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

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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

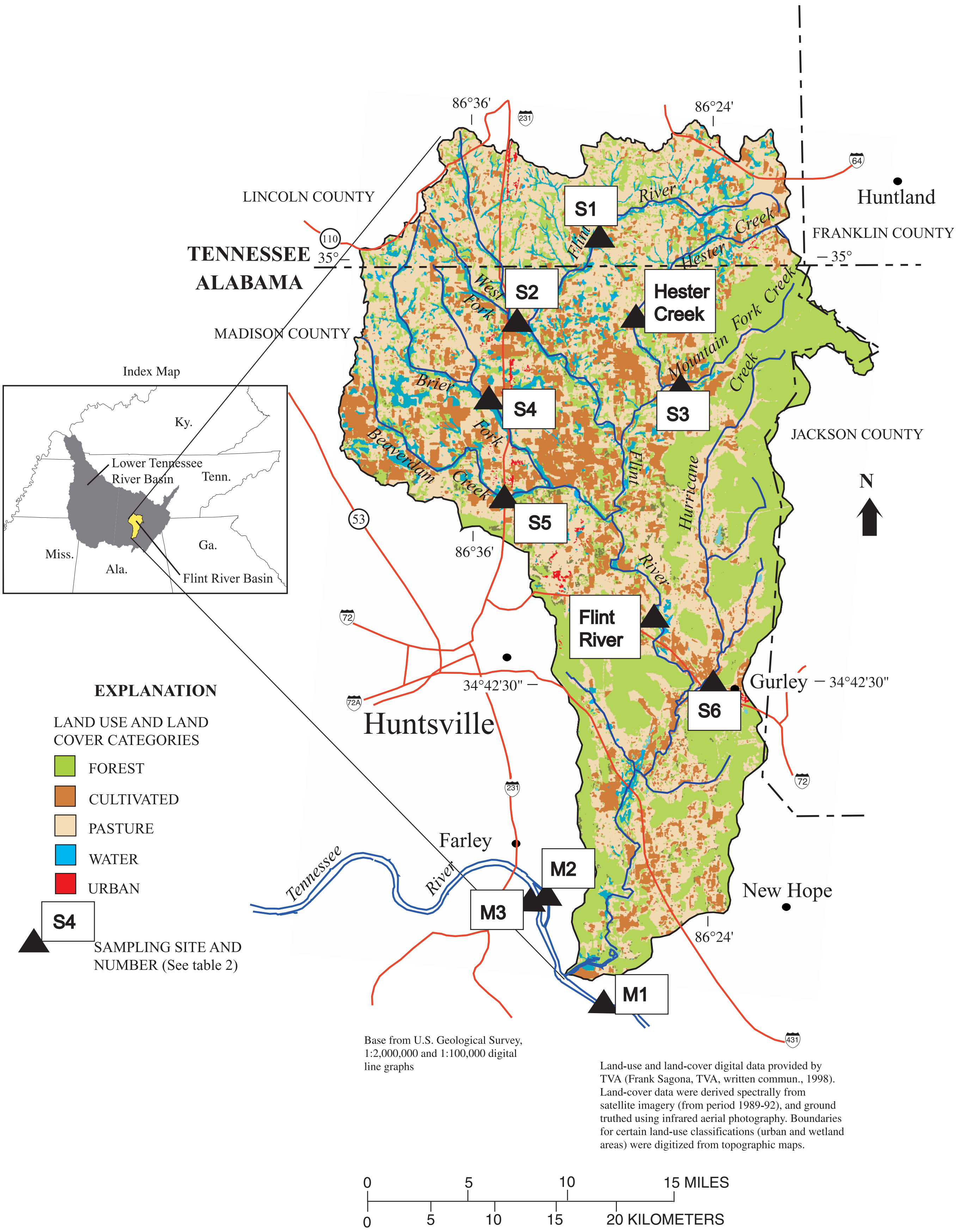
The Flint River, a tributary to the Tennessee River, drains 568 square miles (mi^2) of primarily agricultural land in northern Alabama and south-central Tennessee (fig. 1). Urban and residential land represent a small (less than 1 percent), but growing part of land use in the watershed, as residential 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

