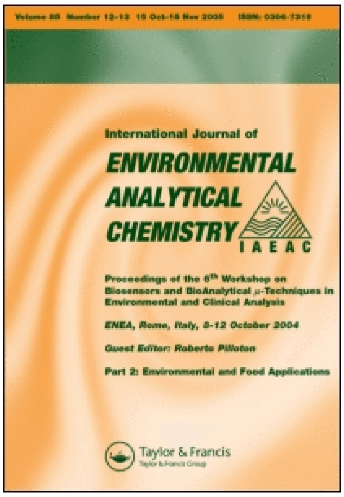

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Herbicide and degradate flux in the Yazoo River Basin

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During 1996–1997, water samples were collected from five sites in the Yazoo River Basin and analysed for 14 herbicides and nine degradates. These included acetochlor, alachlor, atrazine, cyanazine, fluometuron, metolachlor, metribuzin, molinate, norflurazon, prometryn, propanil, propazine, simazine, trifluralin, three degradates of fluometuron, two degradates of atrazine, one degradate of cyanazine, norflurazon, prometryn, and propanil. Fluxes generally were higher in 1997 than in 1996 due to a greater rainfall in 1997 than 1996. Fluxes were much larger from streams in the alluvial plain (an area of very productive farmland) than from the Skuna River in the bluff hills (an area of small farms, pasture, and forest). Adding the flux of the atrazine degradates to the atrazine flux increased the total atrazine flux by an average of 14.5%. The fluometuron degradates added about 10% to the total fluometuron flux, and adding the norflurazon degradate flux to the norflurazon flux increased the flux by 82% in 1996 and by 171% in 1997.

Keywords: Herbicides; Yazoo River Basin; Mississippi; Degradates

1. Introduction

The Yazoo River Basin (figure 1), the largest river basin in Mississippi, covers an area of 34 590 km^2 in north-western Mississippi. The basin is divided almost equally between the alluvial plain, a rich agricultural area that is relatively flat and is characterized by poorly drained soils on the west side of the Yazoo River, and the bluff hills east of the river, an area where the principal land use is small farms, pasture, and forest. The basin is sparsely populated, with no major metropolitan areas [1].

The confluence of the Tallahatchie and Yalobusha Rivers forms the Yazoo River which flows southward from Greenwood along the eastern edge of the alluvial plain until it reaches the Mississippi River at Vicksburg. Discharge from more than 11 400 km^2 of drainage area within the basin is controlled by four flood-control reservoirs (Arkabutla, Sardis, Enid, and Grenada Lakes) located in the uplands.

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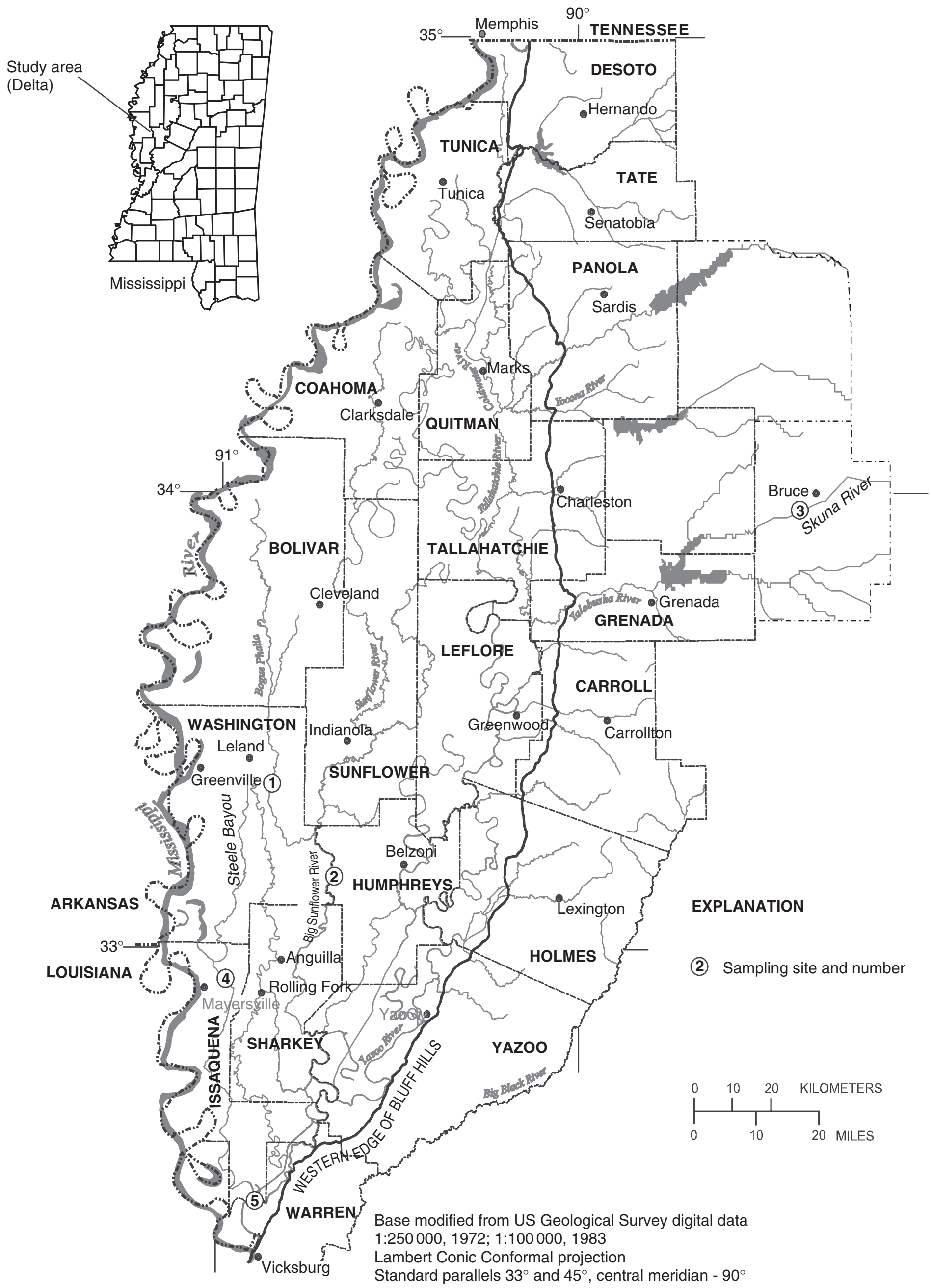

Figure 1. Location of study area and sampling sites, north-western Mississippi.

