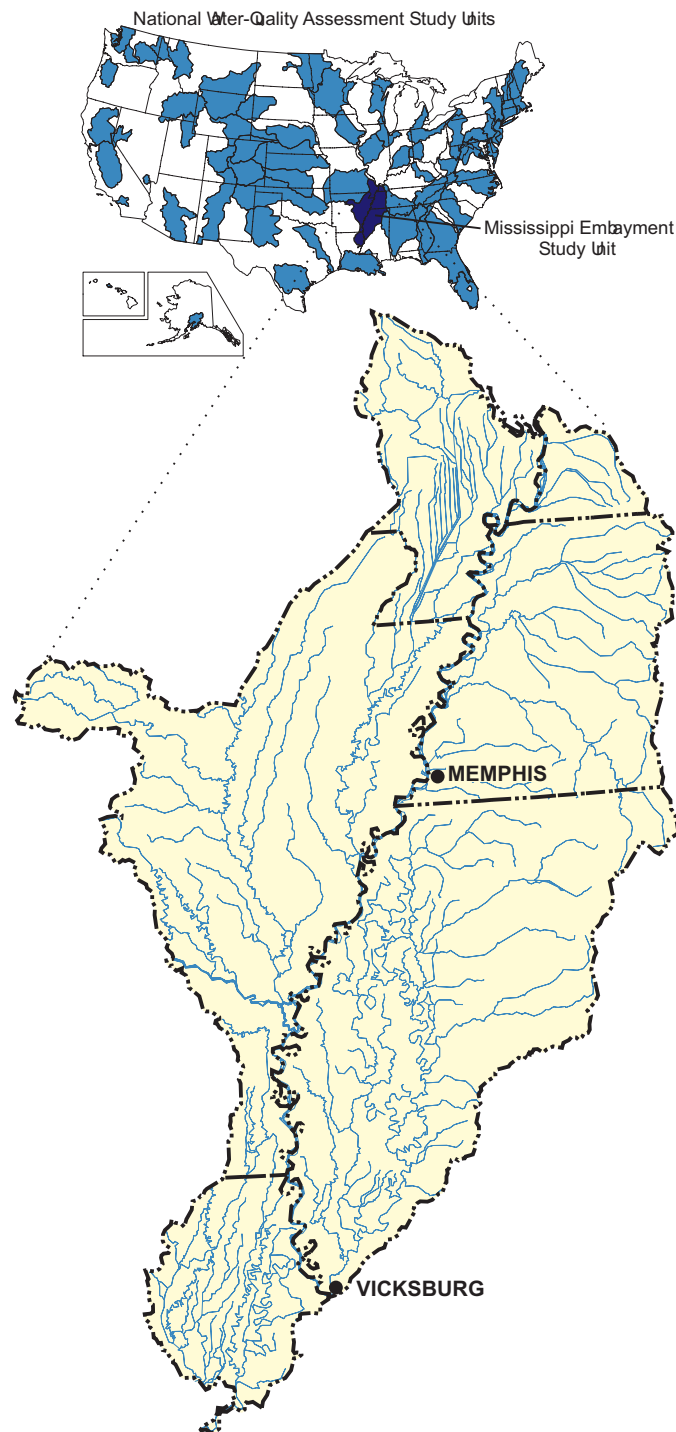
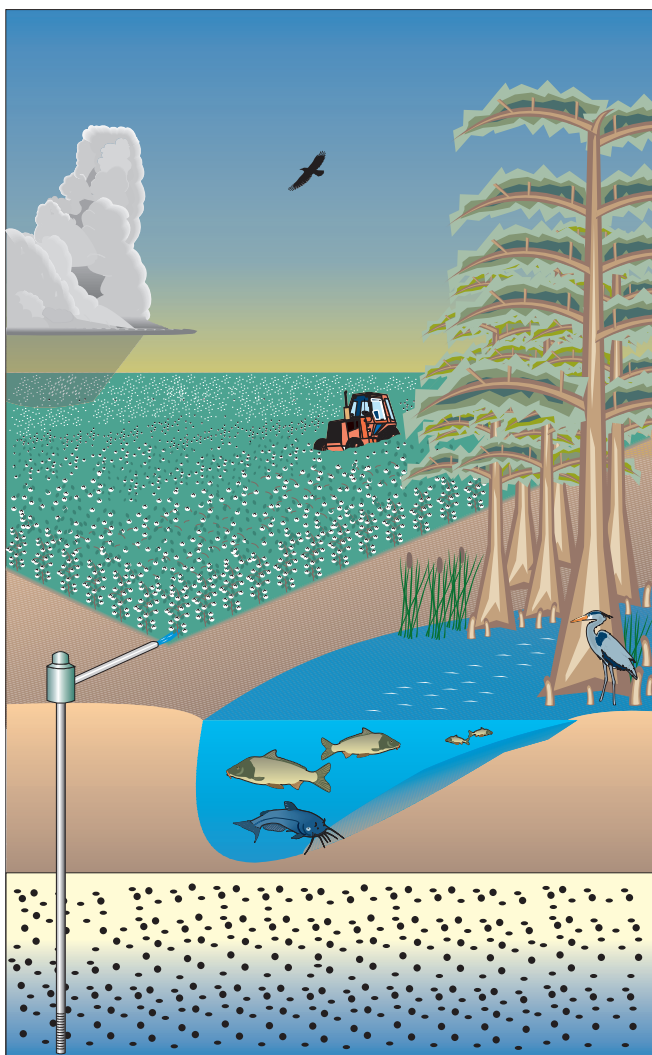


# OCCURRENCE OF PESTICIDES IN FIVE RIVERS OF THE MISSISSIPPI EMBAYMENT STUDY UNIT, 1996-98

U.S. GEOLOGICAL SURVEY  
Water-Resources Investigations Report 99- 4159



National Water-Quality Assessment Program

# Occurrence of Pesticides in Five Rivers of the Mississippi Embayment Study Unit, 1996–98

*By* R.H. Coupe

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U.S. Geological Survey

Water-Resources Investigations Report 99-4159

National Water-Quality Assessment Program

Pearl, Mississippi  
2000



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## FOREWORD

The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth resources of the Nation and to provide information that will assist resource managers and policymakers at Federal, State, and local levels in making sound decisions. Assessment of water-quality conditions and trends is an important part of this overall mission.

One of the greatest challenges faced by water-resources scientists is acquiring reliable information that will guide the use and protection of the Nation's water resources. That challenge is being addressed by Federal, State, interstate and local water-resource agencies and by many academic institutions. These organizations are collecting water-quality data for a host of purposes that include: compliance with permits and water-supply standards; development of remediation plans for a specific contamination problem; operational decisions on industrial, wastewater, or water-supply facilities; and research on factors that affect water quality. An additional need for water-quality information is to provide a basis on which regional and national-level policy decisions can be based. Wise decisions must be based on sound information. As a society we need to know whether certain types of water-quality problems are isolated or ubiquitous, whether there are significant differences in conditions among regions, whether the conditions are changing over time, and why these conditions change from place to place and over time. The information can be used to help determine the efficacy of existing water-quality policies and to help analysts determine the need for and likely consequences of new policies.

To address these needs, the Congress appropriated funds in 1986 for the USGS to begin a pilot program in seven project areas to develop and refine the National Water-Quality Assessment (NAWQA) Program. In 1991, the USGS began full implementation of the program. The NAWQA Program builds upon an existing base of water-quality studies of the USGS, as well as those of other Federal, State, and local agencies.

The objectives of the NAWQA Program are to:

- Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.
- Describe how water quality is changing over time.
- Improve understanding of the primary natural and human factors that affect water-quality conditions.

This information will help support the development and evaluation of management, regulatory, and monitoring decisions by other Federal, State, and local agencies to protect, use, and enhance water resources.

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of more than 50 major river basins and aquifer systems of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within these study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

National synthesis of data analysis, based on aggregations of comparable information obtained from the study units, is a major component of the program. This effort focuses on selected water-quality topics using nationally consistent information. Comparative studies will explain differences and similarities in observed water-quality conditions among study areas and will identify changes and trends and their causes. The first topics addressed by the national synthesis are pesticides, nutrients, volatile organic compounds, and aquatic biology. Discussions on these and other water-quality topics will be published in periodic summaries of the quality of the Nation's ground and surface water as the information becomes available.

This report is an element of the comprehensive body of information developed as part of the NAWQA Program. The program depends heavily on the advice, cooperation, and information from many Federal, State, interstate, Tribal, and local agencies and the public. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch  
Chief Hydrologist



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Conversion Factors, Abbreviations, and Acronyms		
Multiply	By	To obtain
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
square mile (mi <sup>2</sup> )	2.590	square kilometer (km <sup>2</sup> )
acre	0.4047	hectare
pound, avoirdupois (lb)	0.4536	kilogram (kg)
cubic foot per second (ft <sup>3</sup> /s)	0.02832	cubic meter per second (m <sup>3</sup> /s)
g	gram	
L	liter	
µg/L	micrograms per liter	
µm	micron	
BDMC	4-bromo-3, 5-dimethyl phenyl-n-methylcarbamate	
FMS	field matrix spike	
GCMS	gas chromatography/mass spectrometry	
HPLC	high-performance liquid chromatography	
MRL	method reporting level	
MISE	Mississippi Embayment	
SPE	solid phase extraction	
NAWQA	National Water-Quality Assessment	
NWQL	National Water-Quality Laboratory	
COE	U.S. Army Corps of Engineers	
USEPA	U.S. Environmental Protection Agency	
USGS	U.S. Geological Survey	

# Occurrence of Pesticides in Five Rivers of the Mississippi Embayment Study Unit, 1996–98

By R.H. Coupe

## Abstract

The occurrence and temporal distribution of more than 80 pesticides and pesticide metabolites were determined in five rivers of the Mississippi Embayment National Water-Quality Assessment study unit from February 1996 through January 1998. More than 230 samples were collected and analyzed during the 2-year study. The five rivers sampled included three rivers with small, primarily agricultural watersheds; one river with a small urban watershed in Memphis, Tennessee; and one large river with mixed land use (row-crop agriculture, pasture, forest, and urban).

Pesticides, usually herbicides, were frequently detected in water samples from every river. Insecticides were frequently detected (chlorpyrifos and diazinon in all samples) only in the river that drains the urban watershed. The occurrence of pesticides in surface water varied among the agricultural watersheds as well as between the agricultural and urban watersheds. The pesticides detected in the rivers that drain the agricultural watersheds were related to the major crop types cultivated in the watershed—corn is mostly grown in the northern part of the study unit, whereas cotton and rice are mostly grown in the southern part. The occurrence of pesticides in the Yazoo River, which drains the mixed land-use watershed, was similar to pesticide occurrence in the rivers that drain smaller agricultural watersheds, although concentrations were lower

in the Yazoo River. Likewise, simazine, which was detected in all urban stream samples, was also detected in all Yazoo River samples, but in lower concentrations.

The aquatic-life criteria for diazinon and chlorpyrifos was exceeded in 24 of 25 and 12 of 25 urban river samples, respectively, but only once or twice in agricultural and mixed-use watershed samples. Atrazine exceeded the aquatic-life criterion in about 20 percent of the samples from each river, particularly in the spring following pesticide application.

## INTRODUCTION

The goal of the National Water-Quality Assessment (NAWQA) Program is to assess the status and trends in the quality of the Nation's ground- and surface-water resources on a regional or national scale, and to link the status and trends with an understanding of the natural and human factors that affect the quality of water (Gilliom and others, 1995). In 1994, the U.S. Geological Survey (USGS) began an assessment of water quality in the Mississippi Embayment (MISE) study unit. The MISE NAWQA study unit is 1 of over 50 NAWQA study units that contributes to the NAWQA Program by providing water-quality information on a local scale.

The MISE study unit encompasses an area rich in history and natural resources. Some of the most famous examples of pre-Columbian mound building cultures—Poverty Point in northwestern Louisiana and the Toltec Mounds near Little Rock, Arkansas—



are found in the study unit. After thousands of years of accumulated alluvial and eolian deposits, the soils covering much of the study unit are some of the most productive in the world. Productive soils, coupled with a long growing season and a plentiful water supply, make agriculture the dominant economic force in the study unit.

Hernando De Soto in the early 1540's was the first recorded European to explore the study unit. When his battered and bruised entrada reached the banks of the Mississippi River below Memphis, Tenn., they discovered a culture rich in the amenities of life: plentiful food, an active religious life, athletic endeavors, and order and discipline (Wells, 1994). Two hundred canoes filled with 7,000 warriors met De Soto. When French explorers Marquette and Joliet reached the area more than 100 years later, the ravages of endemic diseases introduced by the Spanish had greatly reduced the indigenous population. From the confluence of the Mississippi and the Ohio Rivers to the banks of the Arkansas River, the French explorers only recorded seeing two small bands of natives (McNutt, 1996). In the years since, the study unit has undergone other massive changes. When the first European settlers arrived, most of the study unit was covered by forested wetlands, estimated to have been as much as 90 percent of the Mississippi Alluvial Plain. The subsequent clearing of the forests for agriculture and timber production and the straightening and levying of the streams to control flooding have led to vast changes in the landscape and in the water quality of the area.

The study unit is sparsely populated with the exception of the Memphis urban area, and agriculture is the dominant land use with corn, cotton, soybean, and rice being the most economically important crops. Pesticides are used heavily in the study unit for crop protection due to the warm and humid climate and long growing season that creates intense weed and insect pressure. The use of water-soluble pesticides has been shown to lead to their presence in surface water in many parts of the country.

Most of the older studies on the occurrence of pesticides in the surface waters of the study unit focused on the relatively insoluble insecticides (Willis and others 1983; Cooper, 1987; 1991a,b), many that are no longer used in the United States, such as toxaphene and DDT. These studies showed that many of these compounds exist throughout the ecosystem and persist long after their use has been discontinued.

Many small-scale studies (field or plot size) have examined the runoff potential for the more water-soluble herbicides used in the study unit (Wiese and others, 1980; Smith and others, 1991; Smith, 1992; Southwick and others, 1993; Reddy and others, 1994). More recently, a few localized studies in the study unit have examined the occurrence of pesticides in surface water. Senseman and others (1997) sampled lakes and streams in four counties of eastern Arkansas eight times over a 3-year period. The most frequently detected pesticides in this study, in order of occurrence, were metolachlor (13 percent), atrazine (11.5 percent), norflurazon (8.2 percent), and cyanazine (7.4 percent). Pennington (1996) collected a few surface-water samples in the Yazoo River Basin in June and September 1994 and July 1995; some high-use pesticides were present in nearly every sample. Pereira and Hostettler (1993) collected surface-water samples along the length of the Mississippi River and from the mouth of its major tributaries several times during 1991 and 1992. The results from their study indicated that cotton and rice herbicides only appear in the lower Mississippi River, downstream from the confluence of the Mississippi and Ohio Rivers, and that substantial amounts of these herbicides are being discharged to the Gulf of Mexico.

These few studies indicate that pesticides could be an important component of water quality in the surface waters of the study unit. To gain a better understanding of the effects of pesticide use on surface-water quality, five streams—representing varying land use and drainage size—were sampled from one to five times each month for 2 years.

## **Purpose and Scope**

This report documents the frequency of surface-water sampling, the methods of sample collection and processing, the analytical methods for the determination of pesticides in water samples, and the quality-assurance data collected during the study, as well as provides a statistical and graphical summary of these data. Additionally, this report interprets these data in relation to the seasonal and spatial occurrence of pesticides and relates this occurrence to other areas of the United States. Water samples were collected from one to five times each month from five rivers in the MISE NAWQA study unit from February 1996 to January 1998 and were analyzed for more than 80 water-soluble pesticides.

## Acknowledgments

The following people contributed significantly to the data-collection efforts from February 1996 through January 1998: Michael A. Manning, Charles H. Lee, and Desmond J. Funchess from the USGS office in Pearl, Mississippi; Robert L. Joseph, Larry M. Remsing, A. Dwight Lasker, and Phillip L. Stephens from the USGS office in Little Rock, Arkansas; and Robert E. Whitaker, Howard C. French, Brett D. Gidens, and Kelly R. Brady from the USGS office in Rolla, Missouri.

## Description of the Study Unit

The study unit is situated in the northern part of the Mississippi Embayment, a geological structural trough. The axis of the embayment roughly follows the course of the Mississippi River and gently plunges to the south-southwest. The study unit covers an area of approximately 48,500 mi<sup>2</sup> and includes parts of six States: Arkansas, Kentucky, Louisiana, Mississippi, Missouri, and Tennessee (fig. 1). The Mississippi River, flowing approximately north to south, bisects the study unit.

The study unit is located in the Coastal Plain physiographic province with approximately the western two-thirds of the study unit in the Mississippi Alluvial Plain and one-third (most of the study unit in Kentucky and Tennessee and the eastern part of the Yazoo River Basin) in the East Gulf Coastal Plain physiographic sections. The Mississippi River Alluvial Plain is a low, relatively flat area, with an average gulfward slope of about 0.5 ft/mi. The East Gulf Coastal Plain is gently rolling to hilly and abuts the eastern edge of the alluvial plain. The wind-blown material that formed the Loess Hills rises several hundred feet above the plain. The area where the Loess Hills once met the Mississippi River at Vicksburg, Miss., was what made that city such a formidable fortress during the American Civil War. The northernmost fort in the city sets on a hill about 250 ft above where the Mississippi River once flowed. The Spanish recognized the Loess Hills' dominance over the Mississippi River and built a fort in 1787. On the western boundary of the study unit, small areas of the Ozark Plateaus and Quachita physiographic sections are included in order to conform to drainage basin boundaries.

A distinct characteristic of the Mississippi River and other alluvial valley streams is the formation of natural levees along the banks and the pattern of parallel drainage that results from these levees. When the Mississippi River overflows, sediment is deposited adjacent to the river, forming low, natural levees along the stream with smaller deposits of sediment away from the stream. As a result, the banks of the river are usually 10 to 15 ft above the adjacent lowlands. The formation of these natural levees occurred, for the most part, before the present manmade levee system was built. Because of the natural levees, drainage usually flows away from and parallel to the Mississippi River except where tributary streams join the river.

The Mississippi River has been and continues to be a dominant influence on the Mississippi Alluvial Plain. The soils in this area are some of the most fertile in the world. However, the annual flooding of the alluvial plain that created this fertile soil is not conducive to modern row-crop agriculture, and in the years since the first Europeans arrived, extraordinary efforts have been made to prevent flooding. To this end, most of the rivers and streams in the plain were channelized and straightened. When the Mississippi River rises, the rivers and streams tributary to the Mississippi can be in a backwater condition for months at a time. For example, the U.S. Corps of Engineers (COE) levied the Yazoo River Basin along the Mississippi River and a considerable distance up the Yazoo River. When the Mississippi River rises, the two main rivers that drain the Yazoo River Basin Delta are closed, based on the premise that flooding from the Mississippi River will cause more damage than will flooding from the backed-up tributary rivers. These gates may remain closed for more than a month. One plan under consideration by the COE includes installing pumps to pump the backwater over the levees and into the Mississippi, similar to how backwater conditions are handled in the St. Francis River in Arkansas.

Most of the drainage in the study unit flows into the Mississippi River and eventually into the Gulf of Mexico. The drainage basins wholly contained within the study unit include the Yazoo River Basin in Mississippi, the Hatchie and Obion River Basins and a few smaller basins in Tennessee and Kentucky, and the St. Francis River Basin in Missouri and Arkansas. The White River Basin in Arkansas is not wholly within the study unit, nor is the Arkansas River Basin. The Tensas River Basin in northeastern Louisiana does not flow into the Mississippi River, but becomes part of the Red River and then flows into the Atchafalaya River and into the Gulf of Mexico.

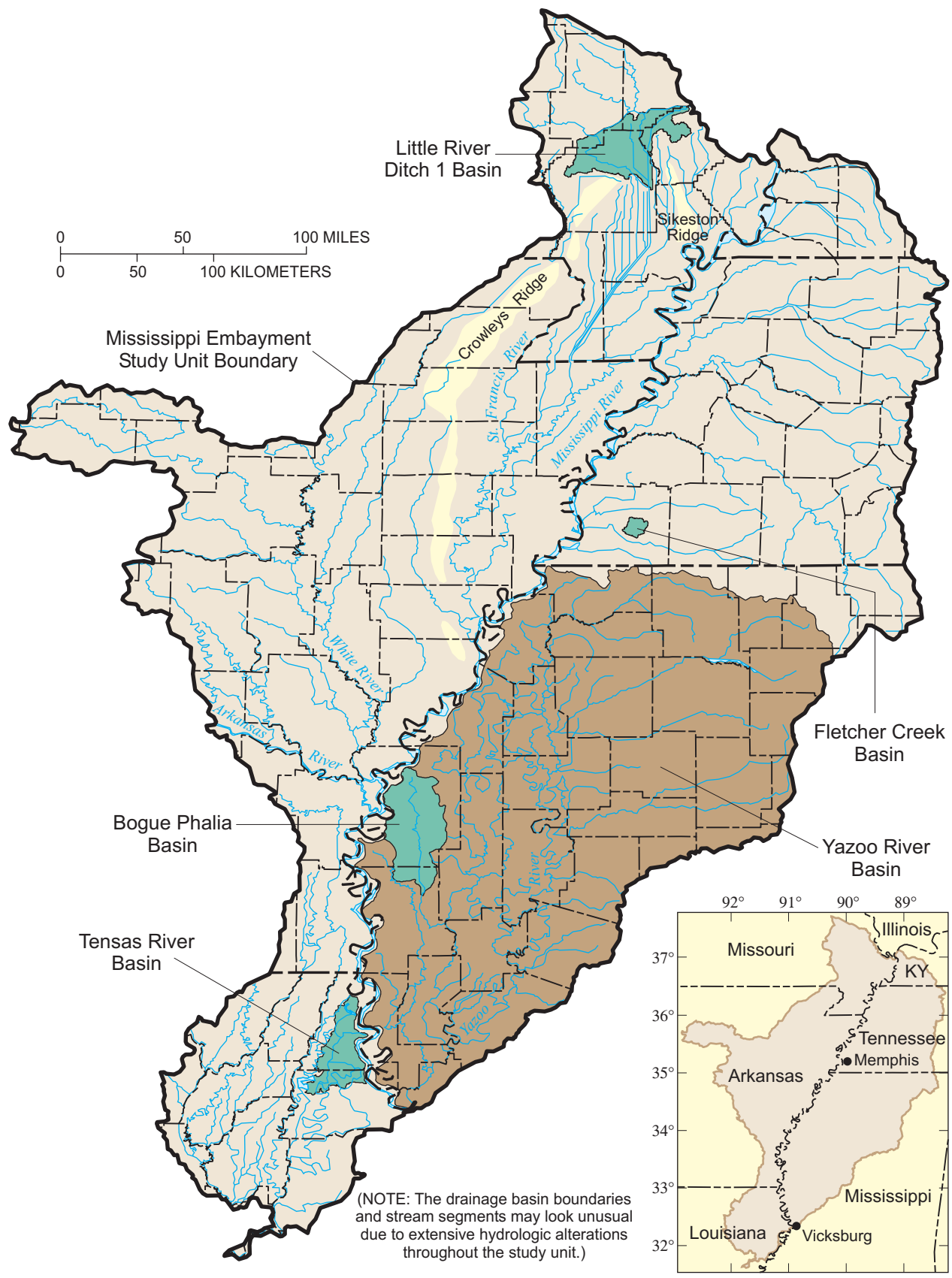


Figure 1. Mississippi Embayment study unit.

The land use in the study unit is almost wholly devoted to agriculture (about 21 million acres), and the only major metropolitan area within the basin is Memphis. Agricultural land use within the study unit is described in table 1. These data were generated from a survey of farmers conducted by the U.S. Department of Agriculture and represent the agricultural land use in 1993 (Stuart and others, 1996). Agricultural land use in the study unit is almost 80 percent row-crop agriculture; 15 percent is pasture and Conservation Reserve Program land (table 1). The major crops in 1993 were soybean and cotton, with smaller amounts of rice, corn, wheat, and a few miscellaneous crops. Only 6.3 percent of the land was listed in the category “other,” which includes fallow fields, building sites, wetlands, wooded areas, or aquaculture.

**Table 1.** Agricultural land-use characteristics of the Mississippi Embayment study unit, 1993

[CRP, Conservation Reserve Program (Stuart and others, 1996)]

Crop	Percentage of land use
Soybean	34.9
Cotton	21.8
Rice	6.8
Corn	5.2
Wheat	5.4
Other crops	4.5
CRP	4.9
Pasture	10.1
Other	6.3

Agriculture in the MISE area changed during the study due to mostly economic factors. Table 2 shows the changes in cotton, soybean, and corn during the 1995-97 growing seasons. As a result of the high cost and risk of growing cotton, and after the disastrous tobacco-budworm infestation in 1995, many farmers growing cotton on land marginally suited for its production, have shifted to soybean or corn production.

