# Water Quality in the Great and Little Miami River Basins

## Ohio and Indiana, 1999–2001

U.S. Department of the Interior
U.S. Geological Survey

Circular 1229

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Front cover: The Little Miami River near Mason, Ohio (photograph by Eric Hatch Photography, Loveland, Ohio). Back cover: Left, Dayton skyline (photograph by Richard Baumer, published with permission); Middle, Little Miami River, near Mason, Ohio, after a summer rainstorm (photograph by Eric Hatch Photography, Loveland, Ohio); Right, municipal supply well near Fairfield, Ohio (photograph by Rhett Moore, U.S. Geological Survey).

# Water Quality in the Great and Little Miami River Basins, Ohio and Indiana, 1999–2001

By Gary L. Rowe, Jr., David C. Reutter, Donna L. Runkle,
Julie A. Hambrook, Stephanie D. Janosy, and Lee H. Hwang

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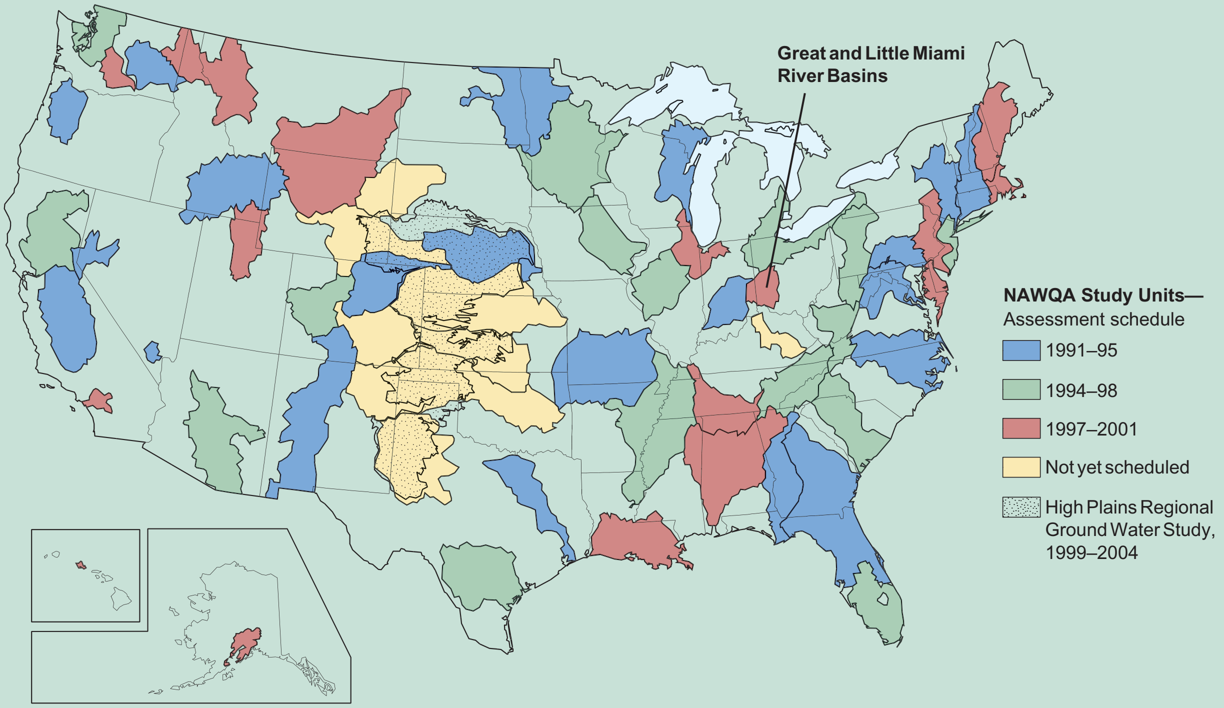
# Contents

# National Water-Quality Assessment Program

The quality of the Nation's water resources is of great interest 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. Recognizing the need for long-term, nationwide assessments of water resources, the U.S. Congress has appropriated funds since 1991 for the USGS to conduct the **National Water-Quality Assessment (NAWQA) Program**. Scientists in the NAWQA Program work with partners in government, research, and public interest groups to assess the spatial extent of water-quality conditions, how water quality changes with time, and how human activities and natural factors affect water quality. This information is useful for guiding water-management and protection strategies, research, and monitoring in different hydrologic and land-use settings across the Nation.



The Great and Little Miami River Basins is one of 51 water-quality assessments initiated since 1991. Together, the 51 major river basins and aquifer systems, referred to as "Study Units," include water resources used by more than 60 percent of the population in watersheds that cover about half of the land area of the conterminous United States. Timing of the assessments varies because of the Program's rotational design, in which one-third of all Study Units are intensively investigated for 3 to 4 years, with trends assessed every 10 years. As indicated on the map, the Great and Little Miami River Basins is part of the third set of intensive investigations, which began in 1997.

# What kind of water-quality information does the NAWQA Program provide?

Water-quality assessments by a single program cannot possibly address all of the Nation's water-resources needs and issues. Therefore, it is necessary to define the context within which NAWQA information is most useful.

- Total resource assessment—NAWQA assessments are long-term and interdisciplinary, and include information on water chemistry, hydrology, land use, stream habitat, and aquatic life. Assessments are not limited to a specific geographic area or water-resource problem at a specific time. Therefore, the findings describe the general health of the total water resource, as well as emerging water issues, thereby helping managers and decision makers to set priorities.
- Source-water characterization—Assessments focus on the quality of the available, untreated resource and thereby complement (rather than duplicate) Federal, State, and local programs that monitor drinking water. Findings are compared to drinking-water standards and health advisories as a way to characterize the resource.
- Compounds studied—Assessments focus on chemical compounds that have well-established methods of investigation. It is not financially or technically feasible to assess all the contaminants in our Nation's waters. In general, the NAWQA Program investigates those pesticides, nutrients, volatile organic compounds, and metals that have been or are currently used commonly in agricultural and urban areas across the Nation. A complete list of compounds studied is on the NAWQA Web site at *water.usgs.gov/nawqa*.
- Detection versus risk—Compounds are measured at very low concentrations, often 10 to 100 times lower than Federal or State standards and health advisories. Detection of compounds, therefore, does not necessarily translate to risks to human health or aquatic life. However, these analyses are useful for identifying and evaluating emerging issues, as well as for tracking contaminant levels over time.
- Multiple scales—Assessments are guided by a nationally consistent study design and uniform methods of sampling and analysis. Findings thereby pertain not only to water quality of a particular stream or aquifer, but also contribute to the larger picture of how and why water quality varies regionally and nationally. This consistent, multi-scale approach helps to determine if a water-quality issue is isolated or pervasive. It also allows direct comparisons of how human activities and natural processes affect water quality in the Nation's diverse environmental settings.

# Introduction to this Report

This report contains the major findings of a 1999–2001 assessment of water quality in the Great and Little Miami River Basins. It is one of a series of reports by the National Water-Quality Assessment (NAWQA) Program that present major findings in 51 major river basins and aquifer systems across the Nation.

In these reports, water quality is discussed in terms of local, State, and regional issues. Conditions in a particular basin or aquifer system are compared to conditions found elsewhere and to selected national benchmarks, such as those for drinking-water quality and the protection of aquatic organisms.

This report is intended for individuals working with water-resource issues in Federal, State, or local agencies, universities, public interest groups, or in the private sector. The information will be useful in addressing a number of current issues, such as the effects of agricultural and urban land use on water quality, human health, drinking water, source-water protection, hypoxia and excessive growth of algae and plants, pesticide registration, and monitoring and sampling strategies. This report is also for individuals who wish to know more about the quality of streams and ground water in areas near where they live and how that water quality compares to the quality of water in other areas across the Nation.

The water-quality conditions in the Great and Little Miami River Basins summarized in this report are discussed in detail in other reports that can be accessed from (*http://oh.water.usgs.gov/miam/intro.html*). Detailed technical information, data and analyses, collection and analytical methodology, models, graphs, and maps that support the findings presented in this report, in addition to reports in this series from other basins, can be accessed from the national NAWQA Web site (*water.usgs.gov/nawqa*).

"Data from the NAWQA supplied critical information for Ohio EPA's Total Maximum Daily Load (TMDL) effort in the Stillwater River Basin, and will continue to provide valuable data for future TMDLs in other subbasins of the Great Miami River. Additionally, the NAWQA study has helped further our understanding of linkages between nutrients, land use, and impairment of aquatic life. The USGS has also been particularly generous in sharing scientific expertise developed by NAWQA with Ohio EPA, especially their expertise in sampling algal communities."

Robert J. Miltner
Aquatic Ecologist
Ohio Environmental Protection Agency

"In partnership with the NAWQA Program, we collected a significant amount of ground-water-quality data that neither agency could have obtained individually. The data provide an important snapshot of the overall health of ground water—the region's primary source of drinking water. The information generated through this partnership will help our region formulate more effective ground-water management strategies in the future."

Michael P. Ekberg
Groundwater Program Manager
Miami Conservancy District

"In southwest Ohio, the USGS NAWQA Program has tapped an extraordinary number of research sources to perform a water-quality assessment of the Great and Little Miami River Basins. NAWQA is developing a picture of water quality that did not previously exist. This is a service for many constituents who rely on the Basins' water resources, including the dozens of public water suppliers who must produce safe drinking water and the towns and cities whose histories and futures are linked to the health of the rivers and the aquifer."

Jane Wittke
Water Quality Program Planner
Ohio-Kentucky-Indiana Regional
Council of Governments

# Summary of Major Findings

## Stream and River Highlights

Since the early 1900s, streams in the Great and Little Miami River Basins have been affected by various human activities, including agriculture, urbanization, discharge of industrial and municipal waste, ditching and tiling of farmland, and channel modification for flood control. Cleanup of contaminants, especially those discharged directly into streams by point sources, began in earnest in the 1970s after passage of the Clean Water Act. Although stream quality has improved significantly since then, elevated concentrations of nutrients and pesticides were frequently detected in streams during 1999–2001, sometimes at levels that exceeded guidelines set for the protection of human health or aquatic organisms. Persistent organic contaminants no longer used, such as polychlorinated biphenyls (PCBs) and organochlorine pesticides, are still present in streambed sediment and fish tissue at concentrations that exceed aquatic-life guidelines.

- At least one pesticide was detected in all streams, sometimes at concentrations at or above drinking-water standards or aquatic-life guidelines. (p. 5, 9–10)

- Two of the most heavily used herbicides, atrazine and metolachlor, were detected in 98 and 94 percent of the samples, respectively, whereas glyphosate, whose use on cropland is approaching that of atrazine, was detected less frequently. (p. 5, 7, 9)

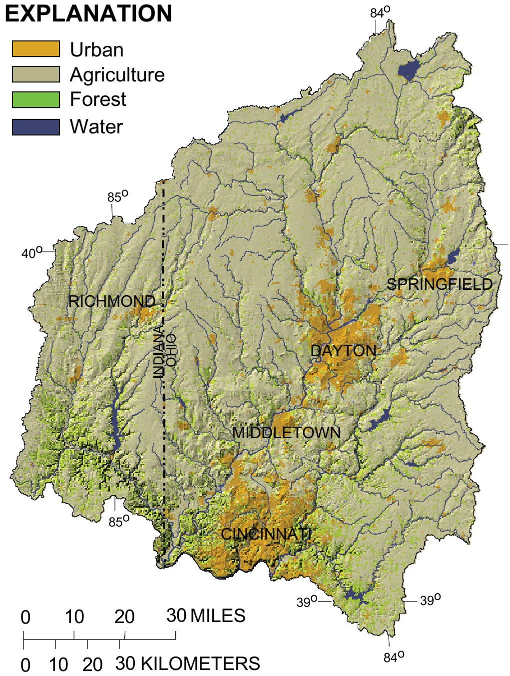
- Insecticides commonly used by homeowners on lawns and gardens, such as diazinon and imidacloprid, were frequently detected in samples from a small urban stream, Holes Creek. Concentrations of diazinon exceeded guidelines for protecting aquatic life in 33 percent of the samples from Holes Creek. (p. 7, 10)

- Degradates (breakdown products) of acetochlor, alachlor, and metolachlor were detected throughout the year at concentrations higher than those of the parent compounds. Some degradates may have equal or greater toxicity and may persist longer in the environment than the parent compound. (p. 10–11)

- Although atrazine concentrations in untreated Harsha Lake water occasionally exceeded the U.S. Environmental Protection Agency (USEPA) drinking-water standard, atrazine concentrations in samples of treated drinking water were always within the standard, particularly after the water-treatment method was changed from powdered activated carbon to granular activated carbon. (p. 10)

- Streams draining agricultural land had the highest mean concentration of nitrogen, whereas streams draining a mix of land uses had the highest mean concentration of phosphorus. Commercial fertilizer and manure applications to agricultural lands are a major source of nitrogen to area streams. Numerous wastewater-treatment discharges at and downstream from Dayton are a primary source of phosphorus to mixed-land-use streams. (p. 20, 22)

- Phosphorus concentrations have decreased by about 50 percent in the Great Miami River and 40 percent in the Little Miami River since 1974. Mean annual concentrations of phosphorus, however, remained above the USEPA recommended guideline of 0.1 milligram per liter. (p. 22)



The Great and Little Miami River Basins drain about 7,354 square miles of southwestern Ohio and southeastern Indiana. More than 2.8 million people reside in the basin, most in and around the Cincinnati and Dayton metropolitan areas. Land use outside the two metropolitan areas is dominated by production of corn and soybeans. Ground-water sources provide most domestic and public drinking-water supplies.

- Sixty-one of the 116 household chemicals and pharmaceuticals for which the samples were analyzed were detected at low concentrations in streams draining mixed-land use and urban land. In a separate study of 29 small streams that drain areas of various land uses, 46 of 58 household chemicals were detected at low concentrations. The number of chemicals detected increased with increasing amounts of urban land. (p. 13–15, 25–26)

- Polychlorinated biphenyls and organochlorine insecticides whose use was canceled or restricted in the 1970s and 1980s continue to persist in fish tissue; many such chemicals were detected at concentrations at or near the maximum concentrations found nationwide by the NAWQA Program. (p. 15, 17)

- Elevated concentrations of polycyclic aromatic hydrocarbons (PAHs) and other semivolatile organic compounds (SVOCs) are widespread in sediment (p. 15–17). The number of synthetic organic compounds (SOCs) detected in streambed sediment increased as the percentage of urban land increased. (p. 26)

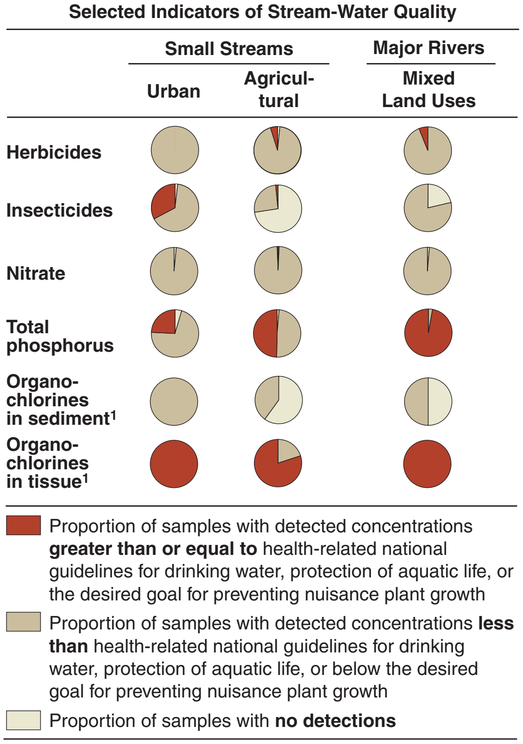
- Excessive growth of algae was found in some large streams with elevated nutrients and relatively open tree canopy. Composition and condition of fish communities in nutrient- and algal-rich streams was variable. (p. 24)

- Stream-water quality declined as the percentage of urban land upstream from the sampling site increased. Increases in the number of household chemicals and pharmaceuticals, concentration of chloride, and total concentration of insecticides in stream water—plus the number of synthetic organic compounds detected in the streambed sediments contributed to the decline. (p. 25–28)

- The structure of biological communities in streams ranging from minimally to highly urbanized reflects a complex combination of water and sediment quality and stream habitat. Certain chemical characteristics, such as elevated trace metals in sediment and pesticides and other organic compounds in water, are associated with decreases in relative abundance and diversity of fish, invertebrates, and algae in some urban streams. (p. 25–28)

## Major Influences on Streams and Rivers

- Runoff from agricultural and urban areas
- Discharges from wastewater-treatment facilities
- Contamination of fish tissue and sediment by persistent organic chemicals


**Selected Indicators of Stream-Water Quality**

[1] DDT and PCB's.

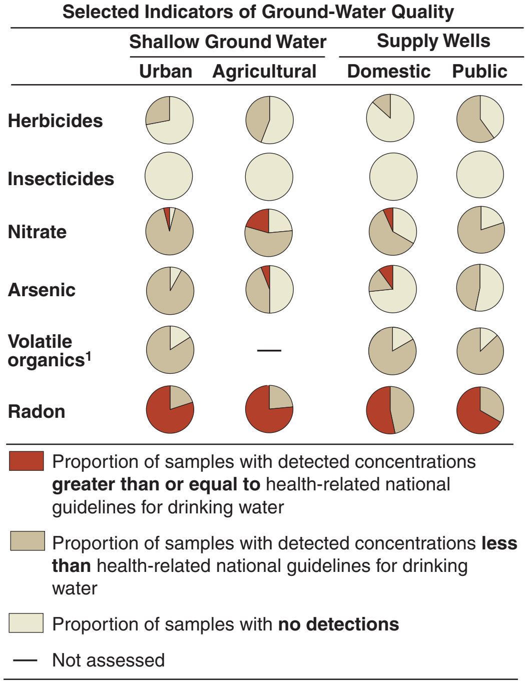
## Ground-Water Highlights

Most residents and many industries in the Great and Little Miami River Basins rely on water pumped from the buried-valley aquifer system, and this demand for ground water is increasing as people move to suburban and rural areas. With few exceptions, ground-water quality is suitable for drinking and other domestic uses. Water from shallow wells (less than 50 feet deep) is vulnerable to contamination by chemicals applied or spilled on the land; hence, shallow-water quality tends to reflect overlying land use and human activities. Water from deeper public-supply wells (median depth 78 feet), also can be vulnerable to contamination because of induced infiltration of stream water, which can reach wells within weeks or even days. Water from domestic wells (median depth 60 feet) in areas not affected by induced infiltration or heavy pumping is, in general, the least vulnerable to contamination.

- One or more pesticides were detected in 63 percent of 96 samples, but no concentrations exceeded drinking-water standards or guidelines. Herbicide degradates (breakdown products) were the most frequently detected class of pesticides. (p. 11–12)
- Pesticides were detected most frequently and at the highest total concentrations in water pumped from public-supply wells near streams, compared to concentrations in water from domestic wells or shallow monitoring wells in agricultural and urban areas. (p. 12)
- Nitrate concentrations in 10 of 104 samples exceeded the USEPA drinking-water standard of 10 milligrams per liter. Concentrations of nitrate in water from shallow monitoring wells in agricultural areas were the highest among area wells and among the highest in the Nation. (p. 19)
- Five of 104 samples exceeded the USEPA drinking-water standard of 10 micrograms per liter for arsenic, which was revised in 2002 (p. 16, 19). Radon concentrations were greater than 300 picocuries per liter, the proposed USEPA drinking-water standard, in 70 percent of the samples. (p. 18)
- Twenty volatile organic compounds were detected in ground water collected from public-supply, domestic, and shallow urban monitoring wells installed in urban areas. No USEPA drinking-water standards or guidelines were exceeded. (p. 13)
- Of the 116 household chemicals and pharmaceuticals for which the samples were analyzed, 16 were detected at very low concentrations in shallow ground water from 19 of 25 monitoring wells in urban areas developed after 1960. (p. 13–15)

## Major Influences on Ground Water

- Geologic and hydrologic factors (type of aquifer material, depth to water, rate of recharge)
- Agricultural and urban land use around well
- Induced infiltration of stream water to public-supply wells


**Selected Indicators of Ground-Water Quality**

[1] Solvents, refrigerants, fumigants, and gasoline compounds.

# Introduction to the Great and Little Miami River Basins

Note: Terms in **bold** are defined in the glossary

Since the 1970s, water quality in the Great and Little Miami River Basins (hereinafter, “Study Unit”) has improved significantly, mainly because of improvements in the treatment of wastewater. As **point-source** pollution has decreased, particularly in larger streams, attention has shifted to **nonpoint sources** and the effects of land use on water quality. Today, water-resource managers and suppliers are interested in the effects of nonpoint-source pollution on contaminant **loads** in streams, health of aquatic organisms, and degradation of streams and **aquifers** used for water supply.

## Past glacial activity influences quality and quantity of water today

Advancing glaciers leveled underlying limestone and shale bedrock and covered most of the Study Unit with thick deposits of **till**—a mix of clay, silt, sand and gravel (fig. 1). The flat to gently rolling landscape is ideal for agriculture. Soils formed from till tend to be fertile but have a high clay content and drain poorly. Clay-rich soils protect underlying ground water by inhibiting downward movement, but they allow sediment and applied chemicals to run off into streams during rainstorms. Near the Ohio River, glacial deposits are thin or absent, and erosion of less resistant shale has produced a more dissected, hilly terrain that is less suitable for farming.

Retreating glaciers filled bedrock valleys with **outwash** deposits of sand and gravel as thick as 250 feet. Such deposits form the buried-valley aquifer system, a major source of drinking water. Depth to water is 20 feet or less in most locations. Soils derived from glacial outwash tend to be well drained, making ground water vulnerable to contamination. In areas with extensive outwash deposits of sand and gravel (fig. 1), discharge of ground water to streams can make up most of the streamflow, particularly during dry summer months and droughts. During dry periods, ground water discharged to streams also can dilute wastewater from point sources. Conversely, contaminants may be added to the stream at locations where contaminated ground water discharges.

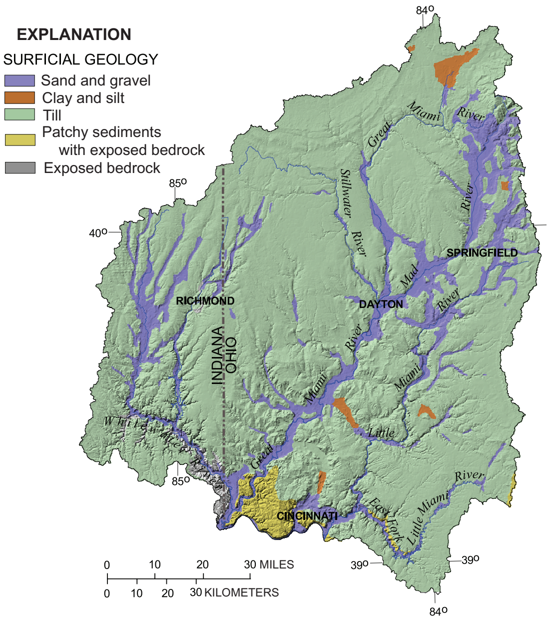


**Figure 1**. Sand-and-gravel deposits—an important source of drinking water—also discharge large volumes of ground water to the Mad and Whitewater Rivers.

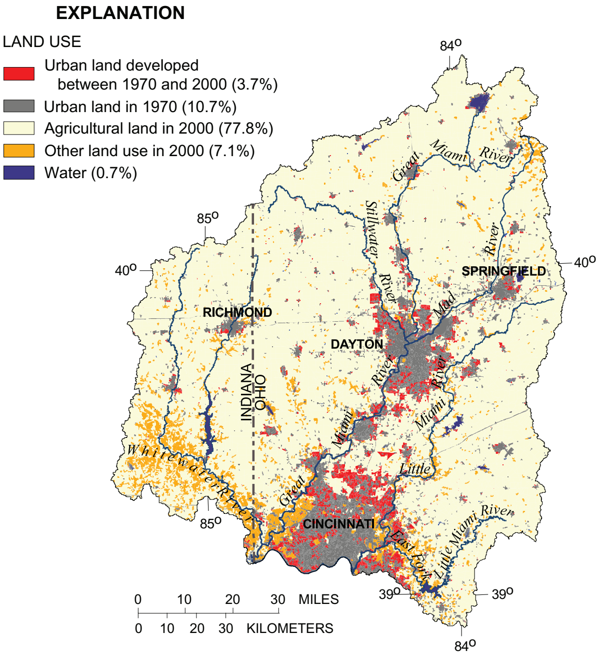


**Figure 2.** Recent urban development is concentrated around the margins of large cities and towns.

## Land use affects water quality and aquatic organisms

Despite increased urban development, agriculture remains the dominant land use, covering about 78 percent of the Study Unit (fig. 2). Corn and soybeans are grown on approximately 2.5 million acres of cropland that surround the heavily urbanized Dayton-Cincinnati corridor. **Fertilizer**, manure, and **pesticides** are applied to cropland to increase production but in excess can **run off** from fields during storms, resulting in high **concentrations** of **nutrients** and pesticides in streams. The practice of ditching, tiling, and channel straightening to improve drainage causes degradation of stream habitat and leads to a reduction in the number of sensitive aquatic organisms. Confined animal feeding operations (CAFOs), mainly for poultry and swine, are concentrated in the northwestern part of the Study Unit, mostly in the Stillwater River Basin. Over the past few decades, animal production in this basin has paralleled the national trend of fewer, larger farms producing more animals.

Land used for residential, commercial, and industrial activities covered about 14 percent of the Study Unit in 2000. Since 1970, more than 270 square miles have been converted from farmland and forest to low-density residential and commercial areas (fig. 2). Census data show declining populations in Cincinnati and Dayton, suggesting relocation of city dwellers to surrounding suburban and rural areas (fig. 3). Conversion of farmland and forest to residential and commercial land can lead to an increase in the amount of runoff, sediment, and wastewater discharged to streams and also can affect aquatic organisms, especially sensitive species, by degrading water quality and physical habitat.

## Public water supplies depend on ground water

In 2000, approximately 1 billion gallons of water per day was used in the Study Unit; about 60 percent from surface water and about 40 percent from ground water (fig. 4). About two-thirds of the surface water is used for power generation. Although many people in Cincinnati obtain drinking water from the Ohio River, most residents and industries in the Study Unit rely on water pumped from the buried-valley aquifer system for drinking water. In the northern part of the Study Unit, where sand- and-gravel deposits are absent, minor amounts of drinking water are pumped from sand-and-gravel lenses in till and from underlying carbonate bedrock.

Water managers are concerned about water-quantity issues associated with urban development along the Miami Valley. Growing towns and cities in upland areas are placing increased demands on well fields that pump water from the buried-valley aquifer in adjacent stream valleys. Many public-supply wells are drilled near streams and rely on induced infiltration of stream water to sustain high pumping rates. Some contaminants in stream water that are not removed by natural filtration through aquifer sediments, however, may be transported to wells.

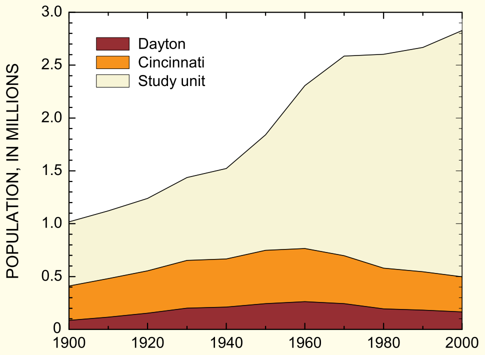


**Figure 3.** Population trends in Dayton and Cincinnati indicate migration of city residents to less densely populated parts of the Study Unit.