Runoff and flooding in the Delta are controlled by two structures, one located at Steele Bayou and the other at the Little Sunflower River. In 1996 and 1997, the gates of both structures were closed continuously for more than 1 month during March–June, and for shorter periods throughout the spring and summer [2, 3].

Herbicides are used heavily in the Yazoo River Basin to protect crops, especially cotton, corn, rice, and soybean, from weed infestation. Although the majority of the herbicides used dissipate quickly, there is concern for offsite movement of a small amount of applied herbicide and subsequent contamination of the environment. In the 1990s, several researchers investigated the occurrence of herbicides in the atmosphere [4, 5] and in surface waters [6–9] of the Yazoo River Basin. All of these researchers detected small amounts of the heavily used herbicides. With the exception of Pereira and Hosttler [9], there was no attempt to quantify the annual flux of herbicides in the streams and rivers of the Yazoo River Basin. Pereira and Hostettler [9] estimated the flux of herbicides from the Yazoo River Basin; however, their estimates were made using limited discharge data and with only a small number of samples.

In order to quantify the flux of herbicides in the Yazoo River Basin, surface-water samples were collected from five sites in the basin (figure 1): (1) Bogue Phalia near Leland, which represents 3.6% of the basin; (2) Big Sunflower River near Anguilla, 19.3%; (3) Skuna River at Bruce, 1.9%; (4) Steele Bayou near Rolling Fork, 3.1%; and (5) Yazoo River below Steele Bayou, which drains the entire basin. The drainage area of these sites is 1250, 6680, 660, 1080, and 34 590 km^2, respectively.

The Bogue Phalia, Big Sunflower River, and Steele Bayou are located in the alluvial plain, and the Skuna River is in the bluff hills. The Bogue Phalia drainage basin is wholly contained within the Big Sunflower Basin. The Yazoo River below Steele Bayou site is located near the mouth of the Yazoo River and integrates land use across the entire basin [1].

The purpose of this study was to characterize the occurrence and to document the flux of selected herbicides in five rivers of the Yazoo River Basin during 1996 and 1997. From January 1996 through December 1997, a total of 224 water samples were collected from five rivers in the Yazoo River Basin: the Bogue Phalia, the Big Sunflower River, the Skuna River, Steele Bayou, and the Yazoo River. The number of samples collected from the rivers ranged from 21 for the Skuna River to 58 for the Bogue Phalia. This article presents the fluxes of selected herbicides from five rivers in the Yazoo River basin for 1996 and 1997.

2. Experimental

For the Bogue Phalia and the Skuna River, the mean daily discharge was calculated and reported by the US Geological Survey (USGS) according to standard procedures [10]. Backwater from the Mississippi River can cause difficulties in measuring flow of the Yazoo River using standard protocol and thus requires an alternate method [11]. The Steele Bayou and Big Sunflower gauging stations are operated by the US Army Corps of Engineers (USACOE) as stage-only stations [12, 13]. A rating curve was developed for the Steele Bayou based on discharge measurements made by the USACOE and applied to the reported gauge heights to calculate a daily discharge. Missing values and periods of backwater were estimated from data collected at nearby gauges upstream and downstream of the gauging station near Rolling Fork, MS. For the Big Sunflower River, a rating curve was developed from discharge measurements made by the USACOE and the USGS. This rating curve could not be applied to every time period, however, because of backwater effects caused by the closure of the control structures during periods of high flow on the Mississippi River. The rating curve was used only when there was greater than a 1.2 m drop in the water level between the gauging station at the Big Sunflower River near Anguilla and the Little Sunflower River control structure. Otherwise, the discharge from the Bogue Phalia and an upstream site on the Big Sunflower River at Sunflower was combined, and discharge for the Anguilla site was calculated using a drainage basin ratio [14]. The stage data reported by the USACOE was an 8:00 a.m. reading and, therefore, is an approximation of the mean daily stage. The quality of the streamflow data from the Yazoo River, Skuna River, and the Bogue Phalia is considered good; however, the data are considered poor for the Steele Bayou and the Big Sunflower River.

The sampling frequency varied annually, seasonally, and between sites, depending upon the sampling objectives at each site, the expected streamflow variability of the site, and the resources available to conduct the sampling. 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, the Big Sunflower River, and Steele Bayou were sampled twice monthly with extra samples collected occasionally during high-flow events. In March 1997, the sampling frequency was increased to weekly through September 1997 and then decreased to twice monthly for the remainder of 1997. Pesticides were not expected to be detected frequently or in high concentrations from the Skuna River because the land use in the Skuna River Basin is small farms, pasture, and forest. Therefore, samples were collected only monthly from this river.

