Seasonal and Annual Load of Herbicides from the Mississippi River Basin to the Gulf of Mexico

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Water samples collected from rivers in the Mississippi River Basin were analyzed for selected herbicides to evaluate their discharge to the Gulf of Mexico and to identify their predominant source areas within the basin. Samples were collected from the Mississippi River at Baton Rouge, LA from 1991 to 1997 and from sites on the upper Mississippi, the Missouri, and the Ohio Rivers from 1996 to 1997. Atrazine, metolachlor, and alachlor ESA (an alachlor metabolite) were the most frequently detected herbicides in the Mississippi River at Baton Rouge, and, in general, were present in the largest concentrations. The peak annual herbicide load was in 1993 when about 640 metric tons of atrazine, 320 metric tons of cyanazine, 215 metric tons of metolachlor, 53 metric tons of simazine, and 50 metric tons of alachlor were discharged to the Gulf of Mexico. The annual load of atrazine and cyanazine was generally 1–3% of the amount annually applied in the Mississippi River drainage basin; the annual load of acetochlor, alachlor, and metolachlor was generally less than 1%. During 1996–1997 the Ohio River contributed about 50% of the discharge and 50% or more of the herbicide load to the Gulf of Mexico.

Introduction

Almost 500 000 metric tons (t) of pesticides are used annually in the United States to control weeds, insects, nematodes, and other pests (*1, 2*). About three-fourths of this amount is used for agriculture, of which about 65% is used for agriculture in the corn and soybean belt of the Midwest (Figure 1). More than 100 000 t of herbicides are used annually on field crops in the Mississippi River Basin. Some of the most heavily used herbicides in the Mississippi River Basin are triazines, such as atrazine and cyanazine, and chloroacetanilides (acetanilides), such as alachlor and metolachlor (*3*). The physiochemical properties of herbicides, and factors such as timing of application, rainfall, and farming practices, are important in governing the quantity and concentration of herbicides in streams. Because most triazine and acetanilide herbicides are water soluble and mobile, they can be transported in surface runoff from agricultural fields to streams. The presence of herbicides in streams is a concern because of potential effects on water quality. Although most herbicides have low acute toxicity to animals, the potential effects on human health are a concern. The U.S. Environmental Protection Agency (USEPA) classifies alachlor as a probable human carcinogen (*4*). Several other herbicides, including atrazine, cyanazine, metolachlor, and simazine, are classified as possible human carcinogens (*4*). In addition, the effects of long-term, low-level concentrations of herbicides or combinations of herbicides and other organic compounds on aquatic ecosystems are largely unknown (*5*).

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FIGURE 1. The Mississippi River Basin and sampling sites.

A number of studies have documented the presence of herbicides in the Mississippi River and its tributaries (*3, 6–12*). Concentrations of herbicides peak for several weeks to several months following their application to farmlands (*8, 10, 11*); concentrations decrease to preplanting levels by late summer. In some small watersheds in the Mississippi River Basin, concentrations of herbicides in streams have been found to exceed 50 μg per L (μg/L) for short periods of time following spring storms (*8, 11*). Discharge from small streams transports herbicides into large rivers such as the Mississippi, Missouri, and Ohio. Although herbicide concentrations in large rivers are generally not as high as in many small streams, the cumulative mass of herbicides, which eventually discharge to the Gulf of Mexico, can be large.

The U.S. Geological Survey (USGS) has collected water samples for herbicide analysis from the Mississippi River at Baton Rouge, LA (Figure 1) since 1991. Additional data were collected in 1996–97 at sites upstream from Baton Rouge on the Mississippi River and at the mouths of the Missouri and Ohio Rivers. Data were collected to examine the occurrence and temporal variability of herbicides that discharge from the Mississippi River Basin to the Gulf of Mexico and to identify the predominant source area of the herbicides detected in the Mississippi River. This paper presents results of these data collection activities.