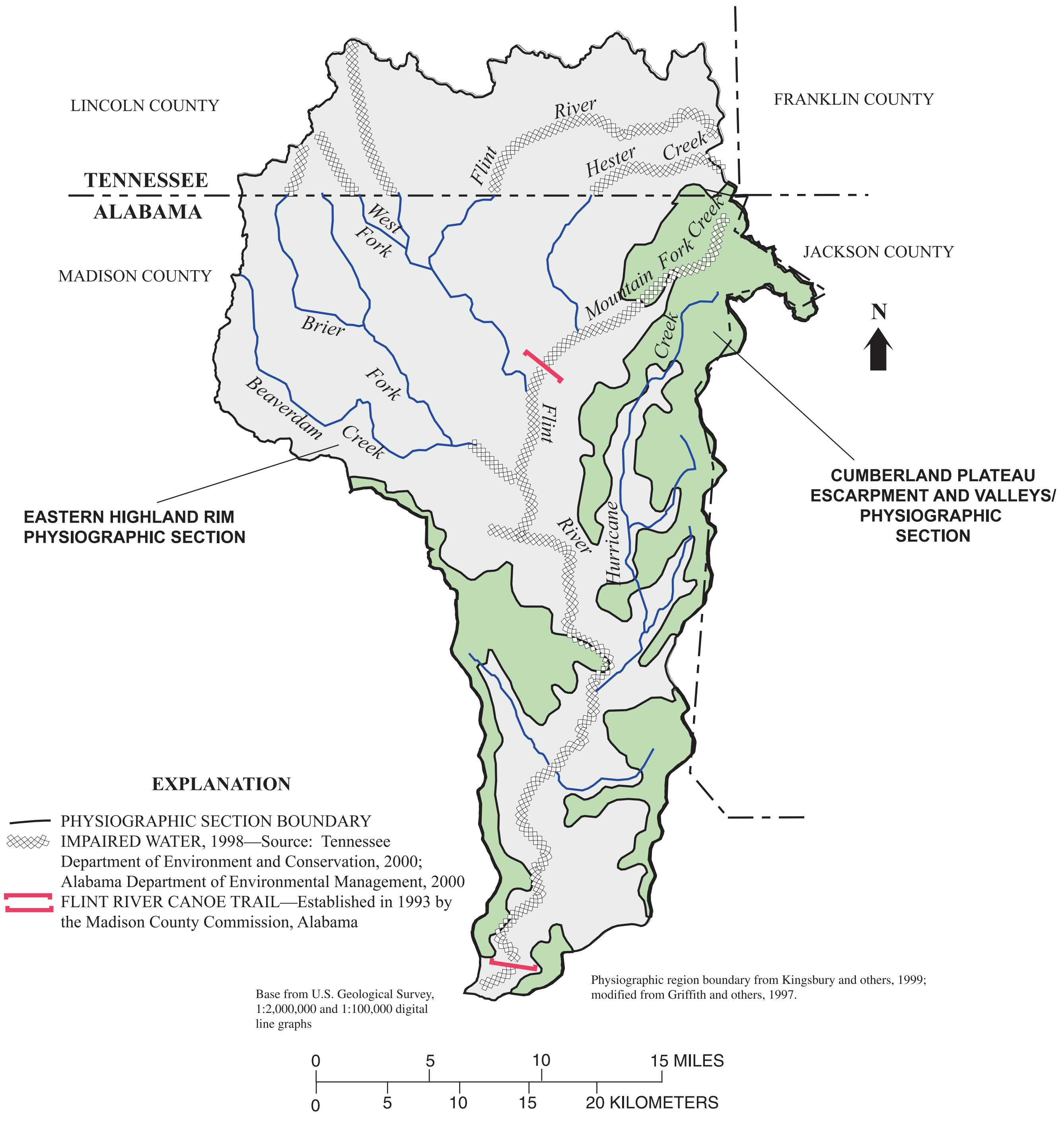
The purposes of this report are to characterize surface-water quality in the Flint River Basin across a range of seasonal and streamflow conditions, and to assess variation of base-flow water quality in relation to land use in the Basin. The water-quality constituents included in the characterization 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.



Base from U.S. Geological Survey, 1:2,000,000 and 1:100,000 digital line graphs

Land-use and land-cover digital data provided by TVA (Frank Sagona, TVA, written commun., 1998). Land-cover data were derived spectrally from satellite imagery (from period 1989-92), and ground truthed using infrared aerial photography. Boundaries for certain land-use classifications (urban and wetland areas) were digitized from topographic maps.

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



Base from U.S. Geological Survey, 1:2,000,000 and 1:100,000 digital line graphs

Physiographic region boundary from Kingsbury and others, 1999; modified from Griffith and others, 1997.

