HERBICIDES IN THE SURFACE WATER OF THE YAZOO RIVER BASIN, MISSISSIPPI

R.H. Coupe
U. S. Geological Survey
Pearl, Mississippi

INTRODUCTION

The U.S. Geological Survey (USGS), through its National Water Quality Assessment program, is studying the effect herbicides have on water quality in the Yazoo River Basin (YRB; Figure 1). As part of the planning process for the study, an analysis of available herbicide data was performed. This paper presents the results of this evaluation for the herbicides atrazine, alachlor, metolachlor, prometryn, cyanazine, fluometuron and molinate. Where the data were sufficient, herbicide data for the YRB were compared to data for the Midwest.

Very little work has been done on a regional scale to understand the characteristics of herbicide transport in the YRB in Mississippi. The YRB, Mississippi's largest river basin, consists of about 13,000 square miles (Figure 1). It is divided almost equally between lowlands in the Mississippi Alluvial Plain (commonly referred to as the Delta), an intensive agricultural area of mostly cotton, rice, and soybean production, and the uplands which generally consist of forests, pastures, and small farms. The YRB is sparsely populated, with no major metropolitan areas. In 1987, there were 760,000 acres of cotton, 176,000 acres of rice, 1,270,000 acres of soybeans, 34,000 acres of corn, and 77,000 acres of grain sorghum harvested in the YRB.

Many streams in the Delta are sluggish with silt bottoms and receive large amounts of sediment and other agricultural constituents. Consequently, many streams have high turbidity, increased nutrient concentrations, and, periodically, high concentrations of toxic substances (Mississippi Department of Environmental Quality 1994). In the Delta, most cotton acres receive multiple applications of herbicides. The average number of applications of herbicides to cotton fields in the Delta is 4.67 (U.S. Department of Agriculture 1992), the highest application rate of any cotton-producing state; the high market value of cotton allows for this. The drainage from the uplands and the Delta is into the Yazoo River, which discharges into the Mississippi River near Vicksburg, Mississippi.

PREVIOUS INVESTIGATIONS

A literature search was conducted, as well as a search of the U.S. Environmental Protection Agency's STORET data base, for herbicide data collected within the YRB. No significant sources other than the USGS were found for the herbicides of interest. The data used in this analysis are from a number of different studies conducted by the USGS and were collected for diverse purposes. The data were not collected for the purpose of making a regional assessment; therefore, the conclusions that were drawn in this report should be viewed as preliminary.

Data were collected as part of the Demonstration Erosion Control (DEC) project as part of an effort to evaluate the effectiveness of the project to alleviate flooding, erosion, sedimentation, and water-quality problems in the YRB (Slack 1992). Samples were collected at eight sites in late winter (February or March) from 1988 through 1994 and analyzed for herbicides (Table 1) by the USGS National Water Quality Lab (NWQL). The data-collection sites are located east of the Yazoo River and represent water quality from small upland drainage basins. Herbicide data for the DEC sites represent the values that could be expected at the end of the annual herbicide cycle of application, runoff, and degradation. Data collected as part of the DEC study will be referred to as DEC data.

As part of a study of the quality of water in the upper Yazoo Basin, six samples were collected in late May or early June 1990 from oxbow lakes; most of the lakes are close to the Yazoo River. The samples were analyzed for herbicides (Table 1) by the NWQL (Slack and Grantham 1991). These samples were collected within a few weeks of planting and may represent the highest concentrations that could be expected. These data will be referred to as oxbow-lake data.

In another study, data were collected as part of a large-scale effort by the USGS to sample the Mississippi River and some of its major tributaries. A Lagrangian sampling strategy was used where a series of cross sections of the Mississippi mainstem and its major tributaries were sampled in downstream sequence (Meade and Stevens 1990; Pereira et al. 1993). The water samples were collected at the mouth of the Yazoo River and are assumed to represent the entire YRB. Samples were collected eight times from December 1987 through May 1992 and were analyzed for a number of constituents including those in Table 1; these data are referred to as large-river data.

