PESTICIDES IN THE YAZOO RIVER AND BOGUE PHALIA, FEBRUARY THROUGH SEPTEMBER 1996

Anubha Dayama and Richard H. Coupe
U. S. Geological Survey
Pearl, Mississippi

INTRODUCTION

A study of pesticides in the Mississippi River during 1991-92 by the U.S. Geological Survey (USGS) indicated that the Yazoo River, a tributary to the Mississippi River, was a major contributor of cotton and rice herbicides to the Mississippi River and subsequently to the Gulf of Mexico (Pereira and Hostettler 1993). In February 1996, the USGS, through its National Water Quality Assessment (NAWQA) program, began a study to determine the status and trends of water quality in the basin of the Yazoo River. As a part of this effort, two streams have been sampled bi-weekly for pesticides from February through September 1996.

The two streams sampled were the Yazoo River near its mouth and the Bogue Phalia which drains a smaller sub-basin of the Yazoo River (Figure 1). The Yazoo River Basin (YRB), Mississippi's largest river basin, consists of about 13,000 square miles. It is divided almost equally betwa een 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. In 1987, there were , 1,270,000 acres of soybeans ,760,000 acres of cotton, 176,000 acres of rice, 77,000 acres of grain sorghum, and 34,000 acres of corn harvested in the YRB. The YRB is sparsely populated with no major metropolitan areas (Coupe 1996). This paper presents the results of the analysis for pesticides in surface-water samples collected from February to September 1996 from the Yazoo River and the Bogue Phalia.

MATERIALS AND METHODS

Sampling Methods

As a part of the intensive study of the water quality in the YRB, the two streams were sampled bi-weekly from February through September 1996. Water samples were collected using standard procedures (Shelton 1994) to ensure representative samples. 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, Mississippi office of the USGS for further processing.

Solid Phase Extraction (SPE) and Sample Analysis

Solid Phase Extraction (SPE) was used prior to pesticide analysis of samples by Gas Chromatography/Mass Spectrometry (GC/MS) or High Performance Liquid Chromatography (HPLC). Using SPE, pesticides are extracted from prefiltered water samples using disposable polypropylene syringe cartridges packed with a specific sorbent material. Samples to be analyzed by GC/MS were extracted by using disposable polypropylene syringe cartridges packed with octadecyl-bonded porous silica (C-18) (Sandstrom et al. 1994), and those analyzed by HPLC were extracted by using 0.5-gram graphitized carbon as the solid phase sorbent (Werner et al. 1996). Regardless of the analytical method, the basic SPE procedure is the same. The SPE cartridges are 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 uL 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 milliliter per minute. The extracted sample on the cartridge can be stored in a cool place (approximately 4°C) for extended periods before analysis. The cartridges were shipped on ice to the National Water Quality Laboratory (NWQL) in Denver, Colorado, where the pesticides were extracted from the cartridges and analyzed by GC/MS or HPLC. Forty-seven pesticides and metabolites were analyzed by GC/MS (Table 1); 41 and pesticide metabolites were analyzed by the HPLC analytical method (Table 2). The two methods have three pesticides in common: carbaryl, carbofuran, and linuron. The method reporting level (MRL) for the HPLC method is higher and therefore the results are sometimes not identical between methods for these three compounds.

RESULTS AND DISCUSSION

The analysis of water samples from both the rivers showed the presence of various pesticides. The samples were analyzed for 85 different pesticides or their metabolites: 38 of these compounds were reported at least once in water samples from the Bogue Phalia or the Yazoo River. The maximum concentrations of the pesticides (except diuron, fluometuron, and norflurazon) was found to be higher in

Bogue Phalia than in the Yazoo River (Table 3). This is to be expected because Bogue Phalia has a much smaller drainage basin and the land-use is more intensive agricultural.