Water samples from the Bogue Phalia, the Skuna River, and Yazoo River were flow-weighted and depth- and width-integrated according to the procedures described by Shelton [15] to ensure that samples were representative of the stream. Water samples were analysed for constituents that are known to be unevenly distributed in the water column, such as total nitrogen, total phosphorus, and sediment. In some cases, because of the low gradient in the alluvial plain, flow-weighted samples were not possible. For the Big Sunflower River and the Steele Bayou, water samples were analysed only for dissolved pesticides, which were assumed to be evenly mixed throughout the stream; hence, samples were collected in an open bottle at the centre of flow. All equipment that came into contact with the sample water was made of Teflon, glass, or stainless steel, and was cleaned with a 0.2% non-phosphate detergent, rinsed with deionized water, rinsed with pesticide-grade methanol, air-dried, wrapped in aluminium foil, and stored in a dust-free environment prior to sample collection.

Water samples were filtered onsite using an aluminium filter plate with a baked 0.7 μm pore size glass fibre filter into 1 L baked amber bottles. The samples were shipped on ice to the USGS Organic Geochemistry Laboratory (OGRL) in Lawrence, KS, for analysis.

The analytical method is documented in a report by Lee and others [16]. Samples were extracted using a preconditioned graphitized carbon column and then eluted from the column using a solution of methylene chloride, methanol, and ammonium hydroxide. The sample components were separated, identified, and measured by injecting the sample into a high-performance liquid chromatograph equipped with a diode array detector and a mass spectrometer detector operated in selected-ion monitoring mode. Compounds were identified by comparing the retention times of the mass spectral signals with the retention times of standards. Further identification was made using selected fragment ions for those compounds that produced fragment ions. The concentration was calculated by determining the ratio of the compound's response to the response produced by an internal standard. This value was compared with the ratio of the responses to the primary standard analysed using the same method. All water samples were analysed for 14 herbicides and nine degradates with a reporting level of $0.05\,\mu g\,L^{-1}$ (table 1).

The field quality-assurance/quality-control programme consisted of the collection and analysis of periodic equipment and field blanks and sample replicates. There were no detections of any pesticides in any blank samples, and the sample replicates (data not shown) indicated good precision. The OGRL also analysed laboratory blanks as part of this study, and there were no detections of pesticides in any sample. Every 10th sample was analysed in replicate, and results (not shown) indicated good analytical precision.

Linear interpolation was used to estimate the daily herbicide flux in five rivers and streams in the Yazoo River Basin. Herbicide concentrations on non-sampled days were estimated by interpolating between concentrations measured on sampled days. Measured or interpolated daily concentrations were multiplied by the mean daily discharge to estimate a daily flux. Daily fluxes were summed to estimate a total flux over a specified period of time.

For herbicide concentrations lower than the compounds reporting limit (censored data), the concentrations were set to zero for flux calculations. This is a conservative estimate of the herbicide concentration and possibly could bias the flux estimates low. Zero was considered by the authors to be an appropriate value (rather than 1/10 or 1/2 of the method report level as used by other authors), because annual fluxes are being calculated, and it is likely that during at least part of the year, the concentrations would be zero. Flux was calculated for 10 herbicides and seven degradates (table 1). These included atrazine and fluometuron and two degradates of each; norflurazon and cyanazine and one degradate of each; as well as alachlor, metolachlor, metribuzin, molinate, prometryn, simazine, and a degradate of propanil.

3. Results and discussion

Herbicides and degradates detected in more than 50% of the samples from at least one sampling site in 1996–1997 were atrazine, deethyl atrazine, cyanazine, cyanazine amide, demethyl fluometuron, demethyl norflurazon, 3,4-dichloroaniline (3,4-DCA), fluometuron, metolachlor, molinate, norflurazon, and simazine. These compounds also had the highest concentrations (table 1).

Of the 14 herbicides, all were detected in at least one sample, but four were detected infrequently (in 15% or less of samples at any site): acetochlor, propanil, propazine, and trifluralin (table 1). Fluxes were not calculated for these herbicides. Other herbicides, such as atrazine, fluometuron, metolachlor, and metribuzin, were detected frequently (generally greater than 20% of the samples) at all sites. Some herbicides such as cyanazine, molinate, norflurazon, prometryn, and simazine were detected frequently in some of the alluvial plain rivers and in the Yazoo River, but not in the bluff hills site on the Skuna River. This probably is a reflection of the differing land use (less agriculture, more forest) in the Skuna River Basin (table 2).

Table 1. List of herbicides and degradates[a].