### Description of the Sampling Stations

A major component of the site-selection process was to target specific watersheds that are primarily influenced by a dominant land use (agriculture or urban) and to investigate the occurrence and distribution of pesticides in surface water. Little River Ditch 1,

Bogue Phalia, and Tensas River were selected to represent streams that drain predominantly agriculture basins; the difference between the basins was the relative amounts of corn, cotton, rice, and soybean acreage. Fletcher Creek was chosen to represent water quality in a rapidly developing urban area. The Yazoo River was chosen to represent a large stream with mixed land use (row-crop agriculture, pasture, forest, and urban).

### Little River Ditch 1, Missouri

The Little River Ditch 1 sampling site is located in Stoddard County near the town of Morehouse, Mo. (fig. 2). This is the northernmost extent of the MISE study unit and mostly consists of lowlands, with hills and ridges that are erosional remnants of a plain. This area is known as the Missouri Bootheel (commonly referred to as “bootheel”) because of its distinctively shaped boundary. Crowley’s Ridge (fig. 1), the most unique feature in the area, can rise 200 ft above the surrounding plain.

**Table 2.** Changes in the amount of cotton, corn, and soybean acreage, 1995-97, by State

[In thousands of acres]

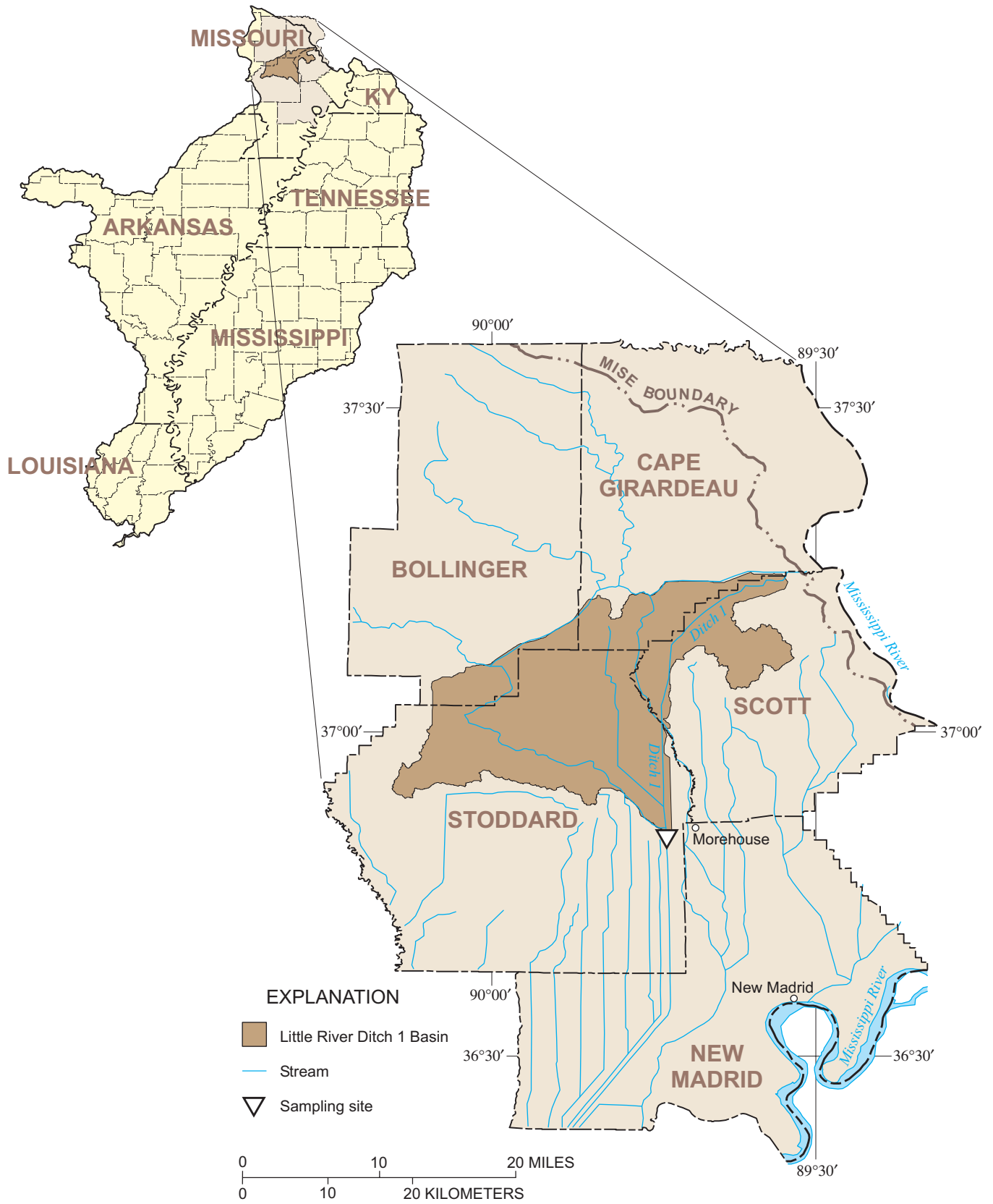
State	1995	1996	1997	Percentage of change
<b>Cotton</b>				
Arkansas <sup>1</sup>	1,170	1,000	962	-18
Louisiana <sup>1</sup>	1,070	895	647	-40
Mississippi <sup>2</sup>	1,460	1,120	985	-33
Missouri <sup>3</sup>	462	390	380	-18
Tennessee <sup>4</sup>	700	540	490	-30
<b>Corn</b>				
Arkansas	95	200	200	110
Louisiana	227	533	400	76
Mississippi	300	630	490	63
Missouri	2,400	2,750	2,950	23
Tennessee	640	770	730	14
<b>Soybean</b>				
Arkansas	3,400	3,500	3,571	5
Louisiana	1,040	1,080	1,260	21
Mississippi	1,850	1,800	2,100	14
Missouri	4,600	4,100	4,900	6.5
Tennessee	1,130	1,200	1,320	17

<sup>1</sup>U.S. Department of Agriculture, 1997 Census of Agriculture, accessed August 1999, URL <http://www.nass.usda.gov>

<sup>2</sup>Gregory and Kenerson, 1999.

<sup>3</sup>Hammer and Schlegel, 1998.

<sup>4</sup>Tennessee Agricultural Statistics Service Staff, 1998.



**Figure 2.** Little River Ditch 1 Basin and the location of the sampling site.

The sampling site is located in the Morehouse Lowlands, between Sikeston and Crowley's Ridges (fig. 1). The drainage basin size upstream of the sampling site is 436 mi<sup>2</sup> and includes parts of Cape Girardeau, Scott, and Stoddard Counties; however, most of the drainage basin is in Stoddard County. In 1996, about 440,000 acres of farmland in Stoddard County included about 128,000 acres of corn, 38,800 acres of cotton, and 29,400 acres of rice (Hamer and Schlegel, 1998). The channel slope is 0.77 ft/mi, and the main channel length above the sampling site is 64.9 mi (G. Wilson, U.S. Geological Survey, written commun., 1999). The mean annual flow at this site (1945-93, 1996-97) was 541 ft<sup>3</sup>/s. The annual mean flow for 1996 and 1997 was 415 and 667 ft<sup>3</sup>/s, respectively.

The French had settled on the terraces of southeastern Missouri by the latter part of the 18th century, and Tecumseh brought part of the Shawnee Tribe to the New Madrid area soon after the turn of the 19th century to escape the encroachment of European settlers in the Ohio River Valley (Sugden, 1998). But much of the bootheel remained undeveloped throughout the 19th century because of the area's vast lowland swamps that were considered unusable except for its timber.

The development of the dragline dredge in the early 20th century had a major impact on the swamps of the bootheel by making it possible to drain the lowland swamps. When only 6 percent of the land had been cleared and cultivated, the Little River Ditches Drainage District was created in the early 20th century. By mid-1950, however, more than 2,000 mi of ditches existed in the area. Current land use in the basin above the Little River Ditch 1 sampling site is more than 84 percent agriculture and 13 percent forest (Vogelmann and others, 1998).

Agriculture is economically important in the bootheel. In 1996, most of the cotton and rice, as well as 20 percent of the Missouri soybean production, was grown in the bootheel region (Hamer and Schlegel, 1998). The bootheel also leads Missouri in the amount of applied herbicides and fertilizer (Wilkison and Maley, 1996). Studies on the occurrence of pesticides in the Little River Ditch 1 or in the bootheel are rare. Luckey (1985) sampled water and bottom sediments in four streams as many as seven times in the bootheel during 1974-78 and reported very few pesticides having concentrations above the reporting level. Most of the analytes of interest in Luckey's study were insecticides, except for 2,4-D. Mesko and Carlson (1988)

analyzed water and bottom-sediment samples for pesticides from five streams in the bootheel (collected once during June 1986) and reported very few pesticides in the water or sediments. Both the Luckey and the Mesko and Carlson studies had much higher reporting levels than those used in this study; sometimes they were more than two orders of magnitude higher.

### **Tensas River, Louisiana**

The Tensas River Basin, located in northeastern Louisiana, flows 165 mi from Lake Providence to Jonesville, where it joins the Ouachita and Little Rivers to form the Black River (fig. 3). The Tensas River drains about 2,517 mi<sup>2</sup> and is theorized to be an abandoned course of the Mississippi River due to its meandering pattern (U.S. Army Corps of Engineers, 1974). Some of the largest remaining tracts of forested wetlands in the Mississippi Valley are located in the basin and are of prime interest to many (Gosselink and others, 1990).

The Tensas River sampling site is located in Madison Parish near the town of Tendal. The drainage area above this point is approximately 309 mi<sup>2</sup> and is located mostly in East Carroll Parish (fig. 3). In 1997 there were 100,000 acres of soybean, 17,200 acres of rice, 39,000 acres of corn, and 39,000 acres of cotton grown in East Carroll Parish (Frank, 1998). The Tensas River headwaters begin in Lake Providence, an oxbow lake separated from the Mississippi River by a levee. The stream length from its headwaters to the sampling point is 44.4 mi and the channel slope is 1.10 ft/mi. The mean annual flow (1936-98) for the Tensas River at this site was 354 ft<sup>3</sup>/s. The annual mean flow for 1996 was 281 ft<sup>3</sup>/s, and for 1997 was 474 ft<sup>3</sup>/s.

During the Civil War, Union General Ulysses S. Grant tried to divert water from the Mississippi River into Lake Providence and then down the Tensas River to transport Federal gunboats below the forts at Vicksburg, Miss. He was unsuccessful, because the stage of the Mississippi River fell faster than the troops could dig (Miles, 1994). Some of the canals remain in existence today.

In October 1907, President Theodore Roosevelt hunted bear on the Tensas Bayou not far from the sampling site and wrote about his experiences in a paper "In the Louisiana Canebrakes" (Roosevelt, 1908). He described a virtual wilderness, with old growth forest and wetlands dominating the landscape, and having a few farms hacked out of the forest; with



Figure 3. Tensas River Basin and the location of the sampling site.

canebrakes 20 ft tall extending for miles; and the bayous teaming with alligators, garfish, and “monstrous snapping turtles, fearsome brutes of the slime.” In 1925, the land under cultivation in the three-parish area of East Carroll, Madison, and Tensas totaled 10,114 acres. By 1940, the total had increased to more than 200,000 acres and by 1990, to more than 580,000 acres.

The Tensas River sampling site from 1975 to 1980 was part of the USGS Pesticide Monitoring Network. Water samples were collected four times each year and analyzed for 11 chlorinated hydrocarbon insecticides, 7 organophosphate insecticides, and 4 herbicides (Gilliom and others, 1985). The Tensas River had the second highest number of organochlorine detections of the 180 sites in the network, with 10 detections of 5 different compounds. There were no organophosphate insecticide detections and few detections of the four herbicides. As recently as 1994, the State of Louisiana was still concerned about the levels of some organochlorine compounds in the fillets of fish caught from the Tensas River (Louisiana Department of Environmental Quality, 1994).

As is typical for most of the Mississippi Alluvial Plain, the basin was mostly forested wetland before the arrival of European settlers. Currently, land use in the basin is 6.5 percent forested wetlands, and more than 87 percent agriculture (Vogelmann and others, 1998).

### **Bogue Phalia, Mississippi**

The Bogue Phalia sampling site is located in Washington County, in west-central Mississippi. The drainage basin above the sampling site near Leland, Miss., is approximately 484 mi<sup>2</sup> and is located mostly in Bolivar County. The basin is 80 percent agricultural (Vogelmann and others, 1998); forested wetlands make up 10.5 percent of the remaining land use (fig. 4). In 1996, Bolivar County cultivated 217,000 acres of soybean, 60,600 acres of cotton, 14,200 acres of corn, and 67,000 acres of rice. In 1996, Washington County cultivated 119,000 acres of soybean, 96,500 acres of cotton, 30,300 acres of corn, and 27,700 acres of rice (Gregory, 1998).

The channel slope is approximately 0.8 ft/mi, and the channel length upstream of the sampling sites is approximately 58.2 mi. (K.V. Wilson Jr., U.S. Geological Survey, written commun., 1998). The stage-only gaging station at the sampling site has been in operation for many years by the COE. Discharge has been measured since October 1995 and the annual mean flow for 1996 and 1997 was 443 and 866 ft<sup>3</sup>/s, respectively.

Historical information on the occurrence of pesticides in the Bogue Phalia is scarce (Coupe, 1996). Pennington (1996) sampled the Bogue Phalia in July 1995 and analyzed for 88 pesticides. She reported the detection of primarily herbicides used in cotton and soybean production (acifluorfen, bentazon, cyanazine, diuron, fluometuron, and norflurazon).

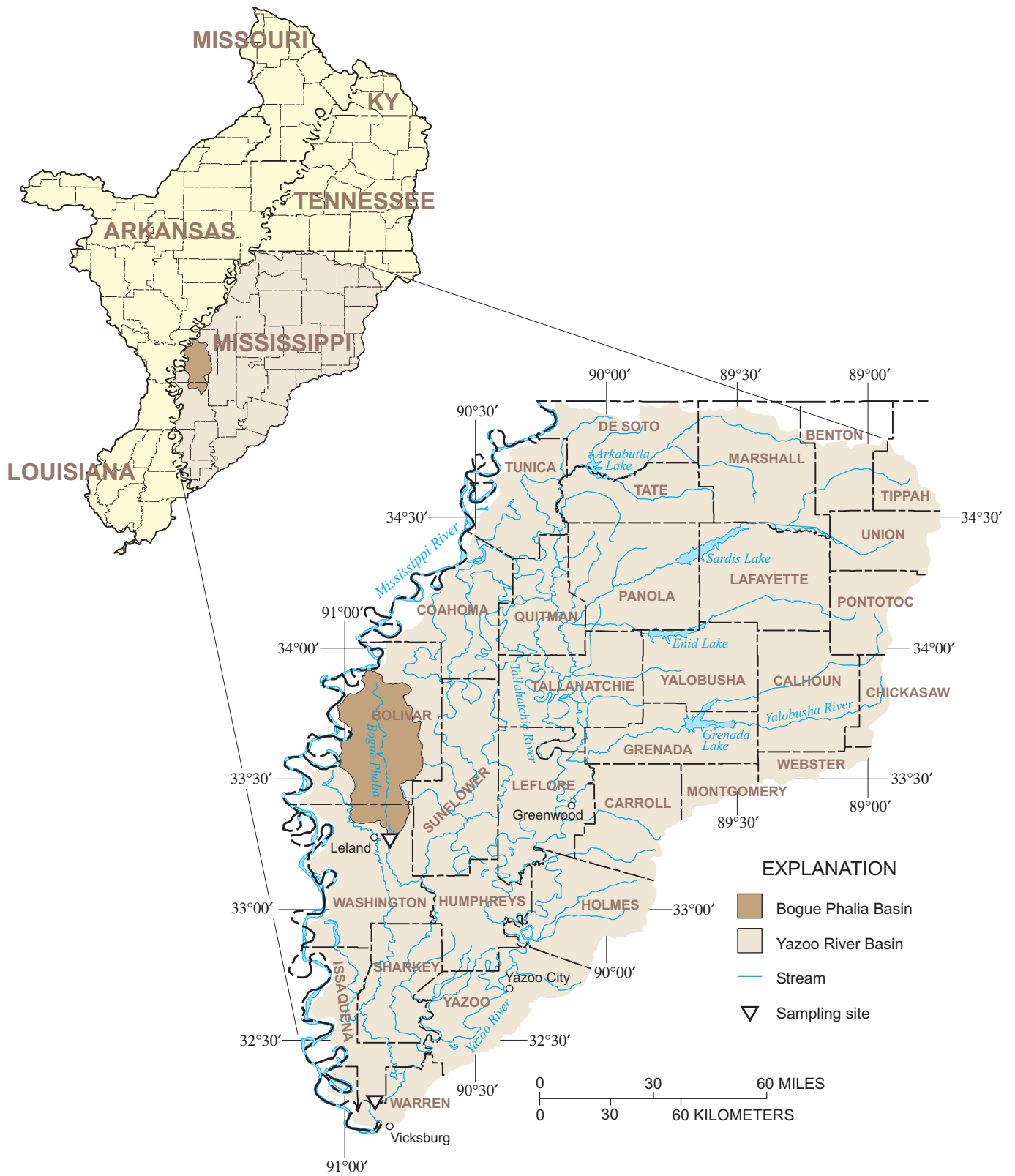
### **Yazoo River, Mississippi**

The Yazoo River Basin (fig. 4), Mississippi's largest river basin, consists of about 13,000 mi<sup>2</sup>. It is divided almost equally between the lowlands and the uplands. The lowlands lie in the Mississippi Alluvial Plain (commonly referred to as the “delta”), an intensive agricultural area of mostly cotton, rice, and soybean production. The uplands generally consist of forests, pastures, and small farms. The Yazoo River Basin is sparsely populated with no major metropolitan areas (Coupe, 1996).

The Yazoo River Basin drains the entire Mississippi Alluvial Plain in Mississippi and is formed by the confluence of the Tallahatchie and Yalobusha Rivers. The Yazoo River flows south from Greenwood along the eastern edge of the alluvial valley until reaching the Mississippi River at Vicksburg. Four flood-control reservoirs (Arkubutla, Sardis, Enid, and Grenada Lakes), which were built between 1940 and 1950, are located in the northeastern part of the basin. These reservoirs control the discharge from more than 4,400 mi<sup>2</sup> of drainage area within the Yazoo River Basin. When combined, the reservoirs provide 3.8 million acre-ft of storage at flood-pool elevation (U.S. Army Corps of Engineers, 1968).

Tributary inflow from the alluvial plain below Yazoo City to the Yazoo River is diverted by a levee located along the right bank of the river channel from Yazoo City to the split of the old channel and the Yazoo River Diversion Channel. In the mid-1960's, the COE constructed a diversion canal that connected Steele Bayou, Deer Creek, Little Sunflower River, and Big Sunflower River drainage basins. Two flood-control structures on the Steele Bayou and Little Sunflower River control runoff from the four basins. The floodgates at Steele Bayou and Little Sunflower are closed when water elevations (Yazoo River stage) approach the pool elevation at each structure. This prevents extensive alluvial flooding by backwater from the Mississippi River. When the stage in the Yazoo River drops below the pool elevation, the flood-control structures are opened, allowing the tributaries to flow into the Yazoo River.





**Figure 4.** Bogue Phalia and Yazoo River Basins and the locations of the sampling sites.

The complex hydrology associated with the Yazoo River has made the measurement of discharge difficult and, historically, there has not been a continuous record of discharge from the Yazoo River Basin. The COE has maintained a gaging station on the Yazoo River upstream at Greenwood, but this site misses the contribution from the delta part of the Yazoo River Basin. With the development of new technology, a continuous record of flow from the Yazoo River began in October 1995 (Manning, 1997).

As with the Bogue Phalia, a subbasin of the Yazoo River, historical data on pesticides in the surface waters of the Yazoo River Basin are scarce. This is especially true for the water-soluble pesticides. Coupe (1996) conducted a literature search and review, as well as a search of the U.S. Environmental Protection Agency's STORET data base, for historical water-soluble herbicide data collected within the Yazoo River Basin, Mississippi, and found only a few isolated studies with a small number of samples. However, these few studies did indicate the potential for offsite movement of many of the heavily used pesticides in the Yazoo River Basin.

More recent studies have examined the effects of pesticide use in agriculture on surface-water quality in the Yazoo River Basin. Pennington (1996) collected a few samples for pesticides as part of an ongoing water-quality study in the delta part of the Yazoo River Basin in Mississippi. There were only three sampling dates in this study, June and September 1994 and July 1995. Concentrations of the cotton herbicides—cyanazine, fluometuron, and norflurazon—were detected in nearly every sample. Pereira and Hostettler (1993) collected surface-water samples along the length of the Mississippi River and from the mouth of its major tributaries several times during 1991 and 1992. The surface-water samples were analyzed for a suite of herbicides—cyanazine, fluometuron, molinate, and norflurazon, as well as one metabolite of molinate and norflurazon. The results of this study indicated that cotton and rice herbicides only appear in the lower Mississippi River, downstream from the confluence of the Mississippi and Ohio Rivers, and that substantial amounts of these herbicides are being discharged to the Gulf of Mexico. The concentrations of these herbicides were highest in the mouth of the Yazoo River. In 1995, Coupe and others (1998b) sampled three streams in the delta part of the Yazoo River Basin and reported substantial amounts of most of the heavily used herbicides—atrazine, cyanazine, fluometuron, and molinate.

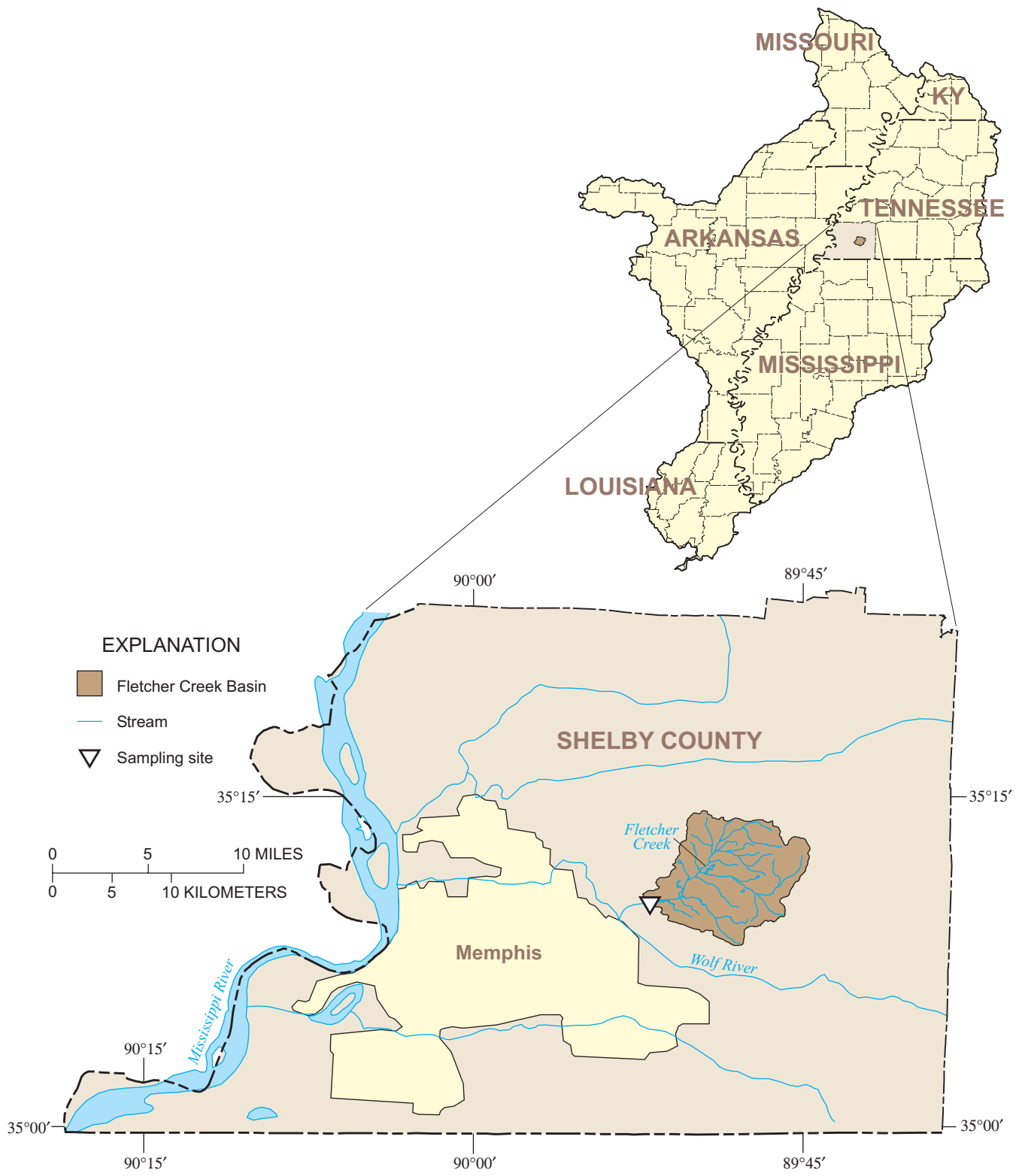
## **Fletcher Creek, Tennessee**

Fletcher Creek is located in the northeastern Memphis metropolitan area (fig. 5). Historically, the land use in this basin has been agriculture, but the basin has undergone recent urbanization. The drainage area for the basin upstream of the sampling site is 30.5 mi<sup>2</sup>. From satellite photography taken in 1991-93, land use was 50 percent developed (urban, industrial, residential), 23 percent forested, and 25 percent agricultural (Vogelmann and others, 1998). The Fletcher Creek sampling site is the only site located in the East Gulf Coastal Plain. The topography in the basin is characterized by gently rolling to steep hills. The stream has been heavily armored with riprap, and rectangular concrete channels have been installed at road crossings to increase the carrying capacity for flood control. Streambed slopes in this area range from about 18 to 70 ft per mile (Neely, 1984). The gaging station at this site was installed in April 1996. The annual mean flow for 1997 was 129 ft<sup>3</sup>/s.

