Trends in Annual Herbicide Loads from the Mississippi River Basin to the Gulf of Mexico

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ABSTRACT

Analyses of water samples collected from the Mississippi River at Baton Rouge, Louisiana, during 1991-97 indicate that hundreds of metric tons of herbicides and herbicide metabolites are being discharged annually to the Gulf of Mexico. Atrazine, metolachlor, and the ethane-sulfonic acid metabolite of alachlor (alachlor ESA) were the most frequently detected herbicides and, in general, were present in the largest concentrations. Almost 80% of the annual herbicide load to the Gulf of Mexico occurred during the growing season from May through August. The concentrations and loads of alachlor in the Mississippi River decreased dramatically after 1993 in response to decreased use in the basin. In contrast, the concentrations and loads of acetochlor increased after 1994, reflecting its role as a replacement for alachlor. The peak annual herbicide load occurred 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 loads of atrazine and cyanazine were generally 1 to 2% of the amount annually applied in the Mississippi River drainage basin; the annual loads of acetochlor, alachlor, and metolachlor were generally less than 1%. Despite a reduction in atrazine use, historical data do not indicate a long-term downward trend in the atrazine load to the Gulf of Mexico. Although a relation (r^2=0.62) exists between the atrazine load and stream discharge during May through August, variations in herbicide use and rainfall patterns within subbasins can have a large effect on herbicide loads in the Mississippi River Basin and probably explain a large part of the annual variation in atrazine load to the Gulf of Mexico.

INTRODUCTION

Current (1999) agricultural practices in the United States rely heavily on pesticides for crop production. Of the more than 500 million kilograms (kg) of pesticides used annually in the United States to control weeds, insects, nematodes, and other pests (Gianessi and Puffer, 1991; Aspelin and others, 1992), about 20% are herbicides applied to field crops in the Mississippi River Basin (fig. 1). Principal herbicides used in the Mississippi River Basin are triazines, such as atrazine and cyanazine, and chloroacetanilides (acetanilides), such as alachlor and metolachlor (Goolsby and Battaglin, 1995). Because most triazine and acetanilide herbicides are water soluble and mobile, they can be transported to streams and ground water. The presence of herbicides in streams is a concern because of potential deleterious effects on water quality. Although most herbicides have low acute toxicity to animals, the potential effects on human health are a concern. For instance, the U.S. Environmental Protection Agency (USEPA) classifies alachlor as a probable human carcinogen, and several other herbicides, including atrazine, cyanazine, metolachlor, and simazine, are classified as possible human carcinogens (Nowell and Resek, 1994). 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 (Larson and others, 1997).

A number of studies have documented the presence of herbicides in the Mississippi River and its tributaries (Pereira and Rostad, 1990; Pereira and Hostettler, 1993). Concentrations of herbicides are largest for several weeks to several months following their application to farmlands (Wauchope, 1978; Thurman and others, 1991; Goolsby and Battaglin, 1993). In some small watersheds in the Mississippi River Basin, concentrations of herbicides in streams have been found to exceed 50 micrograms per liter (µg/L) for short periods of time following spring storms (Thurman and others, 1991; Goolsby and Battaglin, 1993). Discharges from small streams transport herbicides into large rivers such as the Mississippi. Although herbicide concentrations in large rivers are generally lower than in many small streams, the cumulative load of herbicides, which eventually discharges to the Gulf of Mexico, can be large.

