

O C C U R R E N C E
A N D
T R A N S P O R T
O F
A G R I C U L T U R A L
C H E M I C A L S



I N T H E
M I S S I S S I P P I
R I V E R B A S I N
J U L Y T H R O U G H A U G U S T
1 . 9 . 9 . 3



U.S. GEOLOGICAL SURVEY CIRCULAR 1120-C

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 tributary 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 ($\mu\text{g/L}$)	
		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 $\mu\text{g/L}$ (table 3). The four highest atrazine concentrations determined at this site ranged from 3.3 to 4.2 $\mu\text{g/L}$ in 1991 and from 1.3 to 2.6 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ in 1975 and from 1.5 to 4 $\mu\text{g/L}$ 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 Koffsky, 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 $\mu\text{g/L}$, with a few higher values that ranged from 4 to 6 $\mu\text{g/L}$ (Tierney, 1992).

The concentrations of alachlor were less than 1 $\mu\text{g/L}$ and cyanazine ranged from less than 1 to about 2 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ 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

[m³/s, cubic meters per second; μ S, microsiemens per centimeter at 25 degrees Celsius; μ g/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 (μ S)	Nitrate-nitrogen (mg/L)	Alachlor (μ g/L)	Atrazine (μ g/L)	Desethyl-atrazine (μ g/L)	Desisopropyl-atrazine (μ g/L)	Cyanazine (μ g/L)	ESA (μ g/L)	Metolachlor (μ g/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, Louisiana¹												
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

¹Streamflow 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 [m³/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

