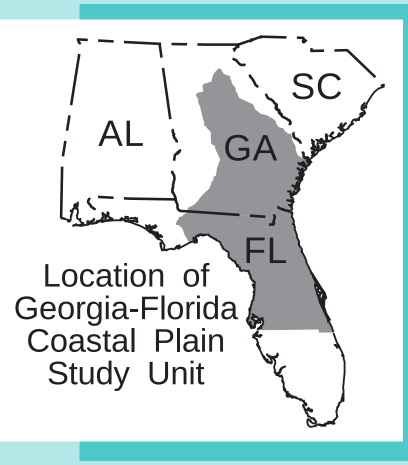
Pesticides in Surface Water from Three Agricultural Basins in South-Central Georgia, 1993-95

By Hilda H. Hatzell

Abstract



Twenty-two of 43 pesticides analyzed were detected in 128 water samples collected from the Tucsawhatchee Creek, the Little River, and the Withlacoochee River. These streams drain agricultural basins in south-central Georgia and were sampled from March 1993 through June 1995. Herbicides were detected more frequently than insecticides. The most frequently detected herbicides were atrazine and metolachlor and the most frequently detected insecticide was carbaryl.

Pesticide concentrations in the three streams were low and did not exceed U.S. Environmental Protection Agency drinking water standards. The maximum pesticide concentration was 2.6 mg/L (micrograms per liter) for propargite, a miticide detected in only one sample. The maximum concentrations of the remaining 21 pesticides were less than 0.25 µg/L. The median concentrations were equal to the method detection limit for all pesticides except atrazine (0.008 µg/L) and metolachlor (0.012 µg/L). The ratio of herbicide detections to nondetections was largest in the planting season, smaller in the harvest season and smallest in the fallow season for the three basins. The same pattern existed for the insecticide ratios in the Little River and the Withlacoochee River.

Pairwise correlations between concentrations of atrazine and metolachlor, and four parameters (discharge, and concentrations of dissolved organic carbon, suspended organic carbon, and suspended sediment) were evaluated for each stream. The strongest correlations existed between metolachlor and mean daily discharge, and metolachlor and sediment in the Withlacoochee River. The only significant correlation for the Little River was between atrazine and suspended sediment.

Introduction

The conditions that influence the transport and degradation of pesticides within a river basin form a complex web of interactions. Understanding these interactions requires evaluating many of the physical, biological, and chemical components of the stream, the pesticides, and the basin. These components include climate, soils, riparian zones, hydrogeology, crops grown, pesticide application rates, channel slope, and surface water discharge. This report provides a foundation for future examinations of the complex interactions of pesticides in south-central Georgia streams by (1) describing pesticide concentrations and occurrence in three streams draining agricultural basins, and (2) evaluating the correlations between the two most frequently detected herbicides, atrazine and metolachlor, and measurements of discharge and concentrations of organic carbon and suspended sediment in the stream. The term “detection” refers to pesticide concentrations that are greater than or equal to the analytic method detection limit for each pesticide (Zaugg and others, 1995).

Pesticides were analyzed in stream water draining three agricultural basins in the northern part of the Georgia-Florida Coastal Plain (GAFL) study unit. The GAFL study unit was selected in 1991 as one of 20 initial study units in the NAWQA Program. The Tucsawhatchee Creek Basin is east of Hawkinsville, Ga. (fig. 1), and is drained by the Tucsawhatchee Creek, a tributary of the Ocmulgee River. The Ocmulgee River is a tributary of the Altamaha River, which discharges into the Atlantic Ocean. The Little River Basin is northwest of Ty Ty, Ga., and is drained by the Little River, a tributary of the Withlacoochee River. The Tucsawhatchee Creek Basin is slightly larger than the Little River Basin (fig. 1). The Withlacoochee River Basin, which is north of Quitman, Ga., is drained by the Withlacoochee River and has a drainage area that is more than 10 times the area of the Little River Basin which is nested within its drainage. The Withlacoochee River is a tributary of the Suwannee River which flows through north Florida and discharges into the Gulf of Mexico.

Land use and pesticide use

Agriculture is the largest land use in the three basins, occupying about one-half to two-thirds of the basin areas (fig. 1). Agricultural land in south-central Georgia is generally in upland elevations and is dissected by forest and wetland areas that occupy both the land sloping toward the stream tributaries and the lowland in the flood plains of main channels.

Major crops harvested in the three basins in 1992 were cotton, peanuts, corn, soybeans, wheat, vegetables, and orchard crops (fig. 2). Other crops such as sorghum, hay, oats, rye, and tobacco represented a small percentage of the acreage harvested. The acreage harvested for crops (fig. 2) represent about 90 to 110 percent of the total harvested crop land acreage. Planting more than one crop on the same acreage within a year makes it possible to account for more than 100 percent of the crop land acreage. Although the type of major crops did not change from 1987 to 1992, acreage of cotton generally increased whereas acreage of soybeans decreased (U.S. Bureau of Census, 1989, 1994).

The pesticides with the most estimated pounds of active ingredient applied in the three basins in 1987 were alachlor, aldicarb, and metolachlor, followed by smaller amounts of atrazine, benfluralin, chlorpyifos, MSMA, and trifluralin (Gianessi and Puffer, 1991, 1992).

