OCCURRENCE AND TRANSPORT OF AGRICULTURAL CHEMICALS

IN THE MISSISSIPPI RIVER BASIN

JULY THROUGH AUGUST 1·9·9·3

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U.S. GEOLOGICAL SURVEY CIRCULAR 1120-C

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Back Cover—View of Spirit of St. Louis Airport, Chesterfield, Mo. (Srenco Photography, St. Louis, Mo.)
Field Hydrologist making streamflow measurements (U.S. Geological Survey)

OCCURRENCE AND TRANSPORT OF AGRICULTURAL CHEMICALS IN THE MISSISSIPPI RIVER BASIN, JULY THROUGH AUGUST 1993

By Donald A. Goolsby, William A. Battaglin, and E. Michael Thurman

Floods in the Upper Mississippi River Basin, 1993

U.S. GEOLOGICAL SURVEY CIRCULAR 1120-C

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FOREWORD

During spring and summer 1993, record flooding inundated much of the upper Mississippi River Basin. The magnitude of the damages—in terms of property, disrupted business, and personal trauma—was unmatched by any other flood disaster in United States history. Property damage alone is expected to exceed $10 billion. Damaged highways and submerged roads disrupted overland transportation throughout the flooded region. The Mississippi and the Missouri Rivers were closed to navigation before and after the flooding. Millions of acres of productive farmland remained under water for weeks during the growing season. Rills and gullies in many tilled fields are the result of the severe erosion that occurred throughout the Midwestern United States farmbelt. The hydrologic effects of extended rainfall throughout the upper Midwestern United States were severe and widespread. The banks and channels of many rivers were severely eroded, and sediment was deposited over large areas of the basin's flood plain. Record flows submerged many areas that had not been affected by previous floods. Industrial and agricultural areas were inundated, which caused concern about the transport and fate of industrial chemicals, sewage effluent, and agricultural chemicals in the floodwaters. The extent and duration of the flooding caused numerous levees to fail. One failed levee on the Raccoon River in Des Moines, Iowa, led to flooding of the city's water treatment plant. As a result, the city was without drinking water for 19 days.

As the Nation's principal water-science agency, the U.S. Geological Survey (USGS) is in a unique position to provide an immediate assessment of some of the hydrological effects of the 1993 flood. The USGS maintains a hydrologic data network and conducts extensive water-resources investigations nationwide. Long-term data from this network and information on local and regional hydrology provide the basis for identifying and documenting the effects of the flooding. During the flood, the USGS provided continuous streamflow and related information to the National Weather Service (NWS), the U.S. Army Corps of Engineers, the Federal Emergency Management Agency (FEMA), and many State and local agencies as part of its role to provide basic information on the Nation's surface- and ground-water resources at thousands of locations across the United States. The NWS has used the data in forecasting floods and issuing flood warnings. The data have been used by the Corps of Engineers to operate water diversions, dams, locks, and levees. The FEMA and many State and local emergency management agencies have used USGS hydrologic data and NWS forecasts as part of the basis of their local flood-response activities. In addition, USGS hydrologists are conducting a series of investigations to document the effects of the flooding and to improve understanding of the related processes. The major initial findings from these studies will be reported in this Circular series as results become available.

U.S. Geological Survey Circular 1120, *Floods in the Upper Mississippi River Basin, 1993*, consists of individually published chapters that will document the effects of the 1993 flooding. The series includes data and findings on the magnitude and frequency of peak discharges; precipitation; water-quality characteristics, including nutrients and man-made contaminants; transport of sediment; assessment of sediment deposited on flood plains; effects of inundation on ground-water quality; flood-discharge volume; effects of reservoir storage on flood peaks; stream-channel scour at selected bridges; extent of flood-plain inundation; and documentation of geomorphologic changes.

Robert M. Hirsch

Acting Director
September 24, 1993

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Occurrence and Transport of Agricultural Chemicals in the Mississippi River, July Through August 1993

By Donald A. Goolsby, William A. Battaglin, *and* E. Michael Thurman

Abstract

Heavy rainfall and severe flooding in the upper Mississippi River Basin from mid-June through early August 1993 flushed extraordinarily large amounts of agricultural chemicals (herbicides and nitrate) into the Mississippi River, many of its tributaries, and, ultimately, the Gulf of Mexico. Even though extremely high streamflows were recorded during the flood in 1993, concentrations of herbicides, such as atrazine, alachlor, cyanazine, and metolachlor, were similar to the maximum concentrations measured during spring and summer 1991 and 1992. It was anticipated that the higher streamflows during the flood would dilute the concentrations of herbicides that are usually flushed into streams in late spring and summer. Instead, concentrations were similar to those measured during much lower flows, but the daily loads of herbicides transported in some reaches of the Mississippi River were higher than those measured in 1991 and 1992. The total atrazine load transported to the Gulf of Mexico from April through August 1993 (539,000 kilograms) was about 80 percent higher than that for the same period in 1991 and 235 percent higher than for the same period in 1992. The concentrations of atrazine and cyanazine in a few individual samples exceeded health-based limits for drinking water. However, because drinking-water regulations are based on the average of at least four quarterly samples, the annual average concentrations in the Mississippi River probably will not exceed these limits for 1993. Nitrate concentrations were similar to those measured during spring and summer 1991 and 1992. The loads of nitrate-nitrogen transported into the Gulf of Mexico during July and August 1993 were as much as 5,734 metric tons per day. These loads generally are similar to those measured in spring 1991 and 1992 but larger than those measured in summer 1991 and 1992. The total nitrate-nitrogen load transported to the Gulf of Mexico from April through August 1993 (827,000 metric tons) was about 37 percent larger than that for this same period in 1991 and 112 percent larger than that for the same period in 1992. The transport of extraordinarily high loads of nitrate and large amounts of fresh-water into the Gulf of Mexico during midsummer when primary production is highest could increase phytoplankton biomass and affect the gulf ecosystem along the Louisiana coast.

INTRODUCTION

Flooding was severe throughout parts of the upper Mississippi River Basin from mid-June through early August 1993 as a result of extraordinary amounts of rainfall. Rainfall during July was more than 200 percent of normal (1961–90) July rainfall over parts of nine upper Midwestern States (Wahl and others, 1993), and record peak discharges were recorded at more than 40 U.S. Geological Survey (USGS) streamflow-gaging stations (Parrett and others, 1993). The cool, wet conditions that preceded the flooding delayed planting by several weeks in some areas (Iowa Agricultural Statistics, 1993). The heavy rainfall and flooding began shortly after most crops were planted and agricultural chemicals, such as herbicides, were applied to cropland. Previous studies by the USGS (Goolsby and others, 1991; Thurman and others, 1991, 1992; Goolsby and

Battaglin, 1993) have shown that large amounts of the herbicides applied to recently planted crops can be flushed from cropland during storm runoff. Consequently, the heavy rainfall that produced the record flooding could flush large amounts of herbicides into streams and ground water. Nitrate concentrations also can be high in some streams during periods of heavy rainfall in spring and early summer (Goolsby and Battaglin, 1993; Lucey and Goolsby, 1993). Therefore, the upper Mississippi River Basin flooded at the time of the year when the potential for adverse effects on the quality of surface and ground water from agricultural chemicals was greatest. High concentrations of agricultural chemicals in streams are of concern because they can affect the suitability of the water for use as public water supplies and can have adverse effects on stream biota.

Purpose and Scope

The purpose of this report is to present and summarize information on the concentrations and transport of agricultural chemicals (herbicides and nitrate) in the Mississippi River during the peak and recession stages of flooding in July and August 1993. Pertinent results from USGS regional studies of agricultural chemicals in streams in the Mississippi River Basin during 1989 and 1990 are discussed, as well as background information on results from a study of the distribution and transport of these chemicals in the Mississippi River from April 1991 through September 1992. Information on the usage and properties of agricultural chemicals frequently detected in streams in the Mississippi River Basin also is presented. The concentrations and loads of herbicides and nitrate during the 1993 flood are compared with those from previous studies. The 1993 flood data presented in this paper are limited to the chemical and hydrologic data available at the end of August 1993.

Sources and Properties of Selected Agricultural Chemicals

The Mississippi River Basin contains the largest and most intensive agricultural region in the country. This region, which includes about 65 percent of the total harvested cropland in the Nation (fig. 1; U.S. Department of Commerce, 1989), produces more than 80 percent of the corn and soybeans grown in the country and much of the cotton, rice, sorghum, and wheat. To increase yields from these crops, large amounts of pesticides and nitrogen fertilizers are used. On the basis of the latest available estimates (1987 through 1989 for pesticides, 1991 for nitrogen fertilizer), it is estimated that more than 100,000 metric tons (t) of pesticides (herbicides, insecticides, fungicides) and about 6.3 million t of nitrogen fertilizers (as nitrogen) were applied to cropland in the Mississippi River Basin in 1991 (U.S. Environmental Protection Agency, 1990; Gianessi and Puffer, 1991; U.S. Department of Agriculture, 1992; J.J. Fletcher, West Virginia University, written commun., 1992).

Herbicides, which are used to control weeds and grasses, account for more than 80 percent of the agricultural use of pesticides in the United States (U.S. Department of Agriculture, 1992). The 20 most heavily used herbicides and the estimated amounts used annually in the United States and in the Mississippi River Basin are shown in figure 2. Herbicides, such as atrazine, alachlor, cyanazine, and metolachlor, used in the production of corn, soybeans, and sorghum are among the most heavily used herbicides. The estimated annual use of these herbicides upstream from selected locations on the Mississippi River and several major tributaries is listed in table 1. The annual estimates for herbicide use shown in figure 2 and table 1 are for 1987 through 1989 (Gianessi and Puffer, 1991). The actual usage for these herbicides in 1993 could be higher or lower than the estimates listed in the table; for example, the nationwide use of cyanazine increased nearly 25 percent between 1989 and 1991 (Dr. Patti Tillotson, Dupont Agricultural Products, written commun., 1993). For atrazine, the annual use probably has decreased in recent years because of a reduction in the recommended application rate (U.S. Department of Agriculture, 1993).

Nitrogen fertilizers are used extensively on crops in the Mississippi River Basin to increase yields. Many forms of commercial fertilizers are used, including anhydrous ammonia, ammonium nitrate, ammonium sulfate, and urea. Other sources of nitrogen in the Mississippi River Basin include animal wastes (cattle, hogs, poultry), domestic sewage, legumes, and mineralization of vegetation and soil organic matter. Very little specific information is available to quantify nitrogen sources other than commercial nitrogen fertilizer. The estimated use of commercial nitrogen fertilizer in 1991 upstream from selected locations on the Mississippi River and several major tributaries is listed in table 1.

