

# OCCURRENCE OF SELECTED COTTON AND RICE HERBICIDES AND THEIR METABOLITES IN STREAMS AND OXBOW LAKES OF WESTERN MISSISSIPPI, NORTHEASTERN LOUISIANA, AND EASTERN ARKANSAS, 1996

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## INTRODUCTION

The U.S. Geological Survey (USGS), through the National Water-Quality Assessment Program, is studying the occurrence of selected pesticides in the Mississippi Alluvial Plain. A reconnaissance study focusing on cotton and rice herbicides and herbicide metabolites was conducted in 1996 to evaluate their persistence in the surface waters of the Mississippi Alluvial Plain (Figure 1).

Contamination of water in the mid-continental United States from pesticide application to corn has been a major water-quality issue over the past decade. Perhaps equally important to water quality in the southeastern United States is the application of herbicides to cotton and rice. Herbicides are applied three to five times annually to cotton in Arkansas, Louisiana, and Mississippi (United States Department of Agriculture 1992). Rice in Arkansas and Louisiana annually receives about one herbicide and one insecticide application. The application rate of pesticides to cotton is three to five times greater per acre than the application rate of pesticides to corn. However, there have been few studies of pesticide fate in the cotton and rice producing areas in the southeastern United States.

In 1994, Mississippi ranked third nationally in cotton production and fifth nationally in rice production; the total economic value was \$738 million for cotton and \$140 million for rice. In 1994, Arkansas ranked first nationally in rice production and fifth nationally in cotton production; the total economic value was \$679 million for rice and \$536 million for cotton.

The Mississippi Alluvial Plain (commonly referred to as the Delta) is an area of intensive agriculture of mostly soybean, cotton, and rice production. The Delta is a sparsely populated area with a few scattered population centers. The study area is located in the alluvial plain of the Mississippi River. The topography is characterized by relatively flat, poorly drained land with slopes of 0.3 to 0.9 feet per mile. The climate is subtropical with long hot summers and short moderate winters. The average annual temperature at Greenville, Mississippi, near the center of the study area, is 18 C. Average monthly temperatures range from 8 C in

January to 33 C in July. Average annual precipitation in Greenville is 51 inches, with the heaviest rainfall occurring from December to April. Minimal rainfall occurs in September and October; however, heavy rainfall producing locally intense runoff can occur at any time of the year. The slow moving streams in the Delta contain silt bottoms and receive large amounts of sediment and other agricultural constituents. Consequently, many streams have relatively high turbidity, elevated nutrient concentrations, and periodically high concentrations of toxic substances (Mississippi Department of Environmental Quality 1992).

This paper focuses on the seasonal occurrence, and the relation of use to occurrence, of eight selected herbicides and two herbicide metabolites in surface water.

## METHODS

A total of 83 samples was collected from 30 streams and oxbow lakes at 46 sites (Figure 1) in February, May, and August of 1996. Water samples were analyzed for 14 pesticides including propanil and molinate, (rice herbicides); cyanazine, fluometuron, and norflurazon (cotton herbicides); and seven herbicide metabolites. Samples were collected at 16 stream and oxbow lake sites in February to determine conditions before the spring application of pesticides. Samples were collected at 35 stream and oxbow lake sites in May after spring planting and the application of pre-emergent herbicides. Samples were collected at 32 stream and oxbow lake sites in August to track the persistence of pre-emergent herbicides and herbicide metabolites as well as to evaluate the occurrence of post-emergent herbicides. Water samples were analyzed by gas chromatography/mass spectrometry by USGS personnel in the Kansas Organics Laboratory.

## SEASONAL OCCURRENCE OF HERBICIDES

Samples collected at 16 stream and oxbow lake sites in February show that selected herbicides were detected frequently, but were found in relatively low concentrations. Twelve of the 21 herbicides and metabolites analyzed were detected above the reporting limit of 0.05 microgram per liter (mg/L); eight of the ten herbicides and metabolites of

focus in this paper were detected. Three herbicides (fluometuron, metolachlor, and norflurazon) and one metabolite 3,4-dichloroaniline (3,4-DCA) (a propanil metabolite) were detected in greater than 40 percent of the samples collected. Two herbicides were detected with concentrations greater than 0.5 mg/L; fluometuron was detected in 9 of the 16 samples (56 percent) with a maximum concentration of 0.80 mg/L, and norflurazon was detected in 7 of the 16 samples (44 percent) with a maximum concentration of 0.73 mg/L. Concentrations of fluometuron, metolachlor, norflurazon, and 3,4-DCA were very similar in all samples collected in February (Figure 2).