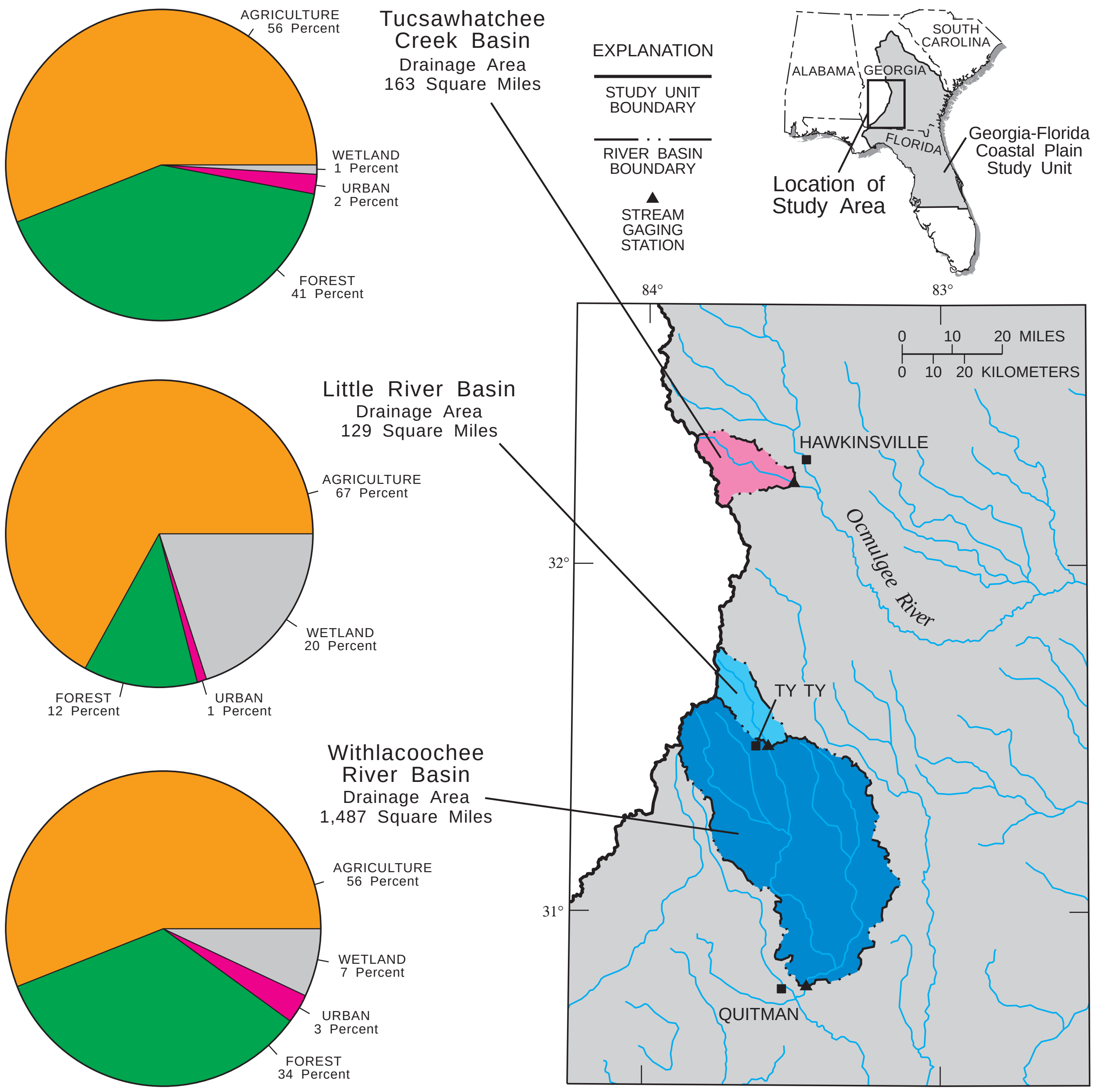


***Figure 1.** Stream water sampling sites and land use for three agricultural basins in the Georgia-Florida Coastal Plain study unit.* Land use is derived from digital data from 1972-78 (U.S. Geological Survey, 1986) updated with 1990 population estimates (Hitt, 1994).

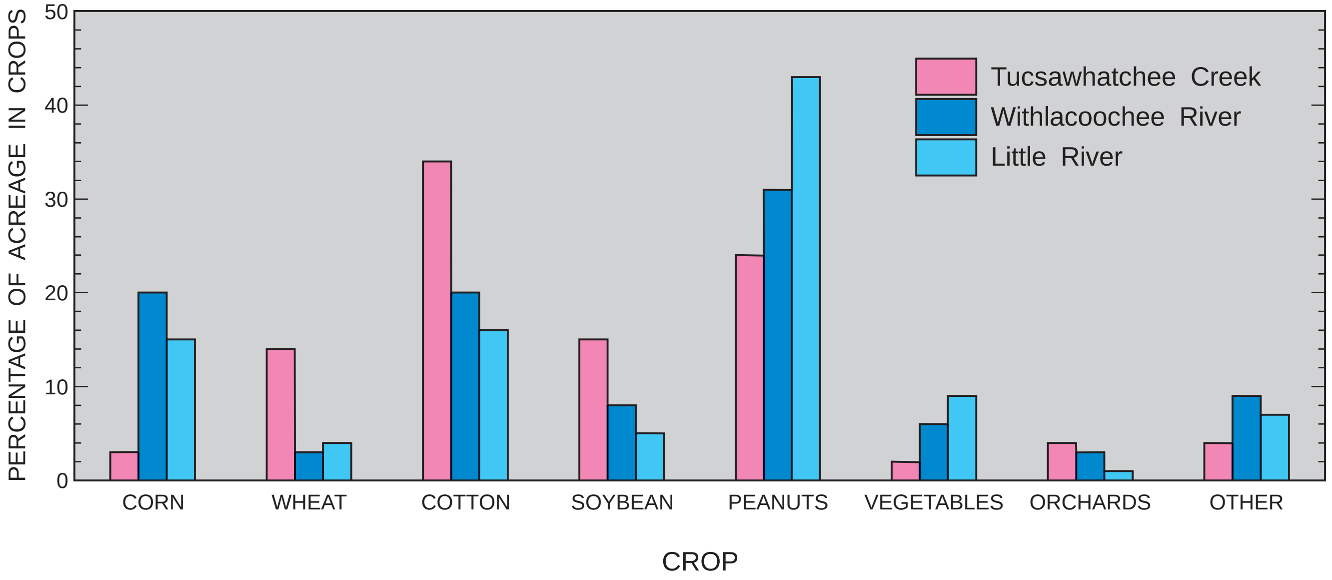


***Figure 2.** Major crops in three agricultural basins in 1992.* The category labeled “other” includes sorghum, hay, oats, rye, and tobacco. Basin crop acreages were derived by apportioning county data (U.S. Bureau of Census, 1994) on the basis of the ratio of agricultural land in the basin part of each county to total agricultural land in the county.

The same pesticides are used for different crop and land uses in Georgia. Atrazine is recommended for weed control in corn and sorghum as well as pine stands; whereas simazine is recommended for corn and for use in peach and pecan orchards (Delaplane, 1992). Stell and others (1995) documented the use of insecticides such as chlorpyrifos, diazinon, malathion, carbaryl, and lindane in pine stands and described the use of the same insecticides as ubiquitous in urban and suburban areas in west Georgia.

The large area of the basins, the high percentages of nonagricultural land, the variety of crops grown, and the use of the same pesticide for different crops and different land uses preclude the identification of specific land-use sources of pesticides in the three basins without additional information.

Sampling and analysis

The primary water-quality sampling site for each basin was located near the stream discharge gage (fig. 1). Water samples from the Tucsawhatchee Creek near Hawkinsville (USGS station 02215100) were collected weekly from March through October 1993 and monthly from November 1993 through June 1995. Water samples from the Little River near Ty Ty (USGS station 02317797) were collected weekly from March through May 1993 and in November 1993 and monthly from December 1993 through June 1995. No water-quality samples were collected from the Little River for June through September 1993, because the Little River had almost no flow in June and July and was dry in August and September. The Withlacoochee River near Quitman (USGS station 02318500) was sampled two to three times per month from March through September 1993 and monthly from October 1993 through June 1995. No samples were collected in May 1994 at any of the sites.

