounts of pesticide detected. One factor that could account for this difference is streamflow. Higher streamflow, especially in the spring, could influence the amount of pesticide in the stream. It appears, however, that the 30-year normals for precipitation and streamflow were similar for the St. Joseph and Black Rivers (fig. 3).

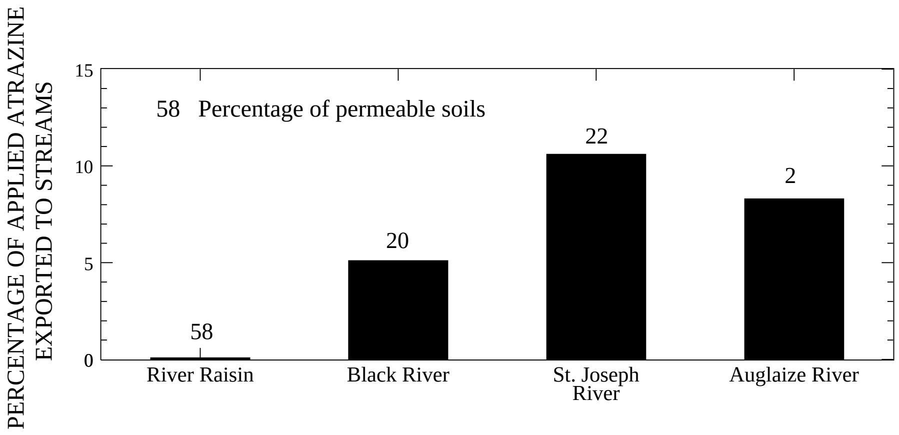

Figure 20. Percentage of applied atrazine exported to streams in row-crop basins and the percentage of permeable soils in each study basin of the Lake Erie-Lake St. Clair Basin, 1996–98.

Summary and Conclusions

As part of the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program, 315 pesticide samples were collected from 10 streams in the Lake Erie-Lake St. Clair Basin. Two agricultural herbicides, metolachlor and atrazine, are the most heavily used pesticides in the Basin. In 1995, approximately 2.0 and 1.7 million pounds of metolachlor and atrazine, respectively, were applied in the Basin. Herbicides are used much more heavily than insecticides in agricultural areas. Seven of the 10 most heavily applied agricultural pesticides were herbicides used primarily on corn and soybeans and include metolachlor, atrazine, cyanazine, acetochlor, alachlor, pendimethalin, and metribuzin. Although data on urban pesticide use are lacking, insecticides usually account for a larger percentage of the overall use in urban areas than in agricultural areas planted in corn and soybeans.

Of the 44 pesticides and three degradates evaluated in this study, 30 were detected at least once. Atrazine was detected in every sample. Deethylatrazine, metolachlor, and simazine were detected in more than 90 percent of the samples. Eight pesticides had a frequency of detection greater than 50 percent. The pesticides that were the most heavily applied in the Basin were generally those most frequently detected in streams in the Basin. Herbicides, therefore, were detected more frequently than insecticides. Diazinon and chlorpyrifos were the most frequently detected insecticides. In general, the number of detections increased with basin size. In the River Raisin near Manchester, Mich., (the smallest basin sampled at 132 mi^2) 14 pesticides were detected at least once; 27 pesticides were detected at the Maumee River at Waterville, Ohio (the largest basin at 6,330 mi^2).

Atrazine and metolachlor were detected at the highest concentrations (85 and 78 µg/L, respectively). Pesticide concentrations in streams showed pronounced seasonal trends. Row-crop herbicides applied in the spring, such as atrazine, had elevated concentrations in the spring; pesticides usually applied in the late summer or early fall, such as diazinon, had maximum measured concentrations at those times. Maximum measured concentrations in streams occurred after application and corresponded with rainfalls that carried the pesticides into the streams. The amount of pesticides detected in streams also was influenced by hydrologic conditions. Differences in the timing and amount of rainfall between 1996 and 1998 influenced the concentrations of pesticides detected. Above-average rainfall in May and June 1996 delayed planting, and maximum measured concentrations of pesticides were detected 2 to 4 weeks later in 1996 than in 1997. Maximum measured and median concentrations were higher in 1996 and 1997 than in 1998 because of the above-average rainfall and streamflow in 1996 and 1997 (compared to the below-average rainfall and streamflow in 1998).

The highest pesticide loads were of atrazine and metolachlor at the Maumee River at Waterville, Ohio, with 47,000 and 44,000 pounds in 1997, respectively. Two basins in which row-crop agriculture dominated—the St. Joseph River near Newville, Ind., and the Auglaize River near Fort Jennings, Ohio—had the highest yields of the herbicides acetochlor, alachlor, atrazine, cyanazine, metolachlor, and simazine. The St. Joseph and Auglaize Rivers had the highest yields of commonly used row-crop herbicides, with atrazine yields of 14 lb/mi^2/yr for both of these streams. Metolachlor yields were 12 and 16 lb/mi^2/yr, respectively. The Cuyahoga River at Cleveland, Ohio, had the highest yields of diazinon and prometon—pesticides typically applied more heavily in urban areas. Pesticide loads in streams as a percentage of the amount applied to cropland in the basin ranged from 3 to 7 percent at the Maumee River at Waterville, Ohio; these percentages tended to be highest in the smaller basins.

All of the herbicide degradates analyzed for were detected in at least 6 of 10 of the samples. Alachlor ESA, metolachlor ESA, and metolachlor oxanilic acid were detected in 100 percent (10 of 10 samples). Acetochlor oxanilic acid had the highest detected concentration (6.76 µg/L). Seasonal variation was similar for the degradates to that of the parent compounds. Acetanilide degradates constituted a much larger fraction of the amount of acetanilide herbicides washing off the fields than triazine degradates did for triazine herbicides. These data, though limited, suggest that degradates—especially acetanilides—can contribute a significant load into Lake Erie.

The annual time-weighted average concentrations did not exceed the primary drinking-water standards or health advisories at any of the surface-water-sampling sites. During May through July, however, when most pesticides run off into streams, time-weighted average concentrations for this time period exceeded the MCL for atrazine at five row-crop sites. There were no exceedences of the acute, longer-term, or lifetime health advisories. Time-weighted average concentrations of atrazine and cyanazine frequently exceeded HA-L guidelines during May through July. For some heavily used herbicides such as atrazine, metolachlor, cyanazine, and acetochlor, elevated concentrations were detected for 4 to 6 weeks after the initial maximum measured concentration in the row-crop basins. Acetochlor was twice detected at levels above 8.00 µg/L in two streams used as a drinking-water supply, which triggers additional sampling as part of the conditional registration for acetochlor.

The percentage of atrazine that was applied and then detected in streams generally increased when the amount of permeable soils decreased within each basin. More permeable soils allow water to percolate into ground water and require less use of tile drains. A lower percentage of atrazine was found in the River Raisin, which has 58 percent permeable soils, compared to the Black River, St. Joseph River, and Auglaize River, which have 20, 22, and 2 percent permeable soils.

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Appendix A

Quality Assurance: Field Blanks, Field Spikes, and Split Replicates
Tables A1–A2
Figure A1

Quality Assurance

Data from field blanks, field and laboratory spikes, and split replicates were used to estimate bias and variability in the measurement of pesticides. A field blank is a pesticide-free water sample that is processed through the sampling equipment and sent to the laboratory for analysis, following the same procedures as those used for environmental samples. Analysis of field blanks provides an estimate to determine whether the equipment, field technicians, transportation of the samples, site atmosphere, laboratory analysis, or other sources could have contaminated the environmental samples.