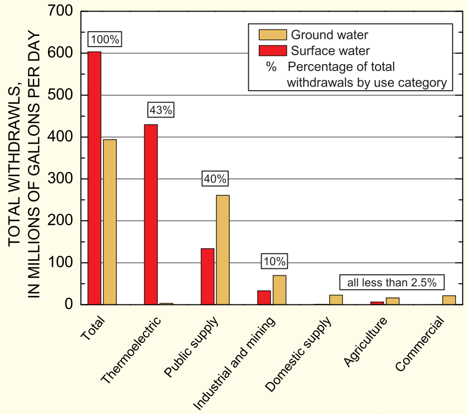


**Figure 4.** Public supply accounts for 40 percent of the water used in the Study Unit.

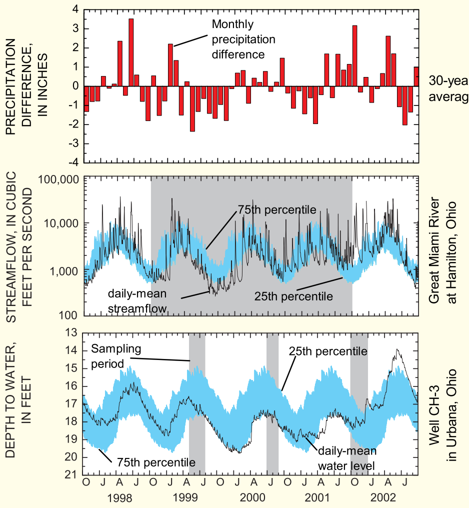


**Figure 5.** Stream-water samples were collected over a range of flows despite widespread drought in 1999 and 2000. Ground-water samples often were collected when rainfall and ground-water levels were below average. (Average and percentiles based on 1971 through 2000 data.)

## Drier than normal weather affected study findings

Water quality in streams and shallow ground water varies in response to hydrologic conditions, so information on precipitation, streamflow, and ground-water levels is critical for assessing water-quality conditions. Streamflow generally fell below the 30-year average during the first 2 years of sampling as a result of moderate to severe drought throughout the Study Unit (fig. 5). Many small streams draining areas underlain by thin glacial deposits or shale bedrock in the southern part of the Study Unit stopped flowing in 1999.

During dry periods when streamflow is low, water quality is affected primarily by discharge of municipal and industrial wastewater, so aquatic organisms may be exposed to higher concentrations of wastewater compounds (such as nutrients) than during periods of normal or high streamflow and may also be affected by algal blooms that reduce dissolved-oxygen concentrations. In wet periods, streamwater quality is affected by urban and agricultural runoff, and aquatic organisms may be temporarily exposed to chemicals spilled, deposited, or recently applied to the land surface.

Ground-water levels in the buried-valley aquifer system also were affected by the drought, but the effects of changing ground-water levels on water quality are difficult to predict. Below-normal rainfall caused water levels in some parts of the buried-valley aquifer to decline before sampling began in May 1999. Water levels remained below the 30-year average for most of 2000 and 2001 (fig. 5).

## Additional Information

For a detailed description of the natural and human factors affecting water quality in the Great and Little Miami River Basins Study Unit, refer to the report by Debrewer and others (2000). The report can be downloaded at http://in.water.usgs.gov/newreports/miami/miami.pdf

# Major Findings

## Pesticides

Pesticides (**herbicides**, **insecticides**, and **fungicides**) are used extensively in agricultural and urban settings in the Study Unit for control of weeds, insects, and fungi. Pesticide use varies by land use. In agricultural areas of the Study Unit, herbicides are applied to virtually all corn and soybean fields, whereas insecticides are used mostly to spot treat infestations in corn (fig. 6).

**Figure 6.** Herbicides are applied to cropland before and after spring planting, mainly from mid-April through June.

Trends in agricultural pesticide use in the Study Unit changed substantially starting in the early 1990s (fig. 7). Such changes include the following:

- Conditional registration by U.S. Environmental Protection Agency (USEPA) in 1994 of the herbicide acetochlor to replace alachlor use on corn
- Increased use of the herbicide glyphosate (Roundup™, Rodeo™, Accord™) in response to introduction of glyphosate-resistant soybeans in 1995 (see p. 9)
- Registration of a more effective form of the herbicide metolachlor (S-metolachlor) in 1999 which, along with the increased use of acetochlor, caused sharp reductions in metolachlor use in Ohio and Indiana (fig. 7).

Atrazine is the most commonly applied herbicide on cropland, in applications of more than 1.1 million pounds per year (table 1). Estimates of pesticide use in urban areas of the Study Unit were not available, but national rankings indicate that 2,4-D is the most commonly applied herbicide to urban areas. Pesticides are commonly used for weed and insect control on lawns, golf courses, road rights-of-way, and home and building perimeters in urban areas.

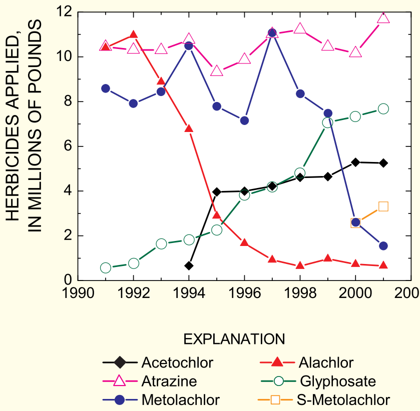


**Figure 7.** Recent trends in agricultural pesticide use in Ohio and Indiana indicate that atrazine and glyphosate were the most abundantly applied herbicides in the Study Unit during 1999-2001. (Data from U.S. Department of Agriculture, 1991–2002.)

**Table 1.** Atrazine is the most commonly used pesticide in agricultural areas of the Study Unit. Pesticide use differs with land use in urban areas across the Nation.

| Study unit ranking of pesticides applied to agricultural areas | | |
|---|---|---|
| Rank | Pesticide | Application, in 1,000 pounds |
| 1 | * Atrazine | 1,120 |
| 2 | * Metolachlor | 944 |
| 3 | * Cyanazine | 476 |
| 4 | * Glyphosate | 410 |
| 5 | * Acetochlor | 337 |
| 6 | * 2,4-D | 161 |
| 7 | * Pendimethalin | 150 |
| 8 | * Alachlor | 109 |
| 9 | * Chlorpyrifos | 106 |
| 10 | * Simazine | 99 |

| National ranking of pesticides applied to urban areas | | |
|---|---|---|
| Rank | Home and garden use | Industrial and commercial use |
| 1 | * 2,4-D | * 2,4-D |
| 2 | * Glyphosate | * Glyphosate |
| 3 | MCPP | Copper sulfate |
| 4 | * Dicamba | * Pendimethalin |
| 5 | * Diazinon | * Chlorpyrifos |
| 6 | * Chlorpyrifos | MSMA |
| 7 | * Carbaryl | * Chlorothalanil |
| 8 | * Benfluralin | * Diuron |
| 9 | * Malathion | * Malathion |
| 10 | * Dacthal | * Triclopyr |

Fungicide 🟦 Herbicide 🟩 Insecticide 🟥

* Pesticides analyzed in this study.

Pesticides applied to urban areas are based on 1998–99 proprietary sales data (Donaldson and others, 2002). Pesticides applied to agricultural areas are based on 1997 estimates (Gail Thelin, U.S. Geological Survey, written commun., 2001) [2,4-D, 2,4-dichlorophenoxyacetic acid; MCPP, 2-(2-methyl-4-chlorophenoxy) propionic acid; MSMA, monosodium methylarsonate]

## Pesticides in Streams

The transport of a pesticide from the site of application depends on the chemical stability of the pesticide, its solubility in water, and its tendency to adsorb to soil particles. Transport by water is the primary way most pesticides get into water supplies—by seeping into ground water and running off to streams. Spray drift and atmospheric transport by volatilization of pesticides are additional ways pesticides can get into our water supplies.

### Pesticides were detected in every stream sample

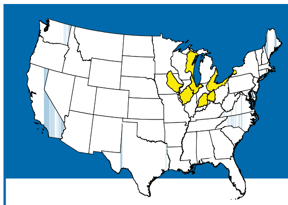
One or more pesticides were detected in each of the 184 samples collected from five stream sites from March 1999 through September 2001. Fifty-eight pesticides were detected in stream water: 37 herbicides, 10 herbicide **degradates**, 9 insecticides, and 2 fungicides. Most samples contained mixtures of 10 to 20 pesticides. Samples collected during runoff events from the East Fork Little Miami River and the Great Miami River contained mixtures of 31 pesticides.

### Heavily used herbicides in agricultural areas were detected in streams

Herbicides applied to cropland were frequently detected in streams draining all three of the major land-use settings (agriculture, Mad River; urban, Holes Creek; mixed, Great Miami River). (See Box 1.) The frequency of detection and the concentrations of herbicides, however, typically were lower in samples

## Additional Information

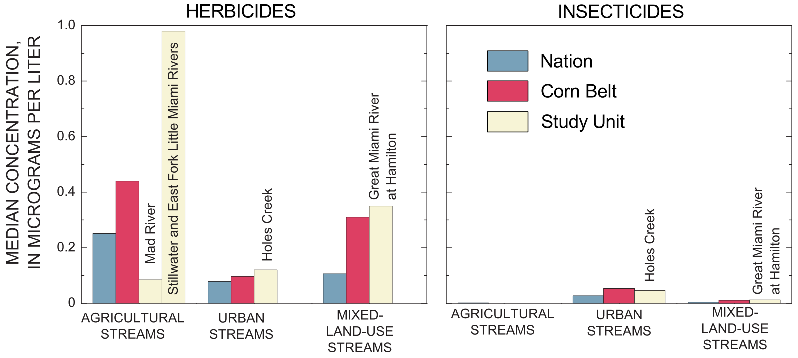
These findings are supported by the Study Unit Design presented on pages 29 and 30 of this report.



# Pesticide occurrence in streams varied in response to ground-water contributions; pesticides in ground water were generally comparable to those in the rest of the Nation and Corn Belt region

## Streams

The **median** concentration of summed herbicides found in the Great Miami River at Hamilton, 0.33 µg/L (microgram per liter), was similar to the median concentration for 13 mixed-land-use streams sampled in the Corn Belt Region by the NAWQA Program from 1991 to 2001 but higher than the median concentration for 47 mixed land-use streams sampled nationwide by the NAWQA Program. The median concentration of summed herbicides in Holes Creek (0.12 µg/L), which drains urban lands, was only slightly higher than values for 4 urban streams sampled in the Corn Belt and the 33 urban streams sampled nationally by NAWQA. The median concentration of summed herbicides was lower for the Mad River (0.08 µg/L), which drains agricultural land and was lower than the median value for 25 agricultural streams sampled in the Corn Belt and 77 streams sampled nationwide by the NAWQA Program. The relatively low concentrations in the Mad River probably are a consequence of the large amounts of ground water discharged to the stream from sand-and-gravel deposits throughout the Mad River Basin (fig. 1). The lower pesticide concentrations in ground water chemically dilutes the stream water.



Pesticide concentrations in streams were among the highest nationwide, but ground-water contributions lowered pesticide concentrations in the Mad River.

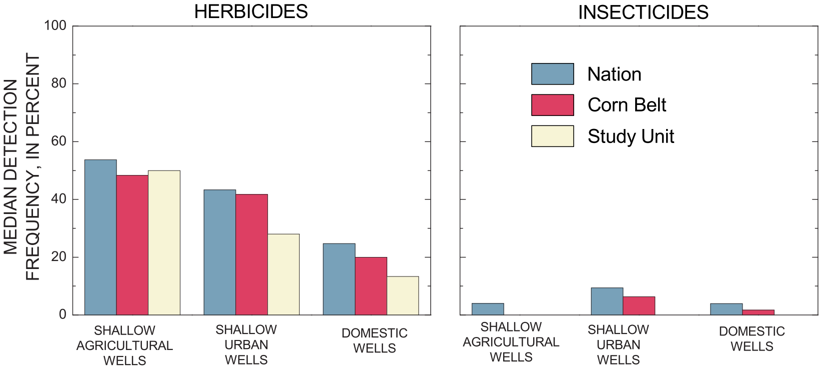
A small number of samples were collected from streams that drain agricultural land in areas of clayey and silty till (Stillwater and East Fork Little Miami Rivers). These streams receive minimal contributions from ground water and are fed by storm runoff and flow from ditches and **tile drains**. The median concentration of herbicides in the samples collected from these streams (0.98 µg/L) was about twice that measured in other agricultural streams sampled for NAWQA studies in the Corn Belt (0.44 µg/L) and about four times that for all agricultural streams s

Unit, Corn Belt, and nationwide. Insecticides were not detected in agricultural streams in these three areas.

## Ground water

The median detection frequencies of herbicides and insecticides in ground-water samples collected in the Study Unit were similar to those found by NAWQA studies in the Corn Belt Region and slightly lower than those found nationwide. One or more herbicides were detected in about 50 percent of samples from NAWQA monitoring wells installed in agricultural areas in the Study Unit, the Corn Belt, and nationwide, but herbicides were detected in 25 percent or less of NAWQA samples from domestic wells.

Insecticides were detected most frequently (in about 10 percent of samples) in NAWQA monitoring wells installed in urban areas in the Corn Belt and nationwide. None of the insecticides ranked in the top 10 pesticides used in agricultural areas or urban areas (table 1), however, were detected in any of the 96 ground-water samples collected in the Study Unit.



In ground water, herbicides were detected more frequently in samples from agricultural wells than in samples from urban and domestic wells.

collected from the Mad River than from the urban and mixed-land-use streams. Because of low concentrations of pesticides in ground water and extensive sand-and-gravel deposits that discharge large quantities of ground water to the Mad River (fig. 1), the stream water is chemically diluted.

Atrazine and metolachlor, the two most commonly used herbicides in the Study Unit, were detected in 98 percent and 94 percent of samples, respectively. Some herbicides used for weed control in both agricultural and urban settings—including 2,4-D, clopyralid, diuron, dicamba, MCPA, pendimethalin, siduron, and triclopyr—were detected more frequently in the urban and mixed-land-use streams than in the agricultural stream. Prometon, a nonagricultural herbicide used exclusively for vegetation control in rights-of-way, was detected in 97 percent of samples from the urban and mixed-land-use streams. Relative to its use, glyphosate was detected less frequently than other high-use herbicides. (See p. 9.)

### Box 1—Detection frequencies

NAWQA reports detection frequencies to describe the occurrence of chemicals in water. All reported detections are used in comparisons of detections for a single chemical between different streams or ground-water networks. Because analytical method sensitivities vary widely from one chemical to another, however, a common reporting level (0.05 µg/L) is sometimes used to establish an equal basis for comparing detection frequencies for multiple chemicals at a single site or network.

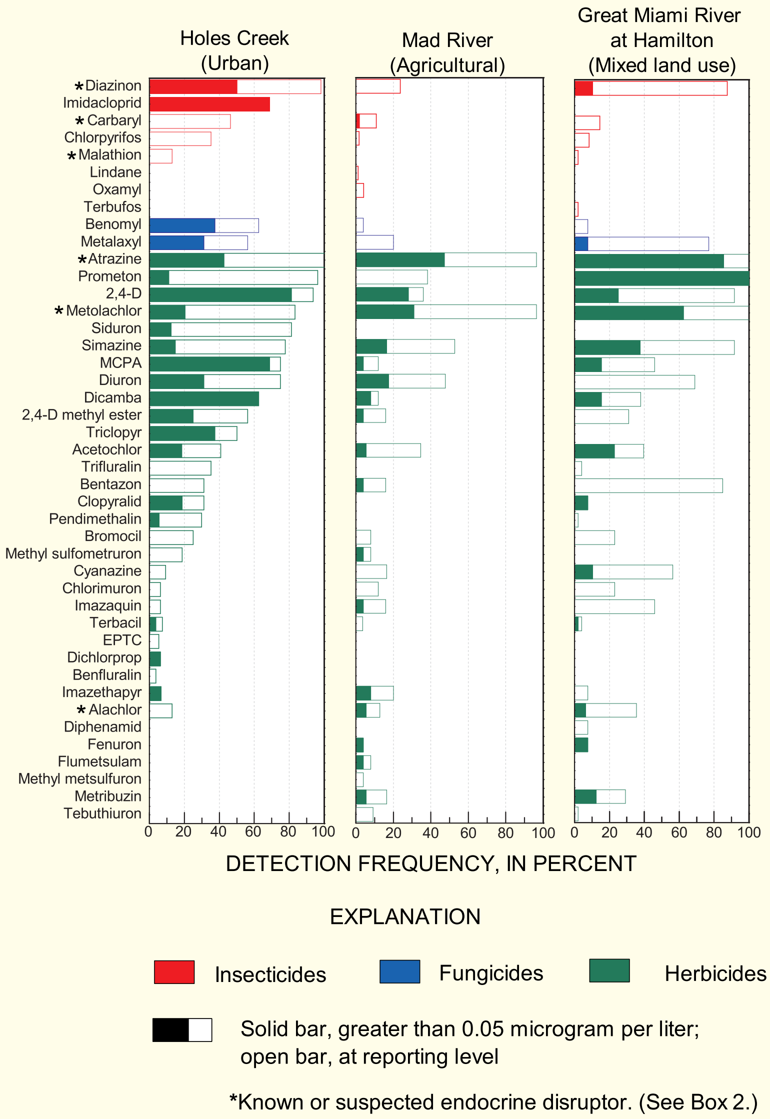


**Figure 8.** Pesticides found in study-unit streams were related to upstream land use. Overall, atrazine, metolachlor, prometon, and 2,4-D were the most frequently detected herbicides. Diazinon and metalaxyl were the most frequently detected insecticide and fungicide, respectively.

### Box 2—Endocrine-disrupting compounds

**Endocrine systems** in animals release hormones that regulate body functions such as growth, embryonic development, and reproduction. Endocrine disruptors are organic chemicals that interfere with or mimic natural hormones and have the potential to cause reproductive or developmental impairment in animals (Smith, 1998). Chemicals believed to be endocrine disruptors include certain pesticides and pesticide degradates, various household chemicals, pharmaceuticals, and wastewater chemicals from industrial and municipal sources. Some chemicals known or suspected to be endocrine disruptors were detected in water, bed sediment, and fish-tissue samples collected in the Study Unit; these include the pesticides atrazine and diazinon and the household chemicals triclosan (found in antibacterial products) and benzophenone (a perfume and soap additive) (Environment Canada, 2002; Zaugg and others, 2002).

## Insecticides and fungicides were detected more frequently in streams receiving runoff from urban areas than from agricultural areas

Diazinon was detected in 90 percent or more of the samples from the urban and mixed-land-use streams (fig. 8) but in less than 30 percent of the samples from the agricultural stream (Mad River). The maximum concentration of diazinon in the urban stream (Holes Creek) was 0.56 µg/L, whereas the maximum in the three agricultural streams (Mad River, Stillwater River, and East Fork Little Miami River) was 0.14, 0.013, and 0.004 µg/L, respectively. Imidacloprid, an insecticide present in turfgrass products used to control grubs, was detected in 70 percent of the samples collected from the urban stream, with a maximum concentration of 0.89 µg/L, but was not found in any samples from the agricultural or mixed-land-use streams. The fungicides benomyl and metalaxyl were detected in slightly more than one-half the samples collected from the urban stream, with maximum concentrations of 0.52 µg/L for benomyl and 1.1 µg/L for metalaxyl.

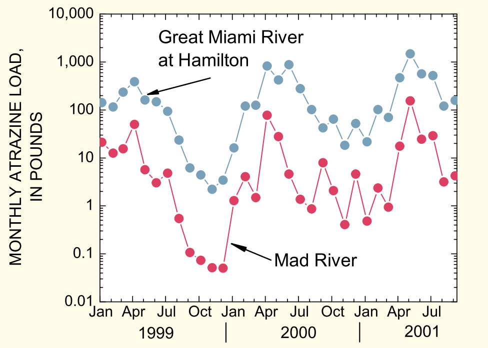


**Figure 9.** Atrazine loads in streams varied in response to runoff events and application periods and were lowest during the 1999 drought, but seasonally were highest in April and May.

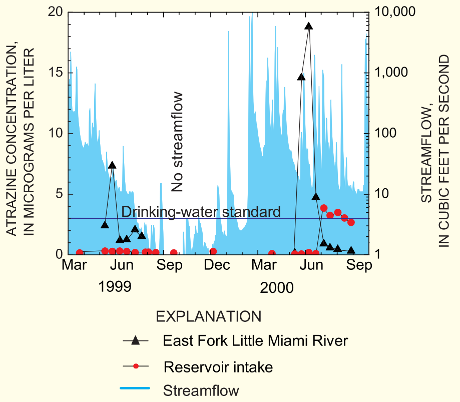


**Figure 10.** Atrazine concentrations in Harsha Lake (reservoir intake) were low and varied little during the 1999 drought, but they increased sharply and remained high during summer 2000.

## Herbicide concentrations and loads varied in response to rainfall and runoff

Seasonal patterns in water quality emerged in agricultural basins, mainly reflecting the timing and amount of herbicide use and the frequency and magnitude of runoff from rainstorms and irrigation. Concentrations and loads of herbicides are highest during runoff following chemical applications. For example, monthly loads of atrazine computed for Mad River (agricultural) and Great Miami River at Hamilton (mixed land use) show this seasonal pattern during the 3-year monitoring period (fig. 9), when peak loads in the Great Miami and Mad Rivers (about 1,500 pounds and 150 pounds) occurred in May 2001. Lower streamflows in the Study Unit during the drought produced the lowest atrazine loads in both rivers in autumn of 1999 (fig. 9).

An understanding of seasonal variations in streamflow and pattens in pesticide use is important because they can significantly affect the timing of the highest concentration in aquatic habitats (possibly affecting, for example, critical life stages of aquatic organisms) and drinking-water supplies. For example, seasonal patterns typically occur in Harsha Lake, an important drinking-water-supply reservoir in the southeastern part of the Study Unit that is fed primarily by the agriculture-draining East Fork Little Miami River. The maximum concentration of atrazine in the East Fork Little Miami River at Williamsburg in 1999 (7 µg/L) was about one-third the maximum concentration in 2000 (about 20 µg/L) (fig. 10). Probably because of the drought, the increase in atrazine concentrations that typically follows the “spring flush” of pesticides applied during the planting season did not occur in Harsha Lake in 1999 (Funk and others, 2003). Instead, atrazine concentrations in

## Box 3—What benchmarks are used for assessing water quality in this report?

Various Federal, State, and Canadian standards, guidelines, criteria, and water-quality goals have been selected for use by the NAWQA Program as benchmarks to compare chemical concentrations in water, sediment, and fish tissue on a national basis. Many benchmarks consist of nonenforceable guidelines designed to protect the health of humans and aquatic organisms. Other benchmarks are used in the regulation of the quality of drinking water and are applicable only to treated drinking water, not the untreated water samples the USGS collects from streams and wells. References in this report to any chemical in “exceedance” of a benchmark concentration are for comparison only and do not imply regulatory violations.

The USEPA is responsible for setting drinking-water standards to protect human health. A Maximum Contaminant Level (MCL), commonly referred to as a primary drinking-water standard, is the maximum allowable concentration of a contaminant in water delivered to any public-water-system user. MCLs are legally enforceable standards for treated drinking water. A Secondary Maximum Contaminant Level (SMCL), commonly referred to as a secondary drinking-water standard, is a nonenforceable guideline for the concentration of a contaminant that may cause undesirable cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water. A Health Advisory Level (HAL) is also a nonenforceable, risk-based guideline. HALs indicate contaminant exposures below which no short- or long-term human-health effects are expected, based on drinking a specific amount of water for a specific period of time. Risk of illness increases with exposure time and concentration. Of 117 pesticides and degradates for which water samples were analyzed for this study, 13 have MCLs and 27 have HALs.

Guidelines to protect aquatic life have been set by several agencies, including the USEPA, Environment Canada, and the International Joint Commission (IJC). The aquatic-life guidelines for water developed by USEPA are based on 4-day average concentrations, are intended to protect 95 percent of the aquatic species, and should not be exceeded more than once in 3 years. The Canadian and IJC aquatic-life guidelines, which are more stringent than those of the USEPA, indicate a single maximum concentration that should never be exceeded. Aquatic-life guidelines for water have been established for only 32 of the 117 pesticides included in this study.

Currently, the United States does not have sediment-quality criteria to protect **benthic** organisms. Canadian Interim Sediment Quality Guidelines were used to evaluate freshwater sediment quality for **semivolatile organic compounds** and trace elements. These sediment-quality guidelines (SQGs) consist of two effect values, the Threshold Effect Level (TEL) and Probable Effect Level (PEL). The TEL defines the contaminant concentration in bed sediment below which adverse biological effects rarely occur, whereas PEL is the contaminant concentration above which adverse biological effects frequently occur. PELs have been established for 22 of the 97 **organochlorine insecticides** and semivolatile organic compounds and 7 of 45 trace elements analyzed for this study.

Harsha Lake remained relatively constant in 1999 and early 2000 until heavier rainfall and runoff in the spring of 2000 transported large quantities of the herbicide into the reservoir. Four of the five untreated reservoir samples collected after June 2000 had atrazine concentrations exceeding the USEPA drinking-water standard of 3 µg/L, but atrazine concentrations in samples collected from the treatment plant were well within this drinking-water standard. (See page 10.)

## Aquatic-life guidelines for pesticides were exceeded in 27 percent of stream samples

Concentrations of pesticides in excess of aquatic-life guidelines were not uncommon in study-unit streams. Pesticides present at concentrations that exceeded aquatic-life guidelines in one or more stream samples included the herbicides atrazine, cyanazine, metribuzin, and metolachlor and the insecticides carbaryl, chlorpyrifos, diazinon, and malathion.

Overall, pesticide concentrations exceeded aquatic-life guidelines in 27 percent of stream samples, but land use, streamflow, and pesticide-application periods were important in determining when, where, and what pesticides exceeded guidelines. Aquatic-life guidelines for herbicides were most frequently exceeded in streams draining agricultural land, whereas aquatic-life guidelines for insecticides were most frequently exceeded in the urban stream, Holes Creek (fig. 11). One or more aquatic-life guidelines were exceeded in 17 percent of samples from streams sampled multiple times over a range of streamflow conditions and land use. In contrast, one or more guidelines were exceeded in 100 percent of spring-runoff samples from streams draining cropland following the application of pesticides. Atrazine concentrations in all of these spring-runoff samples exceeded the aquatic-life guideline of 1.8 µg/L. Of the samples collected in summer 2001, no herbicide concentrations exceeded aquatic-life guidelines; the percentage of samples that exceeded one or more aquatic-life guidelines

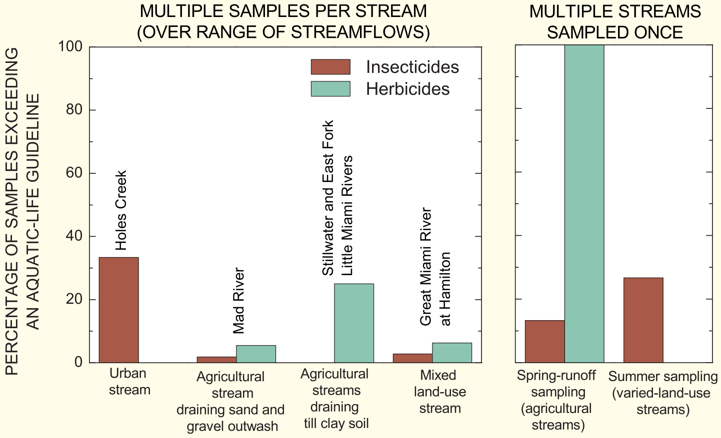


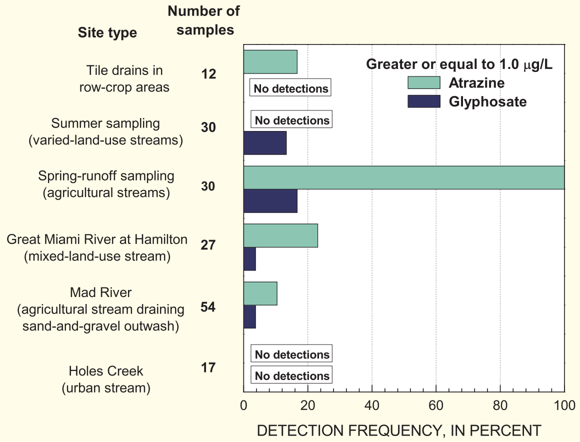
**Figure 11.** Aquatic-life guidelines for insecticides were exceeded most often in Holes Creek, an urban stream, whereas guidelines for herbicides were exceeded most often in agricultural streams during spring runoff.