A total of 128 water samples were collected: 54 from the Tucsawhatchee Creek, 35 from the Little River, and 39 from the Withlacoochee River. Each water sample was analyzed for 44 pesticides and 2 pesticide degradation products. Concentrations of dissolved organic carbon, suspended organic carbon, and suspended sediment were also analyzed. The specific sampling design and procedures are described by Hatzell and others (1995) and Shelton (1994).

Pesticide occurrence in streams

Twenty two pesticides and 2 pesticide degradation products were detected in 1 or more of the 128 samples (fig. 3), whereas 21 pesticides and 1 degradation product were not detected[1]. Some of the pesticides that were not detected might not have been applied in the basins during the sampling period. The remainder of this report discusses the pesticides and degradation products that were detected.

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[1] The 10 herbicides analyzed but not detected in water samples were benfluralin, linuron, molinate, napropamide, pebulate, pronamide, propachlor, propanil, thiobencarb, and triallate. A degradation product of alachlor, 2,6-diethylaniline, was also not detected. The 11 insecticides not detected were alpha-HCH, azinphos-methyl, dieldrin, disulfoton, fonofos, methyl parathion, parathion, permethrin-cis, phorate, terbacil, and terbufos.

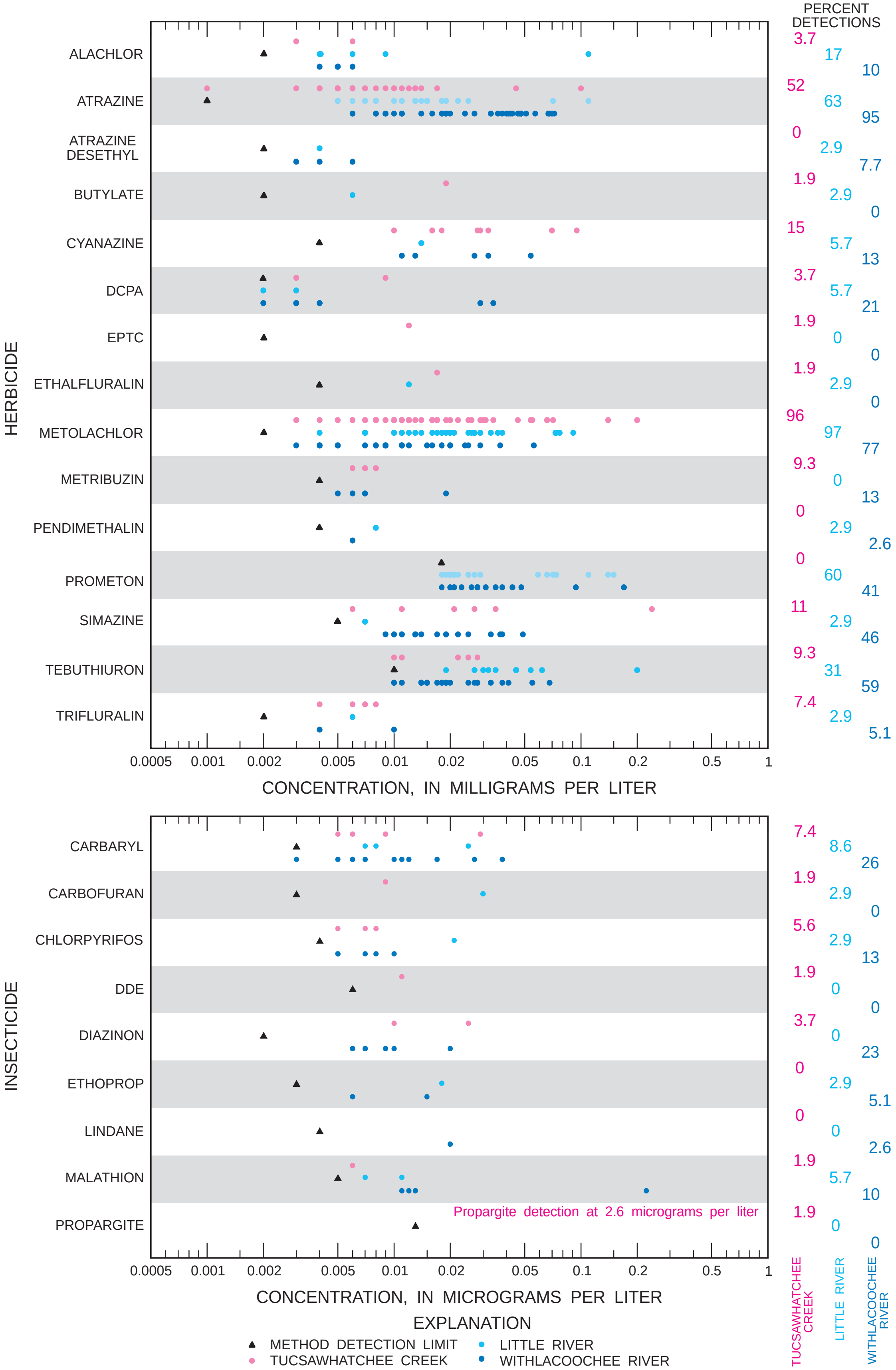

***Figure 3.** Percent detections, and concentrations of pesticides, pesticide degradation products, and method detection limits.* The percent detection for each pesticide at a stream site was calculated by dividing the number of detections by the total number of water samples collected at the stream site.

Pesticide median and maximum concentrations in the three streams were very low and did not exceed the U.S. Environmental Protection Agency maximum contaminant levels (MCL) for drinking water standards or health advisory levels (HAL) for drinking water (Nowell and Resek, 1994). Only two median concentrations were greater than the analytic method detection limit; the medians were 0.008 µg/L for atrazine and 0.012 µg/L for metolachlor. The maximum pesticide concentration was 2.6 µg/L for propargite, a miticide that was detected in only one sample. The maximum concentrations for all other pesticides were less than 0.25 µg/L, and 50 percent of the maximum concentrations were less than or equal to 0.025 µg/L. Carbaryl, chlorpyrifos, and diazinon were detected at concentrations greater than a guideline for the protection of freshwater aquatic life (table 1).

The numbers of pesticide detections and the maximum concentrations were lower in the streams in the GAFL study unit than in streams draining agricultural basins in NAWQA study units in other parts of the country. The number of pesticides with detections in more than 50 percent of samples was two for three streams in south-central Georgia whereas the number was five for three tributaries of the Trinity River in east Texas (Brown, 1996), six for nine sites in the Western Lake Michigan drainages in Wisconsin and Michigan (Sullivan and Richards, 1996), and seven for the White River in Indiana (Crawford, 1995). Each of the above counts included atrazine and metolachlor. Maximum concentrations of atrazine and metolachlor were, respectively: 0.11 and 0.20 µg/L in the GAFL study unit; 4.0 and 1.9 µg/L in the Trinity River; 7.0 and greater than 50 µg/L in the Western Lake Michigan drainages; and 11.0 and 4.9 µg/L in the White River.