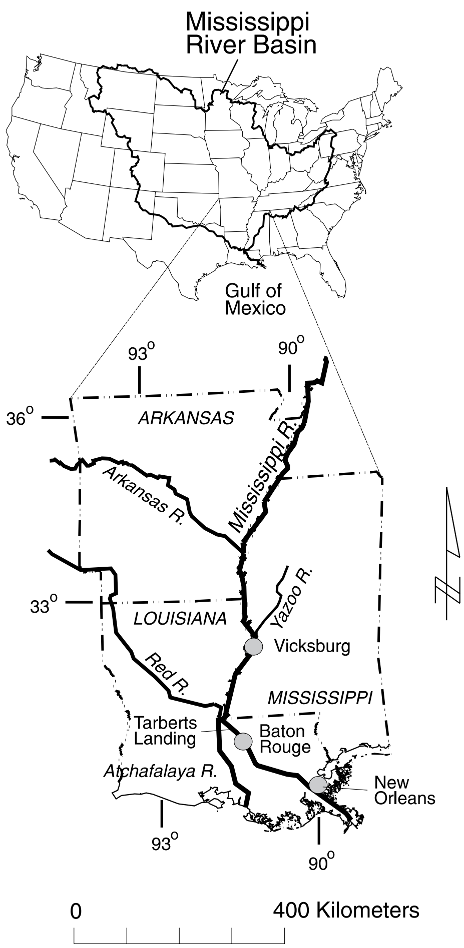

Figure 1. The Mississippi River Basin and sampling sites.

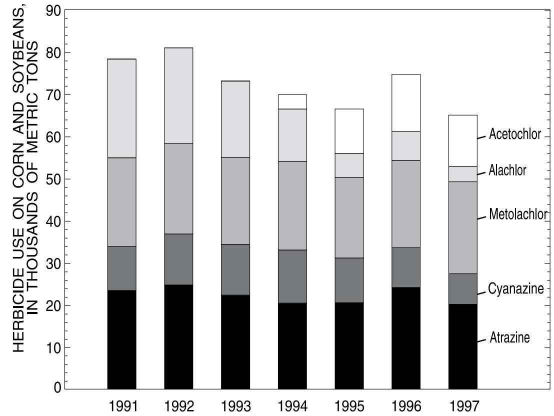

Figure 2. Use of selected herbicides on corn and soybeans in the Mississippi River Basin, 1991-97. (U.S. Department of Agriculture, 1991-97)

During 1991-97, use of five herbicides (acetochlor, alachlor, atrazine, cyanazine, and metolachlor) on corn and soybeans accounted, on average, for about 70% of the annual herbicide use on field crops in the Mississippi River Basin (U.S Department of Agriculture, 1991-97). However, some changes in the quantity and relative use of these herbicides occurred during that time (fig. 2). In 1997, the total amount of acetochlor, alachlor, atrazine, cyanazine, and metolachlor used was about 65,000 metric tons (t), a decrease of about 13,000 t from the amount used in 1991. Although atrazine and metolachlor use remained relatively stable during 1991-97, alachlor use decreased by about 19,000 t, or 85%, and cyanazine use decreased by about 3,100 t, or 30%. The introduction and use of the corn herbicide acetochlor in the United States in 1994 partially offset the decrease in alachlor and cyanazine use and, by 1996, acetochlor was the third most heavily applied herbicide on corn in the Midwestern United States. Because acetochlor has a broader spectrum of weed control than other corn herbicides have, an increase in its use is expected to reduce overall herbicide use in the United States (Capel and others, 1995).

To better understand the occurrence, temporal variability, and load of herbicides in the Mississippi River, the U.S. Geological Survey (USGS) collected herbicide data from the Mississippi River at Baton Rouge, La. (fig.

1), during 1991-97. This paper presents results from the interpretation of these data.

METHODS

Data Collection

A total of 271 water samples were collected from the Mississippi River at Baton Rouge from April 1991 through December 1997. Samples were collected on a weekly to monthly basis and ranged from 17 in 1997 to 60 in 1993. Previous work indicated that dissolved herbicides in the Mississippi River at Baton Rouge are well mixed vertically and laterally at a range of streamflow conditions (Goolsby and others, 1991). Therefore, samples were collected from the upper 6 meters (m) of the water column at the end of a pier extending about 45 m from shore. Samples were collected in glass or Teflon containers, composited in glass or stainless steel containers, and filtered through a nominal 0.7- to 1.0-micrometer pore diameter baked glass-fiber filter into baked glass bottles for shipment to the laboratory. From early March through mid-August 1993, samples were collected by the Jefferson Parish Water Quality Laboratory near New Orleans, La., about 200 kilometers (km) downstream from Baton Rouge. These samples were weekly composites of daily samples collected at two sampling points on opposite banks of the Mississippi River. A review of data collected at comparable times and analyzed by the Jefferson Parish Water Quality Laboratory and USGS laboratories indicated good agreement in analytical results (W.A. Battaglin, USGS, oral communication, 1998).