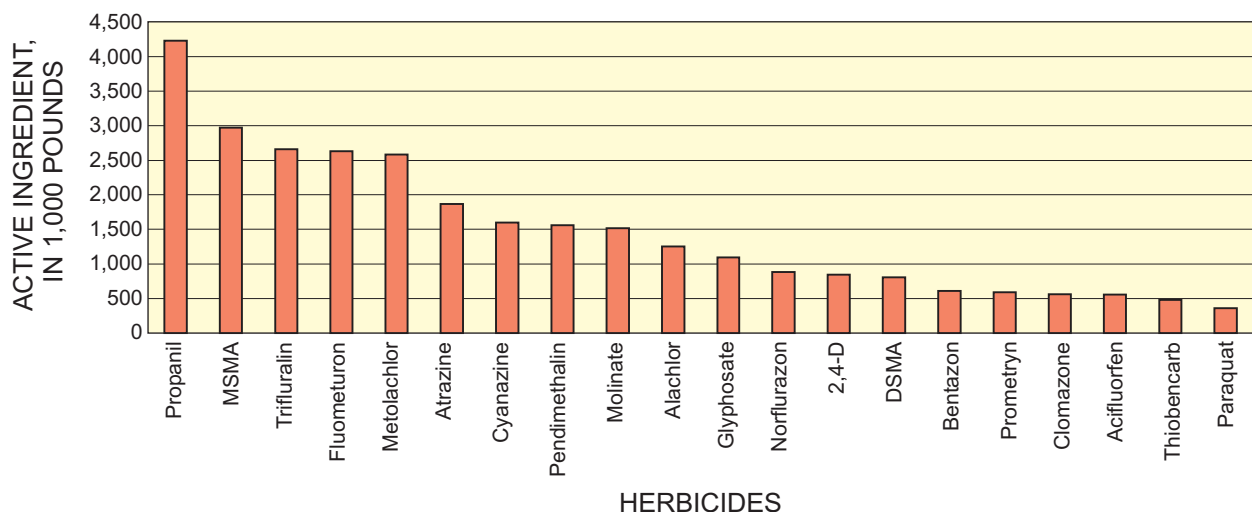
## **Pesticide Use within the Study Unit**

Agricultural activities differ throughout the study unit and change on a north-south and east-west gradient, as well as differ in intensity between the two major physiographic sections. Soybean is the major crop throughout the study unit with more corn acreage and less rice and cotton acreage in the north. The eastern Arkansas part of the study unit is one of the most productive rice growing areas in the country. The delta part of the Yazoo River Basin is a major cotton growing area. The Loess Hills, where silviculture is economically important, is not as intensively farmed as the Alluvial Plain. Consequently, the types of pesticides used and the timing and rates of application are different throughout the study unit.

The amount of active ingredient for the top 20 herbicides used in the study unit from crop acreage data from the 1992 Census of Agriculture (U.S. Department of Commerce, 1995) as well as pesticide-use rates compiled by the National Center for Food and Agricultural Policy (Gianessi and Anderson, 1996) are shown in figure 6. The pesticides for which water-samples were analyzed are listed in table 3. Surface-water samples collected for this study were not analyzed for MSMA, glyphosate, DSMA, clomazone, or paraquat. The amount of active ingredient for the top 20 insecticides used in the study unit, which were compiled from the same data sources as the herbicides, is shown in figure 7.



**Figure 5.** Fletcher Creek Basin and the location of the sampling site.



**Figure 6.** Herbicide use in the National Water-Quality Assessment Mississippi Embayment study unit. (Based on State-level estimates of pesticide-use rates for individual crops, which have been compiled by the National Center for Food and Agricultural Policy (NCFAP) for 1991-93 and 1995, and on county-based crop acreage data obtained from the 1992 Census of Agriculture.)

Surface-water samples collected for this study were not analyzed for profenofos, thiodicarb, acephate, dicrotophos, sulprofos, endosulfan, dimethoate, lambda-cyhalothrin, or cypermethrin. It is worth noting that there are a number of other compounds not easily categorized as herbicides or insecticides, but whose annual use (in pounds) is in the same range as the use of herbicides and insecticides. For example, there are defoliants (such as tribufos, sodium chlorate, and dimethipine), plant growth regulators (such as ethephon and thidiazuron), and fungicides (such as PCNB, mancozeb, and benomyl). These compounds were not included in this study.

## METHODS

The difficulties associated with characterizing the occurrence of pesticides in surface water are immense. Pesticides in surface water are generally detected in concentrations less than 1 µg/L, approximately one part per billion. When sampling for constituents in trace amounts, there is concern that the sample may become contaminated with the constituent of interest during or after the sample has been collected. Therefore, particular care must be given to sample collection and processing to ensure that no contamination occurs. A good quality-control program must be implemented to document levels and sources of contamination, if any. Pesticides are applied seasonally and the use of a particular pesticide may vary from year to year depending on the pest pressure, which in turn may depend on current or antecedent weather conditions.

Pesticides are applied in small amounts to large areas and generally require surface-water runoff to reach streams. The sample-collection frequency, procedures, and processing, as well as the laboratory analytical procedures, should be carefully considered when studying the occurrence of pesticides in surface water. This section describes the selection of pesticide analytes; the sampling frequency, collection, and processing procedures; laboratory techniques; and the results of quality-control samples used in this study to characterize the occurrence of pesticides in five rivers in the study unit.

## Selection of Pesticide Analytes

Pesticides analyzed in surface-water samples were selected from a list of nearly 400 most commonly used pesticides in the United States (Gianessi and Puffer, 1990; 1992). The pesticides were prioritized according to the following factors: a national use of more than 8,000 lbs of active ingredient, inclusion in the analytical schedules of other Federal monitoring or assessment programs, toxicity, leachability, and the ability to trap and extract the analyte from the appropriate solid-phase-concentration matrix (Gilliom and others, 1995). The final target-analyte list (table 3) is a broad spectrum of pesticides that were analyzed by using gas chromatography/mass spectrometry (GCMS) or high-performance liquid chromatography (HPLC) methods.

**Table 3.** Pesticides and pesticide metabolite analytes, method reporting levels, drinking-water standards, and aquatic-life criteria

[Concentrations in micrograms per liter; MCL, maximum contaminate level; HA, health advisories; H, herbicide; --, no standard or guideline; I, insecticide; M, metabolite; F, fungicide; (5), detected in less than 5 percent of samples; (1), detected in less than 1 percent of samples; (ND), not detected in any sample; USEPA, U.S. Environmental Protection Agency]

Pesticide	Type	Method reporting level	Drinking-water standard or guideline MCL or HA	Guideline for aquatic life
<b>Dissolved pesticides analyzed by gas chromatography/mass spectrometry (GCMS)</b>				
Acetochlor	H	0.002	--	--
Alachlor	H	0.002	<sup>1</sup> 2	--
Atrazine	H	0.001	<sup>1</sup> 3	<sup>2</sup> 2
Azinphos-methyl (5)	I	0.001	--	<sup>3</sup> 0.01
Benfluralin (5)	H	0.002	--	--
Butylate	H	0.002	350	--
Carbaryl	I	0.003	700	<sup>4</sup> 0.02
Carbofuran	I	0.003	<sup>1</sup> 40	<sup>2</sup> 1.75
Chlorpyrifos	I	0.004	20	<sup>5</sup> 0.041
Cyanazine	H	0.004	1	<sup>2</sup> 2
DCPA	H	0.002	4,000	--
<i>p,p'</i> -DDE	M	0.006	--	--
Desethylatrazine	M	0.002	--	--
Diazinon	I	0.002	0.6	<sup>4</sup> 0.009
Dieldrin (5)	I	0.001	--	<sup>5</sup> 0.0625
2,6-Diethylaniline (ND)	M	0.003	--	--
Disulfoton (1)	I	0.017	0.3	<sup>4</sup> 0.05
EPTC	H	0.002	--	--
Ethalfuralin (ND)	H	0.004	--	--
Ethoprop (ND)	I	0.003	--	--
Fonofos (ND)	I	0.003	10	--
<i>alpha</i> -HCH (ND)	M	0.002	--	<sup>2</sup> 0.01
<i>gamma</i> -HCH (ND)	I	0.004	<sup>1</sup> 0.2	<sup>5</sup> 0.08
Linuron (5)	H	0.002	--	--
Malathion	I	0.005	200	<sup>3</sup> 0.1
Methyl parathion	I	0.006	2	<sup>2</sup> 7
Metolachlor	H	0.002	70	<sup>2</sup> 8
Metribuzin	H	0.004	100	<sup>2</sup> 1
Molinate	H	0.004	--	--
Napropamide (5)	H	0.003	--	--
Parathion (ND)	I	0.004	--	<sup>5</sup> 0.013
Pebulate (1)	H	0.004	--	--
Pendimethalin	H	0.004	--	--
<i>cis</i> -Permethrin (1)	I	0.005	--	--
Phorate (ND)	I	0.002	--	--
Prometon	H	0.018	100	--
Pronamide	H	0.003	50	--
Propachlor (5)	H	0.007	90	--
Propanil	H	0.004	--	--
Propargite (1)	I	0.013	--	--
Simazine	H	0.005	<sup>1</sup> 4	<sup>2</sup> 10
Tebuthiuron	H	0.01	500	<sup>2</sup> 1.6
Terbacil (1)	H	0.007	90	--
Terbufos (ND)	H	0.013	0.9	--
Thiobencarb	H	0.002	--	--
Triallate (ND)	H	0.001	--	<sup>2</sup> 0.24
Trifluralin	H	0.002	5	<sup>2</sup> 0.1

**Table 3.** Pesticides and pesticide metabolite analytes, method reporting levels, drinking-water standards, and aquatic-life criteria (Continued)

Pesticide	Type	Method reporting level	Drinking-water standard or guideline MCL or HA	Guideline for aquatic life
<b>Dissolved pesticides analyzed by high performance liquid chromatography (HPLC)</b>				
2,4-D	H	0.035	<sup>1</sup> 70	<sup>4</sup> 3
2,4-DB (1)	H	0.035	--	--
2,4,5-T (ND)	H	0.035	70	--
2,4,5-TP (ND)	H	0.031	<sup>1</sup> 50	<sup>4</sup> 1.4
3-Hydroxy-carbofuran (ND)	M	0.014	--	--
Acifluorfen	H	0.035	--	--
Aldicarb (ND)	I	0.55	<sup>1</sup> 7	<sup>2</sup> 1
Aldicarb sulfone (ND)	M	0.1	<sup>1</sup> 7	<sup>2</sup> 1
Aldicarb sulfoxide (1)	M	0.021	<sup>1</sup> 7	<sup>2</sup> 1
Bentazon	H	0.014	200	--
Bromacil (ND)	H	0.035	90	--
Bromoxynil (1)	H	0.035	--	<sup>2</sup> 5
Carbaryl (5)	I	0.008	700	<sup>4</sup> 0.02
Carbofuran	I	0.028	<sup>1</sup> 40	<sup>2</sup> 1.75
Chloramben (ND)	H	0.011	100	--
Chlorothalonil (ND)	F	0.035	--	--
Clopyralid (ND)	H	0.05	--	--
Dacthal, mono-acid (1)	M	0.017	--	--
Dicamba (1)	H	0.035	200	--
Dichlobenil (ND)	H	0.02	--	<sup>4</sup> 37
Dichlorprop (5)	H	0.032	--	--
Dinoseb (1)	H	0.035	<sup>1</sup> 7	<sup>2</sup> 0.05
Diuron	H	0.02	10	<sup>4</sup> 1.6
DNOC (ND)	I,F,H	0.35	--	--
Fenuron (1)	H	0.013	--	--
Fluometuron	H	0.035	90	--
Linuron (5)	H	0.018	--	<sup>2</sup> 7
MCPA (5)	H	0.05	10	<sup>2</sup> 2.6
MCPB (ND)	H	0.035	--	--
Methiocarb (ND)	I	0.026	--	--
Methomyl (5)	I	0.017	200	--
Neburon (1)	H	0.015	--	--
Norflurazon	H	0.024	--	--
Oryzalin (ND)	H	0.019	--	--
Oxamyl (ND)	I	0.018	<sup>1</sup> 200	--
Picloram (ND)	H	0.05	<sup>1</sup> 500	<sup>2</sup> 29
Propham (ND)	H	0.035	100	--
Propoxur (ND)	I	0.035	--	--
Triclopyr	H	0.05	--	--

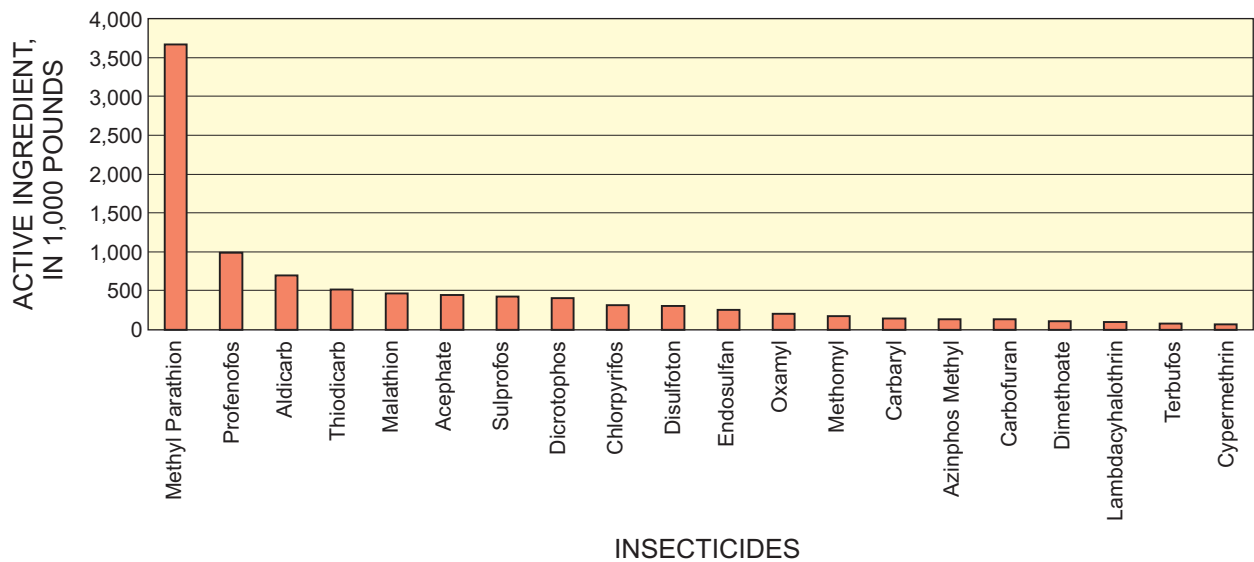
<sup>1</sup>Value is the USEPA maximum contaminant level for drinking water; other values are USEPA lifetime health advisories for a 70-kilogram adult (Nowell and Resek, 1994).

<sup>2</sup>Canadian Government aquatic-life guidelines (Canadian Council of Resource and Environment Ministers, 1991).

<sup>3</sup>USEPA chronic aquatic-life guidelines (Nowell and Resek, 1994).

<sup>4</sup>National Academy of Sciences and National Academy of Engineering aquatic-life guidelines, 1973 (Nowell and Resek, 1994).

<sup>5</sup>USEPA acute aquatic-life guidelines (Nowell and Resek, 1994).



**Figure 7.** Insecticide use in the National Water-Quality Assessment Mississippi Embayment study unit.

The U.S. Environmental Protection Agency’s (USEPA) drinking-water standards (maximum contaminant levels) and health advisories for pesticides, as well as guidelines for the protection of aquatic life issued by several different sources, are listed in table 3. They were included so that the pesticide concentrations measured in the surface waters of the study unit could be put into perspective. The surface waters of the study unit are not used as a drinking-water source, except in a few limited cases; therefore, the maximum contaminant levels are not directly applicable. The aquatic life guidelines issued by the USEPA are used to populate table 3; for those pesticides that have not yet been assigned criteria by the USEPA, criteria from the National Academy of Sciences/ National Academy of Engineers and the Canadian Government are used. The derivation of the aquatic life criteria issued may not be comparable between sources and should be used with caution. For example, USEPA aquatic-life criteria are designed to protect 95 percent of genera tested, not necessarily every locally important, sensitive species; whereas the Canadian guidelines are designed to protect all forms of aquatic life at all life stages.

### Sampling Frequency

The sampling frequency varied annually, seasonally, and between sites, depending upon the sampling objectives at each site, the expected variability of the site, and the resources available to conduct

the sampling. Sampling occurred from February 1996 through January 1998. The Yazoo River, given its large basin size and slow response to hydrologic events, was sampled every other week throughout the sampling period. The Bogue Phalia and Little River Ditch 1 streams were the primary focus for the small basin work, and sample collection was the most intensive at these two sites. Bogue Phalia and the Little River Ditch 1 were sampled twice monthly beginning February 1996, with extra samples occasionally collected during high-flow events. Sampling then increased to weekly from March through September 1997, and then decreased to twice monthly through January 1998. The sampling frequency for the Tensas River was monthly beginning February 1996, with extra samples occasionally collected during high-flow events. Sampling then increased to twice monthly from October 1996 through January 1998.

Because agriculture is the major land use in the study unit, the focus on the occurrence of pesticides in surface waters was related to agriculture. However, urban use of pesticides is well known to affect water quality. Therefore, to compare the occurrence of pesticides in agricultural streams to the occurrence of pesticides in urban streams, an urban stream was sampled for 1 year. Monthly water samples from Fletcher Creek in Memphis, Tenn., were collected and analyzed for pesticides from October 1996 until April 1997. The sampling frequency was increased to two to four times per month from April through September 1997.

## Sample Collection

Surface-water samples were flow-weighted and depth and width integrated according to the procedures in Shelton (1994) to ensure that the sample was representative of the stream. In some cases, because of the low gradient in the Alluvial Plain, flow-weighted samples were not possible. Prior to sample collection, all equipment that came into contact with the sample water was made of Teflon or stainless steel and was cleaned with a 0.2 percent nonphosphate detergent, rinsed with deionized water, rinsed with pesticide-grade methanol, air dried, wrapped in aluminum foil, and stored in a dust-free environment.

## Sample Processing

The water samples were filtered onsite using an aluminum filter plate with a baked 0.7-micrometer pore-size glass fiber filter into 1-liter baked amber bottles. The samples were transported on ice to the Pearl, Miss., or the Rolla, Mo., office of the USGS for further processing. Solid phase extraction (SPE) was used prior to pesticide analysis of samples by gas chromatography/mass spectrometry (GCMS) or high-performance liquid chromatography (HPLC). Using SPE, pesticides were extracted from prefiltered water samples using disposable polypropylene syringe cartridges packed with a specific sorbent material. Samples to be analyzed by GCMS were extracted by using disposable polypropylene syringe cartridges packed with octadecyl-bonded porous silica (C-18) (Zaugg and others, 1995), and those analyzed by HPLC were extracted by using 0.5-gram graphitized carbon as the solid phase sorbent (Werner and others 1996). Sample extraction occurred within 3 days of sample collection. Regardless of the analytical method, the basic SPE procedure was the same. The SPE cartridges were conditioned prior to use by using methanol for the C-18 cartridge and with ascorbic acid for the graphitized carbon. As a quality-assurance measure, samples were spiked with 100- $\mu$ L volume of surrogate compounds before extraction to measure the extraction efficiency. One liter of prefiltered water sample was then pumped through the SPE cartridge at a flow rate of 25 milliliters per minute. The cartridges were shipped on ice to the National Water Quality Laboratory (NWQL) in Arvada, Colo.

## Laboratory Analysis and Quality-Control Assessment

Once at the NWQL, the pesticides were extracted from the cartridges and analyzed by GCMS or HPLC. Forty-seven pesticides and metabolites were analyzed by GCMS; and 39 pesticides and pesticide metabolites were analyzed by the HPLC analytical method (table 3). The two methods were described in Zaugg and others (1995) and Werner and others (1996). There were three pesticides in common between the methods; carbaryl, carbofuran, and linuron. The method reporting level (MRL) for the HPLC method was higher than the GCMS method and, therefore, the results were sometimes not identical between methods for these three compounds.

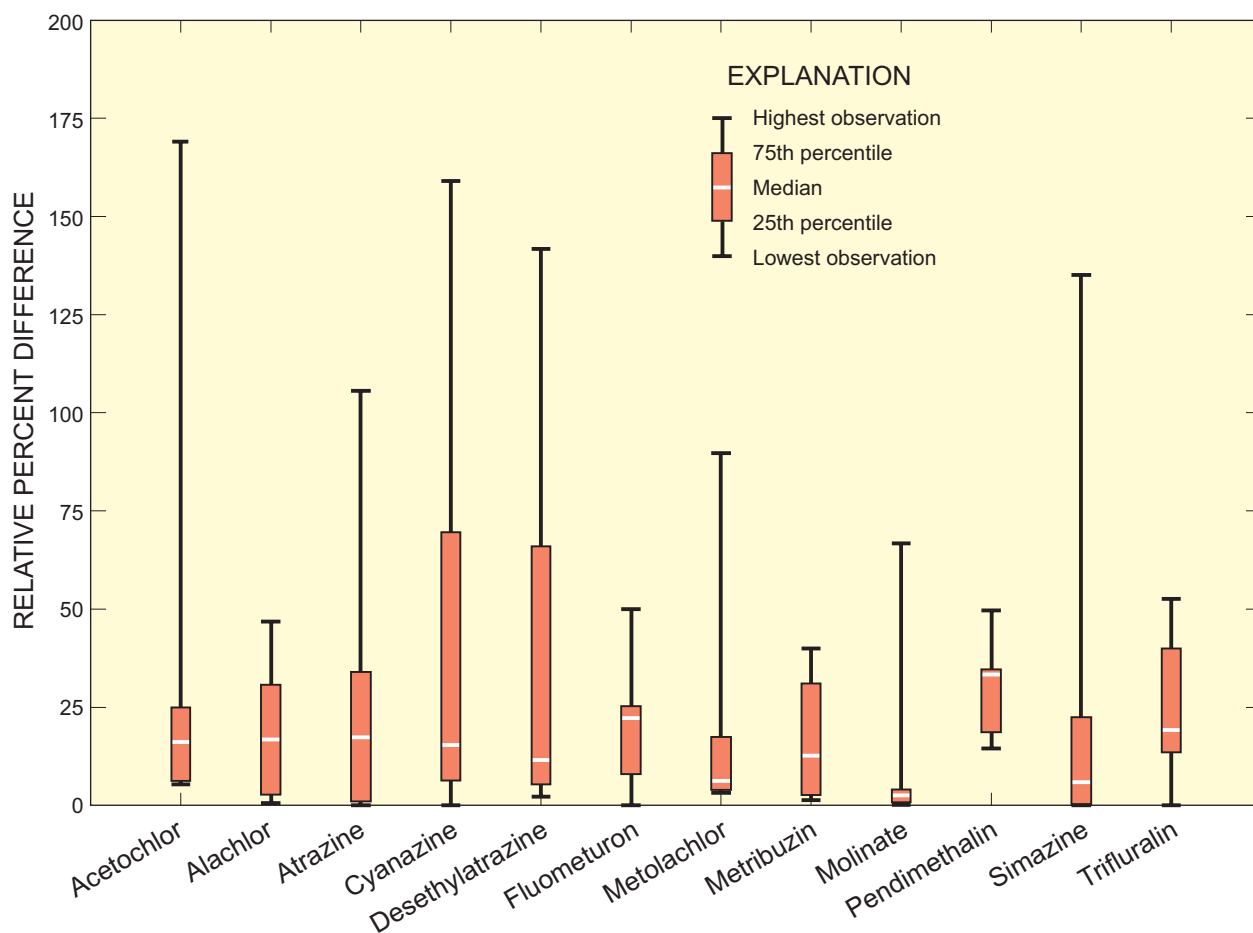
About 15 percent of all samples submitted to the NWQL were quality-control samples which included field-equipment blanks to measure contamination, replicate samples to measure precision, and field-spike samples to measure recovery of analytes. Nine field-equipment blanks were processed and all were free of the pesticides of interest, except for one sample that had a concentration of molinate of 0.002  $\mu$ g/L. This concentration was below the normal reporting level of the NWQL.