Methods

Data Collection. A total of 271 water samples were collected from the Mississippi River at Baton Rouge from April 1991

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TABLE 1. Herbicides and Herbicide Metabolites Analyzed in Samples from the Mississippi River at Baton Rouge, LA, 1991–1997[a]

herbicide or metabolite	type of herbicide	no. of samples	years sampled	analytical reporting limit (μg/L)
acetochlor	acetanilide	120	1994–1997	0.05
alachlor	acetanilide	271	1991–1997	0.05
alachlor ESA	metabolite	160	1993–1997	0.10
ametryn	triazine	198	1991–1995	0.05
atrazine	triazine	271	1991–1997	0.05
cyanazine	triazine	245	1991–1997	0.05–0.20
cyanazine amide	metabolite	88	1994–1997	0.05
deethylatrazine	metabolite	245	1991–1997	0.05
deisopropylatrazine	metabolite	245	1991–1997	0.05
metolachlor	acetanilide	271	1991–1997	0.05
metribuzin	triazine	243	1991–1997	0.05
prometon	triazine	199	1991–1995	0.05
prometryn	triazine	199	1991–1995	0.05
propazine	triazine	199	1991–1995	0.05
simazine	triazine	271	1991–1997	0.05
terbutryn	triazine	115	1993–1995	0.05

[a] μg/L, micrograms per L.

through December 1997. The number of samples collected ranged from 17 in 1997 to 60 in 1993. Samples were collected from the upper 6 m (m) of the water column at the end of a pier extending about 45 m from shore. Previous work indicated that dissolved solutes in the Mississippi River at Baton Rouge are well mixed vertically and laterally (*12*). Samples were collected in glass or Teflon (Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.) containers, composited in glass or stainless steel containers, filtered through baked glass-fiber filters of either 0.7 micrometer (Micro Filtration Systems, type GF75142MM) or 1.0 micrometer (Gelman Sciences, type A–E) pore size into baked glass bottles for shipment to the laboratory. From early March through mid-August 1993, the USGS did not collect samples from the Mississippi River. However, samples were collected during this time period by the Jefferson Parish Water Quality Laboratory near New Orleans, LA, about 200 kilometers (km) downstream from Baton Rouge. The data from the Jefferson Parish Laboratory were used to fill in the 6-month period during 1993 when the USGS did not collect samples, thereby providing a continuous data set from April 1991 through December 1997. The Jefferson Parish Laboratory samples were weekly composites collected continuously at two sampling points on opposite banks of the Mississippi River. A comparison of USGS and Jefferson Parish Laboratory data indicates good agreement for herbicide concentrations in samples collected during the same time period.

The U.S. Army Corps of Engineers provided discharge data for the Mississippi River at Tarberts Landing, LA, located about 130 km upstream from Baton Rouge (John Miller, U.S. Army Corps of Engineers, New Orleans District, written communication). Discharge at Tarberts Landing is similar to the discharge at Baton Rouge. The U.S. Army Corps of Engineers also provided discharge data for water diverted from the Mississippi River to the Atchafalaya River. The sum of the discharge at Tarberts Landing and the discharge diverted to the Atchafalaya River closely represents the total discharge from the Mississippi River to the Gulf of Mexico (*12*).

As part of the USGS National Stream Quality Accounting Network (NASQAN) (*13*), samples from sites in the Mississippi River Basin were collected and analyzed in 1996–1997. NASQAN sites for which data were used in this report include the Mississippi River at Clinton, IA, and at Thebes, IL; the Missouri River at Herman, MO; and the Ohio River at Grand Chain, IL (Figure 1). Samples from NASQAN sites were collected using equal-discharge-increment or equal-width-increment procedures about 15 times per year.

Analytical Procedures

Samples collected in 1991–1997 were analyzed at either the USGS National Water Quality Laboratory (NWQL) in Arvada, CO or a USGS Organic Laboratory in Lawrence, KS. Herbicides were extracted from samples by solid-phase extraction (SPE) on carbon-18 cartridges (*14, 15*) and subsequently removed from the cartridges by a small volume of either 3:1 hexane–2-propanol (NWQL) or ethyl acetate (Kansas Laboratory). The ethanesulfonic acid metabolite of alachlor (alachlor ESA) was removed by a followup elution of the SPE cartridge with methanol (*16*). Sample extracts were evaporated to a final volume of about 100 μL using nitrogen gas and were analyzed by capillary-column gas chromatography/mass spectrometry (GC/MS) with selected-ion monitoring (*14, 17*). Methanol extracts were analyzed for alachlor ESA using enzyme-linked immunosorbent assay (ELISA) (*16*). Samples collected by the Jefferson Parish Water Quality Laboratory during March through August 1993 were analyzed for herbicides by gas chromatography using USEPA protocols (*18*).