Herbicides and nitrogen derived from point and nonpoint sources in the Mississippi River Basin can be transported into the Mississippi River in runoff from agricultural and urban areas, discharge from reservoirs and aquifers, and atmospheric deposition (Goolsby, Thurman, and others, 1993). The physiochemical properties of the herbicides, as well as such factors as usage, rainfall patterns and intensity, and farming practices, are important in governing the amounts and concentrations of these chemicals in streams. Several important physiochemical properties of the most widely used and most frequently detected herbicides in the Mississippi River basin are listed in table 2. These properties include water solubility, soil sorption coefficient (K_{oc}), and soil half-life. Water solubility determines how easily herbicides wash off soil and crop residues and leach through the soil. Herbicides with solubilities of greater than about 30 milligrams per liter (mg/L) are considered to be soluble and are likely to wash off the soil during storms (Becker and others, 1989). Those with solubilities of less than about 1 mg/L are likely to remain on the soil surface. The K_{oc} is a measure of the tendency of a herbicide to attach to soil particles. The larger the K_{oc} value, the more strongly the herbicide will be adsorbed to soil particles. Those with K_{oc} values of less than about 500 milliliters per gram (mL/g) tend to be transported primarily in the dissolved phase (Becker and others, 1989). Those with K_{oc} values of more than 1,000 mL/g are transported primarily on suspended-sediment particles. Soil half-life is the length of time required for herbicides to degrade in the soil to one-half of their previous concentration. The longer the soil half-life, the more persistent the herbicide is and the longer it will be available to wash off in storm runoff. Once herbicides are in surface water, the half-life generally is much longer than in soil because surface water contains much less organic matter and fewer microorganisms to degrade the herbicides.

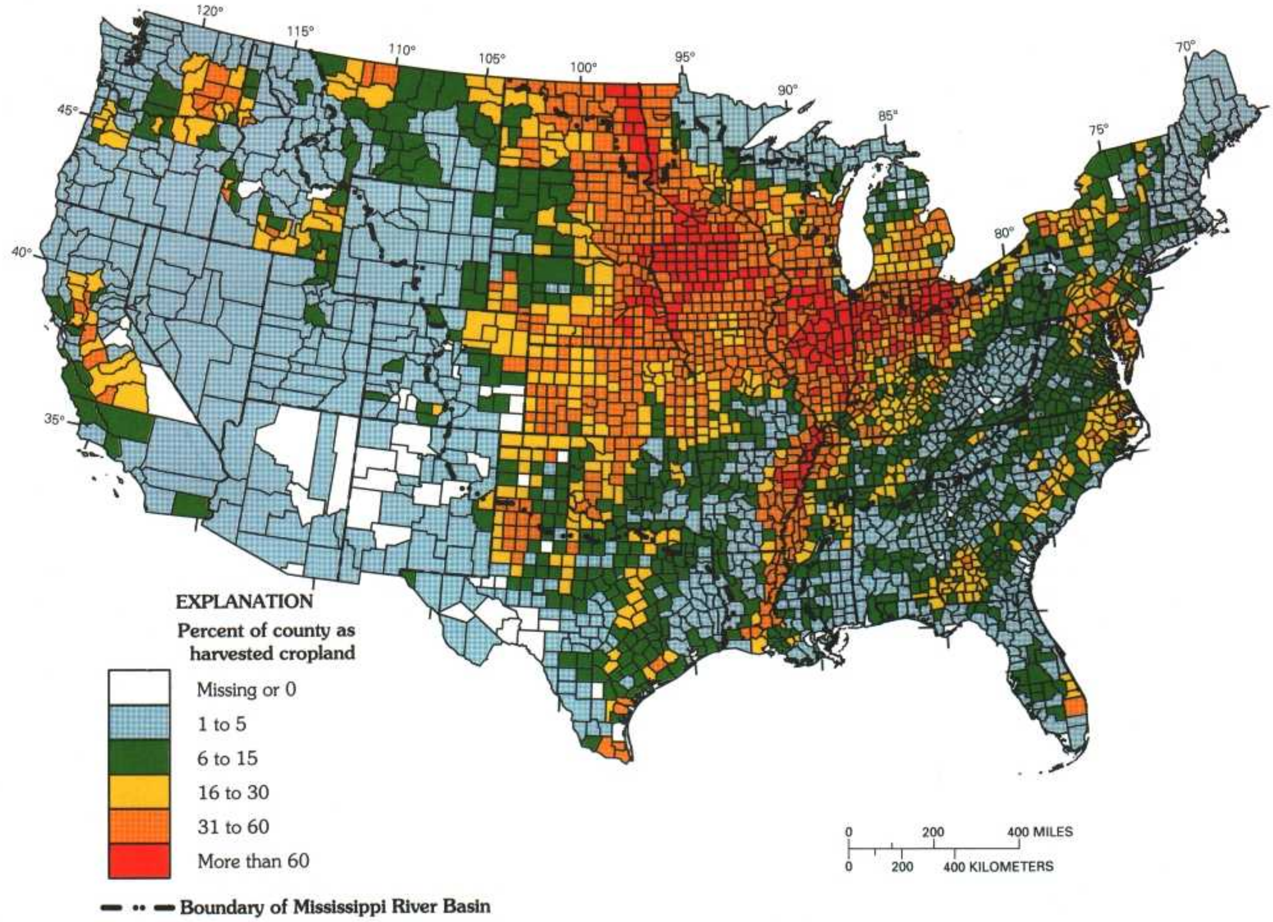

Figure 1. Harvested cropland for each county in the United States, expressed as a percentage of the total area of each county (U.S. Department of Commerce, 1989).

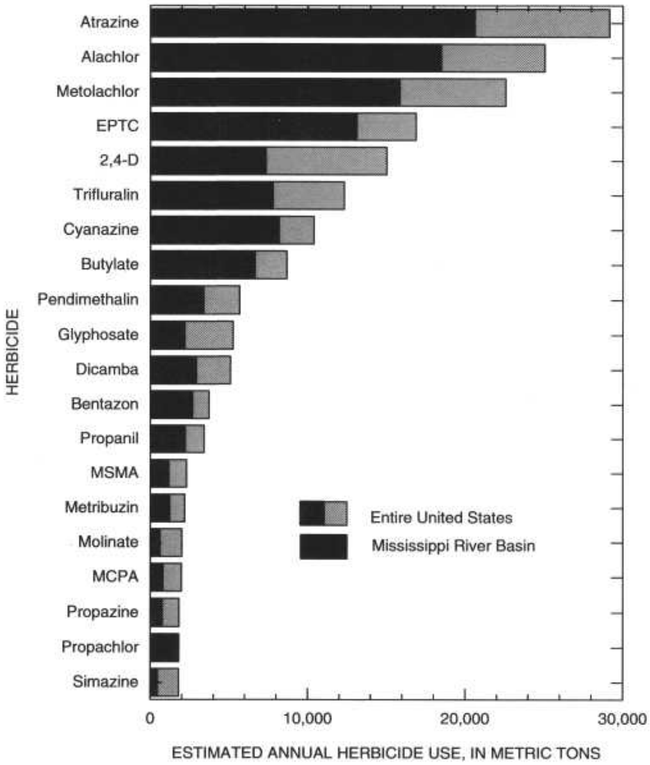

Figure 2. Estimated annual herbicide use in the United States and the Mississippi River Basin from 1987 through 1989 (Gianessi and Puffer, 1991).

Some herbicides can persist for long periods of time in reservoirs where runoff from late spring and summer storms is often stored for many months (Goolsby, Battaglin, and others, 1993). However, little specific information is available on herbicide half-lives in natural water bodies.

The physiochemical properties listed in table 2 indicate that soluble and mobile herbicides, such as atrazine, alachlor, cyanazine, and metolachlor, are transported primarily in the dissolved phase. This group includes the majority of herbicides in use today. However, the soil half-life and such factors as intensity of use; application methods; timing, intensity, and duration of rainfall; and antecedent soil moisture conditions also are important in determining the amounts of herbicides that can be transported into streams.

Much of the nitrogen transported by the Mississippi River is primarily nitrate and various forms of dissolved and particulate organic nitrogen. Small amounts of ammonium and nitrite also are usually present, but these compounds generally are intermediate products in the oxidation of nitrogen compounds to nitrate in well-oxygenated streams. Nitrate is highly soluble and mobile in streams and also is a plant nutrient, which can be readily assimilated in the reproduction and growth of aquatic plants. However, if plant growth and primary production are minimal, as they typically are in streams with high suspended-sediment concentrations and little light penetration, such as the Mississippi River, then nitrate can behave as a conservative solute.

Table 1. Estimated annual use of atrazine, alachlor, cyanazine, and metolachlor from 1987 through 1989, and commercial nitrogen fertilizer during 1991 upstream from selected locations in the Mississippi River Basin

[t, metric tons; km², square kilometers. Source of herbicide data—Gianessi and Puffer (1991); Source of fertilizer data—U.S. Environmental Protection Agency (1990); J.J. Fletcher, West Virginia University, written commun., 1992]

Location	Upstream drainage area, (km^2)	Estimated application (t)				
		Atrazine	Alachlor	Cyanazine	Metolachlor	Nitrogen
Mississippi River at Clinton, Iowa.	222,000	1,440	2,040	1,590	1,630	607,000
Illinois River at Valley City, Illinois.	69,000	1,960	1,880	715	1,760	450,000
Missouri River at Hermann, Missouri.	1,357,000	6,280	4,660	1,970	3,490	1,930,000
Mississippi River at Thebes, Illinois.	1,847,000	13,400	12,200	6,210	11,000	4,055,000
Ohio River at Grand-Chain, Illinois.	526,000	5,060	4,900	1,440	3,440	1,133,000
Mississippi River at Baton Rouge, Louisiana.	2,914,000	20,600	18,500	8,170	15,800	6,263,000

Table 2. Physiochemical properties, health-based limits for drinking water, and Canadian aquatic-life guidelines for selected commonly used herbicides and nitrate

[mg/L, milligrams per liter; mL/g, milliliters per gram; μg/L, micrograms per liter; - -, no data or none available]

Chemical compound	Water solubility[1] (mg/L)	Soil sorption coefficient (K_{oc})[1] (mL/g)	Soil half-life (days)[1]	Maximum contaminant level[2]	Health advisory level[2] (μg/L)	Canadian aquatic-life guidelines (μg/L)
Alachlor	240	170	15	2 μg/L	- -	- -
Atrazine	33	100	60	3 μg/L	3	[3]2
Cyanazine	170	190	14	- -	1	[4]2
Metolachlor	530	200	20	- -	100	[5]8
Metribuzin	1,220	41	30	- -	200	[6]1
Simazine	6.2	138	75	4 μg/L	4	[7]10
Nitrate	Very large..	- -	- -	10 mg/L	- -	- -

[1]Becker and others (1989).
[2]U.S. Environmental Protection Agency (1992).
[3]Trotter and others (1990).
[4]Pauli and others (1991a).
[5]Kent and others (1991).
[6]Pauli and others (1990).
[7]Pauli and others (1991b).

Drinking-Water Standards and Aquatic-Life Guidelines

Maximum contaminant levels (MCL), or drinking-water standards, have been established by the U. S. Environmental Protection Agency (1992) for several herbicides and nitrate (table 2). MCL's for herbicides are based on annual average concentrations and are legally enforceable under the Safe Drinking Water Act (1986). Annual average concentrations of herbicides are determined from analyses of a minimum of four quarterly samples per year, and the standards are violated only if the average concentration in these samples exceeds the MCL. Further, MCL's for herbicides apply to water delivered at the tap and not the raw water source. However, conventional water treatment removes little of the water-soluble herbicides currently (1993) used in the Mississippi River Basin. At present (1993), MCL's have been established only for individual compounds and do not address the possible effects of complex mixtures of herbicides and their degradation products.