The majority of the pesticides that were reported in the Yazoo River and the Bogue Phalia were herbicides. This is due to a number of factors: generally herbicides have a higher water solubility and a lower propensity to sorb to sediment or organic carbon then insecticides. In addition, herbicides are generally applied to bare ground in the spring, when rainfall is frequent. Insecticides are generally applied later in the summer when rainfall is less frequent and the crop canopy has emerged. The insecticides carbaryl, chlorpyrifos, malathion, methyl azinphos all had one detection in either the Yazoo River or the Bogue Phalia. The concentrations were low, less than 0.075 micrograms per liter (ug/L). Methyl parathion was reported twice in each stream, but the concentrations were less than 0.3 ug/L. Carbofuran, the most frequently reported insecticide as it was reported four times in the Yazoo River samples and four times in the Bogue Phalia samples. All of reported concentrations for carbofuran were less than 0.5 ug/L. Tables 1 and 2 list all of the pesticides for which water samples were analyzed. All of the pesticides that were not reported above the MRL in either stream are identified.

Bogue Phalia

Bogue Phalia, a small sub-basin of the YRB has a drainage area of about 480 square miles above the sampling site near Leland, Mississippi. The pesticides reported in more than 75 percent of the surface-water samples were the herbicides atrazine, cyanazine, fluometuron, metolachlor, molinate, thiobencarb and the triazine metabolite deethylatrazine. Four herbicides were reported in every sample collected from the Bogue Phalia: Atrazine, cyanazine, metolachlor and molinate, although much of the time the reported concentrations were very low. Table 3 lists the maximum, minimum and median concentrations of selected pesticides. Molinate, a post-emergent rice herbicide, was the pesticide reported in the highest concentration ranging from 0.03 to 100 ug/L. The median molinate concentration was 0.440 ug/L. Concentrations of molinate were highest in the June and July samples reflecting the use of as a post-emergent herbicide on rice. Metolachlor, a pre-emergent herbicide for corn, cotton, and soybean, was detected in concentrations ranging from 0.057 to 9.2 ug/L. The highest concentrations were in the spring with a median concentration of 0.62 ug/L, metolachlor was the most frequently detected pesticide during the study. This could be due to the high water solubility and large run-off potential of metolachlor (Gross 1992). Similarly, atrazine was found in concentrations ranging from 0.008 to 8.5 ug/L. Cyanazine, fluometuron, diuron and bentazon were detected with mean concentrations of 0.27, 0.21, 0.15 and 0.39 ug/L, respectively. Triclopyr, a post-emergent herbicde used mostly on rice, was most frequently detected in the June and July samples. In a water-quality study of the Delta part of the YRB (Pennington 1996), which included samples from the Bogue Phalia and nearby streams, a few samples were collected for pesticide analyses. The results from the study with regards to the most frequently reported pesticides and the range of concentrations were comparable to this study.

Yazoo River

Although the suite of pesticides detected in the Yazoo River was similar to that found in the Bogue Phalia, the maximum concentrations in the Yazoo River were lower than in the Bogue Phalia, except for the cotton herbicides diuron, fluometuron, and norflurazon. The pesticides that were reported in more than 75 percent of the samples were the herbcides alachlor, atrazine, cyanazine, fluometuron, metolachlor, simazine, and the triazine metabolite deethylatrazine. All of these herbicides, except for alachlor, were present in 100 percent of the water samples from the Yazoo River. Atrazine and metolachlor were found to be in highest concentrations ranging from 0.029 to 6.1 ug/L and 0.031 to 5.8 ug/L, respectively (Table 3). Concentrations of molinate, (ranging from 0.004 to 3.3 ug/L) were much lower in the Yazoo River than in the Bogue Phalia (Table 3) because the percentage of land in rice agriculture is much higher in the Bogue Phalia drainage basin than in the YRB as a whole. The total amount of rice acreage in YRB is small and is concentrated in the Bogue Phalia drainage. The two herbicides that were frequently detected in the Yazoo River, but not in the Bogue Phalia, were alachlor and simazine. Simazine in surface water has been related to its use in urban areas and its concentrations in the Yazoo River probably reflect the small urban area in the YRB (Hippe and Garrett 1997).