		River				
		Big Sunflower (52)	Bogue Phalia (58)	Skuna (21)	Steele Bayou (50)	Yazoo (43)
Compound	Type	Statistics – Percentage of samples above the reporting level, maximum and median concentrations ($\mu g\,L^{-1}$)				
Acetochlor	H	15, 1.68, <0.05	8, 1.91, <0.05	nd, <0.05, <0.05	nd, <0.05, <0.05	6, 0.13, <0.05
Alachlor	H	13, 0.98, <0.05	5, 0.4, <0.05	14, 0.76, <0.05	4, 0.11, <0.05	16, 0.25, <0.05
Atrazine	H	71, 8.49, 0.07	40, 16.6, <0.05	62, 0.92, 0.06	82, 9.21, 0.13	86, 3.74, 0.25
Deethyl atrazine	D	35, 0.42, <0.05	31, 0.37, <0.05	14, 0.1, <0.05	48, 0.61, <0.05	58, 0.34, 0.07
Deisopropyl atrazine	D	42, 0.59, <0.05	28, 0.29, <0.05	10, 0.1, <0.05	50, 0.87, <0.05	42, 0.27, <0.05
Cyanazine	H	85, 5.77, 0.205	52, 2.31, <0.05	10, 0.12, <0.05	90, 6.05, 0.33	51, 1.04, 0.07
Cyanazine amide	D	60, 0.84, 0.08	31, 0.36, <0.05	5, 0.05, <0.05	72, 1.01, 0.12	28, 0.25, <0.05
Fluometuron	H	90, 6.33, 0.26	64, 6.42, 0.08	43, 0.99, <0.05	94, 5.78, 0.435	81, 2.95, 0.21
Demethyl fluometuron	D	49, 0.84, <0.05	31, 1.82, <0.05	33, 0.28, <0.05	60, 1.11, 0.13	74, 0.38, <0.05
3-(Trifluoromethyl)aniline	D	25, 0.45, <0.05	17, 0.14, <0.05	10, 0.21, <0.05	28, 0.2, <0.05	14, 0.3, <0.05
3-(Trifluoromethyl)phenylurea	D	nd, <0.05, <0.05	nd, <0.05, <0.05	nd, <0.05, <0.05	2, 0.14, <0.05	nd, <0.05, <0.05
Metolachlor	H	98, 9.32, 0.21	76, 8.79, 0.1	71, 4.24, 0.12	88, 8.19, 0.19	81, 3.48, 0.2
Metribuzin	H	42, 2.23, <0.05	29, 2.77, <0.05	19, 0.17, <0.05	34, 1.07, <0.05	26, 0.67, <0.05
Molinate	H	63, 53.3, 0.07	71, 63.1, 0.225	nd, <0.05, <0.05	60, 27.4, 0.07	30, 4.32, <0.05
Norflurazon	H	94, 1.54, 0.185	71, 2.24, 0.075	nd, <0.05, <0.05	92, 0.93, 0.185	77, 0.91, 0.07
Demethyl norflurazon	D	96, 1.71, 0.24	78, 1.41, 0.13	nd, <0.05, <0.05	90, 1.27, 0.21	77, 0.74, 0.11
Prometryn	H	42, 0.73, <0.05	21, 3.73, <0.05	5, 0.07, <0.05	46, 2.29, <0.05	35, 0.36, <0.05
Deisopropyl prometryn	D	nd, <0.05, <0.05	2, 0.1, <0.05	nd, <0.05, <0.05	4, 0.11, <0.05	nd, <0.05, <0.05
Propanil	H	4, 1.66, <0.05	3, 2.73, <0.05	nd, <0.05, <0.05	4, 0.11, <0.05	nd, <0.05, <0.05
3,4-Dichloroaniline	D	79, 2.6, 0.175	79, 26.3, 0.14	nd, <0.05, <0.05	72, 5.05, 0.125	21, 0.3, <0.05
Propazine	H	12, 0.11, <0.05	9, 0.11, <0.05	nd, <0.05, <0.05	4, 0.09, <0.05	2, <0.05, <0.05
Simazine	H	46, 0.35, <0.05	29, 0.37, <0.05	nd, <0.05, <0.05	64, 1.16, 0.08	35, 0.29, <0.05
Trifluralin	H	2, 0.06, <0.05	10, 0.12, <0.05	nd, <0.05, <0.05	10, 0.2, <0.05	2, 0.7, <0.05

[a]The number of samples is given in parentheses; H: herbicide; D: degradate; nd: not detected.

Table 2. Drainage basin characteristics for rivers in the Yazoo River Basin.

River	Drainage Area (km^2)	Percent of Yazoo Basin	Percentage of basin in row crop	1996 discharge ($m^3 s^{-1}$)	1997 discharge ($m^3 s^{-1}$)
Skuna	660	1.9	18.9	11	19
Steele Bayou	1080	3.1	53.6	13	20
Bogue Phalia	1250	3.6	71.2	13	26
Big Sunflower	6680	19.3	65.4	54	144
Yazoo	34 590	100	36.8	403	696

Of the nine degradates analysed, seven were frequently (greater than 20% of the samples) detected in water samples from most of the alluvial plain rivers and the Yazoo River (table 1). Demethyl fluometuron was the only degradate detected in more than 20% of the samples from the Skuna River. Two degradates, 3-(trifluoromethyl)-phenylurea and deisopropyl prometryn, were detected only in a few samples from one or two rivers; therefore, fluxes for these two compounds were not calculated. For the degradates of atrazine, cyanazine, and fluometuron, the frequency of occurrence and the median and maximum concentrations were less than those of the parent compounds. This is not the case for norflurazon and propanil. Norflurazon and its degradate demethyl norflurazon have about the same frequency of occurrence. Propanil is rarely detected, but its degradate, 3,4-DCA, is detected in more than 70% of the samples from the three alluvial plain rivers. This would indicate that these degradates are as or more stable than their respective parent compounds. In fact, the half-life of propanil in warm-moist soil is 1–3 days. Although the half life in soil of norflurazon is several weeks, it is rapidly photodegraded (1.04 h) in water [17].

The total herbicide concentration (sum of all herbicides and degradates) in the five rivers varied seasonally (figure 2). Herbicide concentrations were greatest from April through August at all of the sites and showed a bimodal distribution with higher concentrations in the early spring and in late summer. Peak concentrations in streams of the Midwest in the spring have been referred to as the 'spring flush', where pre-emergent herbicides are applied to fields and are moved offsite in the rainfall runoff event after application [18]; concentrations in subsequent runoff events rapidly decline as the pool of available herbicide in the soil declines. Unlike the Midwest, streams in the Yazoo River Basin had a second peak concentration in late summer, probably as a result of a longer growing season (with different herbicide application times for different crops) and the use of post-emergent herbicides. The total herbicide concentration remained above $10\,\mu g\,L^{-1}$ for consecutive months at some sites.