Seven samples were collected on April 6, 1988, from Wolf Lake and some of its tributaries near Yazoo City and were analyzed by the NWQL for the herbicides listed in Table 1. These samples were collected at the beginning of the planting season (Tharpe et al. 1990). These sites are all located in the Delta near the Yazoo River and are relatively close together. Consequently, these data are representative of only a small part of the entire YRB. These data are referred to as Wolf 1 data.

Seven samples were collected on September 26, 1988, and analyzed for herbicides (Table 1) by the NWQL. These samples were collected from different locations in Wolf Lake and Broad Lake (just downstream of Wolf Lake) near Yazoo City. Because these samples were collected at locations close together on the same water body, the chemical analyses of these samples were very similar. Of the five samples collected from Wolf Lake, the only herbicides detected were atrazine and cyanazine. Atrazine was detected in four of the five samples; cyanazine was detected in all five. In the two Broad Lake samples, the only herbicides detected were atrazine in one sample and cyanazine in both samples (Tharpe et al. 1990). These samples likely represent water quality at the end of the growing season. These data are referred to as Wolf 2 data.

Water samples were collected from 149 sites in 122 river basins in the Midwest during March and April (preplanting, 1989-90), May and June (postplanting, 1989-90), and October and November (harvest, 1989) at USGS streamflow-gaging stations. These samples were analyzed for herbicides including those in Table 2 (Thurman et al.1991). These data are referred to as Midwest data.

CHEMICAL AND PHYSICAL CHARACTERISTICS OF SELECTED HERBICIDES

Many studies have been done in the upper Midwest by the USGS to characterize the distribution of herbicides on a regional basis. These studies include short-term large-scale reconnaissance efforts as well as intensive sampling for long periods at a few sites. Herbicides were studied in atmospheric deposition and in reservoirs, and a mass balance of selected herbicides was determined on the largest river system in North America, the Mississippi River.

A number of important conclusions can be drawn from these studies. The first is that although most of the herbicides detected in the studies from the Midwest have relatively short half-lives in the soil (1-60 days typically), once these herbicides reach surface water, they become relatively stable and are present in surface water long after application and far from the point of application. For instance, atrazine discharged from the Mississippi River into the Gulf of Mexico following the 1993 flood was traced around the Florida peninsula and up the Atlantic coast to North Carolina (Goolsby 1994). A second significant conclusion is that the occurrence of many herbicides in surface water is directly related to use, runoff potential determined from soil dissipation rates, water solubility, and the extent of sorption to soil particles across the entire Mississippi River Basin. This implies that runoff of these herbicides is strongly influenced by their chemical and physical properties (Larson et al. 1995).

Properties affecting herbicide runoff include dissipation rates in soil (half-life), water solubility, and the extent of sorption to soil particles (Koc). The half-life of a herbicide, which is related to the chemical and biological loss processes, is important in determining the size and dynamics of the soil reservoir of a chemical. High water solubility enhances surface runoff of herbicides in the dissolved phase, but high water solubility also can contribute to a greater loss of the chemical from the soil due to increased leaching, which would act to diminish the amount of herbicide in runoff. A high soil-water distribution coefficient would inhibit leaching and, therefore, keep the pesticide in the surficial soil; however, a high soil-water distribution coefficient would also act to decrease the amount of herbicide available to runoff in the dissolved phase. Herbicides strongly sorbed to soil particles are removed from agricultural fields through the physical process of soil erosion; herbicides in the dissolved phase are not removed in this manner. The water solubility, soil half-life, soil Koc, and the runoff potential rating for each of the herbicides of interest are listed in Table 3. All of these herbicides have medium to large runoff potentials and have sorptive properties that suggest the herbicides are predominately transported from fields in the dissolved phase.