***Table 1.** Insecticide concentrations that exceeded a guideline*

[Guideline concentrations established for the protection of freshwater aquatic life by the National Academy of Science and National Academy of Engineers are 0.02 µg/L for carbaryl, 0.001 µg/L for chlorpyrifos, and 0.009 µg/L for diazinon (Nowell and Resek, 1994)]

Insecticide	**Concentration (µg/L)**	**Sampling date**
Tucsawhatchee Creek		
Carbaryl	0.029	04/15/93
Chlorpyrifos	0.007	06/22/93
Chlorpyrifos	0.005	07/12/93
Chlorpyrifos	0.008	08/30/93
Diazinon	0.010	06/22/93
Diazinon	0.025	08/30/93
Little River		
Carbaryl	0.025	04/19/93
Chlorpyrifos	0.021	11/11/93
Withlacoochee River		
Carbaryl	0.027	04/21/93
Carbaryl	0.038	06/26/95
Chlorpyrifos	0.008	07/01/93
Chlorpyrifos	0.005	07/08/93
Chlorpyrifos	0.007	04/19/95
Chlorpyrifos	0.005	05/25/95
Chlorpyrifos	0.010	06/26/95
Diazinon	0.010	07/28/93
Diazinon	0.020	06/26/95

In general, herbicides were detected more frequently than insecticides for three streams draining agricultural basins in the GAFL study unit (fig. 3). The most frequently detected herbicides were atrazine and metolachlor and the most frequently detected insecticide was carbaryl.

The occurrence of individual pesticides differed among the three streams (fig. 3). Occurrence of specific pesticides can be expressed as the number of detections for each pesticide as a percentage of the number of water samples collected at the site. Samples from the Withlacoochee River had a much higher percentage of detections for the herbicides, atrazine and simazine, and for the insecticides, carbaryl and diazinon, than those from either the Little River or the Tucsawhatchee Creek. In contrast, the Withlacoochee River had a much lower percentage of metolachlor detections.

Both the Little River and the Withlacoochee River had much higher percentages of prometon and tebuthiuron detections than the Tucsawhatchee Creek; these herbicides are not generally used on crop land but are recommended for weed control on noncropped land such as rights-of-way and industrial storage areas (Delaplane, 1992). Several powerlines are located in the Little River Basin. Atrazine desethyl, a degradation product of atrazine, was detected in the Little River and the Withlacoochee River. DDE, a degradation product of DDT, was detected in the Tucsawhatchee Creek; however, all DDT uses except for public health emergencies were cancelled in the United States on January 1, 1973.

Spatial variation within two basins

To obtain more information on the spatial variation of pesticides in stream water within the Tucsawhatchee Creek and Little River Basins, several stream sites in each basin were sampled once within a brief period. These samples were collected in addition to the regular sampling described earlier. This procedure is an example of synoptic sampling in the NAWQA Program.

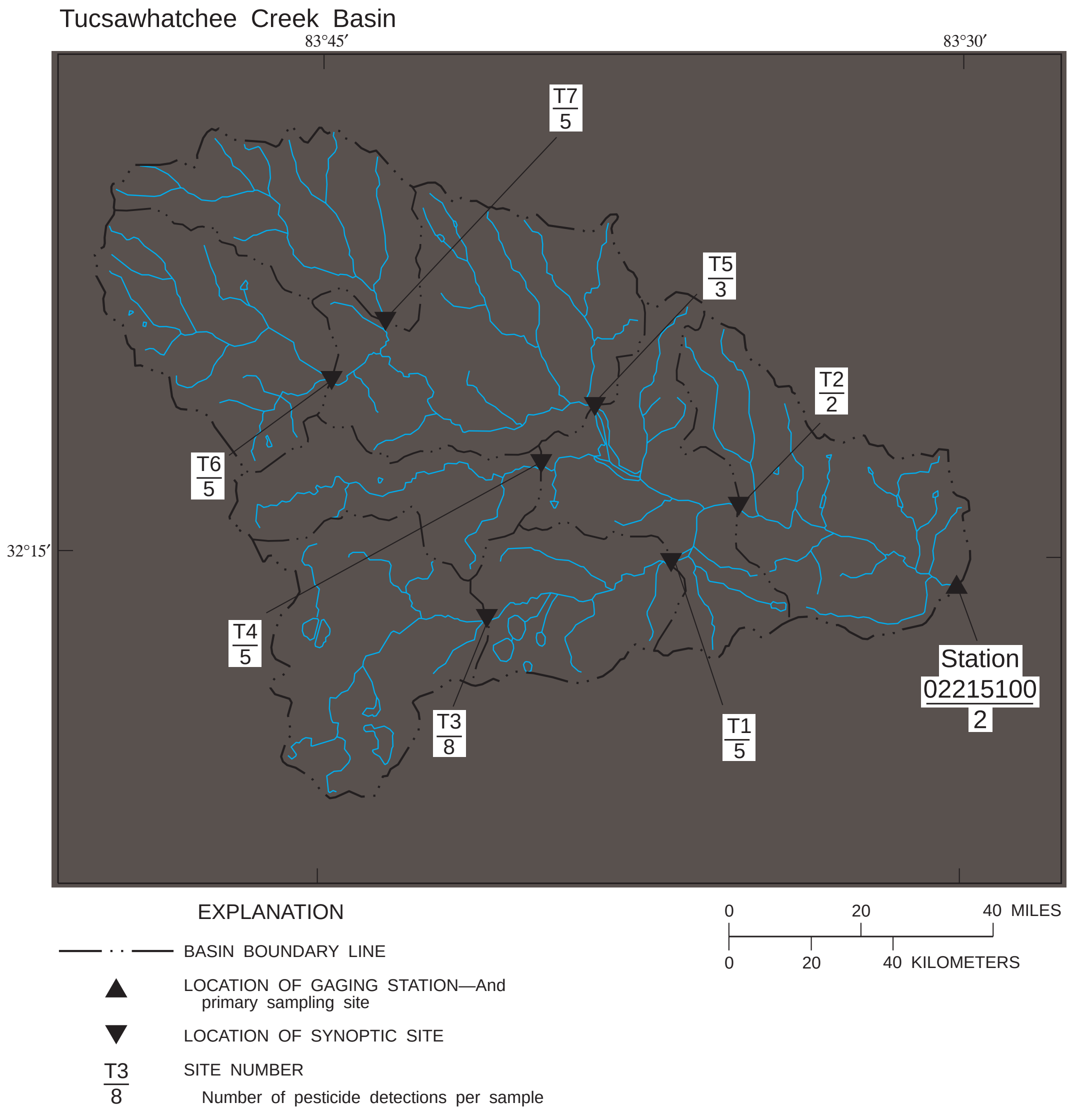

Figure 4. *Synoptic surface-water sampling sites in the Tucsawhatchee Creek River Basin.* The shaded relief image has a vertical exaggeration of 10 and a pixel size of 30 meters; the source is 1:100,000-scale topographic contours.

