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Water Quality of the Flint River Basin, Alabama and Tennessee, 1999-2000

Water-Resources Investigations Report 01-4185
National Water-Quality Assessment Program

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

Cover photos: Top photo is aerial view of the Flint River flood plain near Owens Crossroads, Alabama; photograph taken by Tennessee Valley Press, Inc., Decatur, Ala. Bottom photo is the Flint River at Highway 72, Alabama, courtesy of Susan Weber, Flint River Conservation Association.

Water Quality of the Flint River Basin, Alabama and Tennessee, 1999-2000

By ANNE B. HOOS, JERRY W. GARRETT, and RODNEY R. KNIGHT

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 01-4185

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FOREWORD

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

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

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

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

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

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

Robert M. Hirsch
Associate Director for Water

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Multiply	By	To obtain
inch (in.)	2.54	centimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
cubic feet per second (ft^3/s)	0.02832	cubic meter per second
ton per year (ton/yr)	0.9072	metric ton per year
ton per square mile per year [(ton/mi^2)/yr]	0.003503	metric ton per hectare per year
pound per day (lb/day)	0.4536	kilogram per day
pound per square mile per year [(lb/mi^2)/yr]	0.001751	kilogram per hectare per year

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

ABBREVIATIONS AND ACRONYMS

NAWQA	National Water Quality Assessment
U.S. EPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

WATER-QUALITY ABBREVIATIONS

col./100 mL	Colonies per 100 milliliters
NTU	Nephelometric turbidity units
mg/L	Milligrams per liter

GLOSSARY

Aquatic-life criteria. The level of a pollutant or condition necessary to protect fish and other aquatic life in a stream or lake. Aquatic-life criteria for pesticides specify a maximum concentration that should not be exceeded at any time, or that should not be exceeded beyond specified exposure periods.

Detection frequency. Calculated, for a set of samples, as the proportion of samples in which the concentration of a constituent is greater than or equal to a specified level, such as the detection limit for the analytical method, or a selected threshold of concentration.

Eutrophication. The adverse effects of excess nutrient input to a stream, including overgrowth of plant life and decline of the biological community.

Export. Equivalent to instream load, and used in place of that term in comparisons with input to a watershed. Unit-area export is equivalent to yield.

Flow-weighted mean concentration. The ratio of instream load of a constituent to the mean discharge during the period of transport (dimensions of mass per volume); and equivalent computationally to the flow-weighted mean of the model estimates of daily concentration. Expressed in units of concentration (mg/L). This quantity is used, in place of load or yield, for evaluating average water-quality conditions at the site, and to compare water-quality among sites with differing discharge characteristics.

Input. The mass of a constituent entering a watershed either by deposition on the land surface (land-phase input) or by discharge directly to the stream channel (such as wastewater discharges). Only a portion of the land-phase input reaches the stream channel by overland or subsurface transport processes. Unit-area input is the ratio of input to area of the watershed (dimensions of mass per time per area).

Instream load. The mass of a constituent moving past a specified point in a channel (for example, the mouth of a river basin) during a specified period of time. The instream load can be estimated by monitoring the concentration of the constituent periodically, and streamflow continuously, at the specified point.

Synergistic. Having a combined effect greater than the sum of individual effects.

Yield. The ratio of instream load of a constituent to the area of the watershed (dimensions of mass per time per area). This area-normalized load is used, in place of load, to compare instream loads among watersheds with differing drainage areas, and to compare with inputs to the watershed.

Water Quality of the Flint River Basin, Alabama and Tennessee, 1999-2000

By Anne B. Hoos, Jerry W. Garrett, *and* Rodney R. Knight

ABSTRACT

The U.S. Geological Survey monitored eight stream sites in the Flint River Basin during the period January 1999 through May 2000, to characterize patterns in the occurrence of pesticides, fecal-indicator bacteria, and nutrients in relation to season and streamflow conditions and to land-use patterns. This study is part of the National Water-Quality Assessment Program, which was designed to assess water quality as it relates to various land uses.

Every water sample collected from the Flint River Basin had detectable levels of at least two pesticides; 64 percent of the samples contained mixtures of at least five pesticides. In general, pesticides detected most frequently and at highest concentrations in streams corresponded to the pesticides with the highest rates of use in the watersheds. Detections of fluometuron, norflurazon, and atrazine were more frequent (by a margin of 15 percent or more) in samples from the Flint River when compared with the frequencies of pesticide detections at 62 agricultural stream sites across the Nation. Detections of fluometuron in the Flint River were more frequent even when compared with a cotton-cultivation subset of the 62 sites. For most pesticides, maximum concentrations did not exceed criteria to protect aquatic life; however, maximum concentrations of atrazine, cyanazine, and malathion exceeded aquatic-life criteria in at least one sample. Concentrations near or exceeding the aquatic-life criteria occurred only during the spring and summer (April-July), and generally occurred during storm flows.

Less than 5 percent of the estimated mass of pesticides applied annually to agricultural areas in the Flint River Basin was transported to the stream at the monitoring points on the Flint River near Brownsboro, Alabama, and on Hester Creek near Plevna, Alabama. The pesticides with the highest ratios (greater than 3 percent) of the amount transported instream to the amount applied—atrazine, metolachlor, fluometuron, and norflurazon—are preemergent herbicides applied to the soil before the crops have emerged, which increases the probability of transport in surface runoff.

Concentrations of the fecal-bacteria indicator *Escherichia coli* (*E. coli*) in the Flint River and Hester Creek exceeded the U.S. Environmental Protection Agency criterion for recreation in almost all storm samples, and in many samples collected up to 6 days following a storm. Concentrations in the Flint River were strongly correlated with sample turbidity, suggesting that turbidity might be useful as a surrogate for estimating *E. coli* concentrations. Concentrations of the nutrients nitrogen and phosphorus in samples from the Flint River generally exceeded thresholds indicating eutrophic potential, whereas concentrations in samples from Hester Creek were generally below the thresholds. When compared with nutrient data from a set of 24 agricultural basins across the southeastern region of the United States, concentrations in the Flint River and Hester Creek were slightly above the regional median.

Base-flow concentrations of certain pesticides, nutrients, and *E. coli* were compared to land-use information for eight sites in the Flint

River Basin. The highest base-flow concentrations of aldicarb sulfoxide, fluometuron, and phosphorus were found in the tributaries with the greatest density of cotton acreage in the watershed. Similarly, high base-flow concentrations of total nitrogen were correlated with a high percentage of cultivated land in the watershed. Lack of information about distribution of stream access by livestock weakened the analysis of correlation between livestock and base-flow concentrations of *E. coli* and nutrients.

Input of dissolved and suspended chemicals from the Flint River during storms influences water quality in the reach of the Tennessee River from which the City of Huntsville, Alabama, withdraws about 40 percent of its drinking water. During the storm of April 2-5, 2000, concentrations of several pesticides were at least a factor five times greater in Huntsville's intake water when compared with concentrations in the Tennessee River upstream from the Flint River, although concentrations of all pesticides were below the U.S. Environmental Protection Agency drinking-water standards at all sites on the Tennessee River and in Huntsville's intake water.

INTRODUCTION

The Flint River, a tributary to the Tennessee River, drains 568 square miles (mi^2) of primarily agricultural land in northern Alabama and south-central Tennessee (fig. 1). Urban and residential land represent a small (less than 1 percent), but growing part of land use in the watershed, as residential growth from the City of Huntsville, Alabama, spreads northward and eastward into the watershed. The Flint River is an important recreational and scenic resource; a 34-mile (mi) section of the river (fig. 2) is a popular canoe and tubing area and was designated a canoe trail by the Madison County Commission in 1993. Local agencies are conducting riparian restoration projects to protect and enhance habitat for the diverse aquatic life along the Flint River. Among the several threatened species of fish and aquatic invertebrates found in the Basin are the slackwater darter, Tuscumbia darter, and southern cave fish.

Most of the Flint River Basin lies within the eastern part of the Highland Rim Physiographic section (fig. 2), an area of well drained soils and gently rolling terrain that contains productive farmland (predominantly cotton, corn, and soybeans). The eastern and southwestern edges lie on the escarpment of the Cumberland Plateau (fig. 2), which is characterized by steeply sloping forested land with pasture and cultivated land restricted to the narrow valley floors. Stream channels throughout the Flint River Basin are characterized by gravel and bedrock bottoms with numerous springs and spring-associated fish fauna.

The U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program is currently investigating water quality in the lower Tennessee River Basin (fig. 1, map inset), with several monitoring activities targeted in the Flint River Basin. The purpose of this investigation is to assess surface-water quality related to various land uses. The target issues of this assessment program—nutrients, fecal-indicator bacteria, and pesticides—coincide with assessments conducted by State water-quality regulatory agencies on causes of water-quality impairment in the Flint River Basin (Tennessee Department of Environment and Conservation, 2000; Alabama Department of Environmental Management, 2000, table 6-17), and with concerns of the local watershed group, the Flint River Conservation Association. The water-quality assessments of water (designated as impaired water, 1998, in fig. 2) in the Flint River Basin by State regulatory agencies are presented in this report to add perspective to the interpretations of water-quality data collected for this study; however, this study was not designed to address sources or causes of impairment in specific stream reaches.

Purpose and Scope

The purposes of this report are to characterize surface-water quality in the Flint River Basin across a range of seasonal and streamflow conditions, and to assess variation of base-flow water quality in relation to land use in the Basin. The water-quality constituents included in the characterization are pesticides, fecal-indicator bacteria, and nutrients. The effect of the Flint River Basin on water quality in the main stem of the Tennessee River at a drinking-water intake for the City of Huntsville, Alabama, also is described. This report is based on data collected from January 1999 through May 2000 from eight stream sites in the Flint River Basin and from three sites on the main stem of the Tennessee River.

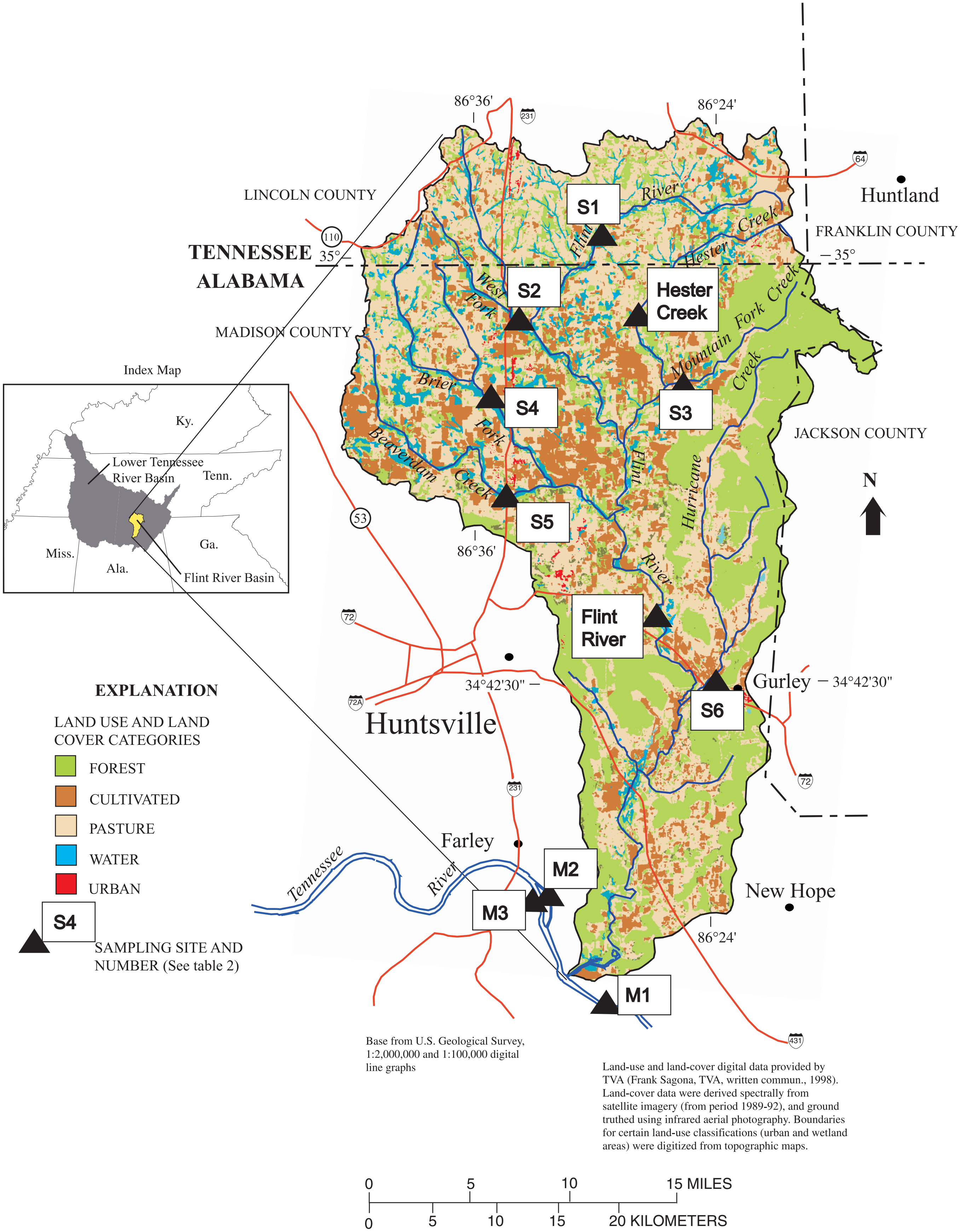


Figure 1. Land use, land cover, and location of sampling sites in the Flint River Basin and adjacent section of the Tennessee River.

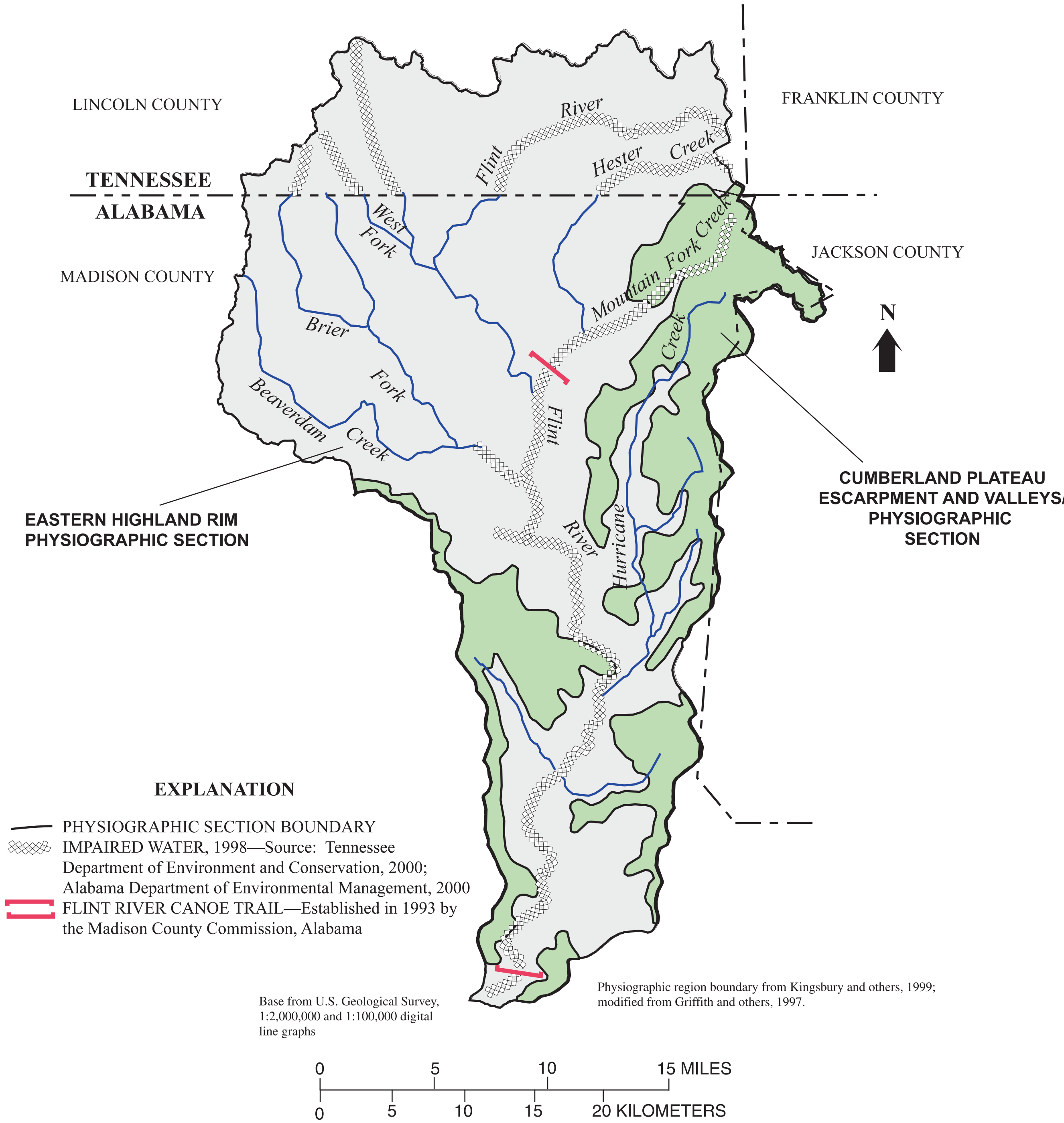


Figure 2. Physiographic sections and impaired waters (1998) in the Flint River Basin, Alabama and Tennessee.