Unlike herbicides, the MCL for nitrate is based on a single sample and not an annual average. If a water sample from a public water supply exceeds 10 mg/L, then a second sample is collected to confirm the original sample. If the average of these two samples exceeds 10 mg/L, then the water supply is not in compliance with the Safe Drinking Water Act.

Health advisory levels (HA) have been established by the U.S.Environmental Protection Agency (USEPA) for several herbicides that do not have MCL's. HA's are the recommended maximum concentrations in drinking water for lifetime exposure and are not legally enforceable. However, in time, the lifetime HA's for some herbicides could become enforceable MCL's. HA's for a few selected herbicides are listed in table 2.

Some herbicides can have adverse effects on aquatic life, but at present (1993), the USEPA has established standards or criteria for aquatic life for few of the current generation herbicides. However, the Canadian Government (Environment Canada) has established water-quality guidelines for specific water uses in Canada that include drinking water, aquatic life, and agricultural uses of water (Wong and Kent, 1988). The guidelines are numerical concentrations recommended to support and maintain a designated water use. Because no U.S. guidelines or criteria for aquatic life have been established for most herbicides in current use, the Canadian herbicide water-quality guidelines, where available, have been included in table 2 as a point of reference for herbicide concentrations measured in the Mississippi River Basin.

Previous Studies of Agricultural Chemicals in the Mississippi River Basin

Several regional studies of herbicides, insecticides, and nitrate in surface waters of the Mississippi River Basin have been done since 1989. These studies show that the occurrence and transport of herbi-

herbicides is seasonal; concentrations are highest within a period of about 3 months after application. A 1989 study of 147 streams that drain areas of from about 200 to more than 100,000 square kilometers (km^2) showed that herbicide concentrations increased from near analytical reporting limits [0.05 microgram per liter (µg/L)] before planting to more 100 µg/L in a few streams during storm runoff after planting (Thurman and others, 1991, 1992; Goolsby and Battaglin, 1993). Median concentrations of alachlor, atrazine, and cyanazine were 0.92, 3.8, and 0.97 µg/L, respectively, during the postplanting sampling period. Median concentrations of these three herbicides before planting and in the fall were less than 0.3 µg/L.

Frequent sampling (two to four times per day during storms) of nine streams during 1990 by using automatic samplers indicated that for periods of several weeks to about 3 months following application of herbicides, elevated herbicide concentrations persisted during storm runoff (Goolsby and Battaglin, 1993). Herbicide concentrations were highest during runoff from the first storms after application (fig. 3). Between storms, as overland flow ceased and streamflow decreased, herbicide concentrations decreased and commonly approached preplanting levels. Peak

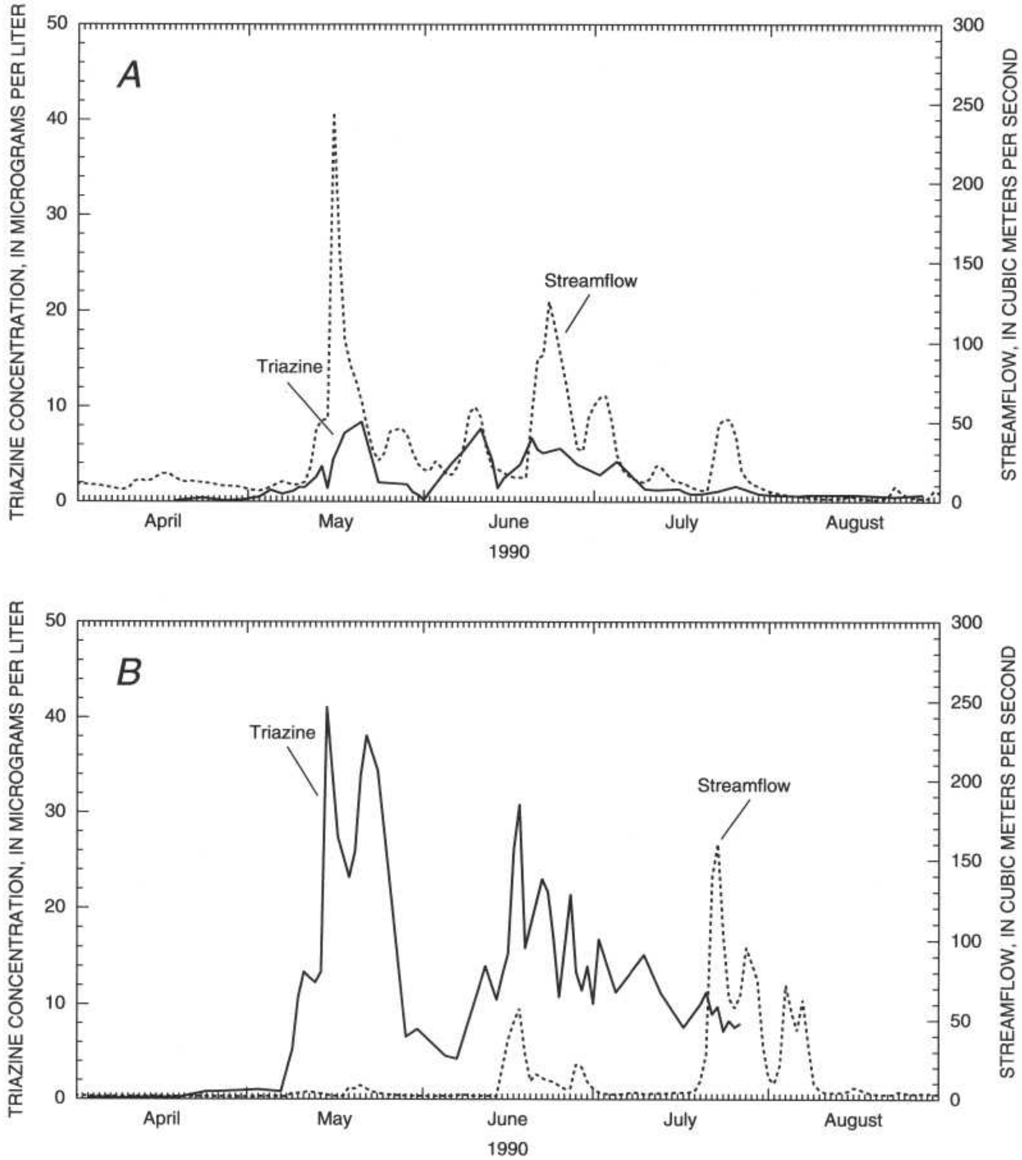

Figure 3. Streamflow and temporal distribution of triazine herbicide concentrations as determined by immunoassay analysis in 1990. *A*, Sangamon River in Illinois; *B*, West Fork Big Blue River in Nebraska.

herbicide concentrations in these streams tended to decrease with runoff from each subsequent storm (fig. 3). Concentrations of triazine herbicides were determined by immunoassay, which is an analytical method that uses antibodies to detect and quantify specific compounds or groups of compounds in water and other materials. The triazine immunoassay primarily measures atrazine but also can indicate the presence of other triazine herbicides, such as simazine and propazine.

The seasonal pattern in herbicide concentrations in the Mississippi River is similar to that described above (Goolsby and others, 1991; Goolsby and Battaglin, 1993). The temporal changes in concentrations of several commonly used herbicides and streamflow in the Mississippi River at Thebes, Illinois, for April 1991 through March 1992 are shown in figure 4. The herbicide concentrations were highest (greater than about 1 μg/L for atrazine) at this site from early May to early July 1991. Low, but detectable, concentrations of atrazine, alachlor, and metolachlor were found year round at this site (fig. 4*A*, *B*), and cyanazine was detected in about 96 percent of the samples (fig. 4*A*). The year-round occurrence of herbicides in the Mississippi River indicates that they are stored in surface reservoirs (Goolsby, Battaglin, and others, 1993) and in aquifers (Squillace and others, 1993). The herbicides are slowly discharged into streams in quantities large enough to produce detectable concentrations year round in the Mississippi River.

Previous studies indicate that nitrate concentrations in streams in the Midwestern States have a seasonal pattern. This pattern, however, is distinctly different from that for herbicides. Unlike herbicides, which are transported primarily in overland flow, nitrate appears to be transported in overland and subsurface flows (Goolsby and Battaglin, 1993; Lucey and Goolsby, 1993). Nitrate concentrations are higher during late fall, winter, and spring and are lower during summer. The lower concentrations in summer are attributed, in part, to assimilation of nitrate by aquatic and terrestrial plants during the growing season, decreased streamflow and ground-water discharge to streams, and greater evapotranspiration, all of which contribute to less leaching of nitrate from the soil and unsaturated zones to streams (Goolsby and Battaglin, 1993).

OCCURRENCE AND TRANSPORT OF AGRICULTURAL CHEMICALS DURING THE 1993 FLOOD

Heavy rainfall and flooding began in many parts of the upper Mississippi River Basin in June 1993, shortly after most crops had been planted. The cool, wet conditions that prevailed over much of the upper Midwest during spring and early summer 1993 delayed or prevented planting of corn in some areas. Because of this delay, more soybeans and less corn were planted than normal in some areas, such as Iowa (Dana Kolpin, U.S. Geological Survey, oral commun., 1993). This could have resulted in the application of less-than-normal amounts of corn herbicides, such as atrazine. The timing and intensity of the rainfall that followed planting was such that large quantities of agricultural chemicals, such as herbicides that are typically applied at the time of planting, could potentially be flushed into streams. However, because of the large volumes of floodwater, it was anticipated that herbicide concentrations would be lower than typically are measured at this time of year because of dilution. To determine the effects of flooding on the occurrence, concentrations, and transport of agricultural chemicals in the Mississippi River, water sampling was begun during early to mid-July at six locations where data had been collected in the 1991–92 study. Three of the sampling locations were on the mainstem of the Mississippi River, and three were on large tributaries. Samples were collected once to twice weekly. At present (early September 1993), the sampling is still underway. The locations of the six sampling sites, in down-river order; the drainage areas; and the date sampling began are as follows:

Site number	Name of sampling site	Drainage area (km^2)	Date sampling began (1993)
05420500	Mississippi River at Clinton, Iowa.	222,000	July 16
05586100	Illinois River at Valley City, Illinois.	69,000	Do.
06345000	Missouri River at Hermann, Missouri.	1,357,000	July 17
07022000	Mississippi River at Thebes, Illinois.	1,847,000	July 20
03612500	Ohio River at Grand Chain, Illinois.	526,000	July 22
07374000	Mississippi River at Baton Rouge, Louisiana.	2,914,000	July 7