SUMMARY

As a part of an ongoing water-quality study of the YRB by the USGS, the Bogue Phalia and the Yazoo River near its mouth were sampled bi-weekly for pesticides from February through September 1996. The herbicides were the most frequently detected class of pesticides in both streams. The insecticides had very few detections and where detected in low concentrations. Atrazine, cyanazine, fluometuron, and the triazine metabolite deethylatrazine were present in more than 75 percent of the water samples from the Bogue Phalia and the Yazoo River. The maximum concentrations of pesticides detected in surface-water samples from the Bogue Phalia were higher than in the Yazoo River, except for diuron, fluometuron, and norflurazon. This was expected because land use in the Yazoo River Basin consists of small farms, pastures and forests in the uplands while the Bogue

Phalia, which forms a smaller sub-basin of YRB in the Delta is an intensively agricultural basin. Among the major pesticides reported in the Bogue Phalia, molinate (a post-emergent rice herbicide) and metolachlor (a pre-emergent herbicide for corn, cotton and soybeans) were found to be in highest concentrations ranging from 0.03 to 100 ug/L and 0.057 to 9.2 ug/L, respectively. Atrazine (a pre-emergent herbicide for corn and sorghum) and metolachlor were the two most frequently detected pesticides found in highest concentrations (6.1 ug/L and 5.8 ug/L respectively) in the Yazoo River. Concentrations of molinate in the Yazoo River, ranging from 0.004 to 3.3 ug/L, were much lower than in the Bogue Phalia.

REFERENCES

Coupe R. H. 1996. Herbicides in the surface water of the Yazoo River Basin, Mississippi. Proceedings of 26th Mississippi Water Resources Conference. 187.

Gross D. W. 1992. Screening procedure for soil and pesticides relative to potential water quality impacts. Weed Technology. 6:701-708.

Hippe D. J., and J. W. Garrett. 1997. The spatial distribution of dissolved pesticides in surface water of the Apalachicola-Chattahoochee-Flint river basin, Georgia, Florida, and Alabama, 1992-95. 1997 Georgia Water Resources Conference.

Pennington K. 1996 Mississippi Delta Surface Water Quality, A Summary. Proceedings of the 26th Mississippi Water Resources Conference. 78.

Pereira W. E., and F. D. Hostettler. 1993. Nonpoint Source Contamination of the Mississippi River and Its Tributaries by Herbicides. Environmental Science and Technology. 6:1542-1552.

Sandstrom M. W., D. S. Wydoski, M. P. Schroeder, J. L. Zamboni, and W. T. Foreman. 1994. Methods of Analysis by the U. S. Geological Survey National Water Quality Laboratory - Determination of Organonitrogen Herbicides in Water by Solid Phase Extraction and Capillary - Column Gas Chromatography/Mass Spectrometry with Selected - Ion Monitoring. U. S. Geological Survey Open-File Report 91-159. 1.

Shelton L. R. 1994. Field Guide For Collecting and Processing Stream-Water Samples for the National Water-Quality Assessment Program. U. S. Geological Survey Open-File Report 94-455. 14.

Werner S. L., M. R. Burkhardt, and S. N. Derusseau. 1996. Methods of Analysis by the U.S. Geological Survey National Water-Quality Laboratory - Determination of Pesticides in Water by Carbopak-B Soild Phase Extraction and High-Performance Liquid Chromatography. U.S.Geological Survey Open-File Report 96-216. 1.

Table 1. Dissolved pesticides analyzed by Gas Chromatography/Mass Spectrometry.

Acetochlor	Methyl Parathion
Alachlor	Metolachlor
Alpha BHC*	Metribuzin
Atrazine	Molinate
Atrazine Deethyl	Napropamide*
Azinphos-Methyl	Parathion*
Benfluralin	Pebulate
Butylate*	Pendimenthalin
Carbaryl[1]	Permethrin-cis*
Carbofuran[1]	Phorate
Chlorpyrifos	Prometon
Cyanazine	Pronamide*
DCPA	Propachlor
DDE-P'P	Propanil
Diazinon	Propargite*
Dieldrin	Simazine
2, 6-Diethylaniline*	Tebuthiuron
Disulfoton*	Terbacil*
EPTC*	Terbufos*
Ethalfluralin*	Thiobencarb
Ethoprop*	Triallate*
Fonofos*	Trifluralin
Lindane*	
Linuron[1]	
Malathion	

Table 2. Dissolved pesticides analyzed by High Performance Liquid Chromatography.