Precision data were obtained from nine sets of replicate samples and are listed in appendix I. The relative percentage differences for those pesticides that were reported in at least five of the nine samples are shown in figure 8. The relative percentage difference (relative percentage difference =  $|A-B|/[(A+B)/2]$ ) ranged from 0 to 194 percent with a median of 15.4 percent. In approximately 12 percent of the samples (18 of 147 pairs), a compound was detected in one sample but not detected in the other.

Recovery data were obtained from four sets of field-matrix spikes (FMS). A FMS set consisted of an environmental sample and two spiked replicates. Water samples were collected and filtered in the field and transported to the USGS District office where they were spiked and extracted. The SPE cartridges were then sent to the NWQL for analysis. The results for the spiked data are shown in figure 9.

Most recoveries of FMS for the GCMS method fell within the expected 60 to 140 percent range; the median recovery was 100 percent. In the method development (Zaugg and others, 1995), five pesticides were identified as having highly variable recoveries (desethylatrazine, methyl-azinphos, carbaryl, carbofuran, and terbacil). Detections for these compounds were highly reliable when they were made, but the





**Figure 8.** Relative percentage difference between replicate samples for selected pesticides.

numerical concentration associated with a detection was not reliable because of poor recovery and high variability. Nondetections were unreliable because the poor recovery results indicated a high potential for false nondetections; that is, samples in which compounds were actually present but were not detected by the analytical method. Other pesticides with median recoveries below 60 percent in the method development were *cis*-permethrin and disulfoton. Although the recoveries were low for these compounds, the method was consistent and the results were considered reliable. Trifluralin and linuron had highly variable FMS recoveries in this study, ranging from 40 to 160 percent.

The method development for the HPLC method (Werner and others, 1996) indicated that the HPLC method had recoveries in organic-free water ranging from 37 to 88 percent. The mean recovery of FMS was slightly lower. Although the majority of these compounds have lower recoveries than what was common for other pesticide methods, Werner and

others (1996) determined that the recovery and precision were generally acceptable for publication and useful for many types of data analysis. The data from this method should be used with care and with the understanding that there will be a higher rate of false negatives from this method and that detected concentrations and detection frequencies are biased low. Three pesticides (chlorothalonil, dichlobenil, and DNOC) were identified as having variable SPE or HPLC performance, or both, and the results were considered to be qualitative only.

The recoveries from the FMS from this study for the HPLC method were generally similar to those reported in the method development with a median recovery of 67 percent. Four pesticides (aldicarb, aldicarb sulfone, clopyralid, and dicamba) had median recoveries of 0 percent; these results should be viewed with caution. The rate of false negatives from laboratory set spikes for these four pesticides was 6, 4, 6, and 1 percent, respectively (J.D. Martin, U.S. Geological Survey, written commun., 1998).

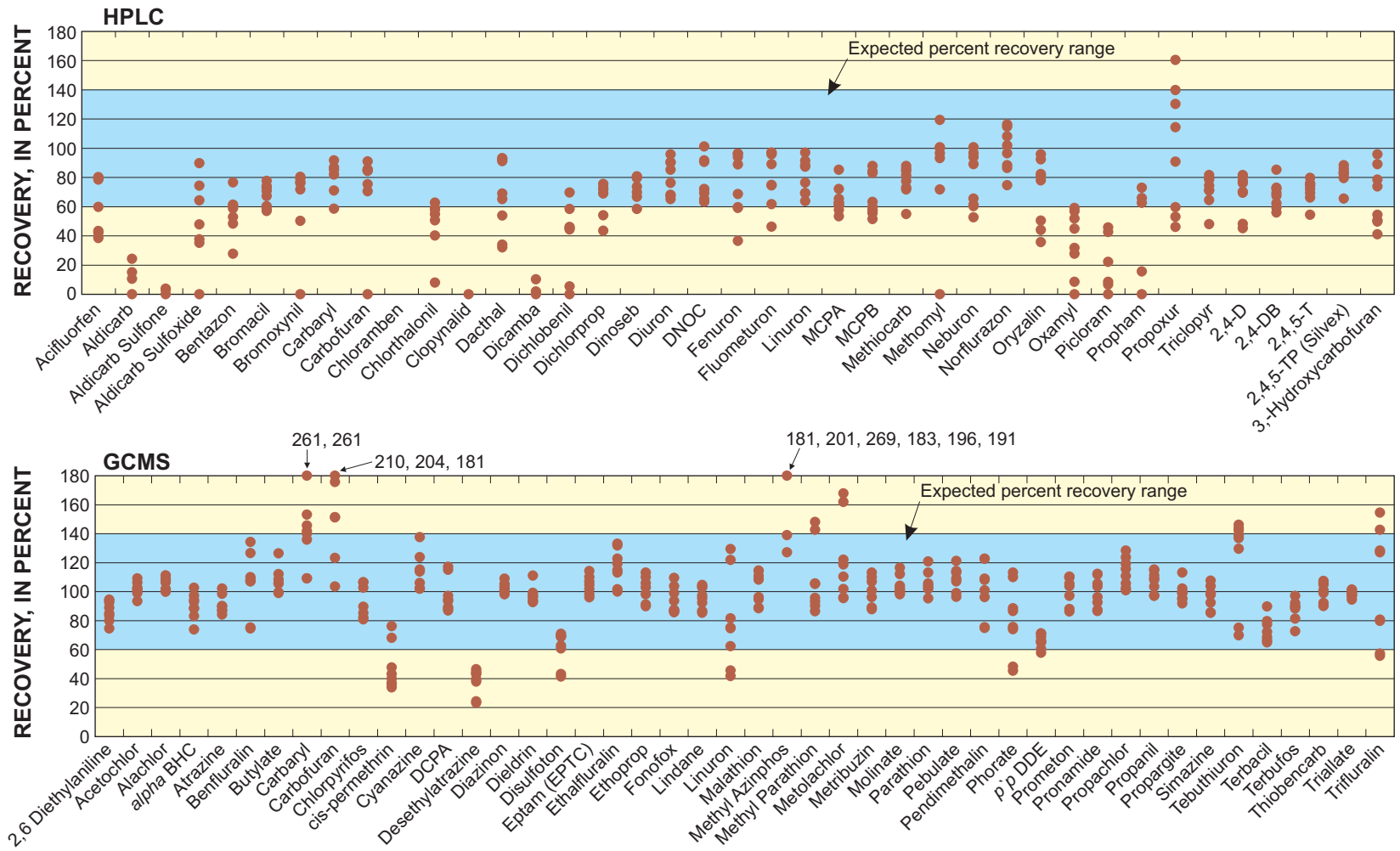
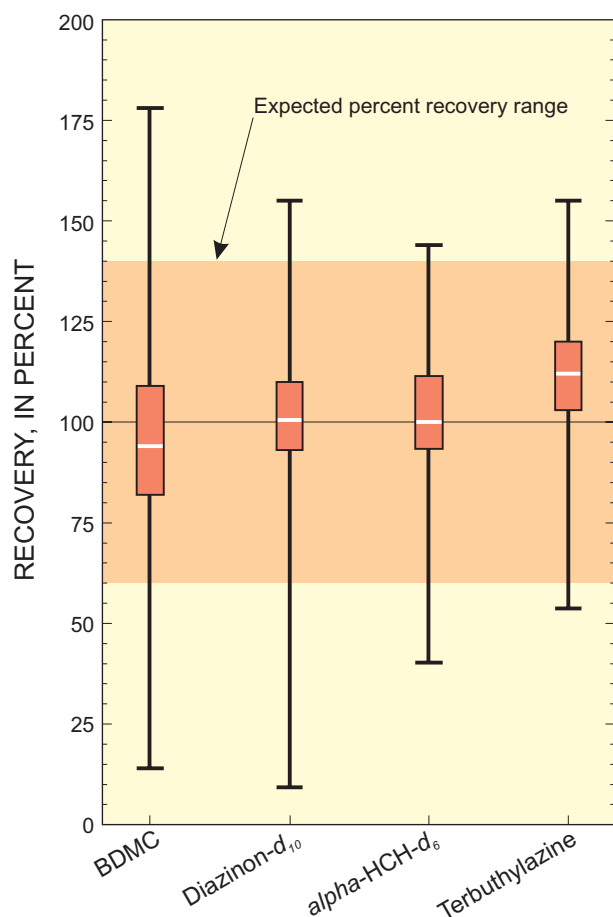


Figure 9. Spike recoveries for pesticides and degradation products analyzed by the HPLC and GCMS methods.

Surrogate solutions were added to the filtered water samples before SPE to measure the extraction efficiency. These surrogate compounds were not expected to be present in the environment, yet were expected to behave similarly to selected target analytes found in the environment. The HPLC method called for the addition of one carbamate surrogate, 4-bromo-3,5-dimethyl phenyl-n-methylcarbamate (BDMC). The GCMS method had three surrogates, an organophosphorus compound (diazinon- $d_{10}$ ), a triazine compound (terbutylazine), and an organochlorine compound ( $\alpha$ -HCH- $d_6$ ). These surrogates were used to assess the recoveries for the targeted analytes. The median overall recoveries for these compounds were 94, 101, 112, and 100 percent, respectively (fig. 10). More than 90 percent of the recovery data fell within the expected range of 60 to 140 percent (Zaugg and others, 1995).



**Figure 10.** Recoveries of surrogate compounds diazinon- $d_{10}$ , terbutylazine,  $\alpha$ -HCH- $d_6$ , and BDMC.

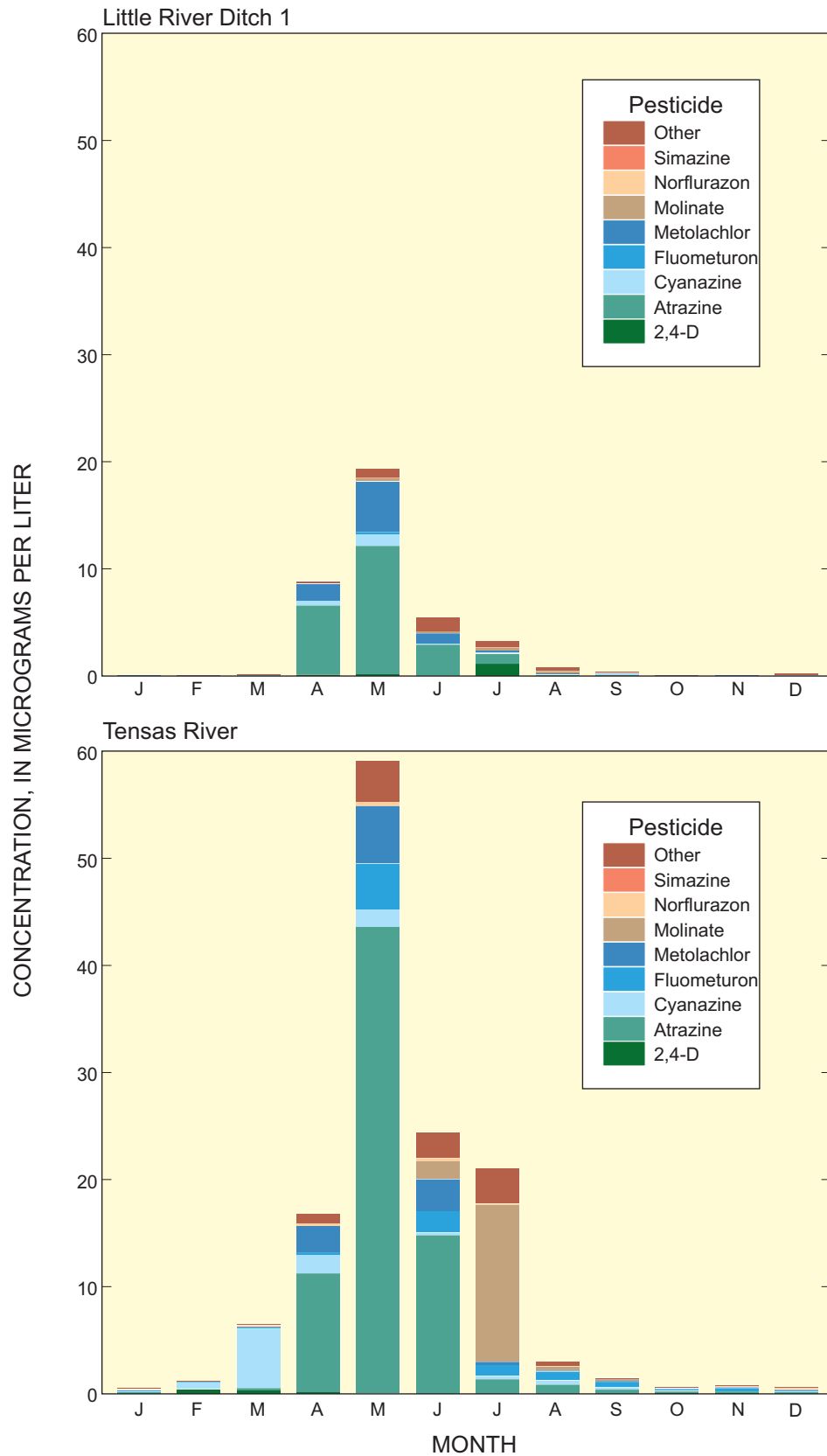
When these data are analyzed by site using an analysis of variance (ANOVA), several anomalies become apparent. The mean surrogate recovery by site from the HPLC method (BDMC) ranged from 90 to 110 percent. The mean range of BDMC recovery for the three agricultural sites (Bogue Phalia, Little River Ditch 1, and the Tensas River) and the large river site (Yazoo River) was 90 to 93 percent. The mean BDMC recovery for the samples collected from the urban stream (Fletcher Creek) was 110 percent. No reason for the significantly larger recovery for BDMC from water samples from Fletcher Creek was apparent. The range of recovery of diazinon- $d_{10}$  and  $\alpha$ -HCH- $d_6$  was significantly lower in water samples from the Little River Ditch 1 than from the other four sites.

From February to September 1996, the SPE of water samples from the Little River Ditch 1 was performed in the Mississippi District; after September 1996, the SPE was performed in the Missouri District. Analyzing the data by site and by the above time period indicates that the recoveries of diazinon- $d_{10}$  and  $\alpha$ -HCH- $d_6$  were significantly lower in water samples extracted in Missouri compared to those extracted in Mississippi. This was attributed to longer holding times in the Missouri District after extraction. Therefore, the concentrations reported for the organophosphorus and organochlorine compounds from water samples collected from the Little River Ditch 1 are considered biased low.

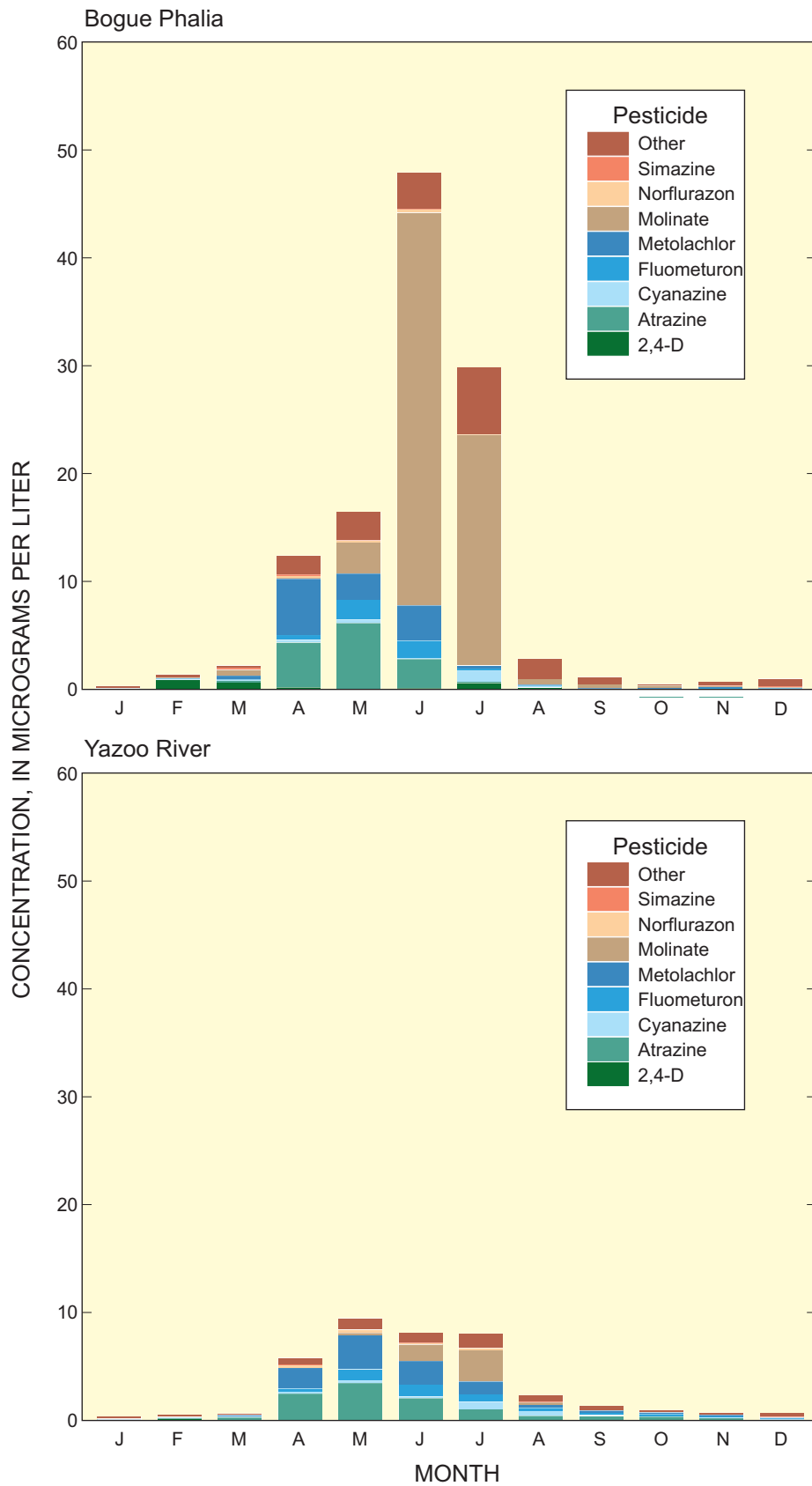
## OCCURRENCE OF PESTICIDES BY SAMPLING STATION

During February 1996 through January 1998, 237 surface-water samples from five rivers were collected and analyzed for more than 80 pesticides and pesticide metabolites; these are described statistically by site in appendix II. Mean monthly total pesticide concentrations are shown graphically in figure 11. The relations of streamflow to pesticide concentrations for selected pesticides are shown in figures 12-17.

The occurrence and the timing of pesticides, especially herbicides, in surface waters of the drainage basins of the study unit can be used as indicators of land use (urban, agricultural, forested) and crop type within agricultural basins.

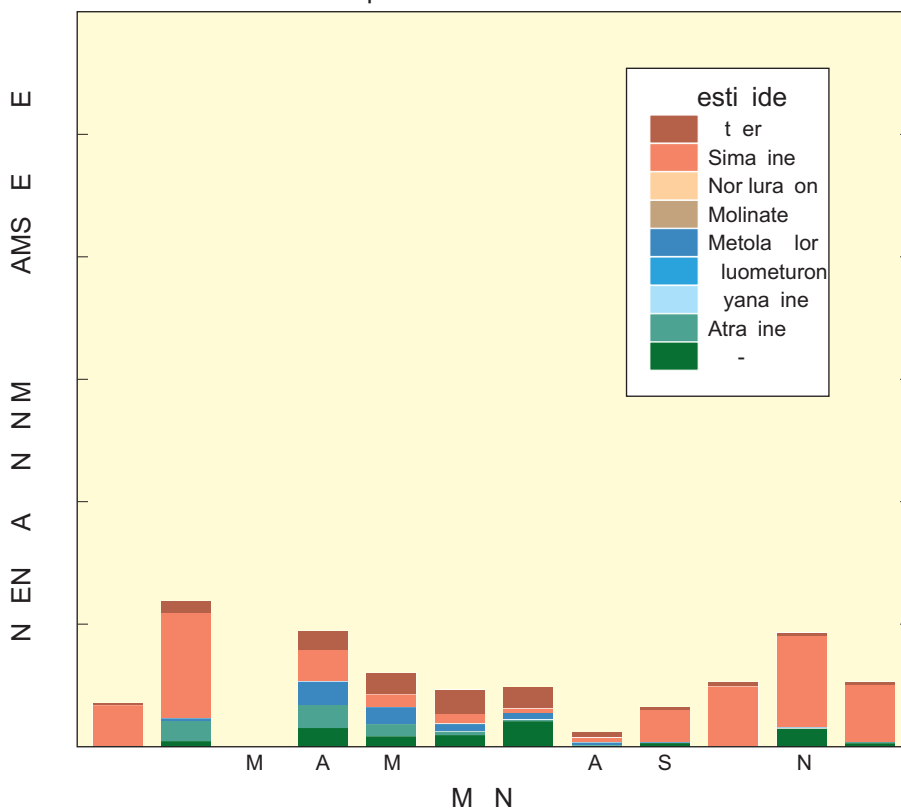


**Figure 11.** Mean monthly total pesticide concentration in five rivers in the Mississippi Embayment study unit, February 1996–January 1998.



**Figure 11.** Mean monthly total pesticide concentration in five rivers in the Mississippi Embayment study unit, February 1996–January 1998. (Continued)

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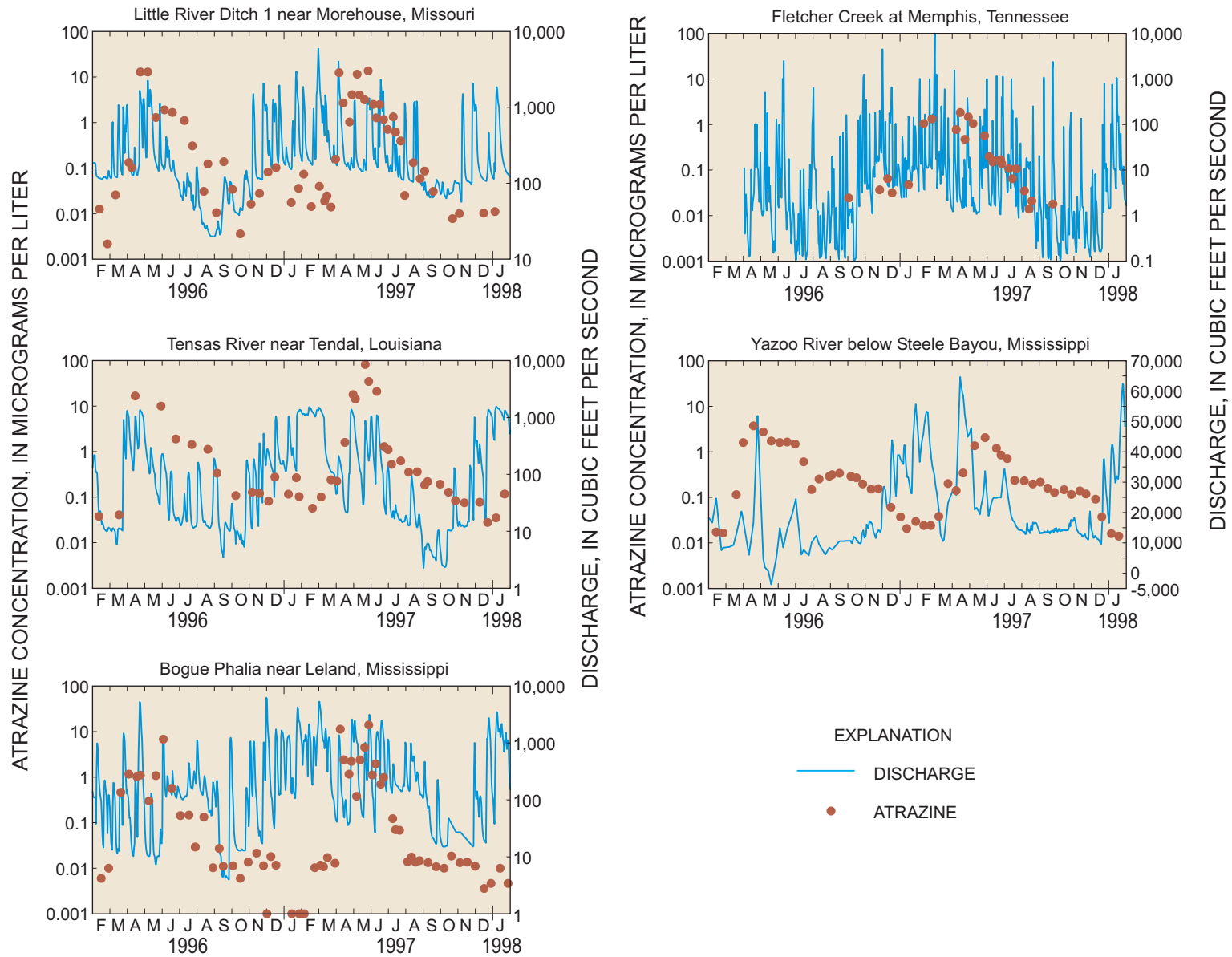
**Figure 11.** Mean monthly total pesticide concentration in five rivers in the Mississippi Embayment study unit, February 1996–January 1998. (Continued)

Atrazine is a triazine herbicide which is used primarily for weed control in corn and grain sorghum in the study unit. It is applied as a preemergent herbicide on corn which is usually one of the first crops planted; therefore, those basins with substantial amounts of corn or grain sorghum within the basin would be expected to have peak atrazine concentrations early in the growing season.