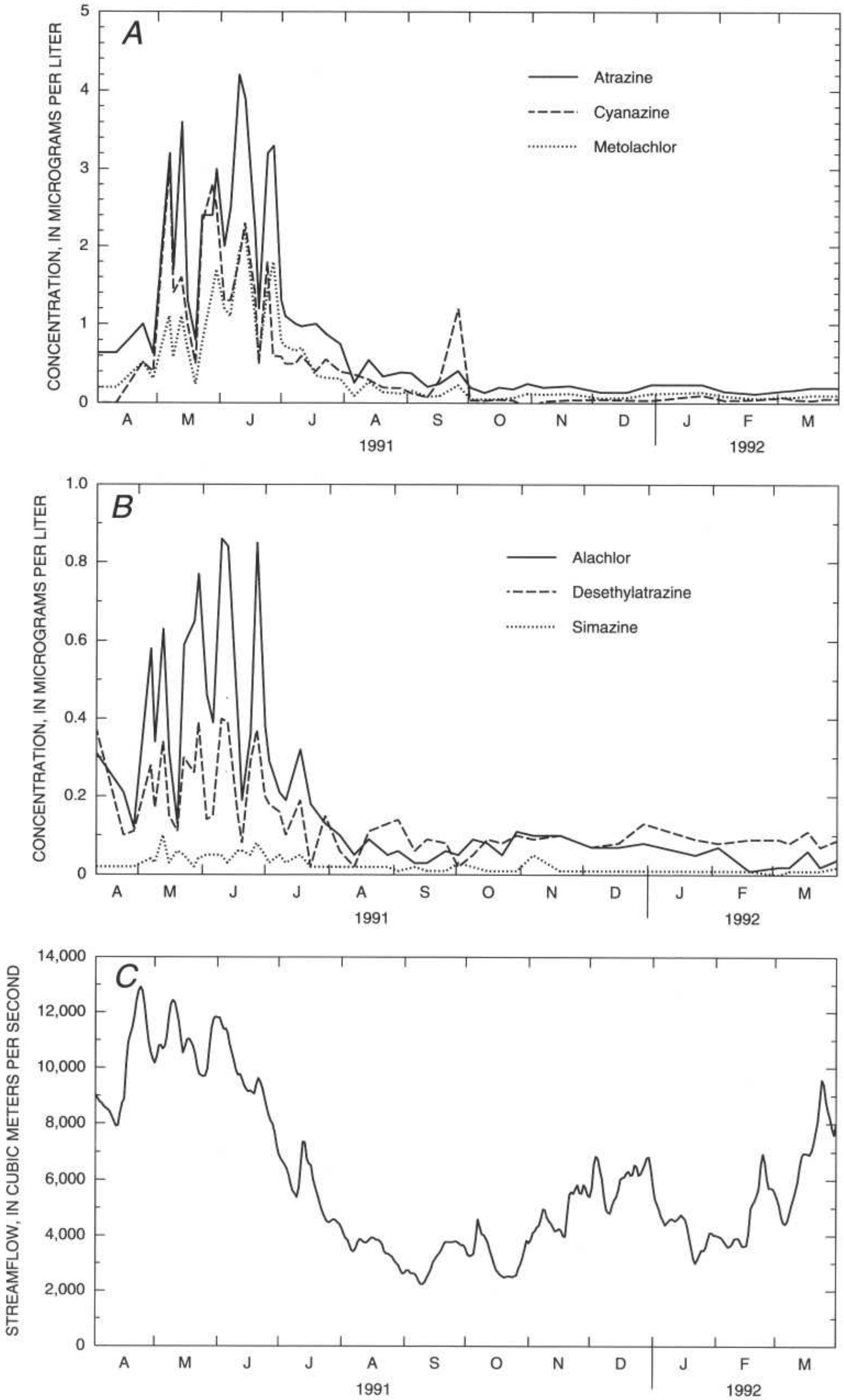

Figure 4. Streamflow and temporal distributions of several major herbicides in the Mississippi River at Thebes, Illinois. *A*, Atrazine, cyanazine, and metolachlor concentrations; *B*, Alachlor, simazine, and desethylatrazine concentrations; *C*, Streamflow.

Except for the Illinois River, these sites had been sampled at approximately weekly intervals from April 1991 through July 1992. Sampling of the Illinois River was discontinued at the end of March 1992. Sampling at the Baton Rouge, Louisiana, site continued through September 1992. The data collected on herbicides and nitrate in the 1991–92 study provide a basis for examining the effects of the 1993 flood on the concentrations and mass transport of these agricultural chemicals in the Mississippi River.

Data-Collection Methods

Methods used to collect, process, and analyze water samples are the same as those used in the 1991–92 study and are described in detail elsewhere (Goolsby and others, 1991). What follows is a brief summary of the methods. Depth-integrated water samples were collected at five or more locations across the river at all sites, except Baton Rouge. Because previous studies indicated dissolved solutes in the river at Baton Rouge were well mixed, a single integrated sample from the upper 7 meters of the water column was collected there. Samples from the river cross-section locations were composited and filtered through glass-fiber filters for herbicides or membrane filters for nitrate and several other dissolved nutrients. All materials used for herbicide sampling were stainless steel, glass, aluminum, or Teflon. The concentrations of 11 herbicides and 2 herbicide metabolites were determined by using gas chromatography/mass spectrometry following extraction on disposable C-18 solid-phase extraction cartridges (Thurman and others, 1990; Meyer and others, 1993). The herbicides analyzed were alachlor, ametryn, atrazine, cyanazine, metribuzin, metolachlor, prometon, propazine, prometryn, simazine, and terbutryn. The herbicide metabolites analyzed were desethylatrazine and desisopropylatrazine, which are primarily metabolites of atrazine. The analytical reporting limits for all herbicides and metabolites analyzed were 0.05 μg/L. In addition, an alachlor soil metabolite, ethanesulfonic acid (ESA), was extracted and isolated by solid-phase extraction and analyzed (reporting limit, 0.1 μg/L) by immunoassay (D.S. Aga, U.S. Geological Survey, written commun., 1993). About 10 percent of the samples analyzed were duplicates or blanks.

The concentrations of dissolved nitrite and nitrite plus nitrate were determined by automated colorimetric methods (Fishman and Friedman, 1989). The concentration of nitrate was calculated as the difference between these two determinations. Dissolved ammonium and orthophosphate also were determined by colorimetric methods (Fishman and Friedman, 1989).

Additional data on herbicide and nitrate concentrations in the lower Mississippi River [sampling site located about 200 kilometers (km) downstream from the USGS sampling site at Baton Rouge] for early March through mid-August 1993 were obtained from the Jefferson Parish Water Quality Laboratory near New Orleans, Louisiana (Wayne Koffskey, written commun., 1993). These samples were weekly composites collected continuously at two sampling points on opposite banks of the Mississippi River by using peristaltic pumps and storing the samples at 4 degrees Celsius. The herbicide samples were analyzed by using the USEPA's Method 505 (U.S. Environmental Protection Agency, 1988). Although the location of the sampling site is close to New Orleans and the sample collection and analytical methods are different from those used by the USGS, these data are still useful in constructing the temporal distribution pattern for herbicides, such as atrazine, in the lower Mississippi River during 1993. Data from the two weekly composite samples were averaged and used to construct a 6-month sequence of atrazine concentrations and loads during 1993 for comparison with previous data from Baton Rouge. The same comparison was made for nitrate.

Streamflow data for all sites, except Baton Rouge, were obtained from USGS offices in Iowa, Illinois, Kentucky, and Missouri. Streamflow data for Baton Rouge were obtained from the U.S. Army Corps of Engineers, New Orleans District (John Miller, U.S. Army Corps of Engineers, written commun., 1993). These data are for a site about 129 km upstream from Baton Rouge but should closely represent the streamflow at Baton Rouge. The Corps of Engineers also provided data on streamflow diverted from the Mississippi River to the Atchafalaya River, which is a distributary of the Mississippi River. This diversion is approximately 30 percent of the streamflow at Baton Rouge. The sum of the streamflow at Baton Rouge and the Atchafalaya diversion closely represents the total discharge from the Mississippi River Basin to the Gulf of Mexico.

Occurrence and Distribution of Herbicides and Nitrate-Nitrogen

Streamflow, herbicide and nitrate concentrations, and several other chemical and physical data collected at the six sites on the Mississippi River and its tributaries during the 1993 flood are listed in tables 3 and 4. The range and median concentrations for selected herbicides, herbicide metabolites, and nitrate determined in water samples collected at the six sites are as follows:

Compound	Number of samples	Concentration (μg/L)	
		Median	Range
Herbicide:			
Alachlor	26	0.20	<0.05–0.38
Atrazine	26	2.22	1.27–3.31
Cyanazine	26	1.18	.45–1.91
Metolachlor	26	.81	.49–1.90
Herbicide metabolite:			
Desethylatrazine	20	.51	.28– .76
Desisopropylatrazine	20	.31	.18– .57
ESA	20	2.0	.5 –4.0
Nitrogen:			
Nitrate	44	2.03 mg/L	.64–3.89 mg/L

Atrazine, ESA, and cyanazine generally had the highest concentrations followed by metolachlor, the two atrazine metabolites, and alachlor. Except for ESA, for which previous data are few, this order is similar to that observed in previous studies and is a reflection of the usage and short-term stability of these compounds in water. The concentrations of herbicides in water samples from the three sites on the Mississippi River were similar to or slightly higher than the maximum concentrations determined at the same three sites during late spring and early summer 1991 and 1992 (see figs. 5–7). For example, at the Thebes site, the concentration of atrazine in four samples collected during July 1993 ranged from about 2.2 to about 3.0 μg/L (table 3). The four highest atrazine concentrations determined at this site ranged from 3.3 to 4.2 μg/L in 1991 and from 1.3 to 2.6 μg/L in 1992 (fig. 5). The only other known data that define the seasonal patterns of herbicides in this reach of the Mississippi River were collected in 1975 and 1976 by the Ciba Geigy Corporation (the manufacturer of atrazine; Tierney, 1992). These data show that the maximum atrazine concentrations in the Mississippi River at St. Louis, Missouri, which is about 215 km upstream from the Thebes site, were from 3 to 4 μg/L in 1975 and from 1.5 to 4 μg/L in 1976.

At the Baton Rouge site during July 1993, concentrations of atrazine, alachlor, and cyanazine were similar to the maximum concentrations during 1991 but were higher than those during 1992 (figs. 5–7). In addition to data collected as part of this study, data on the concentrations of several herbicides for early March through mid-August 1993 were obtained from the Jefferson Parish Water Quality Laboratory (Wayne Koffskey, written commun., 1993). The atrazine data from this laboratory, which represent weekly composite samples collected at a site 200 km downstream from the Baton Rouge site, are shown in figure 5, along with the atrazine data from the Baton Rouge site. These data show that the temporal pattern of atrazine during spring and summer 1993 was similar to that measured in 1991. These data also indicate that the concentration of atrazine at Baton Rouge began to decrease in mid- to late July (fig. 5). From 1978 through 1989, the Ciba Geigy Corporation collected data at Vicksburg, Mississippi, that showed the seasonal patterns in atrazine concentrations in the lower Mississippi River (Tierney, 1992). Data on atrazine concentrations from this site, which are approximately equivalent to that at the Baton Rouge site, show seasonal patterns that are similar to those from 1991 through 1993. The summer maximum concentrations of atrazine reported from 1975 through 1989 varied from year to year but generally were from 1.5 to 3 μg/L, with a few higher values that ranged from 4 to 6 μg/L (Tierney, 1992).

The concentrations of alachlor were less than 1 μg/L and cyanazine ranged from less than 1 to about 2 μg/L at the three Mississippi River sites during July 1993. These concentrations generally were similar to maximum concentration previously measured at the sites in 1991 (figs. 6, 7). The same generally was true for most other herbicides and metabolites, including metolachlor, desethylatrazine, and desisopropylatrazine. The concentrations of ESA ranged from 1.3 to 4 μg/L at the three Mississippi River sites and were similar to those of atrazine. However, no previous data on this compound are available with which the 1993 results can be compared.