Acknowledgments

The authors thank several individuals who gave special assistance in compiling data: Joseph Berry and William Abbott, Natural Resources Conservation Service; Mark Hall, Alabama Cooperative Extension Service; David Qualls, Tennessee Agricultural Extension Service; Victor Payne, Alabama Soil and Water Conservation Committee; and Pat Morgan, City of Huntsville. Susan F. Weber, Flint River Conservation Association, and James Kingsbury and Gregory Clark, USGS, provided excellent technical guidance and review. Thanks to Reavis Mitchell, USGS, for assisting with the design of illustrations. Assistance from Wayne Miller, City of Huntsville, during a special storm sampling effort, is appreciated.

STUDY OBJECTIVES AND APPROACH

The study objectives were to characterize water quality in the Flint River Basin across a range of seasonal and streamflow conditions, to assess spatial variation of base-flow water quality in the Flint River Basin, and to relate water quality in the Flint River to water quality in a drinking-water source for the City of Huntsville.

Design of Monitoring Program

The monitoring program included three separate networks of stream sites and sampling schedules designed to match the different study objectives (tables 1 and 2). The intensive monitoring network, consisting of two sites (Hester Creek and Flint River sites, fig. 1), was used to characterize water quality in the Flint River Basin across a range of seasonal and streamflow conditions. The spatial monitoring network, consisting of the two intensive sites and six additional sites (S1-S6, fig. 1), was used to assess spatial variation of base-flow water quality in the Basin and to compare variation in water quality to variation in land use. The main stem Tennessee River monitoring network, consisting of three sites on the Tennessee River (M1-M3, fig. 1) and the Flint River site (fig. 1),

Table 1. Description of stream monitoring networks in the Flint River Basin and Tennessee River, 1999-2000

[mi^2, square mile]

Study component (number of sites) and objective	Sampling sites	Sampling schedule	Streamflow-data collection
Intensive monitoring network (2 sites) Characterize water quality in the Flint River Basin across a range of seasonal and streamflow conditions.	The Hester Creek site (fig. 1 and table 2), on a tributary to Flint River, and the Flint River site (fig. 1 and table 2), on the Flint River downstream from Hester Creek.	Fixed-frequency schedule (weekly or biweekly during spring and summer; monthly during fall and winter). Plus 18 storm events.	Continuous record, 1999-current year. [1]
Spatial monitoring network (8 sites) Characterize spatial variation of base-flow water quality in the Flint River Basin, and evaluate the representativeness of the intensive monitoring sites.	Six additional tributary sites (S1-S6, fig. 1 and table 2), along with the two intensive sites. The eight sites together drain a total watershed area of 440 mi^2, almost 80 percent of the Flint River Basin.	Two separate base-flow periods: May 12, 1999 (following a 5-day dry period) and September 7-9, 1999 (following a 40-day dry period).	Measurement of instantaneous streamflow at time of sampling.
Main stem Tennessee River monitoring network (4 sites) Relate Flint River water quality to a drinking-water source.	Three sites along the main stem Tennessee River (sites M1 - M3, fig. 1 and table 2), and one site on the Flint River (Flint River, fig. 1).	A single storm event (April 2-5, 2000).	Measurement of instantaneous streamflow at time of sampling. [2]

[1] Historic streamflow record available from a nearby USGS streamflow gaging station, Flint River near Chase, Ala. (03575000), for the period 1930-94.

[2] Hourly streamflow record during the sampling period (April 2-5, 2000) was estimated for graphs in figure 18 by interpolating from continuous streamflow record from Tennessee River at Whitesburg, Ala. (03575500) and measurements of instantaneous streamflow at sites M1 - M3.

Table 2. Watershed characteristics of stream sampling sites in the Flint River Basin and Tennessee River

[mi^2, square miles; land-cover estimates from satellite imagery from period 1989-92 (provided by Frank Sagona, Tennessee Valley Authority, written commun., 1998); density of acreage of cotton, corn, and soybeans calculated based on estimates from 1998 from Joseph Berry (U.S. Natural Resource Conservation Service, written commun., 2000) and William Abbott (U.S. Natural Resource Conservation Service, written commun., 2000) and reported in percentage; density of failing septic systems and livestock calculated based on census estimates from 1998 for the Alabama part of the watersheds (Victor Payne, Alabama Soil and Water Conservation Committee, written commun., 1999) and reported in number per square mile, density estimates are subject to error because the areas for which census estimates were available do not correspond exactly with the watersheds for the sampling sites; site identification denotes monitoring network; <, less than; S denotes spatial network; M denotes main stem Tennessee River monitoring network; --, not estimated]

Site identification (fig. 1)	Surface-water station/Site location			Drainage area (mi^2)	Major land use, in percent					Cotton	Corn	Soybeans	Failing septic systems	Cattle and dairy cows	Chicken and hogs
	Number	Name	River mile		Forest	Pasture	Cultivated	Urban	Other						
Hester Creek	0357479650	Hester Creek at Buddy Williamson Road near Plevna, Ala.	4.6	29.3	27	50	15	< 1	8	9	7	13	11	150	570
Flint River	03575100	Flint River near Brownsboro, Ala.	27.6	374	25	45	20	< 1	10	8	4	11	9	70	150
S1	03574702	Flint River at Lincoln, Tenn.	56.5	52.1	19	59	11	< 1	11	3	6	11	25	30	0
S2	03574750	West Fork Flint River near Hazel Green, Ala.	1.3	39.6	18	52	17	1	12	3	6	11	25	30	0
S3	03574794	Mountain Fork Creek at New Market, Ala.	4.0	37.5	70	15	14	< 1	1	1	3	6	12	54	8
S4	03574823	Brier Fork near Hazel Green, Ala.	5.8	40.8	14	56	14	< 1	16	11	1	8	8	7	40
S5	03574870	Beaverdam Creek near Meridianville, Ala.	2.8	37.2	19	39	30	< 1	12	21	1	16	7	20	0
S6	03575200	Hurricane Creek near Gurley, Ala.	2.4	63.8	63	30	6	< 1	< 1	1	3	6	12	54	8
M1	03574680	Tennessee River near Morgan City, Ala.	340	24,960	--	--	--	--	--				--	--	--
M2	03575480	Tennessee River at State Docks, Ala. (also referred to as "right channel at Hobbs Island")	334[a]	25,610	--	--	--	--	--				--	--	--
M3	03575490	Tennessee River downstream from Hobbs Island, Ala. (also referred to as "left channel at Hobbs Island")	334[a]		--	--	--	--	--				--	--	--

[a] Streamflow in the Tennessee River at river mile 334 is divided by Hobbs Island into right and left channel, sites M2 and M3.

was used to assess the effect of the Flint River on water quality in the Tennessee River at a drinking-water intake for the City of Huntsville, Alabama.

Water-quality constituents analyzed included 113 current-use pesticides (dissolved-phase only), the fecal-indicator bacteria *Escherichia coli* (*E. coli*), and dissolved and suspended phases of nitrogen and phosphorus. Procedures for sample collection and processing followed guidelines for the NAWQA program and are described in Shelton (1994), Gilliom and others (1995), and Mueller and others (1997). Quality-assurance results for the NAWQA program are described in Martin and others (1999).

Watershed Inputs

Inputs of pesticides and nutrients were estimated for the watersheds of two monitoring sites in the Flint River Basin: the Flint River and one of its tributaries, Hester Creek. The methods used to estimate inputs are described in Appendix A; the estimates are presented in Appendixes B and C. Estimates of pesticide inputs represent crop pesticide use only. Herbicides applied in the greatest amounts to crops were glyphosate (cotton and soybeans) and atrazine (corn); insecticides applied in the greatest amounts to crops were aldicarb and dicrotophos (cotton). Density of cultivated land and, therefore, unit-area input estimates of pesticides were larger for the watershed of the tributary site, Hester Creek, than for the larger watershed of the Flint River site.

Inputs of nitrogen and phosphorus to the watersheds were estimated from crop fertilizer, crop nitrogen-fixation, livestock waste, failing septic systems, atmospheric deposition, and wastewater. Input estimates from agricultural activities (crop fertilizer application, crop nitrogen-fixation, and livestock waste) are much larger than estimates from other sources; however, these inputs are distributed across the land surface throughout the watershed, and the percentage transported to streams is unknown. Summed unit-area input estimates were larger (almost double) for the Hester Creek watershed because of the greater density of livestock in the watershed.

HYDROLOGIC CONDITIONS

Precipitation in the Flint River Basin during the period October 1998 through May 2000 was almost 20 percent below normal. Total precipitation for the 20-month period in Huntsville, Ala., was 79.6 in., compared to 97.8 in., the 30-year normal precipitation for the same length of time. The below-normal rainfall resulted in below-normal streamflow during much of this time period, as demonstrated in figure 3 which shows streamflow at the Flint River near Brownsboro, Ala., fell below the 25th percentile of daily mean streamflow (based on 1930-94 historical record) during this time. Despite periods of below-normal streamflow, the mean streamflow yield for 1999 (1.6 cubic feet per second per square mile [$(ft^3/s)/mi^2$]) equaled the mean annual streamflow yield for 1930-94 [1.7 $(ft^3/s)/mi^2$]; this is explained by the above-normal precipitation and runoff in January 1999 offsetting the below-normal precipitation and runoff during other parts of the year.

Water-quality conditions in the Flint River Basin during water years 1999-2000 also may have deviated from normal: transport of water-quality constituents, including pesticides, bacteria, and nutrients, to the streams through storm runoff was probably lower than normal during many months. The below-normal rainfall and recharge during most months also may have resulted in below-normal ground-water flow and transport of constituents to streams.

WATER QUALITY OF THE FLINT RIVER BASIN

Water quality in the Flint River Basin is affected by diverse land-use and natural factors. This section of the report is organized by water-quality issues (pesticides, fecal-indicator bacteria, and nutrients); water-quality conditions are described in relation to these factors. In each category, variation in water quality with season and streamflow is described using data from the intensive monitoring network, then water quality during base flow in the contributing watersheds is evaluated using data from the spatial network.

Pesticides

Physical properties and use restrictions of many pesticides currently in use result in minimum residue available for transport to the aquatic environment. Many pesticides are toxic at low concentrations; therefore, some concern exists about the risk to aquatic life posed by their use. Water samples collected from eight sites in the Flint River Basin were analyzed for 113 pesticides commonly used throughout the United

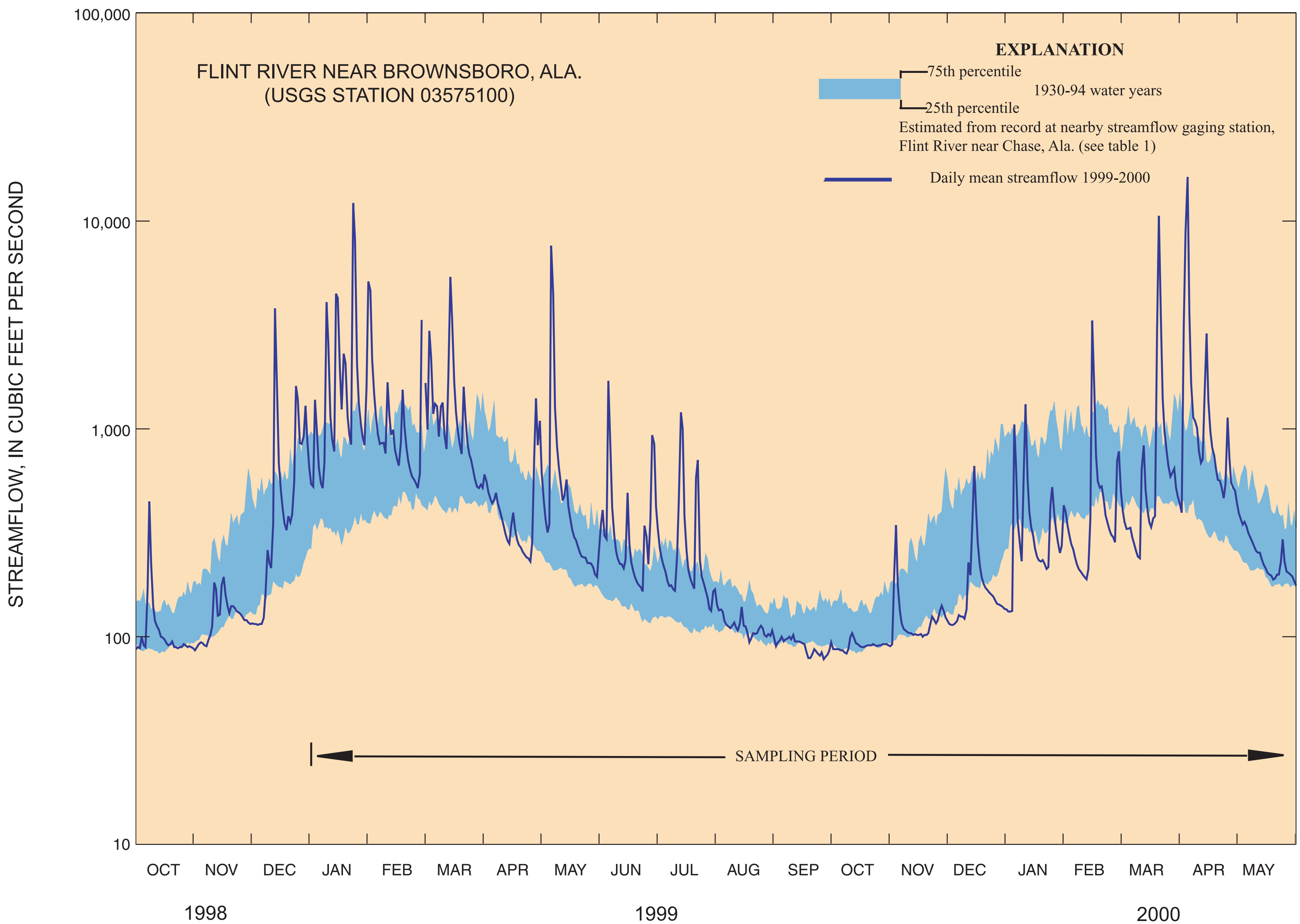


Figure 3. Daily mean streamflows in the Flint River during the fall of 1998 and 1999, and during the winter of 2000, were near or below the 25th percentile of daily mean streamflow for the period of record (1930-94).

States. The reader should note, however, that not all of these pesticides are used in the Flint River Basin. Further, several pesticides used in the Flint River Basin were not included in the analysis; for example, dicrotophos and PCNB (pentachloronitrobenzene).

Of the 113 pesticides analyzed in 75 stream samples from the Flint River and Hester Creek, 55 pesticides were detected at concentrations greater than 0.01 microgram per liter (μg/L). Of these 55 pesticides, 47 were detected in samples from the Flint River, and 35 were detected in samples from Hester Creek. Pesticides that are applied primarily to cotton fields accounted for 17 of the pesticides detected (more than for corn or soybeans). Twenty-one pesticides were detected at concentrations greater than 0.01 μg/L in 10 percent or more of the samples (Appendix B and fig. 4).

Pesticide-detection frequencies for the Flint River and Hester Creek sites were compared with a data set of 62 sites across the Nation that drained predominantly agricultural land (U.S. Geological Survey, 2001) (fig. 4). Fluometuron, norflurazon (both applied to cotton), and atrazine (applied to corn) were detected more frequently (by a margin of 15 percent or greater) in samples from the Flint River and Hester Creek when compared with the national data set. The higher detection frequency of norflurazon in the Flint River Basin may result from a greater density of cotton acreage and thus greater use of fluometuron in the Flint River Basin as compared with use in the agricultural basins represented in the national data set. This statement is supported by a comparison with a subset (15 sites) of the national data set representing cotton cultivation; detection frequencies of norflurazon were about the same for the subset compared with detection frequencies in the Flint River Basin. In contrast, the detection frequency of fluometuron in the Flint River was higher (by a margin of 35 percent) than detection frequencies in the other cotton cultivation basins, suggesting that some factor in addition to cotton acreage contributes to the high detection frequency in the Flint River Basin.