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 (fig. 1). 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 (Goolsby and others, 1991).

Analytical Procedures

Samples collected during 1991-97 were analyzed at the USGS National Water Quality Laboratory (NWQL) in Arvada, Colo., or the USGS Organic Laboratory in Lawrence, Kans. Herbicides were extracted from samples by solid-phase extraction (SPE) on carbon-18 cartridges (Meyer and others, 1993; Zaugg and others, 1995) and subsequently removed from the cartridges by a small volume of either hexane-isopropanol (NWQL) or ethyl acetate (Kansas Laboratory). The ethane-sulfonic acid metabolite of alachlor (alachlor ESA) was removed by a followup elution of the SPE cartridge with methanol (Aga and others, 1994). Sample extracts were evaporated to a final volume using nitrogen gas and were analyzed by capillary-column gas chromatography/mass spectrometry (GC/MS) with selected-ion monitoring (Thurman and others, 1990; Zaugg and others, 1995). Methanol extracts were analyzed for alachlor ESA using enzyme-linked immunosorbent assay (Aga and others, 1994). Samples collected by the Jefferson Parish Water Quality Laboratory during March through August 1993 were analyzed for herbicides by gas chromatography using USEPA protocols (Goolsby and others, 1993).

Twelve triazine and acetanilide herbicides and four breakdown products, or metabolites, are discussed in this report (table 1). These represent the majority of herbicide usage in the Mississippi River Basin (Gianessi and Puffer, 1991) and are the most frequently detected in the Mississippi River (Periera and Rostad, 1990; Periera and Hostettler, 1993; Goolsby and Battaglin, 1995). 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 the samples collected at Baton Rouge were 0.05 μg/L, except for alachlor ESA (0.10 μg/L) and cyanazine (0.05-0.20 μg/L) (table 1).

Table 1. Herbicides and herbicide metabolites analyzed in samples from the Mississippi River at Baton Rouge, Louisiana, April 1991 through December 1997.

[• g/L, micrograms per liter]

Herbicide or Metabolite	Type of herbicide	Number of samples	Years sampled	Analytical reporting limit (• g/L)
Acetochlor	acetanilide	120	1994-97	0.05
Alachlor	acetanilide	271	1991-97	0.05
Alachlor ESA	metabolite	160	1993-97	0.10
Ametryn	triazine	198	1991-97	0.05
Atrazine	triazine	271	1991-97	0.05
Cyanazine	triazine	245	1991-97	0.05-0.20
Cyanazine amide	metabolite	88	1994-97	0.05
Deethylatrazine	metabolite	245	1991-97	0.05
Deisopropylatrazine	metabolite	245	1991-97	0.05
Metolachlor	acetanilide	271	1991-97	0.05
Metribuzin	triazine	243	1991-97	0.05
Prometon	triazine	199	1991-97	0.05
Prometryn	triazine	199	1991-97	0.05
Propazine	triazine	199	1991-97	0.05
Simazine	triazine	271	1991-97	0.05
Terbutryn	triazine	115	1993-97	0.05

Load Calculations

Linear interpolation was used to estimate the herbicide load in the Mississippi River at Baton Rouge. 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. For herbicide concentrations less than reporting or method detection limits (censored data), values of one-tenth the limit were used for load estimates. Sensitivity analysis indicated that using the reporting limit or method detection limit instead of one-tenth the limit resulted in differences of less than 10% in the annual herbicide loads. For the most heavily used herbicides, the differences in load estimates were 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 concentration (sum of the herbicides listed in table 1) in the Mississippi River at Baton Rouge during 1991-97 varied seasonally; concentrations were largest during May through August (fig. 3). This seasonal pattern has been noted in many streams in the Mississippi River Basin and has been termed the “spring flush” (Thurman and others, 1991).