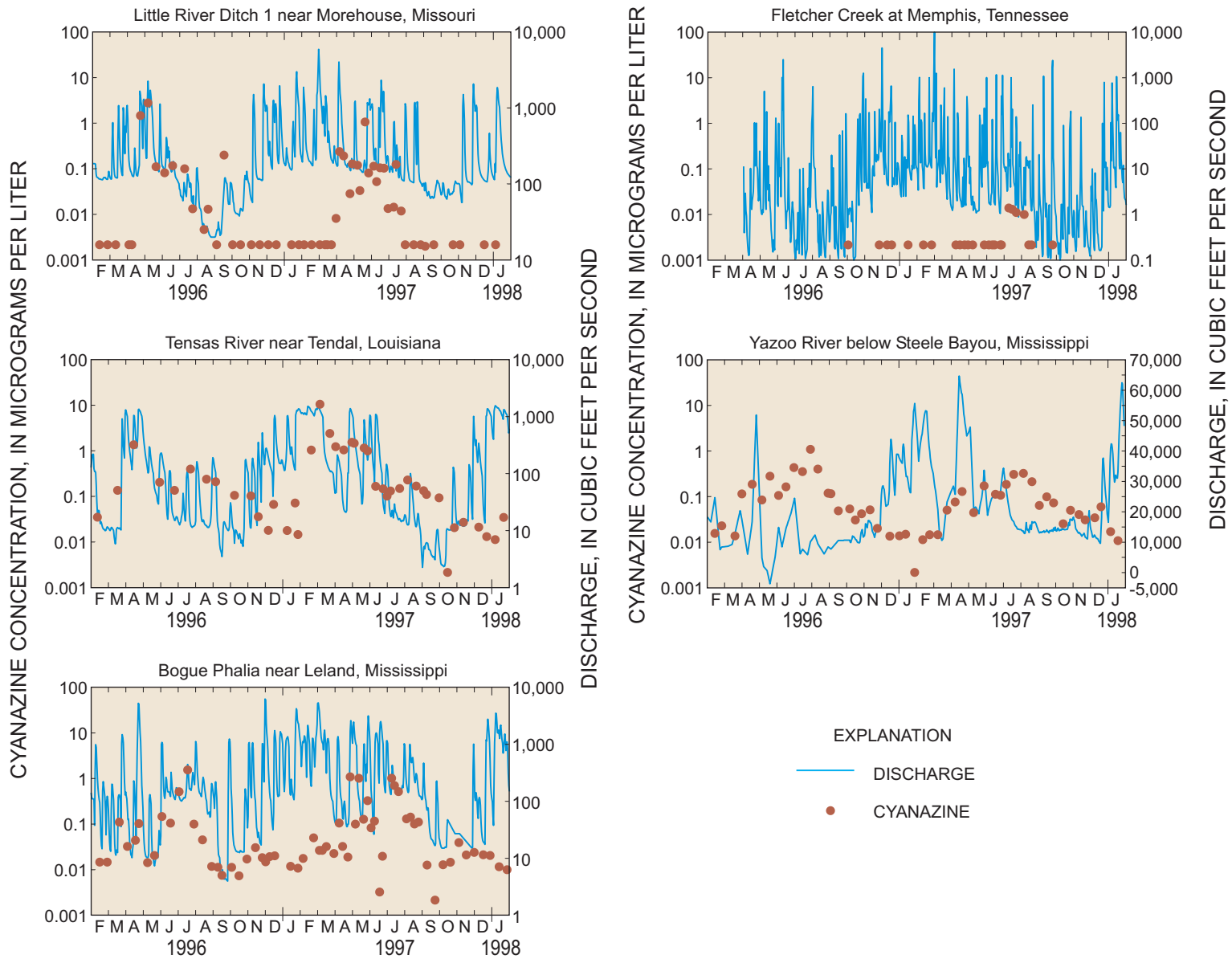
Cyanazine also is a triazine herbicide and is used extensively as a preemergent herbicide on corn in the Midwest; however, it is used primarily as a postemergent herbicide on cotton in the MISE study unit. Therefore, those basins with significant amounts of cotton would be expected to have cyanazine concentrations peaking well after planting has occurred. The Yazoo River data demonstrate this quite well (figs. 12 and 13). Peak concentrations of atrazine in the Yazoo River occurred before the first of June in 1996 and 1997, whereas cyanazine concentrations peaked near the beginning of July in both years.

Fluometuron is used almost exclusively on cotton in the MISE study unit and molinate is used only on rice. Therefore, those basins with significant amounts of cotton and rice (the Tensas, Bogue Phalia, and the Yazoo) would be expected to have more frequent detections and higher concentrations of these herbicides than basins with less cotton and rice (Fletcher Creek and Little River Ditch 1) (figs. 14 and 16).

Simazine, a triazine herbicide, is not used extensively in agriculture within the study unit, but is registered for use for algae control in ponds, for weed control on turf, and for nonselective weed control in industrial areas. The highest concentrations and most frequent detections are in Fletcher Creek that drains an urban watershed. The Yazoo River, which drains a few small urban areas, also had frequent detections (greater than 95 percent) of simazine, but in lower concentrations than those detected in Fletcher Creek.

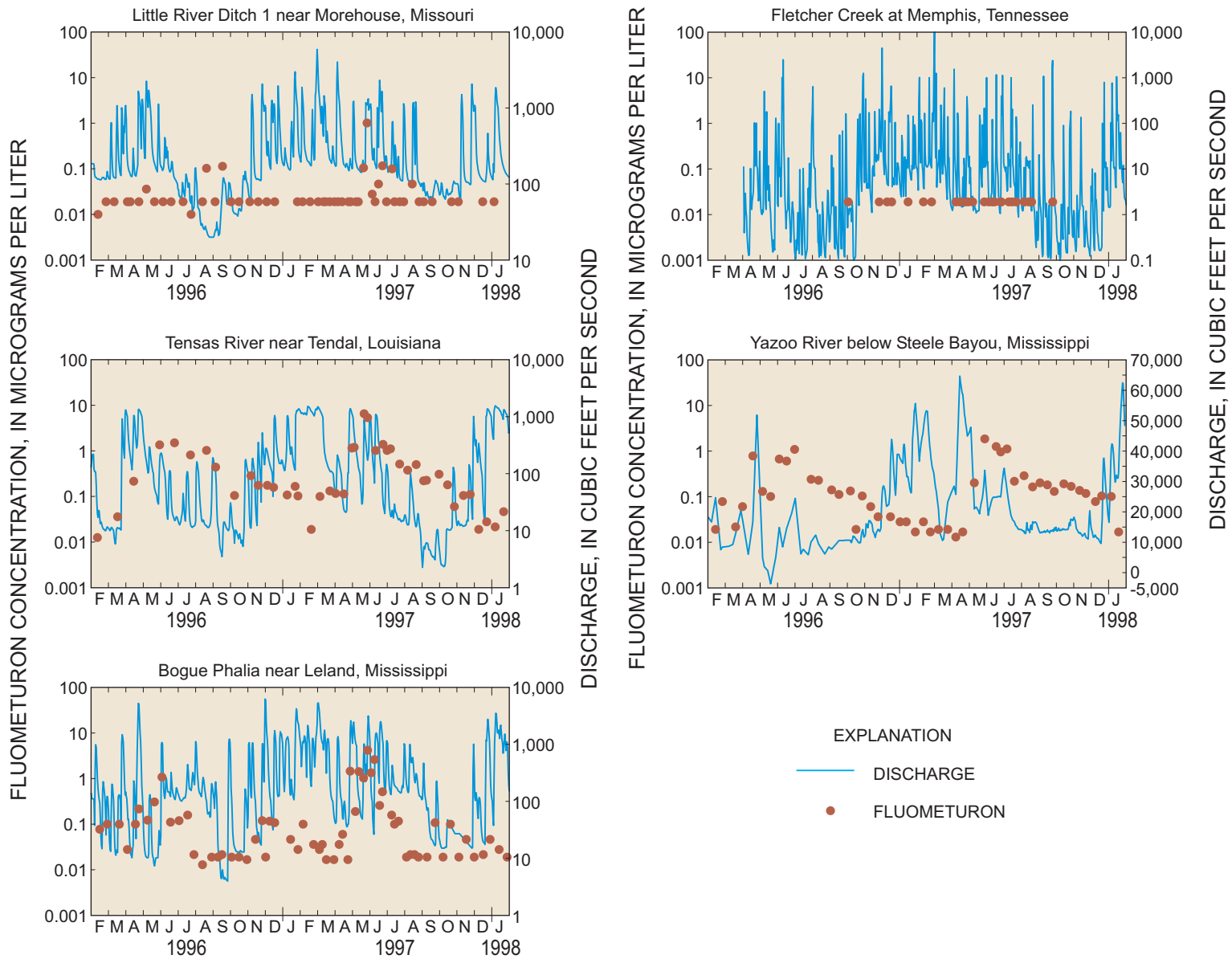


**Figure 12.** Atrazine concentrations and corresponding streamflow in five rivers in the Mississippi Embayment study unit, February 1996—January 1998.

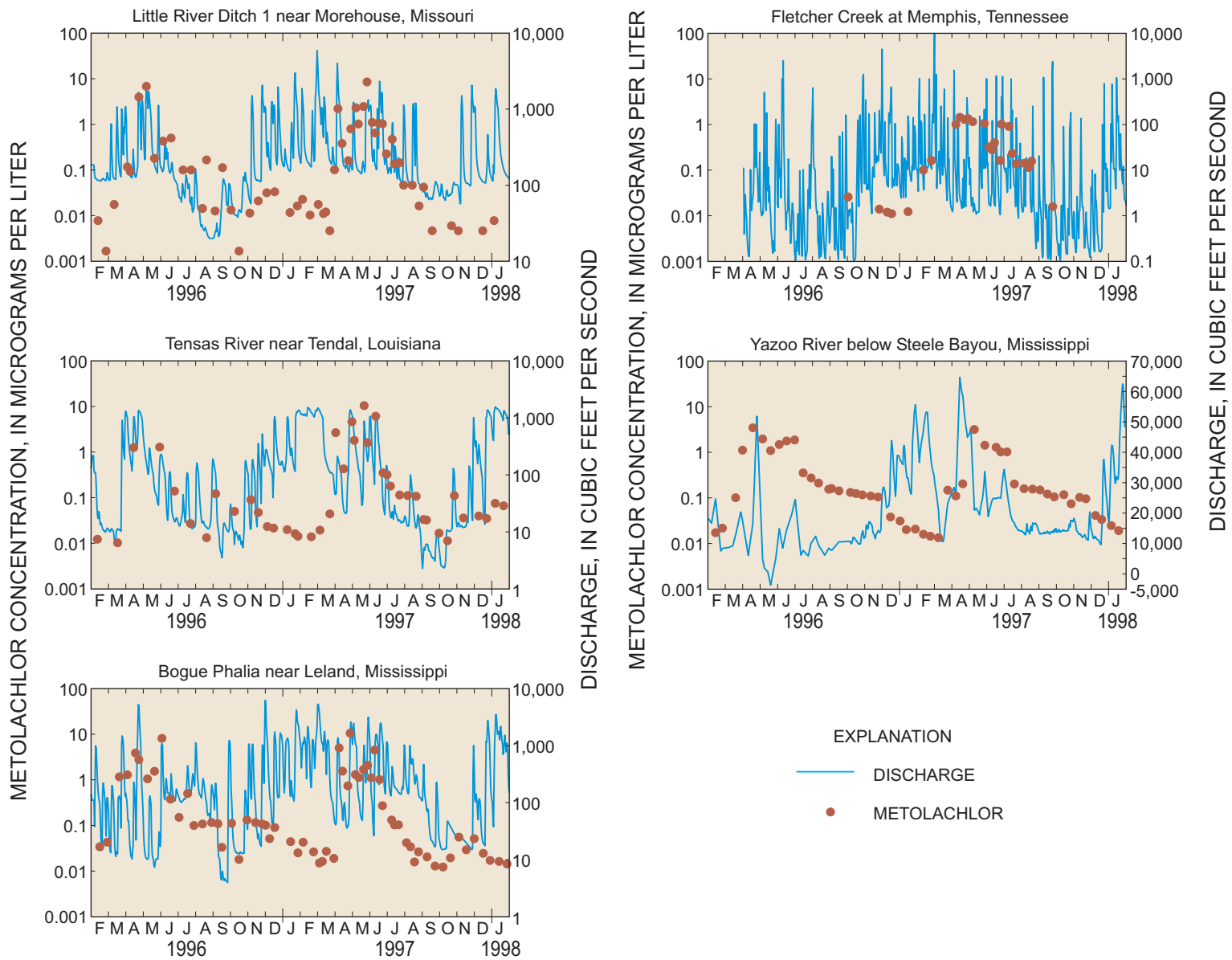


**Figure 13.** Cyanazine concentrations and corresponding streamflow in five rivers in the Mississippi Embayment study unit, February 1996–January 1998.

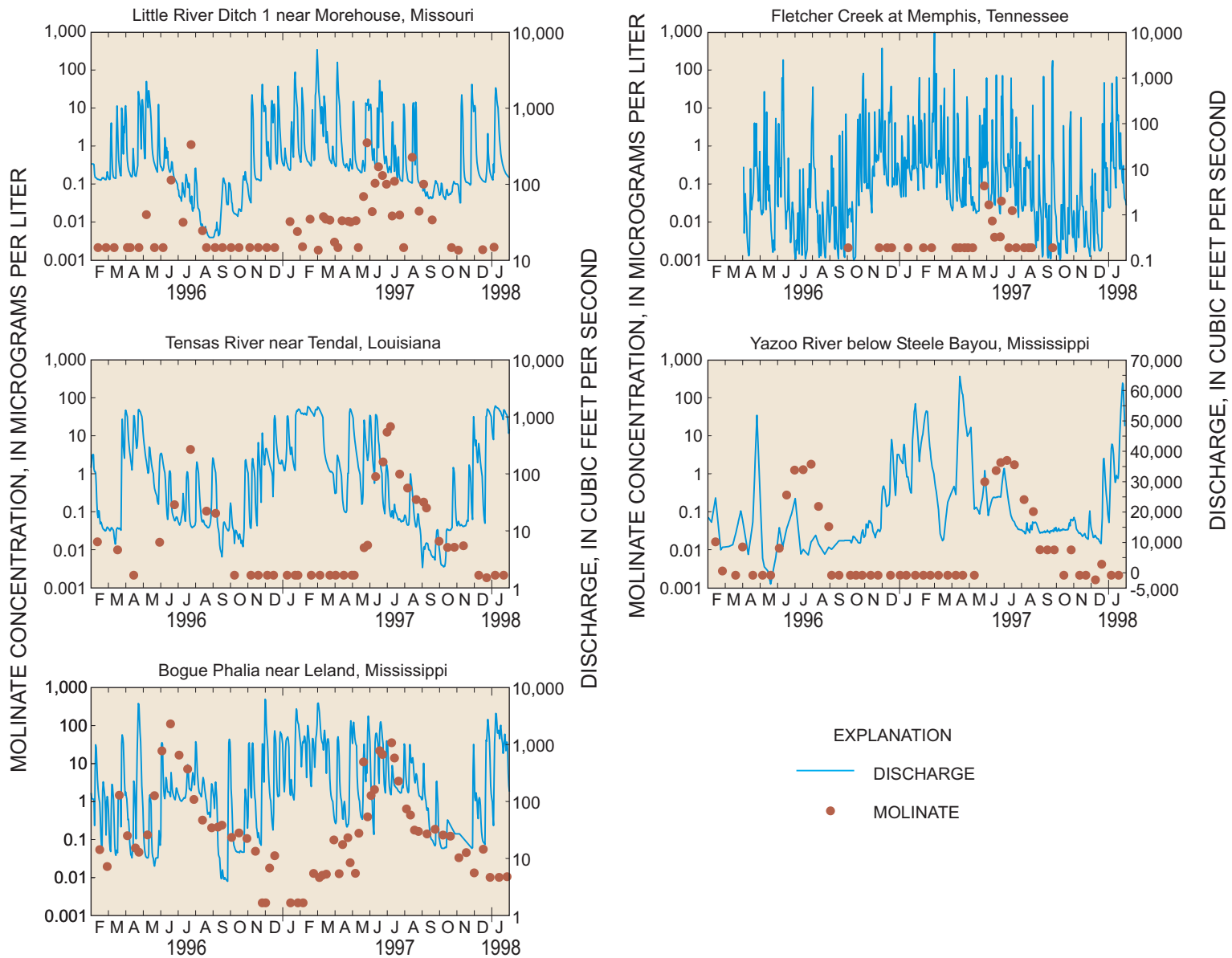




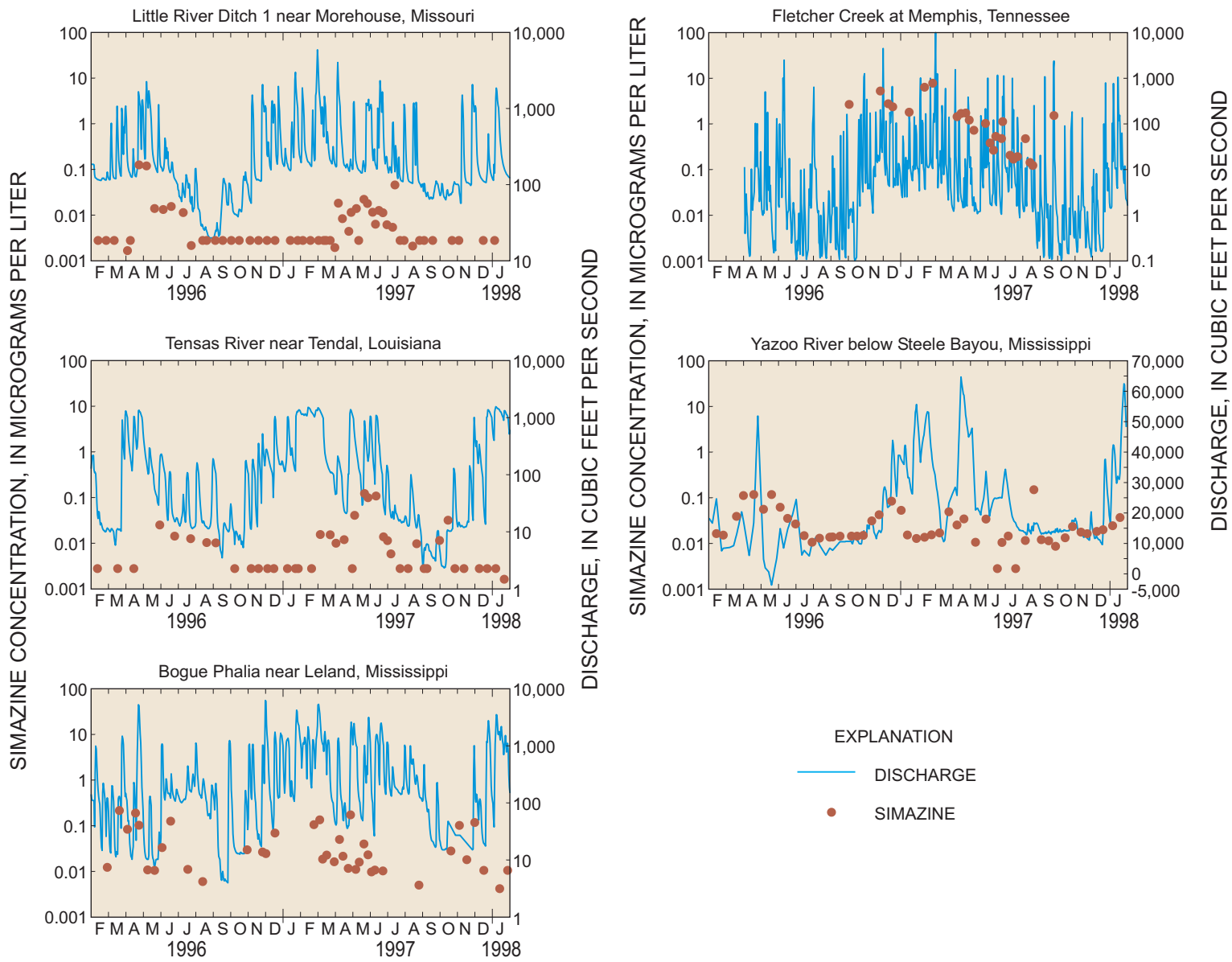
**Figure 14.** Fluometuron concentrations and corresponding streamflow in five rivers in the Mississippi Embayment study unit, February 1996–January 1998.



**Figure 15.** Metolachlor concentrations and corresponding streamflow in five rivers in the Mississippi Embayment study unit, February 1996–January 1998.



**Figure 16.** Molinate concentrations and corresponding streamflow in five rivers in the Mississippi Embayment study unit, February 1996–January 1998.



**Figure 17.** Simazine concentrations and corresponding streamflow in five rivers in the Mississippi Embayment study unit, February 1996–January 1998.

These data were not meant to be a statistical representation of commonly occurring conditions in the surface water of the study unit. Additionally, because the majority of pesticides used for agricultural purposes are applied seasonally and high concentrations of pesticides in streams are related to rainfall runoff events, more sampling was done during these periods. Therefore, the statistics shown in appendix II are not representative of commonly occurring conditions in streams of the study unit, but are probably biased high for some pesticides.

### **Little River Ditch 1, Missouri**

Two pesticides (both herbicides) and an herbicide metabolite were detected in every sample collected from Little River Ditch 1. The herbicides were atrazine, a corn herbicide, and metolachlor which can be used for weed control on corn, cotton, rice, and soybean. The metabolite was desethylatrazine. Additionally, alachlor was detected in more than 75 percent of the samples collected from Little River Ditch 1. The pesticides detected in the highest concentrations were atrazine (22 µg/L) and metolachlor (9.4 µg/L). Figure 11 shows the classic “spring flush” phenomenon described by Thurman and others (1991) in studies of Midwest drainage basins. There were little or no herbicides in the rivers prior to planting, but the concentrations increased with each succeeding runoff event as planting progressed. Eventually, as the reservoir of pesticides in the soil was depleted, the concentrations in the streams dissipated. This is not typical of the other sites in this study unit. There were few insecticides detected in water samples from the Little River Ditch 1, and the few that were detected, were in low concentrations.

There were few detections of fluometuron in the surface waters of the Little River Ditch, indicating that little cotton was being grown in the basin. Molinate was detected in more than 50 percent of the samples, although the concentrations were low, with 95 percent of the concentrations less than 0.75 µg/L.

Atrazine exceeded the guidelines for aquatic life in 14 of 56 samples; most of these samples were collected in April through June. Carbaryl, cyanazine, and diazinon exceeded the guidelines twice each, and 2,4-D exceeded the guidelines once during the study.

### **Tensas River, Louisiana**

The compounds atrazine, cyanazine, desethylatrazine, fluometuron, and metolachlor, all herbicides or herbicide metabolites, were detected above the MRL in all of the water samples from the Tensas River. Tensas River had the highest concentrations for almost all of the pesticides, with the exception of molinate and methyl parathion in the Bogue Phalia, and 2,4-D and simazine in Fletcher Creek. Tensas River had the highest mean total herbicide concentration (more than 15 µg/L) for 4 months (fig. 11). The dominant pesticide was atrazine, a corn herbicide, but there were high concentrations of a number of other herbicides such as cyanazine, fluometuron, metolachlor, and molinate. Gilliom and others (1985) listed the Tensas River as having the second highest number of organochlorine pesticides detections from a network of approximately 180 sites and from more than 1,000 samples. Tensas River also had the highest number of insecticide detections in this study compared to the other agricultural rivers in the study unit, and was the only site where aldicarb sulfoxide, a metabolite of aldicarb, was detected. The insecticide carbofuran was detected in the highest concentration in a water sample collected from the Tensas River.