Comparison of Watershed Inputs to Detection Frequency, Instream Concentrations, and Yields

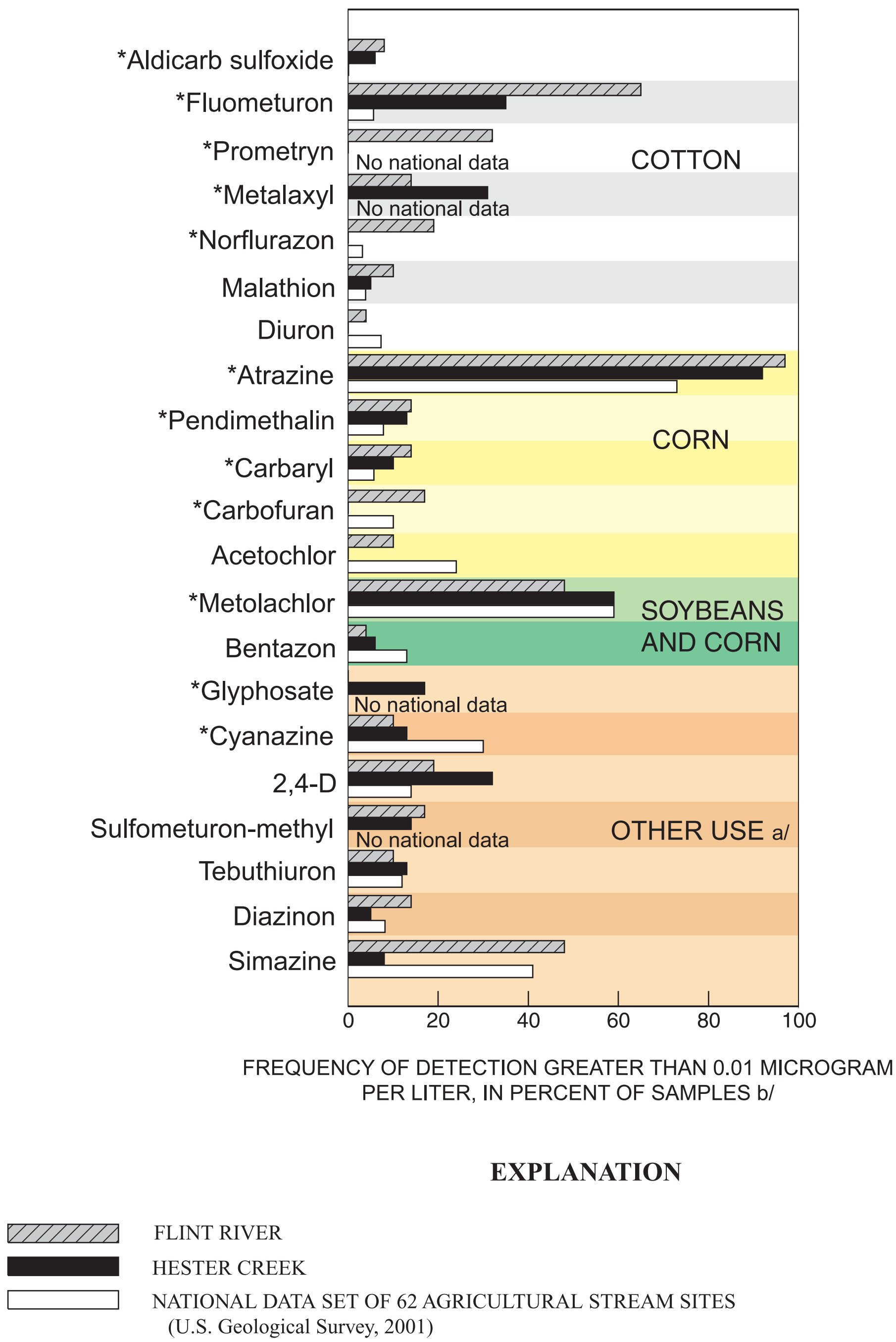
In general, the most heavily applied pesticides were detected most frequently, with the highest concentrations and the highest annual instream yields. For example, atrazine was detected in 100 and 93 percent of the samples from the Flint River and Hester Creek, respectively (Appendix B), and was transported instream from the Flint River and Hester Creek watersheds at the highest rate (an estimated 2.0 and 1.5 pounds per square mile per year [(lb/mi^2)/yr], respectively) (fig. 5 and Appendix B). The instream occurrence of a pesticide is related not only to its application rate, but also to physical and chemical properties controlling the pesticide's mobility in the environment. For example, the most heavily applied pesticide, glyphosate, was detected in only 17 percent of samples from Hester Creek; glyphosate is known to strongly adsorb to soil and, therefore, has a low potential for leaching to runoff or ground water.

Almost two-thirds of the pesticides were detected more frequently in samples from the Flint River than in samples from Hester Creek, although estimated inputs (amounts applied to crops) were higher, on a unit-area basis, for the Hester Creek watershed (fig. 5). Instream yields (unit-area exports) also generally were higher for the Flint River site; the most notable exception was metolachlor, a herbicide applied primarily to manage corn and soybean pests—the yield in Hester Creek was 3.5 (lb/mi^2)/yr compared to the Flint River where the yield was 1.4 (lb/mi^2)/yr. A comparison of concentration distributions during base flow between the two sites, however, showed the opposite pattern: maximum base-flow concentrations were higher in Hester Creek for almost two-thirds of the pesticides detected.

Export ratios were calculated for 10 pesticides as the ratio of watershed export (amount transported instream) to watershed input (amount applied to crops) (fig. 5 and Appendix B). Export ratios ranged from 0.06 percent (trifluralin) to 4.7 percent (norflurazon), and generally, except for metolachlor, were higher for the Flint River than for Hester Creek. The pesticides for which the highest export ratios (greater than 3 percent) were observed—atrazine, metolachlor, fluometuron, and norflurazon—are preemergent herbicides applied to the soil before crops have emerged, thus increasing the likelihood of transport in surface runoff. Metolachlor is commonly applied to the soil surface without incorporation into the soil, further increasing its potential for transport in runoff.

Variation of Concentrations with Season and Streamflow

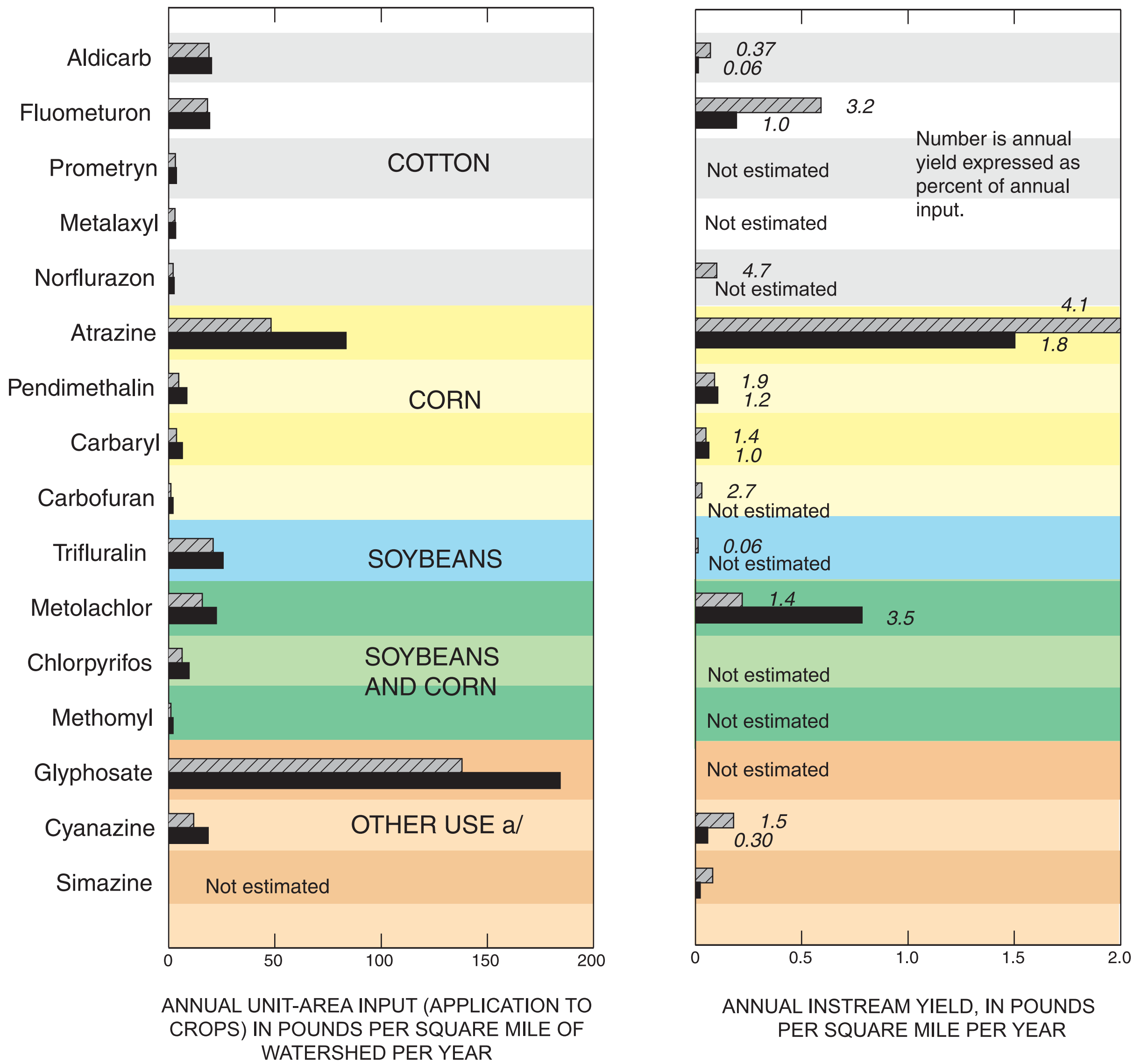
Variation of pesticide concentrations in the Flint River and Hester Creek generally coincided with the pesticide application period. Instream concentrations of the preemergent herbicide atrazine, applied March through May to corn fields, peaked in late April and May at the two stream sites (fig. 6a). Atrazine was detected in stream samples throughout the year, but at



Pesticides are grouped according to common application practices; asterisk indicates pesticides reported as used for crop pest management in the Flint River Basin. Pesticides are arranged within groups in order of estimated input amounts. Results are shown for pesticides detected in at least 10 percent of samples.

a/ OTHER USE refers to use on other crops or other combinations of cotton, corn, and soybeans.
b/ For comparison with a national data set, detection frequencies for aldicarb sulfoxide, fluometuron, norflurazon, diuron, bentazon, and 2,4-D were calculated using a higher (0.05 μg/L) threshold. The frequencies plotted for these pesticides, therefore, do not match values in Appendix B, which were calculated using the 0.01 μg/L threshold.

Figure 4. Detection frequency of pesticides for the Flint River and Hester Creek, 1999-2000, and for a national data set.



EXPLANATION

FLINT RIVER
HESTER CREEK

Annual instream yields were not estimated for prometryn, metalaxyl, norflurazon (at Hester Creek), carbofuran (at Hester Creek), trifluralin (at Hester Creek), chlorpyrifos, or methomyl because most of the observations were below the method detection limit.
Annual instream yields were not estimated for glyphosate because of the small sample set (six samples from Hester Creek, five samples from the Flint River).

a/ OTHER USE refers to use on other crops or other combinations of cotton, corn, and soybeans.

Figure 5. Pesticide use and instream yield for the Flint River and Hester Creek, 1999.

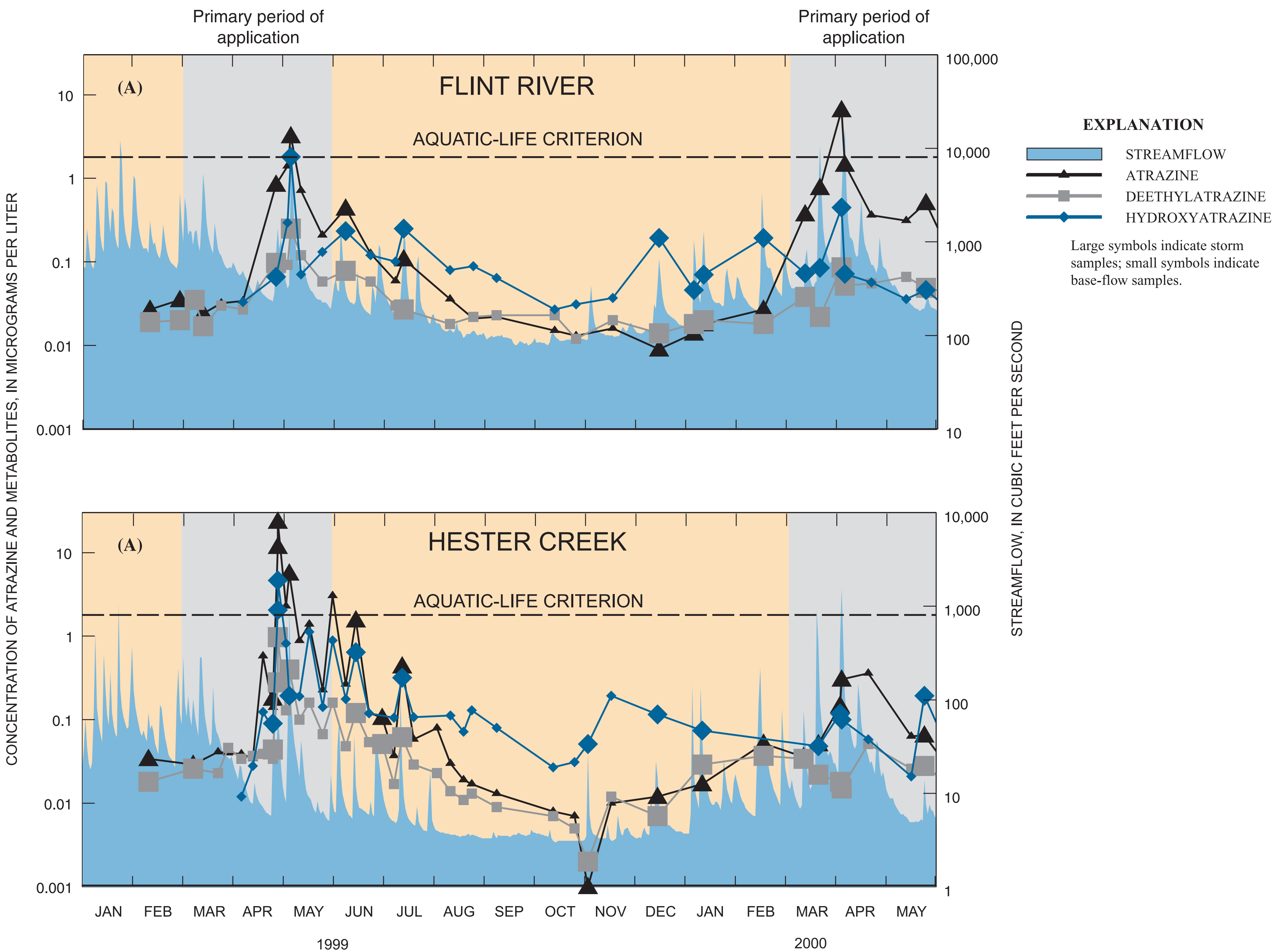


Figure 6. Streamflow and concentration of (A) atrazine and metabolites and (B) cyanazine for the Flint River and Hester Creek, 1999-2000.

