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.

REFERENCES CITED

Adams, J.F., Mitchell, C.C., and Bryant, H.H., 1994, Soil test fertilizer recommendations for Alabama crops: Alabama Agricultural Experiment Station, Auburn University, Agronomy and Soils Department Series No. 178, 68 p.

Alabama Department of Environmental Management, 2000, Alabama's 2000 water quality report to Congress (Clean Water Act 305(b) Report): Alabama Department of Environmental Management, Montgomery, Alabama, variously paginated.

Clark, G.M., Mueller, D.K., and Mast, M.A., 2000, Nutrient concentrations and yields in undeveloped stream basins of the United States: Journal of American Water Resources Association, v. 36, no. 4, p. 849-860.

Crawford, C.G., 1996, Estimating mean constituent loads in rivers by the rating-curve and flow-duration, rating-curve methods: Bloomington, Indiana, Indiana University, Ph.D. dissertation, 245 p.

Dodds, W.K., Jones, J.R., and Welch, E.B., 1998, Suggested classification of stream trophic state: distributions of temperate stream types by chlorophyll, total nitrogen, and phosphorus: Water Research, v. 32, no. 5, p. 1455-1462.

Dolan, D.M., Yui, A.K., and Geist, R.D., 1981, Evaluation of river load estimation methods for total phosphorus: Journal of Great Lakes Research, v. 7, p. 207-214.

Environment Canada, 1999, Canadian water quality guidelines for the protection of aquatic life, Summary tables: accessed December 18, 2000 at URL http://www.ec.gc.ca/ceqg-rcqe.

Gilliom, R.J., Alley, W.M., and Gurtz, M.E., 1995, Design of the National Water-Quality Assessment Program: occurrence and distribution of water-quality conditions: U.S. Geological Survey Circular 1112, 33 p.

Griffith, G.E., Omernik, J.M., and Azevedo, S.H., 1997, Ecoregions of Tennessee: U.S. Environmental Protection Agency National Health and Environmental Effects Research Laboratory EPA/600/R-97/022, 51 p.

Hoos, A.B., Robinson, J.A., Aycock, R.A., Knight, R.R., and Woodside, M.D., 2000, Sources, instream transport, and trends of nitrogen, phosphorus, and sediment in the lower Tennessee River Basin, 1980-96: U.S. Geological Survey Water-Resources Investigations Report 99-4139, 96 p.

International Joint Commission, 1989, Article 5.-Standards, other regulatory requirements, and research, *in* Revised

Great Lakes water quality objectives of 1978, volume 2, an IJC report to the governments of the United States and Canada: Windsor, Ontario, Canada, International Joint Commission, accessed December 18, 2000 at URL http://www.ijc.org/agree/quality.html#art5

Kingsbury, J.A., Hoos, A.B., and Woodside, M.D., 1999, Environmental setting and water-quality issues in the lower Tennessee River Basin: U.S. Geological Survey Water-Resources Investigations Report 99-4080, 44 p.

Martin, J.D., Gilliom, R.J., and Schertz, T.L., 1999, Summary and evaluation of pesticides in field blanks collected for the National Water-Quality Assessment Program, 1992-1995: U.S. Geological Survey Open-File Report 98-412, 102 p.

Miltner, R.J., Baker, D.B., Speth, T.F., and Fronk, C.A., 1989, Treatment of seasonal pesticides in surface waters: Journal of the American Water Works Association, v. 81, no. 1, p. 43-52.

Mueller, D.K., Martin, J.D., and Lopes, T.J., 1997, Quality-control design for surface-water sampling in the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 97-223, 17 p.

Shelton, L.R., 1994, Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94-455, 42 p.

Tennessee Department of Environment and Conservation, 2000, The 1998 303(d) list: Division of Water Pollution Control, accessed December 15, 2000 at URL http://www.state.tn.us/environment/water.htm

U.S. Environmental Protection Agency, 1986, Ambient water quality criteria for bacteria, 1986: Cincinnati, Ohio, U.S. Environmental Protection Agency, EPA 440/5-84-002, 18 p.

———1996, Drinking water regulations and health advisories: Washington, D.C., U.S. Environmental Protection Agency, Office of Water, EPA 822-B-96-002, variously paginated.

———1999a, International notice: cyanazine pesticide voluntarily cancelled and uses phased out: Office of Pesticide Programs, accessed June 22, 2001 at URL http://www.epa.gov/oppfead1/17b/cyanazin.htm

———1999b, Compilation of national recommended water-quality criteria and EPA's process for deriving new and revised criteria: Office of Water, accessed December 18, 2000 at URL http://www.epa.gov/OST/standards/wqcriteria.html

U.S. Geological Survey, 2001, Pesticides in streams; summary statistics; results of the National Water Quality Assessment Program (NAWQA), 1992-1998: U.S. Geological Survey data available on the World Wide Web, accessed December 5, 2001 at URL http://water.wr.usgs.gov/pnsp/pestsw

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