Atrazine exceeded the guidelines for aquatic life in 10 of 42 samples; most of these samples were collected in April through June. Cyanazine exceeded the guidelines for aquatic life in five samples, and the insecticides carbofuran and chlorpyrifos each exceeded the guidelines once. The Tensas River was the only river where metolachlor exceeded the guidelines twice.

### **Bogue Phalia, Mississippi**

Cyanazine and metolachlor, two herbicides, were detected in 100 percent of the samples collected from the Bogue Phalia. Molinate and thiobencarb, two rice herbicides, were detected in more than 50 percent of the samples. Their presence is indicative of the large amount of rice acreage in the basin. Atrazine and fluometuron also were detected in more than 75 percent of the samples from the Bogue Phalia. Methyl parathion, the most heavily used insecticide in the study unit, was detected most frequently and in the highest concentrations in water samples from the Bogue Phalia. It was detected in nearly every sample collected during June, July, and August of 1996 and 1997.

The highest concentration (140 µg/L) of any pesticide detected during this study was the herbicide molinate in a sample collected from the Bogue Phalia on June 18, 1996. Most other pesticides that were detected in this sample were present in low concentrations, with the exception of thiobencarb and triclopyr. These three herbicides can be applied postemergent to rice. The significance of the June 18, 1996, sample is that it was collected at low flow. The streamflow in the Bogue Phalia had been declining since June 10 and was well below the annual mean. Herbicides generally are applied to dry ground and require rainfall or irrigation to move them offsite into surface water. Therefore, high concentrations of herbicides in surface water are related to rainfall runoff events. However, postemergent herbicides applied to rice can be applied directly into the rice flood.

The molinate concentration of 140 µg/L, as well as the relatively high concentrations of thiobencarb and triclopyr, were probably a result of water from rice fields entering the Bogue Phalia in sufficient quantity to result in these high concentrations. The water is drained directly from a rice field or is the result of a break in the levee of a rice field.

During the night of June 18-19, 1996, a thunderstorm crossed the basin, and by 11 a.m. on June 19, the flow in the Bogue Phalia had almost quadrupled. The molinate concentration on June 19 was 13.3 µg/L. The next sample collected on July 3, 1996, again at low flow, had a molinate concentration of 30 µg/L. During the summer 1997, molinate concentrations were again highest in samples collected during low flow. For example, a concentration of 59 µg/L was collected on July 9 when the flow was 664 ft<sup>3</sup>/s, well below the annual mean flow. However, there was a considerable amount of molinate present in samples collected on June 18 (40 µg/L) and June 23 (31 µg/L) at flows more than double the annual mean flow for 1997.

Water samples from the Bogue Phalia exceeded the guidelines for aquatic life eight times for atrazine and once each for carbaryl, chlorpyrifos, cyanazine, malathion, metolachlor, and azinphos-methyl.

## Yazoo River, Mississippi

The water quality of any stream reflects a complex combination of a number of factors such as land use, point sources, and natural factors. The Yazoo River Basin is a large, heterogeneous basin with large areas of rich agricultural land, forest, pasture, and a

number of small urban centers. Consequently, the water-quality of the Yazoo River reflects this varying land use. The Bogue Phalia Basin is wholly contained within the Yazoo River Basin and has a relatively homogeneous land use (80 percent agriculture). The water quality of the Bogue Phalia influences the water-quality of the Yazoo River proportional to the amount of land within the Yazoo River Basin that has a similar land use as the Bogue Phalia.

Water samples from the Bogue Phalia and the Yazoo River had 100 percent detections of cyanazine and metolachlor, as did atrazine and simazine from Yazoo River samples. Although maximum concentrations for atrazine, cyanazine, metolachlor, and simazine were higher in the Bogue Phalia, median concentrations were higher in the Yazoo River.

The maximum concentrations of the rice herbicides molinate, thiobencarb, and triclopyr were 140, 4, and 4.6, µg/L, respectively, in water samples from the Bogue Phalia, and 4.2, 0.16, and 0.3, respectively, from the Yazoo River. Molinate and thiobencarb were detected in more than 50 percent of the samples from the Bogue Phalia. Water samples from the Yazoo River had few detections of thiobencarb, and molinate was detected in less than 50 percent of the samples.

The cotton herbicide fluometuron was detected in water samples in about the same percentage from the Bogue Phalia as from the Yazoo River. The maximum concentration was higher in the Bogue Phalia, but the median and 75th percentile concentrations were higher in the Yazoo River.

The similarities and dissimilarities between pesticides in the Bogue Phalia and in the Yazoo River are evident from these data. All the samples from both sites contained detections of cyanazine and metolachlor; fluometuron was detected in more than 75 percent of the samples. Although the Bogue Phalia had higher maximum concentrations of pesticides than the Yazoo River, the Yazoo River had higher median concentrations.

Reservoirs in the Midwest have been shown to lower the maximum concentrations and to raise the median concentrations compared to streams. This has been shown to be associated with the water storage in reservoirs (Battaglin and Goolsby, 1996). Because reservoirs collect and store water, they tend to lower the maximum concentration of pesticides in the streams, but also to lengthen the amount of time that streams have elevated concentrations of pesticides.

The higher median concentrations of pesticides in the Yazoo River compared to the Bogue Phalia may be related to the long residence times due to shallow slopes in the streams of the delta. This would tend to attenuate the flood peak and thus lower the peak pesticide concentrations. In addition, the flood-control structures that control the movement of water from a large part of the delta into the Yazoo River may be closed for extended periods, causing the lower part of the delta to act as a storage reservoir.

The dissimilarities between pesticides in the Bogue Phalia and in the Yazoo River occur in the concentrations of the rice herbicides such as molinate, thiobencarb, triclopyr, and with simazine, which is used primarily as an urban herbicide in the study unit. The Bogue Phalia had many more detections and higher concentrations of rice herbicides than did the Yazoo River, but the Yazoo River had more frequent detections and a higher median concentration of simazine.

Atrazine exceeded the guidelines for aquatic life in nine water samples from the Yazoo River and once each for carbaryl, diazinon, malathion, metolachlor, and azinphos-methyl.

### **Fletcher Creek, Tennessee**

The distribution of pesticides in the waters of Fletcher Creek was much different than at any other site in this study. This was expected because the land use in the basin is primarily urban as opposed to agriculture in the other basins. Atrazine and metolachlor were detected in 100 percent of the water samples from Fletcher Creek. This is similar to the other sites. However, in addition to atrazine and metolachlor, the insecticides chlorpyrifos and diazinon, as well as the herbicide simazine also were detected in 100 percent of the samples. Two other insecticides, carbaryl and malathion, were detected in more than 50 percent of the water samples. Carbaryl, chlorpyrifos, diazinon, and malathion, as well as the herbicide simazine, are all used heavily in lawn and garden care and for home use in the southeastern United States. The herbicides 2,4-D, pendimethalin, and prometon were detected in more than 50 percent of the water samples.

Molinate, a rice herbicide with no legal urban uses, was detected in more than 25 percent of the water samples (app. II). All of the detections were in late May through July 1997 (fig. 16). Because rice is not grown in the Fletcher Creek Basin (Tennessee Agricultural Statistics Staff, 1998), these molinate detections might indicate atmospheric transport from

rice fields in Mississippi and Arkansas. In a study examining the occurrence of pesticides in rain and air, molinate was detected in 25 percent of the weekly rain samples collected from April through September 1995 in Jackson, Miss. (Coupe and others, 1998a), also an urban area with no known local uses of molinate.

The insecticides diazinon and chlorpyrifos exceeded the guidelines for aquatic life in water samples from Fletcher Creek in 24 of 25, and in 12 of 25 samples, respectively. Atrazine exceeded the guidelines three times, carbaryl twice, and 2,4-D once.

## **OCCURRENCE OF PESTICIDES IN THE STUDY UNIT**

The mean monthly total pesticide concentration for each site is shown in figure 11. The contribution from the eight most frequently detected pesticides are delineated individually, the rest are grouped into the category "other." Fletcher Creek was sampled for pesticides only from October 1996 to September 1997. There were several months when only one sample was collected, and one month (March) when no samples were collected.

The occurrence of pesticides in the surface water of the study unit shows a marked difference between (1) land-use types (urban and agriculture), (2) streams in the north and south of the study unit, and (3) small streams with one primary land use and the large river draining an area of mixed land use.

The herbicides 2,4-D, atrazine, metolachlor, prometon, and simazine were detected in more than 50 percent of the water samples from the urban site, Fletcher Creek. All other sites had detections of 2,4-D and prometon in less than 50 percent of the samples. Simazine was detected in every sample from Fletcher Creek and was the major component of the mean monthly total pesticide concentration for most months. Simazine was also detected in every water sample from the Yazoo River, which drains some small urban areas, but the concentrations were much higher in Fletcher Creek. Simazine was detected much less frequently and in lower concentrations in samples from the Bogue Phalia, Little River Ditch 1, and Tensas River (app. II).

The insecticides carbaryl, chlorpyrifos, diazinon, and malathion were detected in more than 50 percent of the water samples from Fletcher Creek, but were detected in less than 25 percent of the water samples from any other site (app. II).

There is a difference in the seasonal occurrence of pesticides in surface water between urban and agricultural areas (fig. 11). In the agricultural streams, there is a clear seasonal pattern of pesticide occurrence with the highest concentrations occurring in the spring and early summer months, corresponding with planting and application times. In Fletcher Creek, there was no clear pattern in peak concentrations—similar concentrations occurred in the winter months as well as the summer months.

The distribution of the mean monthly total pesticide concentration for the Little River Ditch 1 is typical of a corn and soybean agricultural basin. Most of the pesticides detected in water samples from the Little River Ditch 1 occurred from April through June, with peak concentrations occurring during May. This pattern is typical where planting and pesticide applications occur over a relatively short time period. The major pesticides were atrazine, metolachlor, and cyanazine, typical corn and soybean herbicides.

Little River Ditch 1 was the only stream with more than 75 percent alachlor detections, a corn herbicide used primarily in the Midwest. The Tensas River and the Bogue Phalia had less than 25 percent detections of alachlor. The mean monthly total pesticide concentration is higher and there are a larger number of pesticides making up the mean in the Tensas River and the Bogue Phalia compared to the Little River Ditch 1. This is because of the longer growing season in the southern parts of the study unit that allows for a larger diversity of crops.

The mean monthly total pesticide concentration for the Little River Ditch 1 exceeded 1 µg/L for April through July 1997; but, in the Tensas River and the Bogue Phalia, the mean total pesticide concentration exceeded 1 µg/L from February through September 1997. The mean monthly total pesticide concentration exceeded 1 µg/L in every month that was sampled for Fletcher Creek and exceeded 1 µg/L from April through September 1997 for the Yazoo River.

The pesticides making up the mean monthly total pesticide concentration in the Tensas River and the Bogue Phalia were primarily atrazine and metolachlor, as in Little River Ditch 1. However, there also were herbicides associated with the production of cotton and rice, such as molinate and fluometuron. Insecticides, associated with cotton and rice production, such as carbofuran and methyl parathion, were detected more frequently in the Tensas River and the Bogue Phalia than in Little River Ditch 1 (app. II).

Coupe (1998a) showed that the primary metabolite of the pesticide needs to be enumerated for a full understanding of the total pesticide load in a stream. Water samples in this study unit were analyzed for several metabolites (table 3), but only desethylatrazine was frequently detected. Desethylatrazine is formed by the loss of an ethyl side chain, primarily from the triazine herbicide atrazine but also from other triazine herbicides, such as propazine (Mills and Thurman, 1994). Desethylatrazine was detected in water samples a little less frequently than atrazine, and the maximum and median concentrations were about an order of magnitude lower than those of atrazine, but followed the same pattern. Those sites with the highest median atrazine concentrations also have the highest median desethylatrazine concentrations.

The Yazoo River Basin is more than 20 times the size of the Bogue Phalia, Fletcher Creek, Little River Ditch 1, or Tensas River Basins. Although the concentrations of pesticides were less than those in the smaller basins, the occurrence of pesticides reflects the Yazoo River Basin's mixed land use and includes most of the pesticides detected at other sites, agricultural or urban.

## **OCCURRENCE OF PESTICIDES IN THE MISSISSIPPI EMBAYMENT STUDY UNIT COMPARED TO OTHER NAWQA STUDY UNITS**

The data-collection phase for 20 NAWQA study units that began in 1991 has been completed. The results from pesticide sampling have been aggregated and are available to compare to the results from the MISE study unit (Gilliom and others, 1999). The aggregate NAWQA pesticide data from the first 20 NAWQA study units includes approximately 1,000 water samples from 40 agricultural streams, more than 300 samples from 11 urban streams, and almost 250 samples from 11 large rivers draining mixed land use (Gilliom, R.J., accessed 1998). The water samples in the aggregate NAWQA pesticide data for 1992-96 were collected using the same sampling procedures, sent to the same laboratory, and analyzed by the same methods used in this MISE study. The data are comparable to those collected in the MISE study unit; however, there may be slight differences in the MRL's due to the refinement of the analytical techniques.



Caution should be used when interpreting the results of comparing the occurrence of pesticides in surface water from the MISE study unit to the aggregate NAWQA data for several reasons. First, agriculture is not the same throughout the United States. Climatic differences, soils, availability of water, tradition, market forces, and history all interact to dictate the amounts and types of agriculture in a specific area and the amounts and types of pesticides used. Second, some pesticides, such as atrazine and metolachlor, are used throughout the United States on a variety of crops and could be expected to be detected in much of the Nation's surface water. Other pesticides, used on a few selected crops that are grown in certain regions of the Nation, would not be expected to be detected in streams draining areas where they are not used.

The results from the MISE study unit's three agricultural streams (Little River Ditch 1, Bogue Phalia, and the Tensas River) compared to the aggregate NAWQA pesticide data for agricultural streams indicates some strong similarities and some regional differences, possibly unique to the study unit. In the aggregate data set, the most frequently detected pesticides were atrazine (77 percent), metolachlor (73 percent), and simazine (61 percent). Metolachlor was detected in all of the samples in all three MISE agricultural streams, and atrazine was detected in every sample from Little River Ditch 1, the Tensas River, and in more than 75 percent of the samples from the Bogue Phalia. Simazine was detected in less than 50 percent of the samples from the study unit agricultural streams.

There are regional differences in the occurrence of pesticides in surface water that appear to be unique to the MISE study unit. Pesticides, such as fluometuron and molinate used in cotton and rice production, were detected in less than 5 percent of the samples from the aggregate NAWQA data. At the two MISE agricultural streams in cotton and rice growing areas (Bogue Phalia and the Tensas River), fluometuron was detected in more than 75 percent of the water samples and molinate in more than 50 percent.

Regional differences in pesticides detected in urban streams from the aggregate NAWQA data, compared to pesticides in the MISE urban stream (Fletcher Creek), were not readily apparent. The most frequently detected pesticides in the urban aggregate NAWQA data were simazine (88 percent), atrazine (87 percent), prometon (84 percent), and diazinon (75 percent). Atrazine, diazinon, and simazine were

detected in 100 percent of the water samples from Fletcher Creek, and prometon in more than 50 percent. The insecticides carbaryl and chlorpyrifos were detected in 45 and 41 percent, respectively, of the water samples in the urban aggregate NAWQA data, and 50 and 100 percent, respectively, in Fletcher Creek.

The most frequently detected pesticides in the large river aggregate NAWQA data were atrazine (89 percent), simazine (83 percent), and metolachlor (82 percent). The next most frequently detected pesticide was prometon (62 percent). From the MISE large river sampling site (Yazoo River), atrazine, cyanazine, metolachlor, and simazine were detected in 100 percent of the samples. In the large river aggregate NAWQA data there were less than 10 percent detections of diuron and no detections of fluometuron; but in the Yazoo River, both diuron and fluometuron were detected in more than 75 percent of the samples. Thus, as with the agricultural sites, there are similarities and regional differences in the occurrence of pesticides in large rivers.

## SUMMARY

In 1994, the U.S. Geological Survey, through its National Water-Quality Assessment Program, began an assessment of water quality in the Mississippi Embayment study unit. The study unit is an area rich in agricultural resources with a warm, humid climate, and a long growing season, and is one of the most agriculturally productive areas in the world. The major crops grown in the study unit are corn, cotton, rice, and soybean. Pesticides are heavily used to control weeds and insects. As part of the overall assessment of water quality, more than 230 water samples were collected from five rivers and analyzed for more than 80 pesticides and pesticide metabolites from February 1996 through January 1998.

The five rivers sampled included three rivers draining agricultural areas, one urban river, and one large river with mixed land use. The rivers draining primarily agricultural watersheds were the Little River Ditch 1 located in the Bootheel of Missouri, the Tensas River in northeastern Louisiana, and the Bogue Phalia in west-central Mississippi. The urban stream was Fletcher Creek, located in a rapidly urbanizing area of Memphis, Tenn. The large river with mixed land use (row-crop agriculture, pasture, forest, and urban) was the Yazoo River that drains the relatively flat and heavily agricultural Mississippi Delta and the Loess Hills in the eastern part of the Yazoo River Basin.

Pesticides, usually herbicides, were frequently detected in water samples; the most frequent was metolachlor, detected in 100 percent of samples from all rivers. Metolachlor is used in weed control for corn, cotton, and soybean in the study unit. The next most frequently detected herbicide was atrazine, a corn herbicide, detected in 100 percent of the samples from all rivers except the Bogue Phalia, where it was detected in more than 75 percent of the samples. Desethylatrazine, a major metabolite of atrazine, was detected almost as frequently as atrazine.

Other pesticides that were detected frequently in one or more rivers were alachlor, chlorpyrifos, cyanazine, diazinon, fluometuron, molinate, and simazine. These pesticides show an areal distribution consistent with their use. The insecticides chlorpyrifos and diazinon and the herbicide simazine were detected in 100 percent of the water samples from the urban river, Fletcher Creek. Simazine was also detected in 100 percent of the samples in the Yazoo River, which drains an area of mixed land use, including small urban areas. Fluometuron, a cotton herbicide, and molinate, a rice herbicide, were frequently detected in rivers in cotton and rice growing areas such as the Bogue Phalia and the Tensas River. Alachlor, a corn herbicide that was heavily used in the Midwest, was detected in Little River Ditch 1 in more than 75 percent of the water samples, but much less frequently in the other rivers.

The urban stream (Fletcher Creek) had the greatest number of exceedances of aquatic-life criteria. Diazinon concentrations exceeded the aquatic-life criterion in 24 of 25 samples, and chlorpyrifos exceeded the aquatic-life criterion in 12 of 25 samples. The aquatic-life criteria for diazinon and chlorpyrifos was exceeded only once or twice in water samples from the agricultural (Little River Ditch 1, Bogue Phalia, and Tensas River) and mixed land-use (Yazoo River) watersheds. The aquatic-life criteria of 2 µg/L for atrazine was exceeded in about 20 percent of the samples from each river; most of these exceedances occurred in the spring following application. There were a few other pesticides that exceeded the aquatic-life criteria once or twice in each river (2,4-D, carbaryl, carbofuran, cyanazine, malathion, metolachlor, and azinphos-methyl).

Data from three agricultural streams in the Mississippi Embayment study unit (Little River Ditch 1, Bogue Phalia, and Tensas River) that were compared to the aggregate NAWQA pesticide data (from other NAWQA study units) indicate some strong

similarities and some regional differences. The most frequently detected pesticides were atrazine (77 percent) and metolachlor (73 percent) in the aggregate NAWQA data from agricultural streams. This was quite similar to the results from the MISE study unit. Herbicides, such as molinate and fluometuron, were detected frequently in rivers draining areas of rice and cotton production in the study unit, but were detected in less than 5 percent of the samples from the aggregate NAWQA data. The occurrence of pesticides in an urban stream (Fletcher Creek) was similar nationally to the occurrence in urban streams. The most frequently detected pesticides in the urban aggregate NAWQA data were simazine (88 percent), atrazine (87 percent), and prometon (84 percent). Pesticides detected in the Fletcher Creek were simazine and atrazine (100 percent each), and prometon (50 percent). The insecticides detected in the urban aggregate NAWQA data were carbaryl (45 percent) and chlorpyrifos (41 percent); and in Fletcher Creek, 100 percent and more than 50 percent, respectively.

Atrazine, simazine, and metolachlor were the pesticides most frequently detected in the large river aggregate NAWQA data. Atrazine, cyanazine, metolachlor, and simazine were detected in 100 percent of the water samples from the Yazoo River. There were few detections of diuron and fluometuron in the large river aggregate NAWQA data, but both herbicides were detected in more than 75 percent of the samples from the Yazoo River. Thus, as with the agricultural sites, there are similarities and regional differences in the occurrence of pesticides in large rivers.

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# Appendix I

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**Appendix I.** Concentrations and relative percentage differences for pesticides detected in nine replicate samples [µg/L, micrograms per liter; <, less than; NC, not calculated; H, analyzed by high-performance liquid chromatography; G, analyzed by gas chromatography/mass spectrometry; \*, estimated]

Pesticide	Concentration in duplicates (µg/L)	Relative percent difference
2, 4-D	1.40*	22.2
	1.75	
	<0.035	NC
	0.59	9.2
	0.62	
	0.68	10.5
	0.18	
	0.20	
Acetochlor	0.0305	5.4
	0.0289	25.0
	0.270	
	0.210	6.2
	0.662	
	0.622	
	0.0526	16.2
	0.0447	169
	0.122	
	1.45	
Acifluorfen	<0.035	NC
	0.06	3.6
	0.28	
	0.27	
Alachlor	0.006	15.3
	0.007	
	0.006	18.2
	0.005	0.6
	1.66	
	1.65	2.8
	0.107	
	0.104	
		0.011
0.015		46.8
0.145		
0.90		
Atrazine	0.786	1.0
	0.778	17.3
	0.069	
	0.058	105.6
	17.8	
	5.50	
	1.10	34.0
	0.78	
	1.59	0.0
	1.59	
26.3*	12.5	
23.2*		
	0.32	31.6
	0.44	35.0
	3.09	
	2.17	
	3.50	0.0
3.50		
Benfluralin	0.010	27.3
	0.0076	

Pesticide	Concentration in duplicates (µg/L)	Relative percent difference
Bentazon	0.06*	28.6
	0.08	194
	0.64*	
	0.01	18.9
	0.52	
	0.43	
Butylate	0.061	NC
	<0.002	
Carbaryl	0.14* (H)	7.4
	0.13* (H)	
	0.243* (G)	2.4
	0.249* (G)	
Carbofuran	0.85* (H)	25.2
	0.66* (H)	2.5
	0.39* (G)	
	0.40* (G)	NC
	0.092* (G)	
	<0.003* (G)	2.1
	0.93* (G)	
	0.95* (G)	
Chlorpyrifos	0.0814	8.2
	0.075	NC
<0.004		
	0.008	NC
	<0.004	
	0.016	
Cyanazine	0.600	69.6
	1.24	15.4
	0.140	
	0.120	13.3
	0.040	
	0.035	
	0.649	14.2
	0.563	6.4
	0.0137	
	0.0146	25.6
	0.088	
	0.068	0.0
0.220		
	0.220	
<i>p,p'</i> -DDE	0.004*	28.6
	0.003*	
	0.0093	26.8
	0.0071	NC
	<0.006	
	0.004*	
Desethylatrazine	0.195*	2.6
	0.19*	
	0.0129*	141.7
	0.0022*	
	0.138*	66.0
0.274*		

**Appendix I. Concentrations and relative percentage differences for pesticides detected in nine replicate samples (Continued)**

[µg/L, micrograms per liter; <, less than; NC, not calculated; H, analyzed by high-performance liquid chromatography; G, analyzed by gas chromatography/mass spectrometry; \*, estimated]

Pesticide	Concentration in duplicates (µg/L)	Relative percent difference
	0.065*	11.6
	0.073*	
	0.045*	2.2
	0.046*	
	0.194*	15.6
	0.166*	
	0.0038*	5.4
	0.0036*	
	0.116*	103.3
	0.037*	
	0.22*	8.7
	0.24*	
Diazinon	0.376 0.351	6.9
Dichlorprop	<0.032 0.020*	NC
Dieldrin	0.003*	NC
	<0.001 0.005	NC
	<0.001	
Disulfoton	0.0476 0.0712	39.7
Diuron	0.19 0.13	37.5
	0.09	25.0
	0.07	
	0.01* 0.02*	66.7
DCPA	0.005	NC
	<0.002	
EPTC	0.005 <0.002	NC
Fluometuron	0.15* 0.12 0.20 0.14 0.05	22.2 35.3 50.0
	0.03* 0.04 0.5 0.37 0.37	22.2 0.0
	2.40* 2.60*	8.0
Malathion	0.040 0.043 0.78*	7.2 6.6
MCPA	0.73* 1.28	3.2
Metolachlor	1.24 0.025	17.4