The synoptic sampling within the Tucsawhatchee Creek Basin was completed during July 19-21, 1993, at seven sites in addition to the primary site (fig. 4). A total of 10 herbicides, 1 insecticide, and DDE were detected (table 2). Maximum concentrations of specific pesticides in the synoptic samples were within the ranges of the concentrations for samples taken during the regular sampling at the primary site (fig. 3).

The number of pesticides detected at each site (fig. 4) and the location of the maximum concentrations (table 2) indicate that more pesticides were detected in the southern part of the Tucsawhatchee Creek Basin than in the northern part. The southern

Table 2. *Pesticide detections and concentrations for synoptic water-quality sampling in the Tucsawhatchee Creek Basin*

[Site numbers refer to figure 4]

Pesticide	Number of detections	Maximum concentration	Site number of maximum concentration
Herbicides			
Atrazine	5	0.007	T5
Cyanazine	3	0.031	T3
Ethalfluralin	1	0.059	T3
Metolachlor	8	0.095	T6
Metribuzin	1	0.005	T6
Napropamide	1	0.003	T1
Pendimethalin	1	0.021	T3
Prometon	6	0.063	T4
Tebuthiuron	1	0.014	T7
Trifluralin	3	0.065	T3
Insecticides and Degradation Products			
Chlorpyrifos	2	0.020	T3
DDE	3	0.006	T3,T4,T6

part contains a large plateau with 70 percent agriculture and 8 percent urban land use; it is drained primarily by the tributary at site T3 (fig. 4). Site T3 had the most pesticide detections as well as four of the maximum concentrations. In addition, DDE was detected at three sites in the southern part of the basin (table 2).

The synoptic sampling within the Little River Basin was completed during November 16-18, 1993, at 16 sites in addition to the primary site (fig 5). Only two pesticides, metolachlor and prometon, were detected; both were detected frequently during regular sampling at the primary site (fig. 3). The concentrations of these two herbicides were within the ranges of concentrations for samples taken during regular sampling at the primary site. Metolachlor concentrations were highest in stream water at site L12 on the southwestern branch of the Little River and decreased downstream. Prometon concentrations were highest at site L10 on the northeastern branch of the river and decreased downstream. This pattern of decreasing downstream concentrations is characteristic of dilution and possible degradation.

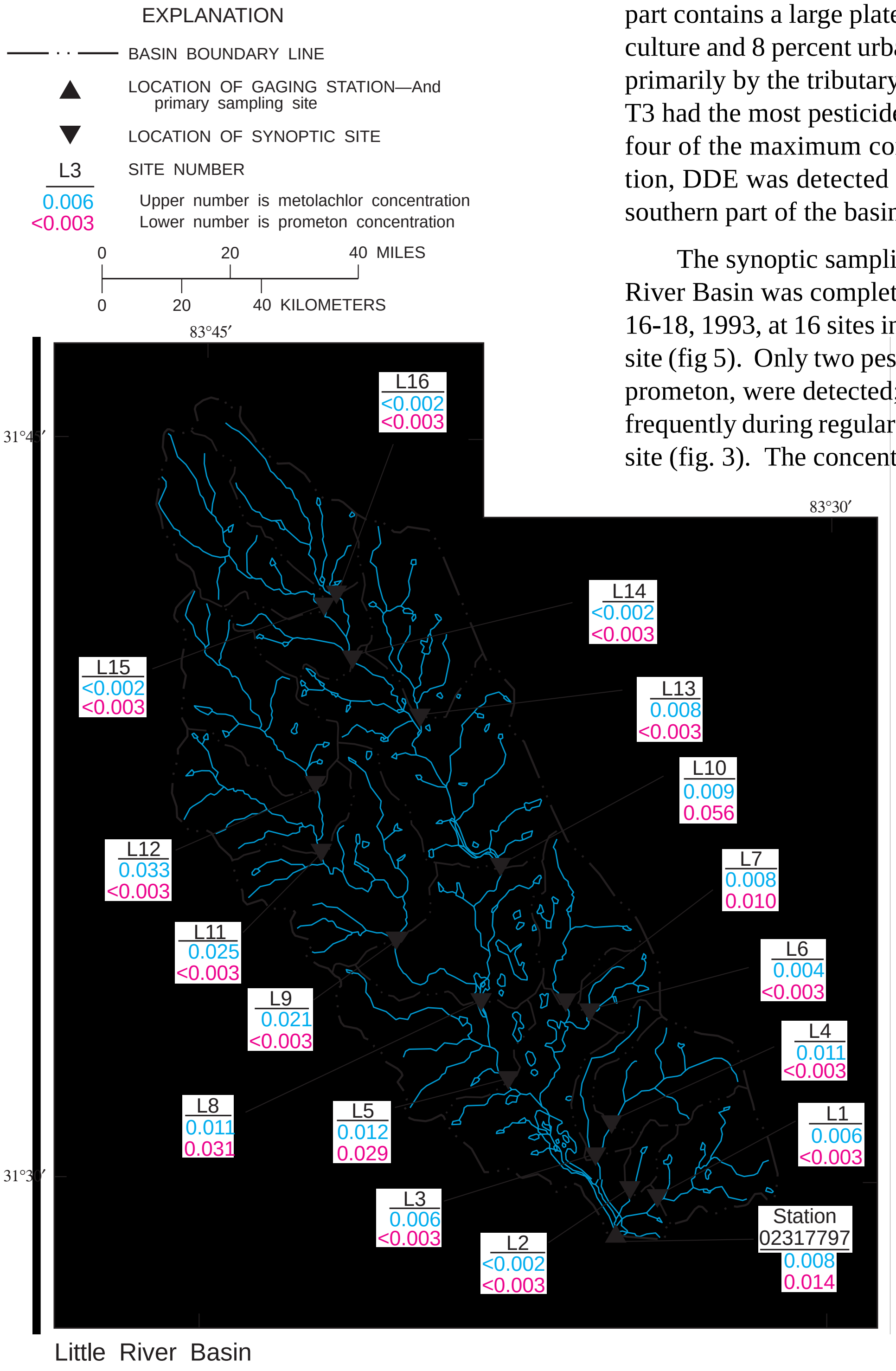

Figure 5. *Synoptic surface-water sampling sites in the Little River Basin.* The shaded relief image has a vertical exaggeration of 10 and a pixel size of 30 meters; the source is 1:100,000-scale topographic contours.