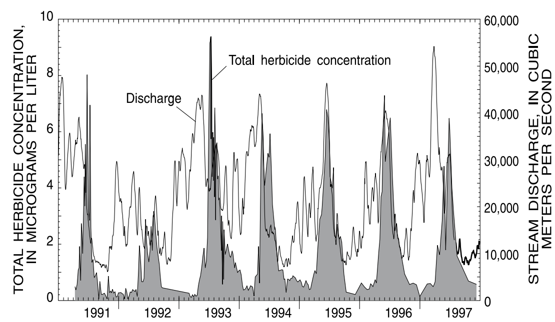

Figure 3. Stream discharge and total herbicide concentration in the Mississippi River at Baton Rouge, Louisiana, April 1991 through December 1997. [The total herbicide concentration represents the sum of the herbicides and metabolites listed in table 1. All herbicides and metabolites, however, were not sampled during all years (see table 1)]

At Baton Rouge, peak herbicide concentrations in the Mississippi River generally followed peak discharge, which typically occurred in late winter or early spring. Although individual herbicide concentrations in some small tributaries to the Mississippi River have been reported to exceed 50 µg/L, no compound exceeded 5 µg/L in the Mississippi River at Baton Rouge during 1991-97, and the total herbicide concentration did not exceed 10 µg/L (fig. 3). Smaller, more drawn-out peak herbicide concentrations in the Mississippi River, compared with those in smaller streams, are attributable to the integrating effect of the Mississippi River, which receives input from many smaller streams (Goolsby and Battaglin, 1995). These smaller streams drain areas of variable land use and crop groups and deliver herbicides to the Mississippi River at different times during the growing season. Peak herbicide concentrations at Baton Rouge also are 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 and subsequently deliver smaller concentrations downstream over longer periods of time (Battaglin and Goolsby, 1998; Stamer and others, 1999).

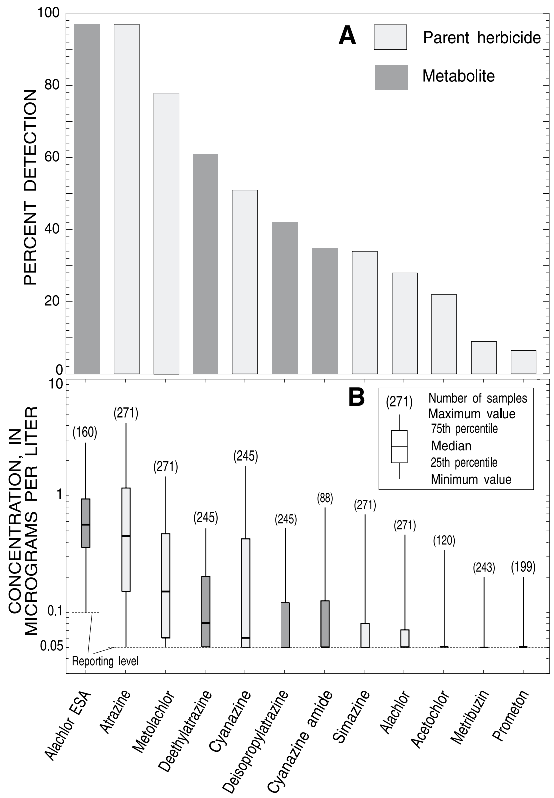

Figure 4. Percent detection and concentrations of herbicides and herbicide metabolites in samples from the Mississippi River at Baton Rouge, Louisiana, April 1991 through December 1997. (The herbicides ametryn, prometryn, propazine, and terbutryn were detected in less than 2% of samples)