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

Acknowledgments

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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

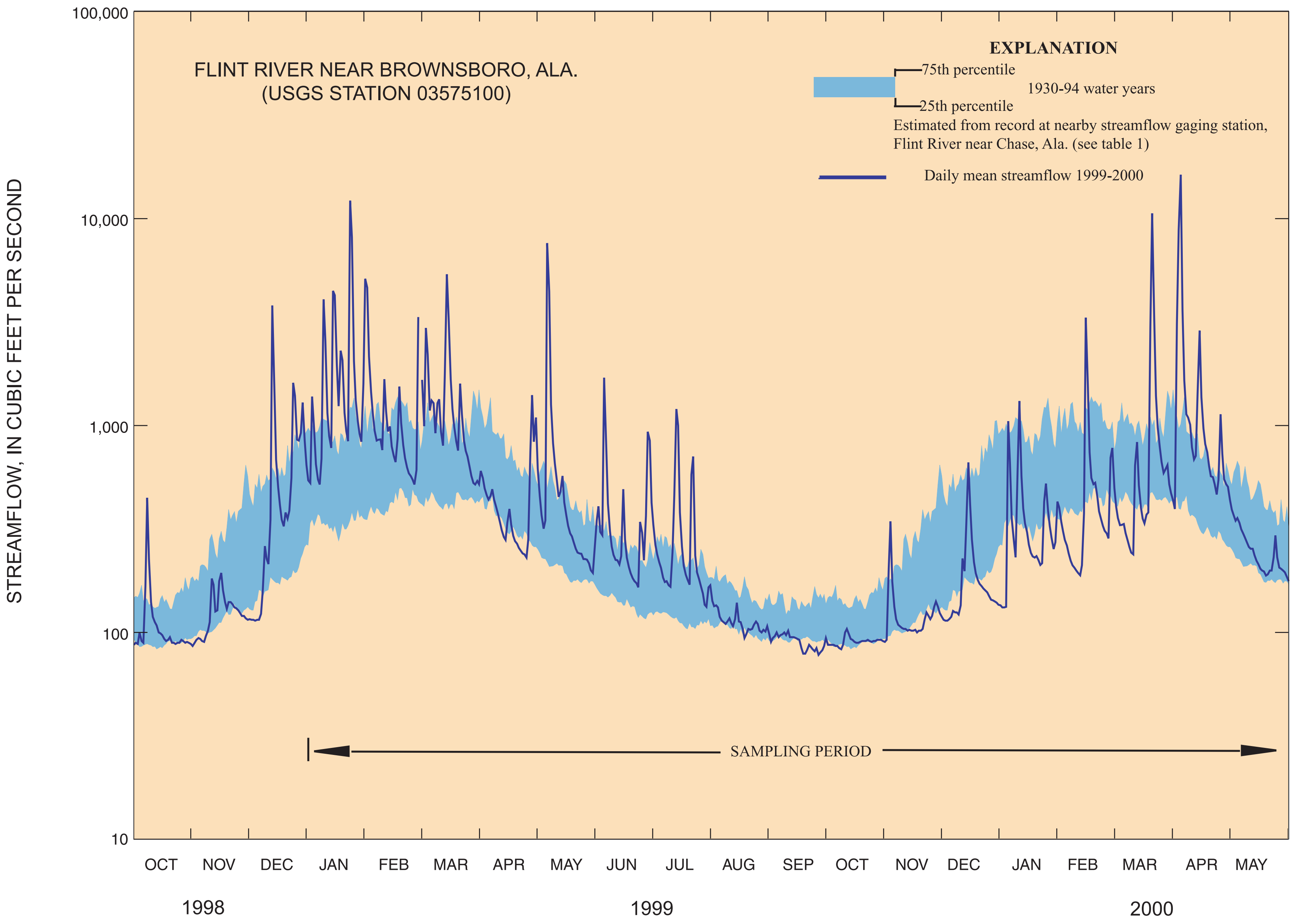


Figure 3. Daily mean streamflows in the Flint River during the fall of 1998 and 1999, and during the winter of 2000, were near or below the 25th percentile of daily mean streamflow for the period of record (1930-94).