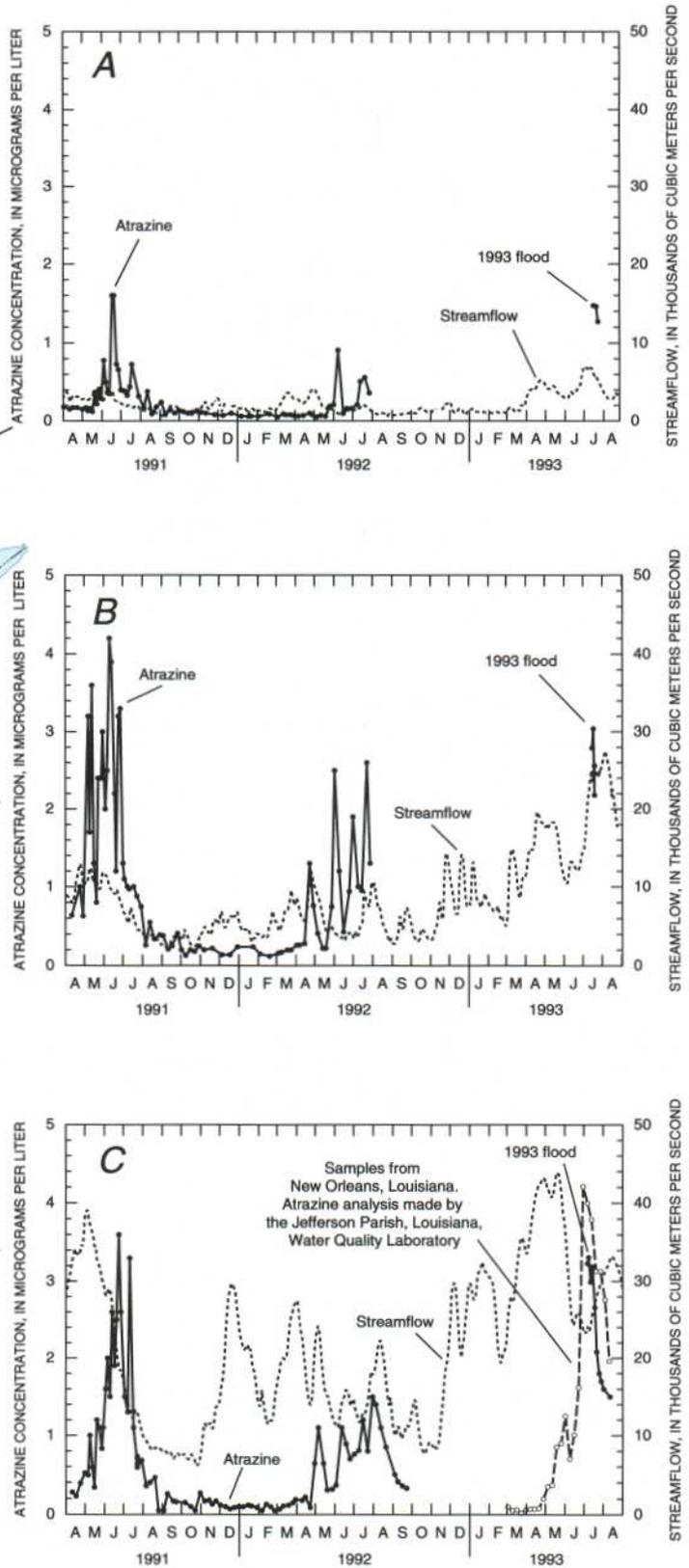
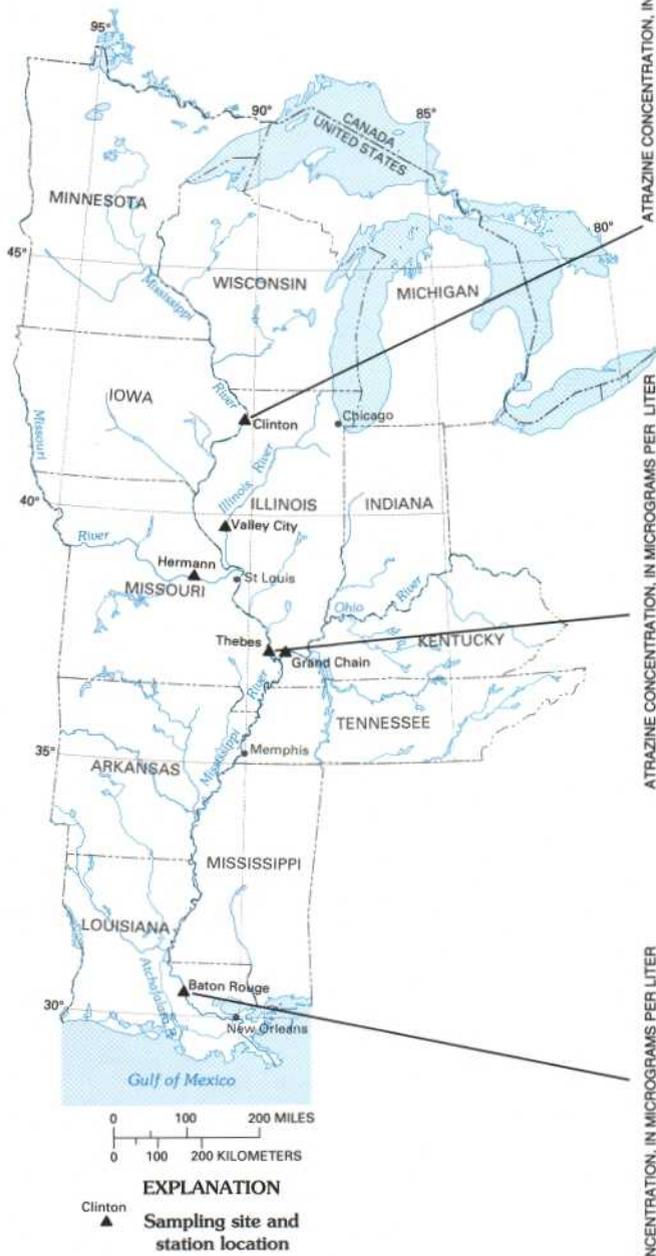


Figure 5. Streamflow and temporal distribution in the concentrations of atrazine at three sites on the Mississippi River from April 1991 through August 1993. A, Clinton, Iowa; B, Thebes, Illinois; C, Baton Rouge, Louisiana.