Acifluorfen	DNOC*
Aldicarb*	Esfenvalerate*
Aldicarb Sulfone*	Fenuron
Aldicarb Sulfoxide*	Fluometuron
Bentazon	3 Hydroxy Carbofuran*
Bromacil*	Linuron*
Bromoxynil*	MCPA*
Carbaryl*	MCPB*
Carbofuran	Methiocarb*
Chloramben*	Methomyl
Chlorothalonil*	1 - Napthol*
Chlopyalid*	Neburon
2, 4, - D	Norflurazon
2, 4 - DB*	Oryzalin*
2, 4, 5 - T*	Oxamyl*
Dacthal Mono-acid*	Picloram*
Dicamba*	Propham*
Dichlobenil*	Propoxur*
Dichlopro*	Silvex*
Dinoseb*	Triclopyr
Diuron	

[1] Note: Both methods have a few analytes in common.

* Pesticides not detected in surface water samples from the Yazoo River or the Bogue Phalia collected February - September 1996

Table 3. Maximum, minimum, and median concentrations of selected dissolved pesticides in the Bogue Phalia and Yazoo River, February through September 1996.
[No., number; all concentrations reported in micrograms per liter]

Yazoo River					Bogue Phalia				
Pesticide	*No. of samples*	*Maximum concentration*	*Minimum concentration*	*Median concentration*	*Pesticide*	*No. of samples*	*Maximum concentration*	*Minimum concentration*	*Median concentration*
Acifluorfen	14	0.46	<0.035	<0.035	*Acifluorfen*	17	1.6	<0.035	0.34
Alachlor	16	0.3	<0.002	0.019	*Alachlor*	17	0.035	<0.002	<0.002
Atrazine	16	6.1	0.029	0.686	*Atrazine*	17	8.5	0.008	0.25
Bentazon	14	0.81	<0.014	<0.014	*Bentazon*	17	2.3	<0.014	0.16
Cyanazine	16	1.3	0.022	0.159	*Cyanazine*	17	2.7	0.009	0.068
Deethyl atrazine	16	0.13	0.003	0.031	*Deethyl atrazine*	17	0.19	<0.002	0.019
Diuron	14	0.6	<0.02	0.06	*Diuron*	17	0.98	<0.02	0.07
Fluometuron	14	1.3	<0.035	0.2	*Fluometuron*	17	1.3	<0.035	0.1
Metribuzin	16	0.44	<0.004	0.043	*Metribuzin*	17	0.88	<0.004	0.022
Metolachlor	16	5.8	0.03	0.54	*Metolachlor*	17	9.2	0.057	0.62
Molinate	16	3.3	<0.04	0.014	*Molinate*	17	100	0.036	0.44
Norflurazon	14	0.68	<0.024	<0.024	*Norflurazon*	17	0.2	<0.024	<0.024
Pendimentalin	16	0.08	<0.004	<0.004	*Pendimentalin*	17	0.48	<0.004	<0.004
Propanil	16	0.012	<0.004	<0.004	*Propanil*	17	0.21	<0.004	0.006
Simazine	16	0.16	0.012	0.038	*Simazine*	17	0.4	<0.005	0.013
Thiobencarb	16	0.074	<0.002	<0.002	*Thiobencarb*	17	4.0	<0.002	0.036
Tebuthiuron	16	0.048	<0.01	0.009	*Tebuthiuron*	17	0.12	<0.010	0.016
Triclopyr	14	0.3	<0.05	<0.05	*Triclopyr*	17	4.6	<0.050	<0.05
Trifluralin	16	0.075	<0.002	0.006	*Trifluralin*	17	0.072	<0.002	<0.002