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

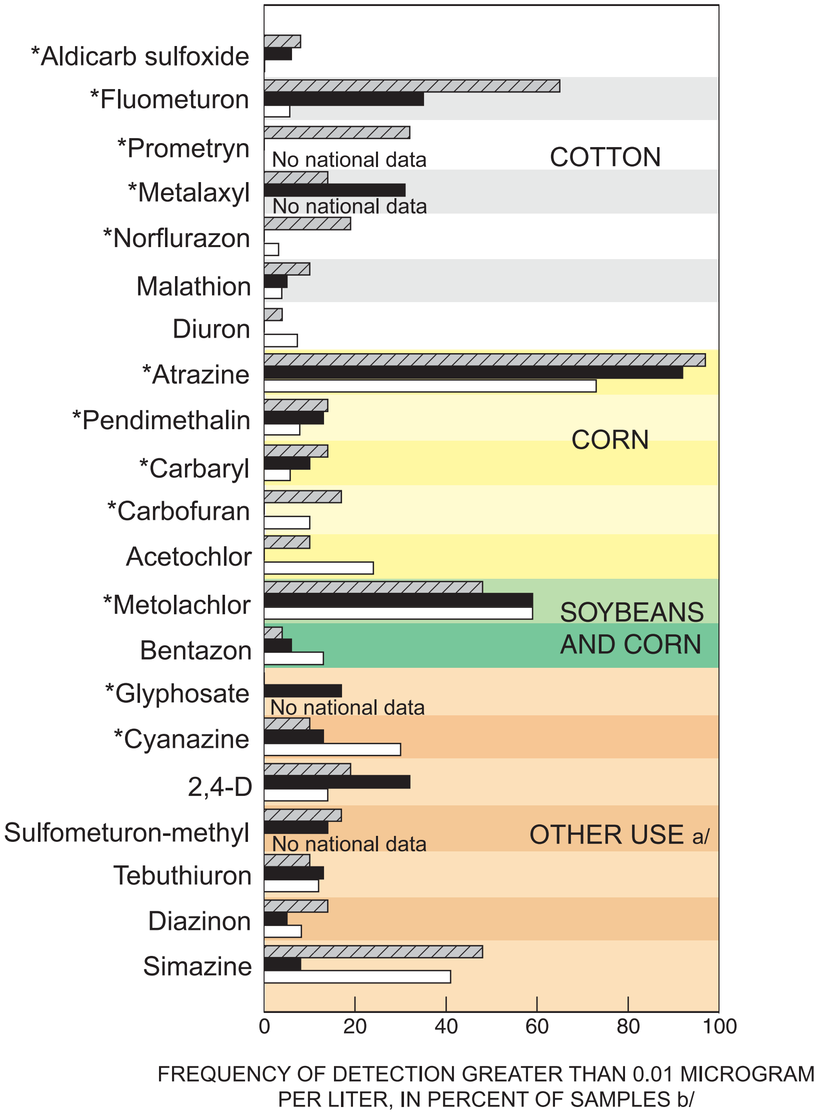
In general, the most heavily applied pesticides were detected most frequently, with the highest concentrations and the highest annual instream yields. For example, atrazine was detected in 100 and 93 percent of the samples from the Flint River and Hester Creek, respectively (Appendix B), and was transported 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