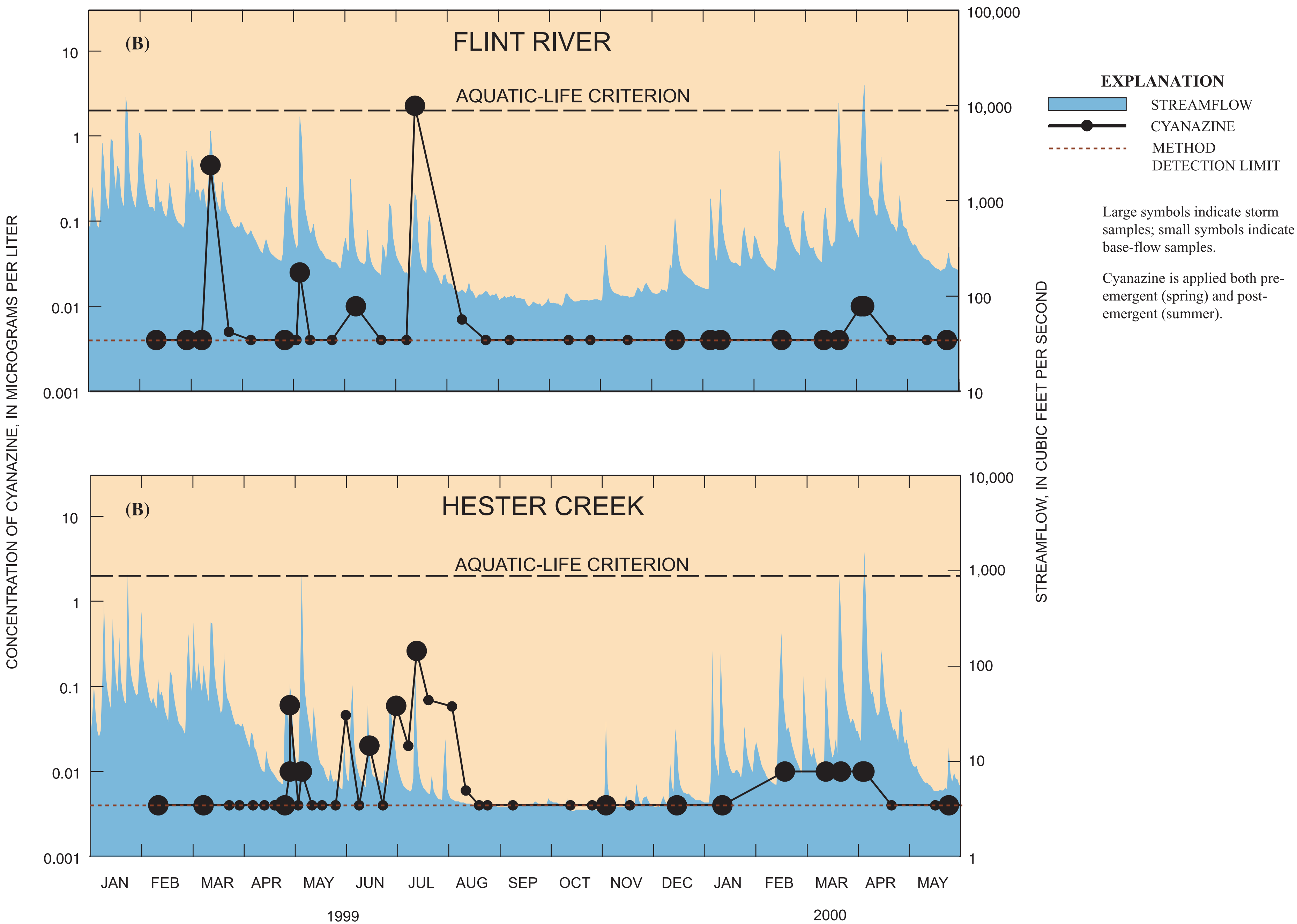


Figure 6. Streamflow and concentration of (A) atrazine and metabolites, and (B) cyanazine for the Flint River and Hester Creek, 1999-2000—Continued.

much lower concentrations (as low as 0.001 μg/L) when compared with April and May samples. Concentrations of the atrazine metabolite, hydroxyatrazine, persisted at higher levels (about 0.1 μg/L) throughout the year. Instream concentrations of cyanazine, which is applied as both a pre- and postemergent herbicide to cotton and corn fields, peaked in the spring and summer months (fig. 6b) corresponding to these different application periods. The lower concentrations of cyanazine observed during spring of 2000 compared with spring 1999 (fig. 6b) may be a result of the change in regulated use of cyanazine. Manufacture of cyanazine ceased at the end of 1999; use of remaining product is allowed during the period from 2000 to 2002, but use has been declining gradually since 1999 (U.S. Environmental Protection Agency, 1999a).

Concentrations of pesticides varied with streamflow as well as with season. Samples were categorized as either base flow or storm flow on the basis of hydrograph analysis and sample turbidity. Peak concentrations of almost all pesticides occurred during storm flows, indicating that the pesticides generally are transported by surface runoff (fig. 7). Concentrations do not increase during every storm, however, because a major factor affecting concentrations of pesticides in storm flow is the period of time between pesticide application and the occurrence of a storm.

Figure 7. Many pesticides are transported to nearby streams by surface runoff from cropland (cotton field in the Hester Creek watershed, April 3, 2000).

For some pesticides, such as atrazine (fig. 6a), concentrations in base-flow samples were almost as high as concentrations in some of the storm samples during the same season, indicating that concentrations in ground water also were elevated. For pesticides such as cyanazine (fig. 6b), concentrations in base-flow samples were low (less than 0.008 μg/L), but increased to detectable levels during a few storms. This pattern indicates that almost all of the mass of cyanazine is transported to the stream during runoff, with negligible amounts transported in ground water. The different base-flow transport patterns of atrazine and cyanazine can be explained by their different physical and chemical properties: residual cyanazine in the soil after application degrades more quickly to its metabolites than does atrazine, and thus, not as much of the parent compound is available for transport to streams in subsequent runoff or to the ground water. Transport of cyanazine metabolites in base flow was not examined because water samples were not analyzed for these metabolites.

Comparison of Concentrations with Criteria to Protect Aquatic Life

The environmental significance of the observed concentrations can be evaluated by comparing concentrations with water-quality criteria that were established to protect aquatic life. Aquatic-life criteria have been established for 23 of the 55 pesticides detected in samples from the Flint River and Hester Creek. Maximum concentrations of pesticides were generally less than the aquatic-life criteria; however, concentrations of atrazine, cyanazine, and malathion exceeded aquatic-life criteria in at least one sample each (fig. 8). Concentrations near or exceeding the aquatic-life criteria occurred from April through July, generally during storm flow (fig. 9). The pattern of concentrations for the insecticide malathion differed from other pesticides: concentrations in the Flint River exceeded the aquatic-life criterion in only one sample, during spring base flow rather than spring runoff, but remained within an order of magnitude of the peak concentration throughout the summer and fall. Concentrations of aldicarb sulfoxide, a metabolite of the insecticide aldicarb, were near, but below, the aquatic-life criterion. Aldicarb was detected in only one sample, suggesting that aldicarb degrades to its metabolite (which is equally toxic) either prior to transport to the stream or rapidly in stream.

Comparison of aquatic-life criteria with maximum (rather than median) concentrations is appropriate because the criteria specify maximum concentrations (acute toxicity) that should not be exceeded at any time (Environment Canada, 1999; International Joint Commission, 1989). The exceptions are the criteria for chlorpyrifos and malathion, which specify the maximum concentration for a 4-day exposure period once every 3 years (U.S. Environmental Protection Agency, 1999b). Pesticide criteria generally are based on the results of single-chemical toxicity tests, and do not consider the synergistic effects of exposure to low-level pesticide mixtures, such as the mixtures detected in samples from the Flint River and Hester Creek. For example, every stream sample had detectable levels of at least two pesticides; 64 percent of the samples contained mixtures of at least five pesticides.

Spatial Variation of Concentrations During Base Flow

Of the 113 pesticides analyzed, 34 were detected at concentrations greater than 0.01 µg/L in at least one of the base-flow samples from the eight stream sites in the Flint River Basin. Variation in concentrations of pesticides during base flow (May 12, 1999) is shown in figure 10. Concentrations during May 1999 did not exceed aquatic-life criteria for any pesticide except for malathion, which exceeded the criterion of 0.1 µg/L at two sites: Mountain Fork Creek (site S3) and the Flint River at Brownsboro, Ala. Base-flow concentrations during May 1999 were close to (within 20 percent of) the criteria for atrazine (at Brier Fork, site S4, fig. 10) and the insecticide methyl azinphos (also at Brier Fork; U.S. Geological Survey, unpub. data, 2001). Base-flow concentrations of pesticides at the eight sites during September 1999 (not shown on fig. 10; U.S. Geological Survey, unpub. data, 2001) were generally less than the method detection limit (MDL) or, for atrazine, were less than 0.03 µg/L.

The spatial pattern of concentrations of selected pesticides during May 1999 base flow was compared to the pattern of various watershed characteristics including percentage of cultivated land in the watershed and acreage of cotton, corn, and soybeans (table 2). The highest base-flow concentrations of aldicarb sulfoxide (fig. 10) and fluometuron were detected in the watersheds with the greatest density of cotton acreage in the watershed. This relation coincides with pesticide use; aldicarb and fluometuron are both applied to cotton fields at planting time in April.

Base-flow concentrations of pesticides (other than malathion) in Hester Creek and the Flint River were similar to those at the tributary sites (S1-S6, fig. 10) during the May and September 1999 monitoring periods, suggesting that base-flow concentrations documented through intensive monitoring at Hester Creek and Flint River are typical of base-flow conditions throughout the Flint River Basin. Base-flow concentrations of malathion, however, ranged much more widely between sites; the base-flow concentration in Mountain Fork Creek (site S3) during May 1999 was almost 1,000 times higher than its concentration in other tributaries. The elevated concentration of malathion in Mountain Fork Creek probably contributed to the malathion detected in the Flint River on the same day, and also may account for detectable concentrations of malathion in base flow in the Flint River throughout the year (fig. 9).

Fecal-Indicator Bacteria

Fecal pollution impairs the quality of streams and rivers for recreational use and adversely affects fish and aquatic life. The following discussion addresses impairment of recreational uses only. Consumption of fecal-contaminated water can cause digestive tract infections, and immersion alone can result in infections of the eyes, ears, nose, and throat. Fecal-indicator bacteria such as *Escherichia coli* (*E. coli*) typically are not disease-causing (pathogenic) bacteria but can be correlated to the presence of human enteric

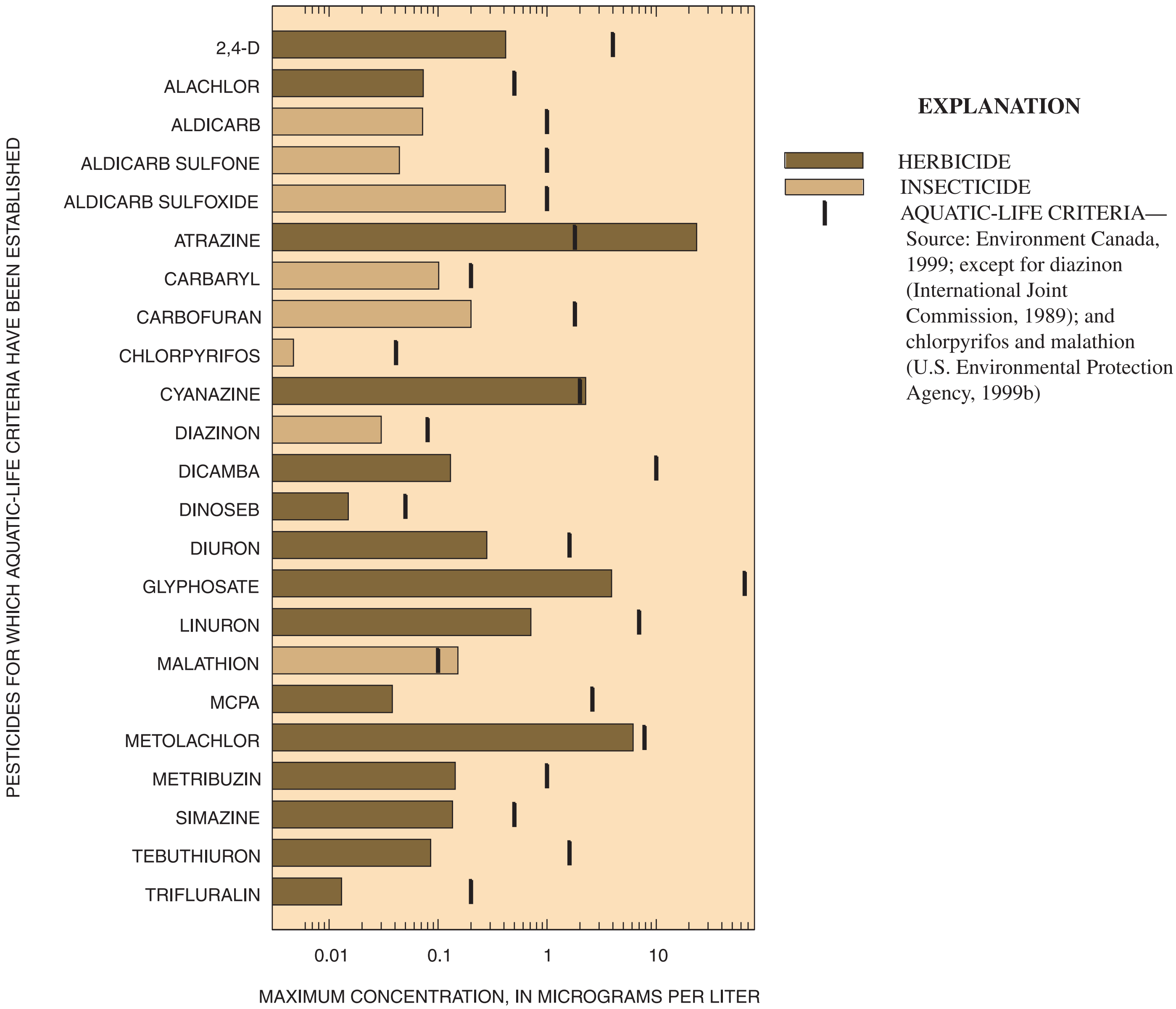


Figure 8. Maximum concentrations of pesticides and aquatic-life criteria for the Flint River and Hester Creek, 1999-2000. Concentrations were below the aquatic-life criteria for all pesticides except for atrazine, cyanazine, and malathion. The aquatic-life criteria were based on the results of single-chemical toxicity tests, and do not consider the synergistic effects of low-level pesticide mixtures.

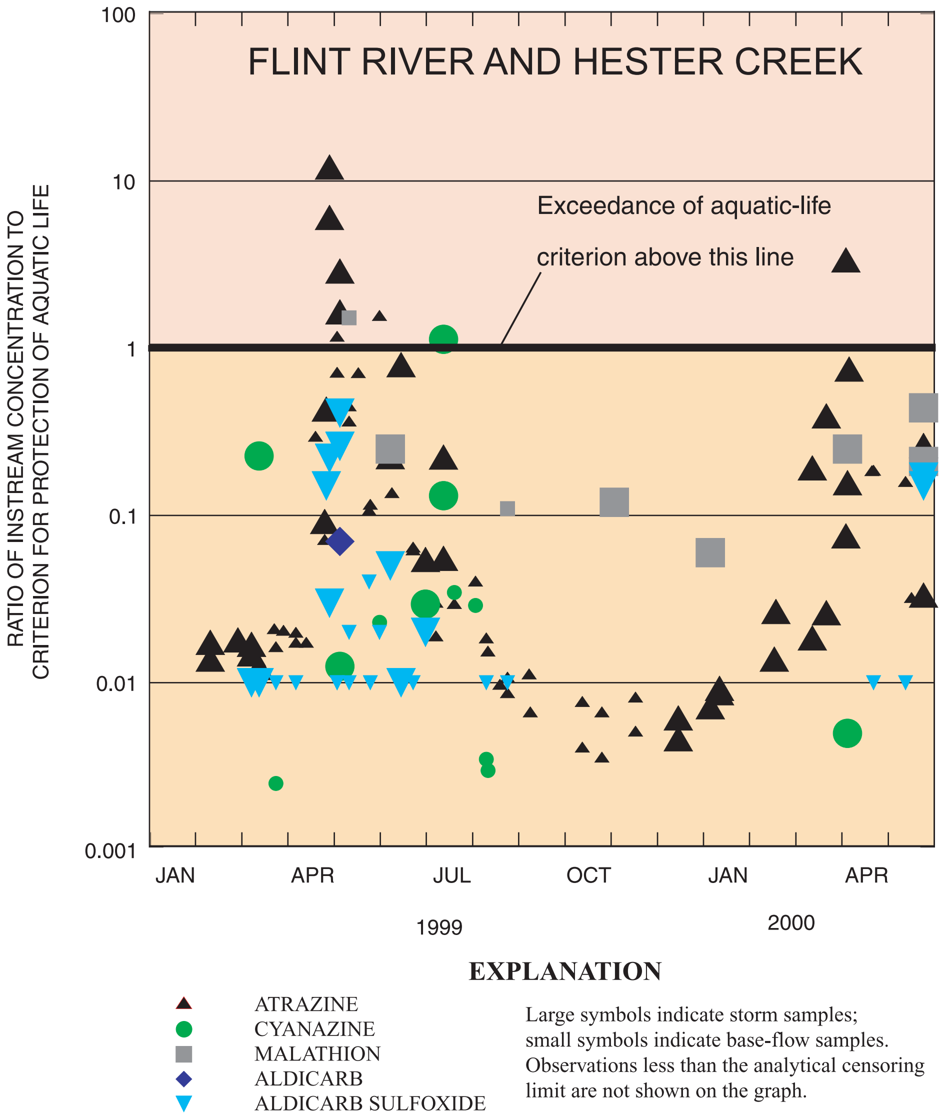


Figure 9. Relation of exceedances of aquatic-life criteria to season and to streamflow for selected pesticides for the Flint River and Hester Creek, 1999-2000. Concentrations near or exceeding the aquatic-life criteria occurred from April through June, and generally during storm flow.

pathogens, and can consequently be used as a measure of whether water is safe for recreational contact. The recommended criterion for *E. coli* concentrations indicating risk to human health in swimming waters is 126 colonies per 100 milliliters (col./100 mL), which applies to the geometric mean of samples collected over a 30-day period. Epidemiological studies at freshwater beaches have indicated that exposure to this level of *E. coli* concentrations causes 8 illnesses per 1,000 swimmers (U.S. Environmental Protection Agency, 1986, table 4). The *E. coli* criterion for a single sample collected from a water body with light to moderate recreational use is 406 col./100 mL.