Samples collected at 35 stream and oxbow lake sites in May show that some herbicides were detected frequently, and some were found in concentrations greater than 30 mg/L. Twenty of the 21 herbicides and metabolites analyzed were detected above the reporting limit of 0.05 mg/L; all ten herbicides and metabolites of focus were detected. Seven herbicides and five metabolites analyzed were detected in greater than 50 percent of the samples. Atrazine was detected in 91 percent of the samples collected and fluometuron, metolachlor, and atrazine all had maximum concentrations greater than 34 mg/L. Alachlor was detected in eight samples; all were in samples collected in May. Concentrations of 3,4-DCA were higher in May than in February, but were much lower than concentrations of fluometuron, metolachlor, and atrazine (Figures 2 and 3).

Samples collected at 32 stream and oxbow lake sites in August show that some herbicides were detected frequently, but generally were found in lower concentrations than in May. Eighteen of the 21 herbicides and metabolites analyzed were detected above the reporting limit of 0.05 mg/L; nine of the ten herbicides and metabolites of focus were detected. Six herbicides and three metabolites analyzed for were detected in greater than 50 percent of the samples. Metolachlor and cyanazine were the herbicides most often detected during the August sampling; they were detected in 81 and 78 percent of the samples, respectively. Four herbicides, (atrazine, cyanazine, fluometuron, and molinate), and one metabolite (cyanazine-amide) were detected at concentrations above 1.0 mg/L. Fluometuron, the herbicide with the highest concentration determined in August, had a maximum concentration of 3.7 mg/L, much lower than the May sampling. These data indicate that herbicides and metabolites were detected most frequently and in highest concentrations shortly after spring applications.

## HERBICIDE USE AND OCCURRENCE

Propanil is a pre-emergent herbicide used on rice and is the herbicide most heavily applied in the study area (Table 1). Although propanil is applied to 90 percent of the rice

acreage in Mississippi (E. Ruth Morgan, Cooperative Extension Service, Mississippi State University, oral communication, 1995), it was detected in only 5 of the 83 samples (6 percent) collected. Propanil concentrations ranged from 0.05 to 0.42 mg/L. 3,4-DCA, a metabolite of propanil, was detected more frequently and in greater concentrations.

3,4-DCA, the metabolite most often detected, was found in 44 percent of the February samples, 83 percent of the May samples, and 72 percent of the August samples. 3,4-DCA was detected in 71 percent of all samples collected and was detected in concentrations as large as 3.5 mg/L. 3,4-DCA was detected more frequently in August (Figure 4) than in February (Figure 2), but concentrations were very similar during those months.

Alachlor is a pre-emergent herbicide applied to corn and soybeans and is the fourth most heavily applied herbicide in the study area. Alachlor was not detected in samples collected in February or August, but was detected in eight samples collected in May. May alachlor concentrations ranged from 0.05 to 0.51 mg/L with a mean concentration of 0.17 mg/L.

Metolachlor is applied to corn, soybeans, and cotton in the Delta and is the fifth most heavily applied herbicide in the study area. Metolachlor was detected in 63 of 83 samples (76 percent). The maximum concentration of metolachlor was 35 mg/L; the mean concentration was 2.3 mg/L. The number of metolachlor detections in May and August are very similar; however, the concentrations in May detections were much higher than in August.

Atrazine is a pre-emergent herbicide used on corn and sorghum. It is the sixth most heavily applied herbicide. Atrazine was detected in 56 of 83 samples (67 percent) and was detected in 26 samples at concentrations greater than 1.0 mg/L; all but one of those was collected in May. Concentrations in samples collected in February and August were generally much lower than those collected in May. The highest concentration of atrazine was 35 mg/L and the mean concentration was 2.5 mg/L.

Fluometuron is a pre-emergent herbicide used on 96 percent of the cotton and a post-emergent herbicide used on 30 percent of the cotton. More fluometuron is used in Mississippi than any other State (Gianessi and Puffer 1990). Fluometuron was detected in 59 of 83 samples (71 percent) and was detected in 7 samples at concentrations greater than 10 mg/L. The maximum concentration of fluometuron was 38 mg/L, which was the highest concentration of a herbicide found during the study. The mean concentration was 3.6 mg/L, the highest of all herbicides analyzed. Fluometuron

concentrations were much greater in May than in the February or August sampling.

Norflurazon is incorporated into the ground prior to planting on about 30 percent of the cotton and used as a pre-emergent herbicide on about 18 percent of the cotton in Mississippi (Byrd 1994). Norflurazon was detected in 52 of 83 samples (63 percent). Norflurazon was detected in concentrations greater than 1.0 mg/L in seven May samples. Norflurazon was not detected in concentrations greater than 1.0 mg/L in February or August. The mean concentration of norflurazon was 0.66 mg/L.

Demethylnorflurazon, a metabolite of norflurazon, was detected in 48 of 83 samples (58 percent). Demethylnorflurazon was detected in 25 percent of May samples and 66 percent of May and August samples. Demethylnorflurazon concentrations ranged from 0.05 to 2.3 mg/L. Three of the 48 samples with detections were greater than 1.0 mg/L, all collected in May.