EXPLANATION

▨ FLINT RIVER

■ HESTER CREEK

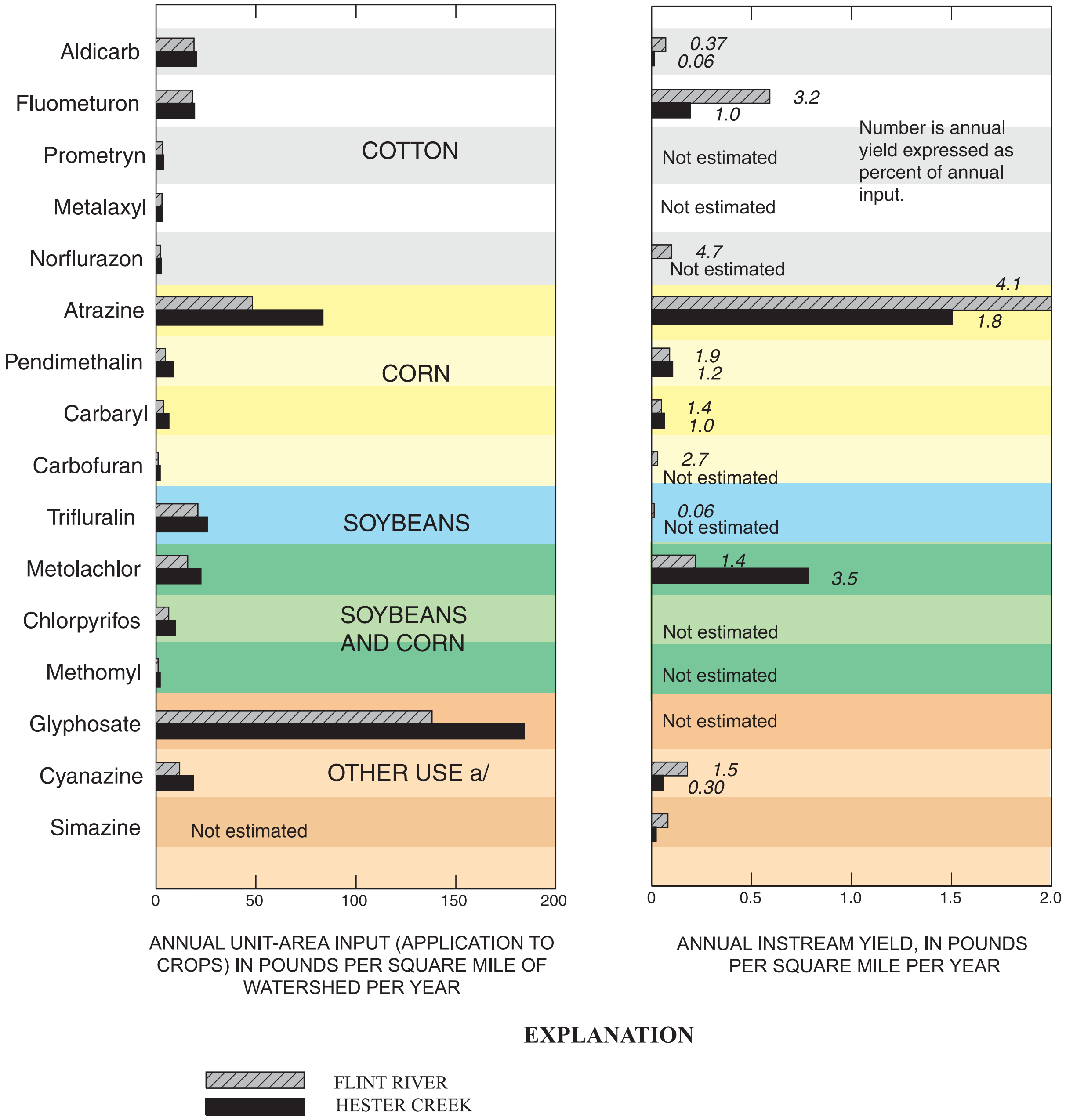
□ NATIONAL DATA SET OF 62 AGRICULTURAL STREAM SITES (U.S. Geological Survey, 2001)

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.



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.