A spike is a sample of streamwater or pesticide-free water used to estimate positive or negative bias in environmental samples caused by matrix interference or pesticide degradation. Matrix interference can cause a positive or negative bias (over- or underestimation of the true amount of pesticides in the sample), and pesticide degradation can cause a negative bias. Matrix interference occurs when compounds in the water prevent accurate measurement of pesticides, using current analytical methods (Mueller and others, 1997). Pesticide degradation occurs when the parent compound breaks down into a metabolite before the sample is analyzed. A spike is a streamwater or pesticide-free water sample that has had a known amount of pesticides added. For each spike, an unspiked streamwater sample (the environmental sample) is collected at the same time to estimate the background concentration (the concentration of pesticides in the spike before the pesticides were added). The percent recovery of each pesticide in the spike is calculated by subtracting the concentration of the pesticide in the spiked sample from the concentration in the environmental sample and dividing by the expected concentration in the spike. The expected concentration is the concentration that would be found if there were 100-percent recovery of the spike compounds added to the sample.

A split replicate is a second environmental sample used to estimate variability. A split replicate is obtained by splitting a large volume of streamwater into two samples (one is considered to be the environmental sample and the other is the split replicate). Because the environmental and split-replicate samples come from the same volume of streamwater, analytical differences between the two samples should reflect the variability associated with either the field or laboratory processes.

Field Blanks

Contamination associated with the pesticide data was estimated, using seven field blanks collected at three surface-water-sampling sites between December 1996 and June 1997. Field-blank samples were collected prior to collecting the environmental samples. Seven pesticides were detected at least once in the field-blank samples (table A1). Of the pesticides with detections, only metolachlor—with six detections—was detected in more than two of the seven field blanks. The median of these detections was 0.004 µg/L, and the maximum was 0.007 µg/L. Even though metolachlor frequently was detected in the field blanks, the concentrations were very low compared to environmental samples. Metolachlor was detected (the method detection limit is 0.002 µg/L) in 99.3 percent of the 305 environmental samples. The frequency of detection would decrease to 96.7 percent if metolachlor were censored at 0.003 µg/L. If censored at 0.007 µg/L, the frequency of detection of metolachlor in the environmental samples would decrease to 84.9 percent.

Diazinon was detected in one sample blank at the highest concentration (0.179 µg/L) of all 458 surface-water blanks collected by all NAWQA 1991 and 1994 Study Units (Jeffrey D. Martin, U.S. Geological Survey, written commun., 2000). The reported value was verified by the NWQL; however, the validity of the sample is questionable because there were no detections in the environmental samples at the previous site or at the site where the blank was collected. Also, the blank does not appear to be a sample switched with an environmental sample because commonly detected pesticides such as atrazine and metolachlor were not detected in the blank.

Table A1. Bias and variability estimates for 7 field blanks and 10 split-replicate samples, Lake Erie-Lake St. Clair Basin, 1996–98

[(µg/L), microgram per liter; E, estimated; nd, not detected]

		Field blanks			**Split replicates**					
Pesticide	**Method detection limit (µg/L)**	**Number of detections**	**Median concentration detected (µg/L)**	**Maximum concentration detected (µg/L)**	**Number of detections**	**Minimum concentration detected (µg/L)**	**Maximum concentration detected (µg/L)**	**Median percent difference for detected pesticides**	**Minimum percent difference for detected pesticides**	**Maximum percent difference for detected pesticides**
Acetochlor	0.002	0	nd	nd	8	0.010	0.518	3.8	0.97	45.2
Alachlor	.002	0	nd	nd	10	.005	.222	5.5	0	26.7
Atrazine	.001	2	.009	.015	10	.033	6.98	3.3	0	21.0
Atrazine, deethyl	.002	0	nd	nd	10	E .006	E .557	13.7	3.2	105.2
Azinphos, methyl	.001	0	nd	nd	0	nd	nd	nd	nd	nd
Benfluralin	.002	0	nd	nd	0	nd	nd	nd	nd	nd
Butylate	.002	0	nd	nd	0	nd	nd	nd	nd	nd
Carbaryl	.003	0	nd	nd	2	E .003	E .015	87.4	40.4	134.4
Carbofuran	.003	0	nd	nd	1	E .003	E .007	77.2	77.2	77.2
Chlorpyrifos	.004	2	.0175	.019	3	.004	.021	75.8	2.5	131.9
Cyanazine	.004	0	nd	nd	10	.010	1.52	4.2	.48	42.3
DCPA	.002	2	E .002	E .002	5	E .0005	.006	51.6	10.8	120.4
DDE, *p,p'*	.006	1	E .002	E .002	0	nd	nd	nd	nd	nd
Diazinon	.002	2	.119	.179	5	.002	.007	18.2	4.2	107.1
Dieldrin	.001	0	nd	nd	0	nd	nd	nd	nd	nd
Diethylanaline-2,6	.003	0	nd	nd	0	nd	nd	nd	nd	nd
Disulfoton	.017	0	nd	nd	0	nd	nd	nd	nd	nd
EPTC	.002	0	nd	nd	1	.003	.003	18.2	18.2	18.2
Ethalfluralin	.004	0	nd	nd	0	nd	nd	nd	nd	nd
Ethoprop	.003	0	nd	nd	0	nd	nd	nd	nd	nd
Fonofos	.003	0	nd	nd	0	nd	nd	nd	nd	nd
alpha-HCH	.002	0	nd	nd	0	nd	nd	nd	nd	nd
gamma-HCH	.004	0	nd	nd	0	nd	nd	nd	nd	nd
Linuron	.002	0	nd	nd	4	.004	.016	14.6	5.8	49.1

Table A1. Bias and variability estimates from 7 field blanks and 10 split-replicate samples, Lake Erie-Lake St. Clair Basin, 1996–98—Continued

		Field blanks			Split replicates					
Pesticide	Method detection limit (μg/L)	Number of detections	Median concentration detected (μg/L)	Maximum concentration detected (μg/L)	Number of detections	Minimum concentration detected (μg/L)	Maximum concentration detected (μg/L)	Median percent difference for detected pesticides	Minimum percent difference for detected pesticides	Maximum percent difference for detected pesticides
Malathion	0.005	1	0.022	0.022	0	nd	nd	nd	nd	nd
Methyl parathion	.006	0	nd	nd	0	nd	nd	nd	nd	nd
Metolachlor	.002	6	.0035	.007	10	.036	4.62	4.9	.80	37.9
Metribuzin	.004	0	nd	nd	9	.004	.207	9.6	0	62.1
Molinate	.004	0	nd	nd	1	.004	.004	13.3	13.3	13.3
Napropamide	.003	0	nd	nd	0	nd	nd	nd	nd	nd
Parathion	.004	0	nd	nd	0	nd	nd	nd	nd	nd
Pebulate	.004	0	nd	nd	0	nd	nd	nd	nd	nd
Pendimethalin	.004	0	nd	nd	0	nd	nd	nd	nd	nd
Permethrin, cis	.005	0	nd	nd	0	nd	nd	nd	nd	nd
Phorate	.002	0	nd	nd	0	nd	nd	nd	nd	nd
Prometon	.003	0	nd	nd	10	.003	.046	9.8	3.8	82.4
Pronamide	.003	0	nd	nd	0	nd	nd	nd	nd	nd
Propachlor	.007	0	nd	nd	0	nd	nd	nd	nd	nd
Propanil	.004	0	nd	nd	0	nd	nd	nd	nd	nd
Propargite	.013	0	nd	nd	0	nd	nd	nd	nd	nd
Simazine	.005	0	nd	nd	10	.004	.682	5.9	0	27.7
Tebuthiuron	.010	0	nd	nd	6	.006	.024	24.6	4.3	67.1
Terbacil	.007	0	nd	nd	0	nd	nd	nd	nd	nd
Terbufos	.013	0	nd	nd	0	nd	nd	nd	nd	nd
Thiobencarb	.002	0	nd	nd	0	nd	nd	nd	nd	nd
Triallate	.001	0	nd	nd	0	nd	nd	nd	nd	nd
Trifluralin	.002	0	nd	nd	1	.003	.004	5.9	5.9	5.9