Of the seven most frequently detected compounds in the Mississippi River at Baton Rouge, four were herbicide metabolites (fig. 4A). Individual herbicides and metabolites detected in more than 50% of the samples were alachlor ESA, atrazine, metolachlor, deethylatrazine, and cyanazine. In general, concentrations of these five herbicides and metabolites also were larger than concentrations of the other herbicides analyzed (fig. 4B). No herbicide or metabolite was detected at a concentration exceeding 5 µg/L. The concentration of atrazine exceeded the maximum contaminant level (MCL) of 3 µg/L (USEPA, 1995) in 11 of 271 samples (fewer than 5%). Cyanazine concentrations exceeded the health advisory (HA) of 1 µg/L in 15 of 245 samples (6%). Alachlor and simazine concentrations did not exceed their MCLs of 2 and 4 µg/L, respectively (USEPA, 1995). However, because MCLs and HAs are based on average concentrations in public water supplies over a specified time period, one or more exceedances of the specified value does not necessarily indicate noncompliance. None of the average annual concentrations of the herbicides examined in this study exceeded MCLs or HAs.

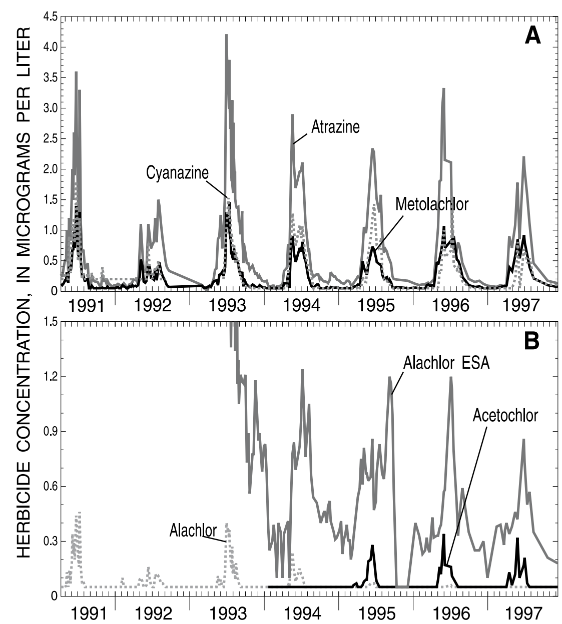

Figure 5. Temporal variation in concentrations of selected herbicides in samples from the Mississippi River at Baton Rouge, Louisiana, April 1991 through December 1997.

Concentrations of atrazine, metolachlor, and cyanazine in the Mississippi River generally peaked simultaneously in late May and early June, then decreased by the end of August (fig. 5A). Acetochlor was first detected in the Mississippi River at Baton Rouge in 1995 (fig. 5B), a year after its introduction for use in the

United States. The increase in the concentrations of acetochlor coincided with a decrease in the concentrations of alachlor (fig. 5B). However, the alachlor metabolite alachlor ESA was detected in nearly all of the samples collected during 1995 through 1997 (fig. 4A). Because it has undergone dechlorination, alachlor ESA is less toxic than the parent compound (Aga and others, 1994) but is more mobile and persistent in the soil and water environment (Thurman and others, 1996). Numerous studies in the Midwest have documented widespread occurrence of alachlor ESA in ground water, whereas alachlor has been detected infrequently (Holden and others, 1992; Baker and others, 1993; Kolpin and others, 1997; Kalkhoff and others, 1998). Because ground-water discharge has been identified as a primary source of herbicides to the Mississippi River during base-flow conditions (Periera and Hostettler, 1993), it also might be responsible for the continued presence of alachlor ESA in the river. The presence of alachlor ESA also has been documented in midwestern reservoirs well past the end of the growing season and at larger concentrations than those of the parent compound (Thurman and others, 1996). Thus, the continued presence of alachlor ESA in the Mississippi River during 1995-97 might 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 residual compounds applied during prior years and released through ground-water and reservoir discharge.