### Glyphosate was detected infrequently in streams and not found in ground water

Glyphosate is a broad-spectrum, non-selective, post-emergent herbicide. It strongly adsorbs onto soil and degrades relatively quickly; moreover, it is believed to be relatively nontoxic to most terrestrial and aquatic organisms (Giesy and others, 2000). Following introduction of genetically modified soybeans in 1995, the acreage planted with glyphosate-tolerant soybeans increased rapidly, and by 2001, accounted for more than 70 percent of the total soybean acreage in Ohio and Indiana (U.S. Department of Agriculture, 1991–2002). Farmers have switched to glyphosate-tolerant soybeans because use of a single herbicide simplifies weed control and lowers costs. As a result, the amount of glyphosate applied to cropland is quickly approaching that of atrazine, the most heavily used herbicide in the Study Unit (fig. 7) and the rest of the Corn Belt. In addition to increased agricultural use, glyphosate is commonly used in urban areas for weed control on lawns and turf, building perimeters, and rights-of-way (table 1).

Glyphosate was detected infrequently in agricultural and mixed-land-use streams at concentrations above 1.0 µg/L and was not detected at this level in small urban streams. Concentrations of glyphosate greater than 1.0 µg/L were detected at about the same frequency in samples of agricultural runoff collected from 30 small subbasins in the rural Stillwater River Basin after a large spring storm and in samples collected from 30 small subbasins (less than 75 square miles) in areas with varying amounts of urban and agricultural land in the Dayton-Cincinnati region during a summer low-flow period. The maximum concentrations of glyphosate for the two groups of samples were 3.6 and 9.2 µg/L, respectively, well below the current drinking-water standard of 700 µg/L and the aquatic-life guideline of 65 µg/L.

Glyphosate was not detected in shallow ground water beneath cropland or in four sets of tile drains sampled before, during, and after the 2001 growing season. Glyphosate is unlikely to be found in ground water because of its strong tendency to adsorb to soil and biodegrade.



Glyphosate was detected less frequently than atrazine in streams draining agricultural and mixed-land-use basins. Although both herbicides are used in large quantities, atrazine is more resistant to degradation than glyphosate and is less likely to bind to soil.

for insecticides, however, was similar to that for Holes Creek. There, concentrations of the insecticide diazinon exceeded the aquatic-life guideline of 0.08 µg/L in 33 percent of the samples collected over a 2.5-year period. Most samples with high concentrations of diazinon were collected from June through September, when many homeowners apply insecticides.

## Potential toxicity of pesticide mixtures varied by season and land use

Aquatic-life guidelines, which are developed for individual pesticides, do not account either for the continuous exposure of fish and benthic organisms to mixtures of pesticides or for seasonal variations in concentrations. Little is known about the possible concurrent or cumulative effects on aquatic life from multiple pesticides at low concentrations, or effects of lengthy periods of low concentrations punctuated by brief seasonal pulses of much higher concentrations. The Pesticide Toxicity Index (PTI) combines pesticide exposure of aquatic organisms with toxicity estimates and is used to rank or compare the relative toxicity of samples or sites (Munn and Gilliom, 2001). High PTI scores are associated with higher toxicities, and in general, insecticides are more toxic than herbicides to benthic **invertebrate**s and fish. Samples from Holes Creek (urban), in which numerous insecticides were detected, almost always had a higher PTI score for benthic invertebrates than samples from Mad River (agricultural) (fig. 12). PTI scores also were shown to increase with increasing percentage of urban land in basins. (See p. 28.) The Mad River occasionally had PTI scores similar to those for Holes Creek, but only when pesticides were applied to agricultural areas in the spring and summer. When agricultural streams within the Stillwater River Basin were sampled during spring runoff, however, PTI scores for those streams were significantly higher than those for Holes Creek (fig. 12). (See Box 4.)

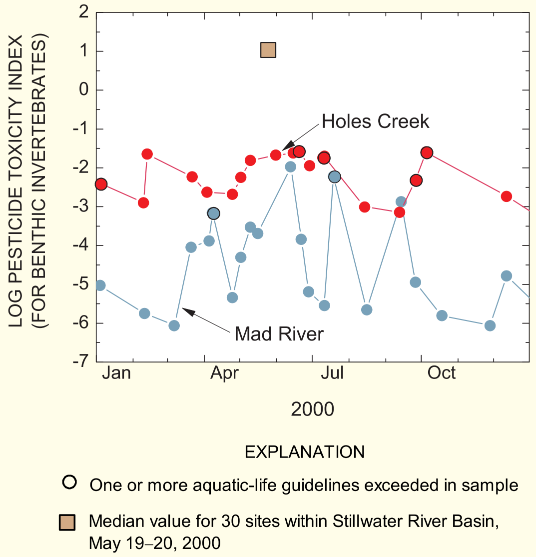


**Figure 12.** Pesticide Toxicity Index scores for the urban Holes Creek were higher than those for the agricultural Mad River, but the scores for Mad River did approach scores for Holes Creek in spring and summer.

### Box 4—Use of the term "Significant"

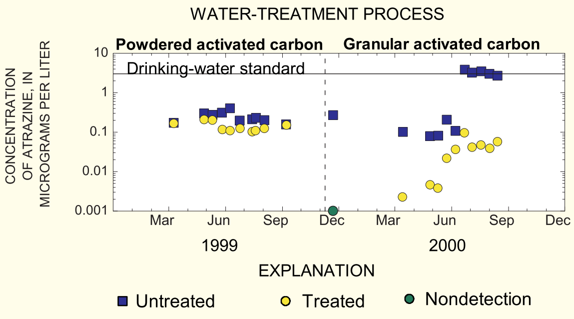
In discussions of statistical analyses, the term "significant" means the analysts believe that the apparent relation has a specific probability of being real and not due to chance. In this report, the selected level of significance is less than 5 percent ($p < 0.05$). Nonparametric statistics were used to evaluate the water-quality datasets because the datasets are small and not normally distributed.

## Pesticide degradates were detected more often than many parent chemicals

Degradates of acetochlor, alachlor, and metolachlor were detected in stream samples throughout the year. The summed concentrations of the oxanilic acid (OA) and ethane-sulfonic acid (ESA) degradates of these herbicides were typically more than 10 times the concentrations of the parent chemicals. Alachlor and acetochlor were detected in streams during the spring application periods but were mostly absent from streams during the remainder of the year. Metolachlor, atrazine, and atrazine degradates were detected in streams throughout the year; the summed concentration

## Atrazine concentrations in treated water from Harsha Lake met drinking-water standard

In 1999, USEPA and USGS initiated a 2-year assessment of pesticide concentrations in drinking water. In support of USEPA's responsibility under the Food Quality Protection Act of 1996, the program was designed as a first step toward a long-term goal of characterizing human exposure to pesticide residues in drinking water derived from surface-water sources. Harsha Lake, which drains primarily agricultural land and supplies drinking water to about 40,000 residents of Clermont County, Ohio, was one of 12 reservoirs sampled in the national assessment of 186 pesticides and degradation products. From March 1999 to September 2000, 21 samples each of untreated and treated water were collected. Drinking-water standards or advisory levels have been established for 19 of the 37 pesticides detected. Analysis of the samples indicate that atrazine concentrations in treated water were always below the drinking-water standard and suggest that the practices employed at the Harsha Lake Water Treatment Plant (activated carbon, oxidation, chlorination) were effective in reducing pesticide concentrations (Funk and others, 2003). Atrazine concentrations in samples of treated water were well below the atrazine drinking-water standard of 3 µg/L, even in samples collected after June 2000 when atrazine concentrations in untreated water from Harsha Lake were consistently at or above the drinking-water standard.



Atrazine concentrations were lowered in treated water when granular activated carbon was used in water treatment.

of atrazine degradates, however, was similar to the concentration of the parent chemical (fig. 13). Little is known about the possible effects of degradates on human health and aquatic life. (See Box 5.)

## Pesticides in Ground Water

Pesticides and other chemicals that dissolve in water can seep into ground water. Shallow wells (less than 50 feet deep) are most vulnerable to contamination by these chemicals, which can move from land surface to the **water table** in a few months to a few years. Deeper **domestic wells** (**median** depth of 60 feet) are generally less vulnerable to contamination, and **recharge** water may take several years to decades to reach deeper wells or parts of the aquifer. In contrast, public-supply wells (median depth of 78 feet) that rely on induced infiltration of stream water can be the most vulnerable to contamination. In fact, studies show that water can move from streams into adjacent public-supply wells quickly, within days to weeks. (See p. 13.)

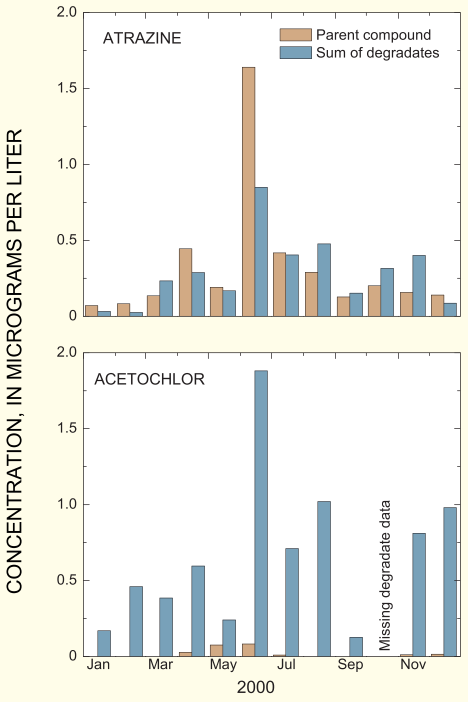


**Figure 13.** Similar concentrations of atrazine and atrazine degradates were measured in the Great Miami River at Hamilton. Concentrations of acetochlor degradates, however, were much higher than concentrations of the parent herbicide.

## Pesticides were detected less frequently and at lower concentrations in ground water than in streams

Thirty-one pesticides were detected in 96 water samples collected from wells completed in the buried-valley aquifer. These include 16 herbicides, 11 herbicide degradates, 2 fungicides, 1 insecticide, and 1 insecticide degradate (fig. 14). About 63 percent of the ground-water samples contained at least one detectable pesticide (or degradate), and almost half the samples contained two or more pesticides. Seventeen pesticides were detected in samples from a public-supply well receiving induced infiltration of water from the Great Miami River and from a shallow **monitoring well** (18 feet deep) in an agricultural area overlain by cropland. The highest concentration of an individual pesticide degradate measured was 3.6 µg/L, for the ESA degradate of alachlor, and the highest parent concentration was 1.3 µg/L, for the fungicide benomyl. Concentrations of most of the pesticides were low; maximum concentrations for 16 of the 31 pesticides detected were less than 0.05 µg/L (fig. 14). None of the pesticides had concentrations greater than USEPA drinking-water benchmarks, although only 11 benchmarks exist for the 31 pesticides and degradates detected. (See Box 3.)

Detection frequencies, concentrations, and number of pesticides detected in ground water were less than those in stream water. For many of these pesticides, the chemical stability or mobility is not sufficient for them to move and persist in the ground-water-flow system long enough to reach a well. In addition, relatively impermeable clay (in glacial till) can impede the vertical movement of pesticides toward the water table.

## Herbicide degradates were the dominant form of pesticides found in ground water

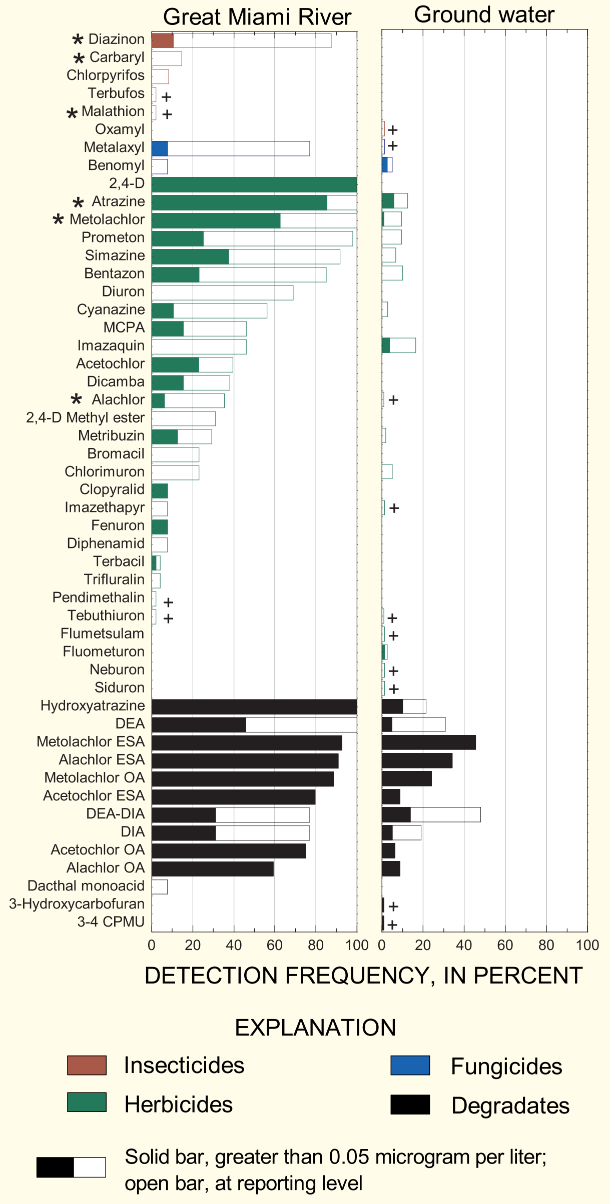
Degradates of atrazine, alachlor, acetochlor, and metolachlor were the most frequently detected contaminants in ground water in the Great and Little Miami River Basins (fig. 14). Atrazine and metolachlor, which were detected in nearly all stream samples, were detected in less than 15 percent of the ground-water samples. The degradates of atrazine, acetochlor, alachlor, and metolachlor, however, made up more than 90 percent of the total pesticide concentration in 80 percent of the samples collected from domestic and

### Box 5—What are degradates and why are they important?

When released into the environment, synthetic organic compounds—including pesticides, VOCs, and pharmaceuticals—may break down by either chemical or biological processes in water, soil, stream sediment, and plant and animal tissue. These processes can result in one or more **breakdown products** (hereinafter termed “degradates”). For example, the herbicide atrazine breaks down to deethylatrazine (DEA), deisopropylatrazine (DIA), deethyldeisopropylatrazine (DEA–DIA), and hydroxyatrazine. Some degradates are produced by the breakdown of more than one parent compound. For example, DIA also can form from the breakdown of the herbicides simazine and cyanazine. Degradates, particularly those of high-use herbicides such as atrazine and metolachlor, are often detected more frequently and at higher concentrations in streams and ground water than are their parent compounds (Clark and others, 1999; Kolpin and others, 2000).

Although many degradates are believed to be less toxic than their parent compounds, some degradates have equal or greater toxicity than the parent compounds (Sinclair and Boxall, 2002). Physical and chemical properties of the degradate may allow it to persist at higher concentrations and for a longer time. Even if a degradate is less toxic than the parent compound, its enhanced stability (or mobility) could lead to increased exposure in humans and aquatic organisms. Health concerns about degradates has prompted USEPA to consider selected atrazine degradates in the reregistration process for atrazine (U.S. Environmental Protection Agency, 2002), although the implications for the atrazine drinking-water standard are uncertain at this time.

public-supply wells. Although the human-health implications of pesticide degradates are not currently known (see Box 5), this finding suggests that monitoring programs that do not analyze for degradates will have an incomplete picture of pesticide occurrence in the buried-valley aquifer system in the Study Unit.



[2,4-D, 2,4-dichlorophenoxyacetic acid; MCPA, (4-chloro-2-methylphenoxy) acetic acid; DEA, deethylatrazine; DEA-DIA, deethyldeisopropylatrazine; DIA, deisopropylatrazine; ESA, ethanesulfonic acid; OA, oxanilic acid; 3-4 CPMU, 3-4(Chlorophenyl) 1-methyl urea; +, compound with only one detection; *, known or suspected endocrine disruptor (see Box 2)]

**Figure 14.** Pesticides frequently detected in streams were found much less frequently in ground water. Degradates of high-use herbicides were the most frequently detected pesticides in ground water.

## Pesticides were detected most frequently and at highest total concentrations in public-supply wells near streams

Pesticides were detected more frequently in water samples from public-supply wells near streams (about 60 percent) than in domestic wells or in shallow monitoring wells in agricultural and urban areas (fig. 15). The median number of pesticides detected per public-supply well (9) also was higher than in shallow agricultural wells (3) and domestic wells (1). With some exceptions, detection frequencies of pesticide degradates were higher in the public-supply wells than in the agricultural and domestic wells (fig. 16). Deethylatrazine (DEA) and the ESA degradates of metolachlor and alachlor were detected in more than 80 percent of the public-supply wells. Bentazon, atrazine, imazaquin, metolachlor, and prometon were detected 2 to 3 times as frequently in public-supply wells as in agricultural wells. The median concentration of pesticides in public-supply wells (1.18 µg/L) was almost 20 times the median concentration of the same group of pesticides in shallow agricultural wells (0.06 µg/L) but was similar to the median concentration found in samples from the Great Miami River (2.11 µg/L).

The most likely source of pesticide contamination of the high-capacity public-supply wells located near streams is induced infiltration of stream water, which can reach the wells in weeks or even days. The rate and volume of pumping, along with the permeability of **streambed sediments** and aquifer materials, governs the degree of interaction between the stream and shallow aquifer and the vulnerability of ground water to contamination. Implications of these findings are important because ground-water contamination is difficult to reverse. Ground-water flow rates are slow compared to streamflow, and a contaminated aquifer can take years or even decades to recover.

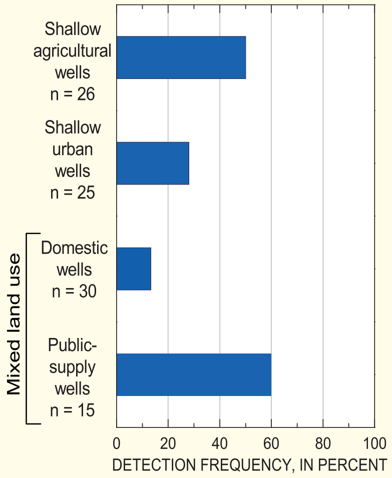
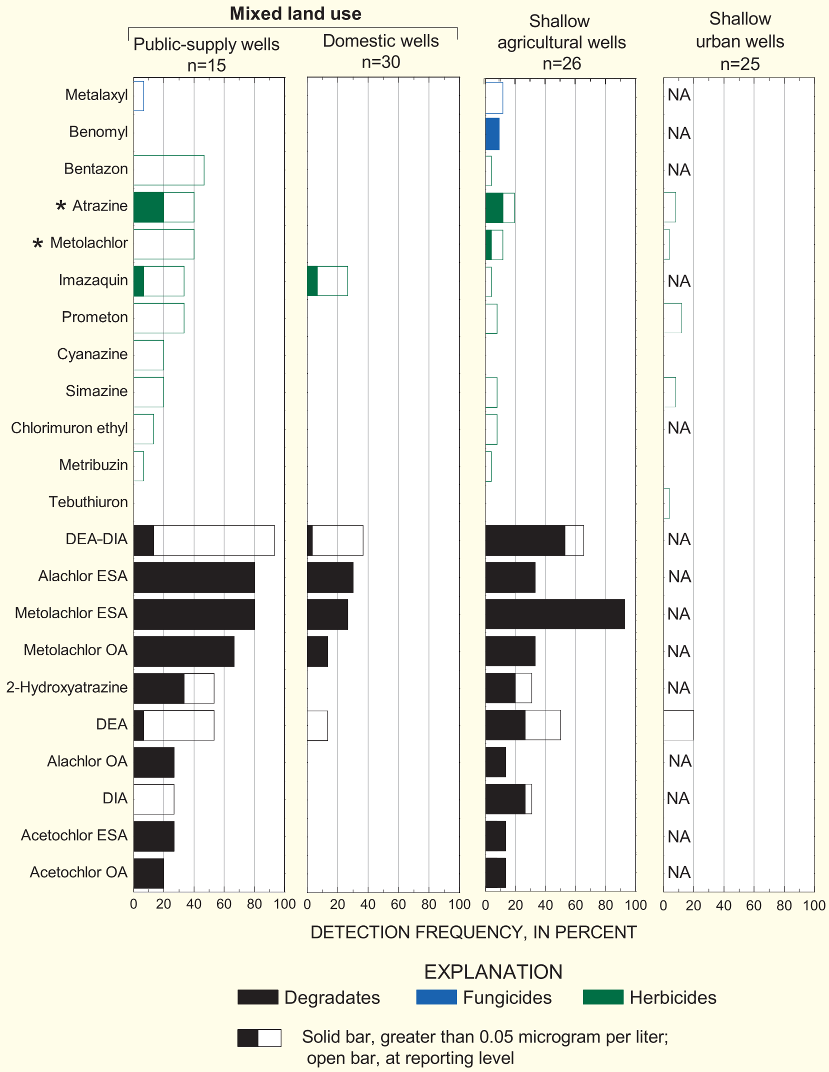


**Figure 15.** One or more pesticides were detected more frequently in high-capacity public-supply wells near streams than in either domestic wells or shallow monitoring wells in agricultural or urban areas.



[DEA, deethylatrazine; DEA–DIA, deethyldeisopropyl atrazine; DIA, deisopropylatrazine; ESA, ethane sulfonic acid; OA, oxanilic acid; n, number of samples; NA, not analyzed; *, known or suspected endocrine disruptor (see Box 2)]

**Figure 16.** Infiltration of stream water containing pesticides is one explanation for why pesticides and degradates were found most often and at highest concentrations in water pumped from high-capacity public-supply wells near streams.

## Other Organic Compounds

**Volatile organic compounds (VOCs)**—used in paints, solvents, fuels, refrigerants, and fumigants—are a water-quality concern because of their widespread use, toxicity, and documented presence at low concentrations in water across the Nation, particularly in urban areas. Thirty of the 86 VOCs for which samples were analyzed were detected in Holes Creek, which drains urban land, and in the Great Miami River at Hamilton, which drains mixed land uses. Three types of VOCs were detected: byproducts of drinking-water disinfection called trihalomethanes (THMs), gasoline chemicals, and various solvents. All three types were detected more frequently in the Great Miami River than in Holes Creek, most likely because the Great Miami River drains a much larger basin, encompasses a larger number of industrial and vehicle sources, and receives treated wastewater from industrial and municipal discharges.

Chloroform (trichloromethane), which is produced during disinfection of drinking water and wastewater, was detected in 100 percent of the samples from the Great Miami River (fig. 17). Benzene was the most commonly detected gasoline product, in about 70 percent of the Great Miami River samples. Methyl *tert*-butyl ether (MTBE), a gasoline additive, was detected in 30 percent of the Great Miami River samples but was not detected in Holes Creek. Trichloroethylene (TCE) was the most commonly detected solvent, in more than 60 percent of the samples from the Great Miami River. Concentrations of VOCs were low, however, and all were well below drinking-water standards and aquatic-life guidelines.

VOCs were detected less frequently in ground water than in streams. A total of 20 VOCs were detected in 70 water samples from domestic, public-supply, and shallow monitoring wells in urban areas. Similar to its presence in streams, chloroform was the most frequently detected VOC in ground water—in more than one-half of the samples from public-supply wells and almost 30 percent of the samples from domestic wells and shallow monitoring wells in urban areas. A commonly used solvent, 1,1,1-trichloroethane, was detected in almost half of the shallow monitoring wells in urban areas. MTBE, which is prevalent in ground water in many parts of the Nation, was detected in 13 percent of public-supply wells. MTBE was not detected in domestic wells or monitoring wells in urban areas. Gasoline chemicals were rarely detected in ground water in the Study Unit; toluene (methylbenzene) and 1,2,4-trimethylbenzene were the only gasoline chemicals detected. As in stream samples, VOC concentrations in ground-water samples were low and all were well below drinking-water standards and aquatic-life guidelines. Chloroform, tetrachloroethylene, and bromodichloromethane were the only chemicals detected in ground water at concentrations greater than 1 µg/L.

### Household chemicals and pharmaceuticals were detected in streams and ground water

Human health and safety have improved through everyday use of household and pharmaceutical chemicals, but these chemicals get into our water supplies when they are disposed of in wastewater. As a result, many of these chemicals have been found at very low concentrations in streams across the country (Kolpin and others, 2002). The effects that many of these chemicals may have on humans or aquatic life at low concentrations is unknown, but several are known or suspected endocrine disruptors. (See Box 2.)

Samples collected monthly from the Great Miami River at Hamilton starting in October 2000 and ending in September 2001, and from 25 wells in urban areas from October through December 2001, were analyzed for household chemicals and pharmaceuticals. Of a total of 116 household chemicals and pharmaceuticals for which the samples were analyzed, 61 were detected at least once in samples collected in study-unit streams and ground water. Most of these chemicals were detected more frequently in streams than in ground water (fig. 18). Twenty-five of the most frequently detected chemicals include personal care products, detergents, drugs and their degradates, flame retardants, and animal-waste products, and nine of the chemicals are known or suspected endocrine disruptors.