In general, herbicide concentrations were slightly lower at the Clinton, Iowa, site (table 3) than elsewhere. This is the most upstream site and drains an area where less land is devoted to crops than farther downstream. Concentrations of herbicides in the three tributaries—the Illinois, the Missouri, and the Ohio Rivers—were not substantially different from those at the Thebes and the Baton Rouge sites (tables 3, 4).

The large volumes of water being discharged by the upper Mississippi River and its tributaries were expected to dilute herbicides and other chemicals transported into the river. However, as noted above, this was not the case. Apparently, flooding and high flows simply flushed larger amounts of herbicides into the rivers than did the lower flows in previous years. This resulted in herbicide concentrations that were typical for the spring runoff period of the year. A possible explanation for the transport of larger amounts of herbicides into rivers is the timing and intensity of the rainfall in the upper Midwest during 1993. Intense and sustained rain fell shortly after planting in many parts of the area and near the time when the most concentrated amounts of herbicides were on the soil. Under these conditions, a larger fraction of herbicides would be transported into rivers than would have been with less rainfall or with rain falling later after herbicide application. A previous study showed that in 1991, less than 2 percent of the herbicides applied that year in the Mississippi River Basin were transported into large rivers (Battaglin and others, 1993; Goolsby and Battaglin, 1993). Because of the heavy rainfall and flooding, it is expected that the fraction of herbicides transported into the Mississippi River in 1993 will be much larger than in 1991.

Nitrate concentrations were less than 3 mg/L as nitrogen in all samples collected in July and August 1993

Table 3. Streamflow, nitrate-nitrogen, and herbicide data for three sites on the Mississippi River during the 1993 flood

[m^3/s, cubic meters per second; μS, microsiemens per centimeter at 25 degrees Celsius; μg/L, micrograms per liter; mg/L, milligrams per liter; kg/d, kilograms per day; t/d, metric tons per day; ESA, ethanesulfonic acid; - -, data not yet available]

Sampling date (1993)	Flow (m^3/s)	Specific conductance (μS)	Nitrate-nitrogen (mg/L)	Alachlor (μg/L)	Atrazine (μg/L)	Desethyl-atrazine (μg/L)	Desiso-propyl-atrazine (μg/L)	Cyana-zine (μg/L)	ESA (μg/L)	Metol-achlor (μg/L)	Atrazine load (kg/d)	Nitrate-nitrogen load (t/d)
Station 05420500—At Clinton, Iowa												
July 16	6,170	409	2.80	0.33	1.47	0.34	0.18	1.40	4.00	0.71	780	1,457
July 20	5,830	435	- -	.27	1.46	.36	.22	1.44	3.10	.64	740	- -
July 23	5,240	436	2.54	.19	1.27	.28	.18	1.09	3.00	.49	580	1,151
August 4	3,340	500	2.28	- -	- -	- -	- -	- -	- -	- -	- -	659
August 13	2,920	495	2.07	- -	- -	- -	- -	- -	- -	- -	- -	522
August 26	3,170	496	2.26	- -	- -	- -	- -	- -	- -	- -	- -	619
Station 07022000—At Thebes, Illinois												
July 16	23,510	- -	- -	.32	2.79	.53	.31	.83	3.10	1.03	5,670	- -
July 18	23,730	- -	- -	.38	3.04	.74	.47	1.82	1.80	1.17	6,240	- -
July 20	25,290	335	2.38	.26	2.18	.56	.39	1.27	2.00	.81	4,770	5,205
	25,290	- -	- -	.32	2.56	- -	- -	1.91	- -	.98	5,599	- -
August 16	21,630	392	1.78	- -	- -	- -	- -	- -	- -	- -	- -	3,330
August 25	17,670	441	1.87	- -	- -	- -	- -	- -	- -	- -	- -	2,858
Station 07374000—At Baton Rouge, Louisiana[1]												
July 7	23,870	351	2.50	.36	3.23	.40	.29	1.42	2.20	1.04	6,750	5,222
July 9	23,650	345	2.40	.37	3.31	.46	.31	1.53	1.90	1.07	6,770	4,908
July 12	24,020	418	2.50	.32	2.99	.52	.31	1.20	2.80	1.07	6,280	5,253
July 15	25,770	414	2.40	.31	3.19	.50	.35	1.34	2.50	.97	7,110	5,348
July 19	27,160	357	2.20	.23	2.66	.52	.33	1.15	1.70	.87	6,250	5,167
July 22	28,120	347	2.00	.17	2.08	.43	.27	.84	1.30	.64	5,060	4,864
July 26	29,110	344	2.10	.15	1.80	- -	- -	1.00	- -	.60	4,530	5,286
July 29	29,850	345	2.00	.14	1.70	- -	- -	.75	- -	.60	4,388	5,162
August 2	30,810	360	2.00	.12	1.60	- -	- -	.73	- -	.50	4,279	5,348
August 5	31,440	380	2.00	- -	- -	- -	- -	- -	- -	- -	- -	5,438
August 6	31,580	394	2.10	- -	- -	- -	- -	- -	- -	- -	- -	5,734
August 9	32,200	378	1.90	- -	- -	- -	- -	- -	- -	- -	- -	5,292
August 12	32,820	358	1.70	.09	1.50	- -	- -	.45	- -	.50	4,257	4,825
August 16	33,190	364	1.70	- -	- -	- -	- -	- -	- -	- -	- -	4,879
August 19	32,740	381	1.70	- -	- -	- -	- -	- -	- -	- -	- -	4,813
August 23	32,000	406	1.70	- -	- -	- -	- -	- -	- -	- -	- -	4,704
August 26	31,320	395	1.50	- -	- -	- -	- -	- -	- -	- -	- -	4,063

[1]Streamflow and atrazine and nitrate loads include the amounts diverted from the Mississippi River into the Atchafalaya River.

from the three sites on the Mississippi River (table 3) and less than 4 mg/L in all samples collected in July and August 1993 from the tributary sites (table 4). These concentrations are similar to those measured in summer 1991 and 1992 (fig. 8). At the three Mississippi River sites, nitrate-nitrogen concentrations generally decreased from mid-July through the end of August (fig. 8). Concentrations of nitrate are typically lower during the summer than during the remainder of the year. Because of the high streamflow and prolonged flushing of the upper Mississippi River Basin, nitrate-nitrogen concentrations during the remainder of 1993 are not expected to be as low as those measured during the preceding 2 years. Additional data on nitrate concentrations in the Mississippi River are needed to answer this question.

Relation to Drinking-Water Standards

As discussed in the section "Drinking-Water Standards and Aquatic-Life Guidelines," the MCL's for herbicides are based on the average concentrations in a minimum of four quarterly samples. Individual samples that exceed these limits do not necessarily constitute noncompliance with the Safe Drinking Water Act. Similarly, HA's are based on annual average concentrations. During July and August 1993, the concentration of atrazine exceeded the MCL of 3 µg/L in 4 of 26 samples (tables 3, 4), and cyanazine exceeded the HA of 1 µg/L in 17 of 26 samples (tables 3, 4). On the basis of previous studies of these herbicides in the Mississippi River Basin, the annual average concentrations for these herbicides probably will not exceed the MCL's or HA's in 1993. During 1991 and 1992, the annual average concentrations for these herbicides were far below the health-based limits (Goolsby and Battaglin, 1993). None of the other herbicides measured during July and August 1993 had concentrations that exceeded the MCL's or HA's. Furthermore, the concentration of nitrate in all samples analyzed was well below the nitrate MCL of 10 mg/L.

Table 4. Streamflow, nitrate-nitrogen, and herbicide data for three sites on the Mississippi River tributaries during the 1993 flood

[m^3/s, cubic meters per second; µS, microsiemens per centimeter at 25 degrees Celsius; µg/L, micrograms per liter; mg/L, milligrams per liter; kg/d, kilograms per day; t/d, metric tons per day; ESA, ethanesulfonic acid; <, less than; - -, data not yet available]

Sampling date (1993)	Flow (m^3/s)	Specific conductance (µS)	Nitrate-nitrogen (mg/L)	Alachlor (µg/L)	Atrazine (µg/L)	Desethyl-atrazine (µg/L)	Desisopropyl-atrazine (µg/L)	Cyanazine (µg/L)	ESA (µg/L)	Metolachlor (µg/L)	Atrazine load (kg/d)	Nitrate-nitrogen load (t/d)
Station 05586100—Illinois River at Valley City, Illinois												
July 16	1,420	505	3.89	0.06	2.87	0.70	0.51	1.30	2.10	0.92	350	478
July 20	1,560	492	3.61	.14	2.62	.76	.57	1.51	2.40	.86	350	486
July 22	1,600	505	3.80	.12	2.47	.73	.57	1.48	2.40	.81	340	526
July 26	2,000	467	3.20	.09	1.95	.66	.47	1.17	2.00	.59	340	553
August 4	1,510	437	2.41	- -	- -	- -	- -	- -	- -	- -	- -	314
August 12	1,305	576	2.65	- -	- -	- -	- -	- -	- -	- -	- -	299
August 19	1,277	565	2.46	- -	- -	- -	- -	- -	- -	- -	- -	272
August 26	- -	593	2.74	- -	- -	- -	- -	- -	- -	- -	- -	- -
August 31	- -	612	2.63	- -	- -	- -	- -	- -	- -	- -	- -	- -
Station 06934500—Missouri River at Hermann, Missouri												
July 17	13,450	263	- -	.33	2.50	- -	- -	1.30	- -	1.90	2,910	- -
July 24	9,100	331	1.13	- -	- -	- -	- -	- -	- -	- -	- -	888
July 27	11,020	- -	- -	.11	1.80	.40	.30	.79	1.10	.62	1,710	- -
August 6	- -	- -	1.39	- -	- -	- -	- -	- -	- -	- -	- -	- -
August 25	- -	- -	1.40	- -	- -	- -	- -	- -	- -	- -	- -	- -
Station 03612500—Ohio River at Grand Chain, Illinois												
July 22	2,270	424	1.97	.21	2.27	.68	.29	.82	1.90	.83	440	386
July 29	3,740	362	1.37	.10	1.59	.49	.33	.69	1.50	.60	510	443
	3,740	362	- -	<.05	1.79	.41	.26	.63	.50	.59	580	- -
August 3	2,920	291	.84	- -	- -	- -	- -	- -	- -	- -	- -	224
August 10	1,480	390	1.29	- -	- -	- -	- -	- -	- -	- -	- -	166
August 19	3,970	361	.72	- -	- -	- -	- -	- -	- -	- -	- -	247
August 25	3,310	292	.72	- -	- -	- -	- -	- -	- -	- -	- -	198