Effects of agricultural seasons

Overall pesticide occurrence varied according to agricultural season (fig. 6). Overall occurrence can be expressed as the ratio of the sum of detections to the sum of nondetections for all pesticides. The durations of the three agricultural seasons were: planting season from April through July, harvesting season from August through November, and fallow season from December through March. These seasons were based on the usual planting and harvesting dates for the major field crops grown in the basins (Georgia Agricultural Statistics Service, 1995).

For herbicides, the ratios of detections to nondetections were largest in the planting season, smaller in the harvest season, and smallest in the fallow season (fig. 6). The same pattern existed for the insecticides in the Little River and the Withlacoochee River although the ratio of detections to nondetections for the Little River was very low. The Tucsawhatchee Creek showed a decrease between the harvesting and fallow seasons but not between the planting and harvesting seasons. The pattern of change in the ratios with season was expected to be different between herbicides and insecticides since herbicides are generally applied in the spring near the time of crop emergence, whereas insecticides are applied as the crop grows and matures. The detections in the fallow season may be related to residual pesticides from the planting and harvesting seasons or to the application of pesticides to cool-season crops such as wheat, rye, oats, spring cabbage, and pecans.

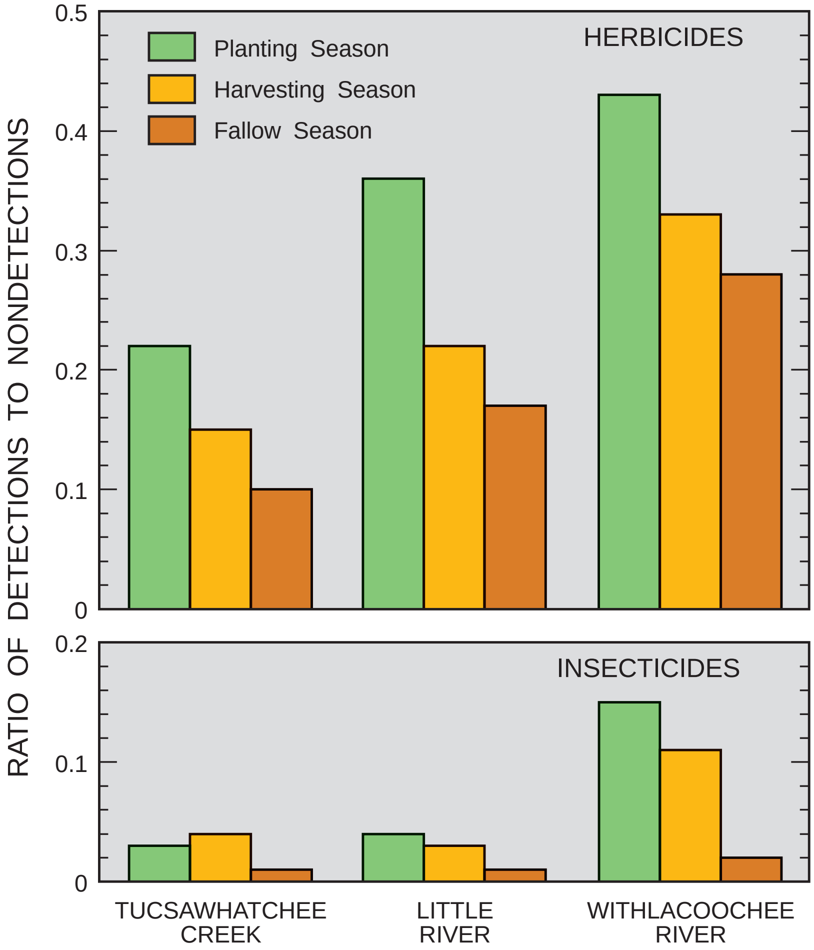

Figure 6. *Changes in the ratio of pesticide detections to nondetections by agricultural season.*

Atrazine and metolachlor concentrations

Atrazine and metolachlor have been frequently detected in stream water from the three basins in this report and in other study units. The large number of detections for these two herbicides throughout the sampling period provided an opportunity to evaluate the relation between pesticide concentrations in streams and agricultural seasons and to compare changes in pesticide concentrations to changes in stream discharge, and concentrations of organic carbon and suspended sediment. Because runoff is a primary source of pesticide concentrations in surface water and runoff contributes to discharge, changes in pesticide concentrations may change with discharge. Organic matter and suspended mineral particles influence pesticide concentrations in soils and stream water by providing chemical sites for the adsorption and desorption of pesticides.

The Kruskal-Wallis test was used to determine if the median concentrations of atrazine and metolachlor were significantly different among seasons. When the Kruskal-Wallis test was significant at an acceptance level (alpha) of 0.05, then differences among seasons were determined by substituting ranks for the original data and performing Tukey’s multiple comparison test (Helsel and Hirsch, 1992).

Atrazine concentrations were statistically higher in the planting season but were the same for the harvesting and fallow seasons (fig. 7). Metolachlor concentrations were statistically the same for the planting and fallow seasons but were lower in the harvesting season (fig. 7). These differences between atrazine and metolachlor are not easily explained by differences in time of application since both herbicides are applied either before or just after the crop emerges. Atrazine is recommended for control of annual broadleaf weeds in corn and sorghum whereas metolachlor is recommended for control of annual grasses in corn, sorghum, and peanuts (Delaplane, 1992). Also, atra-