The frequency of detection of *p,p'*-DDE (14.3 percent) was higher in the seven blanks collected than in the 302 environmental samples (1.3 percent) in the Lake Erie study. This makes the *p,p'*-DDE data questionable. All four detections of *p,p'*-DDE in environmental samples, however, were found in Michigan and the single detection of *p,p'*-DDE was found in a blank collected at the St. Joseph River near Newville, Ind. Furthermore, although *p,p'*-DDE was detected in 14.3 percent of the blanks (1 of 7 blanks) collected in the Lake Erie study, of the 458 blanks collected by all NAWQA Study Units only 2.8 percent had detections (Jeffrey D. Martin, U.S. Geological Survey, written commun., 2000).

Field Spikes

Three sets of field spikes were collected at different concentrations to determine the accuracy with which the National Water Quality Laboratory can measure a known amount of pesticide over a range of concentrations. Fifteen spiked samples were collected. To evaluate recovery at low concentrations, duplicate field spikes (six total samples) at concentrations of 0.1 µg/L were sampled for all 47 pesticides at the St. Joseph River near Newville, Ind., and the Auglaize River near Fort Jennings, Ohio, in December 1996 and at the Black River near Jeddo, Mich., in April 1997. To evaluate recovery at medium concentrations, single field spikes (three total samples) with concentrations of 0.1, 3.0, and 6.0 µg/L, respectively, for 16 heavily used row-crop pesticides were sampled at the St. Joseph River near Newville, Ind., in July 1998. To evaluate recovery at high concentrations, duplicate field spikes (six total samples) with concentrations of 2.0 to 20.0 µg/L were sampled for the same 16 row-crop pesticides at the St. Joseph River near Newville, Ind.; Auglaize River near Fort Jennings, Ohio; and the Maumee River at Waterville, Ohio, in April 1997.

The 15 spiked samples were analyzed, using the gas chromatography/mass spectroscopy (GC/MS) method. Twenty-six of the pesticides had median recovery within 10 percent of 100 percent. For 40 of the 47 pesticides and degradates analyzed in the spikes, using the GC/MS method, the median percent recovery ranged from 71 to 130 percent (table A2). Of the seven compounds outside this range, four were biased low: deethylatrazine (50 percent), disulfoton (56 percent), phorate (57 percent), and *p,p'*-DDE (66 percent). Three were biased high: carbaryl (254 percent), carbofuran (172 percent), and tebuthiuron (136 percent).

Twelve of the 16 pesticides spiked at 0.1, 3.0, and 6.0 µg/L in 1998 had similar recoveries as the 0.1-µg/L field spikes obtained in 1996 and 1997, indicating that bias is not a function of concentration. Recoveries of the four remaining pesticides were a function of concentration; deethylatrazine, cyanazine, carbofuran, and carbaryl showed statistically significant decreases in recovery at higher concentrations (Jeffrey D. Martin, U.S. Geological Survey, oral commun., 1999), indicating that they are underestimated at higher concentrations.

Because replicates were collected for 12 of the 15 spikes, variability can be calculated. The Relative Interquartile Range (RIQR) is a nonparametric measurement of variability around the median. The RIQR is calculated as:

[(75% Quartile - 25% Quartile)/Median) x 100].

The RIQR ranged from 3 for ethoprop to 130 for disulfoton. The median IQR for all pesticides was 20 percent. Ten pesticides had variability with a RIQR greater than 40 percent, including metribuzin (48 percent), propargite (51 percent), tebuthiuron (52 percent), terbacil (52 percent), cis-permethrin (58 percent), terbufos (61 percent), linuron (62 percent), deethylatrazine (84 percent), phorate (123 percent), and disulfoton (130 percent).

A comparison of spikes analyzed by the NQWL for internal quality assurance with the seven field spikes at the same concentrations indicates that the measurement of some compounds may be affected by matrix interference (table A2). Between March 1996 and February 1998, 751 to 754 spikes were analyzed using pesticide-free water at the NWQL. Twenty-eight of the 47 pesticides had median recoveries of 10 percent or less (90–110 percent recovery). The difference between median recoveries in laboratory and field spikes

Table A2. Precision and bias estimates for pesticides in 7 field spikes from the Lake Erie-Lake St. Clair Basin, March 1996–February 1998, and 751 to 754 laboratory spikes for all National Water-Quality Assessment Program Study Units

[IQR, interquartile range]

Compound	Median recovery—field (percent)	Relative IQR—field	Median recovery—laboratory (percent)	Relative IQR—laboratory
Acetochlor	98	7	97	12
Alachlor	101	20	103	11
Atrazine	87	17	100	11
Atrazine, deethyl	50	84	44	42
Azinphos, methyl	118	21	81	70
Benfluralin	107	7	68	32
Butylate	105	8	89	11
Carbaryl	254	10	126	58
Carbofuran	172	30	112	33
Chlorpyrifos	98	5	90	14
Cyanazine	108	39	103	24
DCPA	96	5	104	12
DDE, *p,p’*	66	11	59	23
Diazinon	100	14	84	13
Dieldrin	93	20	82	19
Diethylanaline-2,6	83	25	85	11
Disulfoton	56	130	73	32
EPTC	94	28	91	9
Ethalfluralin	120	12	78	30
Ethoprop	93	3	96	17
Fonofos	89	27	88	14
alpha-HCH	88	8	90	14
gamma-HCH	97	6	92	16

Pesticide	Median recovery—field (percent)	Relative IQR—field	Median recovery—laboratory (percent)	Relative IQR—laboratory
Linuron	102	62	101	28
Malathion	107	16	95	23
Methyl parathion	126	18	90	30
Metolachlor	92	23	106	14
Metribuzin	109	48	78	24
Molinate	98	16	95	9
Napropamide	99	11	94	16
Parathion	130	14	93	23
Pebulate	95	21	92	9
Pendimethalin	126	10	74	32
Permethrin, cis	80	58	46	42
Phorate	57	123	72	27
Prometon	102	27	71	59
Pronamide	105	24	90	15
Propachlor	124	12	105	13
Propanil	103	8	108	15
Propargite	99	51	72	32
Simazine	91	23	101	12
Tebuthiuron	136	52	116	34
Terbacil	101	52	81	36
Terbufos	71	61	76	24
Thiobencarb	97	5	100	15
Triallate	89	13	90	15
Trifluralin	111	32	71	32

was 30 percent or greater for 12 pesticides; in these samples, the laboratory spike values were always less than in the field spikes. These large differences between the field and laboratory spikes for certain pesticides may be explained by (1) matrix interference or (2) improved recovery of spikes using natural waters that have more ions compared to those using pesticide-free water (pesticide recovery is more effective with more ions, using the GC/MS method) (Jeffrey D. Martin, U.S. Geological Survey, oral commun., 1999).