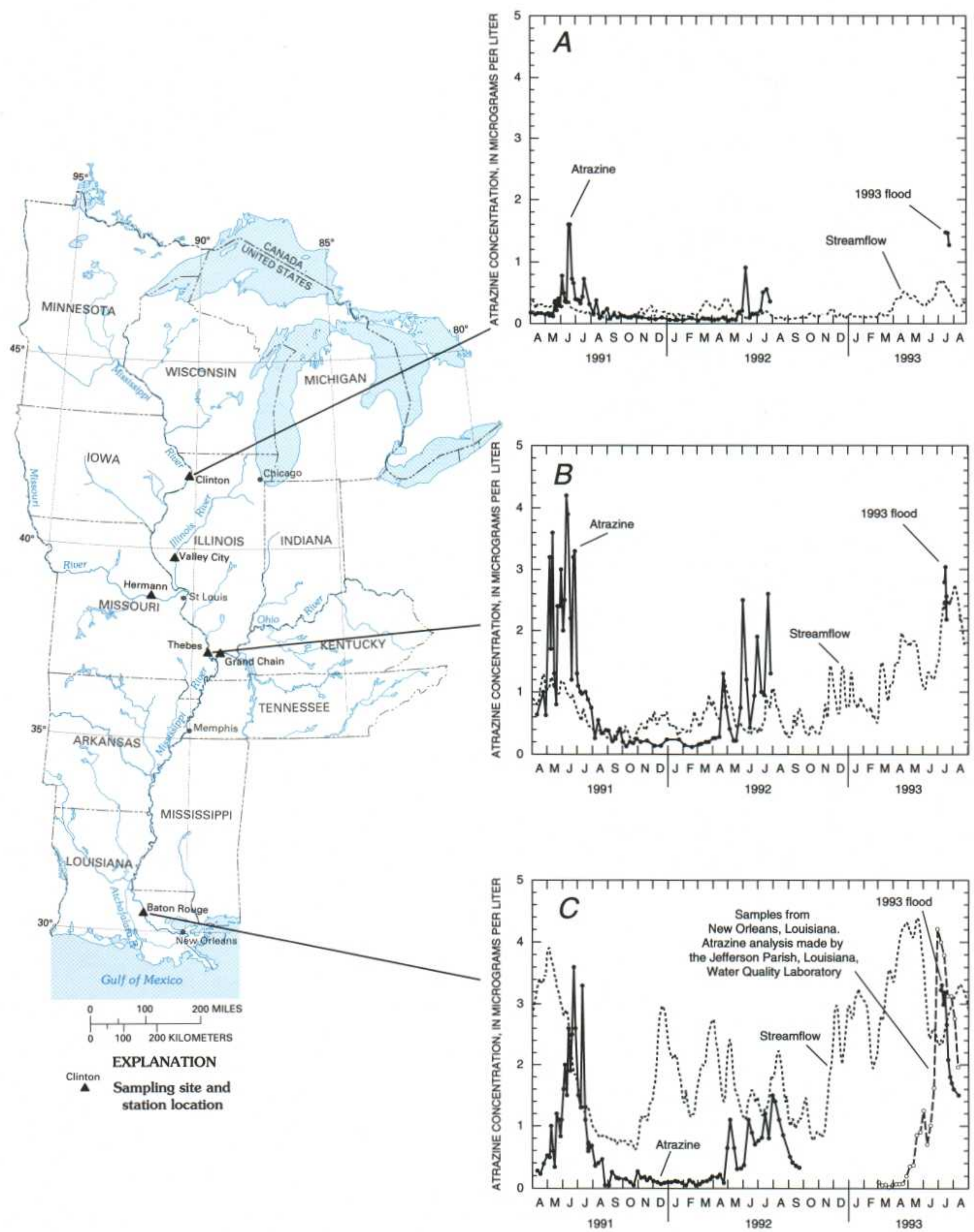

Figure 5. Streamflow and temporal distribution in the concentrations of atrazine at three sites on the Mississippi River from April 1991 through August 1993. *A*, Clinton, Iowa; *B*, Thebes, Illinois; *C*, Baton Rouge, Louisiana.

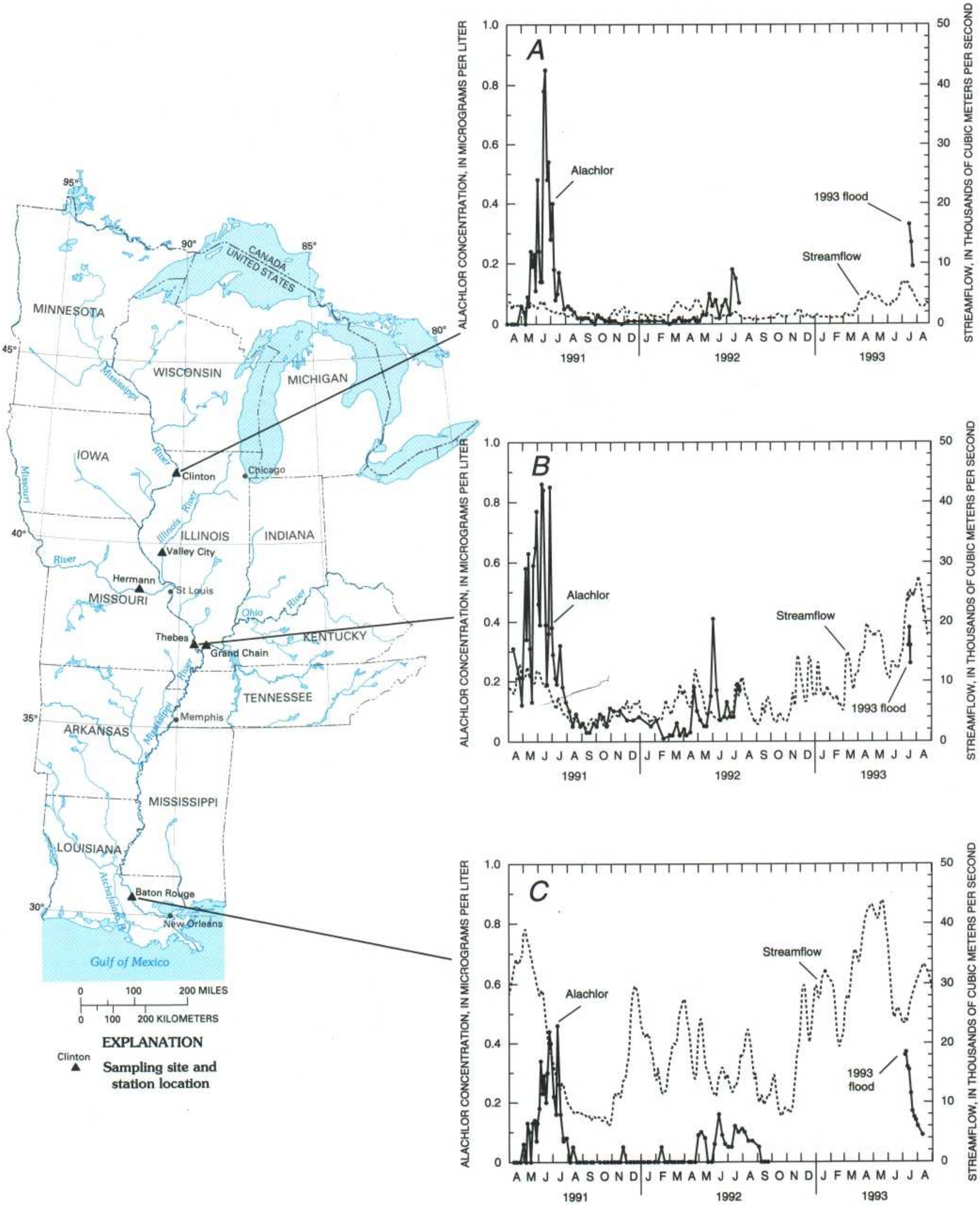

Figure 6. Streamflow and temporal distribution in the concentrations of alachlor at three sites on the Mississippi River from April 1991 through August 1993. *A*, Clinton, Iowa; *B*, Thebes, Illinois; *C*, Baton Rouge, Louisiana.

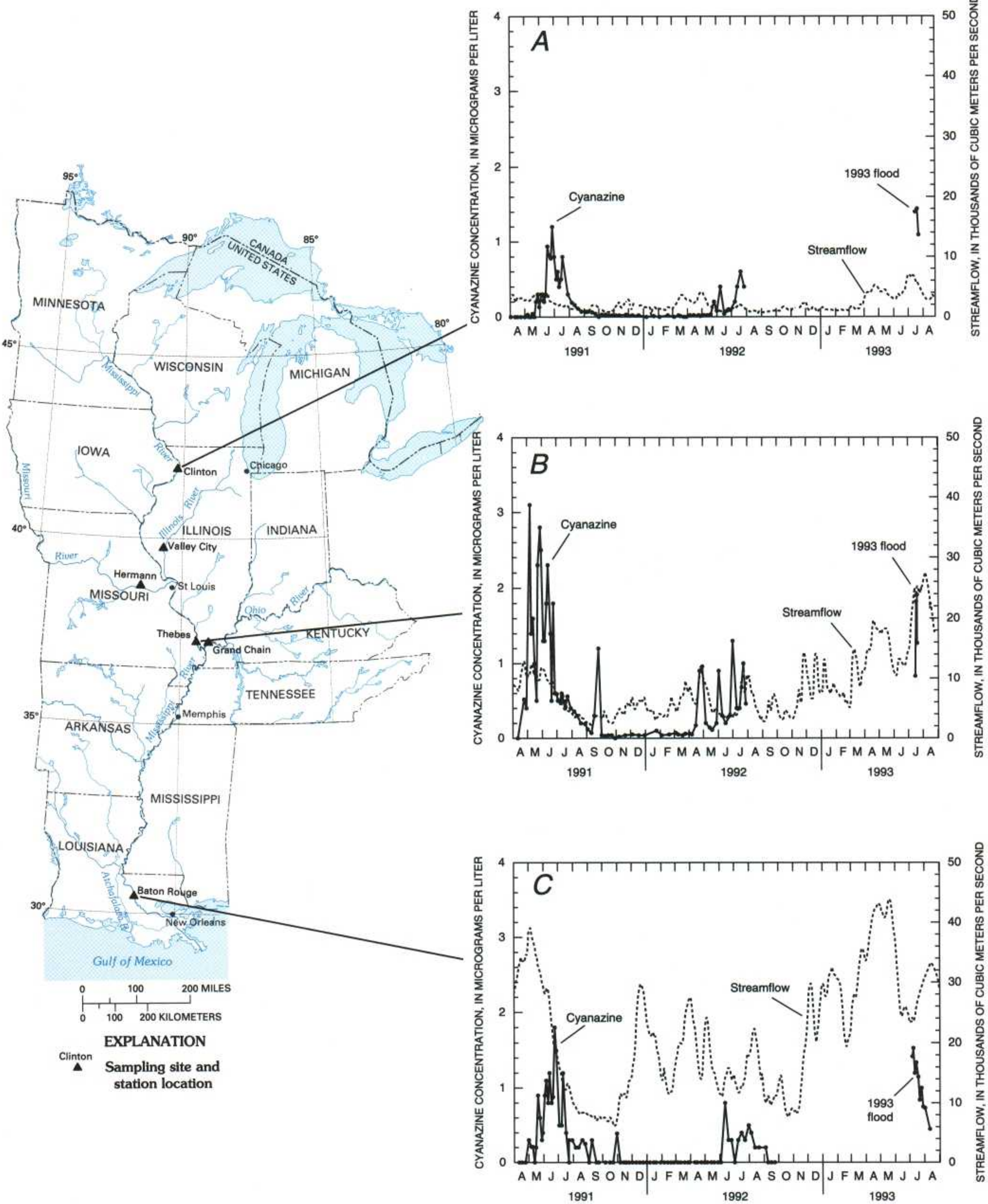

Figure 7. Streamflow and temporal distribution in the concentrations of cyanazine at three sites on the Mississippi River from April 1991 through August 1993. *A*, Clinton, Iowa; *B*, Thebes, Illinois; *C*, Baton Rouge, Louisiana.