Cyanazine is a post-emergent herbicide applied to 69 percent of the cotton in Mississippi (E. Ruth Morgan, Cooperative Extension Service, Mississippi State University, oral communication, 1995). Cyanazine is often the last herbicide applied to cotton by ground equipment before cotton plants become too large. Cyanazine also is used on a small amount of corn acreage and is usually applied by mid-May. Cyanazine was detected in 45 of 83 samples (55 percent). The highest concentration of cyanazine was 3.0 mg/L and the mean concentration was 0.54 mg/L. Cyanazine was detected in 19 percent of samples collected in February, 51 percent of the samples collected in May, and 75 percent of the samples collected in August.

Molinate is a post-emergent herbicide applied to 31 percent of the rice acreage in Mississippi (E. Ruth Morgan, Cooperative Extension Service, Mississippi State University, oral communication, 1995). Molinate was detected in 44 of 83 samples (53 percent). Molinate was detected in two samples in February in low concentrations. Molinate was detected in 71 percent of the May samples and nearly 50 percent of those samples had detections greater than 1 mg/L. The highest concentration of molinate was 9.5 mg/L, and the mean concentration was 1.4 mg/L.

## CONCLUSION

A total of 83 water samples were collected from 30 streams and oxbow lakes at 46 sites in February, May, and August of 1996. This study indicates that herbicide and herbicide metabolite concentrations in surface water are directly influenced by the runoff of herbicides from cotton and rice fields in the Mississippi Alluvial Plain. These results are based upon the observation that herbicides and herbicide metabolites were detected more frequently and in higher concentrations shortly after spring applications. Metolachlor was the herbicide detected most often (76 percent) in samples collected; atrazine, norflurazon, metolachlor, fluometuron, cyanazine, and molinate were detected in more than 50 percent of all samples collected. Propanil, the most heavily applied herbicide in the Delta, was detected only five times during the study, four in the May sampling and once in the August sampling. Concentrations of propanil ranged from 0.05 to 0.42 mg/L. However, 3,4-DCA, a metabolite of propanil, was detected in 71 percent of the samples with concentrations as large as 3.5 mg/L. Fluometuron, the seventh most often applied herbicide, was detected in the highest concentration of all herbicides or metabolites during the study with a maximum concentration of 38 mg/L.

## REFERENCES

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- Gianessi L. P. and Puffer C. 1990 [rev. 1991]. Herbicide use in the United States. Resources for the future. 128.
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Table 1. Herbicide use and number of detections for selected herbicides in the Mississippi Alluvial Plain  
[—, no data; mg/L, micrograms per liter]

Herbicide	Crop Application	Pounds of Active Ingredient Applied (1987-89) <sup>1</sup>	Range of Concentrations (mg/L)	Total Number of Detections	Percentage of Samples With a Detection
Propanil	rice	4,668,460	0.05 - 0.42	5	6
MSMA	cotton	3,185,528	—	—	—
Trifluralin <sup>2</sup>	soybeans, cotton	3,059,728	—	—	—
Alachlor	corn, soybeans	1,789,228	0.05 - 0.51	8	10
Metolachlor	soybeans, cotton	1,734,739	0.05 - 35	63	76
Atrazine	corn, sorghum	1,626,666	0.05 - 35	56	67
Fluometuron	cotton	1,570,100	0.05 - 38	59	71
Norflurazon	cotton	—	0.05 - 7.3	52	63
Cyanazine	cotton, corn	—	0.05 - 3.0	45	54
Molinate	rice	—	0.05 - 9.5	44	53