Twelve triazine and acetanilide herbicides and four metabolites are discussed in this report (Table 1). These represent the majority of herbicide usage in the Mississippi River Basin (*1*) and are the most frequently detected in streams (*6, 7*). Not all of these herbicides or metabolites were analyzed during all 7 years of sampling at Baton Rouge. Alachlor ESA was not included as an analyte until July 1993; analysis for acetochlor and cyanazine amide did not begin until 1994 (Table 1). The analytical reporting limits for samples from Baton Rouge were 0.05 to 0.2 μg/L (Table 1). Reporting limits for samples collected at NASQAN sites in 1996–1997 were 0.001 to 0.005 μg/L (*19*).

Load Calculations

Linear interpolation was used to estimate the herbicide load in the Mississippi River at Baton Rouge and at the four NASQAN sites (Figure 1). Herbicide concentrations on nonsampling days were estimated by interpolating between concentrations measured on sampling days. Measured or interpolated daily concentrations were multiplied by the mean daily discharge to estimate a daily load. Daily loads were summed to estimate a total load over a specified period of time. Herbicide load estimates allow for determination of trends in the transport of herbicides, comparisons of herbicide applications in a drainage basin to the amount leaving the basin in streams, and determination of subbasin contributions in large watersheds.

For herbicide concentrations of less than reporting limits (censored data), values of one-tenth the limit were used for

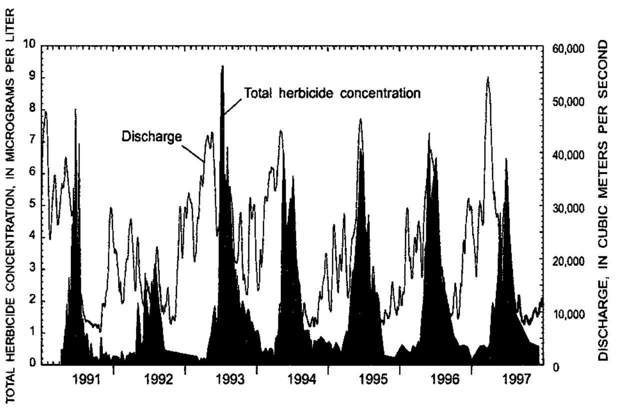

FIGURE 2. Stream discharge and total herbicide concentration in the Mississippi River at Baton Rouge, LA, 1991−1997. (The total herbicide concentration represents the sum of the herbicides and metabolites in Table 1. Note that not all of the compounds listed in Table 1 were analyzed during all years).

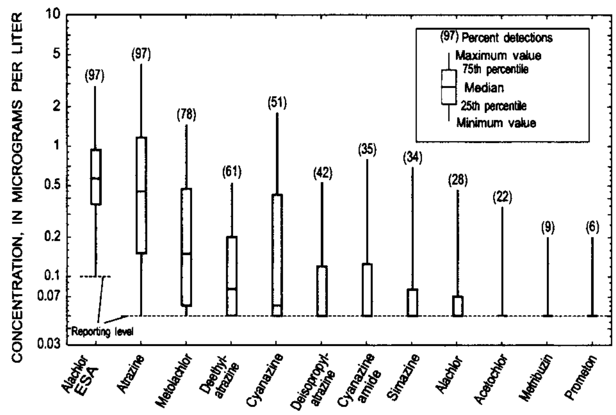

FIGURE 3. Percent detection and concentration distribution of herbicides and herbicide metabolites in samples from the Mississippi River at Baton Rouge, LA, 1991−1997. (Compounds detected in less than 5% of the samples are not shown).