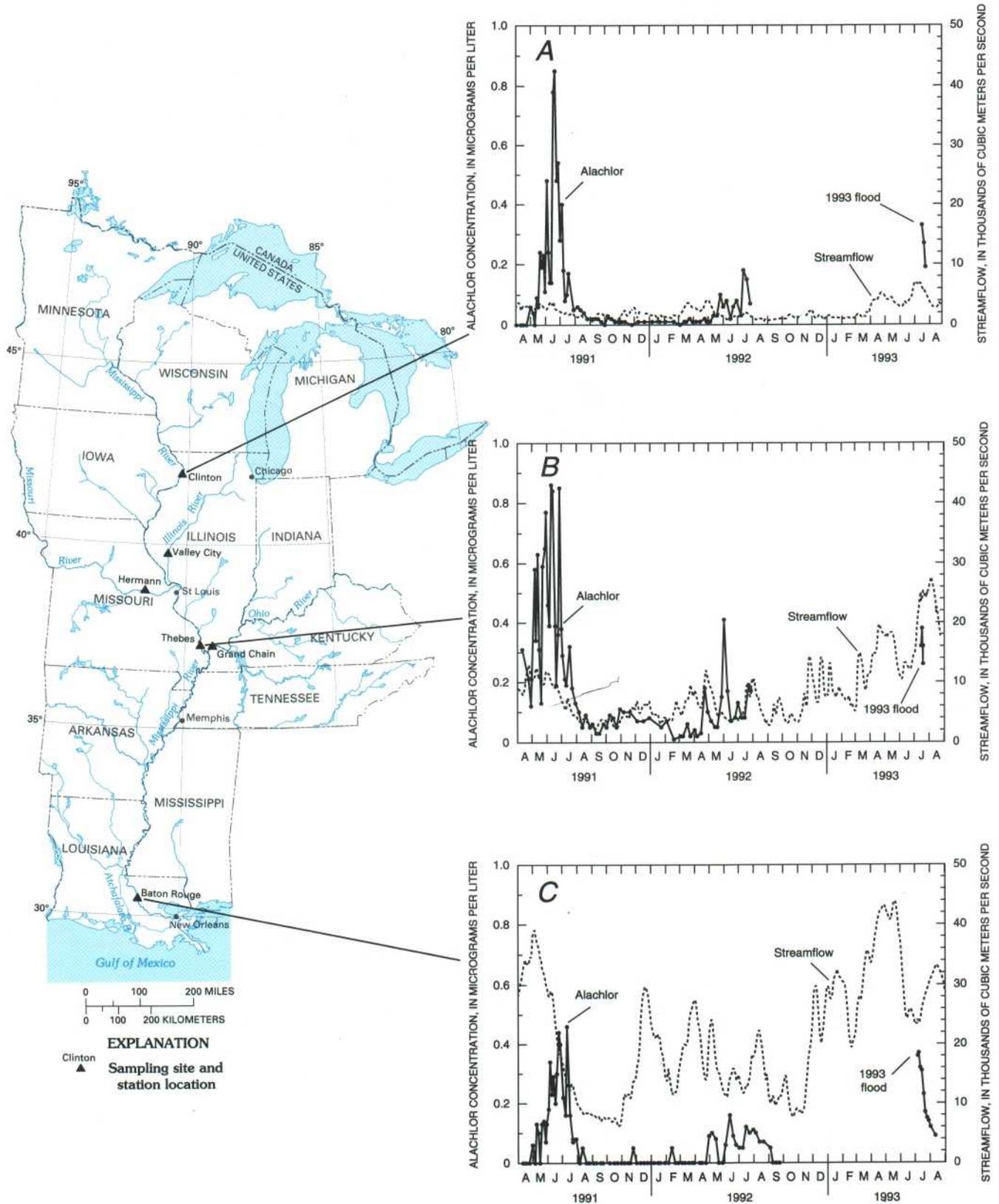


Figure 6. Streamflow and temporal distribution in the concentrations of alachlor at three sites on the Mississippi River from April 1991 through August 1993. A, Clinton, Iowa; B, Thebes, Illinois; C, Baton Rouge, Louisiana.