<sup>1</sup>Compiled from Gianessi and Puffer 1991

<sup>2</sup>Not analyzed in this study

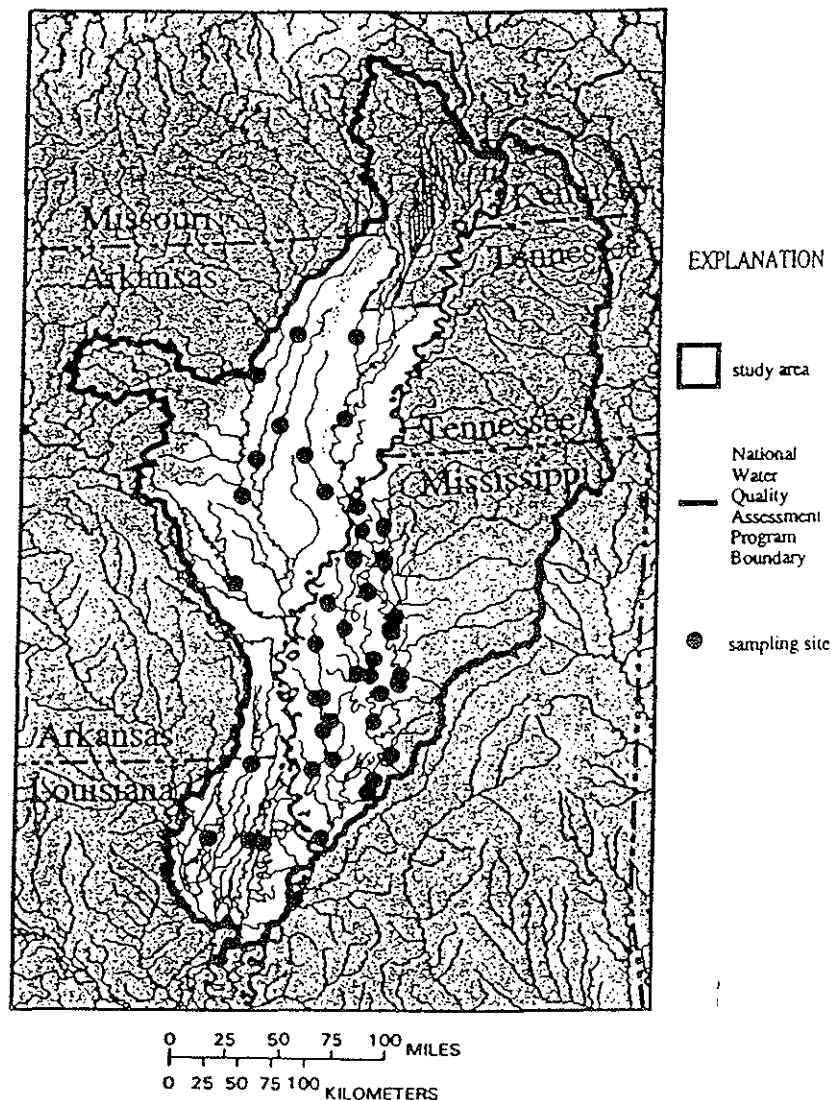


Figure 1.—Location of study area and sampling sites.

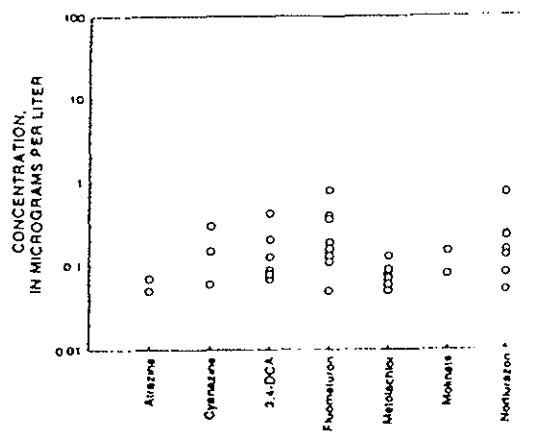


Figure 2. Concentrations of selected herbicides and herbicide metabolites sampled in February 1996.

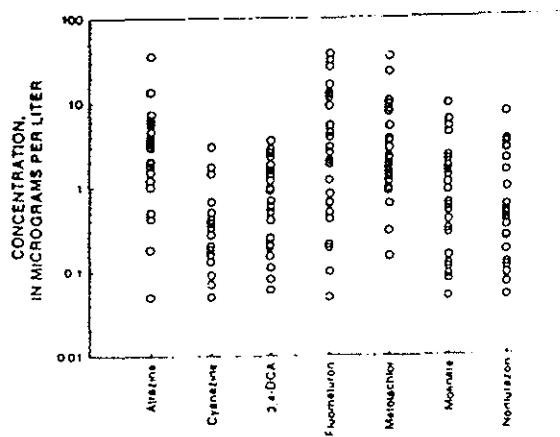


Figure 3. Concentrations of selected herbicides and herbicide metabolites sampled in May 1996.

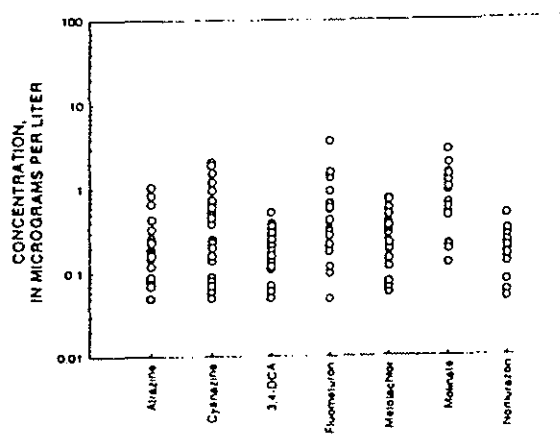


Figure 4. Concentrations of selected herbicides and herbicide metabolites sampled in August 1996.