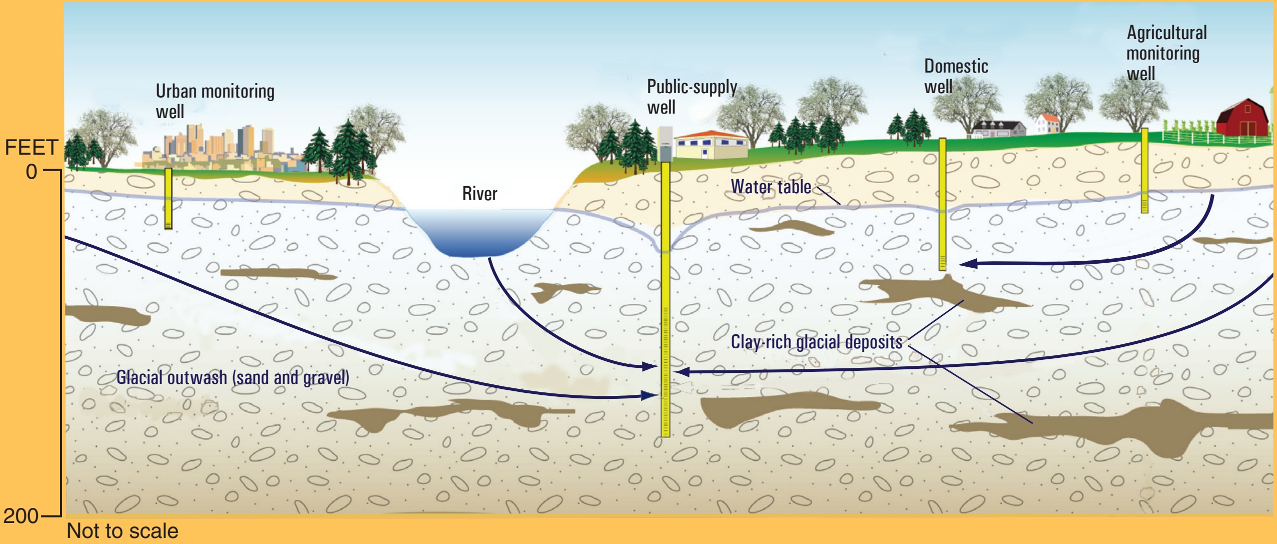
Seven of the household chemicals and pharmaceuticals were detected in more than one-half the samples from the Great Miami River. Acetyl hexamethyl tetrahydronaphthalene (AHTN), a musk fragrance used in many personal care products, was detected in 100 percent of the samples; caffeine and acetaminophen were detected in more than 75 percent

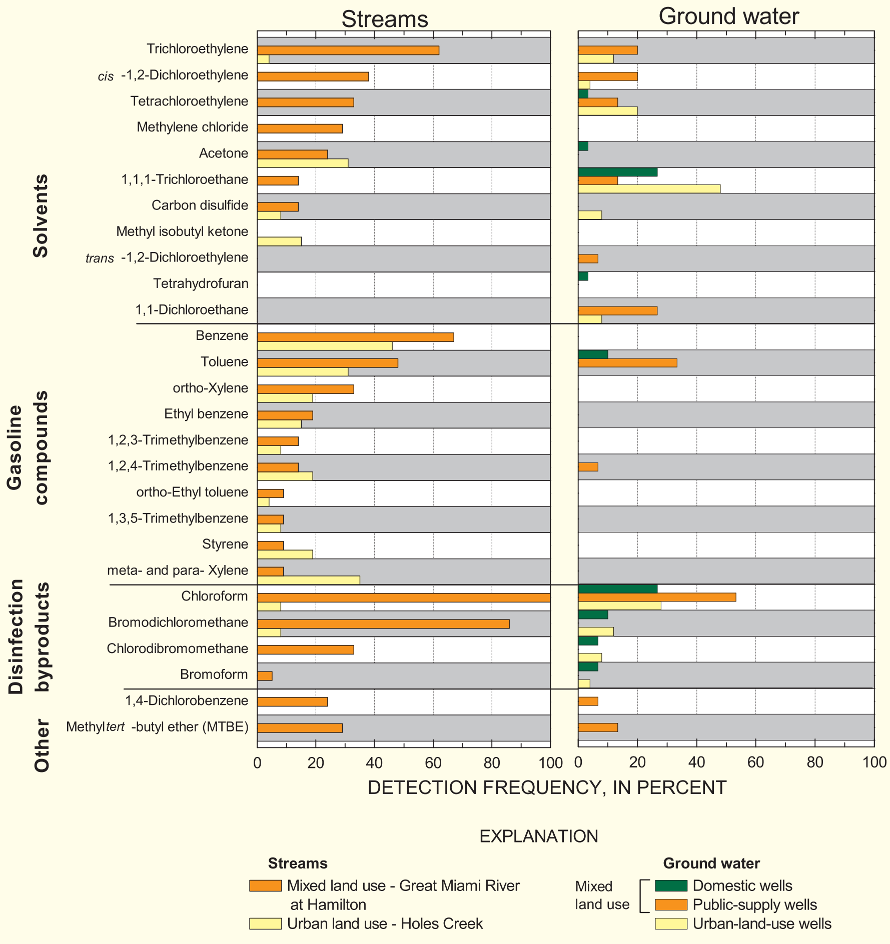
## Hydrogeologic setting, ground-water age, well depth, and construction are key to understanding water quality

Glacial outwash deposits, the source of drinking water to most residents of the Study Unit, are composed of sand and gravel that store and transmit large amounts of water. The same properties that make these deposits an excellent aquifer, such as shallow depth and permeable material, also make ground water vulnerable to contamination. Vulnerability to contamination depends on how fast the aquifer is recharged (ground-water age), which is controlled by various factors, including depth to the water; land use; presence or absence of any overlying, poorly permeable clay layers; amount of water pumped; and distance from sources of contamination. Shallow monitoring wells (less than 50 feet deep) that tap recently recharged ground water are generally considered to be most vulnerable to contamination by chemicals applied to or spilled on the land, so that the quality of shallow ground water tends to reflect overlying land use. For example, the highest concentrations of **nitrate** were found in shallow ground water beneath agricultural areas (see p. 19), and highest concentrations of chloride were found in shallow ground water beneath urban areas (Shindel and others, 2001; 2002; 2003).

Domestic wells are typically deeper than monitoring wells and tap older ground water (recharged within the past few years or decades); they pump small amounts of water and, if properly constructed, are less vulnerable to contamination than are public-supply wells adjacent to streams. Public-supply wells have long well screens, pump large volumes of water, and commonly depend on induced infiltration of stream water to sustain high yields. Because of location and well construction, the public-supply wells have three potential sources of contamination: contaminants introduced at land surface, contaminants found deeper within the aquifer, and contaminants in stream water.

Transport of contaminants to shallow, **unconfined** parts of the aquifer unaffected by heavy pumping may require a few months to a few years. Results of age dating by means of tritium and helium isotopes and sulfur hexafluoride suggest that movement of ground water from the water table to shallow parts of the aquifer (10 to 50 feet deep) takes a year or two. (See Plummer and others [1993] for description of age-dating techniques.) Deeper monitoring wells and domestic wells are recharged more slowly, with median ground-water ages of a decade or more. Age dating of water from high-capacity public-supply wells potentially affected by stream-water infiltration was not attempted because such mixed waters do not yield reliable ages. Studies by Rowe and others (1999) and Sheets and others (2002), however, suggest that water travels from streams to adjacent public-supply wells within relatively short periods (days to months).





[Detection frequency based on reporting level]

**Figure 17.** Volatile organic compounds were detected more frequently in streams than in ground water in the Study Unit.

of samples. In contrast to pesticides, no seasonal pattern was observed in the numbers, types, or concentrations of chemicals found.

A subset of 58 household chemicals and pharmaceuticals were analyzed from samples collected during summer 2001 from 29 small streams with varied land uses. Forty-six chemicals were detected. Seven chemicals were detected in more than one-half of the samples: beta-sitosterol and cholesterol (animal/plant waste products), caffeine (a stimulant), NPEO–2 (a detergent degradate), phenol (multiple uses), tri(2-chloroethyl)phosphate (a plasticizer and flame retardant), and triclosan (a disinfectant/antibacterial chemical). The summed concentration of all chemicals detected in a single sample ranged from 0.26 to 14.1 µg/L, with a median of 3.7 µg/L. No particular group of chemicals was detected more frequently than any other in the small streams, but more chemicals were detected in streams draining larger amounts of urban land. (See p. 25–28.)

Fewer household chemicals and pharmaceuticals (16 out of 116 for which samples were analyzed) were detected in ground water beneath recently developed (post-1960) urban areas than in streams. One or more of the 16 chemicals detected, however, were present at very low concentrations in 19 of 25 shallow monitoring wells in urban areas. The most frequently detected chemical in ground water was 1,7-dimethylxanthine (a caffeine **metabolite**), present in 28 percent of the samples. Most of the chemicals detected in ground water were drugs and their degradates (fig. 18).

## Concentrations of some synthetic organic compounds in the Study Unit ranked among the highest in the Nation

In addition to **polychlorinated biphenyls (PCBs)** (see story on page 17), five organochlorine insecticides or degradates (*cis*- and *trans*-chlordane, *cis*- and *trans*-nonachlor, and aldrin) were detected in fish tissue at concentrations that were among the highest in the Nation (table 2, p. 17). The most common organochlorine insecticides in the Study Unit (*cis*- and *trans*-chlordane, *trans*-nonachlor, and dieldrin) also were among the most frequently detected nationally. These insecticides, whose registrations were canceled during the 1970s and 1980s, were used mainly for termite control and crop protection. They are classified as endocrine disruptors (see Box 2) and are known to cause liver and kidney lesions in fish. Similar to findings for PCBs (see p. 17), organochlorine insecticides were detected more frequently in fish tissue (41 percent) than in bed sediment (16 percent) in the Study Unit. The New York Fish Flesh Criteria (NYFFC) for the protection of fish-eating wildlife (200 µg/kg [micrograms per kilogram] wet weight [Newell and others, 1987]) for total DDT concentration was exceeded in fish tissue (311µg/kg wet weight) from the Mad River. The TEL (see Box 3) for heptachlor epoxide (0.6 µg/kg dry weight) was exceeded in sediment from Holes Creek (1.1 µg/kg dry weight).

Data collected by NAWQA were supplemented by extensive bed-sediment and fish tissue data collected at more than 200 sites within the Study Unit by State agencies in Ohio and Indiana (Janosy, 2002). Dieldrin was the most commonly detected organochlorine insecticide in fish tissue (at 91 percent of the sites) and bed sediment (at 39 percent of the sites). Concentrations of dieldrin in bed sediment exceeded sediment-quality guidelines more often (at 12 sites) than concentrations of any other organochlorine insecticide.

Elevated concentrations of semivolatile organic compounds (SVOCs), such as **polycyclic aromatic hydrocarbons (PAHs)**, were prevalent in bed sediment

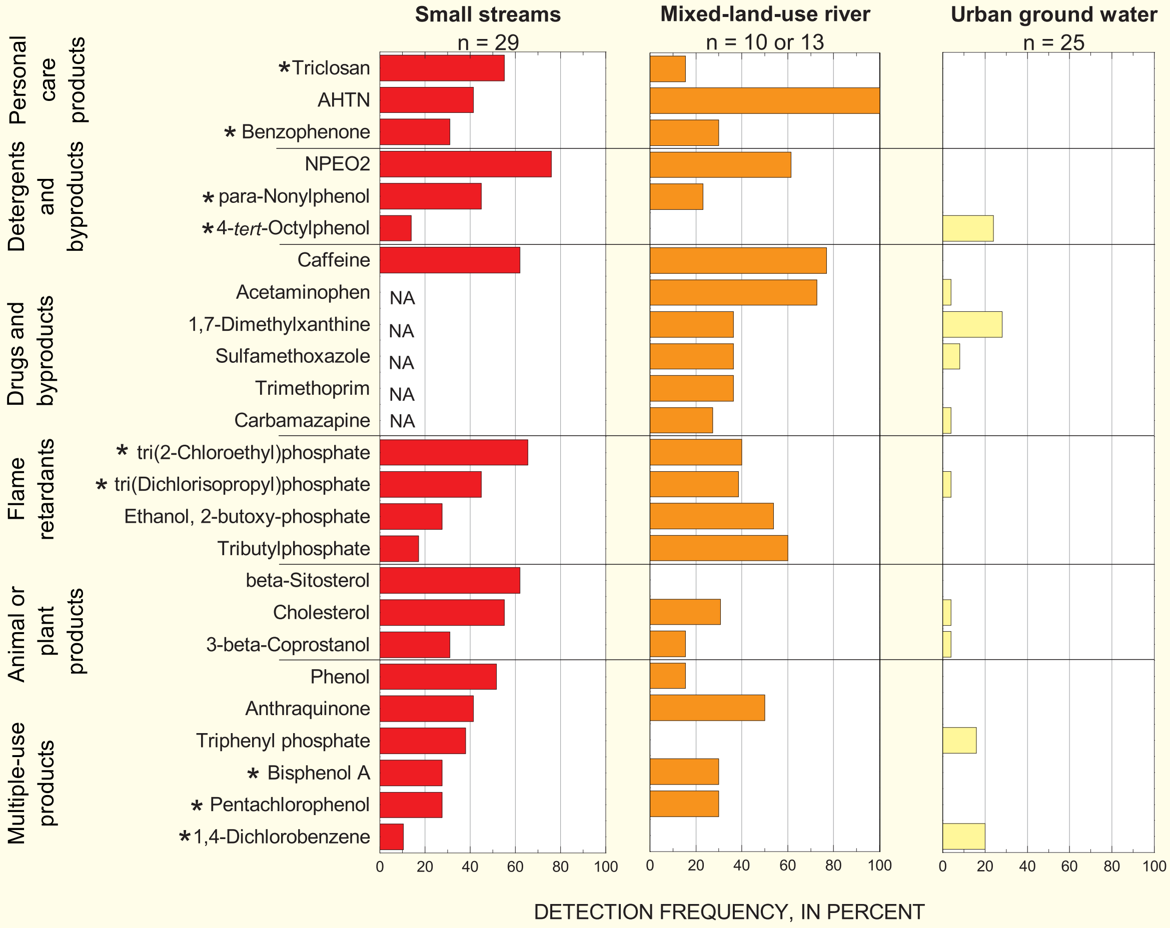


**Figure 18.** Commonly used household chemicals and pharmaceuticals are detected more frequently in streams than in ground water. [n, number of samples; *, known or suspected endocrine disruptor (see Box 2) (Zaugg, 2002); NA, data not available; AHTN, 6-acetyl-1, 1, 2,4, 4,7-hexamethyltetraline; NPEO–2, nonylphenol diethoxylate]

in the Study Unit. Total concentrations of PAHs in sediment from Holes Creek, Great Miami River at Hamilton, and Little Miami River at Milford ranked among the highest 25 percent nationwide for urban and mixed-land-use streams sampled in the NAWQA Program. Forty-seven percent of SVOCs detected were PAHs. Ten PAHs were detected at concentrations exceeding recommended sediment-quality guidelines, although phenanthrene was the only SVOC to exceed a PEL. (See table 2.) Many of the most frequently detected SVOCs in study-unit sediment are components of crude oil and coal tar and are released to the environment through vehicle emissions; coal, oil, and wood-burning stoves and furnaces; and steel and coke production (Janosy, 2002).

## Naturally Occurring Trace Elements

From a national perspective, trace-element concentrations in sediment in the Study Unit generally were below national medians for streams sampled by the NAWQA Program. Although all trace elements of interest were detected at all eight study-unit streams, concentrations were generally below national medians. No PELs were exceeded, but TELs were exceeded for five elements: arsenic, chromium, cadmium, lead, and zinc. Certain trace elements, such as arsenic, occur naturally in the Study Unit and can be redistributed in the environment by human activities, such as waste disposal and fossil-fuel combustion. They also may enter aquatic ecosystems through point- and nonpoint-source releases and atmospheric deposition.

Arsenic, a naturally occurring element associated with the dissolution of arsenic-bearing minerals such as pyrite and iron hydroxides (Welch and others, 2000), is found in ground water in some parts of the Study Unit. Arsenic was detected in 54 percent of the samples from domestic, public-supply, and shallow monitoring wells in agricultural and urban areas. Elevated concentrations of arsenic were typically found in ground-water environments where dissolution of arsenic-bearing minerals is favored, as indicated by low concentrations of nitrate and dissolved oxygen and high concentrations of iron, manganese, and ammonia—conditions typically found at

## Concentrations of PCBs in fish tissue are among the highest in the Nation

Although production of polychlorinated biphenyls (PCBs) was banned in the United States in 1979, PCBs are still present in fish tissue from the Great and Little Miami River Basins, frequently at concentrations near or at the maximum concentrations found nationwide. PCB concentrations in fish tissue at four of five agricultural streams in the Study Unit were among the highest in the Nation, ranking in the top 25 percent of 208 streams sampled nationwide by the NAWQA Program. Tissue samples from the urban and mixed-land-use streams also ranked in the top 25 percent of streams sampled nationally. Elevated concentrations of PCBs in fish at seven of the eight sampled sites exceeded the New York Fish Flesh Criteria (NYFFC) for the protection of fish-eating wildlife (110 µg/kg wet weight) (Newell and others, 1987). Common carp, targeted for this study, are potentially exposed to PCBs through contact with contaminated sediments or consumption of contaminated plant and animal material. Study-unit results were similar to national results; elevated concentrations of PCBs in fish tissue were found at many sites where concentrations of PCBs in sediment were below detection levels. Frequent detection of PCBs and elevated concentrations in fish tissue is related to the ability of PCBs to **bioaccumulate** in fish and fish-eating wildlife. Possible sources of PCBs in streams and sediment include atmospheric deposition, landfills, industrial facilities, incinerators, and leakage of PCB-containing materials still in use, such as electrical transformers. (Use of PCBs in equipment already in service was not banned in 1979.) Because of past widespread use and their environmental persistence—half-lives of individual PCBs in sediment range from months to years—PCBs are expected to remain in the environment for the foreseeable future (U.S. Environmental Protection Agency, 1999b).

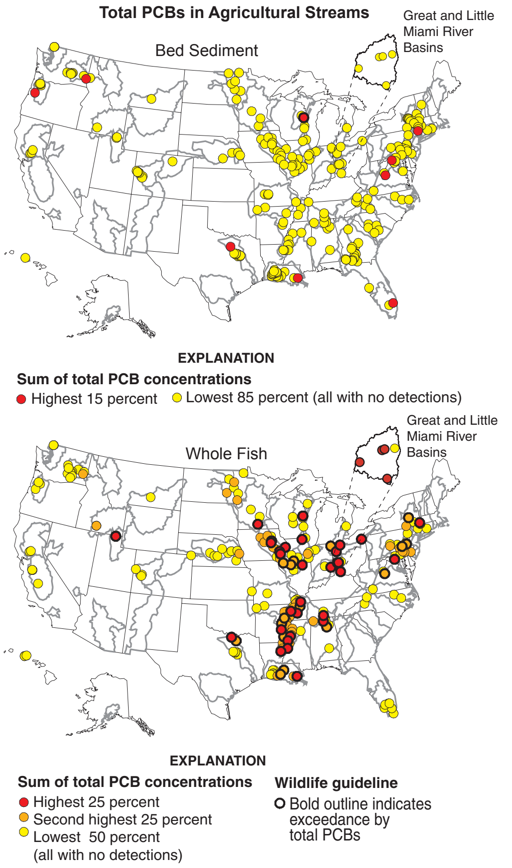


**Table 2.** Concentrations of many organic compounds in fish tissue and sediment ranked in the top 25 percent of all streams sampled in the NAWQA Program. Trace-element concentrations in sediment, however, were typically at or below national medians.

| Land use | Site | Fish tissue[1] (percentile) | | | | | | | Fish-tissue guidelines | Bed sediment[1] (percentile) | | | | | | | Sediment-quality guidelines (number of exceedances) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *cis*-Chlordane | *trans*-Chlordane | *cis*-Nonachlor | *trans*-Nonachlor | Aldrin | Dieldrin | PCBs | Number of exceedances | Phenanthrene | Pyrene | Fluoranthene | Arsenic | Chromium | Lead | Zinc | Probable Effect Level | Threshold Effect Level |
| Mixed | Little Miami River at Milford | | 95 | 95 | 95 | x | 95 | 50 | 1 (PCB) | x | 75 | 75 | 50 | 25 | 50 | 50 | 0 | 14 |
| | Great Miami River at Hamilton | 95 | 95 | 90 | 95 | **max** | 90 | 95 | 1 (PCB) | 75 | 75 | 75 | 50 | 25 | 50 | 50 | 1 (phenanthrene) | 14 |
| Urban | Holes Creek near Kettering | 75 | 75 | 75 | 75 | x | 50 | 75 | 1 (PCB) | 25 | 25 | 25 | 75 | 25 | x | x | 0 | 13 |
| Agriculture | E. F. Little Miami River near Williamsburg | x | x | 75 | 50 | x | 50 | 75 | 1 (PCB) | x | 50 | 50 | 50 | 50 | 50 | 75 | 0 | 4 |
| | Whitewater River near Nulltown | 90 | 90 | x | 90 | x | 75 | 90 | 1 (PCB) | x | 50 | 50 | 50 | x | 50 | 25 | 0 | 2 |
| | Stillwater River near Union | | 90 | 95 | 95 | x | 95 | 75 | 1 (PCB) | x | 50 | 50 | 75 | 50 | 50 | 75 | 0 | 3 |
| | Great Miami River near Tipp City | | 75 | 90 | 90 | x | 75 | 95 | 1 (PCB) | 90 | 90 | 90 | 75 | x | 75 | 75 | 0 | 12 |
| | Mad River near Springfield | **max** | **max** | **max** | **max** | x | 75 | x | 1(total DDT) | 75 | 75 | 90 | 75 | 25 | 50 | 50 | 0 | 8 |

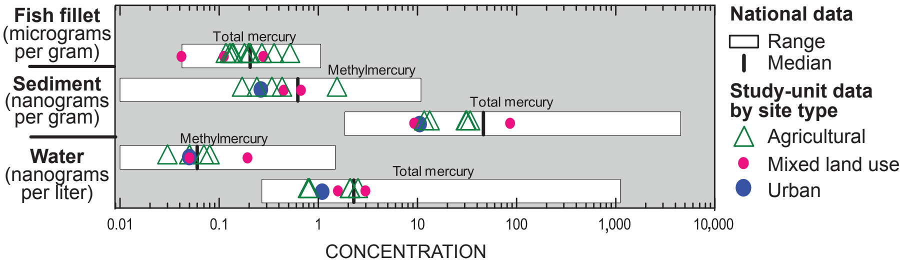
[1] Percentile ranking of concentration with respect to NAWQA studies nationwide; x, less than 25th percentile; **max**, maximum found nationally

## Concentrations of mercury in water and sediment were lower than the national median, despite higher atmospheric deposition rates

Mercury, a highly toxic trace element, is one of the most widespread contaminants affecting our Nation's streams. Mercury reaches most aquatic ecosystems by way of atmospheric deposition. Sources of mercury are coal combustion, ore mining, metal processing, and waste incineration (Krabbenhoft and Rickert, 1997; Eisler, 1985–99). Bacteria in sediment convert inorganic mercury to the more toxic methylmercury, an organic form that accounts for 90 to 100 percent of the total mercury found in fish tissue. Methylmercury, along with PCBs, is responsible for most of the human fish-consumption advisories issued in Ohio and Indiana (Ohio Department of Health, 2002; Lanetta Alexander, Indiana State Department of Health, written commun., 2003).

Analyses of samples collected in the Great and Little Miami River Basins in 1998 indicate that concentrations of total mercury and methylmercury in water and sediment were near or below the median for 106 streams sampled across the Nation, even though the atmospheric deposition rate of mercury in the Study Unit was the sixth highest among the 21 NAWQA Study Units examined (Krabbenhoft and others, 1999). The relatively low concentrations, despite higher atmospheric deposition, most likely are a consequence of the general absence of environmental conditions associated with high rates of methylation (such as high wetland density, organic-rich sediment, and low pH) in the Study Unit.

Concentrations of total mercury (most of which is methylmercury) in sport-fish fillets also were relatively low when compared to those in other NAWQA Study Units (ranking below the national median) (Janosy, 2002). The highest concentrations of mercury in fish fillets sampled from the Study Unit (0.52 and 0.36 µg/g (microgram per gram), wet weight) were found in smallmouth bass collected from the East Fork Little Miami River near Williamsburg, Ohio; these concentrations exceeded the USEPA human-health criterion of 0.3 µg/g (U.S. Environmental Protection Agency, 2001). No correlations were found between concentrations of mercury in fish tissue and methylmercury concentrations in water or sediment, despite the finding nationally that methylmercury concentrations in water correlated strongly with bioaccumulation rates in fish.



EXPLANATION

National data

▭ Range

| Median

Study-unit data by site type

△ Agricultural

● Mixed land use

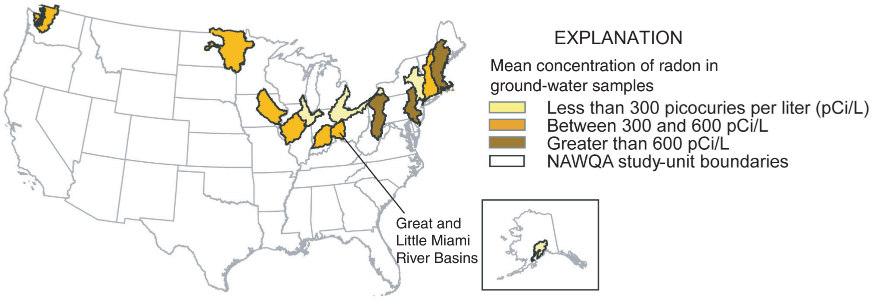
● Urban

## Proposed drinking-water standard for radon commonly was exceeded, but concentrations were similar to those in other glaciated areas

Concentrations of radon were greater than 300 pCi/L (picocuries per liter), the proposed USEPA drinking-water standard, in 65 percent of 104 wells sampled in the Great and Little Miami River Basins. Public water systems must comply with the new standard beginning January 23, 2006. Concentrations of radon ranged from 100 to 1,390 pCi/L, with a median concentration of 395 pCi/L.

Concentrations of radon did not vary significantly among domestic, public-supply, and shallow monitoring wells and did not vary significantly with well depth or ground-water age. Radon concentrations in ground water underlying the Study Unit are about average when compared to concentrations in wells tapping glacial aquifers in 13 other NAWQA Study Units across the Nation. Because sources of radon are related to the geologic material making up the aquifer, only the data from those NAWQA Study Units with glacial aquifers were used in comparisons of radon concentrations.

Radon is a colorless and odorless radioactive gas that forms during the decay of natural uranium in rocks and soil. Radon gas is carried in water pumped from wells and is released to the air as the water is agitated during domestic uses such as cooking or showering (Otton, 1992). Breathing radon increases the risk of lung cancer (U.S. Environmental Protection Agency, 1999a).



EXPLANATION

Mean concentration of radon in ground-water samples

- ▭ Less than 300 picocuries per liter (pCi/L)
- ▭ Between 300 and 600 pCi/L
- ▭ Greater than 600 pCi/L
- ▭ NAWQA study-unit boundaries

depths greater than 50 feet in the aquifer. High concentrations of arsenic also were associated with high concentrations of strontium and silica, constituents that indicate the relative amount of water-rock reaction (Rowe and others, 1999). Concentrations of arsenic generally were lower than the USEPA drinking-water standard of 10 µg/L (reduced from 50 µg/L in August 2002, but public-water suppliers must comply with the 10-µg/L standard beginning January 23, 2006). Five of 104 ground-water samples collected in the Study Unit exceeded the standard of 10 µg/L. Concentrations in two samples, one from a 100-foot-deep domestic well and the other from a 45-foot-deep agricultural monitoring well, exceeded the older standard of 50 µg/L.

The five samples with arsenic concentrations above the drinking-water standard were from wells deeper than 23 feet and in ground water recharged before 1982. No significant correlations between arsenic concentration, well depth, and ground-water age could be identified, however, when data from all wells were considered. Although the arsenic drinking-water standard was exceeded in only five samples, further investigation is warranted because of arsenic's toxicity and unpredictable occurrence in the aquifer.

# Nutrients—Too Much of a Good Thing

Human activities in the Study Unit—including agricultural and urban uses of fertilizer, agricultural use of manure from confined animal feeding operations, and disposal of domestic and municipal wastewater—have contributed to increases in nitrogen and **phosphorus** in streams and nitrate in shallow ground water (fig. 19). Plants need nutrients to grow and produce good crop yields; however, nutrients applied to the land can seep into ground water or run off to streams during rainstorms.

Excessive nitrogen and phosphorus in streams can contribute to overgrowth of algae and other nuisance plants, whose death and subsequent decay can cause oxygen levels in streams to decline substantially during warm weather and at night. Some sensitive aquatic organisms cannot live in low-oxygen environments. High nutrient concentrations in streams have also been associated with an increase in the number of deformities, eroded fins, lesions, and tumors on fish (Ohio Environmental Protection Agency, 1995, 1997).