The total herbicide concentrations were highest from the three streams located in the alluvial plain; the Big Sunflower River, the Steele Bayou, and the Bogue Phalia. The lowest total herbicide concentrations were measured at the site located in the bluff hills: the Skuna River. The total herbicide concentrations in the Yazoo River were intermediate between the alluvial plain sites and the bluff hills site. The largest component of the total herbicide concentration for samples from the alluvial plain sites was atrazine and/or metolachlor in the spring and molinate in the summer.

The majority (greater than 90%) of the herbicide flux occurred during the months from April through July in both 1996 and 1997 (figure 3). The highest monthly flux for 1996 occurred in April; the highest monthly flux in 1997 occurred in June. In 1996, the monthly flux of herbicides for May from the Yazoo River to the

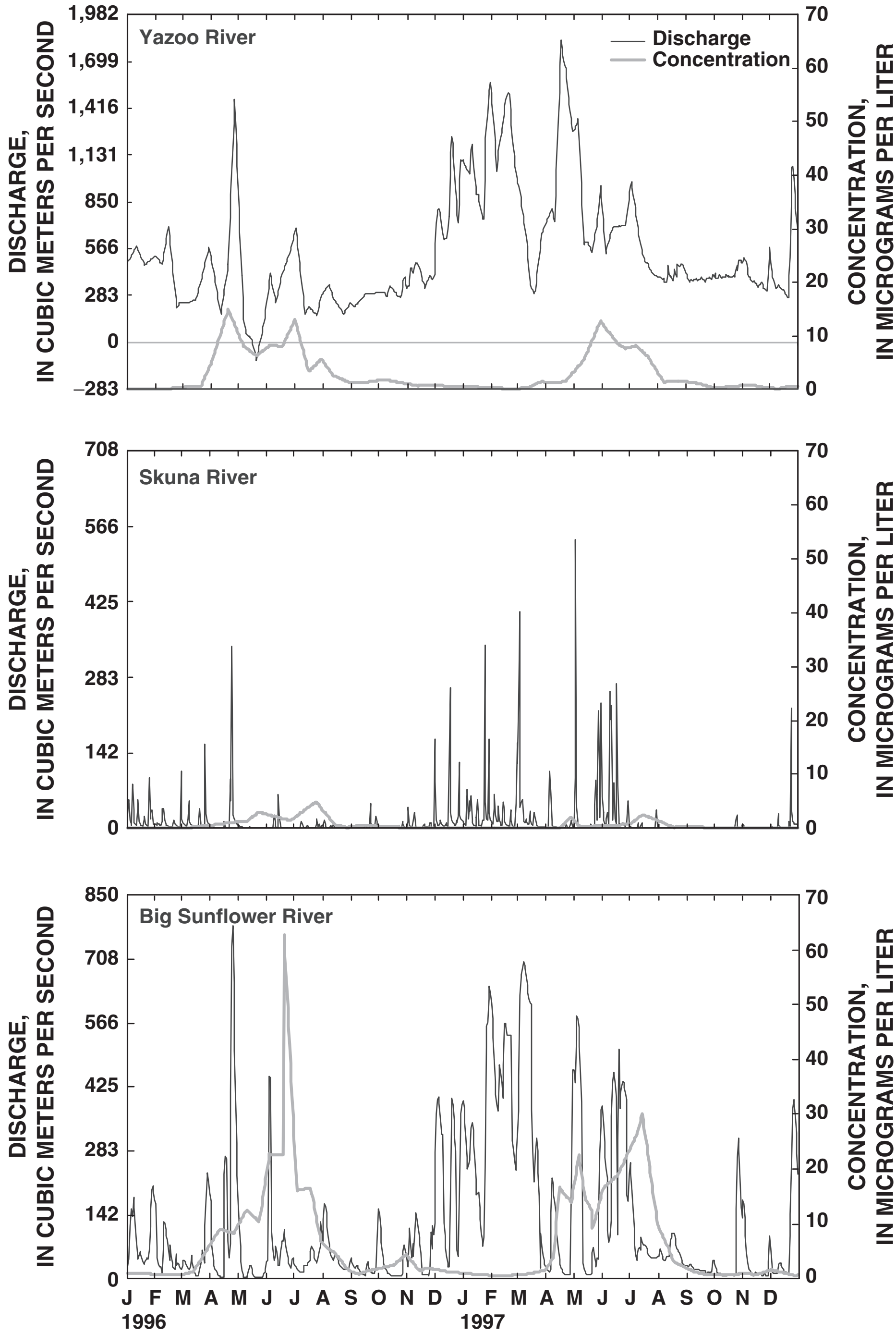

Figure 2. Steam discharge and total herbicide concentration in five rivers of the Yazoo River Basin, MS, 1996–1997; Yazoo River, Skuna River, Big Sunflower River, Bogue Phalia, and Steel Bayou.