The variability (median RIQR) was approximately the same for the laboratory (19 percent) and field spikes (20 percent). The range, however, was smaller for the laboratory spikes than for the seven field spikes. The RIQR for the laboratory spikes ranged from 9 for ethoprop to 70 for disulfoton, with a median of 20 percent. A smaller RIQR is expected because of the large number of samples (more than 750). Eight pesticides had high variability (RIQR greater than 30 percent) in field or laboratory spikes. Five pesticides (deethylatrazine, disulfoton, linuron, phorate, and terbufos) had much greater variability associated with the field spikes (greater than 30 percent difference between the field and laboratory RIQRs); three pesticides (methyl azinphos, carbaryl, and prometon) had much greater variability associated with the laboratory spikes.

Split Replicates

The precision of the pesticide data was estimated, using 10 split-replicate samples collected at four surface-water-sampling sites between December 1996 and June 1997. Of the 47 compounds that were analyzed, 19 were detected at least once; therefore relative differences in concentrations could be calculated (table A1). For replicates with one detection and one nondetection, the MDL concentration was used. The percent difference between replicates was calculated as:

$$[EC - RC/(EC+RC)/2] \text{ x } 100,$$

where,

EC is the concentration of the environmental sample and

RC is the concentration of the split-replicate.

The median percent differences for these 19 pesticides ranged from 3.3 (atrazine) to 87.4 percent (carbaryl). Compounds having the most variability were carbaryl, carbofuran, chlorpyrifos, and DCPA—all of which had median percent differences greater than 50 percent or more. Some of the variability associated with these pesticides results from detections near the MDL, where percent differences are greatest (Mueller and others, 1997). Only eight compounds were detected at concentrations above 1 µg/L. As concentrations approached the MDL, the variability increased (fig. A1). Of the remaining 15 pesticides that were detected, 4 had individual replicates that had maximum percent differences greater than 50 percent. Two (carbofuran and prometon) had maximum percent differences between 75.0 and 99.9 percent, and two (metribuzin and tebuthiuron) had maximum percent differences between 50.0 and 74.9 percent. In these four samples, carbofuran and metribuzin were detected near the MDL. Three pesticides (carbofuran, EPTC, and molinate) were detected only once.

The results of the quality-assurance blank samples indicate that, for most pesticides, bias was low. Metolachlor was an exception. Because the contamination of metolachlor was at low levels, the analysis was unaffected and the data were uncensored. The results of the field and laboratory spikes indicate that the recovery of pesticides, using GC/MS analysis, was effective for most of the compounds analyzed; 28 of the 47 had recoveries between 90 and 110 percent. Some pesticides consistently were biased low in recovery, and reported concentrations were probably low, including those for deethylatrazine, *p,p'*-DDE, disulfoton, and phorate. Some pesticides were consistently biased high in recovery, and reported concentrations were probably high, including carbaryl, carbofuran, and tebuthiuron. The results of the split-replicate samples indicate that intra-sample variability is low for those pesticides most frequently detected. The variability was greater for some pesticides (carbaryl, carbofuran, and chlorpyrifos) because of the low number of detections in the split-replicate samples. These results indicate that the reproducibility, and thus the quality of the samples, was good.

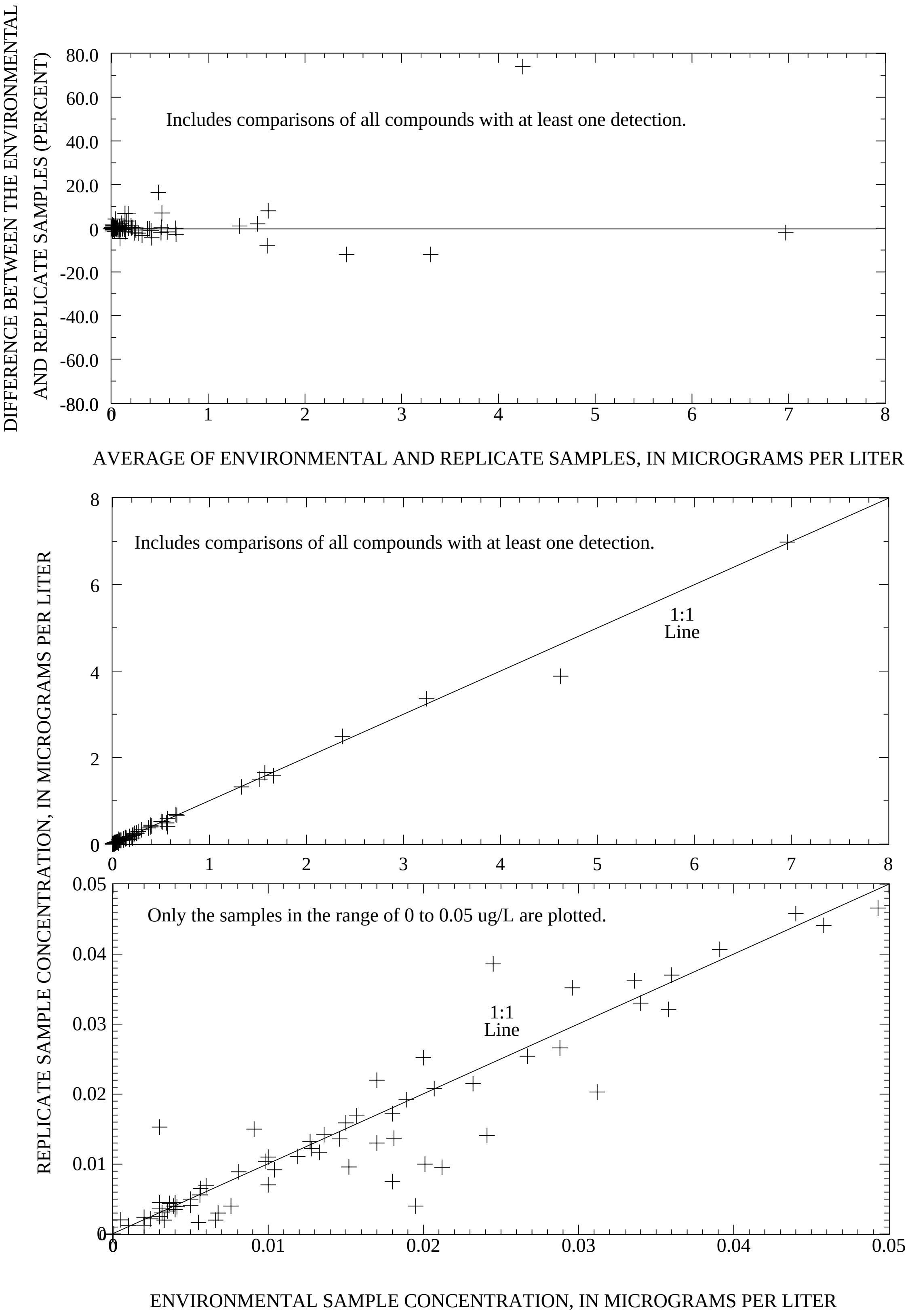

Figure A1. Percent differences and differences in concentration between the 10 environmental and split-replicate samples for the Lake Erie-Lake St. Clair study, 1996–98.

Appendix B

Compounds Analyzed; Method Detection Limit; Number of Analyses; Frequency of Detection; and the Median, 95th Percentile, and Maximum Concentration for Each Pesticide for Each Basin

Tables B1–B10

Table B1. Compounds analyzed; method detection limit; number of analyses; frequency of detection; and the median, 95th percentile, and maximum concentrations for samples from the River Raisin near Manchester, Mich.