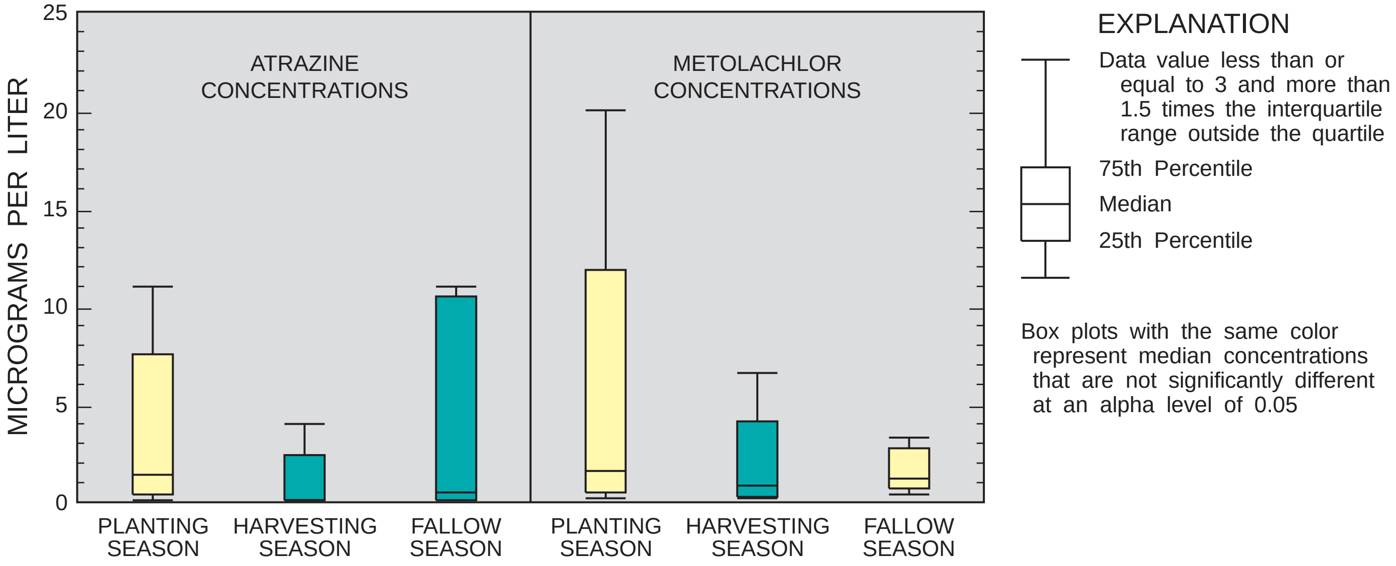

Figure 7. *Differences in atrazine and metolachlor concentrations by agricultural seasons.*

zine and metolachlor can be applied together for weed control in corn (Delaplane, 1992). The differences in atrazine and metolachlor concentrations among seasons may be related to differences in the solubility of the two herbicides as well as their interactions with soil particles and microorganisms. For example, atrazine has been rated as slightly soluble in water whereas metolachlor has been rated as soluble in water (Briggs, 1992). Atrazine adsorbs and desorbs readily from soil particles; metolachlor is readily adsorbed by soil organic matter (Herbicide Handbook Committee, 1983).

Changes in atrazine and metolachlor concentrations were compared to changes in four parameters: mean daily discharge, and concentrations of dissolved organic carbon, suspended organic carbon, and suspended sediment. Suspended sediment concentrations were measured as the weight of fine-grained sediments with a diameter of 0.062 mm or less per liter of water. The strength of the associations between the concentrations of the two herbicides and the four parameters were statistically evaluated by calculating Spearman's rho, which is a correlation coefficient based on ranks (Helsel and Hirsch, 1992).
The larger the absolute value of rho, the stronger the correlation. A positive rho value indicates that the pesticide and the parameter increased or decreased together whereas a negative rho value indicates that as one increased, the other decreased. A correlation was considered significant at an alpha level of 0.05.

Rho values for the same combinations of atrazine and metolachlor with the four parameters were different among the three basins, and both positive and negative correlations were found (table 3). In the Tucsawhatchee Creek, atrazine correlated negatively with dissolved organic carbon and positively with suspended sediment, whereas metolachlor correlated positively with discharge and suspended sediment. In the Little River, the positive correlation between atrazine and suspended sediment was the only significant combination. In the Withlacoochee River, atrazine correlated negatively with discharge, dissolved organic carbon, and suspended sediment but metolachlor correlated positively with the same parameters. The highest rho value was 0.62 for the association between metolachlor and suspended sediment in the Withlacoochee River.

Table 3. *Spearman's rho correlation coefficients for combinations of atrazine and metolachlor concentrations with four parameters*

[Coefficients are significant at an alpha level of 0.05. NS is not significant]

Parameters	**Tucsawhatchee Creek**	**Little River**	**Withlacoochee River**
	Atrazine Concentration		
Mean daily discharge	NS	NS	-0.46
Dissolved organic carbon	-0.36	NS	-0.44
Suspended organic carbon	NS	NS	NS
Suspended sediment	0.34	0.44	-0.33
	Metolachlor Concentration		
Mean daily discharge	0.32	NS	0.61
Dissolved organic carbon	NS	NS	0.47
Suspended organic carbon	NS	NS	NS
Suspended sediment	0.33	NS	0.62

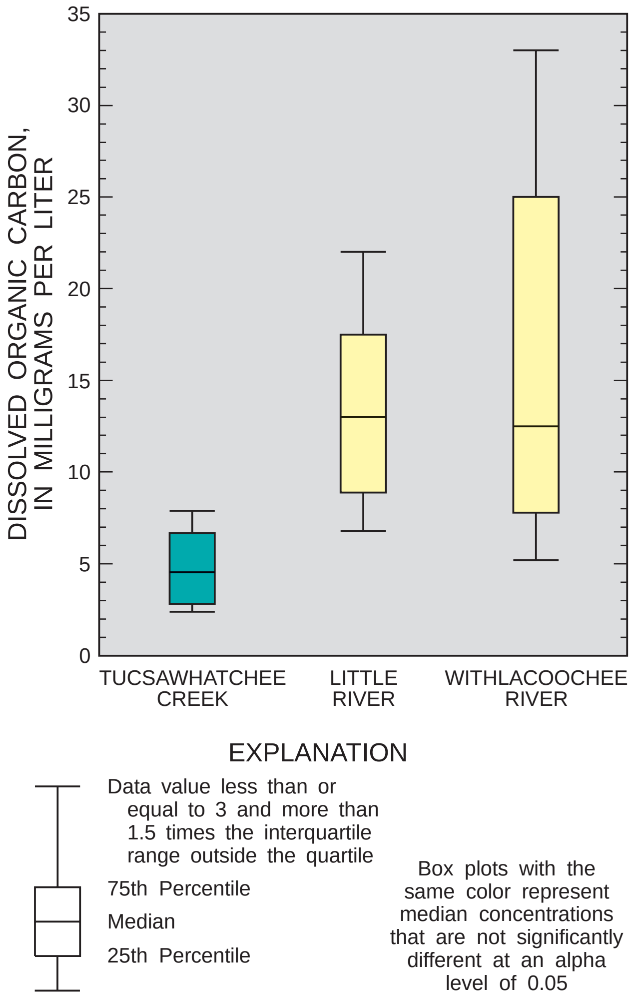

Figure 9. *Differences in concentrations of dissolved organic carbon by basins.*

The correlations between the two herbicides and the four parameters may be influenced by several factors, including differences among the basin drainages, differences in the parameters among the basins, and correlations among the parameters. The Tucsawhatchee Creek and the Little River drainages may differ in the rate of water movement through the basins (figs. 4 and 5). The drainage in the northern part of the Tucsawhatchee Creek Basin is more incised into the landscape and has narrower flood plains than in the Little River Basin. The drainage in the Little River Basin is characterized by meandering in the main channel and by ponds at the inception of the stream tributaries. Depending on antecedent conditions, runoff entering the Little River is likely to move through the basin more slowly than the Tucsawhatchee Creek and part of the runoff can be stored in the numerous ponds. Slowing the movement of water increases the potential for degradation by providing additional time for the herbicides to interact with the stream environment.