DISCUSSION

Atrazine

Atrazine was the most frequently detected herbicide in surface-water samples in the Midwest: 91 percent of the preplanting, 98 percent of the postplanting, and 76 percent of the harvest water sample concentrations of atrazine were above the reporting level. In the YRB, atrazine is used on 62 percent of the corn acreage and on 8 percent of the grain sorghum acreage (Table 3), but the total acreage for corn and sorghum is small when compared to the amount of cotton, rice, and soybean acreage in the YRB. Atrazine would not be expected to be detected as frequently in the YRB as in the Midwest. The DEC data appear to support this hypothesis because there are very few detections of atrazine in the data. However, the DEC data were collected before the annual application of herbicides. All but one of the large-river and oxbow-lake samples had atrazine concentrations above the reporting level. Atrazine concentrations in the oxbow-lake samples ranged from 0.1 to 7.2 micrograms per liter (ug/L) with a median value of 0.4 ug/L. Furthermore, atrazine concentrations in the large-river samples ranged from 0.04 to 0.58 ug/L. A few atrazine concentrations in the large-river data were between the reporting level used on that study (0.005 ug/L) and the reporting level used for the other studies (0.1 ug/L). Atrazine concentrations in three of seven Wolf 1 samples were above the reporting level; these samples could have been collected before application. Atrazine concentrations in five of seven samples were above the reporting level. These data indicated that atrazine is present in the surface water of the YRB, although atrazine is not detected with the same frequency as in the Midwest.

Alachlor and metolachlor

Alachlor is used extensively in the Midwest as a preemergent herbicide in corn and soybean production. Alachlor was detected in 86 percent of the postplanting surface-water samples from the Midwest, but only in 18 and 12 percent of the preplanting and harvest samples, respectively. Estimates of alachlor use on soybean acreage in Mississippi ranged from 0 to 20 percent; in addition, alachlor was used on 8 percent of the corn and 15 percent of the grain sorghum acreage (Table 4). The annual use of alachlor as a preemergent herbicide in the YRB (Table 2) is 115,000 pounds active ingredient. Alachlor has a half-life of 15 days; therefore, it might be expected that alachlor would only be found in the surface water of the YRB immediately following application in the spring. Two samples in the DEC data had concentrations of alachlor above the reporting level. None of the samples in the Wolf 1, Wolf 2, or the oxbow-lake data had concentrations of alachlor above the reporting level of 0.1 ug/L. Concentrations of alachlor in seven of eight large-river samples were above the reporting level of 0.005 ug/L, but only two of eight samples had alachlor concentrations above the 0.1 ug/L reporting level used in the other studies. These two samples were collected in June 1989 and May 1992. Although the total amount of alachlor used in the YRB is close to the total atrazine used (Table 3), the number of detections are far less, probably as a result of alachlor's relatively short half-life. The frequency of detection of alachlor in the YRB is less than in the Midwest.

Metolachlor is used in the Midwest on corn and soybean as a preemergent herbicide. Metolachlor was the second most frequently detected herbicide in surface-water samples in the Midwest data. It was detected in 34, 83, and 44 percent of the preplanting, postplanting, and harvest samples, respectively. In the YRB, metolachlor is used on 2 to 4 percent of the soybean acreage, 8 to 16 percent of the cotton acreage, 10 percent of the corn acreage, and 15 percent of the grain sorghum acreage (Table 4). None of the DEC or Wolf 2 samples had concentrations of metolachlor above the reporting level; the Wolf 1 samples had one sample with a metolachlor concentration above the reporting level. The oxbow-lake samples had concentrations of metolachlor above the reporting level in five of six samples ranging from 0.4 to 5.2 u/gL with a median value of 1.9 ug/L. All eight of the samples from the large-river data had detections of metolachlor, with five of the eight concentrations above the 0.1 ug/L reporting level used in the other studies. The three highest concentrations of metolachlor, 1.7, 0.66, and 0.34 ug/L, occurred in June 1989 and 1990, and May 1992. The lowest concentration in the large-river data was 0.027 ug/L and was for a sample collected in December 1987. The oxbow-lake and large-river data indicate that metolachlor can be found in the surface water of the YRB during the late spring and early summer months.