[µg/L, micrograms per liter; ld, less than method detection limit; E, pesticides detected and concentrations estimated; --, no data]

Compound	Method detection limit (µg/L)	Number of analyses	Frequency of detection (percent)	Median (µg/L)	95th percentile (µg/L)	Maximum (µg/L)
Acetochlor	0.002	27	29.6	ld	0.042	0.045
Alachlor	.002	27	25.9	ld	.017	.040
Atrazine	.001	27	100	.022	.248	.280
Atrazine, deethyl	.002	27	100	E .008	E .036	E .045
Azinphos, methyl	.001	27	0	--	--	--
Benfluralin	.002	27	0	--	--	--
Butylate	.002	27	0	--	--	--
Carbaryl	.003	27	0	--	--	--
Carbofuran	.003	27	0	--	--	--
Chlorpyrifos	.004	27	0	--	--	--
Cyanazine	.004	27	66.7	.008	.030	.152
DCPA	.002	26	3.7	ld	ld	E .001
DDE, *p,p'*	.006	27	3.7	ld	ld	E .002
Diazinon	.002	27	37.0	ld	.008	.009
Dieldrin	.001	27	0	--	--	--
Diethylanaline-2,6	.003	27	0	--	--	--
Disulfoton	.017	27	0	--	--	--
EPTC	.002	27	0	--	--	--
Ethalfluralin	.004	27	0	--	--	--
Ethoprop	.003	27	0	--	--	--
Fonofos	.003	27	3.7	ld	ld	E .003
HCH, alpha	.002	27	0	--	--	--
HCH, gamma	.004	27	0	--	--	--
Linuron	.002	27	0	--	--	--
Malathion	.005	27	0	--	--	--
Metolachlor	.002	27	92.6	.007	.038	.067
Metribuzin	.004	27	11.1	ld	.023	.024
Molinate	.004	27	0	--	--	--
Napropamide	.003	27	0	--	--	--
Parathion	.004	27	0	--	--	--
Parathion, methyl	.006	27	0	--	--	--
Pebulate	.004	27	0	--	--	--
Pendimethalin	.004	27	0	--	--	--
Permethrin, cis	.005	27	0	--	--	--
Phorate	.002	27	0	--	--	--
Prometon	.003	27	44.4	ld	.017	.018
Pronamide	.003	27	0	--	--	--
Propachlor	.007	27	0	--	--	--
Propanil	.004	27	0	--	--	--
Propargite	.013	27	0	--	--	--
Simazine	.005	27	100	.042	1.09	1.63
Tebuthiuron	.010	27	7.4	ld	E .002	E .004
Terbacil	.007	27	0	--	--	--
Terbufos	.013	27	0	--	--	--
Thiobencarb	.002	27	0	--	--	--
Triallate	.001	27	0	--	--	--
Trifluralin	.002	27	0	--	--	--

Table B2. Compounds analyzed; method detection limit; number of analyses; frequency of detection; and the median, 95th percentile, and maximum concentrations for samples from the Clinton River at Sterling Heights, Mich.

[µg/L, micrograms per liter; ld, less than method detection limit; E, pesticides detected and concentrations estimated; --, no data]

Compound	Method detection limit (µg/L)	Number of analyses	Frequency of detection (percent)	Median (µg/L)	95th percentile (µg/L)	Maximum (µg/L)
Acetochlor	0.002	37	29.7	ld	0.022	0.320
Alachlor	.002	37	29.7	ld	.019	.087
Atrazine	.001	37	100	.026	.117	.410
Atrazine, deethyl	.002	37	97.3	E .008	E .018	E .022
Azinphos, methyl	.001	37	0	--	--	--
Benfluralin	.002	37	5.4	ld	E .003	E .004
Butylate	.002	37	0	--	--	--
Carbaryl	.003	37	35.1	ld	E .102	E .139
Carbofuran	.003	37	0	--	--	--
Chlorpyrifos	.004	37	18.9	ld	.011	.011
Cyanazine	.004	37	29.7	ld	.014	.022
DCPA	.002	37	18.9	ld	.003	.005
DDE, *p,p'*	.006	37	0	--	--	--
Diazinon	.002	37	67.6	.012	.152	.197
Dieldrin	.001	37	0	--	--	--
Diethylanaline-2,6	.003	37	0	--	--	--
Disulfoton	.017	37	0	--	--	--
EPTC	.002	37	0	--	--	--
Ethalfluralin	.004	37	0	--	--	--
Ethoprop	.003	37	0	--	--	--
Fonofos	.003	37	0	--	--	--
HCH, alpha	.002	37	0	--	--	--
HCH, gamma	.004	37	0	--	--	--
Linuron	.002	37	0	--	--	--
Malathion	.005	37	5.4	ld	.010	.026
Metolachlor	.002	37	100	.010	.078	.260
Metribuzin	.004	37	13.5	ld	.024	.035
Molinate	.004	37	0	--	--	--
Napropamide	.003	37	0	--	--	--
Parathion	.004	37	0	--	--	--
Parathion, methyl	.006	37	0	--	--	--
Pebulate	.004	37	0	--	--	--
Pendimethalin	.004	37	16.2	ld	.015	.144
Permethrin, cis	.005	37	0	--	--	--
Phorate	.002	37	0	--	--	--
Prometon	.003	37	94.5	.015	.139	.228
Pronamide	.003	37	0	--	--	--
Propachlor	.007	37	0	--	--	--
Propanil	.004	37	0	--	--	--
Propargite	.013	37	0	--	--	--
Simazine	.005	37	97.3	.014	.049	.070
Tebuthiuron	.010	37	8.1	ld	E .005	E .006
Terbacil	.007	37	0	--	--	--
Terbufos	.013	37	0	--	--	--
Thiobencarb	.002	37	0	--	--	--
Triallate	.001	37	0	--	--	--
Trifluralin	.002	37	16.2	ld	.004	.006

Table B3. Compounds analyzed; method detection limit; number of analyses; frequency of detection; and the median, 95th percentile, and maximum concentrations for samples from the Auglaize River near Fort Jennings, Ohio

[µg/L, micrograms per liter; ld, less than method detection limit; E, pesticides detected and concentrations estimated; --, no data]]

Compound	Method detection limit (µg/L)	Number of analyses	Frequency of detection (percent)	Median (µg/L)	95th percentile (µg/L)	Maximum (µg/L)
Acetochlor	0.002	36	86.1	0.017	5.06	5.13
Alachlor	.002	36	97.2	.022	3.32	4.59
Atrazine	.001	36	100	.379	E 40	E85
Atrazine, deethyl	.002	36	100	E .063	E 1.05	E 1.51
Azinphos, methyl	.001	35	0	--	--	--
Benfluralin	.002	36	0	--	--	--
Butylate	.002	36	0	--	--	--
Carbaryl	.003	36	11.1	ld	E .024	E .432
Carbofuran	.003	36	8.3	ld	E .007	E .007
Chlorpyrifos	.004	35	22.2	ld	.024	.051
Cyanazine	.004	36	97.2	.095	6.98	7.00
DCPA	.002	35	8.3	ld	E .001	E .002
DDE, *p,p'*	.006	36	0	--	--	--
Diazinon	.002	36	44.4	ld	.037	.048
Dieldrin	.001	36	2.8	ld	ld	.004
Diethylanaline-2,6	.003	36	0	--	--	--
Disulfoton	.017	36	0	--	--	--
EPTC	.002	36	0	--	--	--
Ethalfluralin	.004	36	0	--	--	--
Ethoprop	.003	36	0	--	--	--
Fonofos	.003	36	0	--	--	--
HCH, alpha	.002	36	0	--	--	--
HCH, gamma	.004	36	0	--	--	--
Linuron	.002	36	2.8	ld	ld	.023
Malathion	.005	36	2.8	ld	ld	.019
Metolachlor	.002	36	100	.529	E37	E78
Metribuzin	.004	36	88.9	.033	3.31	5.36
Molinate	.004	36	0	--	--	--
Napropamide	.003	36	0	--	--	--
Parathion	.004	36	0	--	--	--
Parathion, methyl	.006	36	0	--	--	--
Pebulate	.004	36	0	--	--	--
Pendimethalin	.004	36	8.3	ld	.045	E .113
Permethrin, cis	.005	36	0	--	--	--
Phorate	.002	36	0	--	--	--
Prometon	.003	36	94.4	.027	.149	.174
Pronamide	.003	36	0	--	--	--
Propachlor	.007	36	0	--	--	--
Propanil	.004	36	0	--	--	--
Propargite	.013	36	0	--	--	--
Simazine	.005	36	97.2	.052	2.57	3.05
Tebuthiuron	.010	36	22.2	ld	.013	.013
Terbacil	.007	36	0	--	--	--
Terbufos	.013	36	0	--	--	--
Thiobencarb	.002	36	0	--	--	--
Triallate	.001	36	0	--	--	--
Trifluralin	.002	36	11.1	ld	.004	.009