Herbicide Load to the Gulf of Mexico

During 1991-97, the annual load of herbicides from the Mississippi River Basin to the Gulf of Mexico ranged from about 450 t in 1992 to 1,920 t in 1993 (fig. 6A), when extensive flooding occurred in the upper Mississippi and Missouri River Basins. During 1993, about 640 t of atrazine, 320 t of cyanazine, 215 t of metolachlor, 53 t of simazine, and 50 t of alachlor were discharged to the Gulf of Mexico. Not all of the compounds listed in table 1 were analyzed during all years from 1991 through 1997. Nearly 80% of the annual herbicide load was discharged during May through August (fig. 6B). The monthly load of herbicides was largest during June, when an average of about 300 t, or

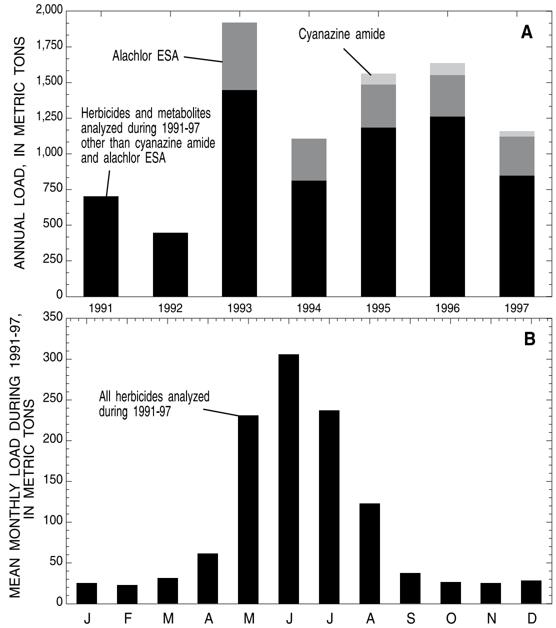

Figure 6. Annual and monthly loads of herbicides discharged from the Mississippi River Basin to the Gulf of Mexico, 1991-97. (The 1993 load of alachlor ESA represents July through December only)

25% of the annual total, was discharged. In June 1995, nearly 650 t of herbicides was discharged to the Gulf of Mexico, the largest single monthly load of herbicides in the Mississippi River during 7 years of sampling.

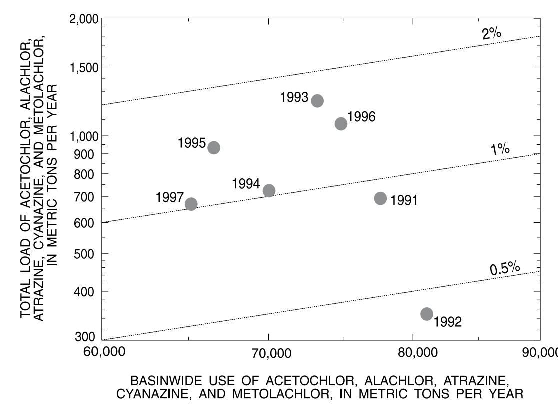

Figure 7. Relation of total annual load and use for five herbicides discharged from the Mississippi River Basin to the Gulf of Mexico, 1991-97. (Lines are annual load as a constant percentage of annual use)

The total loads of acetochlor, alachlor, atrazine, cyanazine, and metolachlor as a percentage of total basinwide use varied during 1991-97 (fig. 7). Use of these five herbicides was largest in 1992, when more than 81,000 t was applied to crops in the Mississippi River Basin. However, the total load of these five herbicides in 1992 was only about 350 t, less than 0.5% of the use total. Conversely, in 1993 the use total was about 73,000 t, but the total load was about 1,200 t, or about 1.6% of the use.