Prometryn and cyanazine

Prometryn was not detected above the reporting level in any of the surface-water samples from the Midwest (Table 3), not unexpectedly, because prometryn is not labeled for use on any of the major Midwest crops. Prometryn is used in the YRB as a postemergent herbicide on 19 percent of the cotton acreage (Table 4). Prometryn is also used to prepare fallow/stale seedbed on about 3 percent of the cotton acreage; this application could occur sometime from November 1 until 30 days prior to planting, approximately March 15. Thus, prometryn would not be expected to be found in spring runoff, but later during June and July. Prometryn was detected in all four samples from the large-river samples collected at the mouth of the Yazoo River. The highest concentration -- 0.09 and 0.075 ug/L -- which are below the reporting level used in the other studies, occurred during late June and early August, respectively. Prometryn was detected once in the DEC data, probably a result of a fallow/stale seedbed application. The oxbow-lake and Wolf 2 samples each had one sample with a prometryn concentration above the reporting level. However, the Wolf 1 data had five of seven samples above the reporting level, with a median concentration of 0.3 ug/L. Prometryn can be found in the surface water of the YRB, but the concentrations generally are low.

Cyanazine, used mainly as a preemergent herbicide on corn in the Midwest, was the third most frequently detected herbicide in a year-long study conducted by the USGS. Cyanazine also had the second highest load to the Gulf of Mexico from the Mississippi River, although cyanazine was eighth in total use (Goolsby and Battaglin 1993). Cyanazine use in the Midwest is less than half that of the top three herbicides: atrazine, metolachlor, and alachlor. In the Midwest surface-water samples, cyanazine was detected in 5, 63, and 0 percent of the preplanting, post application, and harvest samples, respectively. The major use of cyanazine in the YRB is as a postemergent or layby application, 68 and 80 percent of the cotton acreage, respectively (Table 4). Cyanazine is used to prepare fallow/stale seedbed (3 percent of cotton acreage) and as a preemergent herbicide (1 percent of cotton acreage). Cyanazine is labeled for use as a preemergent herbicide for corn in the YRB and is used on 2 percent of the corn acreage.

Although cyanazine has a medium runoff potential, it is clear from the Midwest study that cyanazine is mobile and can be found in the surface water of the Midwest following spring application. Cyanazine use in the YRB is large when compared to the use of other herbicides; therefore, given cyanazine's use and demonstrated mobility one might expect to find cyanazine in the surface water of the YRB in the runoff following application. Because the major application of cyanazine is not preemergent in April or May, but postemergent in late June and July, the highest concentrations should be found in the summer -- unlike in the Midwest samples where it was found in the spring. Cyanazine was detected above the reporting level once in the DEC data. This probably is reflective of the smaller amount of cotton grown in the uplands and the early season sampling period. The Wolf 1 samples had four of seven cyanazine concentrations above the reporting level, but the median concentration was 0.1 ug/L, the reporting level. In the Wolf 2 data collected in September, all samples had concentrations above the reporting level, with a median concentration of 0.4 ug/L. The oxbow-lake data, collected about mid-season, had 5 of 6 samples above the reporting level, with a median concentration of 0.4 ug/L. The six samples from the large-river data had concentrations above the reporting level used in that study (0.025); four of the six large-river samples had concentrations above the reporting level of 0.1 ug/L used in the other studies. These data generally showed a trend of smaller values in May and early June with the larger values later (late June and early August).