Ingestion of drinking water with high nitrate concentrations can cause low oxygen levels in the blood of infants, a potentially fatal condition known as methemoglobinemia, or "blue baby syndrome" (Spaulding and Exner, 1993). Because of these health concerns, the USEPA set the drinking-water standard for nitrate at 10 mg/L (milligrams per liter) (U.S. Environmental Protection Agency, 1986).

## Drinking-water standard for nitrate was exceeded more frequently in ground water than in streams, except during spring runoff

Concentrations of nitrate exceeded the drinking-water standard more frequently in ground water than in agricultural, urban, and mixed-land-use streams (fig. 20). Specifically, nitrate concentrations in 10 percent of the ground-water samples (10 of 104 samples) and less than 1 percent of the stream samples exceeded the drinking-water standard of 10 mg/L. In streams, this pattern can vary seasonally, however, particularly during spring runoff following fertilizer application to cropland. Samples collected May 19–20, 2000, at 30 stream sites in the agricultural Stillwater River Basin during a runoff event had a median nitrate concentration of 22 mg/L; the maximum concentration was 45 mg/L. Most of the nitrogen in these stream samples came from soil nitrogen and inorganic fertilizer, as indicated by nitrogen isotope analysis. (See p. 23.)

**Figure 19.** Manure from animals can be an important source of nutrients to some streams in the Great and Little Miami River Basins, but most nitrogen and phosphorus in agricultural streams is from fertilizer applied to cropland. Discharge of municipal and industrial wastewater is a significant source of nutrients to large streams in the Study Unit, particularly during low streamflow.

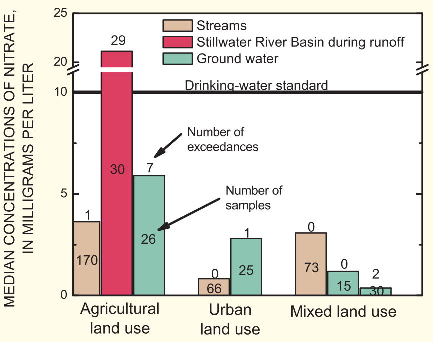


**Figure 20.** Concentrations of nitrate were highest in samples collected in agricultural streams during a runoff event.

Elevated concentrations of nitrate in ground water were strongly related to land use, well depth, and age of water (fig. 21). For example, the median concentration of nitrate in shallow monitoring wells (median depth 26 feet) in agricultural areas was 5.9 mg/L and was higher than that for shallow monitoring wells (median depth 39 feet) in urban areas (median about 2.5 mg/L).

In addition, concentrations of nitrate are greater in wells less than 60 feet deep, generally recharged since 1990, than in the deeper wells, which were recharged before 1990. As water moves deeper into the aquifer system, chemicals such as nitrate can change. For example, in low-oxygen (about 1.0 mg/L) conditions, nitrate is broken down to nitrogen gas and water (referred to as **denitrification**), such as documented in ground water underlying the Dayton area (Rowe and others, 1999). The relatively slow movement of ground water, combined with the right environmental conditions, allows the aquifer to naturally rid itself of nitrate with depth.

## Commercial fertilizer applications to agricultural lands are greatest nonpoint source of nutrients

Major nonpoint sources of nutrients to the Study Unit include atmospheric deposition and applications of manure and commercial fertilizer to agricultural lands. Commercial fertilizer accounted for an estimated two-thirds of nitrogen and phosphorus applied or deposited to the Great Miami River Basin during the 2-year monitoring period October 1998 through September 2000 (Reutter, 2003). Cropland applications of manure generated from a high number of confined animal-feeding operations in the Stillwater River Basin accounted for about 9 percent of the nitrogen applied or deposited on the Great Miami River Basin. Commercial fertilizer accounted for about 74 percent of nitrogen and 81 percent of phosphorus applied or deposited on the Little Miami Basin (fig. 22).

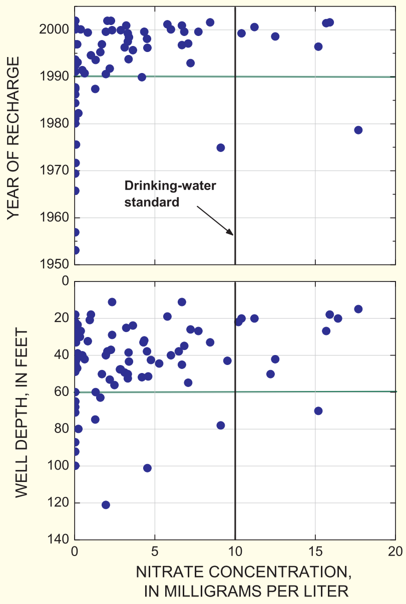


**Figure 21.** Nitrate concentrations tend to be highest in ground water recharged after 1990 and in wells less than 60 feet deep.

Although the amounts of nutrients reaching streams generally increase as nonpoint nutrient inputs increase, not all nutrients applied or deposited onto the basins enter the streams. Only 13 percent of total nitrogen from nonpoint sources was transported to the Great Miami and Little Miami Rivers and only 5 percent of total phosphorus from nonpoint sources was transported to the rivers (Reutter, 2003). This result is consistent with the fact that nitrate, the dominant form of nitrogen in study-unit streams, tends to dissolve in water and be transported readily with surface and **tile**-drainage runoff. In contrast, most phosphorus occurs as solids, or is bound to soil, and is less likely to dissolve in water that runs off to streams or seeps to ground water; hence, most phosphorus from nonpoint sources is transported during large storms when heavy runoff and high streamflows mobilize soil- and sediment-bound phosphorus. Total nitrogen from nonpoint sources accounted for 78 percent of the instream load of the Great Miami River at Hamilton and 66 percent of the instream load of the Little Miami River at Milford over the 2-year monitoring period. Total phosphorus from nonpoint sources accounted for 48 percent of the instream load of the Great Miami River at Hamilton and 52 percent of the instream load of the Little Miami River at Milford. Point-source discharges of phosphorus were primarily from wastewater-treatment plants in urban areas.

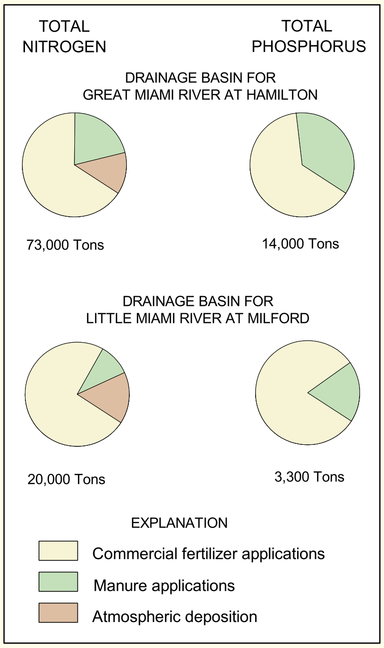


**Figure 22.** Most nonpoint total nitrogen and total phosphorus applied to or deposited on the Great and Little Miami River Basins was from commercial fertilizer.

## Nutrient loads in streams varied seasonally

During the 2-year monitoring period, nutrient loads in the study-unit streams were highest during winter and spring and lowest during summer and autumn. For example, nitrate loads to the Great Miami River at Hamilton decreased from a peak of about 3,000 tons in January 1999 to less than 50 tons in September 1999 (fig. 23), mostly in response to drought in summer and autumn 1999. Nutrient loads from point-source discharges to the Great Miami River at Hamilton were actually higher than the computed nitrate and total phosphorus instream loads during much of summer and autumn 1999. Thus, during periods of low streamflow, point-source discharges can be the dominant source of nutrients in streams. The difference between nutrient inputs and actual loads also indicates that uptake of nutrients by algae and other aquatic plants is an important process during summer and autumn months.

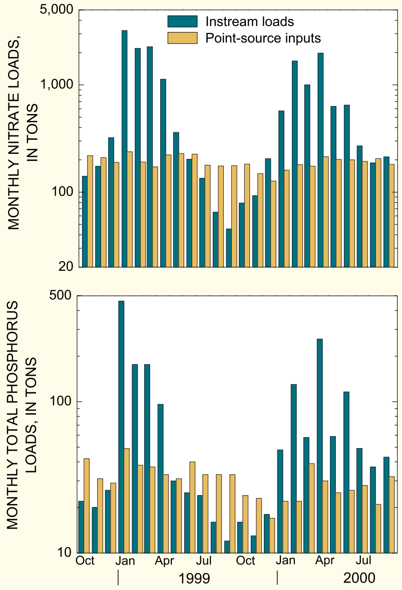
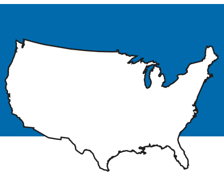
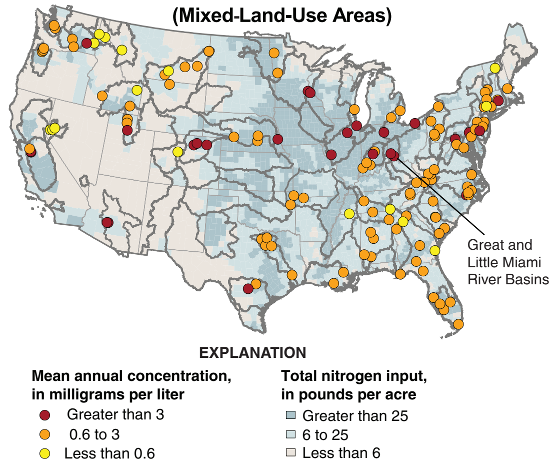


**Figure 23.** In the spring, nonpoint sources (instream loads) were the largest contributor of nitrate and total phosphorus to the Great Miami River at Hamilton. In summer, point sources became an important contributor.

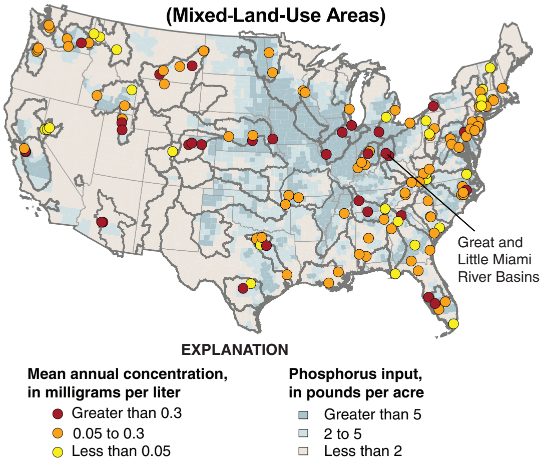


# Nutrients in mixed-land-use streams and nitrate in shallow agricultural wells were among the highest in the Nation

Total N in Streams 1993-2001 (Mixed-Land-Use Areas)



Total P in Streams 1993-2001 (Mixed-Land-Use Areas)



## High nutrient concentrations in streams draining mixed-land-use areas are a concern locally and nationally

The Ohio Environmental Protection Agency (OEPA) has attributed excessive algal growth to high concentrations of nutrients at several locations in the Great Miami River between Dayton and the Ohio River. The OEPA also reported that elevated nutrient loads were associated with a large number of deformities, eroded fins, lesions, and tumors on fish from the Great and Little Miami Rivers (Ohio Environmental Protection Agency, 1995, 1997).

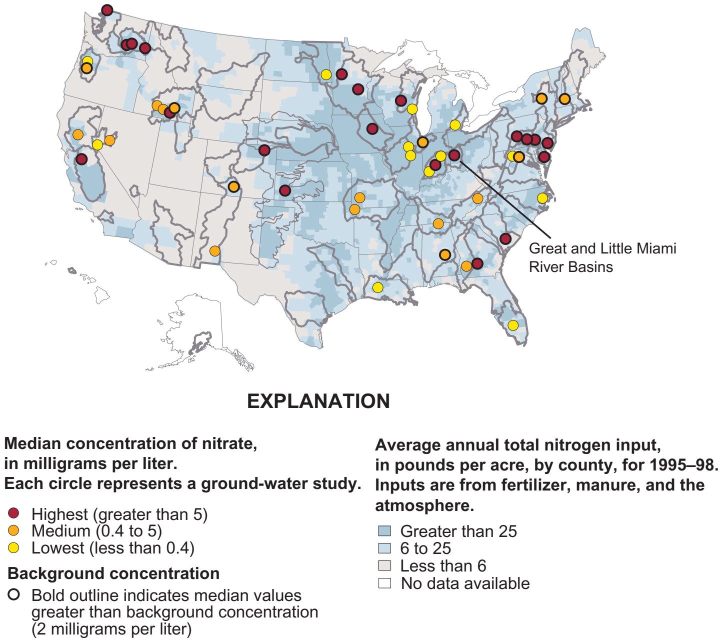
Mean annual concentrations of nitrogen and phosphorus for the Great and Little Miami Rivers (generally greater than 3 and 0.3 mg/L, respectively) were among the highest reported for large, mixed-land-use streams monitored by the NAWQA Program nationwide. Goolsby and others (1999) found that the Great Miami River Basin produced high **yields** of nitrogen (5.7 tons per square mile) and phosphorus (700 pounds per square mile) in comparison to the rest of the Mississippi River Basin, which yielded 1.4 tons per square mile of nitrogen and 240 pounds per square mile of phosphorus. The transport of large amounts of nutrients from the Mississippi River Basin to the Gulf of Mexico, particularly transport associated with spring runoff, has increased algal growth in the Gulf of Mexico and led to seasonal oxygen depletion (hypoxia).

## High nitrate concentrations in shallow ground water common in agricultural areas

Agriculture is a major industry in the Study Unit, and tons of fertilizer are applied to the land surface annually to increase crop yields. The underlying shallow aquifer is composed of highly permeable sand and gravel and is capable of transmitting large amounts of water. Land use, high permeability, and shallow depth increase the vulnerability of the buried-valley aquifer to contamination. Because of these conditions, the median concentration of nitrate (5.9 mg/L) in shallow monitoring wells screened in sand and gravel deposits in agricultural areas was among the highest in the Nation, ranking in the upper 25 percent of all values.

NITRATE

SHALLOW GROUND WATER IN AGRICULTURAL AREAS



## Phosphorus concentrations have decreased since 1974 in the Great Miami and Little Miami Rivers

Concentrations of total phosphorus decreased from 1974 through 2000 in Little Miami River at Milford and Great Miami River at Hamilton, both of which receive numerous wastewater and other point-source discharges (fig. 24). Specifically, total phosphorus concentrations decreased about 40 percent in the Little Miami River at Milford and 50 percent in the Great Miami River at Hamilton. Decreases are likely due to increased use of phosphorus-free detergents, increased adoption of no-till farming and other best-management practices that reduce soil transport to streams, and improved wastewater treatment. Benefits have been reported by the Ohio Environmental Protection Agency (1995, 1997), including improved habitat and aquatic **community** response for many stream sections. Despite declining nutrient concentrations, median concentrations of total phosphorus for the Great and Little Miami Rivers were still above the USEPA recommended goal of 0.1 mg/L.

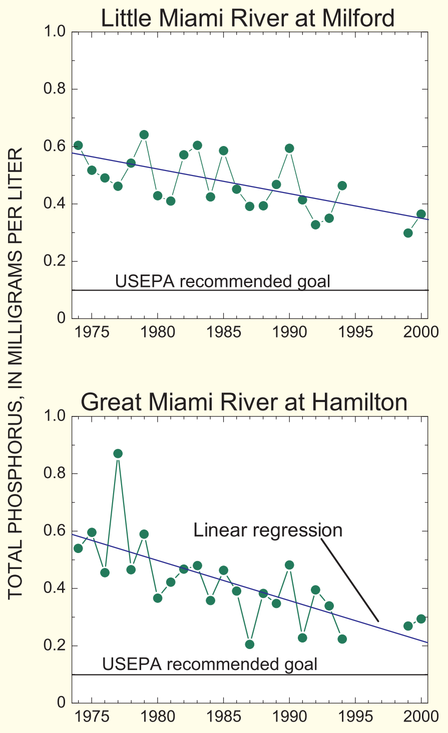


**Figure 24.** Annual flow-weighted mean concentrations of total phosphorus for the Great Miami River at Hamilton and the Little Miami River at Milford decreased from 1974 through 2000 (data from USGS National Water Information System).

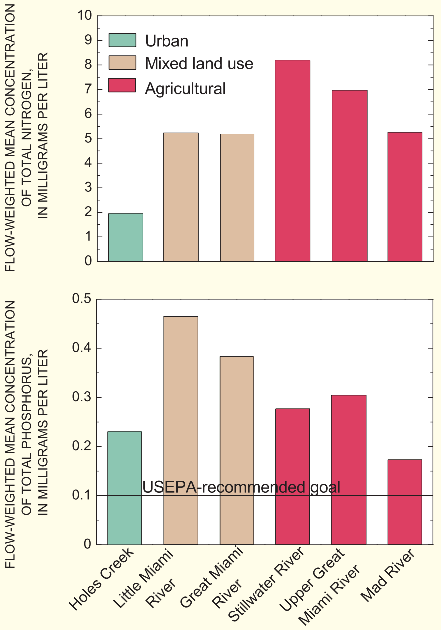


**Figure 25.** Agricultural streams had the highest total nitrogen concentrations, whereas mixed-land-use streams had the highest total phosphorus concentrations.

## Highest nitrogen concentrations in streams were in agricultural areas, but highest phosphorus concentrations were in streams with numerous point sources

Concentrations of nitrogen and phosphorus in study-unit streams varied among land uses (fig. 25). For example, Holes Creek, which drains urban areas, had the lowest **flow-weighted mean** concentration for nitrogen (about 2 mg/L), whereas the agricultural Stillwater, Mad, and Upper Great Miami Rivers had the highest (greater than 5 mg/L). The highest flow-weighted mean concentrations of total phosphorus (about 0.4 mg/L) were detected in the Great and Little Miami Rivers, which drain a mix of land uses and receive discharge from numerous wastewater-treatment plants at or downstream from Dayton. Total phosphorus was elevated not only in the mixed streams; in fact, the flow-weighted mean concentration of total phosphorus in streams draining all land uses exceeded the USEPA goal for total phosphorus of 0.1 mg/L. This goal is designed to prevent excessive growth of algae and other aquatic plants in flowing streams that do not discharge directly into lakes or impoundments. This goal also was exceeded in most samples collected from agricultural streams in the Stillwater River Basin during spring runoff. The median concentration of total phosphorus was 0.34 mg/L, and the maximum concentration was 0.73 mg/L.

## Ground water contributed nitrate to some streams

Concentrations of nitrate in stream water during periods of low streamflow were significantly correlated with the amount of **base flow** (fig. 26). Both the Mad River and Whitewater River drain basins in which sand-and-gravel outwash deposits discharge large quantities of ground water to streams (fig. 1). For streams that do not receive large quantities of effluent from wastewater-treat-

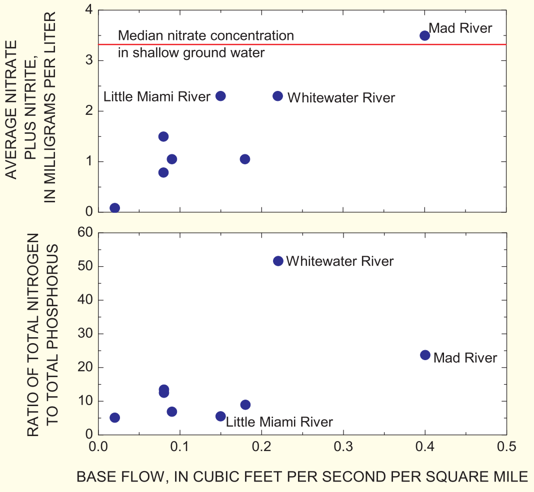
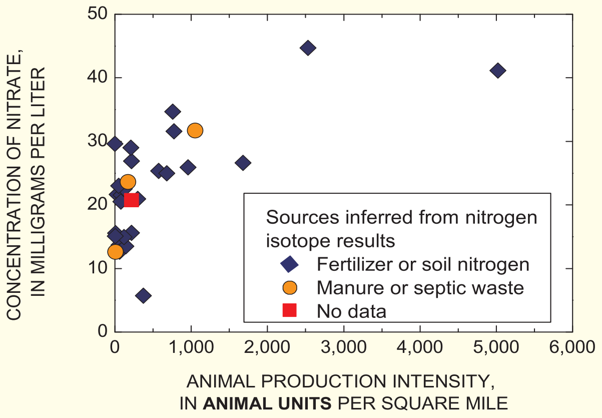


**Figure 26.** The amount of nitrate in study-unit streams in July during the 1999 drought increased with increased ground-water discharge (base flow) to the stream. Streams with a large base flow, such as the Mad and Whitewater Rivers, tend to have higher ratios of total nitrogen to total phosphorus.

## Confined animal feeding operations (CAFOs) contributed additional nutrients and trace amounts of antibiotics to streams

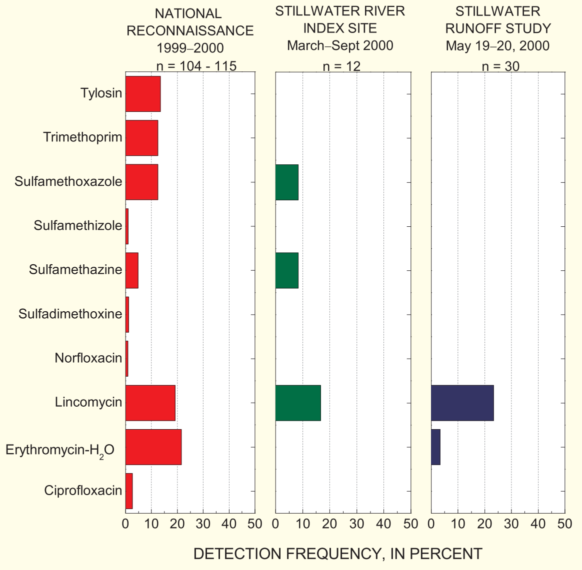
A snapshot of water-quality conditions in the Stillwater River Basin was obtained in May 2000 by collecting high streamflow (runoff) samples from 30 subbasins after a single rainstorm (Charles Schalk, U.S. Geological Survey, written commun., 2003). Although nitrate concentrations in the 30 subbasins were significantly correlated with animal density, nitrate yields were not (although the highest yields among the subbasins were associated with the two subbasins having the highest animal densities). In a separate comparison of daily mean nutrient yields estimated for the Stillwater River and the adjacent upper Great Miami and Mad Rivers, yields of total nitrogen and phosphorus from the Stillwater River Basin were 1.2 to 1.5 times those of the other basins, which have similar levels of crop production but do not have substantial numbers of CAFOs (Reutter, 2003). This finding suggests that, on an annual basis, the large number of CAFOs in the Stillwater River Basin probably contribute additional nutrients to the Stillwater River.



Nitrate concentrations in agricultural runoff increased as the number of animals in a basin increased. Despite this, nitrogen isotope data from only three basins were consistent with a manure or septic-waste source.

Antibiotics, which are used in CAFOs to promote growth and prevent disease, have recently received increased attention because little is known about the fate of these drugs and their degradates in the environment, the potential health effects on humans and animals exposed to low levels of these chemicals, and their potential role in the development of antibiotic-resistant bacteria (Boxall and others, 2003). Lincomycin and erythromycin-$H_2O$, two antibiotics approved for use in animals and humans, were detected in runoff and were among the antibiotics most frequently detected (19.2 and 21.5 percent, respectively) in a sampling of 104 streams nationwide in 1999–2000 (Kolpin and others, 2002). Lincomycin was found in runoff from seven sites in the Stillwater River Basin (23.5 percent) at concentrations that ranged from 0.02 to 0.25 µg/L. Erythromycin-$H_2O$, a degradate of the antibiotic erythromycin, co-occurred with lincomycin at one site at a concentration of 0.06 µg/L. Traces of lincomycin, sulfamethazine, and sulfadimethoxine were detected in runoff samples from the Stillwater River index site in early spring 2000. No antibiotics were detected, however, in subsequent samples collected during late spring and summer 2000. Most detections of lincomycin (6 of 7) were in the northern part of the Stillwater River Basin, in small subbasins where large poultry and swine CAFOs are located. The highest concentrations of lincomycin (0.25, 0.10 µg/L) were in runoff from the North Fork Stillwater River and Swamp Creek Basins, the two subbasins with the highest animal-production intensities (Charles Schalk, written commun., 2003).

*Campylobacter* and *Salmonella* bacteria were not detected in any runoff. *Escherichia coli* bacteria were detected at 60 percent of sites, and *Enterococcus* sp. bacteria were detected at all sites. Samples of *Escherichia coli* and *Enterococcus* bacteria isolated from the runoff samples were tested for resistance to a wide variety of human and veterinary antibiotics (Charles Schalk, written commun., 2003). As expected, resistance to some antibiotics that have been used for decades in humans and animals (tetracycline and sulfa-class antibiotics) was noted in some samples. But resistance to antibiotics considered critical for treatment of humans, such as fluoroquinolones, generally was not observed. The exception involved three sites where samples of *Enterococcus* bacteria demonstrated resistance to the antibiotic vancomycin. This antibiotic is used to treat multi-drug-resistant enterococci infections in humans and is not approved for use in animals.



Lincomycin, which is used as a growth promoter for swine and poultry, was the only antibiotic detected at multiple runoff sites and in more than one sample from the Stillwater River index site.

ment plants, inflowing ground water can be an important source of nitrogen, particularly during summer months and drought periods when streamflow is reduced. This condition is especially true of nitrate, which was detected in shallow ground water beneath agricultural and urban areas at concentrations comparable to those observed in the Mad and Whitewater Rivers (fig. 26). Because shallow ground water generally contains little phosphorus, ground-water-dominated streams will tend to have higher ratios of total nitrogen to total phosphorus than streams draining till-rich (high clay) basins whose flows are dominated by surface runoff; this condition is especially true in rural areas with few point sources of nitrogen and phosphorus. Streams dominated by sewage effluent at low flows, such as the Little Miami River (Buchberger and others, 1997), also have high nitrate concentrations but will have lower ratios of total nitrogen to total phosphorus because of higher phosphorus concentrations (fig. 26). For ground-water-dominated streams such as the Mad and Whitewater Rivers, nitrate from base flow could be of consequence in establishing nutrient criteria or total maximum daily loads (TMDLs).

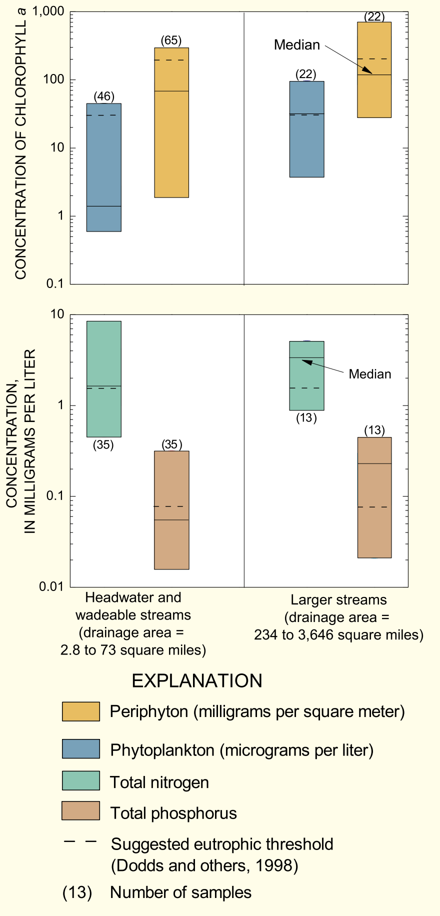


**Figure 27.** Smaller streams generally had less chlorophyll *a* than larger streams during July 2000 and 2001. Median values for nitrogen and phosphorus in larger streams exceeded the suggested eutrophic thresholds.