Table B4. Compounds analyzed; method detection limit; number of analyses; frequency of detection; and the median, 95th percentile, and maximum concentrations for samples from the Cattaraugus Creek at Gowanda, N.Y.

[µg/L, micrograms per liter; ld, less than method detection limit; E, pesticides detected and concentrations estimated; --, no data]

Compound	Method detection limit (µg/L)	Number of analyses	Frequency of detection (percent)	Median (µg/L)	95th percentile (µg/L)	Maximum (µg/L)
Acetochlor	0.002	24	4.2	ld	ld	0.005
Alachlor	.002	24	16.7	ld	.015	.018
Atrazine	.001	24	100	.011	.306	.347
Atrazine, deethyl	.002	24	100	E .006	E .022	E .023
Azinphos, methyl	.001	24	0	--	--	--
Benfluralin	.002	24	0	--	--	--
Butylate	.002	24	0	--	--	--
Carbaryl	.003	24	4.2	ld	ld	E .011
Carbofuran	.003	24	0	--	--	--
Chlorpyrifos	.004	24	0	--	--	--
Cyanazine	.004	24	8.3	ld	.006	.023
DCPA	.002	24	0	--	--	--
DDE, *p,p'*	.006	24	0	--	--	--
Diazinon	.002	24	0	--	--	--
Dieldrin	.001	24	0	--	--	--
Diethylanaline-2,6	.003	24	0	--	--	--
Disulfoton	.017	24	0	--	--	--
EPTC	.002	24	4.2	ld	ld	E .002
Ethalfluralin	.004	24	0	--	--	--
Ethoprop	.003	24	0	--	--	--
Fonofos	.003	24	0	--	--	--
HCH, alpha	.002	24	0	--	--	--
HCH, gamma	.004	24	0	--	--	--
Linuron	.002	24	0	--	--	--
Malathion	.005	24	0	--	--	--
Metolachlor	.002	24	100	.004	.304	.367
Metribuzin	.004	24	0	--	--	--
Molinate	.004	24	0	--	--	--
Napropamide	.003	24	0	--	--	--
Parathion	.004	24	0	--	--	--
Parathion, methyl	.006	24	0	--	--	--
Pebulate	.004	24	0	--	--	--
Pendimethalin	.004	24	0	--	--	--
Permethrin, cis	.005	24	0	--	--	--
Phorate	.002	24	0	--	--	--
Prometon	.003	24	12.5	ld	E .003	E .003
Pronamide	.003	24	0	--	--	--
Propachlor	.007	24	0	--	--	--
Propanil	.004	24	0	--	--	--
Propargite	.013	24	0	--	--	--
Simazine	.005	24	79.2	.003	.011	.227
Tebuthiuron	.010	24	0	--	--	--
Terbacil	.007	24	0	--	--	--
Terbufos	.013	24	0	--	--	--
Thiobencarb	.002	24	0	--	--	--
Triallate	.001	24	0	--	--	--
Trifluralin	.002	24	0	--	--	--

Table B5. Compounds analyzed; method detection limit; number of analyses; frequency of detection; and the median, 95th percentile, and maximum concentrations for samples from the Black River near Jeddo, Mich.

[µg/L, micrograms per liter; ld, less than method detection limit; E, pesticides detected and concentrations estimated; --, no data]

Compound	Method detection limit (µg/L)	Number of analyses	Frequency of detection (percent)	Median (µg/L)	95th percentile (µg/L)	Maximum (µg/L)
Acetochlor	0.002	28	75.0	0.018	1.49	E 3.80
Alachlor	.002	28	96.4	.027	1.03	1.32
Atrazine	.001	28	100	.237	7.21	7.32
Atrazine, deethyl	.002	28	100	E .037	E .542	E .622
Azinphos, methyl	.001	28	0	--	--	--
Benfluralin	.002	28	0	--	--	--
Butylate	.002	28	7.1	ld	.011	.021
Carbaryl	.003	28	7.1	ld	E .013	E .019
Carbofuran	.003	28	3.6	ld	ld	E .006
Chlorpyrifos	.004	28	7.1	ld	.005	.018
Cyanazine	.004	28	100	.060	2.76	3.39
DCPA	.002	27	10.7	ld	E .002	E .003
DDE, *p,p’*	.006	28	10.7	ld	E .002	E .003
Diazinon	.002	28	7.1	ld	.010	.028
Dieldrin	.001	28	0	--	--	--
Diethylanaline-2,6	.003	28	0	--	--	--
Disulfoton	.017	28	0	--	--	--
EPTC	.002	28	53.6	.001	.176	.177
Ethalfluralin	.004	28	0	--	--	--
Ethoprop	.003	28	0	--	--	--
Fonofos	.003	28	7.1	ld	.008	.021
HCH, alpha	.002	28	0	--	--	--
HCH, gamma	.004	28	0	--	--	--
Linuron	.002	28	28.6	ld	.068	.090
Malathion	.005	28	0	--	--	--
Metolachlor	.002	28	100	.451	E25.9	E 37
Metribuzin	.004	28	82.1	.021	.640	.866
Molinate	.004	28	0	--	--	--
Napropamide	.003	28	0	--	--	--
Parathion	.004	28	0	--	--	--
Parathion, methyl	.006	28	0	--	--	--
Pebulate	.004	28	0	--	--	--
Pendimethalin	.004	28	17.9	ld	.056	.071
Permethrin, cis	.005	28	0	--	--	--
Phorate	.002	28	0	--	--	--
Prometon	.003	28	64.3	.006	.025	.032
Pronamide	.003	28	0	--	--	--
Propachlor	.007	28	0	--	--	--
Propanil	.004	28	0	--	--	--
Propargite	.013	28	0	--	--	--
Simazine	.005	28	96.4	.009	.104	.140
Tebuthiuron	.010	28	10.7	ld	E .004	E .005
Terbacil	.007	28	14.3	ld	E .013	E .021
Terbufos	.013	28	0	--	--	--
Thiobencarb	.002	28	0	--	--	--
Triallate	.001	28	0	--	--	--
Trifluralin	.002	28	25.0	ld	.005	.006

Table B6. Compounds analyzed; method detection limit; number of analyses; frequency of detection; and the median, 95th percentile, and maximum concentrations for samples from the Grand River at Harpersfield, Ohio

[µg/L, micrograms per liter; ld, less than method detection limit; E, pesticides detected and concentrations estimated; --, no data]