The above pattern was also noted in data collected from a Georgia basin (Hippe et al. 1995). Weekly samples were collected from a small (62 mi2) agricultural basin (46 percent agriculture mostly cotton and peanuts, 34 percent forested, 20 percent wetland). Cyanazine was detected in the surface water in May, but the highest concentration of cyanazine and the only herbicide detected was in August. Cyanazine was also detected in January, probably as a result of fallow/stale seedbed preparation.

Fluometuron

Fluometuron, first introduced for public use in 1965, is a substituted urea herbicide labeled for use in cotton and sugarcane for the control of both grasses and broadleaf weeds and is widely used in cotton production in the YRB (Table 4). Mississippi uses more fluometuron than any other State (Gianessi and Puffer 1990). Fluometuron is ranked 29th according to national use. Fluometuron is used on almost all cotton acreage in Mississippi and has the highest herbicide usage in the YRB. It is used as a preemergent herbicide on 96 percent of the cotton acres and then used again on 30 percent as a postemergence application. This means that the potential supply of fluometuron to the surface water of the YRB might be fairly continuous for a period of 4 to 5 months. Given fluometuron's half-life of 85 days and its long application period, it might be expected that fluometuron would be found year round in surface water. Previous research indicates that as much as 2 percent of the applied fluometuron can be expected to be lost in runoff, depending on the slope of the land and rainfall amount (Wiese et al. 1980).

Only a few samples from the large-river data were analyzed for fluometuron; they were collected in August and November 1991 and in May 1992. All samples had concentrations above the reporting level, 0.4, 0.2, and 0.5 ug/L, respectively. These data are representative of the entire YRB and suggest that fluometuron may be found year round in the surface water.

Molinate

Molinate is a carbamate herbicide used mainly for postemergent control of barnyardgrass in rice. One barnyardgrass plant per square foot has been shown to reduce yields from a good stand of rice by 25 percent. Therefore, rice producers have an incentive for controlling barnyardgrass and given that molinate is applied at a high rate of 3 to 5 pounds per acre (lb/acre), the potential exists for molinate to reach the surface water in detectable amounts in rice-growing areas.

Molinate is usually applied directly into the flooded rice; therefore, molinate might not be detected in the surface water until the flood is released. The rice fields are drained approximately 14 days before harvest, in late July or early August. Thus, one might expect that molinate concentrations have a sharp increase in late July or August, corresponding to the release of the water from the rice fields.

The only existing data on molinate are three samples collected as part of the large-river study from the mouth of the Yazoo River. The samples were collected in August and November 1991 and in May 1992; the concentrations of molinate were 2.58, 0.024, and <0.005 ug/L, respectively. These data clearly show the expected pattern.

CONCLUSIONS

A comparison between large-scale studies from the Midwest on the occurrence and the distribution of herbicides and a number of small-scale studies from the YRB indicate that there are similarities and significant differences between the two areas in the occurrence and distribution of herbicides in surface water. The most striking feature from the Midwest reconnaissance data was that large concentrations of herbicides were flushed from the cropland and transported through the surface-water system as pulses in response to late spring and early summer rainfall ("spring flush"). This implies that the major application of herbicides occurs at or before planting. In the YRB, one of the major crops is cotton, which receives an average of 4.67 applications of herbicides during its long growth period. In addition, because of the unique nature of rice agriculture, the herbicides that are applied directly to the flood might not be detected in the surface water of the Yazoo River Basin until the flood is released just before harvest in late July or early August. This implies that instead of a single "spring flush" in the YRB, there could be a continuing flush of herbicides throughout the growing period whenever there is sufficient rainfall to produce runoff. The small studies in the Yazoo River Basin substantiate this, but further work on a larger scale is needed.