## Responses of algae and fish communities to high nutrient concentrations are variable

Mean annual concentrations of nitrogen and phosphorus in the Great and Little Miami Rivers were among the highest in the Nation (p. 21), and individual samples over a range of stream sizes included concentrations above the suggested eutrophic threshold (Dodds and others, 1998) (fig. 27). Algal growth as periphyton (algae attached to the stream bottom) or phytoplankton (algae floating in the water column) can reach nuisance levels when nutrient concentrations are high and sunlight is plentiful. Although nuisance algal growth was visible at several study-unit streams (fig. 28), concentrations of chlorophyll *a* (an indicator of algal productivity) were generally less than those that indicate stream **eutrophication**. This was especially true of smaller streams, where vegetation on the banks (median 92 percent canopy cover) limit light and thus limit undesirable algal blooms. In contrast, phytoplankton chlorophyll *a* measured in larger streams (median shading 57 percent) was commonly above the suggested eutrophic threshold for preventing nuisance algal conditions.

Excess algal growth can cause declines in dissolved oxygen to concentrations below those necessary to support fish and other aquatic life. Although concentrations of dissolved oxygen fluctuated as much as 9.3 mg/L over 48 hours during summer low-flow conditions, minimum concentrations measured in small and large streams (4.2 and 6.4 mg/L, respectively) were above the minimum water-quality standard for dissolved oxygen in Ohio and Indiana streams (4.0 mg/L) (Shindel and others, 2001, 2002; Ohio Environmental Protection Agency, 2003; Indiana Administrative Code, 2003). Therefore, despite high concentrations of nutrients and excessive algal growth in places, concentrations of dissolved oxygen in study-unit streams met current water-quality standards.

Ecologic response to the high nutrient concentrations and excess algal growth is mixed: fish-community assessments (**Index of Biotic Integrity [IBI] scores**) indicate a range of fair to excellent fish populations in small and large streams considered at risk for eutrophication (fig. 29). This finding indicates that, for many streams, factors other than high nutrient concentrations (habitat, suspended sediment, other contaminants in water and sediment) affect fish-community response.

**Figure 28.** Nuisance algal growth, such as the *Rhizoclonium* sp. algae shown here from the Mad River, was visible in many study-unit streams.

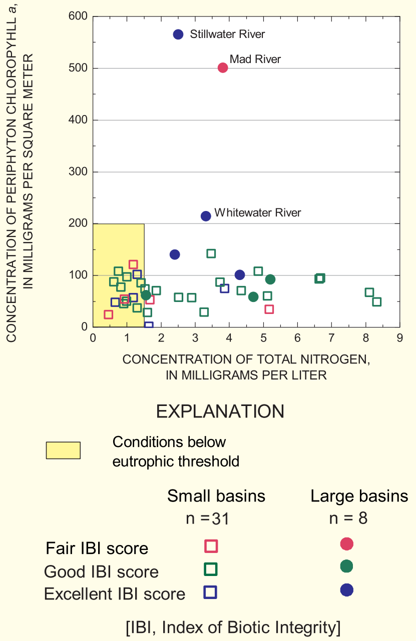


**Figure 29.** Fish-community responses vary with trophic conditions.

# Influence of Urbanization on Stream Quality

The chemical, biological, and physical condition of streams and rivers draining basins undergoing suburban and urban development is of concern to water-resource managers and the public. Research has shown that the quality of streams commonly declines as development increases in basins that previously were forested or sparsely populated (Paul and Meyer, 2001). The overall quality of urban streams can be affected adversely by degradation of water quality or stream habitat, contamination of streambed sediments, or alteration of natural streamflow patterns. Combinations of those factors often result in loss of sensitive species and overall declines in the well-being of biological communities.

The influence of suburban and urban development in and around the Dayton and Cincinnati metropolitan areas was examined at 30 stream sites during summer 2001; land cover upstream from these sites ranged from 0 to about 50 percent urban (fig. 30). This is in contrast to other metropolitan areas studied by NAWQA, where the proportion of urban land in the most developed basins exceeded 80 or 90 percent (p. 28). Streams in the Great and Little Miami River Basins with minimal urban development were influenced by drainage from intensive row-crop agriculture, whereas streams in developed basins generally drained residential and commercial lands that formerly were farms or undisturbed (forested) lands.

## Urban-land percentage affects water and streambed-sediment chemistry

Results from this study showed that stream-water quality in the Great and Little Miami River Basins declined as the percentage of urban land upstream of the sampling site increased. For example, concentrations of chloride in water samples were significantly higher with higher percentage of urban land use (p. 28), possibly in response to use of road salt during winter and the influence of urban wastewater and septic-tank discharges. Higher concentrations of insecticides, particularly those commonly used on lawns and commercial areas (such as diazinon), were detected in streams draining basins with higher percentages of urban land (fig. 31). As a result, the potential toxicity of pesticide mixtures to aquatic organisms increased rapidly at relatively low percentages of urban land cover (less than 10 percent) and then remained high, especially compared to the potential toxicity of herbicide-dominated mixtures found in agricultural streams. (See p. 9–10, 28.) The number of pharmaceutical and household chemicals detected in streams—an indicator of the influence of urban wastewater discharges on water quality (p. 15–17)—was larger at higher percentages of urban land in the basin (fig. 31). In addition, the number of synthetic organic compounds detected in streambed sediment, such as polycyclic aromatic hydrocarbons (PAHs), increased as the percentage of urban land increased (fig. 32).

Some wastewater discharges contribute excessive nutrient loads to stream systems; but concentrations of nitrate as nitrogen in the streams examined for this study actually decreased with increases in the percentage of urban land (p. 28). Although nitrogen-based fertilizers commonly are used on residential lawns and commercial areas, fertilizer applications

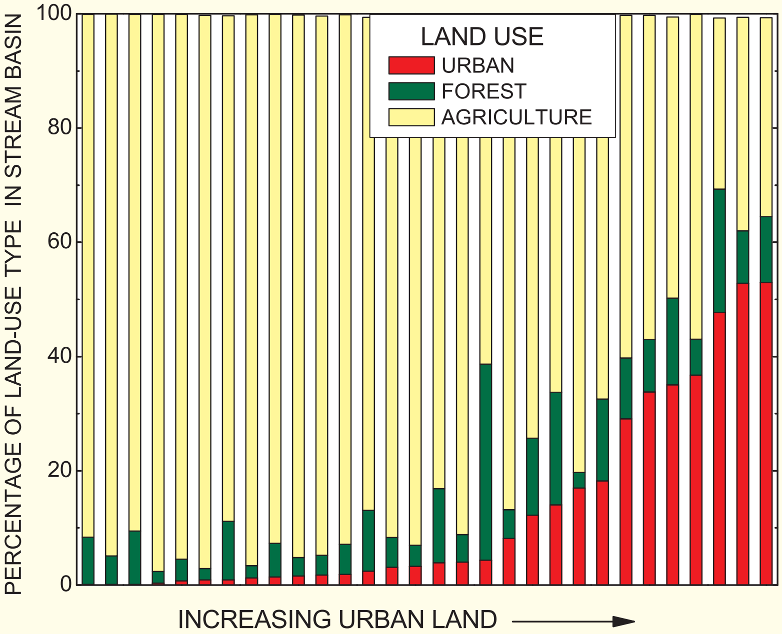


**Figure 30.** Basins used to examine the effects of urbanization on water quality and aquatic communities in the Dayton/Cincinnati area reflect the recent (post-1970) trend of converting agricultural and forested land around large metropolitan areas to residential and commercial uses.

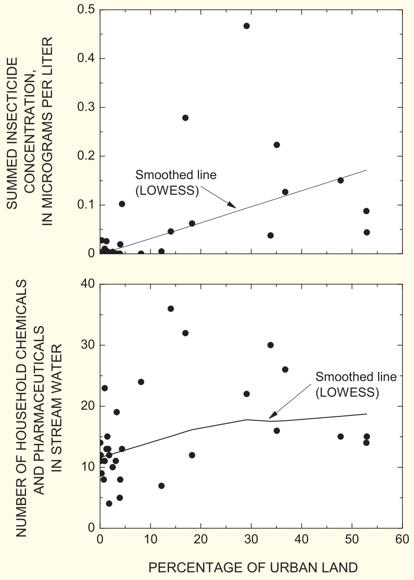


**Figure 31.** Total insecticide concentrations and the number of household chemicals and pharmaceuticals detected in stream water increased with the percentage of urban land in the stream basin. Smoothed lines in these and subsequent figures are shown where the correlation (Spearman rank) between the plotted variables is significant at a probability value less than 0.05.)

on urban land appear to be less than those on farmland in basins with low urban-land percentages, at least on the basis of annual nutrient yields estimated for the urban stream Holes Creek (fig. 24, Reutter, 2003). In cities where forested land is developed for urban uses, however (for example, Boston; p. 28), nitrate concentrations in streams increased with the percentage of urban land.

## Aquatic-community reflects urban influences

Biological indicators of stream quality, such as the presence or absence of invertebrates, fish, and algae sensitive to contamination, commonly are used to assess the effects of urbanization on a stream. For example, data collected in four major metropolitan areas (p. 28) indicated that the numbers of pollution-sensitive aquatic insects—specifically, the numbers of mayfly, stonefly, and caddisfly **taxa** (orders Ephemeroptera, Plecoptera, and Trichoptera, or "**EPT** richness")—generally decreased as the percentage of urban land increased. Analyses of samples of aquatic organisms collected from the Dayton/Cincinnati area, however, indicated an initial decline of EPT richness in streams in basins with less than 15 percent urban land cover, an increase in EPT richness in streams in basins with urban land cover greater than 15 percent, and considerable variability in EPT richness among streams draining predominantly agricultural land (that is, urban land cover less than 10 percent). The high degree of variability in EPT richness observed in the Dayton/Cincinnati streams may be partially attributable to variations in stream velocity: EPT richness increased significantly with stream velocity. Variations in stream velocity are related to minor differences in land-surface topography, channel slope, and other stream-habitat features in those basins. Of the streams examined in this study, higher stream velocities and associated favorable habitat features, such as riffles, were generally associated with streams draining more urbanized basins, hence greater EPT richness at some of the more urbanized sites.

Results from this and other NAWQA urban studies indicate that application of insecticides to lawns, homes, and commercial buildings in urban areas may also adversely affect aquatic-community structure, particularly benthic invertebrates (p. 28). EPT richness in Dayton/Cincinnati-area streams decreased significantly with increased Pesticide Toxicity Index (PTI) values (fig. 33). PTI values increased sharply in the 0- to 15-percent range of urban land cover and then remain relatively unchanged at moderate to high percentages of urban land (p. 28). Higher PTI values reflect the increased occurrence and higher concentrations of more toxic organophosphate insecticides, such as diazinon and chlorpyrifos, in urbanized stream basins. Improved aquatic-community structure in streams affected by urban development may be seen in the future as a result of the USEPA decision in 2000 to eliminate residential use of some of the more toxic organophosphate pesticides.

The relative abundance of pollution-**tolerant** fish in Dayton/Cincinnati area streams increased in concert with the number of household and pharmaceutical chemicals detected in water samples—an indicator of the influence of point-source discharges (fig. 34). Increases in pollution-tolerant organisms associated with wastewater discharges to streams have been well documented (Kemp and others, 1967).

The number of **diatom** species declined with increases in the number of potentially toxic metals that were detected in streambed sediments at concentrations above a Threshold Effect Level (fig. 34; Box 3, p. 8). The metals of concern were arsenic, cadmium, chromium, copper, lead, and zinc. Diatoms are known to be sensitive to metal contamination (Austin and Deniseger, 1985), and these metals, individually or in combination, may be important in reducing diatom community richness. In urban environments, common sources of metals are treated wood products (arsenic, chromium, and cop-

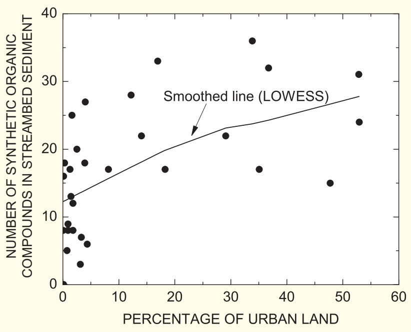


**Figure 32.** The number of synthetic organic compounds detected in streambed sediments increased with urban-land percentage in the stream basin.

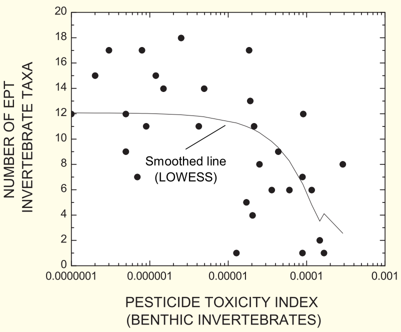


**Figure 33.** The number of sensitive invertebrate species (EPT; Ephemeroptera, Plecoptera, and Trichoptera) declined significantly as the Pesticide Toxicity Index (PTI) increased.

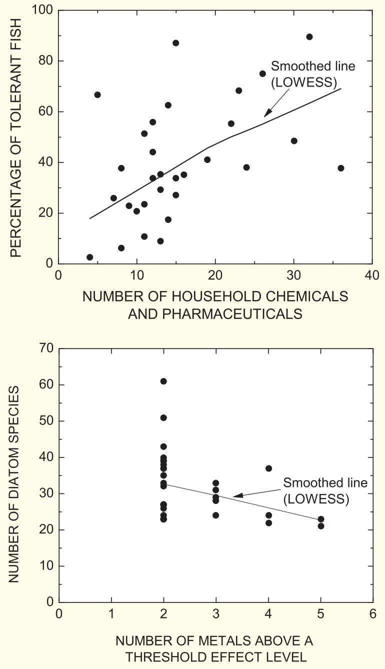
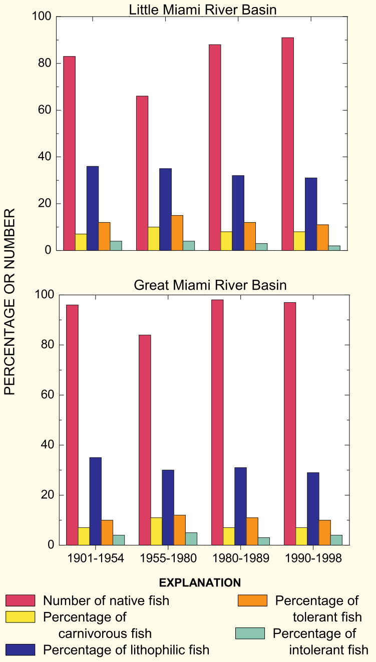


**Figure 34.** Increases in indicators of the effects of urban wastewater and runoff on water quality (number of household chemicals and pharmaceuticals) and sediment quality (number of metals with concentrations above a Threshold Effect Level) were associated with higher percentages of tolerant fish species and fewer diatom species.

## Changes observed in the Fish Community, 1900-98

Historically, 133 fish species representing 25 families have been documented in the Great and Little Miami River Basins. That number has declined over the last century, with 132 species reported since 1901, 123 since 1955, 117 since 1980, and 113 post-1990 (Harrington, 1999). Natural processes and human activities, especially channel modifications, wastewater discharges, and increased use of chemicals, have altered fish communities.

Fish communities may respond to environmental disturbances by changes in the population, including **abundance**, **richness**, and **composition** (Ohio Environmental Protection Agency, 1987). Index of Biotic Integrity components were divided into three groups (fish community composition, **trophic** composition, and fish condition), and representative components were calculated using available data in the Study Unit from 1900 through 1998. Although historically a decline in the total number of species has been documented, an increase in the number of native species from the 1955 to 1980 period to the 1980 to 1989 period indicates improvement in water quality. In the Little Miami River Basin, however, fish-community composition indicates continued stress as the percentages of **carnivores**, **intolerant species**, and **lithophilic** species, all indicators of good water quality, continued to decline through 1998. In the Great Miami River Basin, no consistent trend in composition was observed.



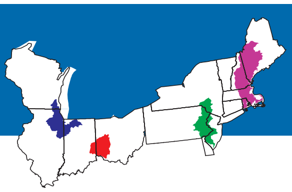
per), rubber tires (zinc), wheel weights (lead), brake pads (copper), and oil and grease additives (lead, nickel, and zinc). Although the presence of these metals at elevated levels in streambed sediments is usually attributed to urban sources, some metals may also be derived from natural sources, such as soils or eroded bedrock. For example, erosion of marine-shale outcrops in the banks and bottom of streams draining the Kentucky River Basin yields sediment that commonly contains elevated concentrations of cadmium, lead, and zinc (Porter and others, 1995).

High-quality physical features—forested ravines and steep channel slopes—in urban streams in the Great and Little Miami River Basin may help to explain somewhat anomalous trends in aquatic-community structure compared to NAWQA findings elsewhere. For example, sensitive EPT taxa did not continue to decline with increasing urban land as reported in other urban areas (p. 28) but rather began to increase in basins with greater than 15 percent urban land. Similarly, no significant trends with increasing urban land were found for Ohio's fish-community-based IBI (Index of Biotic Integrity, p. 24) or benthic algal biomass (chlorophyll-*a*). In contrast to other urban areas studied by NAWQA, physical habitat along streams in the Dayton/Cincinnati areas is substantially more degraded in the least urbanized agricultural basins than in the more developed basins examined by this study. For example, physical features associated with the predominantly agricultural basins (little or no urban land) reflect poorly drained, flat land and streams with few riffles and relatively high percentages of fine clay substrate; together, these features make for unfavorable stream habitat (fig. 35).

In summary, results from NAWQA studies in urban areas across the Nation indicate that the condition of biological communities reflects a complex combination of factors associated with greater urban development, including degradation of water and sediment quality, stream habitat, and modification of streamflow and temperature (Couch and Hamilton, 2002). The relative association of these factors can also vary spatially and with seasonal and year-to-year differences in rainfall and runoff. Hence, results of these studies—which reflect summer low-flow conditions—may not be representative of seasonal or long-term variations. Nevertheless, improved understanding of how these factors vary in the Great and Little Miami River Basins along a gradient of urban land use will help to define the progression of stream degradation with respect to basin development. Furthermore, studies here and elsewhere in the Nation will identify settings where stream restoration and protection resources need to be focused and where water-quality management actions are likely to have the greatest benefits.

**Figure 35.** Stream-habitat characteristics in urban areas (top) were generally better than those in more highly agricultural basins (bottom).

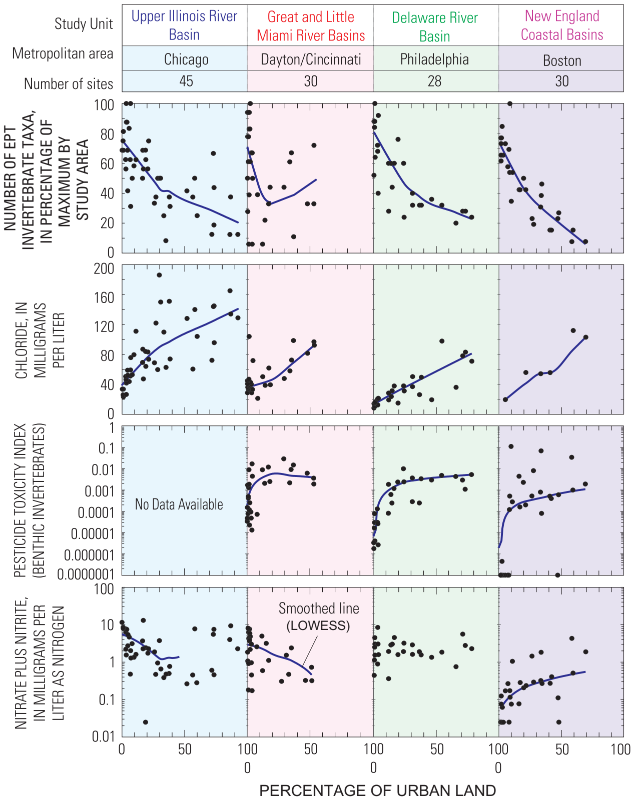
# Stream quality degrades as urbanization increases in four major metropolitan areas



Urbanization can degrade water quality and affect sensitive aquatic life, according to a comparison of NAWQA findings among studies in the major metropolitan areas of Boston (New England Coastal Basins), Philadelphia (Delaware River Basin), Dayton and Cincinnati (Great and Little Miami River Basins), and Chicago (upper Illinois River Basin). These studies, which compared conditions among streams in basins ranging from minimally to highly urbanized, showed declines in indicators of biological-community health—and increases in chemical indicators of human activity—with increases in percentage of urban land. For example, the number of benthic invertebrate species sensitive to pollution, such as the "EPT insects" (mayflies [Ephemeroptera], stoneflies [Plecoptera], and caddisflies [Trichoptera]), generally decreased with increasing urban-land percentage in all four metropolitan areas. The declines in EPT insects were steepest from 0 to about 20 percent urban land, and with the exception of Dayton/Cincinnati, the decline continues with increased urbanization. The anomalous pattern in the Dayton/Cincinnati area may be associated, in part, with effects of high percentages of agricultural land in some of its less urbanized basins, as well as the absence of study sites with much more than 50 percent urban land.

Over space and time, invertebrate communities integrate the effects of many factors, including chemical changes, physical habitat alterations, and changes in types of food available to invertebrate consumers. Among the chemical changes noted with increasing urban land in the metropolitan areas studied were increased chloride concentrations and increased potential pesticide toxicity to benthic invertebrates. Chloride sources include municipal and industrial discharges, septic systems, and road-salt runoff. Other organic and inorganic chemicals may be associated with chloride from these sources. The potential toxicity of the mixture of pesticides detected in stream water increased with increasing urban land percentage, according to the Pesticide Toxicity Index (a measure for ranking sites based on summed concentrations of detected pesticides and the toxicity of each pesticide to benthic invertebrates [Munn and Gilliom, 2001]). The increase was especially pronounced at relatively low percentages of urban land. Contributing factors may include the amount, relative toxicity, and timing of pesticides—particularly insecticides—that are applied in urban settings.

Patterns of nitrate concentration with increasing urban land were not consistent among the four metropolitan areas. In fact, the only clear increase in nitrate concentrations with urbanization was in the Boston area. This is, in part, because nutrients in Boston-area streams are associated primarily with urban sources and are not affected by additional sources, such as fertilizers applied on agricultural land. Moreover, basins with minimal urban land in the Boston area are mainly forested, and nitrate concentrations in those streams are low (less than 0.1 mg/L). In contrast, nitrate concentrations in streams decreased with increasing urbanization in the Dayton/Cincinnati area and in minimally to moderately urban settings of the Chicago area, whereas in the Philadelphia area they neither increased nor decreased; fertilizers applied to crops contribute to the higher nitrate concentrations in some less urbanized basins in these settings. Sewage may be a factor contributing to the high nutrient concentrations in some highly urban Chicago streams.



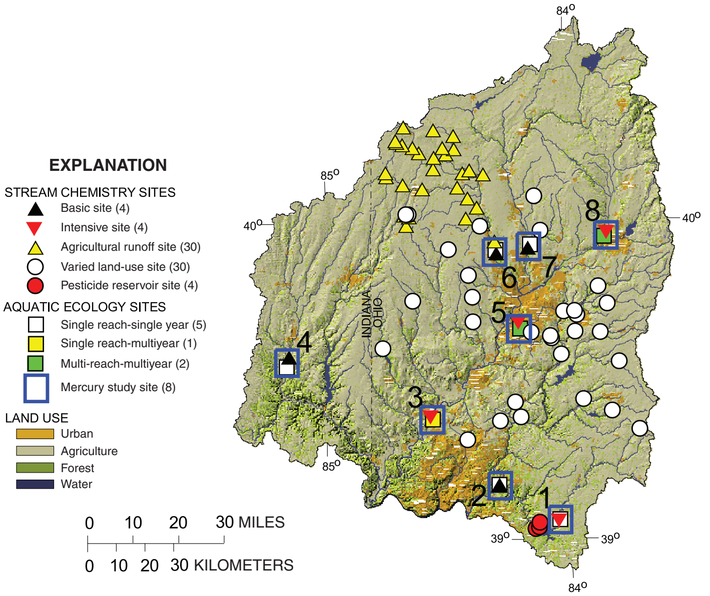
Selected examples of biological and chemical indicators in relation to urbanization. Smoothed lines are shown where the correlation (Spearman rank) between the biological or chemical factor and percentage of urban land is statistically significant at a probability value of less than 0.05.

In summary, biological and chemical characteristics in streams respond to increases in urban land in their respective basins. However, the responses may differ in pattern and in rate, so approaches for monitoring the effects of urbanization on streams may need to be tailored to specific metropolitan areas. Findings of these NAWQA studies may help in developing and prioritizing optimal management strategies for a particular setting.

# Study Unit Design

Stream-chemistry studies were designed to measure how natural factors and human activities affect water quality (see p. 30):

- Eight drainage basins representing the dominant hydrologic and land-use settings in the Study Unit were selected for the stream-chemistry network (four **basic** and four **intensive** sites). Seasonal variations in stream chemistry were measured for a range of streamflows.
- Samples were collected at 30 sites in the Stillwater River Basin after heavy spring rains to determine concentrations of chemicals in agricultural runoff.
- During summer low-flow conditions, streamwater quality was assessed in 30 small stream basins with varying amounts of agricultural and urban land in areas surrounding Cincinnati and Dayton ("varied land-use" sites).
- Treated and untreated drinking-water samples were collected to assess pesticide concentrations in a water-supply reservoir (Harsha Lake).

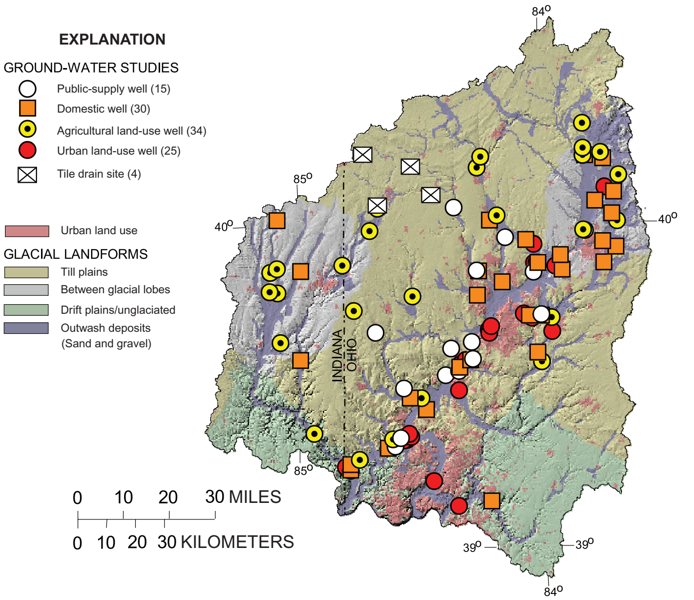


| Site number | Site name | Setting | Basin area (square miles) | Site number | Site name | Setting | Basin area (square miles) |
|---|---|---|---|---|---|---|---|
| 1 | East Fork Little Miami River near Williamsburg, Ohio | Cropland/ Drift Plains | 234 | 5 | Holes Creek near Kettering, Ohio | Urban/ Till Plains | 20.0 |
| 2 | Little Miami River near Milford, Ohio | Mixed land use/ Till-Drift Plains | 1,203 | 6 | Stillwater River near Union, Ohio | Cropland/ Till Plains | 646 |
| 3 | Great Miami River at Hamilton, Ohio | Mixed land use/ Till Plains | 3,630 | 7 | Great Miami River near Vandalia, Ohio | Cropland/ Till Plains | 1,142 |
| 4 | Whitewater River near Alpine, Indiana | Cropland/ Interlobate | 529 | 8 | Mad River near Eagle City, Ohio | Cropland/ Interlobate | 310 |

Fish tissue and bed sediment were analyzed for environmental contaminants at each of the basic and intensive stream-chemistry sites (eight sites total). Surveys of fish, benthic invertebrates, algae, and stream habitat were done one to four times to assess aquatic-community status. Multiple-reach surveys were done at two sites; reaches ranged from 655 to 1,640 feet in length. Periphyton, phytoplankton, chlorophyll, and streambed-sediment samples were collected to compare concentrations of nutrients, algae, and selected organic contaminants in 30 small stream basins with varying amounts of agricultural and urban land. Water, streambed sediment, and sport fish fillet samples were analyzed for mercury and methylmercury at eight stream-chemistry sites.