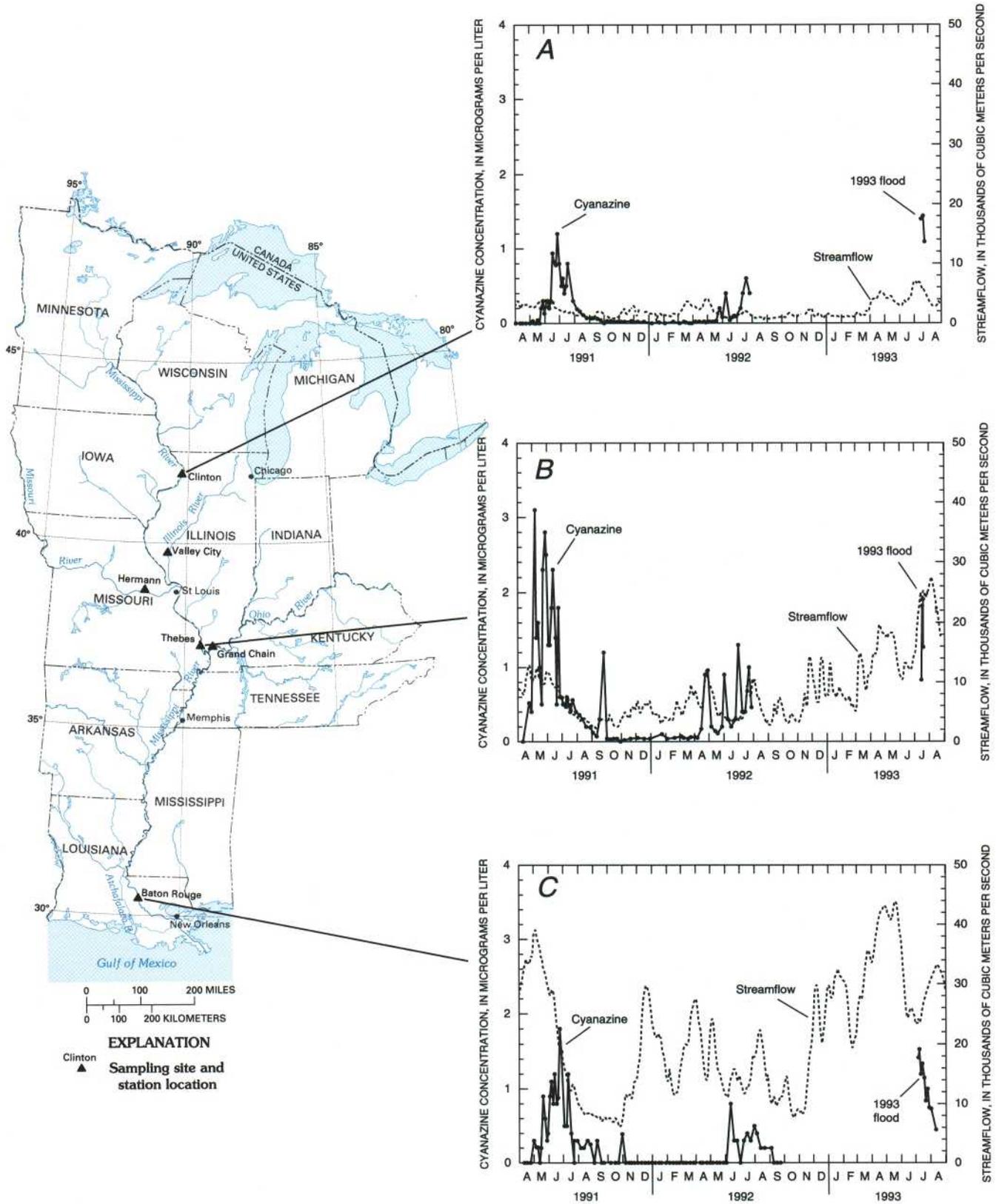


Figure 7. Streamflow and temporal distribution in the concentrations of cyanazine at three sites on the Mississippi River from April 1991 through August 1993. A, Clinton, Iowa; B, Thebes, Illinois; C, Baton Rouge, Louisiana.