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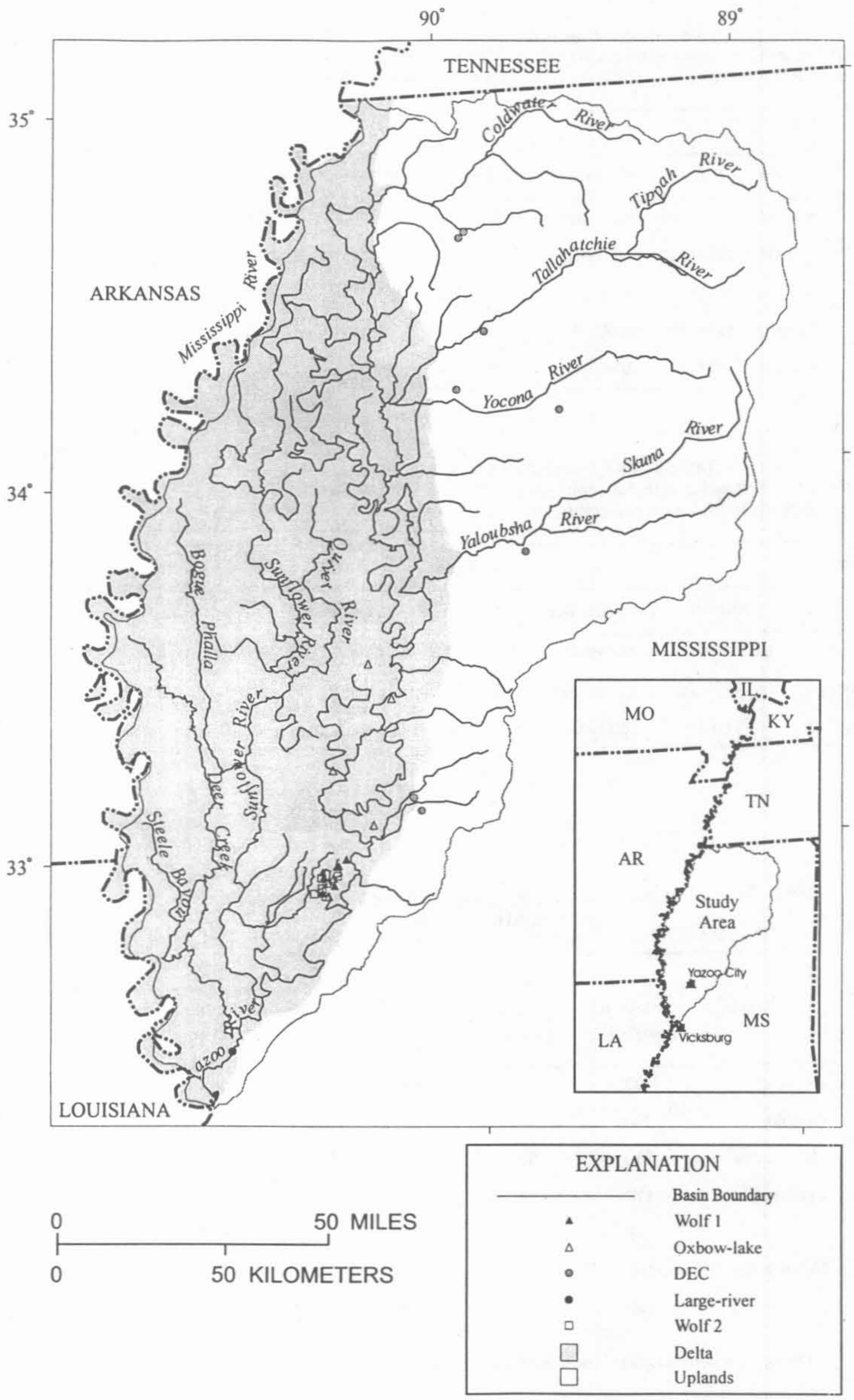

Figure 1. Location of data-collection sites in the Yazoo River Basin.