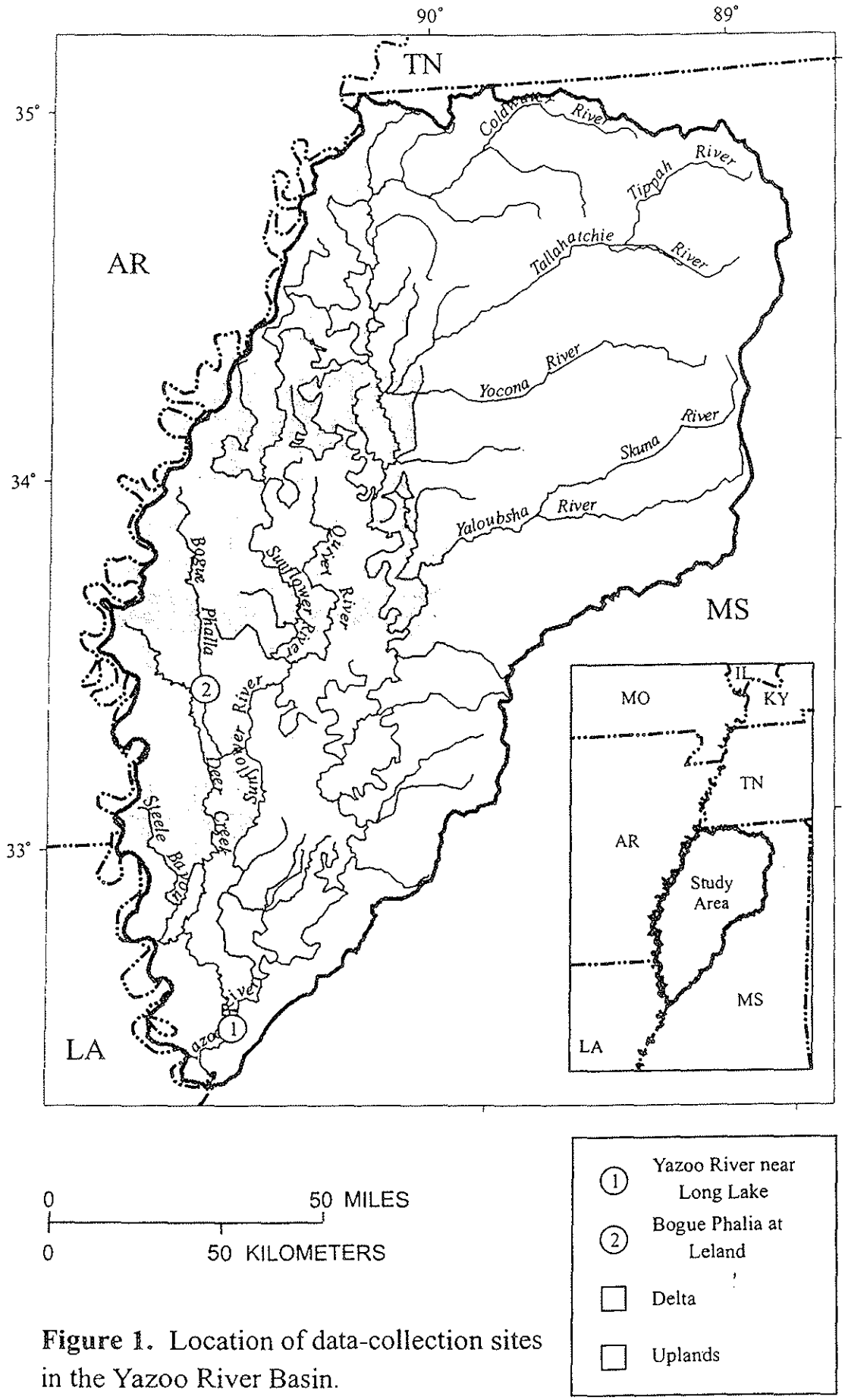

Figure 1. Location of data-collection sites in the Yazoo River Basin.