Concentrations of *E. coli* exceeded the U.S. EPA criterion of 126 col./100 mL for human health during certain summer months in the Flint River and Hester Creek. Monthly mean concentrations of *E. coli* for the Flint River, in the reach used for recreational boating (figs. 2 and 11), were less than the criterion in June (111 col./100 mL) and August (45 col./100 mL) and exceeded the criterion during July (255 col./100 mL). Monthly mean concentrations of *E. coli* in Hester Creek exceeded the criterion in June (760 col./100 mL), July (640 col./100 mL), and August (380 col./100 mL). The monthly mean concentrations were calculated as the geometric mean of

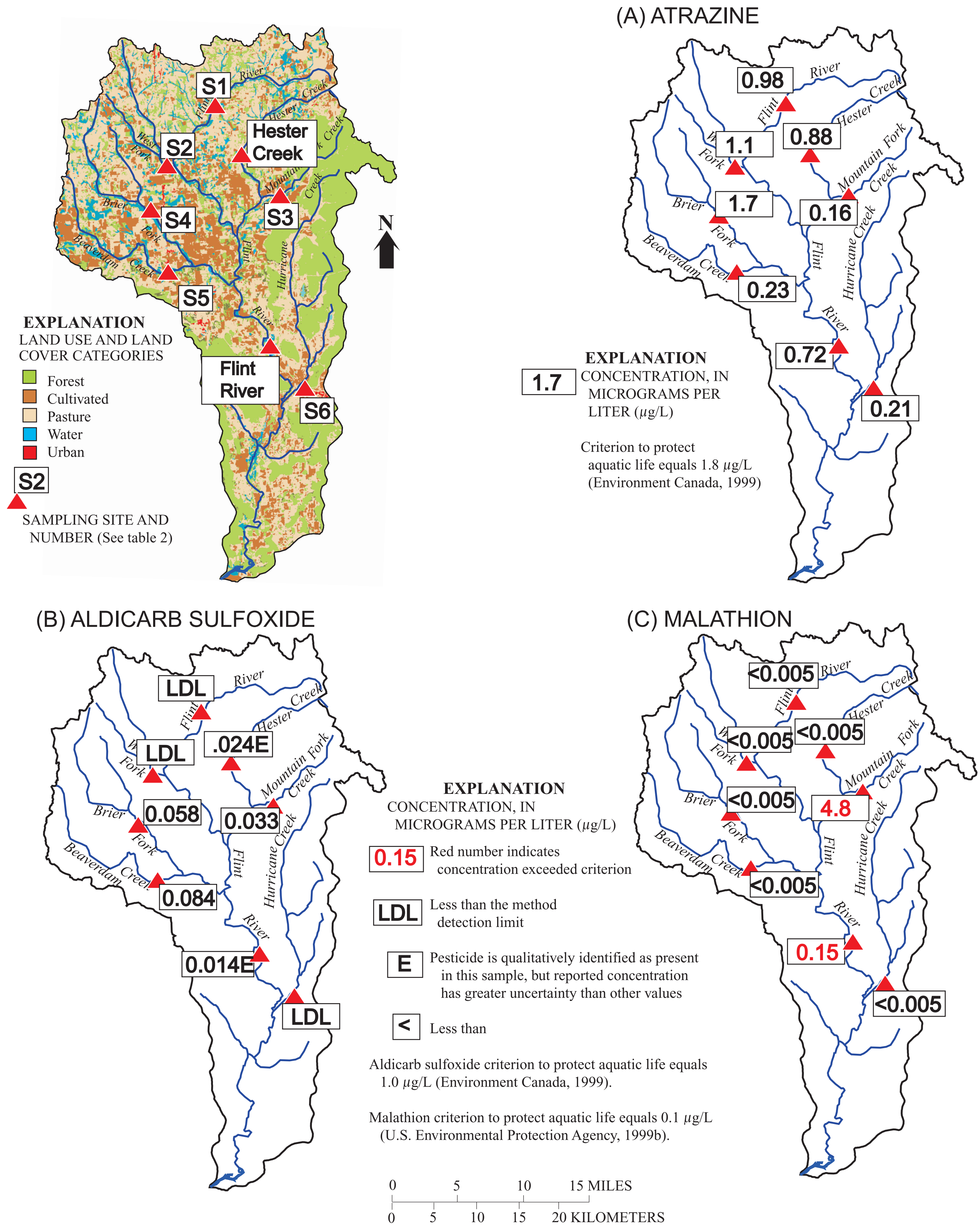


Figure 10. Land use and land cover, and spatial variation of concentrations of (A) atrazine, (B) aldicarb sulfoxide, and (C) malathion in the Flint River Basin during base flow, May 1999.

Figure 11. The Flint River, designated as a canoe trail by the Madison County Commission in Alabama, is a popular water recreation resource used for canoeing and tubing. (Photograph by Susan F. Weber, Flint River Conservation Association.)

three samples (Flint River) or four samples (Hester Creek) collected over a 30-day period.

Variation of Concentrations with Streamflow and Turbidity

Concentrations of *E. coli* in the Flint River and Hester Creek are significantly different ($p < 0.001$, Wilcoxon rank-sum test) between base flow and storm flow (fig. 12). Concentrations of *E. coli* in the 11 base-flow samples from the Flint River, in the reach used for recreational boating, generally did not exceed the single-sample criterion, whereas *E. coli* concentrations in 12 out of the 13 storm samples exceeded the single-sample criterion. The median value for all base-flow samples from the Flint River was 50 col./100 mL, less than both the single-sample and geometric-mean criteria. However, the median value for samples collected 3 to 6 days after a storm was higher, almost equal to the geometric mean criterion, suggesting that the bacteriological risk remains elevated at least 6 days after a storm. Concentrations of *E. coli* were higher in Hester Creek when compared with the Flint River concentrations; concentrations in 3 of 14 base-flow samples from Hester Creek exceeded the single-sample criterion, and *E. coli* concentrations in 14 of 16 storm samples, and concentrations in 7 of 9 samples collected 3 to 6 days after a storm, exceeded the single-sample criterion (fig. 12).

Concentrations of *E. coli* did not vary as greatly with season ($p > 0.40$; Wilcoxon rank sum test) as with streamflow. Mass loading of *E. coli* was much greater in winter, however, because of more frequent occurrences of storms. Based on instream load calculations, 84 percent of the estimated annual instream load of *E. coli* in the Flint River was calculated for the 3-month period of December through February, whereas only 2 percent was calculated for the 3-month period of June through August; for Hester Creek, 54 percent of the estimated annual load was calculated for the period of December through February, and 2 percent for the period of June through August.

Concentrations of *E. coli* were strongly correlated with turbidity for the Flint River throughout the range of concentration values ($r > 0.9$, $p < 0.001$ for log-transformed data); correlation was not as strong for Hester Creek, especially for *E. coli* concentrations less than 1,000 col./100 mL (fig. 13). Turbidity, therefore, may be useful as a surrogate for estimating concentrations of *E. coli* in the Flint River. For example, a turbidity value of 22 nephelometric turbidity units (NTU) was estimated from a linear regression of the data (fig. 13) for the Flint River to be the value at which the *E. coli* concentration would be expected to exceed the single-sample criterion (406 col./100 mL).

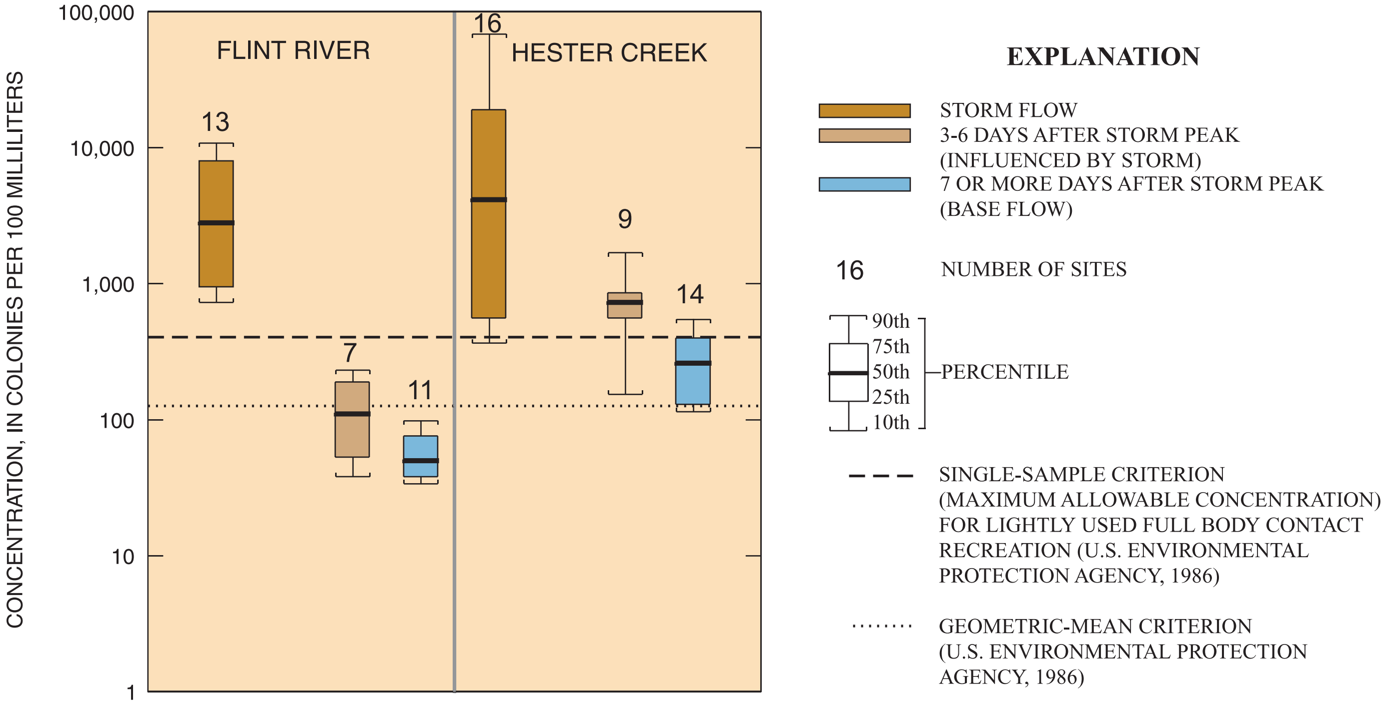


Figure 12. Concentrations of *E. coli* in the Flint River and Hester Creek during storm flows frequently exceed U.S. Environmental Protection Agency criteria for recreation. *E. coli* concentrations remain elevated at least 6 days after storm peaks in streamflow.

Spatial Variation of Concentrations During Base Flow

E. coli-concentration data were collected from the network of eight stream sites in the Flint River Basin during base flow in May and September 1999 (fig. 14). Concentrations exceeded the single-sample criterion for recreation (406 col./100 mL) at two sites: Hester Creek and West Fork Flint River, site S2. The spatial pattern of *E. coli* concentrations was compared to the pattern for various watershed characteristics including percentage of pastureland and percentage of cultivated land, density of livestock population, and failing septic systems (table 2). The reader should note that input from livestock is not necessarily represented by density of population; stream access may also be an important factor, but one that was not considered in this analysis. Correlation was significant ($r > 0.9$, $p < 0.006$) between *E. coli* concentration during May 1999 and density of livestock population (highest for Hester Creek). A weaker correlation ($r = 0.7$, $p = 0.10$) was observed between *E. coli* concentrations during September 1999 and density of failing septic systems (highest for West Fork Flint River, site S2). These correlations suggest that, of the four variables considered, livestock populations were the most likely source of fecal material to streams during base flow in May 1999; whereas failing septic systems were the most likely source during base flow in September 1999, when sampling followed a prolonged 40-day dry period. Correlations should be interpreted with caution, however, because of the small number of observations ($n = 8$).

The *E. coli*-concentration data from the spatial network can be used to identify which tributaries in the Flint River Basin contribute the largest amount of fecal material to the Flint River during base flow. During May 1999, Hester Creek contributed the largest amount (41 percent) of the tributary load to the Flint River, and Beaverdam Creek (site S5) contributed the second largest amount (26 percent). Bacterial loading differed during September 1999 after a prolonged dry period, when West Fork Flint River (site S2) contributed the largest amount (56 percent).

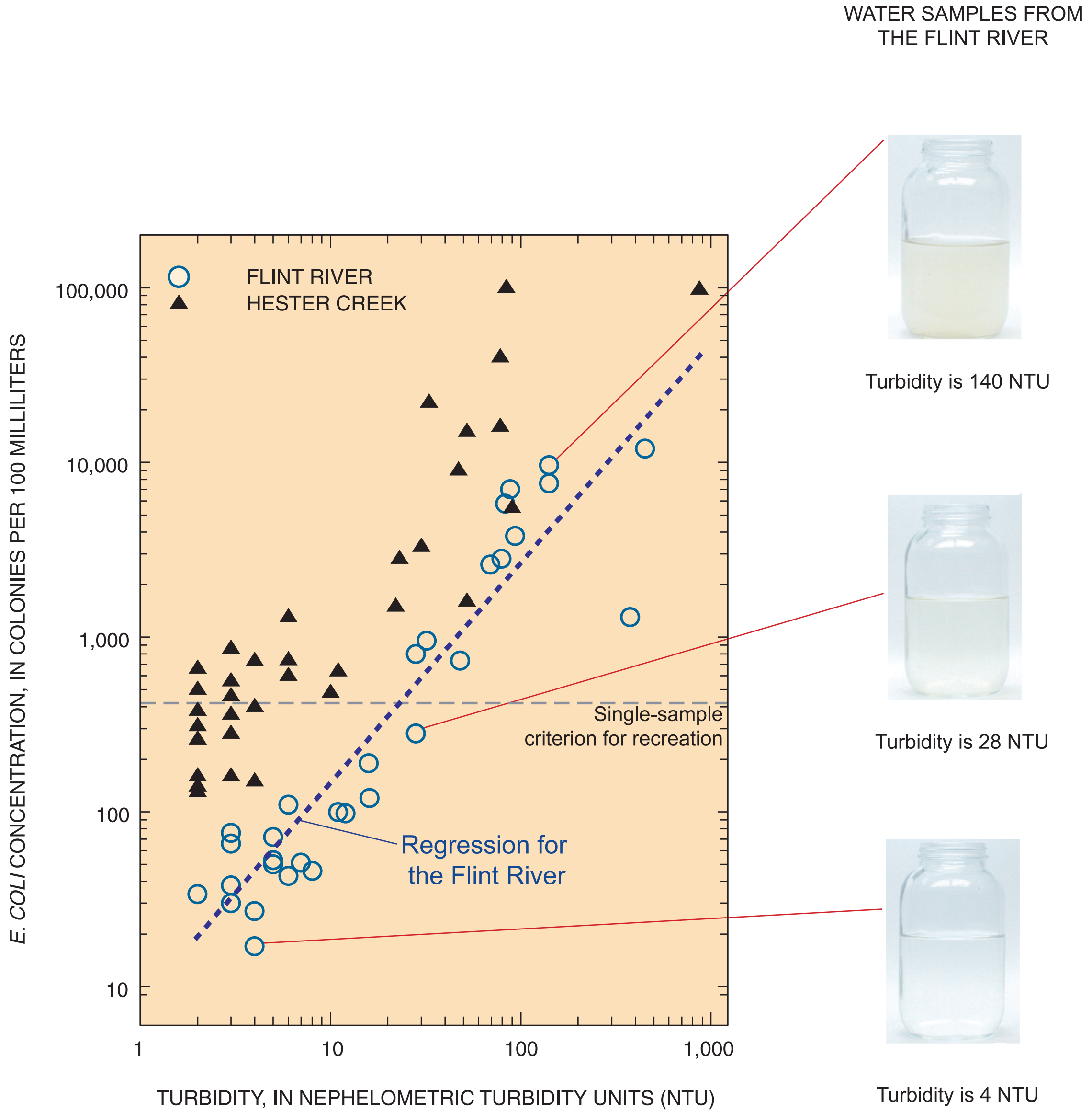


Figure 13. *E. coli* concentration and turbidity for the Flint River and Hester Creek. The strong correlation between *E. coli* concentration and turbidity for the Flint River and Hester Creek suggests that turbidity might be useful as a surrogate for estimating concentrations of *E. coli*. The photographs of water samples from the Flint River demonstrate the physical appearance of water with turbidity values below, near, and above 22 NTU, the value with expected *E. coli* concentration equal to the single-sample criterion for recreation.