Table 1. Yazoo River Basin short-term study results
[order: Number of samples with concentrations above reporting level; number of samples; reporting level; all concentrations in micrograms per liter; N/A, not applicable]

Study	Herbicide						
	Atrazine	Alachlor	Cyanazine	Fluometuron	Metolachlor	Molinate	Prometryn
large-river	8/8/0.005	7/8/0.005	6/6 /0.025	3/3/0.005	8/8/0.005	2/3/0.005	4/4/0.005
DEC	4/54/0.10	2/54/0.10	1/54/0.10	N/A	0/54/0.10	N/A	0/54/0.10
oxbow-lake	5/6/0.10	0/6/0.10	5/6/0.10	N/A	5/6/0.10	N/A	1/6/0.10
Wolf 1	2/7/0.10	0/7/0.10	4/7/0.10	N/A	1/7/0.10	N/A	5/7/0.10
Wolf 2	5/7/0.10	0/7 0.10	7/7/0.10	N/A	0/7/0.10	N/A	1/7/0.10

Table 2. 1989 Midwest reconnaissance data
[order: Number of samples with concentrations above reporting level; number of samples; reporting level; all concentrations in micrograms per liter; N/A, not applicable]

Timing	Herbicides				
	Atrazine	Alachlor	Cyanazine	Metolachlor	Prometyrn
Preplanting	136/149/0.05	27/149/0.05	7/149/0.2	51/149/0.05	0/149/ 0.05
Postplanting	146/149/0.05	128/149/0.05	94/149/0.2	124/149/0.05	0/149/0.05
Harvest	113/149/0.05	18/149/0.05	0/149/0.2	66/149/0.05	0/149 /0.05

Table 3. Selected chemical and physical properties, and runoff-potential ratings of selected herbicides.

Herbicide	Water solubility (mg/L)[1]	Half-life in soil (days)[1]	Soil Sorption coefficient (K_{OC})[1]	Runoff potential[1]
Atrazine	33	60	100	large
Alachlor	240	15	170	medium
Metolachlor	530	90	200	large
Cyanazine	170	14	190	medium
Prometryn	33	60	400	large
Fluometuron	100	85	100	large
Molinate	970	21	190	medium

[1]Physical property data and runoff-potentials from Gross, 1992.

Table 4. Mississippi statewide herbicide use statistics (data from Gianessi and Puffer, 1990, unless otherwise indicated)
[pre, preemergent; uk, unknown; post, postemergent; -- not applicable]

Herbicide	Crop	Application timing	Percent of crop National average	Percent of crop State average	Total Yazoo River Basin use (pounds active ingredient)	Percent of total use in United States
Atrazine	corn	pre	66	62[a]	--	--
	sorghum	pre	52	8[a]	--	--
		--	--	--	121,000	0.19
Alachlor	corn	pre	26	8[a]	--	--
	soybean	pre	15	20[a] 0[b]	--	--
	sorghum	pre	12	15[a]	--	--
		--	--	--	115,000	0.21
Cyanazine	cotton	post and layby	15	69[a] 152[c,d]	--	--
	corn	pre	18	2[a]	--	--
		--	--	--	432,000	1.9
Fluometuron	cotton	pre and post	30	126[c,e]	590,000	24.7
Metolachlor	soybean	pre	11	4[a] 2[b]	--	--
	corn	pre	26	10[a]	--	--
	cotton	pre	3	16[a] 8[b]	--	--
	sorghum	pre	19	15	--	--
		--	--	--	294,000	0.59
Molinate	rice	post	46	31a	176,000	4.0
Prometryn	cotton	post	16	38[a] 19[b,f]	122,000	6.8

a. Oral commun. E. Ruth Morgan, Cooperative Extension Service, Mississippi State University, 1995
b. From United States Department of Agriculture, 1992
c. From Byrd, 1994
d. Fallow/stale seedbed 3 percent, preemergent 1 percent, postemergent 68 percent, and layby 80 percent
e. Preemergent 96 percent, postemergent 30 percent
f. Prometryn is also used to prepare fallow/stale seedbed on 3 percent of the cotton acreage in Mississippi