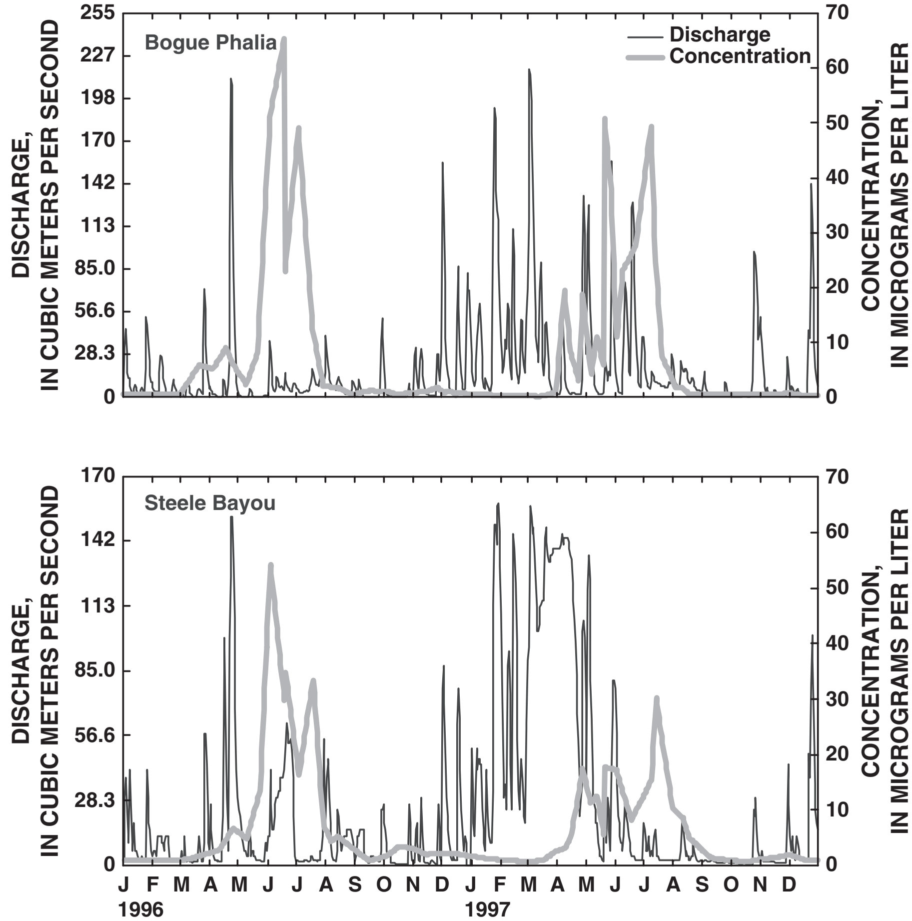

Figure 2. Continued.

Mississippi River was quite low compared with April or June of 1996 or April through July of 1997. This was a result of conditions in the greater Mississippi River Basin rather than in the Yazoo River Basin. The flow in the Mississippi River increased and caused backwater conditions in the Yazoo River to occur to such an extent that net reverse flow occurred [9, 11]. The control structures were closed during 5–28 May 1996, allowing no water from the alluvial plain into the Yazoo River.

Aerially, the land area of the Big Sunflower River at Anguilla represents about 19.3% of the Yazoo River Basin (table 2). If the total herbicide concentration acted conservatively and if pesticide use across the basin was homogenous, then it might be expected that the flux from the Big Sunflower River would contribute about 20% of the flux of the Yazoo River. However, the monthly flux from the Big Sunflower River for June 1996 and April through July 1997 far exceeded 20% of the flux of the Yazoo River and, in some months, nearly equalled the flux of the Yazoo River. This is probably due to the large contribution that molinate, a herbicide used on rice, makes to the total herbicide concentration.

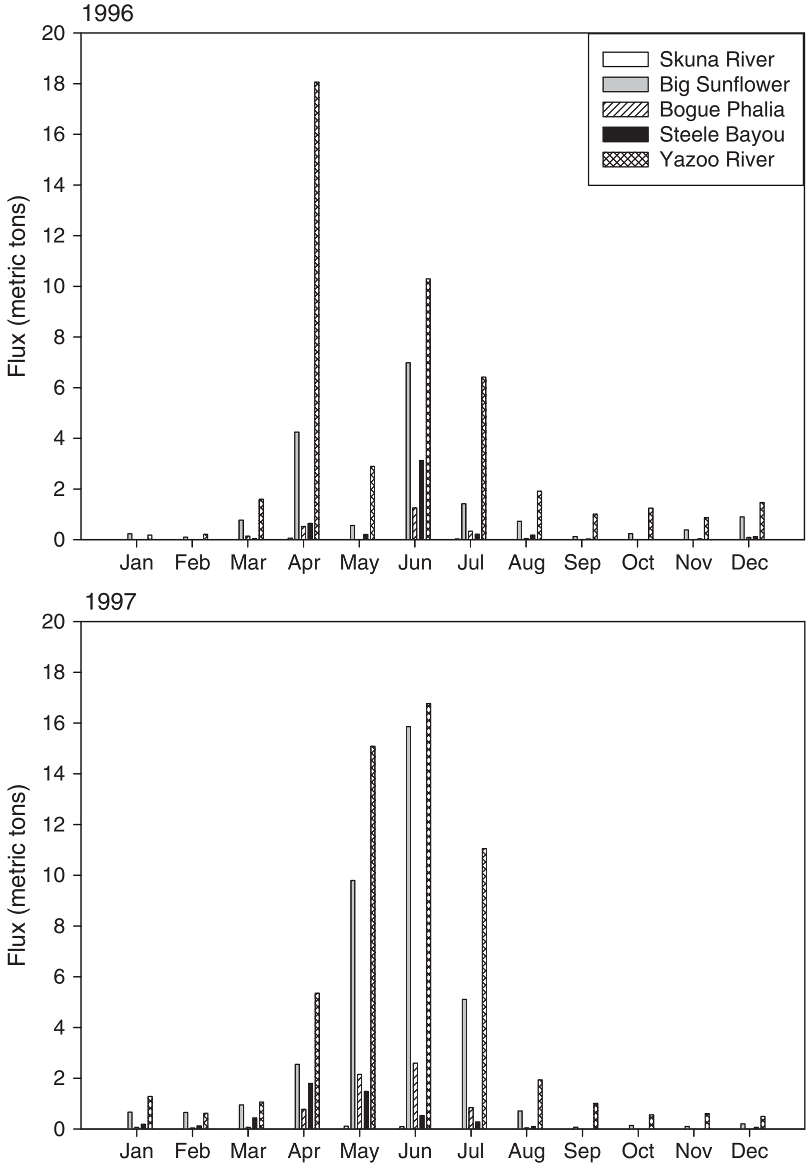

Figure 3. Monthly total herbicide fluxes for 1996 and 1997 from streams in the Yazoo River Basin.