Pesticide	Concentration in duplicates (µg/L)	Relative percent difference
	0.021 4.81 4.52	6.2
	0.930 0.620	40.0
	0.918 0.882	4.0
	4.22 3.89	8.1
	0.029	3.5
	0.028 2.08	89.7
	5.46 0.240 0.230	4.3
methyl Parathion	0.054 0.072	28.6
Metribuzin	0.190 0.260 0.016 0.013 0.075 0.076	31.1 20.7 1.3
	3.74 3.92 0.004 0.006 0.482	4.7 40.0 NC
	<0.004 0.0037 0.038	2.7
Molinate	0.0962 0.0964 0.0719 0.071	0.2 1.3
	153 140	8.9
	0.149 0.143 0.653 0.658 0.260 0.270	4.1 0.8 3.8
Norflurazon	0.05 0.05 <0.024	0.0 NC
	0.08 0.15 0.15 0.44 0.43	0.0 2.3
Pebulate	0.005 0.005	0.0



**Appendix I.** Concentrations and relative percentage differences for pesticides detected in nine replicate samples (Continued)  
 [µg/L, micrograms per liter; <, less than; NC, not calculated; H, analyzed by high-performance liquid chromatography; G, analyzed by gas chromatography/mass spectrometry; \*, estimated]

Pesticide	Concentration in duplicates (µg/L)	Relative percent difference	Pesticide	Concentration in duplicates (µg/L)	Relative percent difference
Pendimethalin	0.332	14.5		0.062	135
	0.287			0.012	
	0.0864	18.7		0.024	0.0
	0.0716			0.024	
	0.088	34.7	Tebuthiuron	0.027	29.8
	0.062			0.02	
	0.028	NC		0.015	6.5
	<0.004			0.016	
	1.09	33.3		0.0049*	NC
	0.779			<0.01	
	0.065	49.7	Thiobencarb	0.083	11.4
	0.108			0.0093	
Propanil	0.0196	6.3		0.0644	5.3
	0.0184			0.0611	
	0.180	4.3		0.510	21.7
	0.188			0.410	
	0.011	31.6		0.009	NC
	0.008			<0.002	
	0.108	25.1		0.396	36.4
	0.0839			0.274	
Prometon	0.291	19.3		0.022	NC
	0.353			<0.002	
	0.0035*	25.0	Triclopyr	0.20	93.3
	0.0045*			0.55	
	0.004*	22.2		1.5*	14.3
	0.005*			1.3	
	0.008*	31.6		0.38	5.1
	0.011*			0.40	
Propachlor	0.004*	0.0	Tirfluralin	0.025	29.4
	0.004*			0.0186	
Simazine	1.08	1.8		0.008	19.2
	1.10			0.0066	
	0.0323	24.0		0.002*	0.0
	0.0411			0.002*	
	0.210	10.0		0.006	15.4
	0.190			0.007	
	0.016	0.0		0.0931	13.5
	0.016			0.0813	
	0.0527	21.0		0.012	52.6
	0.0427			0.007	
	0.0219	0.5		0.003*	40.0
	0.0218			0.002*	

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## Appendix II

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**Appendix II.** Summary statistics for selected pesticides analyzed in water samples collected from five rivers in the Mississippi Embayment study unit, 1996-98

[<, less than; \*\*, estimated concentration; (HPLC), high performance liquid chromatography; (GCMS), gas chromatography mass spectrometry; \*, value is estimated by using a log-probability regression to predict values of data below the detection limit]

Compound	Number	Maximum	Minimum	Mean	Percentage				
		(micrograms per liter)			95	75	50	25	5
<b>Fletcher Creek at Memphis, Tennessee—October 1996 to September 1997</b>									
2,4,5-T	25	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
2,4-D	25	5.53	<0.035	0.944*	4.84	0.68	0.18	<0.035	<0.035
2,4-DB	25	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
2,6-Diethylaniline	25	<0.003	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
3-Hydroxy-carbofuran	25	<0.014	<0.014	--	<0.014	<0.014	<0.014	<0.014	<0.014
Acetochlor	25	0.043	<0.002	--	0.013	<0.002	<0.002	<0.002	<0.002
Acifluorfen	25	0.060	<0.035	--	0.060	<0.035	<0.035	<0.035	<0.035
Alachlor	25	0.017	<0.002	0.002*	0.011	<0.002	<0.002	<0.002	<0.002
Aldicarb	25	<0.016	<0.016	--	<0.016	<0.016	<0.016	<0.016	<0.016
Aldicarb sulfone	25	<0.016	<0.016	--	<0.016	<0.016	<0.016	<0.016	<0.016
Aldicarb sulfoxide	25	<0.021	<0.021	--	<0.021	<0.021	<0.021	<0.021	<0.021
alpha-HCH	25	<0.030	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Atrazine	25	3.37	0.023	0.601	3.11	0.839	0.229	0.060	0.026
Benfluralin	25	0.008	<0.002	--	0.007	<0.002	<0.002	<0.002	<0.002
Bentazon	25	<0.014	<0.014	--	<0.014	<0.014	<0.014	<0.014	<0.014
Bromacil	25	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Bromoxynil	25	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Butylate	25	<0.002	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Carbaryl (HPLC)	25	0.26	<0.008	--	0.19	<0.008	<0.008	<0.008	<0.008
Carbaryl** (GCMS)	25	0.359	<0.003	0.074*	0.249	0.099	0.041	<0.050	<0.003
Carbofuran (HPLC)	25	<0.028	<0.028	--	<0.028	<0.028	<0.028	<0.028	<0.028
Carbofuran** (GCMS)	25	0.016	<0.003	--	<0.020	<0.003	<0.003	<0.003	<0.003
Chloramben	25	<0.011	<0.011	--	<0.011	<0.011	<0.011	<0.011	<0.011
Chlorothalonil**	25	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Chlorpyrifos	25	0.251	0.017	0.056	0.220	0.071	0.036	0.026	0.017
Clopyralid	25	<0.050	<0.050	--	<0.050	<0.050	<0.050	<0.050	<0.050
Cyanazine	25	0.023	<0.004	--	0.020	<0.004	<0.004	<0.004	<0.004
monoacid-DCPA	25	<0.017	<0.017	--	<0.017	<0.017	<0.017	<0.017	<0.017
DCPA	25	0.002	<0.002	--	0.002	<0.002	<0.002	<0.002	<0.002
p,p' DDE	25	0.006	<0.006	--	<0.006	<0.006	<0.006	<0.006	<0.006
desethyl-Atrazine**	25	0.283	<0.002	0.051*	0.190	0.067	0.019	0.005	<0.002
Diazinon	25	1.05	0.012	0.206	0.880	0.322	0.127	0.067	0.013
Dicamba	25	0.090	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Dichlobenil**	25	<0.020	<0.020	--	<0.020	<0.020	<0.020	<0.020	<0.020
Dichlorprop	25	0.290	<0.032	--	0.070	<0.032	<0.032	<0.032	<0.032
Dieldrin	25	<0.001	<0.001	--	<0.001	<0.001	<0.001	<0.001	<0.001
Dinoseb	25	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035

**Appendix II.** Summary statistics for selected pesticides analyzed in water samples collected from five rivers in the Mississippi Embayment study unit, 1996-98 (Continued)  
 [<, less than; \*\*, estimated concentration; (HPLC), high performance liquid chromatography; (GCMS), gas chromatography mass spectrometry; \*, value is estimated by using a log-probability regression to predict values of data below the detection limit]

Compound	Number	Maximum	Minimum	Mean	Percentage				
		(micrograms per liter)			95	75	50	25	5
Disulfoton	25	<0.017	<0.017	--	<0.017	<0.017	<0.017	<0.017	<0.017
Diuron	25	0.23	<0.020	0.053*	0.22	0.090	<0.020	<0.020	<0.020
DNOC**	25	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
EPTC	25	0.013	<0.002	--	0.008	<0.002	<0.002	<0.002	<0.002
Ethalfuralin	25	<0.004	<0.004	--	<0.004	<0.004	<0.004	<0.004	<0.004
Ethoprop	25	<0.003	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
Fenuron	25	<0.013	<0.013	--	<0.013	<0.013	<0.013	<0.013	<0.013
Fluometuron	25	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Fonofox	25	<0.003	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
Lindane	25	<0.004	<0.004	--	<0.004	<0.004	<0.004	<0.004	<0.004
Linuron (HPLC)	25	<0.018	<0.018	--	<0.018	<0.018	<0.018	<0.018	<0.018
Linuron (GCMS)	25	<0.002	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Malathion	25	0.56	<0.005	0.271*	0.379	0.071	0.011	<0.005	<0.005
MCPA	25	0.73	<0.050	0.29*	0.68	0.31	<0.050	<0.050	<0.050
MCPB	25	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Methiocarb	25	<0.026	<0.026	--	<0.026	<0.026	<0.026	<0.026	<0.026
Methomyl	25	<0.017	<0.017	--	<0.017	<0.017	<0.017	<0.017	<0.017
methyl-Parathion	25	0.061	<0.006	--	0.050	<0.006	<0.006	<0.006	<0.006
methyl-Azinphos	24	0.043	<0.001	--	<0.001	<0.001	<0.001	<0.001	<0.001
Metolachlor	25	2.42	0.014	0.653	2.35	1.06	0.293	0.073	0.015
Metribuzin	25	0.188	<0.004	0.020*	0.106	0.011	<0.030	<0.004	<0.004
Molinate	25	0.096	<0.004	0.012*	0.061	0.007	<0.004	<0.004	<0.004
Napropamide	25	<0.040	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
Neburon	25	<0.015	<0.015	--	<0.015	<0.015	<0.015	<0.015	<0.015
Norflurazon	25	<0.024	<0.024	--	<0.024	<0.024	<0.024	<0.024	<0.024
Oryzalin	24	<0.019	<0.019	--	<0.019	<0.019	<0.019	<0.019	<0.019
Oxamyl	25	<0.018	<0.018	--	<0.018	<0.018	<0.018	<0.018	<0.018
Parathion	25	<0.004	<0.004	--	<0.004	<0.004	<0.004	<0.004	<0.004
Pebulate	25	<0.004	<0.004	--	<0.004	<0.004	<0.004	<0.004	<0.004
Pendimethalin	25	0.372	<0.004	0.100*	0.293	0.105	0.083	<0.010	<0.004
cis-Permethrin	25	<0.005	<0.005	--	<0.005	<0.005	<0.005	<0.005	<0.005
Phorate	25	<0.002	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Picloram	25	<0.050	<0.050	--	<0.050	<0.050	<0.050	<0.050	<0.050
Prometon	25	0.353	<0.018	0.055*	0.155	0.054	0.026	<0.018	<0.018
Pronamide	25	0.131	<0.003	0.022*	0.091	0.018	<0.003	<0.003	<0.003
Propachlor	25	<0.007	<0.007	--	<0.007	<0.007	<0.007	<0.007	<0.007
Propanil	25	0.055	<0.004	--	0.042	<0.004	<0.004	<0.004	<0.004
Propargite	25	<0.013	<0.013	--	<0.013	<0.013	<0.013	<0.013	<0.013

**Appendix II.** Summary statistics for selected pesticides analyzed in water samples collected from five rivers in the Mississippi Embayment study unit, 1996-98 (Continued)  
 [<, less than; \*\*, estimated concentration; (HPLC), high performance liquid chromatography; (GCMS), gas chromatography mass spectrometry; \*, value is estimated by using a log-probability regression to predict values of data below the detection limit]

Compound	Num-ber	Maximum	Minimum	Mean	Percentage				
		(micrograms per liter)			95	75	50	25	5
Propham	25	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Propoxur	25	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Silvex	25	<0.021	<0.021	--	<0.021	<0.021	<0.021	<0.021	<0.021
Simazine	25	9.03	0.182	2.54	8.79	3.85	1.46	0.553	0.199
Tebuthiuron	25	0.028	<0.010	0.012*	0.026	0.014	<0.010	<0.010	<0.010
Terbacil**	25	<0.007	<0.007	--	<0.007	<0.007	<0.007	<0.007	<0.007
Terbufos	25	<0.013	<0.013	--	<0.013	<0.013	<0.013	<0.013	<0.013
Thiobencarb	25	0.009	<0.002	--	0.009	<0.002	<0.002	<0.002	<0.002
Triallate	25	<0.001	<0.001	--	<0.001	<0.001	<0.001	<0.001	<0.001
Triclopyr	25	1.24	<0.050	--	0.55	<0.050	<0.050	<0.050	<0.050
Trifluralin	25	0.037	<0.002	0.004*	0.019	0.004	<0.002	<0.002	<0.002
<b>Little River Ditch No. 1 near Morehouse, Missouri—February 1996 to January 1998</b>									
2,4,5-T	55	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
2,4-D	55	5.83	<0.035	0.194*	0.590	0.110	<0.035	<0.035	<0.035
2,4-DB	55	<0.240	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
2,6-Diethylaniline	56	<0.003	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
3-Hydroxy-carbofuran	55	<0.014	<0.014	--	<0.014	<0.014	<0.014	<0.014	<0.014
Acetochlor	56	0.220	<0.002	0.019*	0.099	0.010	<0.002	<0.002	<0.002
Acifluorfen	55	0.640	<0.035	0.059*	0.340	0.040	<0.035	<0.035	<0.035
Alachlor	56	5.46	<0.002	0.388*	2.54	0.212	0.010	0.003	<0.002
Aldicarb	55	<0.550	<0.016	--	<0.016	<0.016	<0.016	<0.016	<0.016
Aldicarb sulfone	55	<0.100	<0.016	--	<0.016	<0.016	<0.016	<0.016	<0.016
Aldicarb sulfoxide	55	<0.021	<0.021	--	<0.021	<0.021	<0.021	<0.021	<0.021
alpha-HCH	56	<0.002	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Atrazine	56	22.1	0.004	2.69	20.0	2.10	0.146	0.045	0.009
Benfluralin	56	<0.002	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Bentazon	55	1.31	<0.014	0.12*	0.63	0.080	0.020	<0.014	<0.014
Bromacil	55	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Bromoxynil	55	0.080	<0.012	--	<0.035	<0.035	<0.035	<0.035	<0.035
Butylate	56	<0.002	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Carbaryl (HPLC)	55	0.020	<0.008	--	<0.008	<0.008	<0.008	<0.008	<0.008
Carbaryl** (GCMS)	56	0.029	<0.003	0.002*	0.021	<0.003	<0.003	<0.003	<0.003
Carbofuran (HPLC)	55	0.32	<0.028	--	<0.120	<0.028	<0.028	<0.028	<0.028
Carbofuran** (GCMS)	56	0.280	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
Chloramben	55	<0.420	<0.011	--	<0.011	<0.011	<0.011	<0.011	<0.011
Chlorothalonil**	55	<0.480	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Chlorpyrifos	56	0.010	<0.004	--	0.004	<0.004	<0.004	<0.004	<0.004
Clopyralid	55	<0.230	<0.050	--	<0.050	<0.050	<0.050	<0.050	<0.050
Cyanazine	56	5.00	<0.004	0.211*	1.25	0.10	<0.004	<0.004	<0.004

**Appendix II.** Summary statistics for selected pesticides analyzed in water samples collected from five rivers in the Mississippi Embayment study unit, 1996-98 (Continued)  
 [<, less than; \*\*, estimated concentration; (HPLC), high performance liquid chromatography; (GCMS), gas chromatography mass spectrometry; \*, value is estimated by using a log-probability regression to predict values of data below the detection limit]

Compound	Number	Maximum	Minimum	Mean	Percentage				
					(micrograms per liter)				
					95	75	50	25	5
monoacid-DCPA	55	0.060	<0.017	--	<0.017	<0.017	<0.017	<0.017	<0.017
DCPA	56	0.027	<0.002	0.002*	0.002	<0.002	<0.002	<0.002	<0.002
<i>p,p'</i> DDE	56	<0.006	<0.006	--	<0.006	<0.006	<0.006	<0.006	<0.006
desethyl-Atrazine**	56	0.570	0.001	0.070	0.335	0.076	0.013	0.004	0.001
Diazinon	56	0.018	<0.002	--	0.006	<0.002	<0.002	<0.002	<0.002
Dicamba	55	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Dichlobenil**	55	<1.200	<0.020	--	<0.020	<0.020	<0.020	<0.020	<0.020
Dichlorprop	55	0.240	<0.032	--	<0.032	<0.032	<0.032	<0.032	<0.032
Dieldrin	56	<0.001	<0.001	--	<0.001	<0.001	<0.001	<0.001	<0.001
Dinoseb	55	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Disulfoton	56	<0.017	<0.017	--	<0.017	<0.017	<0.017	<0.017	<0.017
Diuron	55	0.150	<0.020	0.014*	0.030	<0.020	<0.020	<0.020	<0.020
DNOC**	55	<0.420	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
EPTC	56	<0.002	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Ethalfuralin	56	<0.004	<0.004	--	<0.004	<0.004	<0.004	<0.004	<0.004
Ethoprop	56	<0.003	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
Fenuron	55	<0.013	<0.013	--	<0.013	<0.013	<0.013	<0.013	<0.013
Fluometuron	55	1.05	<0.010	0.041*	0.15	<0.035	<0.035	<0.035	<0.035
Fonofox	56	<0.003	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
Lindane	56	<0.004	<0.004	--	<0.004	<0.004	<0.004	<0.004	<0.004
Linuron (HPLC)	55	<0.018	<0.018	--	<0.018	<0.018	<0.018	<0.018	<0.018
Linuron (GCMS)	56	<0.002	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Malathion	56	0.016	<0.005	--	<0.005	<0.005	<0.005	<0.005	<0.005
MCPA	55	<0.170	<0.050	--	<0.050	<0.050	<0.050	<0.050	<0.050
MCPB	55	<0.140	<0.021	--	<0.035	<0.035	<0.035	<0.035	<0.035
Methiocarb	55	<0.026	<0.026	--	<0.026	<0.026	<0.026	<0.026	<0.026
Methomyl	55	<0.017	<0.017	--	<0.017	<0.017	<0.017	<0.017	<0.017
methyl-Parathion	56	0.099	<0.006	--	<0.006	<0.006	<0.006	<0.006	<0.006
methyl-Azinphos	56	<0.010	<0.001	--	<0.001	<0.001	<0.001	<0.001	<0.001
Metolachlor	56	9.38	0.003	0.887	6.72	0.698	0.083	0.018	0.006
Metribuzin	56	0.190	<0.004	0.015*	0.089	0.009	<0.004	<0.004	<0.004
Molinate	56	1.84	<0.004	0.106*	0.739	0.027	0.008	<0.004	<0.004
Napropamide	56	0.019	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
Neburon	55	<0.015	<0.015	--	<0.015	<0.015	<0.015	<0.015	<0.015
Norflurazon	55	<0.024	<0.024	--	<0.024	<0.024	<0.024	<0.024	<0.024
Oryzalin	55	<0.310	<0.019	--	<0.019	<0.019	<0.019	<0.019	<0.019
Oxamyl	55	<0.018	<0.018	--	<0.018	<0.018	<0.018	<0.018	<0.018
Parathion	56	<0.004	<0.004	--	<0.004	<0.004	<0.004	<0.004	<0.004

**Appendix II.** Summary statistics for selected pesticides analyzed in water samples collected from five rivers in the Mississippi Embayment study unit, 1996-98 (Continued)  
 [<, less than; \*\*, estimated concentration; (HPLC), high performance liquid chromatography; (GCMS), gas chromatography mass spectrometry; \*, value is estimated by using a log-probability regression to predict values of data below the detection limit]

Compound	Number	Maximum	Minimum	Mean	Percentage				
		(micrograms per liter)			95	75	50	25	5
Pebulate	56	<0.004	<0.004	--	<0.004	<0.004	<0.004	<0.004	<0.004
Pendimethalin	56	0.330	<0.004	0.020*	0.091	<0.004	<0.004	<0.004	<0.004
<i>cis</i> -Permethrin	56	<0.005	<0.005	--	<0.005	<0.005	<0.005	<0.005	<0.005
Phorate	56	<0.002	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Picloram	55	<0.050	<0.050	--	<0.050	<0.050	<0.050	<0.050	<0.050
Prometon	56	0.108	<0.018	0.011*	0.030	0.004	<0.018	<0.018	<0.018
Pronamide	56	<0.003	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
Propachlor	56	<0.007	<0.007	--	<0.007	<0.007	<0.007	<0.007	<0.007
Propanil	56	2.05	<0.004	--	0.260	<0.004	<0.004	<0.004	<0.004
Propargite	56	0.061	<0.013	--	<0.013	<0.013	<0.013	<0.013	<0.013
Propham	55	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Propoxur	55	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Silvex	55	<0.021	<0.021	--	<0.021	<0.021	<0.021	<0.021	<0.021
Simazine	56	0.190	<0.005	0.016*	0.069	0.015	<0.005	<0.005	<0.005
Tebuthiuron	56	0.017	<0.010	0.010*	0.013	<0.010	<0.010	<0.010	<0.010
Terbacil**	56	<0.007	<0.007	--	<0.007	<0.007	<0.007	<0.007	<0.007
Terbufos	56	<0.013	<0.013	--	<0.013	<0.013	<0.013	<0.013	<0.013
Thiobencarb	56	0.061	<0.002	--	0.041	<0.002	<0.002	<0.002	<0.002
Triallate	56	<0.001	<0.001	--	<0.001	<0.001	<0.001	<0.001	<0.001
Triclopyr	55	<0.250	<0.032	--	<0.050	<0.050	<0.050	<0.050	<0.050
Trifluralin	56	0.032	<0.002	0.003*	0.010	0.002	<0.002	<0.002	<0.002
<b>Bogue Phalia near Leland, Mississippi—February 1996 to January 1998</b>									
2,4,5-T	63	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
2,4-D	63	2.99	<0.035	0.26*	0.93	0.34	<0.035	<0.035	<0.035
2,4-DB	63	<0.240	<0.013	--	<0.240	<0.035	<0.035	<0.035	<0.035
2,6-Diethylaniline	63	<0.003	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
3-Hydroxy-carbofuran	63	<0.014	<0.014	--	<0.014	<0.014	<0.014	<0.014	<0.014
Acetochlor	62	2.28	<0.002	--	0.067	<0.002	<0.002	<0.002	<0.002
Acifluorfen	63	1.60	<0.035	0.16*	0.84	0.17	<0.035	<0.035	<0.035
Alachlor	62	0.492	<0.002	--	0.035	<0.002	<0.002	<0.002	<0.002
Aldicarb	63	<0.550	<0.016	--	<0.550	<0.016	<0.016	<0.016	<0.016
Aldicarb sulfone	63	<0.100	<0.016	--	<0.100	<0.016	<0.016	<0.016	<0.016
Aldicarb sulfoxide	63	<0.021	<0.021	--	<0.021	<0.021	<0.021	<0.021	<0.021
<i>alpha</i> -HCH	62	<0.020	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Atrazine	62	23.2	<0.001	1.36*	6.89	0.860	0.032	0.013	<0.001
Benfluralin	63	0.008	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Bentazon	63	2.30	<0.014	0.30*	1.53	0.40	<0.014	<0.014	<0.014
Bromacil	63	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Bromoxynil	63	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035

**Appendix II.** Summary statistics for selected pesticides analyzed in water samples collected from five rivers in the Mississippi Embayment study unit, 1996-98 (Continued)  
 [<, less than; \*\*, estimated concentration; (HPLC), high performance liquid chromatography; (GCMS), gas chromatography mass spectrometry; \*, value is estimated by using a log-probability regression to predict values of data below the detection limit]