Ground-water studies focused exclusively on sand-and-gravel deposits, known as the buried-valley aquifer system, a major source of drinking water aquifer in the Study Unit. (See p. 30.) Ground-water studies were designed to measure water quality in the following:

- Domestic wells screened at various depths in the aquifer
- High-capacity public-supply wells next to large streams
- Shallow ground water in areas overlain by agricultural or urban land use (monitoring wells)
- Tile drains beneath croplands to assess the quality of infiltrating soil water.



SUMMARY OF DATA COLLECTION IN THE GREAT AND LITTLE MIAMI RIVER BASINS, 1998–2001

| Study component | | What data were collected and why | Types of sites sampled | Number of sites | Sampling frequency and period |
|---|---|---|---|---|---|
| **Stream and Lake Chemistry** | | | | | |
| Basic sites | | Streamflow, nutrients, major ions, bacteria, organic carbon, suspended sediment, and physical parameters. **To determine how often and how much of a constituent is present, over time, in response to different seasonal or land-use patterns.** | Sites were selected to represent the range of hydrologic and land-use settings in the Study Unit, including basin outflow sites. | 4 | Monthly; storm and low-flow events, for two years (October 1998–September 2000) |
| Intensive sites | | Same as above plus VOCs, pesticides, and pesticide degradates. VOCs sampled at urban and large-river sites only. **To determine how often and how much of a chemical is present, over time, in response to different seasonal or land-use patterns.** | Includes small urban basin (Holes Creek), two larger row-crop agricultural basins (Mad River, East Fork Little Miami River), and large river, mixed-land-use site (Great Miami River at Hamilton). | 4 | Weekly to monthly; storm and low-flow events for 2 years, three sites sampled monthly for third year |
| Special Studies | Agricultural-runoff sites | Streamflow, physical properties, nutrients, major ions, bacteria, organic carbon, suspended sediment, pesticides, nitrogen isotopes, and antibiotics. **To evaluate concentrations and sources of agrichemicals in streams during a rainfall and runoff event.** | 30 streams draining agricultural basins ranging in size from 1.5 to 609 square miles with varying amounts of animal production intensity in the Stillwater River Basin. | 30 | Once following heavy rains May 19–20, 2000. Biweekly samples at basin outlet March–September 2000 |
| | Varied-land-use streams | Streamflow, physical properties, major ions, nutrients, organic carbon, bacteria, suspended sediment, pesticides, and household chemicals and pharmaceuticals. **To evaluate stream quality with varying amounts of agricultural and urban land.** | 30 streams draining basins ranging in size from 2.8 to 65 square miles with varying amounts of agricultural and urban land. | 30 | Once in July 2001 |
| | Reservoir pesticide study | Physical properties, pesticides, and pesticide degradates. **To provide information on pesticide concentrations in treated and untreated drinking water withdrawn from supply reservoirs across the Nation.** | 2 stream sites representing major inflow and reservoir outflow sites; 1 treated and 1 untreated drinking-water site at East Fork Lake reservoir (Harsha Lake). | 4 | Quarterly throughout year except biweekly during spring-summer months, 1999–2000 |
| **Stream Ecology, Fish Tissue, and Streambed Sediment** | | | | | |
| Stream ecology | | Algal, benthic-invertebrate, and fish communities and the condition of stream habitat. **To determine the effects of water quality and habitat on aquatic biota**. | Sites collocated at or near basic and intensive stream sites. | 8 | One to four times September 1998–August 2001 |
| Streambed sediment and fish tissue | | Organochlorine pesticides and semivolatile organic compounds in sieved sediment and whole fish (common carp). Trace elements in sieved sediment and carp livers. **To measure how much the occurence of a chemical changes because of different land- or chemical-use patterns.** | Sites collocated at or near basic and intensive stream sites. | 8 | Once in September 1998 |
| Varied land-use streams | Aquatic biota | Algal (periphyton and phytoplankton) communities and the condition of stream habitat. **To evaluate response of aquatic biota with varying amounts of agricultural and urban land**. | Sites collocated with varied-land-use stream sites. | 30 | One to four times in September 1998–August 2001 |
| | Streambed sediment | Organochlorine pesticides, semivolatile organic compounds, and trace elements in sieved sediment. **To evaluate streambed sediment chemistry with varying amounts of agricultural and urban land.** | Sites collocated with varied-land-use stream sites. | 30 | Once in July 2001 |
| Special study: mercury in water, sediment, and fish tissue | | Mercury and methylmercury in water column, streambed sediment, and sport fish (smallmouth bass) fillets. **To evaluate factors for mercury occurrence and the potential for mercury methylation across the Nation.** | Sites collocated at or near basic and intensive stream sites; part of larger national mercury study. | 8 | Once in September 1998 |
| **Ground-Water Chemisty** | | | | | |
| Existing wells | Domestic-well study | Water-level, physical properties, nutrients, major ions, bacteria, organic carbon, trace elements, pesticides, pesticide degradates, VOCs, tritium and helium isotopes. **To evaluate quality of ground water withdrawn for domestic use from the buried-valley aquifer system.** | 29 domestic and 1 supply well screened at varying depths in the buried-valley aquifer system throughout the Study Unit. | 30 | Once in May–July 1999 |
| | Public-supply-well study | Same as domestic-well study above except tritium and helium isotopes were not collected. **To evaluate quality of ground water pumped from high-capacity public-supply wells located adjacent to large streams**. | Public-supply wells adjacent to streams in the buried-valley aquifer system throughout the Great Miami River drainage basin. | 15 | Once in May–June 1999 |
| Monitoring wells | Agricultural-land-use study | Same as domestic-well study except bacteria and VOCs were not collected. **To evaluate effects of row-crop agriculture on shallow ground-water quality.** | Installed 26 shallow monitoring wells in areas where the buried-valley aquifer system is overlain by row-crop agriculture. At 8 sites, intermediate depth monitoring wells were also installed. | 34 total<br>26 shallow | Once in July–August 2000 |
| | Urban land-use study | Same as domestic-well study except bacteria, pesticide degradates, tritium and helium isotopes were not sampled. Selected household chemicals and pharmaceuticals, and sulfur hexafluoride also were collected. **To evaluate effects of residential-commercial development on shallow ground-water quality.** | Installed 25 shallow monitoring wells in areas where the buried-valley aquifer system is overlain by residential-commercial areas developed in the last 30–40 years. | 25 | Once in October–December 2001 |
| Tile-drain study | | Physical properties, discharge, nutrients, seleced pesticides, and pesticide degradates. **To assess occurrence of nutrients, pesticides, and pesticide degradates in tile drainage.** | 4 tile drains beneath corn and soybean fields in Darke County, Ohio. Part of regional assessment of tile-drain water quality across the Midwest. | 4 | Three times (pre-plant, post-plant, post-harvest) spring–fall 2001. |

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# Glossary

**Abundance** Number of individuals in a community, habitat, or sample.

**Animal Unit (AU)** The number of animals of various sizes and species which are equivalent to one slaughter or feeder beef with regard to daily waste production; thus, 1 AU is equivalent to 1 slaughter or beef cattle, 0.7 mature dairy cow, 0.5 horse, 2.5 swine weighing more than 25 kilograms, and 100 laying hens.

**Aquifer** A water-bearing layer of soil, sand, gravel, or rock that will yield usable quantities of water to a well.

**Base flow** Sustained, low flow in a stream; ground-water discharge is the source of base flow in most places.

**Basic Fixed Sites** Sites on streams at which streamflow is measured and samples are collected for temperature, salinity, suspended sediment, major ions and metals, nutrients, and organic carbon to assess the broad-scale spatial and temporal character and transport of inorganic constituents of streamwater in relation to hydrologic conditions and environmental settings.

**Benthic** Refers to plants or animals that live on the bottom of lakes, streams, or oceans.

**Bioaccumulation** The net accumulation of a substance by an organism as a result of uptake from all environmental sources, including gills, epithelial tissues, and dietary sources.

**Breakdown products** See Degradate.

**Carnivore** Flesh-eating organism.

**Community** In ecology, the species that interact in a common area.

**Composition** General makeup of the species present in a community, along with a measure of their relative abundance.

**Concentration** The amount or mass of a substance present in a given volume or mass of sample. Usually expressed as micrograms per liter (µg/L) or milligrams per liter (mg/L) for water samples or micrograms per kilogram (µg/kg) or micrograms per gram (µg/g) for sediment or tissue samples. Radon is reported in picocuries per liter (pCi/L). Periphyton organisms, which attach to rocks and other structures, are measured in mass per area, such as milligrams per square meter (mg/m$^2$).

**Degradate** A compound derived by chemical, biological, or physical action upon a organic substance. The breakdown is a natural process that may result in a more toxic or a less toxic compound and a more persistent or less persistent compound.

**Denitrification** A process by which oxidized forms of nitrogen such as nitrate ($NO_3^-$) are reduced to form nitrites, nitrogen oxides, ammonia, or free nitrogen; commonly brought about by the action of denitrifying bacteria and usually resulting in the escape of nitrogen to the air.

**Diatoms** Single-celled, colonial, or filamentous algae with siliceous cell walls constructed of two overlapping parts.

**Domestic well** A private home well, or a well that serves fewer than 15 households or 25 individuals.

**EPT** Organisms in three insect orders —mayflies (*Ephemeroptera*), stoneflies (*Plecoptera*), and caddisflies (*Trichoptera*)— that are composed primarily of species considered to be relatively intolerant to environmental alterations.

**Endocrine system** The collection of glands in animals that secrete hormones, which influence growth, gender, and sexual maturity.

**Eutrophication** The process by which water becomes enriched with plant nutrients, most commonly phosphorus and nitrogen.

**Fertilizer** Any of a large number of natural or synthetic materials, including manure, and nitrogen, phosphorus, and potassium compounds, spread or worked into soil to increase its fertility.

**Flow-weighted mean** A concentration calculated by first multiplying each sample concentration by its associated streamflow value, then dividing the sum of these products by the sum of the streamflows. The resultant mean value accounts for the effects of variable streamflow on concentrations.

**Fungicide** A chemical or other agent applied for the purpose of killing undesirable fungi. See also Pesticide.

**Herbicide** A chemical or other agent applied for the purpose of killing undesirable plants. See also Pesticide.

**Index of Biotic Integrity (IBI)** An aggregated number, or index, based on several attributes or metrics of a fish community that provides an assessment of biological conditions.

**Insecticide** A substance or mixture of substances intended to kill or repel insects. See also Pesticide.

**Intensive Fixed Sites** Basic Fixed Sites with increased sampling frequency during selected seasonal periods and analysis of dissolved pesticides for 1 year. Most NAWQA Study Units have one to two integrator Intensive Fixed Sites and one to four indicator Intensive Fixed Sites.

**Intolerant species** Organisms that are not adaptable to human alterations to the environment and thus decline in numbers where human alterations occur. See also Tolerant species.

**Invertebrate** An animal having no backbone or spinal column.

**Lithophilic** Refers to fish that exhibit simple spawning behavior and require clean gravel and (or) cobble substrates for successful reproduction.

**Load** General term that refers to a material or constituent in solution, in suspension, or in transport; usually expressed in terms of mass or volume.

**LOWESS smooth** LOcally WEighted Scatterplot Smoothing, a statistical method of defining a smooth curve through the middle of a scatterplot to highlight trends or patterns in the data.

**Median** The middle or central value in a distribution of data ranked in order of magnitude. The median is also known as the 50th percentile.

**Metabolite** See Degradate.

**Monitoring well** A well designed for measuring water levels and testing ground-water quality.

**Nitrate** An ion consisting of nitrogen and oxygen ($NO_3^-$). Nitrate is a plant nutrient and is very mobile in soils. In this report, the term “nitrate” is used as shorthand for “nitrate plus nitrite, reported as nitrogen.”

**Nonpoint source** A pollution source that cannot be defined as originating from a discrete point such as a pipe discharge.

**Nutrient** Element or compound essential for animal and plant growth. Common nutrients in fertilizer include nitrogen, phosphorus, and potassium.

**Organochlorine insecticide** A class of organic insecticides containing a high percentage of chlorine. Includes dichlorodiphenylethanes (such as DDT), chlorinated cyclodienes (such as chlordane), and chlorinated benzenes (such as lindane). Most organochlorine insecticides were banned because of their carcinogenicity, tendency to bioaccumulate, and toxicity to wildlife.

**Outwash** Sediment deposited by streams fed by glacial meltwater.

**Pesticide** A chemical applied to crops, rights-of-way, lawns, or residences to control weeds, insects, fungi, nematodes, rodents, or other “pests.”

**Phosphorus** A nutrient essential for growth that can play a key role in stimulating aquatic growth in lakes and streams.

**Point source** A pollution source at a discrete location such as discharge pipe, drainage ditch, tunnel, well, concentrated livestock operation, or floating craft.

**Polychlorinated biphenyls (PCBs)** A mixture of chlorinated derivatives of biphenyl, marketed under the trade name Aroclor with a number designating the chlorine content (such as Aroclor 1260). PCBs were used in transformers and capacitors for insulating purposes and in gas pipeline systems as a lubricant. Further sale for new use was banned by law in 1979.

**Polycyclic aromatic hydrocarbon (PAHs)** A class of organic compounds with a fused-ring aromatic structure. PAHs result from incomplete combustion of organic carbon (including wood), municipal solid waste, and fossil fuels. PAHs include benzo[*a*]pyrene, fluoranthene, and pyrene.

**Recharge** Water that infiltrates the ground and reaches the saturated zone.

**Richness** Number of species in a community, habitat, or sample.

**Runoff** Rainwater or snowmelt that is transported to streams by overland flow, tile drains, or ground water.

**Semivolatile organic compound (SVOC)** Operationally defined as a group of synthetic organic compounds that are solvent extractable and can be determined by gas chromatography/mass spectrometry. SVOCs include phenols, phthalates, and polycyclic aromatic hydrocarbons (PAHs).

**Streambed sediment** The material that temporarily is stationary on the bottom of a stream or other watercourse.

**Taxon (plural taxa)** Any identifiable group of taxonomically related organisms.

**Tile drain** A buried perforated pipe designed to remove excess water from soils.

**Till** Unconsolidated sediment that contains a mixture of clay to boulder-sized particles, deposited by advancing and retreating glaciers.

**Tolerant species** Those species that are adaptable to (tolerant of) human alterations to the environment and often increase in number when human alterations occur.

**Trophic** A level in the food pyramid.

**Unconfined aquifer** An aquifer whose upper surface is a water table; an aquifer containing unconfined ground water.

**Volatile organic compounds (VOCs)** Organic chemicals that have a high vapor pressure relative to their water solubility. VOCs include components of gasoline, fuel oils, and lubricants, as well as organic solvents, fumigants, some inert ingredients in pesticides, and some by-products of chlorine disinfection.

**Water table** The point below the land surface at which ground water is first encountered and below which the earth is saturated. Depth to the water table varies widely across the country.

**Yield** With reference to water quality, the mass of material or constituent transported by river in a specified period of time divided by the drainage area of the river basin.

# Appendix—Water-Quality Data from the Great and Little Miami River Basins in a National Context

Concentrations and detection frequencies of the most commonly detected constituents, constituents that exceed a drinking-water standard or aquatic-life guideline, or constituents that are of regulatory or scientific importance are presented below. Plots of other pesticides, nutrients, VOCs, and trace elements assessed in the Great and Little Miami River Basins are available at our Web site at:

**http://water.usgs.gov/nawqa/graphs**

These summaries of chemical concentrations and detection frequencies from the Great and Little Miami River Basins are compared to findings from 51 NAWQA Study Units investigated from 1991 to 2001 and to water-quality benchmarks for human health, aquatic life, fish-eating wildlife, or prevention of nuisance plant growth. These graphical summaries provide a comparison of chemical concentrations and detection frequencies between (1) surface- and ground-water resources, (2) agricultural, urban, and mixed land uses, and (3) shallow ground water and aquifers commonly used as a source of drinking water. Please note that these graphical summaries do not include results from special studies of stream and lake chemistry (agricultural runoff sites, varied-land-use streams, and reservoir pesticide study), public-supply wells, or eight intermediate-depth agricultural monitoring wells, as described in the table on page 30.

For example, the graph for atrazine shows that detections and concentrations in the Great and Little Miami River Basins are (1) somewhat higher than national findings in small urban streams and in large rivers draining mixed land use but similar to other agricultural streams (2) only rarely greater than the USEPA drinking water standard and (3) greater in streams than in ground water.

NOTE to users:

- The analytical detection limit varies among the monitored chemicals, thus, frequencies of detections are not comparable among chemicals.
- It's important to consider the frequency of detection along with the concentration. For example, atrazine, deethylatrazine, and metolachlor were detected in every sample collected from mixed-land-use streams in the Great and Little Miami River Basins compared to 91, 78, and 76 percent for mixed-land-use streams nationwide with concentrations of each compound generally above the national median.

Quality-control data for the following analytes indicate relatively frequent low-level contamination of samples during sample processing for analysis. Results for these analytes cannot, therefore, be presented using the generalized methods that were applied to other analytes in this appendix. Analysis of results for analytes potentially affected by contamination requires special statistical treatment beyond the scope of this report. For more information about these analytes and how to interpret data on their occurrence and concentrations, please contact the Study Unit.

**Trace elements in ground water**: aluminum, barium, boron, cadmium, chromium, cobalt, copper, lithium, nickel, strontium, zinc
**SVOCs in bed sediment:** phenol, bis(2-ethylhexyl)phthalate, butylbenzylphthalate, di-*n*-butylphthalate, diethylphthalate
**Insecticides in water:** *p,p'*-DDE

## CHEMICALS IN WATER

**Concentrations and detection frequencies, Great and Little Miami River Basins, 1999–2001**

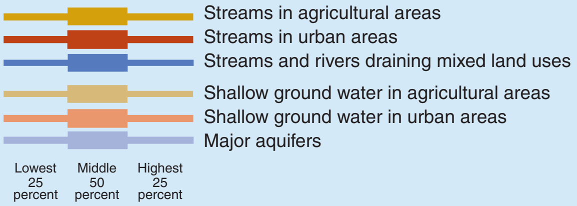
◆ Detected concentration in Study Unit

66 38 Frequencies of detection, in percent. Detection frequencies were not censored at any common reporting limit. The left-hand column is the study-unit frequency, and the right-hand column is the national frequency

-- Not measured or sample size less than two

*12* Study-unit sample size. For ground water, the number of samples is equal to the number of wells sampled

**National ranges of detected concentrations, by land use, in 51 NAWQA Study Units, 1991–2001**—Ranges include only samples in which a chemical was detected



**National water-quality benchmarks**

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

| Drinking-water quality (applies to ground water and surface water)

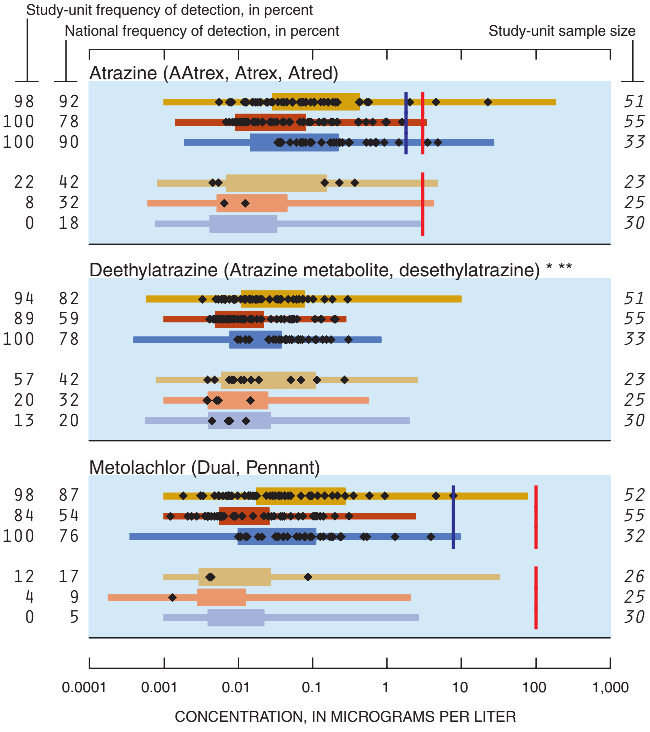
| Protection of aquatic life (applies to surface water only)

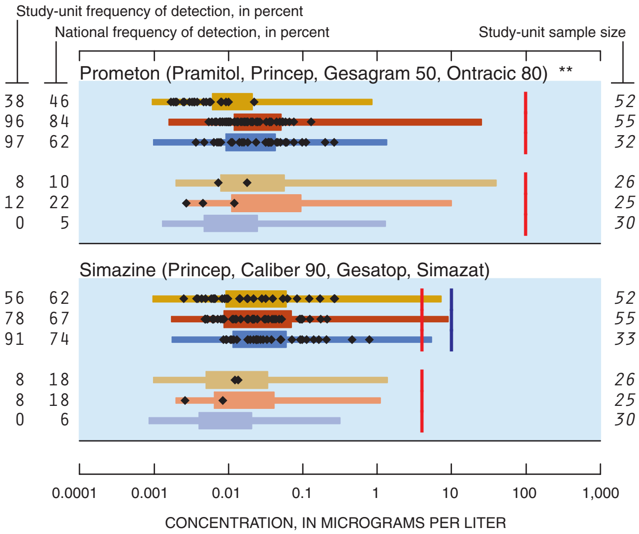
| Prevention of nuisance plant growth in streams

* No benchmark for drinking-water quality

** No benchmark for protection of aquatic life

## Pesticides in water—Herbicides





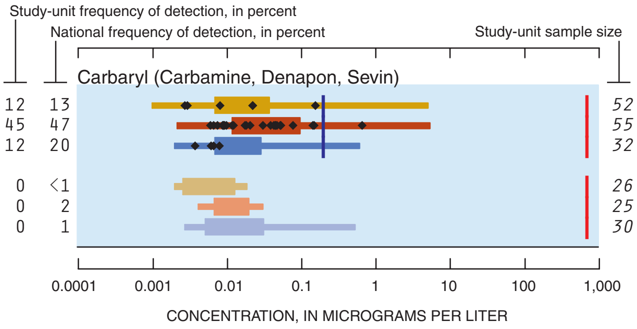
### Other herbicides detected

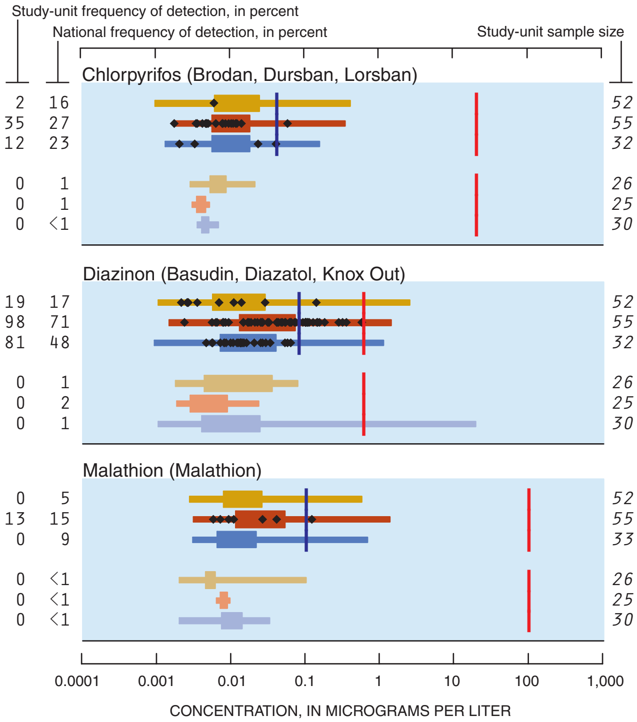
Acetochlor (Harness Plus, Surpass) * **
Alachlor (Lasso, Bronco, Lariat, Bullet) **
Benfluralin (Balan, Benefin, Bonalan, Benefex) * **
Cyanazine (Bladex, Fortrol)
EPTC (Eptam, Farmarox, Alirox) * **
Metribuzin (Lexone, Sencor)
Pendimethalin (Pre-M, Prowl, Weedgrass Control, Stomp, Herbadox) * **
Tebuthiuron (Spike, Tebusan)
Terbacil (Sinbar) **
Trifluralin (Treflan, Gowan, Tri-4, Trific, Trilin)

### Herbicides not detected

Chloramben, methyl ester (Amiben methyl ester) * **
Butylate (Sutan +, Genate Plus, Butilate) **
DCPA (Dacthal, chlorthal-dimethyl) **
2,6-Diethylaniline (metabolite of Alachlor) * **
Ethalfluralin (Sonalan, Curbit) * **
Linuron (Lorox, Linex, Sarclex, Linurex, Afalon) *
Molinate (Ordram) * **
Napropamide (Devrinol) * **
Pebulate (Tillam, PEBC) * **
Pronamide (Kerb, Propyzamid) **
Propachlor (Ramrod, Satecid) **
Propanil (Stam, Stampede, Wham, Surcopur, Prop-Job) * **
Thiobencarb (Bolero, Saturn, Benthiocarb, Abolish) * **
Triallate (Far-Go, Avadex BW, Tri-allate) *

## Pesticides in water—Insecticides





### Other insecticides detected

gamma-HCH (Lindane, gamma-BHC, Gammexane)
Terbufos (Contraven, Counter, Pilarfox) **

### Insecticides not detected

Azinphos-methyl (Guthion, Gusathion M) *
Carbofuran (Furadan, Curaterr, Yaltox)
Dieldrin (Panoram D-31, Octalox)
Disulfoton (Disyston, Di-Syston, Frumin AL, Solvirex, Ethylthiodemeton) **
Ethoprop (Mocap, Ethoprophos) * **
Fonofos (Dyfonate, Capfos, Cudgel, Tycap) **
alpha-HCH (alpha-BHC, alpha-lindane) **
Methyl parathion (Penncap-M, Folidol-M, Metacide, Bladan M) **
Parathion (Roethyl-P, Alkron, Panthion) *
*cis*-Permethrin (Ambush, Astro, Pounce) * **
Phorate (Thimet, Granutox, Geomet, Rampart) * **
Propargite (Comite, Omite, Ornamite) * **