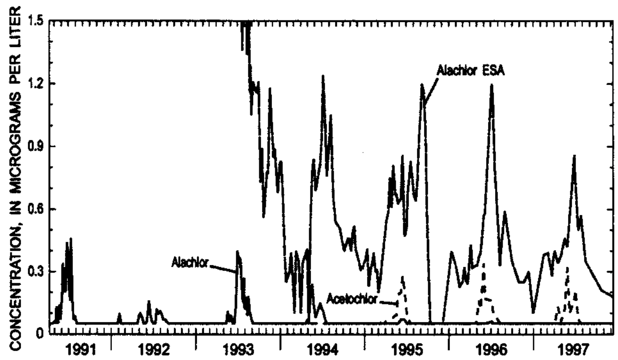

FIGURE 4. Temporal variation in concentrations of selected herbicides in samples from the Mississippi River at Baton Rouge, LA, 1991−1997.

load estimates. Sensitivity analysis indicated that for censored data, substitution of the reporting limit for one-tenth the limit resulted in a difference of less than 10% in the annual herbicide load. For the most heavily used herbicides, the difference in load estimates was substantially less than 10% because of the high frequency of detection and generally larger concentrations.

Results and Discussion

Herbicide Occurrence and Concentrations. The total herbicide concentrations (sum of the herbicides listed in Table 1) in the Mississippi River at Baton Rouge in 1991−1997 varied seasonally; the largest concentrations were in May through August (Figure 2). This seasonal pattern has been noted in many streams in the Mississippi River Basin and has been termed the "spring flush" (*11*). At Baton Rouge, peak herbicide concentrations in the Mississippi River generally lagged peak discharge, which typically occurred in late winter or early spring. Although individual herbicide concentrations in some Mississippi River Basin streams have been reported to exceed 50 μg/L, total herbicide concentrations in the Mississippi River at Baton Rouge did not exceed 10 μg/L in 1991−1997 (Figure 2). Smaller, more drawn-out herbicide peaks in the Mississippi River, compared with peaks in smaller streams, is attributable to the integrating effect of the Mississippi River, which receives input from many smaller streams. These smaller streams may drain areas of variable land use and crop groups and may deliver herbicides to the Mississippi River at different times during the growing season. Peak herbicide concentrations at Baton Rouge also may be attenuated by the presence of upstream reservoirs. Data collected at outlets of 76 Midwestern reservoirs indicate that reservoirs collect and store the spring flush of herbicides, subsequently delivering smaller concentrations downstream for longer periods of time (*20*).

Herbicides and metabolites detected in more than 50% of the samples from the Mississippi River at Baton Rouge were alachlor ESA, atrazine, metolachlor, deethylatrazine, and cyanazine (Figure 3). In general, concentrations of these five herbicides and metabolites were higher than concentrations of the other herbicides analyzed (Figure 3); although none exceeded 5 μg/L. The concentration of atrazine exceeded the maximum contaminant level (MCL) of 3 μg/L (*21*) in 11 of 271 samples (fewer than 5%). Cyanazine concentrations exceeded the health advisory (HA) of 1 μg/L (*21*) in 15 of 245 samples (6%). However, because MCLs and HAs are based on an annual average concentration, one or more exceedances of the specified value does not necessarily indicate noncompliance. Alachlor and simazine concentrations did not exceed their MCLs of 2 and 4 μg/L (*21*), respectively, and none of the average annual concentrations of the herbicides examined in this study exceeded MCLs or HAs.

Acetochlor, an acetanilide herbicide with a chemical structure and properties similar to those of alachlor and metolachlor, was first detected in the Mississippi River at Baton Rouge in 1995 (Figure 4). In 1994, the first year that acetochlor was used in the United States, it was the fifth most heavily applied corn herbicide in the Midwest (*22*). By 1996, only atrazine and metolachlor use exceeded that of acetochlor on corn in the Midwestern United States (*23*). Because acetochlor has a broader spectrum of weed control than other corn herbicides, an increase in its use is expected to reduce overall herbicide use in the United States (*24*).

The increase in the acetochlor concentrations coincided with a decrease in the concentrations of alachlor (Figure 4). However, the alachlor metabolite alachlor ESA was detected in nearly all of the samples collected during 1995 through 1997 (Figure 4). Because it has undergone dechlorination, alachlor ESA is less toxic than the parent compound (*21*) but is more mobile and persistent in the soil and water environment (*16, 25*). Numerous studies in the Midwest have documented widespread occurrence of alachlor ESA in groundwater, whereas alachlor has been detected infrequently (*26−29*). Because groundwater discharge has been identified as a primary source of herbicides to the Mississippi River during base-flow conditions (*7*), it may also be responsible for the continued presence of alachlor ESA in the river. The presence of alachlor ESA has also been documented in midwestern reservoirs well past the end of