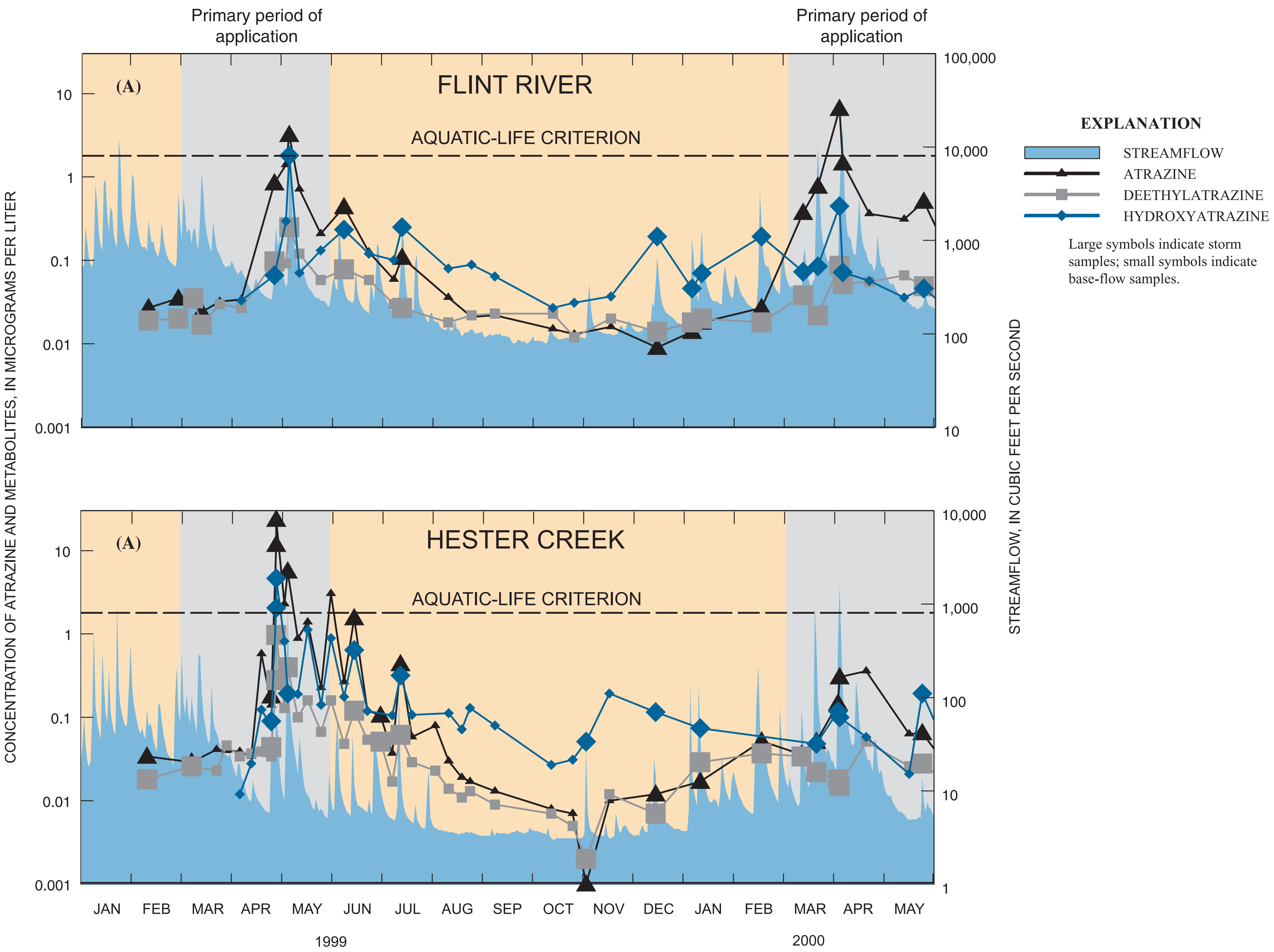


Figure 6. Streamflow and concentration of (A) atrazine and metabolites and (B) cyanazine for the Flint River and Hester Creek, 1999-2000.