The maximum concentration of molinate generally is an order of magnitude higher in the three delta streams (ranging from 27.4 to 63.1 $\mu g\,L^{-1}$) than the maximum concentration of the other herbicides. The maximum concentration in the Yazoo River was 4.32 $\mu g\,L^{-1}$. The primary route of loss for molinate after application is through volatilization (75–85%) which is quite rapid, with rate constants ranging from 0.11 to 0.43/day [19]. Capel and others [20] modelled the in-stream loss of molinate and estimated that 79% of the molinate in the stream was lost after 15 days. This probably accounts for the large loss of molinate mass between the Big

Table 3. Flux of selected herbicides from five rivers in the Yazoo River Basin 1996 and 1997[a].

	River									
	Skuna		Steele Bayou		Bogue Phalia		Big Sunflower		Yazoo	
Compound	1996	1997	1996	1997	1996	1997	1996	1997	1996	1997
Alachlor	3.4	13.7	0	0	0	5.6	253	44	451	291
Atrazine	53.8	71	169	802	193	1040	2480	3820	13 390	11 490
Dethyl atrazine	5.7	3.1	24.8	47.9	15.6	38.1	126	377	905	1100
Deisopropyl atrazine	3	11.4	20.2	65.5	19.1	29.2	164	312	824	743
Cyanazine	0.4	0.5	140	183	55.5	126	899	1480	2030	2010
Cyanazine amide	0.4	0	68.5	64.1	11.3	28.1	279	281	239	493
Fluometuron	10.1	23.9	175	420	63.5	574	1750	3000	5240	8290
Demethyl fluometuron	2.2	9.6	60.8	123	24.8	154	426	390	355	493
TFMA	0.6	23.9	2.25	17.7	0.5	18.3	44.9	130	18	581
Metolachlor	81	80	376	637	527	919	3620	7340	13 820	10 700
Metribuzin	2.5	0.4	8	140	33.3	305	305	1839	1066	2050
Molinate	0	0	223	286	1260	2490	3840	12 300	2160	10 050
Norflurazon	0	0	73.3	134	57.6	182	835	1120	2330	2320
Demethyl norflurazon	0	0	87.7	199	57.6	195	835	1760	1910	3960
Prometryn	0.5	0	17.8	8	26.2	36.1	143	156	516	380
3,4-Dichloro aniline	0	0	36.1	244	102	419	451	1910	131	717
Simazine	0	0	135	57.1	41.9	60.7	210	495	744	682

[a]TFMA: 3-(trifluoromethyl)aniline; flux is in kg/yr.

Sunflower River sampling site and the Yazoo River. Additionally, since molinate is used exclusively on rice in Mississippi, and rice is only grown in the alluvial plain portion of the Yazoo River Basin, streams in the alluvial plain would be expected to contribute more of the total mass than the amount expected based on land area.

Table 3 shows the annual fluxes for those herbicides and degradates for which there were sufficient data to calculate fluxes. The annual mean streamflow at each site was much higher in 1997 than in 1996 (table 2). Generally, the fluxes from the alluvial plain sites and the bluff hill site followed this pattern (i.e. higher fluxes in 1997). However, for the Yazoo River, there is no clear pattern among the herbicides and degradates in annual fluxes. Four compounds had higher fluxes in 1996 than in 1997 (alachlor, atrazine, metolachlor, and prometryn), nine compounds had higher fluxes in 1997 than in 1996 (deethyl atrazine, cyanazine-amide, fluometuron, demethyl fluometuron, TFMA, metribuzin, molinate, demethyl-norflurazon, and 3,4-DCA), and four compounds had virtually the same flux in 1996 as in 1997 (deisopropyl atrazine, cyanazine, norflurazon, and simazine). The reasons for this are not clear but could be related to the complicated hydrology in the lower Yazoo River, the timing of herbicide applications, change in cropping patterns between the two years, or the precision of the data.

With the exception of molinate, the Yazoo River Basin herbicide flux as a percentage of use (FAPU) was very similar in 1996 and 1997 (figure 4). The molinate FAPU was 2.1 in 1996 and 9.9 in 1997. The FAPU of atrazine and metolachlor was nearly 10% annually. In other studies from the Midwest, these values generally fall into the 1–5% range [21, 22]. Capel and Larson [23] showed that the FAPU for atrazine was relatively invariant of watershed size, but that weather, especially substantial rainfall in the spring and early summer, and the percentage of soils in the watershed

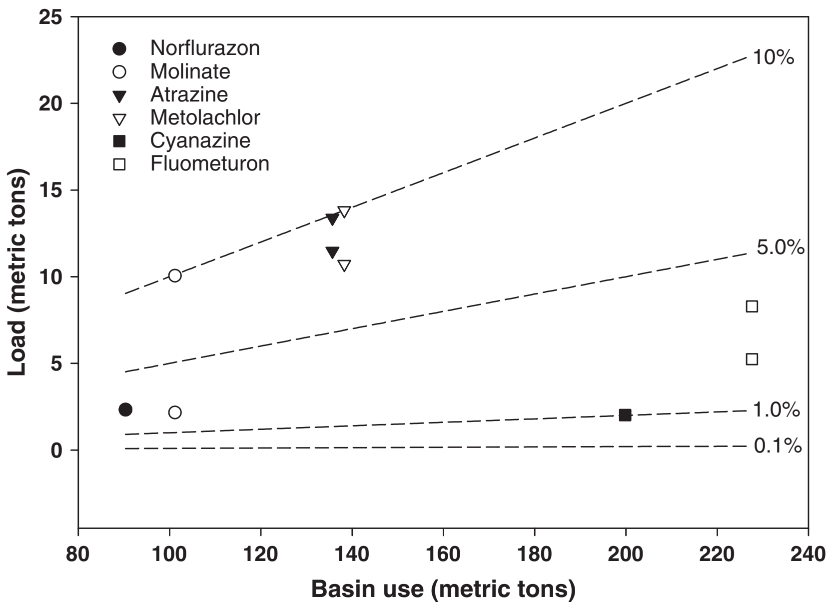

Figure 4. Relation of flux and basin use in the Yazoo River Basin, 1996–1997. Dashed lines represent the percentage of basin use; flux values are from the Yazoo River below Steel Bayou (1996–1997).

with fine texture could increase the FAPU. The FAPU was between 1 and 5% for fluometuron, norflurazon, and cyanazine.