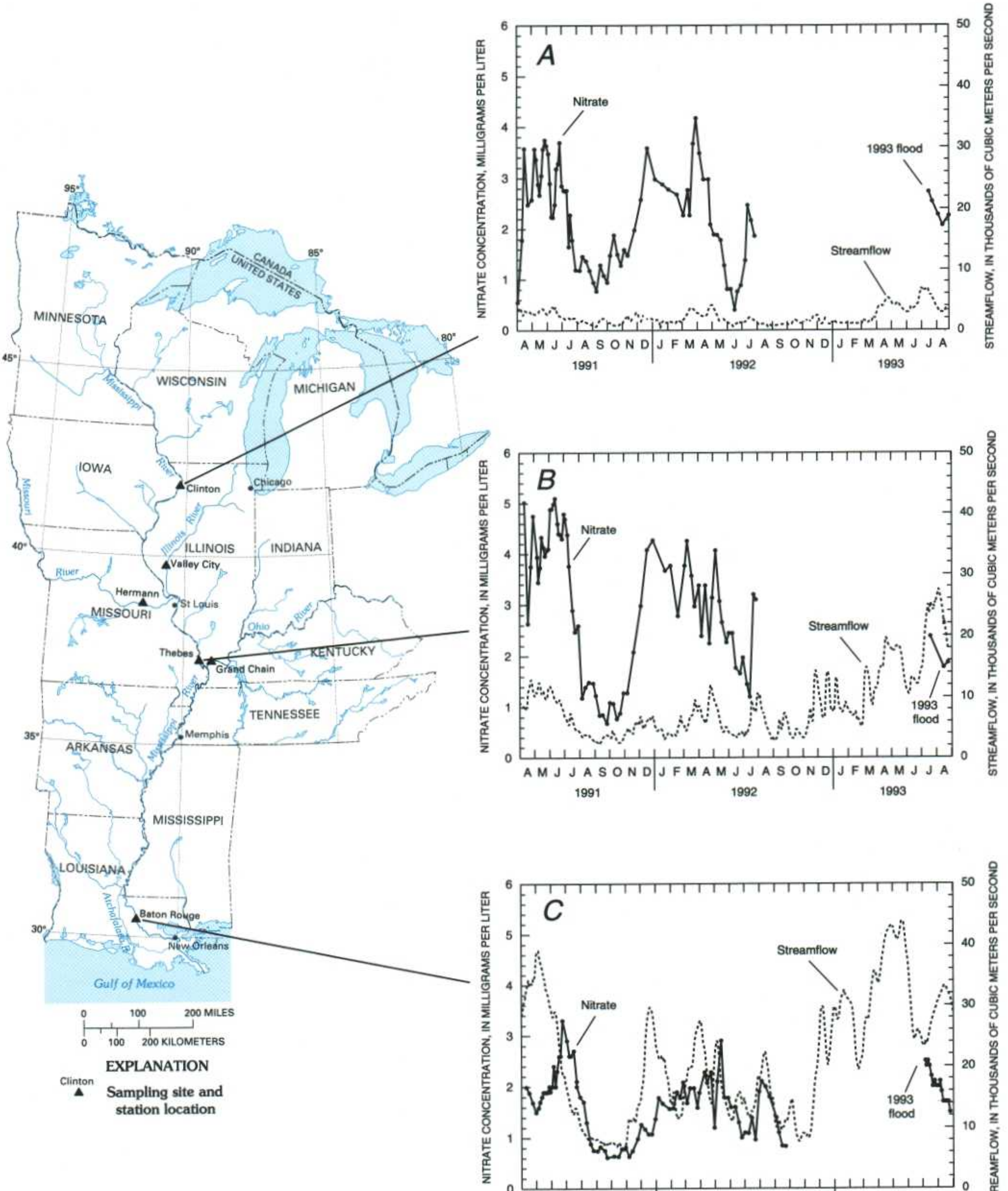

Figure 8. Streamflow and temporal distribution in the concentrations of nitrate-nitrogen at three sites on the Mississippi River from April 1991 through August 1993. *A*, Clinton, Iowa; *B*, Thebes, Illinois; *C*, Baton Rouge, Louisiana.

Transport of Herbicides and Nitrate

The transport of agricultural chemicals (herbicides and nitrate) by rivers is a function of the concentration of these compounds and the volume of water that flows in the river. During the 1993 flood, concentrations of agricultural chemicals were similar to those measured at the same time of the year in 1991 and 1992; however, the volume of water transported by the upper Mississippi River was much larger than normal for midsummer. The resulting estimates of the daily loads of agricultural chemicals transported by the Mississippi River are large relative to estimates calculated from data collected in 1991 and 1992.

Calculation Methods

The amount (loads) of herbicides or nitrate transported each day by rivers was calculated by multiplying daily mean streamflow by herbicide or nitrate concentration. The resulting estimates of daily agricultural chemical loads (kilograms or metric tons) can then be compared with estimates of daily agricultural chemical loads calculated from data collected in other studies. The daily load at Baton Rouge was estimated from concentrations of agricultural chemicals measured at Baton Rouge and the combined streamflow for Baton Rouge and the Atchafalaya diversion. The daily load estimate for Baton Rouge, therefore, closely represents the total load of agricultural chemicals from the Mississippi River to the Gulf of Mexico.

In earlier studies, estimates of seasonal or annual loads of agricultural chemicals were calculated by multiplying daily mean streamflow by measured or estimated daily herbicide or nitrate concentration and then accumulating these estimates for a period of interest, such as 1 year (Battaglin and others, 1993; Goolsby and Battaglin, 1993). Estimates of the loads of atrazine and nitrate transported by the Mississippi River from April through August 1993 were calculated for comparison with loads transported from April through August 1991 and 1992.

Transport of Herbicides

The combination of high herbicide concentrations, which are typical during late spring and summer, and high streamflow resulted in large loads of herbicides in the upper Mississippi River during the 1993 flood. Estimates of the loads of atrazine from April 1991 through August 1992 and from mid-July through mid-August 1993 at three sites on the Mississippi River are shown in figure 9. The three largest daily load estimates for atrazine, alachlor, cyanazine, and metolachlor in 1991 and 1992 and during the 1993 flood are listed in table 5. Also shown in figure 9 are the atrazine load estimates at New Orleans from March through August 1993.

At the Thebes site, the maximum daily atrazine load during the 1993 flood was 6,240 kilograms (kg) (fig. 9; table 5), or approximately 1.7 times that of 1991 and more than three times that of 1992. The maximum daily cyanazine load during the 1993 flood (4,180 kg) was about 1.5 times the maximum observed in 1991 and about five times that in 1992 (fig. 9; table 5). For metolachlor, the maximum daily load during the 1993 flood (2,400 kg) was approximately 1.3 times that in 1991 and about six times that of 1992 (fig. 9; table 5). Finally, the maximum daily load of alachlor during the 1993 flood (780 kg) was the same as that of 1991 and about five times that of 1992. Similar proportions among maximum daily herbicide load during the 1993 flood and those during 1991 and 1992 are noted at the Clinton site (fig. 9; table 5). At the Baton Rouge site, large maximum daily herbicide loads were estimated during the 1993 flood. The total amount of atrazine discharged to the Gulf of Mexico from April through August 1993 is estimated to be 539,000 kg compared with 296,000 kg during this same period in 1991 and 160,000 kg in 1992. The 1993 atrazine load for this 5-month period was 80 and 235 percent larger, respectively, than in 1991 and 1992. The much larger transport in 1993 is attributed to extensive flushing of atrazine from the upper Mississippi River Basin during the 1993 flood.

Transport of Nitrate

Near-normal nitrate-nitrogen concentrations of 2 to 3 mg/L during July and August 1993 combined with high streamflows resulted in the transport of large amounts of nitrate in the upper Mississippi River during the 1993 flood. The maximum daily loads of nitrate-nitrogen during the 1993 flood at the Thebes and the Baton Rouge sites were more than 5,000 t. These loads were larger than those measured in 1992 but similar to those measured in spring and early summer 1991 (fig. 10; table 6). The annual load of nitrate-nitrogen transported by the Mississippi River during 1993 is expected to be much larger than that estimated for 1991 or 1992 because large loads of nitrate-nitrogen are being transported in the summer. For example, the nitrate-nitrogen load transported to the gulf of Mexico from April through August 1993 was 827,000 t compared with 603,000 t in 1991 and 390,000 t in