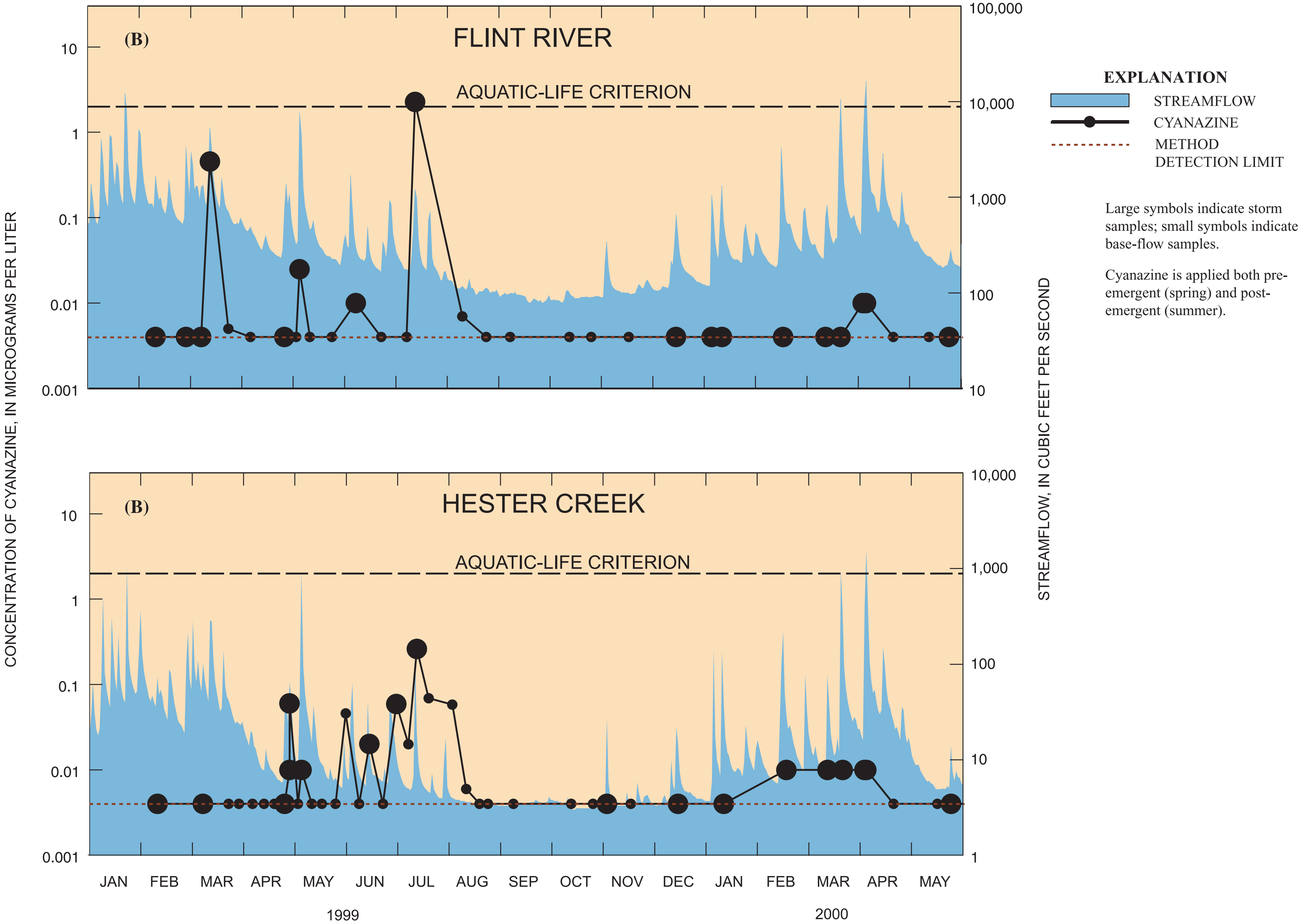


Figure 6. Streamflow and concentration of (A) atrazine and metabolites, and (B) cyanazine for the Flint River and Hester Creek, 1999-2000—Continued.