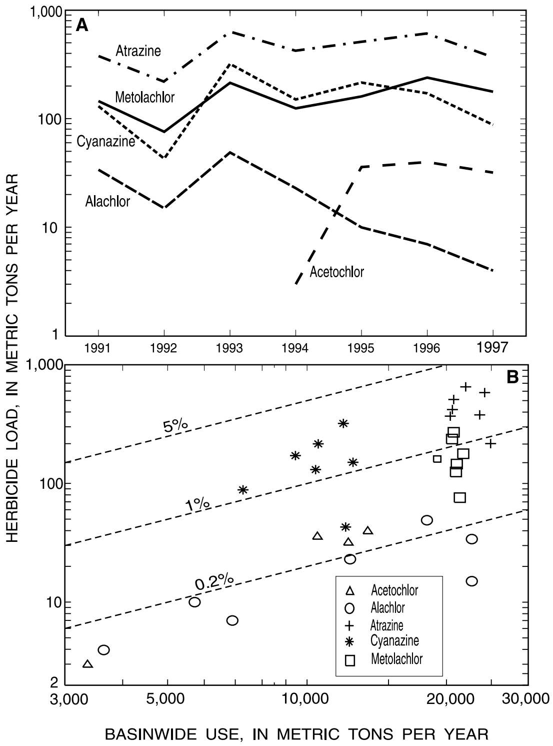

Figure 8. Annual loads and relation of total annual load and use for five herbicides discharged from the Mississippi River Basin to the Gulf of Mexico, 1991-97. (Lines in B are annual load as a constant percentage of annual use)

Of the herbicides analyzed, atrazine accounted for the largest proportion of the annual load to the Gulf of Mexico and ranged from about 220 t in 1992 to about 640 t in 1993 (fig. 8A). During 1991-97, the average annual load of atrazine represented about 2% of its basinwide use. Only in 1992 (0.9%) was the annual load of atrazine less than 1.5% of annual use (fig. 8B). If the loads of atrazine metabolites (deethylatrazine and deisopropylatrazine) were included with the load of atrazine, the average annual load would represent about 3% of the annual basinwide use of atrazine. The annual load of cyanazine as a percentage of use was similar to that of atrazine (fig. 8B), averaging about 1.5% of basinwide use during 1991 through 1997. Only in 1992 did the cyanazine load represent less than 1% of the annual use. During 1995 through 1997, the combined load of cyanazine and cyanazine amide (the primary metabolite of cyanazine), on average, accounted for about 2.4% of the cyanazine used in the Mississippi River Basin.

Of the acetanilide herbicides, metolachlor accounted for the largest proportion of the annual load to the Gulf of Mexico and ranged from 76 t in 1992 to 240 t in 1996 (fig. 8A). The load of acetochlor increased from less than 5 t in 1994 to 40 t in 1996 in response to its increased basinwide use, whereas the load of alachlor decreased from 49 t in 1993 to less than 5 t in 1997. The annual load of acetanilide herbicides, in general, represented a smaller percentage of the total basinwide use than the loads of atrazine and cyanazine (fig. 8B). The average annual loads of metolachlor, acetochlor, and alachlor, all acetanilide herbicides, represented 0.8, 0.3, and 0.15% of their basinwide use, respectively.

Long-Term Atrazine Load

Atrazine data for the Mississippi River at Vicksburg, Miss., from 1975 to 1990, in combination with the data collected for this study during 1991-97, provide information about long-term trends in the atrazine load to the Gulf of Mexico. Starting in 1975, in response to concerns about the city of New Orleans' drinking-water supply, Ciba-Geigy Corporation established a monitoring program to evaluate the presence of atrazine in the Mississippi River (Ciba-Geigy Corporation, 1992). Width-integrated samples were collected from the Mississippi River at Vicksburg 20 to 50 times per year and analyzed by gas chromatography with confirmation by GC/MS. Daily discharge data for the Mississippi River at Vicksburg were provided by the U.S. Army Corps of Engineers and were assumed to be comparable to discharge in the Mississippi River at Baton Rouge plus the discharge diverted to the Atchafalaya River.