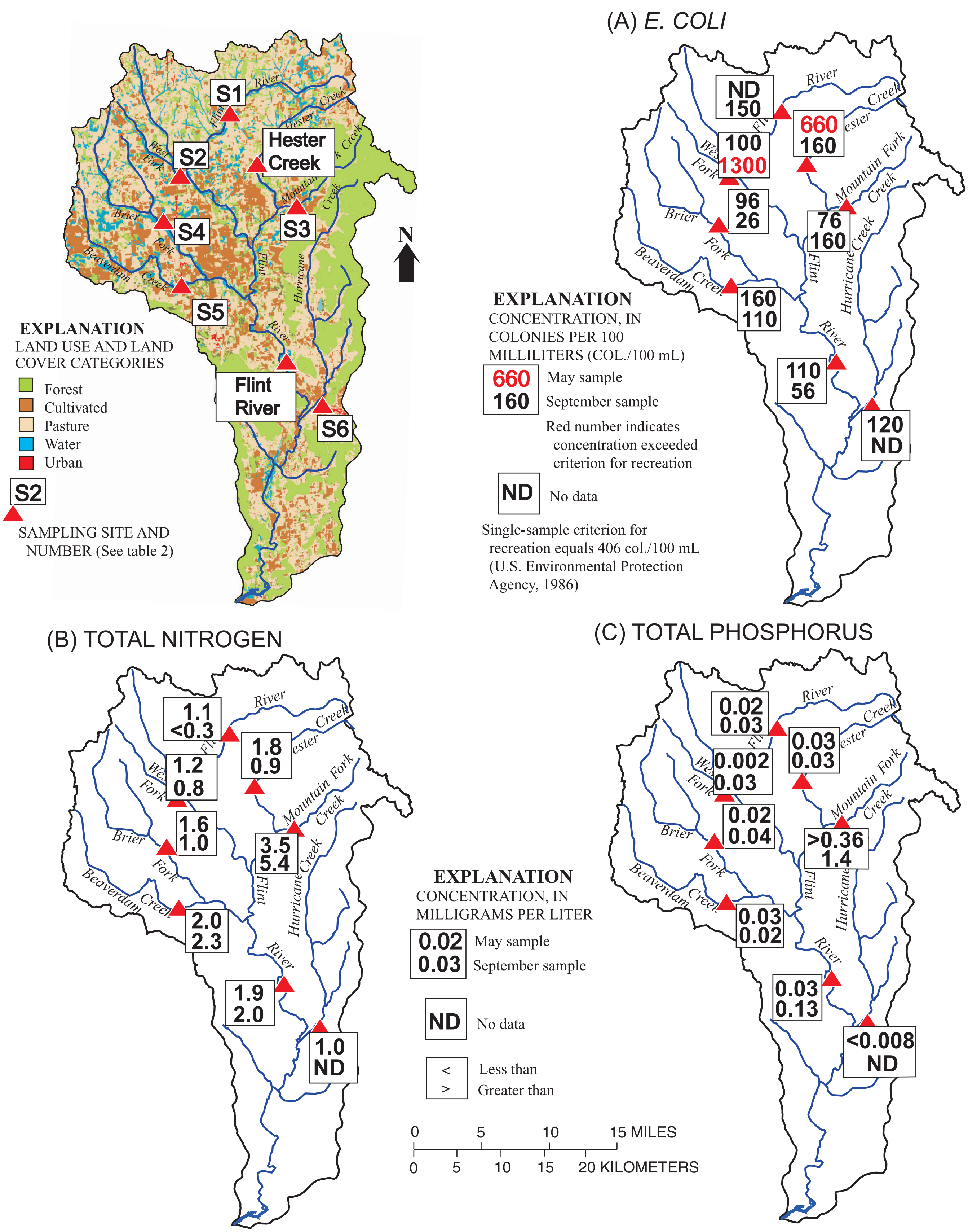


Figure 14. Land use and land cover, and spatial variation of concentrations of (A) *E. coli*, (B) total nitrogen, and (C) total phosphorus in the Flint River Basin during base flow, 1999.

Nutrients

Nutrient overenrichment of streams can promote excess growth of aquatic plants, resulting in recreational impairment and adverse effects on aquatic life. In the Flint River Basin, Hester Creek and its tributaries and the upper part of the Flint River (from the Alabama/Tennessee State line to headwaters) and its tributaries were assessed as impaired by nutrients in 1998 (fig. 2) (Tennessee Department of Environment and Conservation, 2000).

Variation of Concentrations with Season and Streamflow

Concentrations of the nutrients nitrogen and phosphorus in samples from the Flint River generally exceeded thresholds indicating eutrophic potential, whereas concentrations in samples from Hester Creek generally were below the thresholds (fig. 15). The threshold indicating eutrophic potential should be compared with conditions during the summer period of aquatic-plant growth (Dodds and others, 1998). The median total nitrogen concentrations for the Flint River and Hester Creek during the summer growth period were 2.0 and 1.2 milligrams per liter (mg/L), respectively, compared with a threshold value of 1.5 mg/L for temperate streams. The median total phosphorus concentrations for the Flint River and Hester Creek during the summer growth period were 0.12 and 0.05 mg/L, compared with a threshold value of 0.075 mg/L for temperate streams.

Comparisons of the thresholds indicating eutrophic potential with the Flint River Basin data during 1999 should be made with caution for the following reasons.

1. Nutrient concentrations above the threshold do not necessarily cause eutrophication because other factors, such as turbidity and stream shading, influence the relation between nutrient concentrations and aquatic-plant productivity.
2. Conversely, eutrophication may occur even where observed nutrient concentrations are well below the threshold.
3. Comparison of nutrient concentrations in 1999 with thresholds may be of limited use for evaluating long-term conditions in the Flint River Basin because of the below-normal rainfall and streamflow during the sampling period.

The seasonal pattern of nitrogen (specifically nitrate) and phosphorus concentrations differed between the Flint River and Hester Creek sites. Base-flow concentrations of nitrate (fig. 15) and dissolved phosphorus in Hester Creek were significantly lower ($p < 0.05$, Wilcoxon rank sum test) during the period August through November 1999 when compared with the rest of the study period; this pattern partly is attributed to nutrient uptake by aquatic plants. In contrast, base-flow concentrations of these constituents in the Flint River during the summer equaled or exceeded base-flow concentrations during other seasons. The higher base-flow concentrations of nitrate and phosphorus during the summer accounted for the higher median concentration in the Flint River when compared with concentrations in Hester Creek and also when compared with threshold values indicating eutrophic potential. Base-flow concentrations of nitrogen and phosphorus also were elevated in the tributary Mountain Fork Creek during May and September (discussed in the following section).

Estimates of unit-area inputs of nitrogen and phosphorus to the watersheds for the Hester Creek and Flint River sites are similar, except for inputs from livestock waste, which are higher (almost double) for Hester Creek when compared with the Flint River (Appendix C). In contrast to unit-area inputs, annual instream yields for nitrogen and phosphorus were higher for the Flint River when compared with Hester Creek: 3.0 and 2.1 tons per square mile per year [(tons/mi^2)/yr], respectively, for total nitrogen, and 0.34 and 0.20 (tons/mi^2)/yr, respectively, for total phosphorus (Appendix C). Consequently, the ratios of unit-area export (instream yield) to unit-area input for nitrogen and phosphorus are about three times greater for the Flint River when compared with Hester Creek (Appendix C). This disparity in the ratio may be due to differences in the processes by which the inputs from the two watersheds are transported from the land surface to the stream channel, or to inaccurate or inappropriate estimates of input, or to other important sources of nutrients not quantified in this analysis.

Despite differences between the two sites in seasonal- and streamflow-related patterns of concentrations and differences in median concentrations and instream yield, estimates of flow-weighted mean concentrations of nutrients compare closely (Appendix C; flow-weighted mean concentration is calculated as the ratio of annual instream load to annual mean streamflow). The flow-weighted mean concentrations for water year 1999 for both sites were 1.8 and 0.2 mg/L for total nitrogen and total phosphorus, respectively.

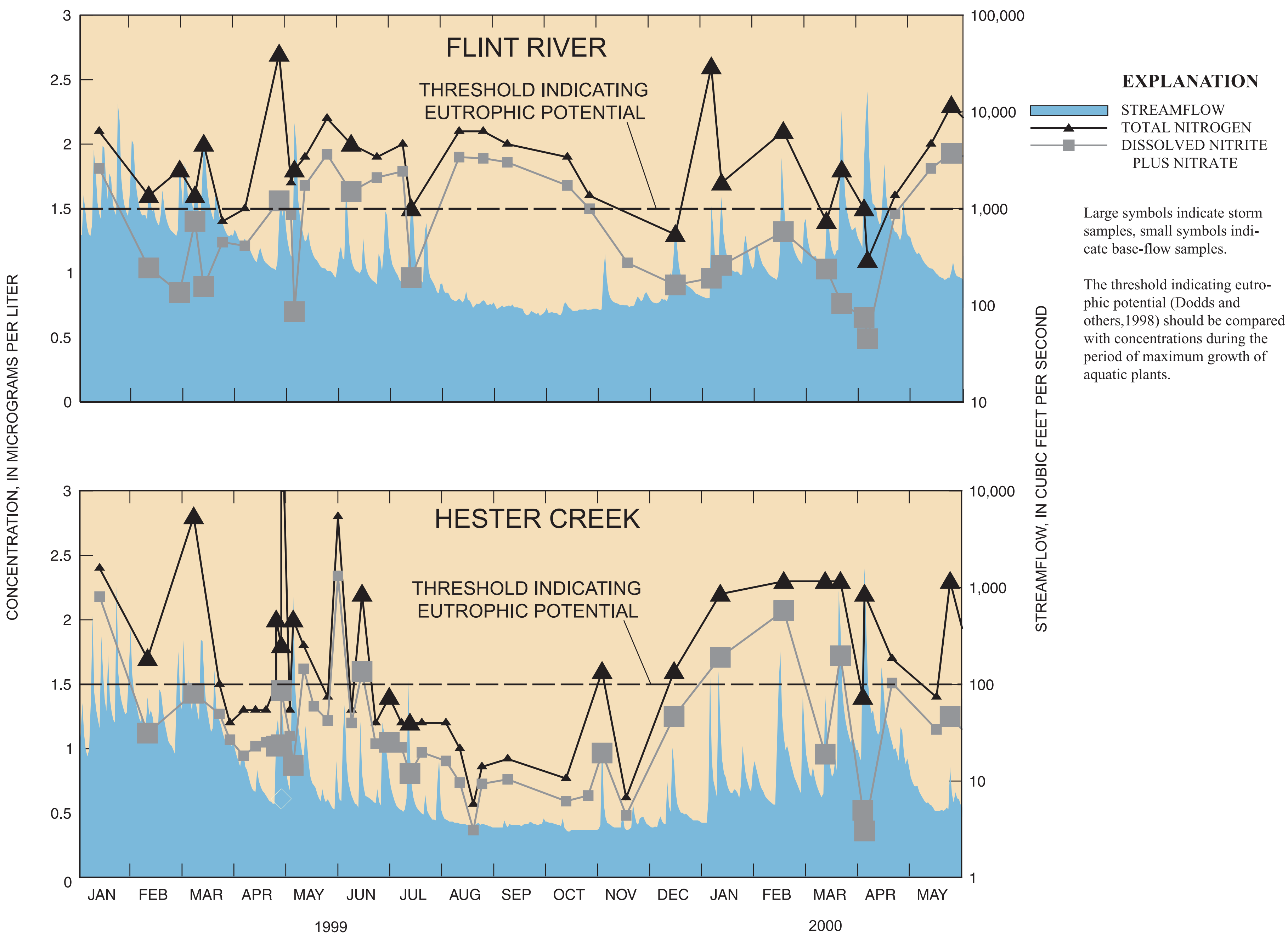


Figure 15. Streamflow and concentration of total nitrogen and dissolved nitrite plus nitrate for the Flint River and Hester Creek, 1999-2000.

These values can be placed in a regional context by comparing with the statistical distribution of estimated values of annual flow-weighted mean concentrations from two different USGS nutrient data sets from the southeastern region of the United States. The first data set is from 16 streams draining undeveloped basins, monitored during 1990-95 (Clark and others, 2000). The second data set is from 24 streams draining mainly agricultural basins (agricultural land use in the watershed exceeds 50 percent) that were monitored during 1993-97 (J. Stoner, U.S. Geological Survey, written commun., 2000). The values for total nitrogen and total phosphorus at Flint River and Hester Creek are well above the 90th percentile values of their respective distributions for undeveloped basins in the southeastern region of the United States (fig. 16), indicating that these sites are nutrient enriched compared with background levels. When compared with concentrations from the set of 24 agricultural basins in the southeastern region, the concentrations from the Flint River and Hester Creek were slightly above the regional median.

Spatial Variation of Concentrations During Base Flow

Nutrient-concentration data were collected from the network of eight stream sites in the Flint River Basin during base flow in May and September 1999 (fig. 14). The spatial pattern of nutrient concentrations was compared with the pattern for various watershed characteristics including percentage of pastureland and percentage of cultivated land; acreage of cotton, corn, and soybeans; and density of livestock and failing septic systems (table 2). Base-flow nitrogen concentrations did not correlate with any of these watershed characteristics; concentrations were highest for Mountain Fork Creek (site S3), but watershed characteristics that would indicate high nutrient input were not in the high ends of their respective ranges for the Mountain Fork Creek watershed (table 2). When this site was removed from the data set ($n = 7$ for the trimmed set), correlation was significant ($p = 0.01$) between percent of watershed in cultivated land and total nitrogen concentration, and was stronger for total nitrogen concentration during September ($r = 0.9$) when compared with the concentration during May ($r = 0.7$). Correlation also was significant ($r = 0.8$, $p = 0.02$) between cotton acreage and total phosphorus concentration (May only). Correlations were not significant between density of livestock or failing septic systems and base-flow nutrient concentrations; however, this analysis may not accurately evaluate the contribution from livestock, as stream access by livestock was not considered.

The elevated concentrations of nitrogen and phosphorus at Mountain Fork Creek (site S3) may be caused by input from a nutrient source not included in this analysis. During a separate base-flow sampling project of the Mountain Fork Creek watershed on May 15, 2000, concentrations of dissolved nitrate were elevated (greater than 2 mg/L) in samples from three sites near the downstream end of Mountain Fork Creek, but concentrations were at trace levels (0.1 mg/L) in samples from two upstream sites (U.S. Geological Survey, unpub. data, 2001). The Mountain Fork Creek tributary made the largest contribution of nutrients to the Flint River during base flow; 42 and 74 percent of the summed tributary load of total nitrogen during May and September 1999 sampling, respectively, and 85 and 98 percent of the summed tributary load of total phosphorus during May and September 1999 sampling, respectively. The elevated concentrations of nitrogen and phosphorus in Mountain Fork Creek may have contributed to the elevated base-flow concentrations of nitrate and phosphorus observed in the Flint River as compared to Hester Creek (discussed in the previous section).

RELATION OF STORM TRANSPORT OF SELECTED PESTICIDES IN THE FLINT RIVER BASIN TO CONCENTRATIONS IN THE SOURCE FOR DRINKING WATER FOR THE CITY OF HUNTSVILLE, ALABAMA

About 40 percent of the public water supply for the City of Huntsville, Ala., is withdrawn from the right bank of the Tennessee River at mile 334 (South Parkway Water Treatment Plant), about 5 mi. downstream of the confluence with the Flint River (also on the right bank, at river mile 339). The watershed and presumed source area for the Tennessee River at the Huntsville intake encompasses a 25,000-mi^2 area that is predominantly (about 60 percent) forested land. Numerous impoundments along the Tennessee River upstream from the Huntsville intake regulate streamflow and dampen short-term fluctuations in streamflow and water quality caused by runoff. During storms, however, the quality of water at the intake is greatly affected by the smaller (570 mi^2),

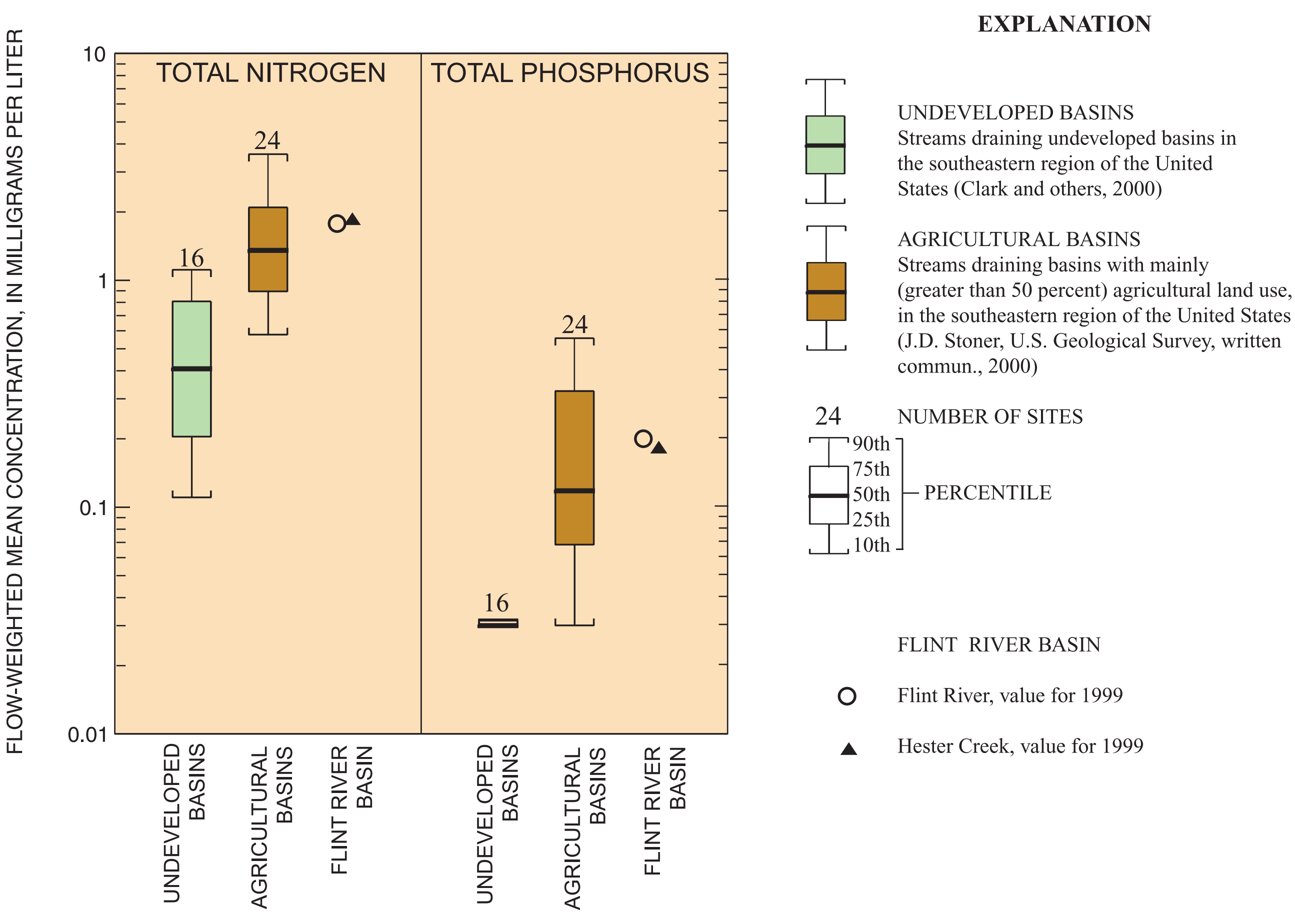


Figure 16. Flow-weighted mean concentrations of total nitrogen and total phosphorus for the Flint River and Hester Creek, 1999, as compared to undeveloped and agricultural basins in the southeastern region of the United States.

predominantly agricultural Flint River Basin as a result of two factors: larger percentages of flow from the Flint River to the regulated Tennessee River during storms (as high as 30 percent, compared with the drainage-area ratio of 2 percent), and incomplete mixing at the confluence of the Flint and Tennessee Rivers. Comparison of turbidity measured in samples from the Huntsville intake water with runoff events in the Flint River (fig. 17) demonstrates the influence of inputs of streamflow from the Flint River on suspended material in the Tennessee River and at the intake.