## Volatile organic compounds (VOCs) in water

*These graphs represent data from 32 Study Units, sampled from 1994 to 2001*

### VOCs detected

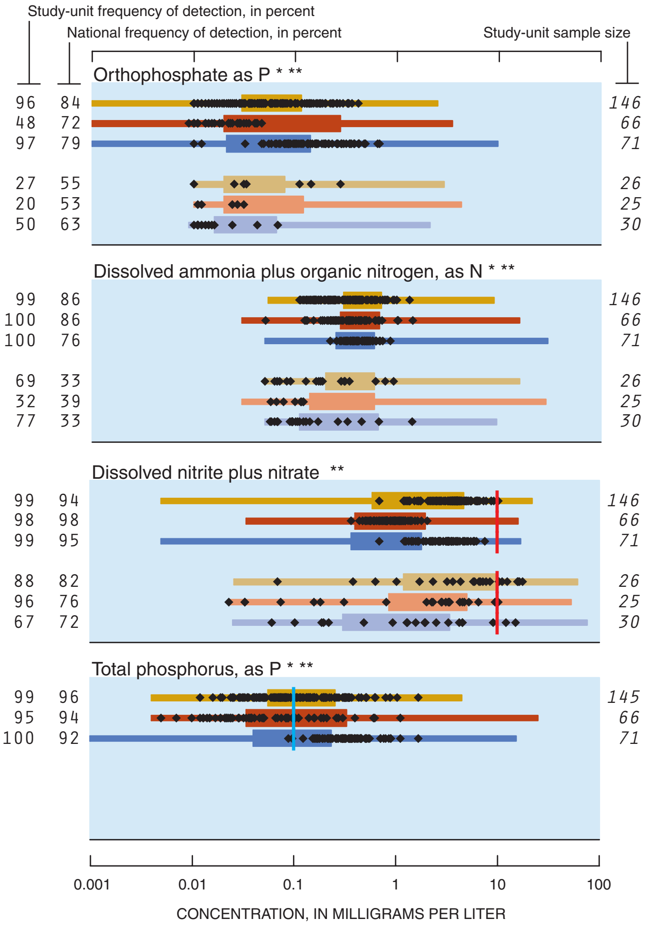
Acetone (Acetone) * **
Benzene
Bromodichloromethane (Dichlorobromomethane) **
2-Butanone (Methyl ethyl ketone (MEK)) **
Carbon disulfide * **
Chloromethane (Methyl chloride) **
Dibromochloromethane (Chlorodibromomethane) **
Dibromomethane (Methylene dibromide) * **
Dichlorodifluoromethane (CFC 12, Freon 12) **
1,1-Dichloroethane (Ethylidene dichloride) * **
*cis*-1,2-Dichloroethene ((Z)-1,2-Dichloroethene) **
Dichloromethane (Methylene chloride)
1,2-Dimethylbenzene (*o*-Xylene) **
1,3 & 1,4-Dimethylbenzene (*m*-&*p*-Xylene) **

Ethenylbenzene (Styrene) **
Ethylbenzene (Phenylethane)
2-Ethyltoluene (*o*-Ethyltoluene) * **
4-Methyl-2-pentanone (Methyl isobutyl ketone (MIBK)) * **
Methylbenzene (Toluene)
Tetrachloroethene (Perchloroethene)
Tetrahydrofuran (Diethylene oxide) * **
Tribromomethane (Bromoform) **
1,1,1-Trichloroethane (Methylchloroform) **
Trichloroethene (TCE)
Trichloromethane (Chloroform)
1,2,3-Trimethylbenzene (Hemimellitene) * **
1,2,4-Trimethylbenzene (Pseudocumene) * **
1,3,5-Trimethylbenzene (Mesitylene) * **

**VOCs not detected**

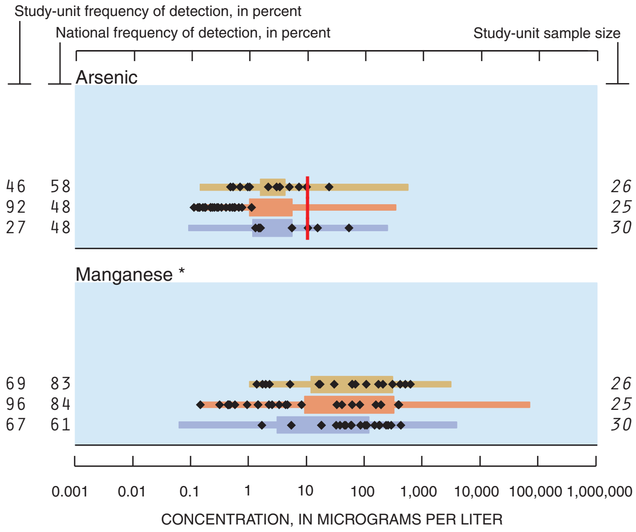
Bromobenzene (Phenyl bromide) * **
Bromochloromethane (Methylene chlorobromide) **
Bromoethene (Vinyl bromide) * **
Bromomethane (Methyl bromide) **
*n*-Butylbenzene (1-Phenylbutane) * **
*sec*-Butylbenzene ((1-Methylpropyl)benzene) * **
*tert*-Butylbenzene ((1,1-Dimethylethyl)benzene) * **
3-Chloro-1-propene (3-Chloropropene) * **
1-Chloro-2-methylbenzene (*o*-Chlorotoluene) **
1-Chloro-4-methylbenzene (*p*-Chlorotoluene) **
Chlorobenzene (Monochlorobenzene)
Chloroethane (Ethyl chloride) * **
Chloroethene (Vinyl chloride) **
1,2-Dibromo-3-chloropropane (DBCP, Nemagon) **
1,2-Dibromoethane (Ethylene dibromide, EDB) **
*trans*-1,4-Dichloro-2-butene ((Z)-1,4-Dichloro-2-butene) * **
1,3-Dichlorobenzene (*m*-Dichlorobenzene)
1,4-Dichlorobenzene (*p*-Dichlorobenzene, 1,4-DCB)
1,2-Dichloroethane (Ethylene dichloride)
1,1-Dichloroethene (Vinylidene chloride) **
*trans*-1,2-Dichloroethene ((E)-1,2-Dichlorothene) **
1,2-Dichloropropane (Propylene dichloride) **
2,2-Dichloropropane * **
1,3-Dichloropropane (Trimethylene dichloride) * **
*trans*-1,3-Dichloropropene ((E)-1,3-Dichloropropene) **
*cis*-1,3-Dichloropropene ((Z)-1,3-Dichloropropene) **
1,1-Dichloropropene * **
Diethyl ether (Ethyl ether) * **
Diisopropyl ether (Diisopropylether (DIPE)) * **
Ethyl methacrylate (Ethyl methacrylate) * **
Ethyl *tert*-butyl ether (Ethyl-t-butyl ether (ETBE)) * **
1,1,2,3,4,4-Hexachloro-1,3-butadiene (Hexachlorobutadiene)
1,1,1,2,2,2-Hexachloroethane (Hexachloroethane) **
2-Hexanone (Methyl butyl ketone (MBK)) * **
Iodomethane (Methyl iodide) * **
Isopropylbenzene (Cumene) * **
*p*-Isopropyltoluene (*p*-Cymene, 1-Isopropyl-4-methylbenzene) * **
Methyl acrylonitrile (Methacrylonitrile) * **
Methyl methacrylate (Methyl-2-methacrylate) * **
Methyl *tert*-butyl ether (MTBE) **
Methyl-2-propenoate (Methyl acrylate) * **
Naphthalene
2-Propenenitrile (Acrylonitrile) **
*n*-Propylbenzene (Isocumene) * **
1,1,2,2-Tetrachloroethane **
1,1,1,2-Tetrachloroethane (1,1,1,2-TeCA) **
Tetrachloromethane (Carbon tetrachloride)
1,2,3,4-Tetramethylbenzene (Prehnitene) * **
1,2,3,5-Tetramethylbenzene (Isodurene) * **
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113, CFC 113) * **
1,2,4-Trichlorobenzene
1,2,3-Trichlorobenzene (1,2,3-TCB) *
1,1,2-Trichloroethane (Vinyl trichloride) **
Trichlorofluoromethane (CFC 11, Freon 11) **
1,2,3-Trichloropropane (Allyl trichloride) **
*tert*-Amyl methyl ether (TAME) * **

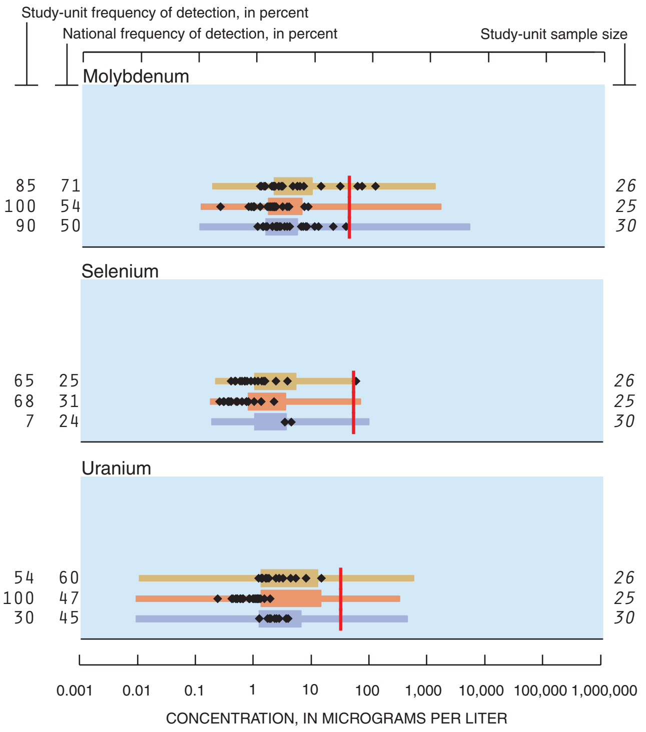
## Nutrients in water

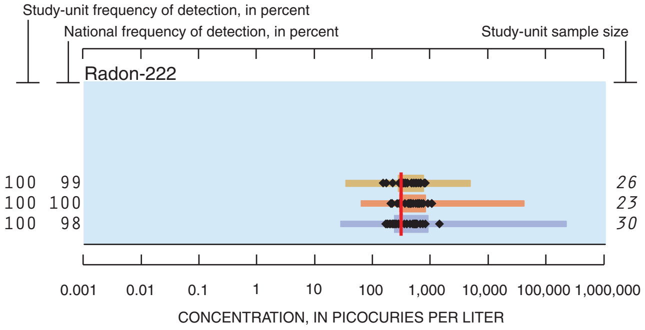


**Other nutrient detected**
Ammonia *

## Trace elements in ground water







**Other trace elements detected**

Antimony
Lead
Thallium
Vanadium *

**Trace elements not detected**

Beryllium
Silver

## CHEMICALS IN FISH TISSUE AND BED SEDIMENT

**Concentrations and detection frequencies, Great and Little Miami River Basins, 1999–2001—**Study-unit frequencies of detection are based on small sample sizes; the applicable sample size is specified in each graph

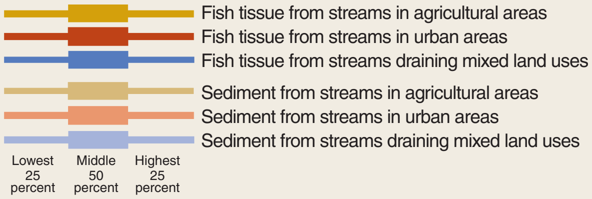
◆ Detected concentration in Study Unit

66 38 Frequencies of detection, in percent. Detection frequencies were not censored at any common reporting limit. The left-hand column is the study-unit frequency and the right-hand column is the national frequency

-- Not measured or sample size less than two

*12* Study-unit sample size

**National ranges of concentrations detected, by land use, in 51 NAWQA Study Units, 1991–2001—**Ranges include only samples in which a chemical was detected


Fish tissue from streams in agricultural areas
Fish tissue from streams in urban areas
Fish tissue from streams draining mixed land uses
Sediment from streams in agricultural areas
Sediment from streams in urban areas
Sediment from streams draining mixed land uses

**National benchmarks for fish tissue and bed sediment**

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

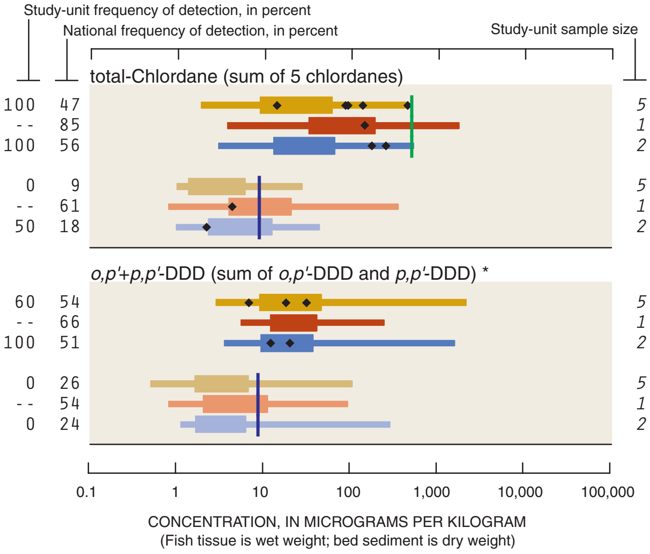
| Protection of fish-eating wildlife (applies to fish tissue)

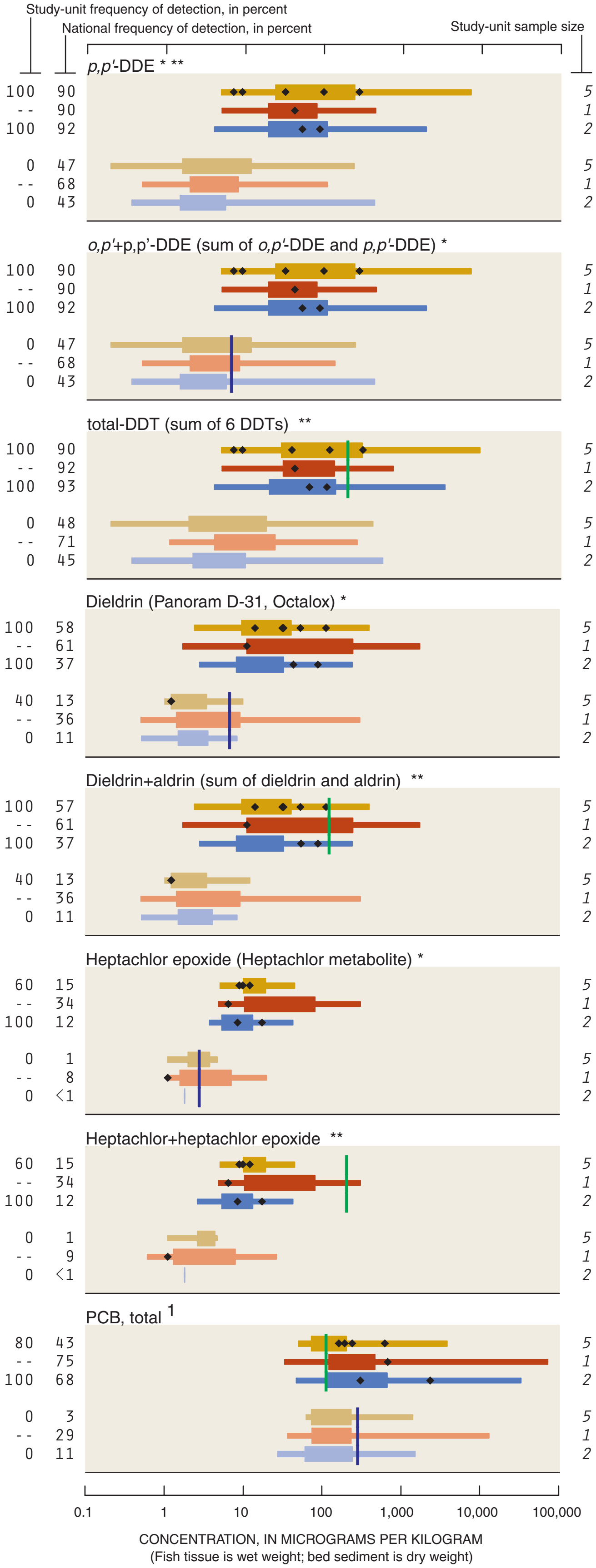
| Protection of aquatic life (applies to bed sediment)

* No benchmark for protection of fish-eating wildlife

** No benchmark for protection of aquatic life

## Organochlorines in fish tissue (whole body) and bed sediment



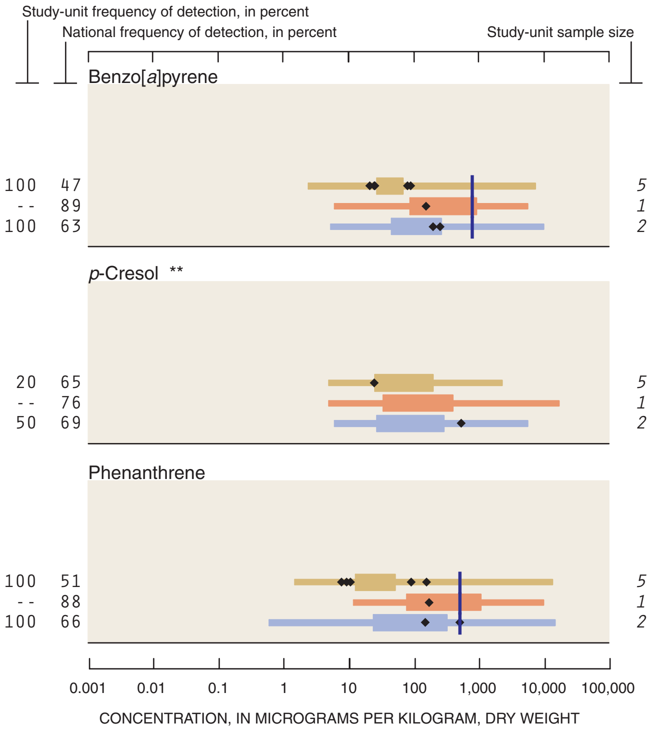


**Other organochlorines detected**

Hexachlorobenzene (HCB) **
Pentachloroanisole (PCA, pentachlorophenol metabolite) * **

**Organochlorines not detected**
Chloroneb (chloronebe, Demosan) * **
DCPA (Dacthal, chlorthal-dimethyl) * **
*o,p'*+*p,p'*-DDT (sum of *o,p'*-DDT and *p,p'*-DDT) *
Endosulfan I (alpha-Endosulfan, Thiodan) * **
Endrin (Endrine)
gamma-HCH (Lindane, gamma-BHC, Gammexane) *
Total HCH (sum of alpha, beta, gamma, and delta-HCH) **
Isodrin (Isodrine, Compound 711) * **
*p,p'*-Methoxychlor (Marlate, methoxychlore) * **
*o,p'*-Methoxychlor * **
Mirex (Dechlorane) **
*cis*-Permethrin (Ambush, Astro, Pounce) * **
*trans*-Permethrin (Ambush, Astro, Pounce) * **
Toxaphene (Camphechlor, Hercules 3956) * **

## Semivolatile organic compounds (SVOCs) in bed sediment



**Other SVOCs detected**
Acenaphthene
Acenaphthylene
Acridine **
Anthracene
Anthraquinone **
Benz[*a*]anthracene
Benzo[*b*]fluoranthene **
Benzo[*g,h,i*]perylene **
Benzo[*k*]fluoranthene **
9*H*-Carbazole **
Chrysene
Dibenz[*a,h*]anthracene
Dibenzothiophene **

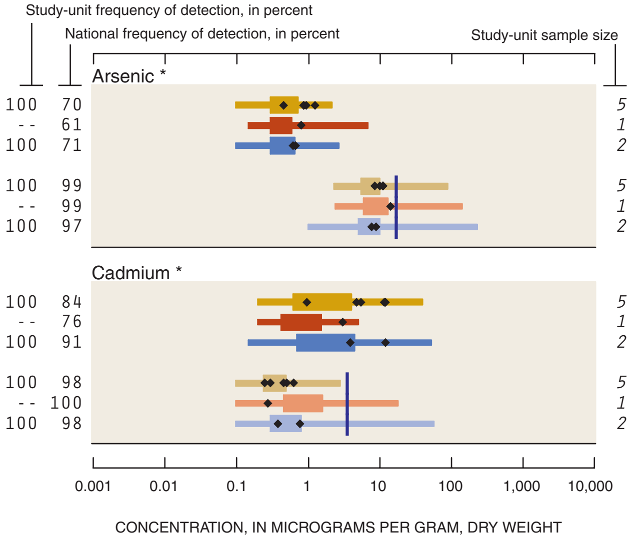
---

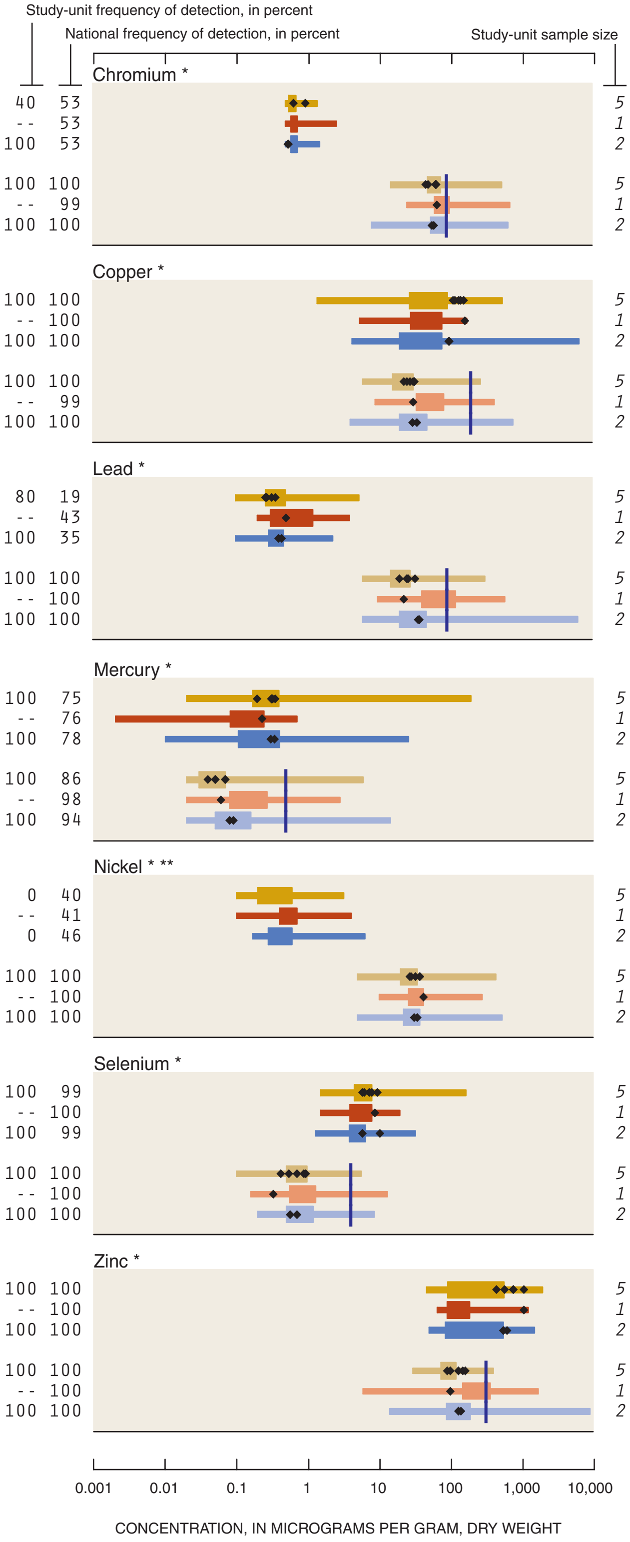
[1] The national detection frequencies for total PCB in sediment are biased low because about 30 percent of the samples nationally had elevated detection limits compared to this Study Unit. See http://water.usgs.gov/nawqa/ for additional information.

2,6-Dimethylnaphthalene **
Fluoranthene
9*H*-Fluorene (Fluorene)
Indeno[1,2,3-*c,d*]pyrene **
2-Methylanthracene **
4,5-Methylenephenanthrene **
1-Methylphenanthrene **
1-Methylpyrene **
Pyrene

**SVOCs not detected**
C8-Alkylphenol **
Azobenzene **
Benzo[*c*]cinnoline **
2,2-Biquinoline **
4-Bromophenyl-phenylether **
4-Chloro-3-methylphenol **
bis (2-Chloroethoxy)methane **
2-Chloronaphthalene **
2-Chlorophenol **
4-Chlorophenyl-phenylether **
Di-*n*-octylphthalate **
1,2-Dichlorobenzene (*o*-Dichlorobenzene, 1,2-DCB) **
1,3-Dichlorobenzene (*m*-Dichlorobenzene) **
1,4-Dichlorobenzene (*p*-Dichlorobenzene, 1,4-DCB) **
1,2-Dimethylnaphthalene **
3,5-Dimethylphenol **
Dimethylphthalate **
2,4-Dinitrotoluene **
Isophorone **
Isoquinoline **
1-Methyl-9*H*-fluorene **
Naphthalene
Nitrobenzene **
*N*-Nitrosodi-*n*-propylamine **
*N*-Nitrosodiphenylamine **
Pentachloronitrobenzene **
Phenanthridine **
Quinoline **
1,2,4-Trichlorobenzene **
2,3,6-Trimethylnaphthalene **

## Trace elements in fish tissue (livers) and bed sediment





Coordination with agencies and organizations in the Great and Little Miami River Basins was integral to the success of this water-quality assessment. We thank those who served as members of our liaison committee.

**Federal Agencies**
U.S. Army Corps of Engineers
U.S. Department of Agriculture
U.S. Environmental Protection Agency

**State Agencies**
Ohio Department of Natural Resources
Ohio Environmental Protection Agency
Indiana Department of Environmental Management
Indiana Department of Natural Resources

**Local Agencies**
Butler County Department of Environmental Services
City of Cincinnati
City of Dayton
City of Fairfield
City of Hamilton
Clermont County Office of Environmental Quality
Ohio State University Extension Southwest District
Hamilton County Health District
Hamilton to New Baltimore Ground Water Consortium
Miami Conservancy District
Miami Valley Regional Planning Commission
Ohio-Kentucky-Indiana Regional Council of Governments

**Universities**
Earlham College
Heidelburg College
Miami University
University of Cincinnati
University of Dayton
Wright State University

**Other public and private organizations**
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Little Miami Incorporated
Mill Creek Watershed Project
Ohio Farm Bureau Federation
Procter and Gamble Corporation
Stillwater Watershed Council
Terran Corporation

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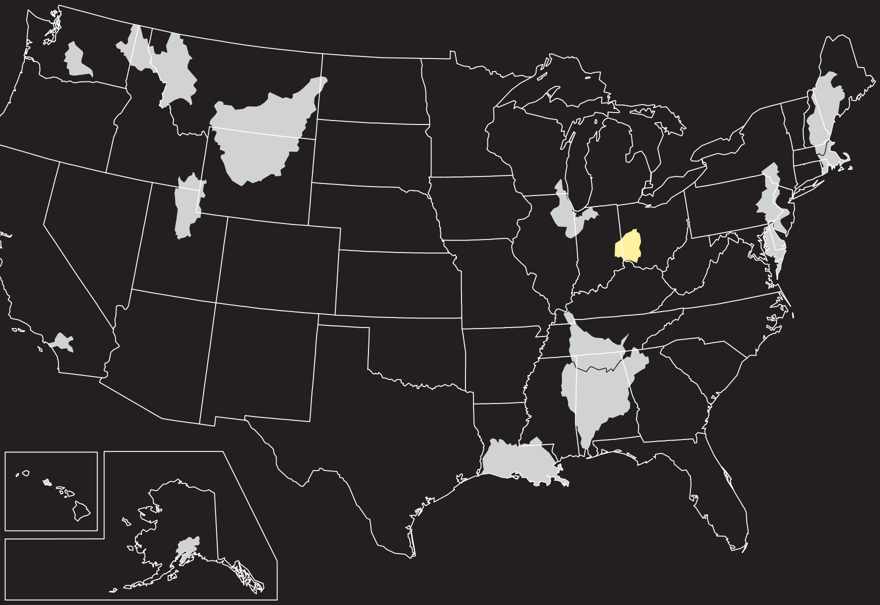
# NAWQA

## National Water-Quality Assessment (NAWQA) Program
## Great and Little Miami River Basins



Rowe and others—Water Quality in the Great and Little Miami River Basins
U.S. Geological Survey Circular 1229

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