Annual use estimates of herbicides in the Mississippi River Basin indicate that atrazine use has declined substantially since the mid-1970’s and early 1980’s (Gianessi, 1992). In 1976, about 38,000 t of atrazine was applied in the Mississippi River Basin. Applications declined to about 32,000 t in 1982 and to 20,000-25,000 t during 1991-97. However, estimates of the annual load of atrazine to the Gulf of Mexico during 1975-97 do not reflect the reduction in its annual basinwide use over the same period (fig. 9). During 1975-80 and 1987-92 (excluding 1990, when atrazine data at Vicksburg were unavailable), the atrazine load to the Gulf of Mexico was, in general, less than the 22-year average of about 370 t (fig. 9). In contrast, the annual atrazine load during 1981-86 and 1993-96 exceeded the long-term average.

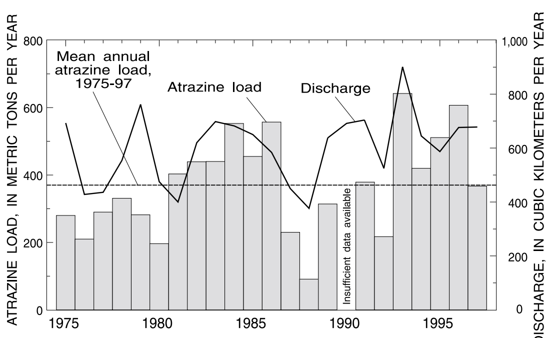

Figure 9. Annual discharge and atrazine load from the Mississippi River Basin to the Gulf of Mexico, 1975-97.

Annual variations in stream discharge during the growing season appear to be a better predictor of atrazine load in the Mississippi River than does annual atrazine use in the basin. Regression of the atrazine load with stream discharge during May through August explains a large part (r^2=0.62) of the annual variation (fig. 10A). However, on the basis of the regression residuals, a long-term downward trend in atrazine load from 1975 to 1997 is not apparent as a result of the decrease in basinwide atrazine use (fig. 10B). An apparent increase in the annual May through August 1975-97 discharge in the Mississippi River (fig. 10C) might be responsible for offsetting the basinwide decrease in atrazine use during the same period. Numerous factors influence the load of atrazine in the Mississippi River, and available data are insufficient to observe gradual trends in atrazine load to the Gulf of Mexico. Variations in herbicide application rates and storm patterns within subbasins can have a large effect on the herbicide load in the Mississippi River and probably explain a large part of the annual variation in atrazine load to the Gulf of Mexico. Subbasins contribute variable amounts of herbicides to the Mississippi River each year, depending on farming practices and climatic conditions. Long-term data from individual subbasins are needed to explain long-term variability in the loads of herbicides to the Gulf of Mexico.

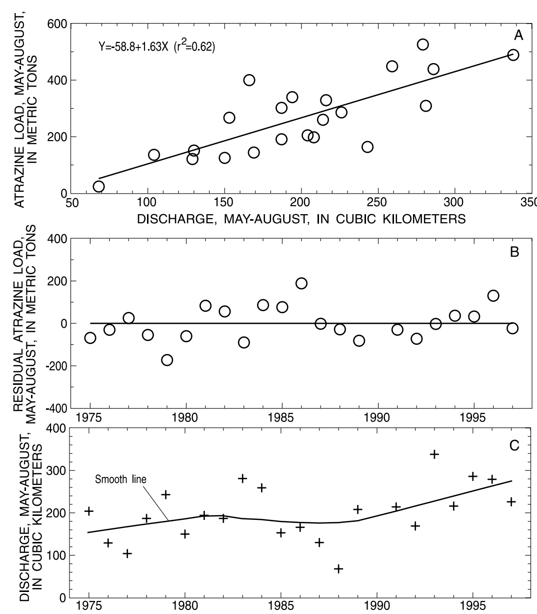

Figure 10. Relation of discharge and atrazine load, May-August, in the Mississippi River at Vicksburg, Mississippi, and Baton Rouge, Louisiana, 1975-97. (1975-89 data are for Vicksburg; 1991-97 data are for Baton Rouge)

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