Three of the four parameters that were correlated to atrazine and metolachlor were different among the basins. During the sampling period, the peak discharges for both the Tucsawhatchee Creek and the Little River ranged between about 1,500 cubic feet per second (ft^3/s) and 3,500 ft^3/s with the exception of one flood event in July 1994 for the Tucsawhatchee Creek (fig. 8). In contrast, peak discharges for the Withlacoochee River ranged from about 8,000 ft^3/s to 20,000 ft^3/s (fig. 8).

Median concentrations of dissolved organic carbon were not significantly different for the Little River and the Withlacoochee River at an alpha level of 0.05 but were significantly higher than the median concentration for the Tucsawhatchee Creek (fig. 9). The median concentrations of suspended organic carbon for the Tucsawhatchee Creek (0.4 mg/L) and the Withlacoochee River (0.2 mg/L) were not significantly different but were significantly lower than the median concentration for the Withlacoochee River (0.6 mg/L). The median concentrations of the suspended sediment were not significantly different among the basins; the median concentration for all suspended sediment samples was 9.12 mg/L. Higher concentrations of organic carbon and suspended sediment may provide more adsorption sites for atrazine and metolachlor.

When the data are combined for the three basins, several of the four parameters were correlated to each other (table 4). Discharge was positively correlated with concentrations of dissolved organic carbon and suspended sediment. Suspended sediment concentrations were positively correlated with concentrations of dissolved and suspended organic carbon.

The above differences among the basin drainages, differences in the parameters among the basins, and correlations among the parameters demonstrate the complexity and interactions of factors that can influence concentrations of atrazine and metolachlor in streams draining agricultural basins in the GAFL study unit.

Table 4. *Spearman's rho correlation coefficients among four parameters*

[Data were combined for three streams. Rho values are significant at an alpha level of 0.05. All other combinations of parameters were not significant]

Parameter	Parameter	Spearman's rho
Mean daily discharge	Suspended sediment	0.49
Mean daily discharge	Dissolved organic carbon	0.39
Suspended sediment	Dissolved organic carbon	0.24
Suspended sediment	Suspended organic carbon	0.39

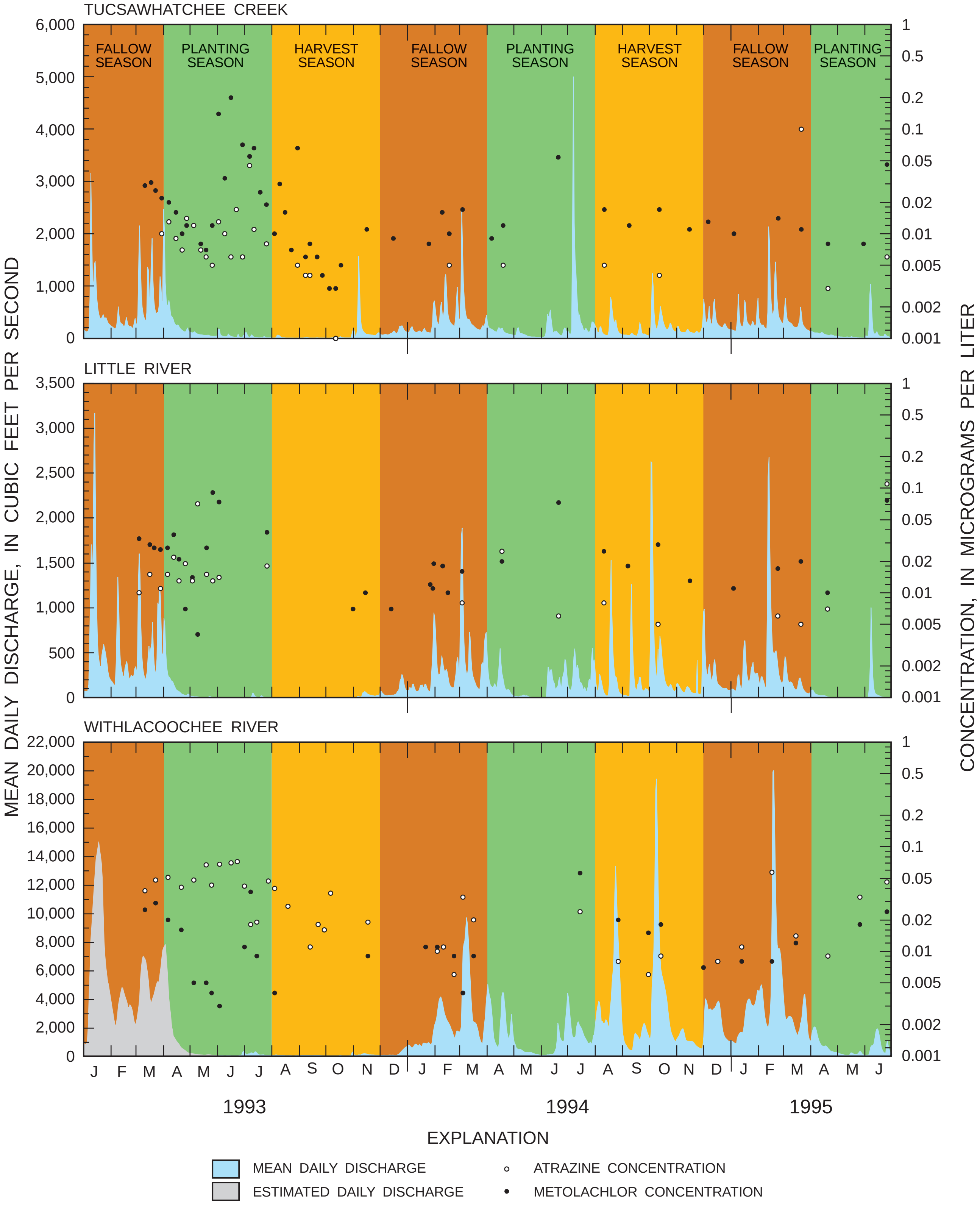

Figure 8. *Mean daily discharge, concentrations of atrazine and metolachlor, and agricultural seasons for three streams.* Estimated mean daily discharge values for the primary site at the Withlacoochee River near Quitman, Ga., were derived from discharge records for the Withlacoochee River near Pinetta, Fla. (USGS station 02319000).

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NAWQA Program

The objectives of the USGS National Water-Quality Assessment Program (NAWQA) are to describe the water-quality conditions for a large part of the Nation’s freshwater streams, rivers, and aquifers, describe how water quality changes over time, and improve understanding of the primary natural and human factors that affect water-quality conditions (Hirsch and others, 1988). These objectives are achieved through the national synthesis of data from investigations completed by 60 study units located in the Nation’s most important river basins and aquifers. Reports such as this one are elements in the comprehensive body of information developed as a part of the NAWQA Program.