One of the objectives of this study was to determine whether the observed incomplete mixing in the Tennessee River also affects transport of dissolved constituents; that is, constituents that may not be removed during treatment (filtration) of the intake water supply. Other studies have shown that several pesticides commonly transported in the dissolved phase (for example, atrazine, cyanazine, and metolachlor, which were detected frequently at sites throughout the Flint River Basin) are not completely removed during conventional water treatment (Miltner and others, 1989). A special storm sampling project was conducted April 2-5, 2000, with the assistance of staff of the South Parkway Water Treatment Plant, in order to test the hypothesis that during high flow events in the Flint River Basin, the quality of water (both suspended and dissolved material) withdrawn from the right bank of the Tennessee River at the South Parkway intake is more similar to water quality of the Flint River than to water quality of the main channel of the Tennessee River. Rainfall amounts during April 2-5 were greater in the Flint River Basin (about 5 in.) than in the rest of the Tennessee Valley (about 1 in.); consequently, the Flint River contributed almost 15 percent of the total streamflow in the Tennessee River at mile 334 (TRM 334) during this

EXPLANATION

FLINT RIVER STREAMFLOW

INTAKE TURBIDITY (Wayne Miller, City of Huntsville, written commun., 2000)

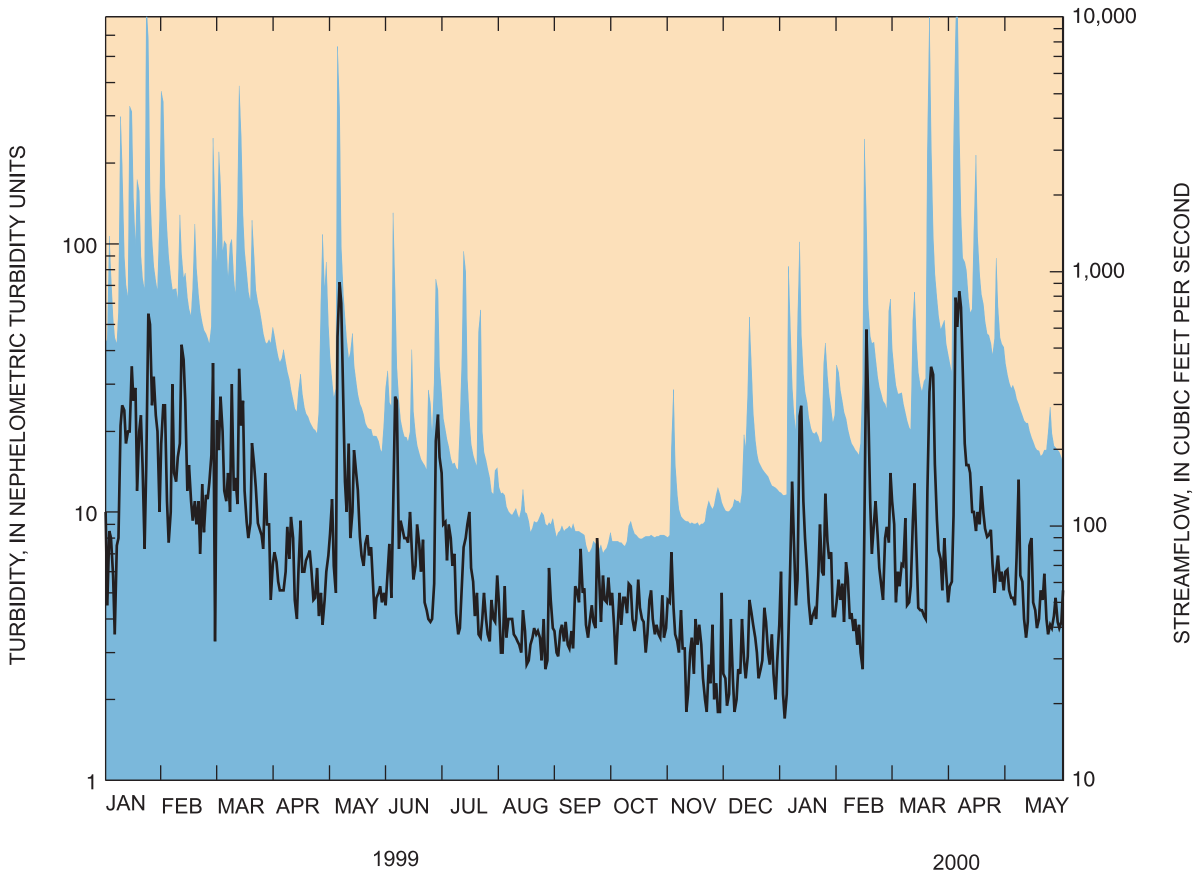


Figure 17. Relation between turbidity of intake water for the City of Huntsville water-treatment plant (South Parkway Plant) and streamflow in the Flint River near Brownsboro, Ala., 1999-2000.

period. The sampling sites for the Tennessee River are described in tables 1 and 2. Streamflow and atrazine concentrations in the Flint and Tennessee Rivers during the storm are shown in figure 18.

In water samples collected at the South Parkway intake, peak concentrations of all target pesticides for which drinking-water standards have been established were below those standards. Comparison of concentrations among the four sites supports the hypothesis that the chemical load from the Flint River (entering at TRM 339) strongly influenced water quality at TRM 334 near the intake during this storm. Concentrations of atrazine (fig. 18), acetochlor, carbofuran, diazinon, and metolachlor were at least a factor of five times greater in the intake water compared to the Tennessee River upstream from the Flint River. In addition, the higher concentrations in the intake and right channel of the Tennessee River main stem compared with the lower concentrations in the left channel of the main stem near Hobbs Island (all at TRM 334) indicate that the mass of dissolved chemicals contributed by the Flint River is not completely mixed with the Tennessee River between TRM 339 and TRM 334, influencing water quality more strongly than would be expected from mass balance considerations. For example, the expected peak concentration of atrazine in the intake water (based on mass balance calculations using data from the Flint River and TRM 340) is 0.62 µg/L, the

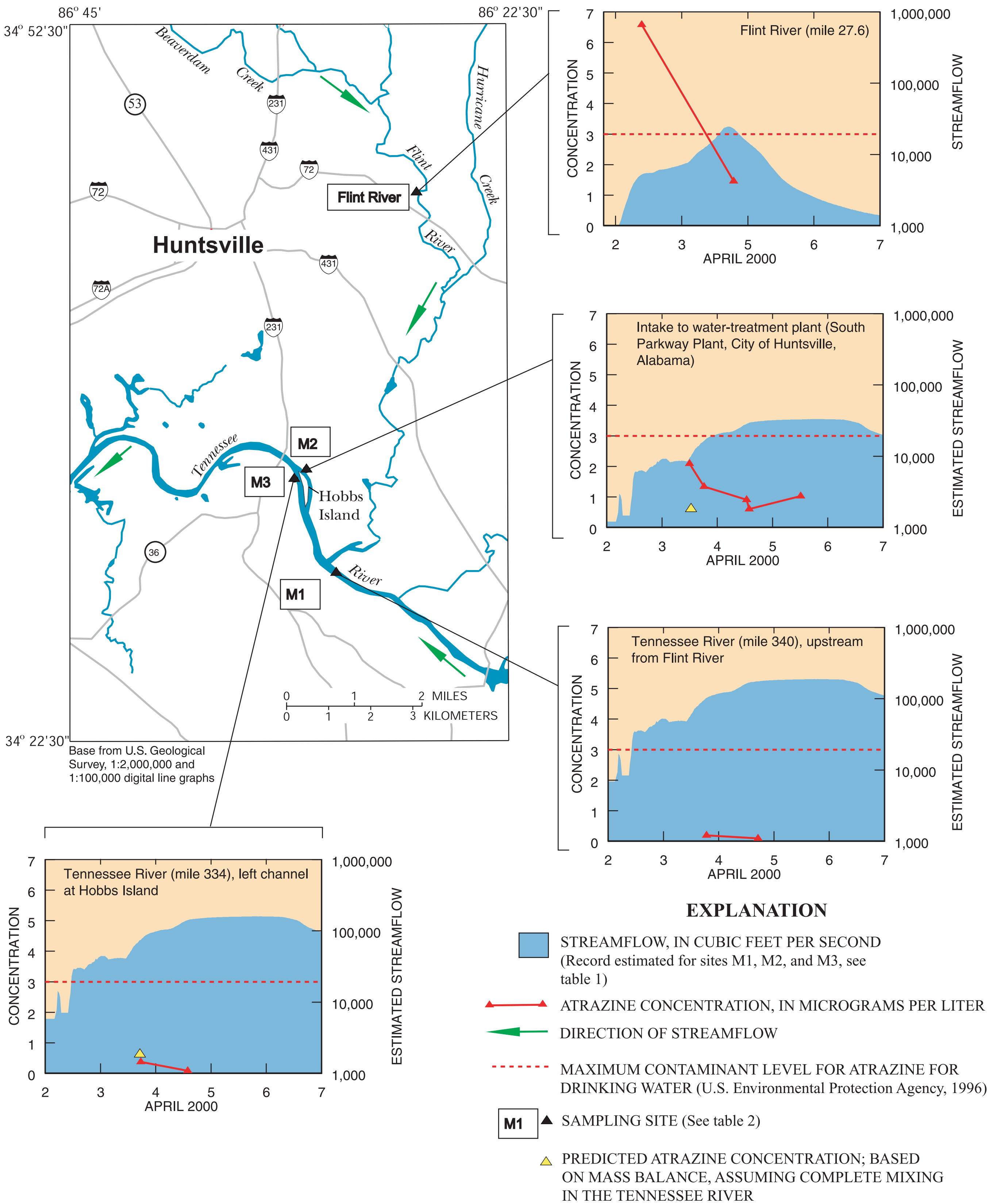
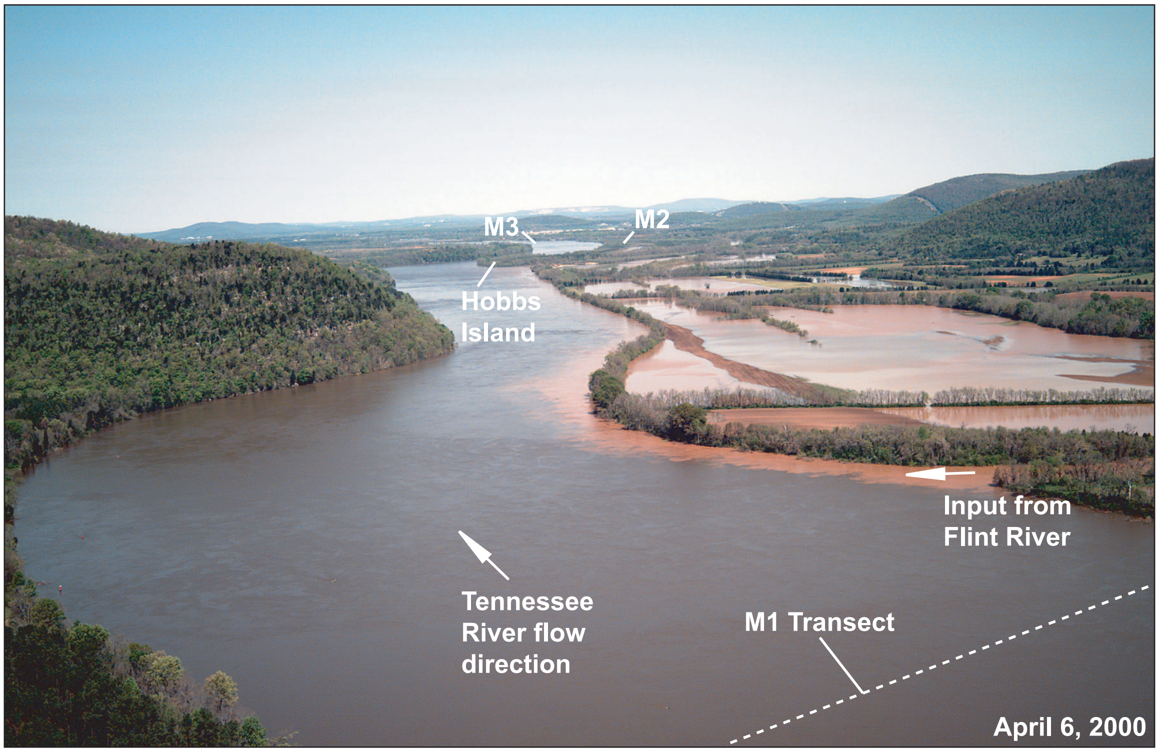


Figure 18. Streamflow and atrazine concentrations in the Flint River, the Tennessee River, and at the intake to the City of Huntsville's water-treatment plant, April 2-7, 2000. Atrazine concentrations were ten times greater in the intake water compared with concentrations in the Tennessee River upstream from the Flint River, and more than triple the concentration that would be expected with complete mixing in the Tennessee River.



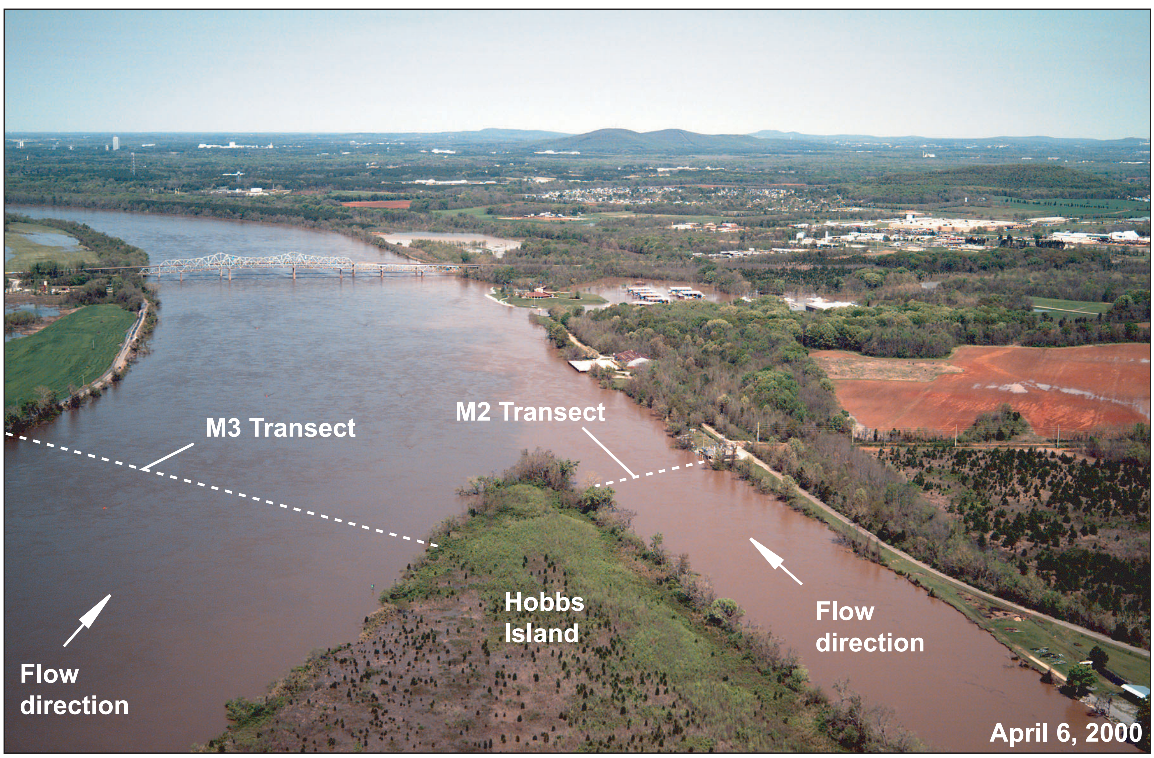


Figure 18. Streamflow and atrazine concentrations in the Flint River, the Tennessee River, and at the intake to the City of Huntsville's water-treatment plant, April 2-7, 2000—Continued.

observed peak concentration was 2.1 μg/L (compare with the drinking-water standard of 3 μg/L). The discussion of Flint River water quality in previous sections of this report, therefore, has implications for drinking-water quality for the City of Huntsville.