Compound	Method detection limit (µg/L)	Number of analyses	Frequency of detection (percent)	Median (µg/L)	95th percentile (µg/L)	Maximum (µg/L)
Acetochlor	0.002	28	57.1	0.007	0.165	0.410
Alachlor	.002	28	35.7	ld	.075	.138
Atrazine	.001	28	100	.185	2.45	2.57
Atrazine, deethyl	.002	28	100	E .029	E .200	E .211
Azinphos, methyl	.001	28	0	--	--	--
Benfluralin	.002	28	0	--	--	--
Butylate	.002	28	0	--	--	--
Carbaryl	.003	28	17.9	ld	E .013	E .031
Carbofuran	.003	28	0	--	--	--
Chlorpyrifos	.004	28	17.9	ld	.021	.106
Cyanazine	.004	28	50.0	ld	.091	.113
DCPA	.002	28	14.3	ld	E .001	E .002
DDE, *p,p'*	.006	28	0	--	--	--
Diazinon	.002	28	32.1	ld	.049	.092
Dieldrin	.001	28	0	--	--	--
Diethylanaline-2,6	.003	28	0	--	--	--
Disulfoton	.017	28	0	--	--	--
EPTC	.002	28	0	--	--	--
Ethalfluralin	.004	28	0	--	--	--
Ethoprop	.003	28	0	--	--	--
Fonofos	.003	28	0	--	--	--
HCH, alpha	.002	28	0	--	--	--
HCH, gamma	.004	28	0	--	--	--
Linuron	.002	28	3.6	ld	ld	.054
Malathion	.005	28	3.6	ld	ld	.008
Metolachlor	.002	28	100	.105	1.37	1.51
Metribuzin	.004	28	28.6	ld	.073	.120
Molinate	.004	28	0	--	--	--
Napropamide	.003	28	0	--	--	--
Parathion	.004	28	0	--	--	--
Parathion, methyl	.006	28	0	--	--	--
Pebulate	.004	28	0	--	--	--
Pendimethalin	.004	28	0	--	--	--
Permethrin, cis	.005	28	0	--	--	--
Phorate	.002	28	0	--	--	--
Prometon	.003	28	75.0	.008	.044	.055
Pronamide	.003	28	0	--	--	--
Propachlor	.007	28	0	--	--	--
Propanil	.004	28	0	--	--	--
Propargite	.013	28	0	--	--	--
Simazine	.005	28	89.3	.023	.167	.177
Tebuthiuron	.010	28	0	--	--	--
Terbacil	.007	28	3.6	ld	ld	E .014
Terbufos	.013	28	0	--	--	--
Thiobencarb	.002	28	0	--	--	--
Triallate	.001	28	0	--	--	--
Trifluralin	.002	28	0	--	--	--

Table B7. Compounds analyzed; method detection limit; number of analyses; frequency of detection; and the median, 95th percentile, and maximum concentrations for samples from the St. Joseph River near Newville, Ind.

[µg/L, micrograms per liter; ld, less than method detection limit; E, pesticides detected and concentrations estimated; --, no data]

Compound	Method detection limit (µg/L)	Number of analyses	Frequency of detection (percent)	Median (µg/L)	95th percentile (µg/L)	Maximum (µg/L)
Acetochlor	0.002	35	82.9	0.012	4.68	5.61
Alachlor	.002	35	97.1	.023	3.43	4.94
Atrazine	.001	35	100	.357	17	E23
Atrazine, deethyl	.002	35	100	E .045	E .479	E .510
Azinphos, methyl	.001	34	0	--	--	--
Benfluralin	.002	35	2.9	ld	ld	E .003
Butylate	.002	35	2.9	ld	ld	E .002
Carbaryl	.003	35	0	--	--	--
Carbofuran	.003	35	2.9	ld	ld	E .004
Chlorpyrifos	.004	34	22.9	ld	.020	E .211
Cyanazine	.004	35	100	.081	4.68	4.75
DCPA	.002	35	17.1	ld	E .002	E .005
DDE, *p,p'*	.006	35	0	--	--	--
Diazinon	.002	35	14.3	ld	.007	.007
Dieldrin	.001	35	0	--	--	--
Diethylanaline-2,6	.003	35	2.9	ld	ld	E .001
Disulfoton	.017	35	0	--	--	--
EPTC	.002	35	2.9	ld	ld	E .002
Ethalfluralin	.004	35	0	--	--	--
Ethoprop	.003	35	0	--	--	--
Fonofos	.003	35	0	--	--	--
HCH, alpha	.002	35	0	--	--	--
HCH, gamma	.004	35	0	--	--	--
Linuron	.002	35	28.6	ld	.394	.434
Malathion	.005	35	2.9	ld	ld	.011
Metolachlor	.002	35	100	.270	12	14
Metribuzin	.004	35	82.9	.019	1.62	2.02
Molinate	.004	35	0	--	--	--
Napropamide	.003	35	0	--	--	--
Parathion	.004	35	0	--	--	--
Parathion, methyl	.006	35	0	--	--	--
Pebulate	.004	35	0	--	--	--
Pendimethalin	.004	35	8.6	ld	.015	.152
Permethrin, cis	.005	35	0	--	--	--
Phorate	.002	35	0	--	--	--
Prometon	.003	35	74.3	.010	.065	.210
Pronamide	.003	35	0	--	--	--
Propachlor	.007	35	0	--	--	--
Propanil	.004	35	0	--	--	--
Propargite	.013	35	0	--	--	--
Simazine	.005	35	100	.042	1.4	2.16
Tebuthiuron	.010	35	48.6	ld	.040	.070
Terbacil	.007	35	0	--	--	--
Terbufos	.013	35	0	--	--	--
Thiobencarb	.002	35	0	--	--	--
Triallate	.001	35	0	--	--	--
Trifluralin	.002	35	2.9	ld	ld	E .001

Table B8. Compounds analyzed; method detection limit; number of analyses; frequency of detection; and the median, 95th percentile, and maximum concentrations for samples from the Cuyahoga River at Cleveland, Ohio

[µg/L, micrograms per liter; ld, less than method detection limit; E, pesticides detected and concentrations estimated; --, no data]

Compound	Method detection limit (µg/L)	Number of analyses	Frequency of detection (percent)	Median (µg/L)	95th percentile (µg/L)	Maximum (µg/L)
Acetochlor	0.002	28	25.0	ld	0.122	0.198
Alachlor	.002	28	25.0	ld	.021	.027
Atrazine	.001	28	100	.063	.572	.761
Atrazine, deethyl	.002	28	96.4	E .013	E .038	E .038
Azinphos, methyl	.001	28	0	--	--	--
Benfluralin	.002	28	0	--	--	--
Butylate	.002	28	0	--	--	--
Carbaryl	.003	28	42.9	ld	E .110	E .143
Carbofuran	.003	28	0	--	--	--
Chlorpyrifos	.004	28	46.4	ld	.023	.025
Cyanazine	.004	28	35.7	ld	.080	.126
DCPA	.002	28	14.3	ld	E .002	E .003
DDE, *p,p'*	.006	28	0	--	--	--
Diazinon	.002	28	92.9	.036	.160	.290
Dieldrin	.001	28	0	--	--	--
Diethylanaline-2,6	.003	28	0	--	--	--
Disulfoton	.017	28	0	--	--	--
EPTC	.002	28	3.6	ld	ld	E .004
Ethalfluralin	.004	28	0	--	--	--
Ethoprop	.003	28	0	--	--	--
Fonofos	.003	28	0	--	--	--
HCH, alpha	.002	28	0	--	--	--
HCH, gamma	.004	28	0	--	--	--
Linuron	.002	28	0	--	--	--
Malathion	.005	28	14.3	ld	.015	.016
Metolachlor	.002	28	100	.021	.266	.386
Metribuzin	.004	28	3.6	ld	ld	.030
Molinate	.004	28	0	--	--	--
Napropamide	.003	28	0	--	--	--
Parathion	.004	28	0	--	--	--
Parathion, methyl	.006	28	0	--	--	--
Pebulate	.004	28	0	--	--	--
Pendimethalin	.004	28	3.6	ld	ld	.021
Permethrin, cis	.005	28	0	--	--	--
Phorate	.002	28	0	--	--	--
Prometon	.003	28	96.4	.038	.135	.162
Pronamide	.003	28	0	--	--	--
Propachlor	.007	28	0	--	--	--
Propanil	.004	28	0	--	--	--
Propargite	.013	28	0	--	--	--
Simazine	.005	28	71.4	.012	.063	.064
Tebuthiuron	.010	28	21.4	ld	.016	.030
Terbacil	.007	28	3.6	ld	ld	E .014
Terbufos	.013	28	0	--	--	--
Thiobencarb	.002	28	0	--	--	--
Triallate	.001	28	0	--	--	--
Trifluralin	.002	28	10.7	ld	.006	E .007