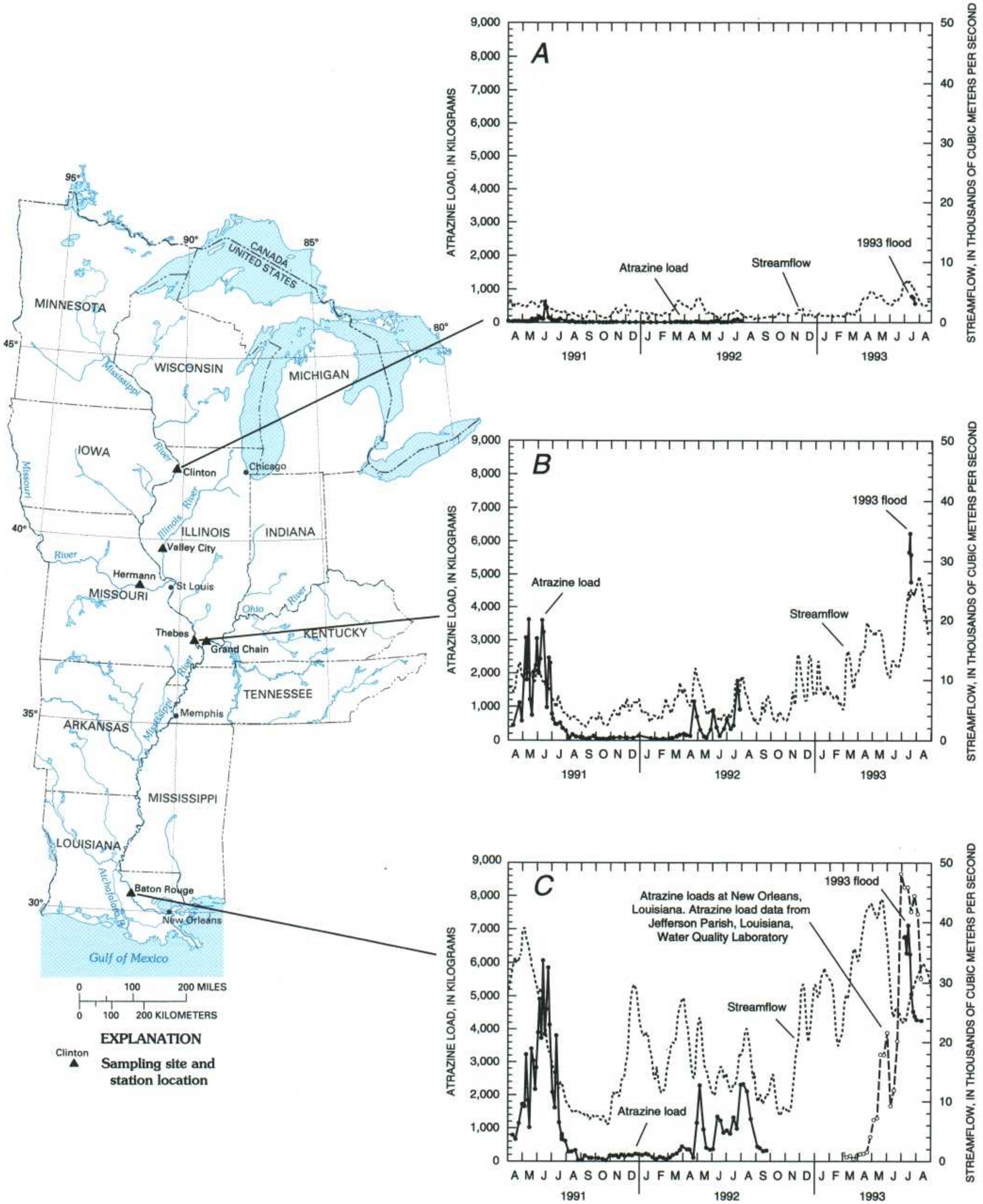

Figure 9. Streamflow and temporal distribution of daily load of atrazine at three sites on the Mississippi River from April 1991 through August 1993. *A*, Clinton, Iowa; *B*, Thebes, Illinois; *C*, Baton Rouge, Louisiana.

Table 5. Three largest daily load estimates for atrazine, alachlor, cyanazine, and metolachlor at three sampling sites on the Mississippi River in 1991 and 1992 and during the 1993 flood

[In kilograms per day]

Herbicide	1991			1992			1993 flood		
	First	Second	Third	First	Second	Third	First	Second	Third
Station 05420500—At Clinton, Iowa									
Atrazine	530	430	180	96	75	73	780	740	580
Alachlor	260	230	110	27	26	15	180	140	86
Cyanazine	310	240	220	100	59	53	750	730	490
Metolachlor	190	190	170	46	45	27	380	320	220
Station 07022000—At Thebes, Illinois									
Atrazine	3,620	3,600	3,240	1,780	1,160	910	6,240	5,670	5,600
Alachlor	780	740	700	160	150	130	780	700	650
Cyanazine	2,980	2,610	2,540	890	800	680	4,180	3,730	2,780
Metolachlor	1,830	1,730	1,630	430	410	370	2,400	2,140	2,090
Station 07374000—At Baton Rouge, Louisiana[1]									
Atrazine	6,060	5,860	4,910	2,330	2,310	2,290	7,110	6,770	6,750
Alachlor	840	720	680	210	200	170	760	750	690
Cyanazine	2,930	2,800	2,700	980	770	660	3,130	2,990	2,970
Metolachlor	2,280	2,260	1,910	1,080	780	630	2,250	2,190	2,170

[1]Includes the amounts of herbicides diverted from the Mississippi River into the Atchafalaya River.

1992. The 1993 load for this period was 37 and 112 percent, respectively, larger than in 1991 and 1992. Nitrate-nitrogen loads generally are much lower in the summer months than in the remainder of the year (Battaglin and others, 1993; Goolsby and Battaglin, 1993).

The transport of extraordinarily large loads of nitrate from the Mississippi River Basin into the Gulf of Mexico during the summer months of 1993 could affect the gulf ecosystem along the Louisiana coast by stimulating algal growth. The National Oceanic and Atmospheric Administration has monitored the concentrations of nitrate, dissolved oxygen, and other characteristics in the gulf to determine the effects of the flooding. The data indicate that during July 1993, salinity of surface water in the gulf shelf was lower than average for this time of year and that phytoplankton biomass was higher than average (Michael Dowgiallo, National Oceanic and Atmospheric Administration, written commun., 1993). These effects could be attributed to larger-than-average seasonal inflows of freshwater and nutrients, such as nitrate.

SUMMARY

Water samples for the analysis of herbicides and nitrate were collected during July and August 1993 to determine the effects of record flooding on the concentrations and transport of these common agricultural chemicals in the Mississippi River Basin. Samples were collected at three sites on the mainstem of the Mississippi River and at sites near the mouths of three large tributaries—the Illinois, the Missouri, and the Ohio Rivers. Results from these samples were compared with those from a previous study of the Mississippi River conducted in 1991 and 1992. The results show that the heavy rainfall and severe flooding from mid-June through early August 1993 flushed extraordinarily large amounts of agricultural chemicals into the Mississippi River, many of its tributaries, and, ultimately, the Gulf of Mexico. Concentrations of herbicides, such as atrazine, alachlor, cyanazine, and metolachlor, were similar to the maximum concentrations measured during spring and summer 1991 and 1992, even though high streamflows were recorded. Consequently, the record flooding did not dilute the concentrations of herbicides as was anticipated. Instead, larger-than-average amounts of herbicides were flushed into streams and concentrations of herbicides remained about the same as typical for this time of the year. The maximum daily load of atrazine transported by the Mississippi River in the vicinity of Thebes during the flood of 1993 was as much as 70 percent higher than that measured in 1991. The total load of atrazine discharged to the Gulf of Mexico from April through

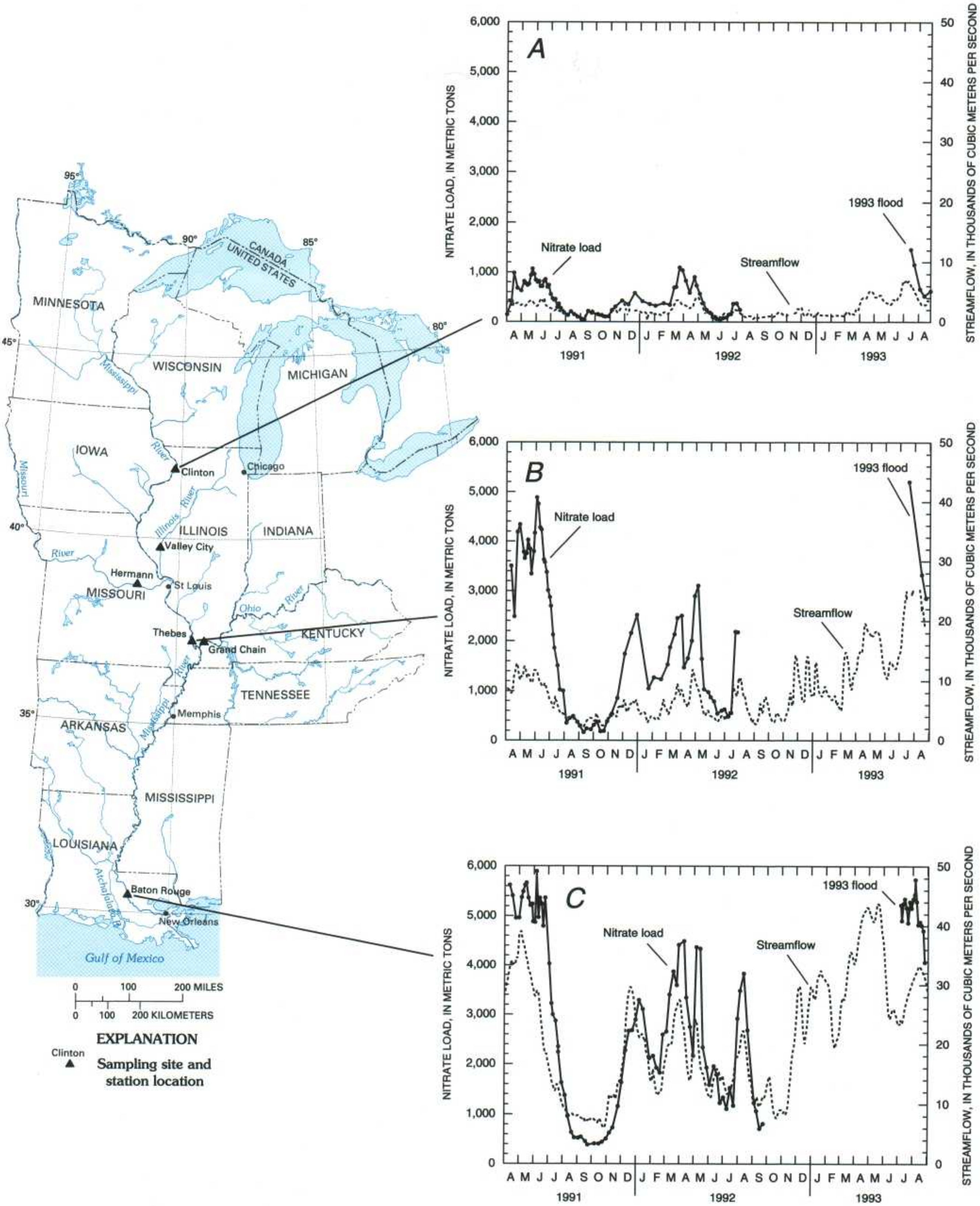

Figure 10. Streamflow and temporal distribution of daily load of nitrate at three sites on the Mississippi River from April 1991 through August 1993. *A*, Clinton, Iowa; *B*, Thebes, Illinois; *C*, Baton Rouge, Louisiana.

Table 6. Three largest daily load estimates for nitrate-nitrogen at three sampling sites on the Mississippi River in 1991 and 1992 and during the 1993 flood

[In metric tons per day]

Site	1991			1992			1993 flood		
	First	Second	Third	First	Second	Third	First	Second	Third
Station 05420500 at Clinton Iowa.	1,070	990	960	1,100	1,040	910	1,495	1,151	660
Station 07022000 at Thebes, Illinois.	4,890	4,760	4,340	3,110	2,900	2,510	5,205	3,330	2,858
Station 0737400 at Baton Rouge, Louisiana.[1]	5,900	5,670	5,630	4,500	4,420	4,380	5,734	5,437	5,348

[1]Includes amounts of nitrate diverted from the Mississipi River into the Atchafalaya River.

August 1993 (539,000 kg) was about 80 percent larger than that for the same period in 1991 and 235 percent larger than that for this same period in 1992. The concentrations of atrazine and cyanazine in a few samples exceeded health-based limits for drinking water. However, compliance with drinking-water regulations is based on the average of at least four quarterly samples; the annual average concentrations of these herbicides in the Mississippi River probably will not exceed these limits for 1993. Nitrate concentrations also remained typical for this time of the year, although nitrate loads generally were higher than those measured in spring and summer 1991 and 1992. It is estimated that 827,000 t of nitrate-nitrogen was discharged to the Gulf of Mexico from April through August 1993. This amount is about 37 percent larger than that for the same period in 1991 and about 112 percent larger than that for the same period in 1992. The discharge of extraordinarily high loads of nitrate and large amounts of freshwater into the Gulf of Mexico during midsummer when primary production is highest could increase phytoplankton biomass and affect the gulf ecosystem along the Louisiana coast.

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