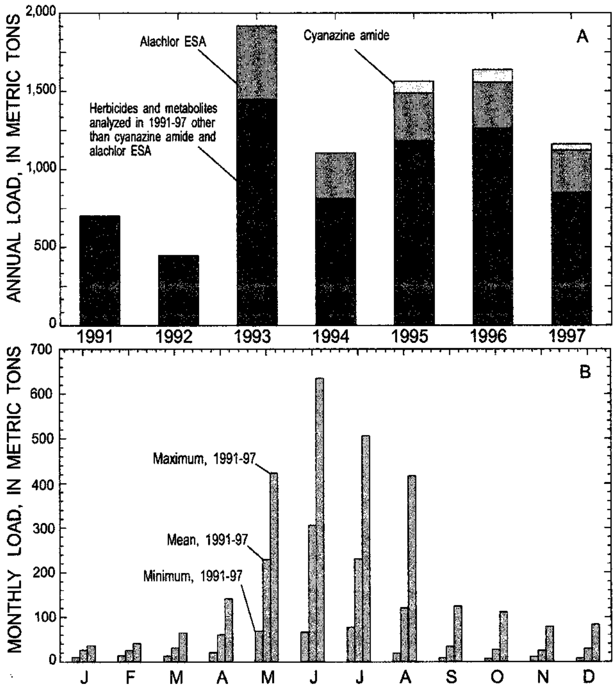

FIGURE 5. Annual and monthly loads of herbicides discharged from the Mississippi River Basin to the Gulf of Mexico, 1991−1997. (Monthly loads represent the total load of herbicides and metabolites listed in Table 1. Loads for January, February, and March are for 1992−1997; all other months are for 1991−1997).

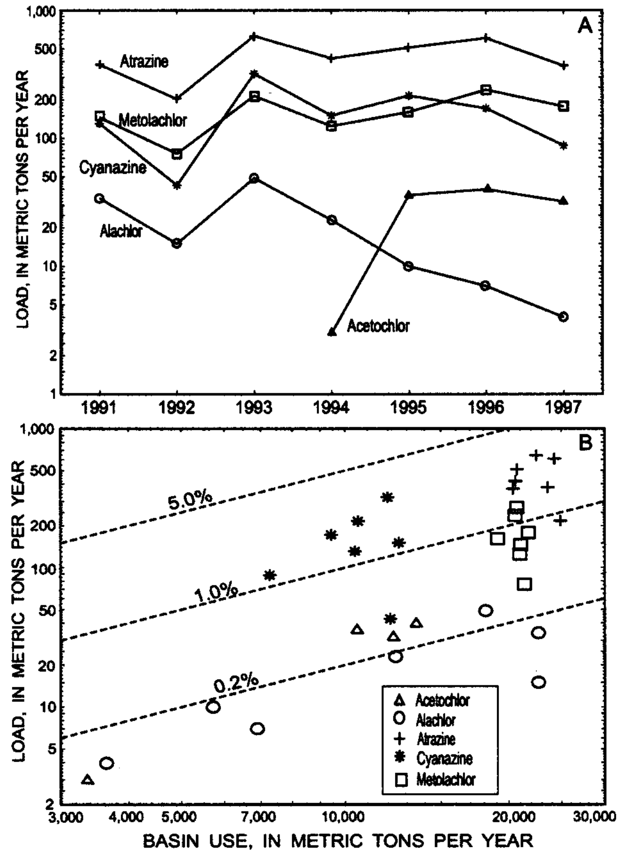

FIGURE 6. Annual load and relation of annual load and use for selected herbicides discharged to the Gulf of Mexico, 1991−1997. (Dashed lines in B are annual loads as a constant percent of annual use).

the growing season and at larger concentrations than the parent compound (*25*). Thus, the continued presence of alachlor ESA in the Mississippi River during 1995−1997 may be attributable to a number of factors. These include degradation of current-year applications of alachlor in upstream parts of the Mississippi River Basin and release of residual compound from prior year applications via ground-water and reservoir discharge.