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

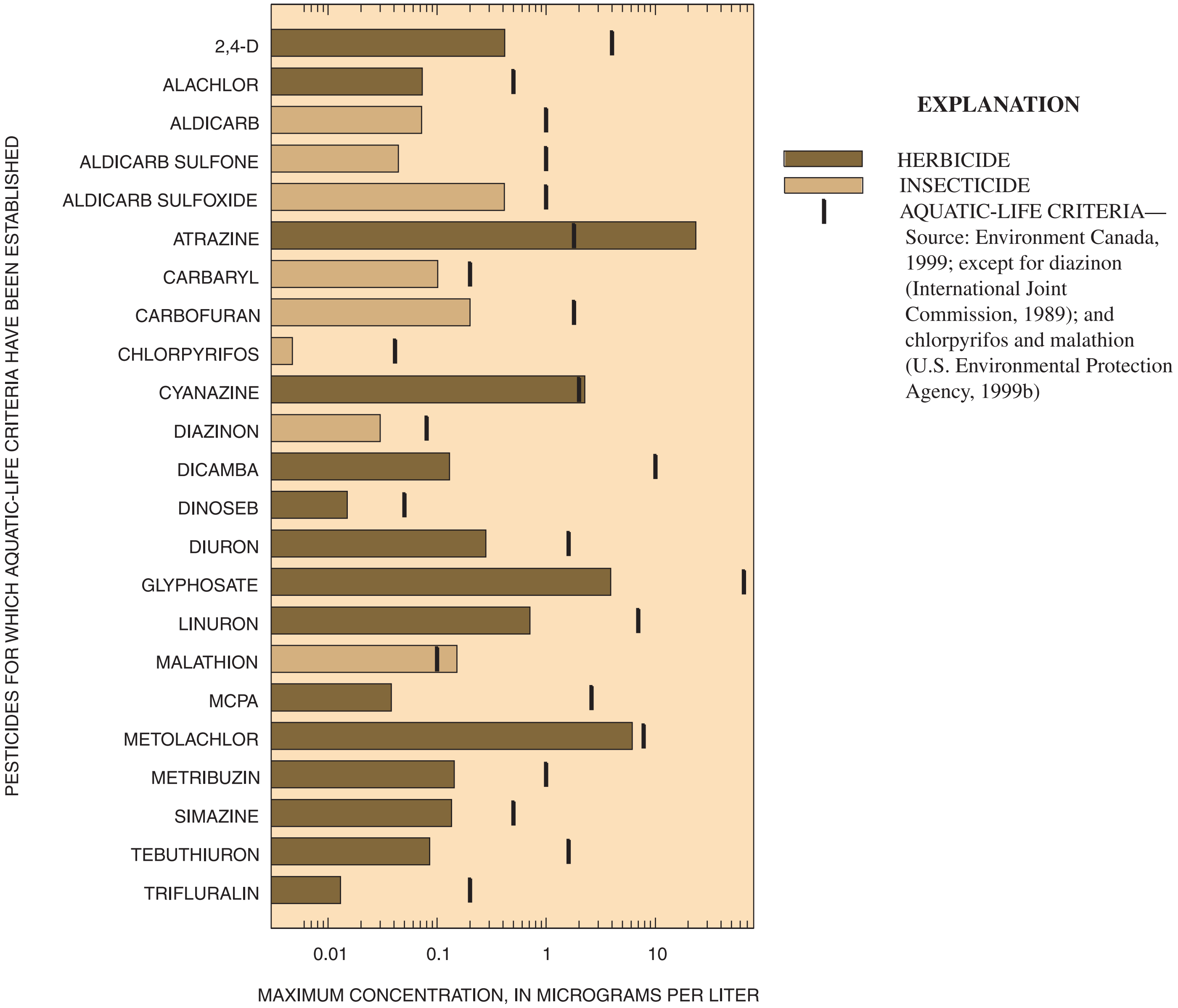


Figure 8. Maximum concentrations of pesticides and aquatic-life criteria for the Flint River and Hester Creek, 1999-2000. Concentrations were below the aquatic-life criteria for all pesticides except for atrazine, cyanazine, and malathion. The aquatic-life criteria were based on the results of single-chemical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

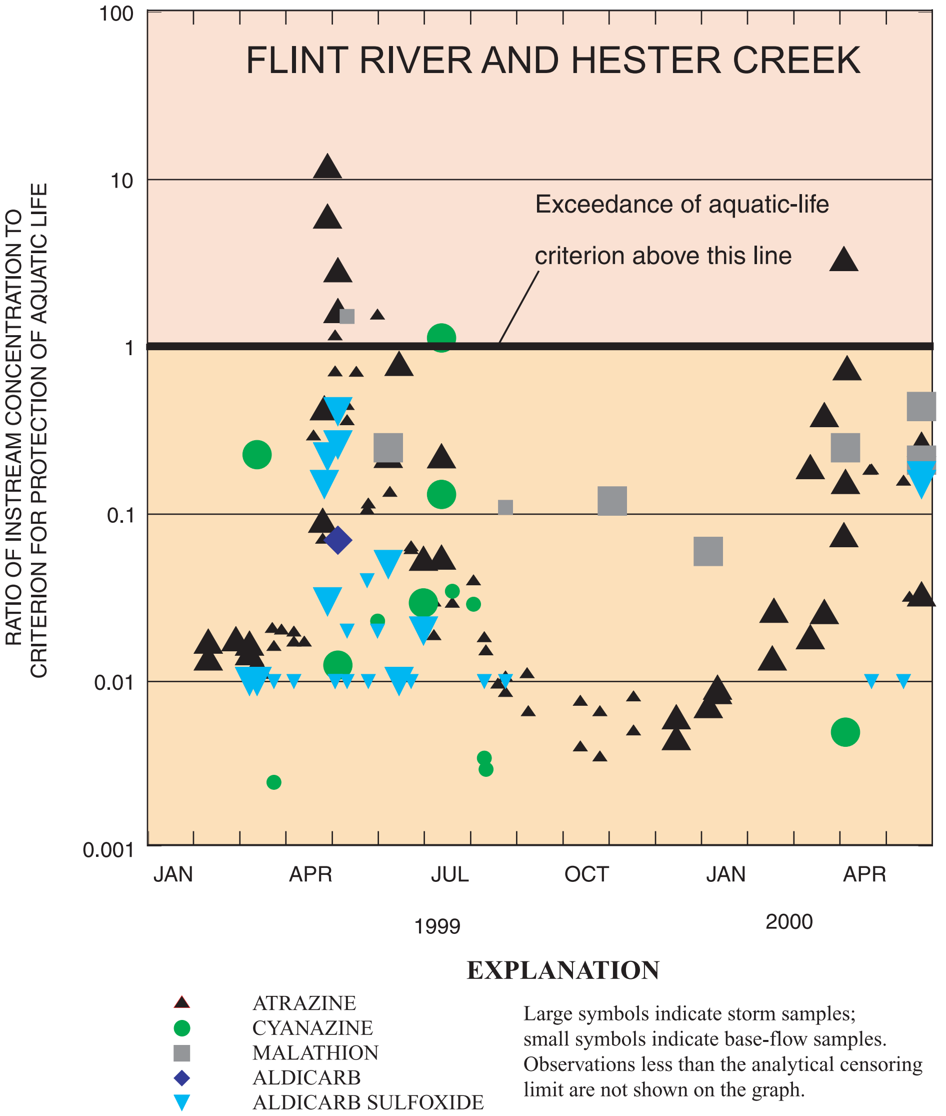


Figure 9. Relation of exceedances of aquatic-life criteria to season and to streamflow for selected pesticides for the Flint River and Hester Creek, 1999-2000. Concentrations near or exceeding the aquatic-life criteria occurred from April through June, and generally during storm flow.

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