Table B9. Compounds analyzed; method detection limit; number of analyses; frequency of detection; and the median, 95th percentile, and maximum concentrations for samples from the Maumee River at New Haven, Ind.

[µg/L, micrograms per liter; ld, less than method detection limit; E, pesticides detected and concentrations estimated; --, no data]

Compound	Method detection limit (µg/L)	Number of analyses	Frequency of detection (percent)	Median (µg/L)	95th percentile (µg/L)	Maximum (µg/L)
Acetochlor	0.002	29	75.9	0.014	4.58	8.88
Alachlor	.002	29	96.5	.027	2.54	3.63
Atrazine	.001	29	100	.485	E28	E37
Atrazine, deethyl	.002	29	100	E .052	E .738	E 1.09
Azinphos, methyl	.001	28	0	--	--	--
Benfluralin	.002	29	3.4	ld	ld	E .004
Butylate	.002	29	0	--	--	--
Carbaryl	.003	29	31.0	ld	E .033	E .141
Carbofuran	.003	29	10.3	ld	E .044	E .188
Chlorpyrifos	.004	28	27.6	ld	.045	.092
Cyanazine	.004	29	100	.115	5.53	5.97
DCPA	.002	29	10.3	ld	.002	.006
DDE, *p,p’*	.006	29	0	--	--	--
Diazinon	.002	29	55.2	.006	.130	.201
Dieldrin	.001	29	0	--	--	--
Diethylanaline-2,6	.003	29	0	--	--	--
Disulfoton	.017	29	0	--	--	--
EPTC	.002	29	3.4	ld	ld	.010
Ethalfluralin	.004	29	0	--	--	--
Ethoprop	.003	29	0	--	--	--
Fonofos	.003	29	3.4	ld	ld	.005
HCH, alpha	.002	29	0	--	--	--
HCH, gamma	.004	29	0	--	--	--
Linuron	.002	29	20.7	ld	.077	.438
Malathion	.005	29	10.3	ld	.007	.009
Metolachlor	.002	29	100	.395	18	E23
Metribuzin	.004	29	72.4	.032	1.25	1.69
Molinate	.004	29	0	--	--	--
Napropamide	.003	29	0	--	--	--
Parathion	.004	29	0	--	--	--
Parathion, methyl	.006	29	0	--	--	--
Pebulate	.004	29	0	--	--	--
Pendimethalin	.004	29	13.8	ld	.094	.142
Permethrin, cis	.005	29	0	--	--	--
Phorate	.002	29	0	--	--	--
Prometon	.003	29	89.7	.026	.220	.248
Pronamide	.003	29	0	--	--	--
Propachlor	.007	29	0	--	--	--
Propanil	.004	29	0	--	--	--
Propargite	.013	29	0	--	--	--
Simazine	.005	29	100	.063	2.25	3.00
Tebuthiuron	.010	29	48.3	ld	.093	.155
Terbacil	.007	29	0	--	--	--
Terbufos	.013	29	0	--	--	--
Thiobencarb	.002	29	0	--	--	--
Triallate	.001	29	0	--	--	--
Trifluralin	.002	29	10.3	ld	.004	.006

Table B10. Compounds analyzed; method detection limit; number of analyses; frequency of detection; and the median, 95th percentile, and maximum concentrations for samples from the Maumee River at Waterville, Ohio

[µg/L, micrograms per liter; ld, less than method detection limit; E, pesticides detected and concentrations estimated; --, no data]

Compound	Method detection limit (µg/L)	Number of analyses	Frequency of detection (percent)	Median (µg/L)	95th percentile (µg/L)	Maximum (µg/L)
Acetochlor	0.002	33	93.9	0.026	6.68	10.6
Alachlor	.002	33	97.0	.036	4.34	6.70
Atrazine	.001	33	100	.337	E21	E22
Atrazine, deethyl	.002	33	100	E .084	E .763	E 1.02
Azinphos, methyl	.001	33	0	--	--	--
Benfluralin	.002	33	3.0	ld	ld	E .002
Butylate	.002	33	6.1	ld	.001	.005
Carbaryl	.003	33	12.1	ld	E .026	E .084
Carbofuran	.003	33	9.1	ld	E .079	E .247
Chlorpyrifos	.004	32	42.4	ld	.025	.030
Cyanazine	.004	33	100	.096	9.92	9.97
DCPA	.002	33	15.2	ld	E .001	E .003
DDE, *p,p'*	.006	33	0	--	--	--
Diazinon	.002	33	66.7	.005	.022	.023
Dieldrin	.001	33	6.1	ld	.004	.009
Diethylanaline-2,6	.003	33	6.1	ld	E .002	E .002
Disulfoton	.017	33	0	--	--	--
EPTC	.002	33	12.1	ld	E .004	E .004
Ethalfluralin	.004	33	0	--	--	--
Ethoprop	.003	33	0	--	--	--
Fonofos	.003	33	0	--	--	--
HCH, alpha	.002	33	3.0	ld	ld	E .004
HCH, gamma	.004	33	0	--	--	--
Linuron	.002	33	24.2	ld	.055	.370
Malathion	.005	33	3.0	ld	ld	.008
Metolachlor	.002	33	100	.372	17	20
Metribuzin	.004	33	87.9	.052	3.50	4.92
Molinate	.004	33	0	--	--	--
Napropamide	.003	33	0	--	--	--
Parathion	.004	33	0	--	--	--
Parathion, methyl	.006	33	3.0	ld	ld	.008
Pebulate	.004	33	0	--	--	--
Pendimethalin	.004	33	12.1	ld	.039	.064
Permethrin, cis	.005	33	0	--	--	--
Phorate	.002	33	0	--	--	--
Prometon	.003	33	87.9	.020	.114	.128
Pronamide	.003	33	0	--	--	--
Propachlor	.007	33	3.0	ld	ld	.008
Propanil	.004	33	0	--	--	--
Propargite	.013	33	0	--	--	--
Simazine	.005	33	97.0	.047	1.84	1.99
Tebuthiuron	.010	33	78.8	.016	.066	.090
Terbacil	.007	33	0	--	--	--
Terbufos	.013	33	0	--	--	--
Thiobencarb	.002	33	0	--	--	--
Triallate	.001	33	0	--	--	--
Trifluralin	.002	33	12.1	ld	.002	.005