Herbicide Load to the Gulf of Mexico. From 1991 through 1997, the annual load of herbicides from the Mississippi River Basin to the Gulf of Mexico ranged from about 450 t in 1992 to 1920 t in 1993, when extensive flooding occurred in the upper Mississippi and Missouri River Basins (Figure 5A). On average, nearly 80% of the annual herbicide load was discharged during May through August (Figure 5B). The largest mean monthly load of herbicides from 1991 to 1997 occurred during June, when an average of about 300 t, or 25% of the annual total, was discharged. In June 1995, nearly 650 t of herbicides were discharged to the Gulf of Mexico, the largest single monthly load of herbicides during 7 years of sampling.

Of the herbicides analyzed, atrazine had the largest load to the Gulf of Mexico ranging from 217 t in 1992 to 642 t in 1993. From 1991 through 1997 the annual atrazine load ranged from 0.9 to 2.9% of the total annual use in the Mississippi River Basin (Figure 6B). Only in 1992 (0.9%) was the annual load of atrazine less than 1.5% of annual use. The percentage of atrazine load would be much larger if its metabolites were included in the estimates. However, part of the metabolite load is probably residual from use during prior years. Although deisopropylatrazine is a metabolite of atrazine, it is also a metabolite of cyanazine and simazine (*30*); therefore, its presence may not be entirely attributable to atrazine use. Nevertheless, significant concentrations of deethylatrazine and deisopropylatrazine in the Mississippi River indicate that the estimates of annual percentage of atrazine load shown in Figure 7B may be conservatively low.

The annual load of cyanazine as a percentage of use was similar to that of atrazine (Figure 6B). Only in 1992 did the cyanazine load represent less than 1% of the annual use. The percentage of cyanazine load in Figure 7B also may be conservatively low because of the presence of cyanazine metabolites, primarily cyanazine amide and deisopropyla-trazine.

Of the acetanilide herbicides, metolachlor accounted for the largest proportion of the annual load to the Gulf of Mexico ranging from 76 t in 1992 to 240 t in 1996 (Figure 6A). The load of acetochlor increased from 3 t in 1994 to 40 t in 1996 in response to its increased basinwide use, while the alachlor load decreased from 49 t in 1993 to 4 t in 1997. The annual load of acetanilide herbicides, in general, represented a smaller percentage of the total basin use compared with atrazine and cyanazine (Figure 6B). The load of metolachlor was consistently about 1% of annual use, except in 1992, when the load was only 0.4% of use. The load of acetochlor was about 0.3% of annual use in 1995−1997 but less than 0.1% in 1994, the first year of acetochlor applications. The alachlor load was consistently less than 0.2% of annual use, except in 1993, when the alachlor load was about 0.3% of annual use.

Herbicide Load in Subbasins. Comparisons of load in the Mississippi River and major tributaries indicate which Mississippi River subbasins contribute the largest quantities of herbicides to the Gulf of Mexico. From January 1996 through September 1997, sites on the Mississippi River at Clinton, IA, and Thebes, IL, on the Missouri River at Herman, MO, and the Ohio River at Grand Chain, IL, were monitored for herbicides (Figure 1). Samples from the most upstream site at Clinton had the smallest concentrations of nearly all the herbicides analyzed. Atrazine concentrations at the

TABLE 2. Flux of Selected Herbicides in the Mississippi, Missouri, and Ohio Rivers from January 1996 through September 1997[a]

site	drainage area (thousands of km^2)	discharge (km^3)	flux (metric tons) acetochlor	alachlor	atrazine	cyanazine	metolachlor	simazine
Mississippi River at Clinton, IA	222	102 000	3	1	15	3	15	1
Missouri River at Herman, MO	1357	179 000	13	7	192	39	79	2
sum for sites at Clinton and Herman	1579	281 000	16	8	207	42	94	3
Mississippi River at Thebes, IL	1847	401 000	51	12	468	109	217	13
Ohio River at Grand Chain, IL	526	628 000	48	16	648	87	249	66
sum from sites at Thebes and Grand Chain	2373	1 029 000	99	28	1,116	196	466	79
Mississippi River at Baton Rouge, LA	2914	1 277 000	72	11	963	252	412	60

[a] km^2, square kilometers; km^3, cubic kilometers.