Compound	Number	Maximum	Minimum	Mean	Percentage				
		(micrograms per liter)			95	75	50	25	5
Butylate	62	<0.002	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Carbaryl (HPLC)	63	<0.008	<0.008	--	<0.008	<0.008	<0.008	<0.008	<0.008
Carbaryl** (GCMS)	62	0.065	<0.003	--	<0.02	<0.003	<0.003	<0.003	<0.003
Carbofuran (HPLC)	62	0.80	<0.028	--	<0.120	<0.028	<0.028	<0.028	<0.028
Carbofuran** (GCMS)	63	0.745	<0.003	--	0.280	<0.003	<0.003	<0.003	<0.003
Chloramben	63	<0.420	<0.011	--	<0.420	<0.011	<0.011	<0.011	<0.011
Chlorothalonil**	62	<0.480	<0.035	--	<0.480	<0.035	<0.035	<0.035	<0.035
Chlorpyrifos	61	0.072	<0.004	--	<0.004	<0.004	<0.004	<0.004	<0.004
Clopyralid	63	<0.230	<0.050	--	<0.230	<0.050	<0.050	<0.050	<0.050
Cyanazine	62	2.70	0.004	0.199	1.07	0.120	0.046	0.025	0.009
monoacid-DCPA	62	<0.017	<0.017	--	<0.017	<0.017	<0.017	<0.017	<0.017
DCPA	62	0.025	<0.002	--	0.001	<0.002	<0.002	<0.002	<0.002
<i>p,p'</i> DDE	62	0.007	<0.002	0.003*	0.005	<0.010	<0.006	<0.006	<0.006
desethyl-Atrazine**	62	0.190	<0.002	0.026*	0.123	0.035	0.003	<0.002	<0.002
Diazinon	62	0.005	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Dicamba	63	0.43	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Dichlobenil**	63	<1.200	<0.020	--	<1.200	<0.020	<0.020	<0.020	<0.020
Dichlorprop	63	<0.032	<0.032	--	<0.032	<0.032	<0.032	<0.032	<0.032
Dieldrin	62	0.003	<0.001	--	<0.001	<0.001	<0.001	<0.001	<0.001
Dinoseb	63	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Disulfoton	62	0.071	<0.017	--	<0.017	<0.017	<0.017	<0.017	<0.017
Diuron	63	2.08	<0.010	0.150*	0.39	0.13	0.050	<0.050	<0.020
DNOC**	63	<0.420	<0.035	--	<0.420	<0.035	<0.035	<0.035	<0.035
EPTC	62	<0.010	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Ethalfuralin	62	0.004	<0.004	--	<0.004	<0.004	<0.004	<0.004	<0.004
Ethoprop	62	0.003	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
Fenuron	62	0.013	<0.013	--	<0.013	<0.013	<0.013	<0.013	<0.013
Fluometuron	63	6.60	<0.035	0.43*	2.38	0.17	0.070	0.030	<0.035
Fonofox	62	<0.003	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
Lindane	62	<0.004	<0.004	--	<0.004	<0.004	<0.004	<0.004	<0.004
Linuron (HPLC)	63	0.070	<0.018	--	<0.018	<0.018	<0.018	<0.018	<0.018
Linuron (GCMS)	62	0.051	<0.002	--	0.008	<0.002	<0.002	<0.002	<0.002
Malathion	62	0.325	<0.005	0.012*	0.030	<0.005	<0.005	<0.005	<0.005
MCPA	63	<0.170	<0.050	--	<0.170	<0.050	<0.050	<0.050	<0.050
MCPB	63	<0.140	<0.035	--	<0.140	<0.035	<0.035	<0.035	<0.035
Methiocarb	63	<0.026	<0.026	--	<0.026	<0.026	<0.026	<0.026	<0.026
Methomyl	63	0.650	<0.017	0.057*	0.260	<0.017	<0.017	<0.017	<0.017
methyl-Parathion	62	0.422	<0.006	0.043*	0.230	0.006	<0.006	<0.006	<0.006



**Appendix II.** Summary statistics for selected pesticides analyzed in water samples collected from five rivers in the Mississippi Embayment study unit, 1996-98 (Continued)  
 [<, less than; \*\*, estimated concentration; (HPLC), high performance liquid chromatography; (GCMS), gas chromatography mass spectrometry; \*, value is estimated by using a log-probability regression to predict values of data below the detection limit]

Compound	Num-ber	Maximum	Minimum	Mean	Percentage				
		(micrograms per liter)			95	75	50	25	5
methyl-Azinphos	61	0.065	<0.001	--	<0.300	<0.001	<0.001	<0.001	<0.001
Metolachlor	62	12.2	0.018	1.22	7.23	1.25	0.111	0.049	0.024
Metribuzin	62	3.92	<0.004	0.212*	0.880	0.059	0.010	<0.004	<0.004
Molinate	62	140.0	<0.004	6.66*	40.0	0.825	0.150	0.032	<0.004
Napropamide	62	0.021	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
Neburon	63	<0.015	<0.015	--	<0.015	<0.015	<0.015	<0.015	<0.015
Norflurazon	62	1.24	<0.024	0.096*	0.37	0.11	<0.024	<0.024	<0.024
Oryzalin	63	<0.310	<0.019	--	<0.310	<0.019	<0.019	<0.019	<0.019
Oxamyl	62	<0.018	<0.018	--	<0.018	<0.018	<0.018	<0.018	<0.018
Parathion	62	0.004	<0.004	--	<0.004	<0.004	<0.004	<0.004	<0.004
Pebulate	62	0.005	<0.004	--	<0.004	<0.004	<0.004	<0.004	<0.004
Pendimethalin	62	2.05	<0.004	0.105*	0.480	0.041	<0.004	<0.004	<0.004
cis-Permethrin	62	0.005	<0.005	--	<0.005	<0.005	<0.005	<0.005	<0.005
Phorate	62	<0.002	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Picloram	63	<0.050	<0.050	--	<0.050	<0.050	<0.050	<0.050	<0.050
Prometon	62	0.014	<0.018	--	<0.018	<0.018	<0.018	<0.018	<0.018
Pronamide	62	0.038	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
Propachlor	62	0.007	<0.007	--	<0.007	<0.007	<0.007	<0.007	<0.007
Propanil	62	0.600	<0.004	0.030*	0.167	0.007	<0.004	<0.004	<0.004
Propargite	62	0.013	<0.013	--	<0.013	<0.013	<0.013	<0.013	<0.013
Propham	63	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Propoxur	63	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Silvex	63	<0.021	<0.021	--	<0.021	<0.021	<0.021	<0.021	<0.021
Simazine	62	0.400	<0.005	0.049*	0.217	0.050	0.012	<0.005	<0.005
Tebuthiuron	62	0.120	<0.010	0.013*	0.041	0.012	<0.010	<0.010	<0.010
Terbacil**	62	<0.007	<0.007	--	<0.007	<0.007	<0.007	<0.007	<0.007
Terbufos	62	<0.013	<0.013	--	<0.013	<0.013	<0.013	<0.013	<0.013
Thiobencarb	62	4.00	<0.002	0.172*	0.360	0.047	0.010	<0.020	<0.002
Triallate	62	<0.001	<0.001	--	<0.001	<0.001	<0.001	<0.001	<0.001
Triclopyr	63	4.60	<0.050	0.38*	2.27	<0.250	<0.050	<0.050	<0.050
Trifluralin	62	0.113	<0.002	0.011*	0.079	0.007	<0.002	<0.002	<0.002
<b>Yazoo River below Steele Bayou, Mississippi—February 1996 to January 1998</b>									
2,4,5-T	48	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
2,4-D	48	0.50	<0.035	0.050*	0.24	<0.150	<0.035	<0.035	<0.035
2,4-DB	48	<0.240	<0.035	--	<0.240	<0.035	<0.035	<0.035	<0.035
2,6-Diethylaniline	50	<0.003	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
3-Hydroxy-carbofuran	48	<0.014	<0.010	--	<0.014	<0.014	<0.014	<0.014	<0.014
Acetochlor	50	1.45	<0.002	--	0.320	0.007	<0.002	<0.002	<0.002
Acifluorfen	48	0.46	<0.035	0.050*	0.21	<0.035	<0.035	<0.035	<0.035

**Appendix II.** Summary statistics for selected pesticides analyzed in water samples collected from five rivers in the Mississippi Embayment study unit, 1996-98 (Continued)  
 [<, less than; \*\*, estimated concentration; (HPLC), high performance liquid chromatography; (GCMS), gas chromatography mass spectrometry; \*, value is estimated by using a log-probability regression to predict values of data below the detection limit]

Compound	Number	Maximum	Minimum	Mean	Percentage				
					(micrograms per liter)				
					95	75	50	25	5
Alachlor	50	0.300	<0.002	0.028*	0.110	0.019	0.009	<0.002	<0.002
Aldicarb	48	<0.550	<0.016	--	<0.550	<0.016	<0.016	<0.016	<0.016
Aldicarb sulfone	47	<0.100	<0.016	--	<0.100	<0.016	<0.016	<0.016	<0.016
Aldicarb sulfoxide	47	<0.021	<0.021	--	<0.021	<0.021	<0.021	<0.021	<0.021
<i>alpha</i> -HCH	50	<0.002	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Atrazine	50	6.10	0.023	0.887	4.28	0.816	0.361	0.092	0.029
Benfluralin	50	<0.002	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Bentazon	48	0.82	<0.014	0.084*	0.40	0.050	<0.014	<0.014	<0.014
Bromacil	48	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Bromoxynil	48	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Butylate	50	0.061	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Carbaryl (HPLC)	48	<0.008	<0.008	--	<0.008	<0.008	<0.008	<0.008	<0.008
Carbaryl** (GCMS)	50	0.027	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
Carbofuran (HPLC)	48	0.33	<0.028	--	<0.120	<0.028	<0.028	<0.028	<0.028
Carbofuran** (GCMS)	50	0.196	<0.003	0.016*	0.070	<0.003	<0.003	<0.003	<0.003
Chloramben	48	<0.420	<0.011	--	<0.420	<0.011	<0.011	<0.011	<0.011
Chlorothalonil**	48	<0.480	<0.035	--	<0.480	<0.035	<0.035	<0.035	<0.035
Chlorpyrifos	50	0.035	<0.004	0.002*	0.012	<0.004	<0.004	<0.004	<0.004
Clopyralid	48	<0.230	<0.050	--	<0.230	<0.050	<0.050	<0.050	<0.050
Cyanazine	50	1.30	0.004	0.182	0.654	0.220	0.078	0.041	0.014
monoacid-DCPA	48	<0.017	<0.017	--	<0.017	<0.017	<0.017	<0.017	<0.017
DCPA	50	0.005	<0.002	0.001*	0.002	<0.002	<0.002	<0.002	<0.002
<i>p,p'</i> DDE	50	0.006	<0.006	0.002*	0.003	<0.006	<0.006	<0.006	<0.006
desethyl-Atrazine**	50	0.180	0.002	0.034	0.130	0.040	0.022	0.005	0.003
Diazinon	50	0.025	<0.002	--	0.006	<0.002	<0.002	<0.002	<0.002
Dicamba	48	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Dichlobenil**	48	<1.200	<0.020	--	<1.200	<0.020	<0.020	<0.020	<0.020
Dichlorprop	48	<0.032	<0.032	--	<0.032	<0.032	<0.032	<0.032	<0.032
Dieldrin	50	0.015	<0.001	--	<0.001	<0.001	<0.001	<0.001	<0.001
Dinoseb	48	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Disulfoton	50	<0.017	<0.017	--	<0.017	<0.017	<0.017	<0.017	<0.017
Diuron	48	0.60	<0.020	0.11*	0.37	0.15	0.070	0.020	<0.020
DNOC**	48	<0.420	<0.035	--	<0.420	<0.035	<0.035	<0.035	<0.035
EPTC	50	0.010	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Ethalfuralin	50	<0.004	<0.004	--	<0.004	<0.004	<0.004	<0.004	<0.004
Ethoprop	50	<0.003	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
Fenuron	48	<0.013	<0.013	--	<0.013	<0.013	<0.013	<0.013	<0.013
Fluometuron	48	3.37	<0.035	0.37*	1.39	0.37	0.14	0.050	<0.035

**Appendix II.** Summary statistics for selected pesticides analyzed in water samples collected from five rivers in the Mississippi Embayment study unit, 1996-98 (Continued)  
 [<, less than; \*\*, estimated concentration; (HPLC), high performance liquid chromatography; (GCMS), gas chromatography mass spectrometry; \*, value is estimated by using a log-probability regression to predict values of data below the detection limit]

Compound	Num-ber	Maximum	Minimum	Mean	Percentage				
		(micrograms per liter)			95	75	50	25	5
Fonofox	50	<0.003	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
Lindane	50	<0.004	<0.004	--	<0.004	<0.004	<0.004	<0.004	<0.004
Linuron (HPLC)	48	0.040	<0.018	--	<0.026	<0.018	<0.018	<0.018	<0.018
Linuron (GCMS)	50	0.075	<0.002	--	0.030	<0.002	<0.002	<0.002	<0.002
Malathion	50	0.523	<0.005	0.023*	0.097	0.009	<0.005	<0.005	<0.005
MCPA	48	<0.170	<0.050	--	<0.170	<0.050	<0.050	<0.050	<0.050
MCPB	48	<0.140	<0.035	--	<0.140	<0.035	<0.035	<0.035	<0.035
Methiocarb	48	<0.026	<0.026	--	<0.026	<0.026	<0.026	<0.026	<0.026
Methomyl	46	0.090	<0.017	--	<0.017	<0.017	<0.017	<0.017	<0.017
methyl-Parathion	50	0.110	<0.006	0.011*	0.081	<0.006	<0.006	<0.006	<0.006
methyl-Azinphos	48	0.126	<0.001	--	<0.900	<0.050	<0.001	<0.001	<0.001
Metolachlor	50	5.80	0.021	0.788	4.44	0.702	0.193	0.064	0.026
Metribuzin	50	0.596	<0.004	0.067*	0.440	0.044	<0.004	<0.004	<0.004
Molinate	50	4.19	<0.004	--	3.30	0.065	<0.004	<0.004	<0.004
Napropamide	50	<0.030	<0.003	--	<0.010	<0.003	<0.003	<0.003	<0.003
Neburon	48	<0.015	<0.015	--	<0.015	<0.015	<0.015	<0.015	<0.015
Norflurazon	48	0.68	<0.024	0.100*	0.49	0.13	<0.024	<0.024	<0.024
Oryzalin	48	<0.310	<0.019	--	<0.310	<0.019	<0.019	<0.019	<0.019
Oxamyl	47	<0.018	<0.018	--	<0.018	<0.018	<0.018	<0.018	<0.018
Parathion	50	<0.004	<0.004	--	<0.004	<0.004	<0.004	<0.004	<0.004
Pebulate	50	<0.004	<0.004	--	<0.004	<0.004	<0.004	<0.004	<0.004
Pendimethalin	50	0.130	<0.004	0.018*	0.080	<0.004	<0.004	<0.004	<0.004
cis-Permethrin	50	<0.005	<0.005	--	<0.005	<0.005	<0.005	<0.005	<0.005
Phorate	50	<0.002	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Picloram	48	<0.050	<0.050	--	<0.050	<0.050	<0.050	<0.050	<0.050
Prometon	50	0.014	<0.018	0.009*	0.012	0.005	<0.018	<0.018	<0.018
Pronamide	50	<0.003	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
Propachlor	50	0.008	<0.007	--	<0.007	<0.007	<0.007	<0.007	<0.007
Propanil	50	0.018	<0.004	--	<0.004	<0.004	<0.004	<0.004	<0.004
Propargite	50	<0.013	<0.013	--	<0.013	<0.013	<0.013	<0.013	<0.013
Propham	48	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Propoxur	48	<0.035	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Silvex	48	<0.021	<0.021	--	<0.021	<0.021	<0.021	<0.021	<0.021
Simazine	50	0.255	0.005	0.047	0.160	0.059	0.029	0.022	0.007
Tebuthiuron	50	0.048	<0.010	0.011*	0.027	0.011	<0.010	<0.010	<0.010
Terbacil**	50	0.059	<0.007	--	<0.007	<0.007	<0.007	<0.007	<0.007
Terbufos	50	<0.015	<0.013	--	<0.013	<0.013	<0.013	<0.013	<0.013
Thiobencarb	50	0.162	<0.002	0.011*	0.061	<0.002	<0.002	<0.002	<0.002

**Appendix II.** Summary statistics for selected pesticides analyzed in water samples collected from five rivers in the Mississippi Embayment study unit, 1996-98 (Continued)  
 [<, less than; \*\*, estimated concentration; (HPLC), high performance liquid chromatography; (GCMS), gas chromatography mass spectrometry; \*, value is estimated by using a log-probability regression to predict values of data below the detection limit]

Compound	Number	Maximum	Minimum	Mean	Percentage				
		(micrograms per liter)			95	75	50	25	5
Triallate	50	<0.001	<0.001	--	<0.001	<0.001	<0.001	<0.001	<0.001
Triclopyr	48	0.30	<0.050	--	<0.250	<0.050	<0.050	<0.050	<0.050
Trifluralin	50	0.075	<0.002	0.007*	0.028	0.007	<0.002	<0.002	<0.002
<b>Tensas River at Tendal, Louisiana—February 1996 to January 1998</b>									
2,4,5-T	43	<0.060	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
2,4-D	43	0.88	<0.035	0.12*	0.500	<0.150	<0.035	<0.035	<0.035
2,4-DB	43	0.040	<0.035	--	<0.240	<0.035	<0.035	<0.035	<0.035
2,6-Diethylaniline	42	<0.003	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
3-Hydroxy-carbofuran	43	<0.024	<0.014	--	<0.014	<0.014	<0.014	<0.014	<0.014
Acetochlor	42	0.115	<0.002	--	0.007	<0.002	<0.002	<0.002	<0.002
Acifluorfen	43	1.04	<0.035	--	0.28	<0.035	<0.035	<0.035	<0.035
Alachlor	42	0.028	<0.002	--	0.004	<0.002	<0.002	<0.002	<0.002
Aldicarb	43	<0.550	<0.016	--	<0.550	<0.016	<0.016	<0.016	<0.016
Aldicarb sulfone	43	<0.100	<0.016	--	<0.100	<0.016	<0.016	<0.016	<0.016
Aldicarb sulfoxide	43	1.91	<0.021	--	<0.036	<0.021	<0.021	<0.021	<0.021
alpha-HCH	42	<0.002	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Atrazine	42	92.3	0.050	7.35	55.7	2.10	0.429	0.110	0.059
Benfluralin	42	<0.002	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Bentazon	43	1.76	<0.014	--	0.17	<0.014	<0.014	<0.014	<0.014
Bromacil	43	<0.060	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Bromoxynil	43	<0.060	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Butylate	42	<0.002	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Carbaryl (HPLC)	43	<0.014	<0.008	--	<0.008	<0.008	<0.008	<0.008	<0.008
Carbaryl** (GCMS)	42	<0.003	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
Carbofuran (HPLC)	42	2.82	<0.028	0.16*	0.66	<0.120	<0.028	<0.028	<0.028
Carbofuran** (GCMS)	42	2.63	<0.003	0.250*	1.15	<0.120	<0.003	<0.003	<0.003
Chloramben	43	<0.420	<0.011	--	<0.420	<0.011	<0.011	<0.011	<0.011
Chlorothalonil**	43	<0.480	<0.035	--	<0.480	<0.035	<0.035	<0.035	<0.035
Chlorpyrifos	41	0.052	<0.004	0.004*	0.016	<0.004	<0.004	<0.004	<0.004
Clopyralid	43	<0.230	<0.050	--	<0.230	<0.050	<0.050	<0.050	<0.050
Cyanazine	42	12.0	0.004	0.856	4.17	0.730	0.216	0.059	0.016
monoacid-DCPA	43	<0.029	<0.017	--	<0.017	<0.017	<0.017	<0.017	<0.017
DCPA	42	<0.002	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
p,p' DDE	42	0.006	<0.006	0.003*	0.004	0.002	<0.006	<0.006	<0.006
desethyl-Atrazine**	42	3.03	0.004	0.222	0.830	0.188	0.070	0.016	0.008
Diazinon	42	0.005	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Dicamba	43	<0.060	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Dichlobenil**	43	<1.200	<0.020	--	<1.200	<0.020	<0.020	<0.020	<0.020
Dichlorprop	43	<0.055	<0.032	--	<0.032	<0.032	<0.032	<0.032	<0.032

**Appendix II.** Summary statistics for selected pesticides analyzed in water samples collected from five rivers in the Mississippi Embayment study unit, 1996-98 (Continued)  
 [<, less than; \*\*, estimated concentration; (HPLC), high performance liquid chromatography; (GCMS), gas chromatography mass spectrometry; \*, value is estimated by using a log-probability regression to predict values of data below the detection limit]

Compound	Num-ber	Maximum	Minimum	Mean	Percentage				
		(micrograms per liter)			95	75	50	25	5
Dieldrin	42	<0.001	<0.001	--	<0.001	<0.001	<0.001	<0.001	<0.001
Dinoseb	43	0.030	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Disulfoton	42	<0.017	<0.017	--	<0.017	<0.017	<0.017	<0.017	<0.017
Diuron	43	0.13	<0.020	0.019*	0.090	0.020	<0.020	<0.020	<0.020
DNOC**	43	<0.420	<0.035	--	<0.420	<0.035	<0.035	<0.035	<0.035
EPTC	42	<0.002	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Ethalfuralin	42	<0.004	<0.004	--	<0.004	<0.004	<0.004	<0.004	<0.004
Ethoprop	42	<0.003	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
Fenuron	43	<0.022	<0.013	--	<0.013	<0.013	<0.013	<0.013	<0.013
Fluometuron	43	8.34	0.019	0.93	6.57	1.09	0.33	0.12	0.035
Fonofox	42	<0.003	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
Lindane	42	<0.004	<0.004	--	<0.004	<0.004	<0.004	<0.004	<0.004
Linuron (HPLC)	43	0.010	<0.018	--	<0.018	<0.018	<0.018	<0.018	<0.018
Linuron (GCMS)	42	<0.002	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Malathion	42	0.073	<0.005	--	<0.005	<0.005	<0.005	<0.005	<0.005
MCPA	43	<0.170	<0.050	--	<0.170	<0.050	<0.050	<0.050	<0.050
MCPB	43	<0.140	<0.035	--	<0.140	<0.035	<0.035	<0.035	<0.035
Methiocarb	43	<0.044	<0.026	--	<0.026	<0.026	<0.026	<0.026	<0.026
Methomyl	43	0.080	<0.017	--	<0.017	<0.017	<0.017	<0.017	<0.017
methyl-Parathion	42	0.061	<0.006	--	<0.006	<0.006	<0.006	<0.006	<0.006
methyl-Azinphos	40	<0.500	<0.001	--	<0.300	<0.001	<0.001	<0.001	<0.001
Metolachlor	42	11.7	0.011	1.09	7.92	0.563	0.079	0.039	0.015
Metribuzin	42	6.61	<0.004	0.336*	1.12	0.068	0.008	<0.004	<0.004
Molinate	42	32.0	<0.004	1.57*	6.80	0.193	0.010	<0.004	<0.004
Napropamide	42	<0.110	<0.003	--	<0.010	<0.003	<0.003	<0.003	<0.003
Neburon	43	0.030	<0.015	--	<0.015	<0.015	<0.015	<0.015	<0.015
Norflurazon	43	0.51	<0.024	0.16*	0.43	0.20	<0.024	<0.024	<0.024
Oryzalin	43	<0.310	<0.019	--	<0.310	<0.019	<0.019	<0.019	<0.019
Oxamyl	43	<0.031	<0.018	--	<0.018	<0.018	<0.018	<0.018	<0.018
Parathion	42	<0.004	<0.004	--	<0.004	<0.004	<0.004	<0.004	<0.004
Pebulate	42	<0.004	<0.004	--	<0.004	<0.004	<0.004	<0.004	<0.004
Pendimethalin	42	0.303	<0.004	0.040*	0.220	<0.004	<0.004	<0.004	<0.004
cis-Permethrin	42	<0.005	<0.005	--	<0.005	<0.005	<0.005	<0.005	<0.005
Phorate	42	<0.002	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Picloram	43	<0.086	<0.050	--	<0.050	<0.050	<0.050	<0.050	<0.050
Prometon	42	0.011	<0.018	--	<0.018	<0.018	<0.018	<0.018	<0.018
Pronamide	42	<0.003	<0.003	--	<0.003	<0.003	<0.003	<0.003	<0.003
Propachlor	42	0.012	<0.007	--	<0.007	<0.007	<0.007	<0.007	<0.007

**Appendix II.** Summary statistics for selected pesticides analyzed in water samples collected from five rivers in the Mississippi Embayment study unit, 1996-98 (Continued)

[<, less than; \*\*, estimated concentration; (HPLC), high performance liquid chromatography; (GCMS), gas chromatography mass spectrometry; \*, value is estimated by using a log-probability regression to predict values of data below the detection limit]

Compound	Number	Maximum	Minimum	Mean	Percentage				
					(micrograms per liter)				
					95	75	50	25	5
Propanil	42	0.079	<0.004	--	0.008	<0.004	<0.004	<0.004	<0.004
Propargite	42	<0.013	<0.013	--	<0.013	<0.013	<0.013	<0.013	<0.013
Propham	43	<0.060	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Propoxur	43	<0.060	<0.035	--	<0.035	<0.035	<0.035	<0.035	<0.035
Silvex	43	<0.036	<0.021	--	<0.021	<0.021	<0.021	<0.021	<0.021
Simazine	42	0.131	<0.005	0.016*	0.065	0.017	<0.005	<0.005	<0.005
Tebuthiuron	42	<0.010	<0.010	--	<0.010	<0.010	<0.010	<0.010	<0.010
Terbacil**	42	<0.007	<0.007	--	<0.007	<0.007	<0.007	<0.007	<0.007
Terbufos	42	<0.013	<0.013	--	<0.013	<0.013	<0.013	<0.013	<0.013
Thiobencarb	42	0.008	<0.002	--	<0.002	<0.002	<0.002	<0.002	<0.002
Triallate	42	<0.001	<0.001	--	<0.001	<0.001	<0.001	<0.001	<0.001
Triclopyr	43	1.43	<0.050	0.11*	0.48	<0.250	<0.050	<0.050	<0.050
Trifluralin	42	0.110	<0.002	0.011*	0.056	0.004	<0.002	<0.002	<0.002