SUMMARY

Eight stream sites in the Flint River Basin, Alabama and Tennessee, were monitored during January 1999 through May 2000 to characterize patterns in the occurrence of pesticides, fecal-indicator bacteria, and nutrients in relation to season and streamflow conditions and to land-use patterns. In addition, three sites on the Tennessee River near the confluence with the Flint River were monitored to relate water quality in the Flint River to water quality in a drinking-water source for the City of Huntsville. Water-quality conditions in the Flint River Basin during the monitoring period may have deviated from normal as a result of below-normal rainfall and streamflow. Transport of water-quality constituents, including pesticides, bacteria, and nutrients, in storm runoff to the streams was probably lower than normal during many months.

Occurrence of pesticides in the Flint River and its tributary Hester Creek was compared to information about agricultural pesticide use in the watershed. In general, pesticides detected most frequently and at the highest concentrations in streams corresponded to the pesticides with the highest rates of use in the watersheds and with the highest potential (based on the pesticide's chemical and physical properties) for transport in runoff or ground water. For example, atrazine, which is the second most heavily applied pesticide, or one of its metabolites was detected in 100 and 93 percent of the samples from the Flint River and Hester Creek, respectively. In contrast, glyphosate, the most heavily applied pesticide, was detected in only 17 percent of samples from Hester Creek; this contrast between rate of use and instream occurrence may be caused by glyphosate's strong affinity to soil particles and its resulting low potential for leaching to runoff or ground water. Detections of fluometuron, norflurazon, and atrazine were more frequent (by a margin of 15 percent or greater) in samples from the Flint River as compared to pesticide detection frequencies at 62 agricultural stream sites across the Nation. Detections of fluometuron in the Flint River were more frequent even when compared to a cotton-cultivation subset of the 62 sites.

Less than 5 percent of the estimated mass of pesticides applied annually to agricultural areas in the Flint River Basin was transported to the stream at the monitoring points on the Flint River near Brownsboro, Ala., and on Hester Creek near Plevna, Ala. The amount transported instream ranged from 0.06 percent (for trifluralin) to 4.7 percent (for norflurazon) of the amount applied. The pesticides for which the highest ratios (> 3 percent) were observed—atrazine, metolachlor, fluometuron, and norflurazon—are preemergent herbicides applied to the soil before the crops have emerged, which increases the likelihood of their transport in surface runoff.

The environmental significance of the observed pesticide concentrations was evaluated by comparing these concentrations with water-quality criteria to protect aquatic life. For most pesticides, maximum concentrations did not exceed aquatic-life criteria; however, maximum concentrations of atrazine, cyanazine, and malathion exceeded aquatic-life criteria in at least one sample each. Concentrations near or exceeding the aquatic-life criteria occurred only during the spring and summer months (April through July), and generally occurred during storm flows. The aquatic-life criteria generally are based on the results of single-chemical toxicity tests and do not consider the synergistic effects of exposure to low-level pesticide mixtures, such as the mixtures detected in samples from the Flint River and Hester Creek sites. For example, every stream sample had detectable levels of at least two pesticides; 64 percent of the samples contained a mixture of at least five pesticides.

E. coli concentrations in the Flint River and Hester Creek exceeded the U.S. Environmental Protection Agency single-sample criterion of 406 col./100 mL for recreation in almost all storm samples, and in samples collected up to 6 days following a storm. Concentrations in the Flint River were strongly correlated with sample turbidity. Exceedance of the single-sample *E. coli* criterion for recreation can be estimated empirically from turbidity measurements using linear regression. For the Flint River site, a sample with turbidity equal to 22 NTU has an expected *E. coli* concentration equal to the criterion for recreation.

When compared with nutrient data from a set of 24 agricultural basins across the southeastern region of the United States, concentrations of nitrogen and phosphorus in the Flint River and Hester Creek were slightly above the regional median. Nutrient

concentrations in the Flint River generally exceeded thresholds indicating eutrophic potential, whereas nutrient concentrations in samples from Hester Creek were generally below the thresholds. Seasonal variation of nutrient concentrations in the Flint River, marked by increased base-flow concentrations of nitrate and phosphorus during the period May through October, differed from the pattern expected based on nutrient dynamics. The seasonal increase in base-flow concentrations accounted for the higher median concentration in the Flint River compared with the threshold values indicating eutrophic potential. Nutrient input from the Mountain Fork Creek tributary may have contributed to this pattern. During two base-flow periods in May and September 1999, Mountain Fork Creek contributed more than 40 percent of the summed tributary load of total nitrogen, and more than 80 percent of the summed tributary load of total phosphorus.

The base-flow concentrations of certain pesticides, *E. coli*, and nutrients at eight sites in the Flint River Basin were compared with land-use information. The highest base-flow concentrations of aldicarb sulfoxide, fluometuron, and phosphorus occurred in the tributaries with the greatest density of cotton acreage in the watershed. Similarly, base-flow concentrations of total nitrogen were correlated with the percentage of cultivated land in the watershed. Base-flow concentrations of *E. coli* during May were correlated most strongly with watershed density of livestock population, whereas concentrations of *E. coli* during September, after a prolonged dry period, were correlated most strongly with the estimated density of failing septic systems in the watershed. Lack of information about distribution of stream access by livestock, however, weakened the analysis of correlation between livestock and base-flow concentrations of *E. coli* and nutrients.

Input of dissolved and suspended chemicals from the Flint River during storms influences water quality in the reach of the Tennessee River from which the City of Huntsville, Alabama, withdraws about 40 percent of its drinking water. The increased influence during storms is a result of two factors: larger percentages of flow from the Flint River to the flow-regulated Tennessee River during storms, and incomplete mixing at the confluence of the Flint and Tennessee Rivers. During the storm of April 2-5, 2000, concentrations of several pesticides were at least a factor of five times greater in Huntsville's intake water compared with concentrations in the Tennessee River upstream from the Flint River, although concentrations of all pesticides were below the U.S. EPA drinking-water standards at all sites on the Tennessee River and in Huntsville's intake water.

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APPENDIXES

APPENDIX A. METHODS FOR ESTIMATING WATERSHED INPUT AND INSTREAM YIELD OF PESTICIDES, NITROGEN, AND PHOSPHORUS FOR THE FLINT RIVER BASIN, ALABAMA AND TENNESSEE

Watershed Input

The estimated agricultural inputs of pesticides presented in Appendix B were summed from estimates of application to three major crops (corn, cotton, and soybeans), which were calculated from crop acreage and pesticide application rates. Estimates in Appendix B are for unit-area input, or the ratio of mass of pesticide to the total area of the watershed. Information about pesticide application rates was provided by Joseph Berry (U.S. Natural Resource Conservation Service, Ala., written commun., 2000), William Abbott (U.S. Natural Resource Conservation Service, Tenn., written commun., 2000), Mark Hall (Agricultural Extension Service, Madison County, Ala., oral commun., 2000), and David Qualls (Agricultural Extension Service, Lincoln County, Tenn., written commun., 2000). Crop-acreage estimates for 1999-2000 were provided by Joseph Berry and William Abbott (U.S. Natural Resource Conservation Service, written commun., 2000). Although nonagricultural inputs of certain pesticides (home and garden use and roadway maintenance) account for part of the pesticide input to the watershed, these were not estimated for this study.

Inputs of nitrogen and phosphorus from various agricultural and nonagricultural sources in a watershed were estimated for the Flint River and Hester Creek using local information, along with methods and coefficients described in Hoos and others (2000). Inputs from fertilizer were estimated using application recommendations from Adams and others (1994) for the three major crops. Wastewater inputs of nitrogen and phosphorus were calculated based on 1999 to 2000 effluent monitoring data provided by Pat Morgan (City of Huntsville, Ala., written commun., 2000). Inputs of nitrogen and phosphorus from failing septic systems and livestock waste were calculated based on census estimates from Victor Payne (Alabama Soil and Water Conservation Committee, written commun., 1999); these estimates were extrapolated from the Alabama part of the watershed to the entire watershed on a per-unit-area basis.

Instream Yield

Instream loads of selected pesticides and nutrients were estimated for the Flint River and Hester Creek by either the rating-curve or ratio-estimator method, using the program LOADEST2 (Crawford, 1996). For most pesticides, instream loads were estimated using the rating-curve method with a seasonal covariate function to account for the spring pulse in pesticide loads. This approach effectively creates two rating-curve models for each pesticide data set: one model for the pesticide-application season and another for the rest of the year (C.G. Crawford, written commun., 1999). The ratio-estimator method (Dolan and others, 1981) was used in place of the rating-curve method to estimate instream loads for five pesticides (cyanazine, carbaryl, carbofuran, trifluralin, and pendimethalin) for which 85 percent or more of the samples had concentrations less than the method detection limit. The estimates from the ratio-estimator method are less reliable than those from the rating-curve method because they do not account for seasonal- and streamflow-related variability.

Estimates of annual instream yield (Appendixes B and C) were calculated by dividing instream load by watershed area. These estimates are considered interim results (instream yields may be recalculated after additional years of planned data collection) and should be interpreted with caution as the calibration data set is limited to 17 months of data, and includes fewer than 40 samples for most constituents.

Appendix B. Input and export estimates and detection frequency of selected pesticides for the Flint River and Hester Creek, 1998-2000

[Unit-area input reported in pounds of active ingredient per square mile of total watershed area per year; input estimates are for use on crops during 1998; unit-area export reported in pounds per square mile per year; export estimates are for water year 1999; export ratio reported in percent and calculated as (export/input)*100; frequency of detection reported in percent and calculated for the period January 1999 - May 2000; >, greater than; µg/L, micrograms per liter; I, insecticide; H, herbicide; F, fungicide; NRU, not estimated because no reported use for crop pest management in the Flint River Basin; ND, no data (not targeted for analysis); --, data not sufficient for estimating export because most observations were below the method detection limit]

Chemical (trade name)	Type	Watershed for Flint River near Brownsboro, Ala.				Watershed for Hester Creek at Buddy Williamson Road near Plevna, Ala.			
		Unit-area input	Unit-area export	Export ratio, in percent	Frequency of detection > 0.01 µg/L	Unit-area input	Unit-area export	Export ratio, in percent	Frequency of detection > 0.01 µg/L
Pesticides reported as used for crop pest management in the Flint River Basin									
Aldicarb (Temik) [a, b]	I	19	0.071	0.37	48	20	0.011	0.06	21
Atrazine (Aatrex) [a]	H	48	2.0	4.1	100	83	1.5	1.8	93
Carbaryl (Sevin) [b]	I	3.6	0.050	1.4	14	6.2	0.062	1.0	10
Carbofuran (Furadan) [b]	I	1.1	0.028	2.7	17	1.8	--	--	0
Chlorpyrifos (Lorsban)	I	6.4	--	--	0	9.3	--	--	0
Cyanazine (Bladex)	H	12	0.18	1.5	10	18	0.055	0.30	13
Dicrotophos (Bidrin)	I	6.6	ND	ND	ND	6.9	ND	ND	ND
Fluometuron (Cotoran)	H	18	0.59	3.2	87	19	0.19	1.0	76
Glyphosate (Roundup)	H	140	--	--	[c] 0	183	--	--	[c] 17
Metalaxyl (Ridomil)	F	2.9	--	--	14	3.0	--	--	31
Metolachlor (Dual)	H	16	0.22	1.4	48	22	0.78	3.5	59
Methomyl (Lannate) [a]	I	1.1	--	--	0	1.8	--	--	[c] 7
Norflurazon (Zorial) [b]	H	2.1	0.10	4.7	87	2.2	--	--	7
Pendimethalin (Prowl)	H	4.8	0.094	1.9	14	8.3	0.10	1.2	13
PCNB (Terraclor)	I	29	ND	ND	ND	30	ND	ND	ND
Prometryn (Cotton Pro)	H	3.2	--	--	[c] 32	3.3	--	--	[c] 0
Trifluralin (Treflan) [b]	H	21	0.013	0.061	3	25	--	--	0
Pesticides for which input was not estimated (not reported as used for crop pest management in the Flint River Basin), but which were detected at concentrations > 0.01 µg/L in 10 percent or more of samples									
2,4-dichlorophenoxyacetic acid (2,4-D)	H	NRU	--	--	[c] 22	NRU	--	--	[c] 34
Acetochlor (Surpass)	H	NRU	--	--	10	NRU	--	--	0
Bentazon (Basagran)	H	NRU	--	--	9	NRU	--	--	10
Diazinon (Spectracide)	I	NRU	--	--	14	NRU	--	--	5
Diuron (Karmex or Direx)	H	NRU	--	--	[c] 13	NRU	--	--	[c] 0
Malathion (Cythion)	I	NRU	--	--	10	NRU	--	--	5
Simazine (Princep)	H	NRU	0.075	--	48	NRU	0.022	--	8
Sulfometuron-methyl (Oust)	H	NRU	--	--	[c] 17	NRU	--	--	[c] 14
Tebuthiuron (Spike)	H	NRU	--	--	10	NRU	--	--	13

[a] Export estimates and detection frequency include estimated mass and detection frequency of metabolites.

[b] Estimates of export and export ratio are subject to error because concentrations were reported with the "E" data qualifier, signifying that although the pesticide was qualitatively identified as present, the reported concentration has greater uncertainty than other values.

[c] Reported value for detection frequency is a minimum estimate because some observations were reported as less than a value that was larger than the 0.01 µg/L threshold.

Appendix C. Input and export estimates of nitrogen and phosphorus for the Flint River and Hester Creek, 1998-99

[Unit-area inputs reported in tons of element per square mile per year; input estimates are for 1998, with some exceptions (noted in the table); unit-area export reported in tons per square mile per year; estimates of export and flow-weighted mean concentration are for water year 1999; export ratio reported in percent and calculated as (export/input)*100; flow-weighted mean concentration reported in milligrams per liter and calculated as the ratio of export to mean streamflow, with appropriate unit conversions; -, negative number because crop harvest represents a nutrient sink; balance of input to agricultural lands calculated as sum of inputs from fertilizer application, livestock waste, and (for nitrogen) crop fixation, minus removal as crop harvest]

	Watershed for Flint River near Brownsboro, Ala.				Watershed for Hester Creek at Buddy Williamson Road near Plevna, Ala.			
		Export, 1999 data				Export, 1999 data		
Source and nutrient	Unit-area input	Unit-area export	Export ratio	Flow-weighted mean concentration	Unit-area input	Unit-area export	Export ratio	Flow-weighted mean concentration
Agricultural activities								
Cropland fertilizer								
Nitrogen	5.0				5.8			
Phosphorus	0.99				1.2			
Crop fixation								
Nitrogen	3.5				4.3			
Livestock waste								
Nitrogen	3.4				7.7			
Phosphorus	1.1				2.5			
Harvest								
Nitrogen	-7.7				-10			
Phosphorus	-0.83				-1.1			
Balance of input to agricultural lands								
Nitrogen	4.2				7.4			
Phosphorus	1.3				2.7			
Wastewater (1999)								
Nitrogen	0.035				0			
Phosphorus	0.010				0			
Atmospheric deposition (1999)								
Nitrogen	0.14				0.13			
Failing septic systems								
Nitrogen	0.085				0.10			
Phosphorus	0.025				0.029			
Sum of all inputs								
Nitrogen	4.4				7.6			
Phosphorus	1.3				2.7			
Nitrogen		3.0	67	1.8		2.1	27	1.8
Phosphorus		0.34	26	0.20		0.20	7.6	0.18