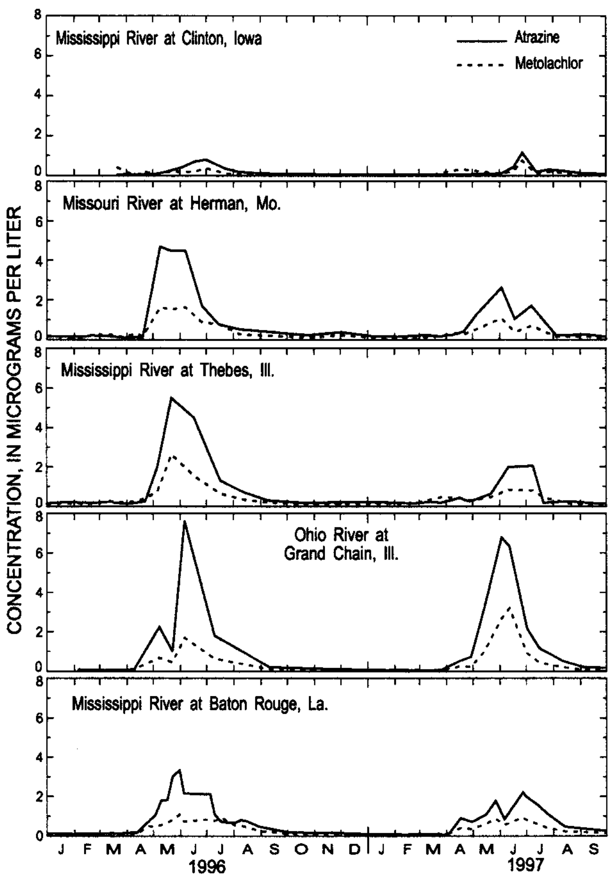

FIGURE 7. Concentrations of atrazine and metolachlor in the Mississippi, Missouri, and Ohio Rivers January 1996 through September 1997.

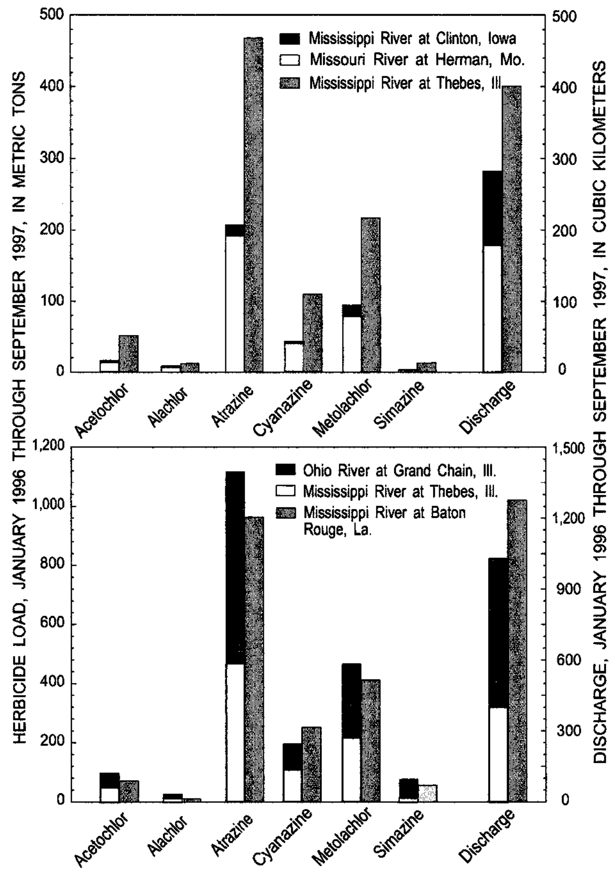

FIGURE 8. Load of selected herbicides in the Mississippi, Missouri, and Ohio Rivers January 1996 through September 1997.