There are a number of factors (agricultural practices, climatic factors, and soil conditions) that could be contributing to the high FAPU values from the Yazoo River Basin as compared with other geographic areas. Because of the high rainfall and the high clay content of the soils, the runoff volume from the Yazoo River Basin is among the highest in the nation [24]. Because of the long-growing season, crops are planted and pesticides used over a much longer period than in the Midwest and, with rainfall being plentiful throughout the spring and early summer, the chances of having a rainfall-runoff event soon after application are increased. The amount of pesticide moving offsite has been inversely correlated with the amount of time between application and the first rainfall-runoff event [24].

Adding the flux of the atrazine degradates to the atrazine flux from the Yazoo River increased the total atrazine flux by about 13% in 1996 and about 16% in 1997. The fluometuron degradates increased the total flux by about 7% in 1996 and 13% in 1997. The flux of norflurazon from the Yazoo River increased by 82% in 1996 when the flux of the demethyl degradate was added to the flux of the parent compound, and in 1997 the flux increased by about 171%. The cyanazine degradate increased the cyanazine flux by approximately 12 and 25% for 1996 and 1997, respectively.

Several researchers [9, 21, 25] have calculated the loads of herbicides from the Mississippi River into the Gulf of Mexico. It is of interest to calculate the contribution of the Yazoo River Basin to the flux of herbicides into the Gulf of Mexico. The Yazoo River Basin drainage area is only a little over 1% of the drainage area of the Mississippi River, and the flow of the Yazoo River in 1996 and 1997 was only a few percent of the total flow of the Mississippi River. Therefore, for those herbicides that are used

Table 4. Percentage contribution from the Yazoo River Basin to the flux of herbicides to the Gulf of Mexico (unless otherwise noted, fluxes for the Gulf of Mexico were from Kelly *et al.* [21]).

Herbicide	1996	1997
Alachlor	2.3	1.5
Atrazine	1.6	2
Deethyl atrazine	2.6	3.3
Cyanazine	1.3	2.5
Fluometuron[a]	29.1	46
Metolachlor	4.5	4.1
Metribuzin	15.2	18.1
Molinate	94.2	96.5
Norflurazon[a]	23	23
Simazine	1.5	1.6

[a]Based on the flux for 1991 from Pereira and Hostettler [9].

throughout the Mississippi River Basin, it would be expected that the flux from the Yazoo River would only be a few percent of the flux in the Mississippi River. This is the case for alachlor, atrazine, deethyl atrazine, cyanazine, metolachlor, and simazine (table 4). Only metribuzin shows an anomalously high percentage of flux from the Yazoo River. Fluometuron, molinate, and norflurazon are used almost exclusively in the rice- and cotton-growing regions of the lower Mississippi River Valley. The percentage of flux of these herbicides from the Yazoo River is much higher than the percentage of drainage area or flow. Of particular note is the molinate flux. The flux of molinate from the Yazoo River was five times higher in 1997 than in 1996, but the percentage of flux from the Yazoo River to the Gulf of Mexico was about the same in both years and quite high, 94.2 and 96.5. This would indicate that most of the molinate flux to the Gulf of Mexico originates from the Yazoo River Basin; this is not the expected result and needs further investigation. Because Arkansas has five times the rice area of Mississippi, and it could be assumed that weed-control practices would be similar, it would be hard to understand how the Yazoo River could account for over 90% of the molinate flux to the Gulf of Mexico.

4. Conclusions

Several herbicides that are used for crop protection and herbicide degradates were frequently detected in the rivers and streams of the Yazoo River Basin. Herbicides were more frequently detected in streams from the alluvial plain (an area of high agricultural productivity) than in streams in the bluff hills (an area of small farms, forest, and pasture) portion of the Yazoo River Basin. Most degradates were found less frequently and in lower concentrations then their parent compounds; the exceptions were norflurazon and propanil. A degradate of norflurazon, demethylnorflurazon, was reported as frequently as its parent compound and in about the same concentrations. Propanil was detected in fewer than 4% of the samples, but 3,4-DCA, a degradate of propanil, was detected frequently (greater than 70% of samples) in streams from the alluvial plain where rice is grown.

Fluxes generally were higher in 1997 than in 1996 due to greater rainfall in 1997 than 1996. The annual mean streamflow for the Yazoo River in 1997 (696 311 $L\,s^{-1}$) was nearly twice that of 1996 (403 232 $L\,s^{-1}$). Fluxes of herbicides were much larger from streams in the alluvial plain (an area of very productive farmland) than from the Skuna River in the bluff hills (an area of small farms, pasture, and forest). Adding the flux of the atrazine degradates to the atrazine flux increased the annual total atrazine flux by an average of 14.5%. The fluometuron degradates added about 10% to the total fluometuron flux, and adding the norflurazon degradate flux to the norflurazon flux increased the flux by 82% in 1996 and by 171% in 1997.

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