Clinton site did not exceed 2 μg/L during 21 months of sampling (Figure 7). Not only were concentrations of herbicides smaller at the Clinton site, but they also generally peaked in late June or early July, about a month later than peak concentrations at the other sites. Although discharge of the Mississippi River at Clinton accounted for about 25% of the discharge downstream at Thebes, the herbicide load at Clinton accounted for less than 10% of the herbicide load at Thebes (Table 2 and Figure 8). The combined discharge of the Mississippi River at Clinton and the Missouri River at Herman, MO, accounted for about 70% of the discharge measured in the Mississippi River at Thebes. However, for most herbicides, the load at Clinton and Herman accounted for less than 50% of the load in the Mississippi River at Thebes (Figure 8). Apparently, rivers draining most of Iowa and Illinois, including the Iowa, Des Moines, and Illinois Rivers, accounted for about 30% of the discharge at Thebes and more than half of the acetochlor, atrazine, cyanazine, metolachlor, and simazine in 1996–1997. Data collected in 1991–1992 indicated that, during those years, the Illinois River alone accounted for about 20% of the herbicide load in the Mississippi River at Thebes (*9*).

Although the Ohio River Basin constitutes less than 20% of the Mississippi River Basin, from January 1996 through September 1997, it contributed about 50% of the discharge and as much as 50% or more of the herbicide load to the Gulf of Mexico. Atrazine concentrations in samples from the Ohio River at Grand Chain, IL exceeded 6 μg/L in both 1996 and 1997 (Figure 7). The load of atrazine in the Ohio River during the 21 months of sampling was about 38% larger than the load of atrazine in the Mississippi River at Thebes (Table 2 and Figure 8). The Ohio River Basin also contributed more metolachlor and simazine and about the same amount of acetochlor and alachlor as did the Mississippi River Basin upstream from Thebes. These results contrast with results of studies conducted in 1991 and 1992, when the Mississippi River Basin upstream from Thebes contributed 60% or more of the herbicide load to the Gulf of Mexico, and the Ohio River Basin contributed less than 20% (*9, 31*). Abnormally wet years in the Ohio River Basin in 1996 and 1997 probably account for this discrepancy in basin loads.

From January 1996 through September 1997, the combined discharge in the Mississippi River at Thebes and the Ohio River at Grand Chain accounted for about 80% of the discharge to the Gulf of Mexico (Table 2). However, for most herbicides, the combined load at these two sites exceeded the load to the Gulf of Mexico (Figure 8). Cyanazine, used extensively on cotton in the lower part of the Mississippi River Basin (*23*), was the only herbicide that showed a net increase in load from the confluence of the Mississippi and Ohio Rivers to the Mississippi River at Baton Rouge. Previous studies (*7*) have identified the Yazoo River Basin as a primary source of cyanazine to the lower Mississippi River. For the rest of the herbicides analyzed, some degradation of the parent compound may have occurred in the Mississippi River downstream from its confluence with the Ohio River. A study conducted during 1991 and 1992 (*9*) found that the annual alachlor load in the Mississippi River between the Ohio River confluence and Baton Rouge decreased by 30% and attributed this loss to degradation. However, in contrast to this study, the study conducted during 1991 and 1992 found that loads of atrazine and metolachlor increased in the lower Mississippi River and loads of cyanazine and simazine remained relatively unchanged.

Another possible explanation for the loss of herbicides in the lower Mississippi River during 1996 and 1997 is error in the load estimates. Several factors contribute uncertainty to the load estimates shown in Table 2. These factors include errors associated with the technique used to estimate loads, streamflow measurement, sample collection, and analytical technique. Studies have demonstrated that concentrations of herbicides in streams are highly variable during the growing season, and, during this study, the NASQAN sites were sampled only once or twice per month. Thus, large errors in load estimation can occur if peak concentrations are missed during sampling. Because different laboratories were used to analyze samples collected at the NASQAN sites and those collected at Baton Rouge, a small bias in the results from either laboratory may also result in load estimation errors.

Data collected during this and previous studies indicate that a number of factors play an important role in the occurrence and transport of herbicides in streams in the Mississippi River Basin. Factors such as temporal and spatial variations in climate, application patterns, and crop rotations may result in considerable variation in the primary source area of herbicides and in the annual herbicide load delivered to the Gulf of Mexico. In addition, because herbicide metabolites are known to exist in streams in large quantities, an understanding of their properties and transport is essential to evaluate the overall fate of herbicides in the Mississippi River Basin. Because little information currently exists, more study is also needed to evaluate the potential buildup of these compounds in the off-shore environment of the Gulf of Mexico and to understand the environmental effects on the biological communities contained therein.

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