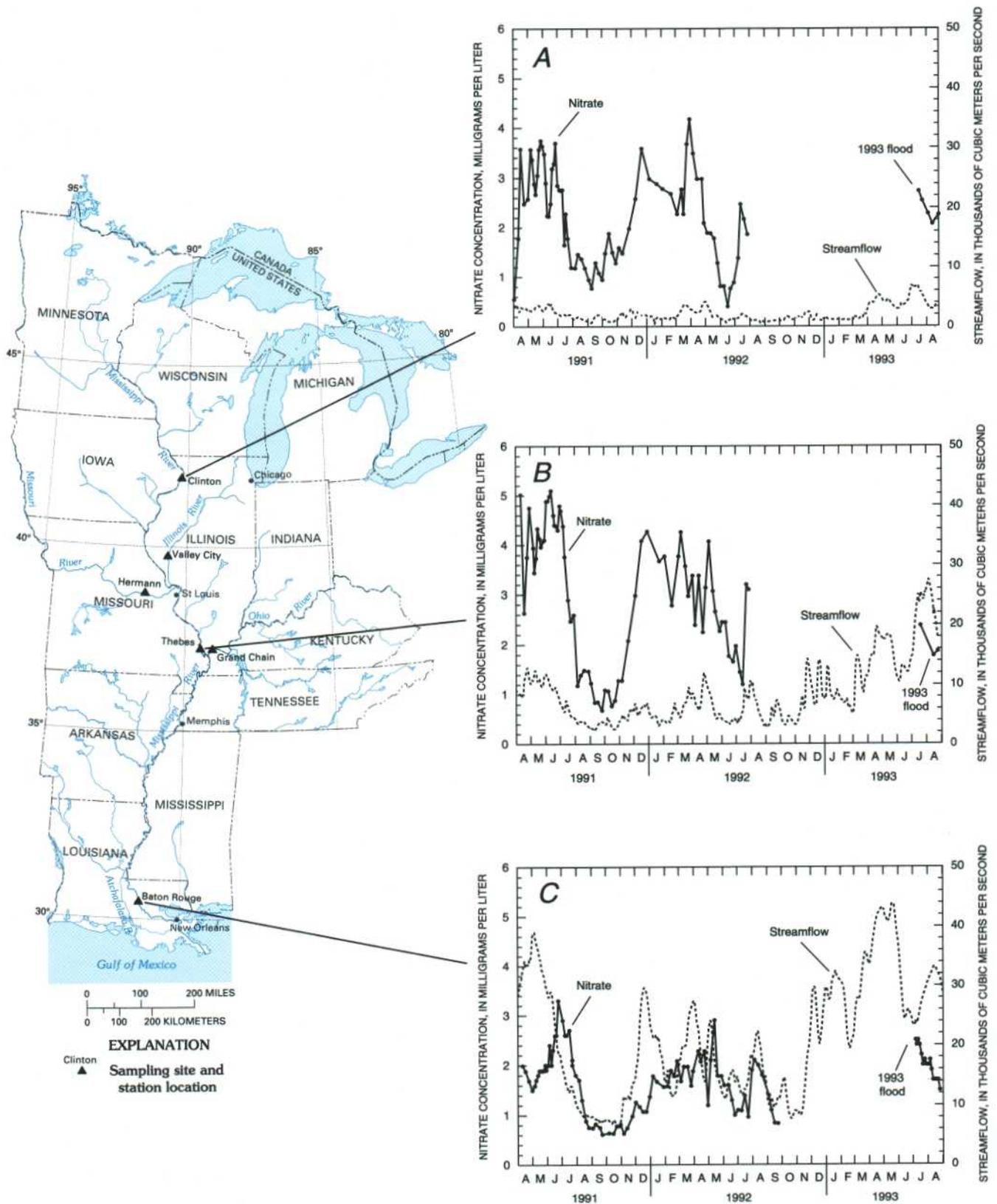


Figure 8. Streamflow and temporal distribution in the concentrations of nitrate-nitrogen at three sites on the Mississippi River from April 1991 through August 1993. A, Clinton, Iowa; B, Thebes, Illinois; C, Baton Rouge, Louisiana.

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

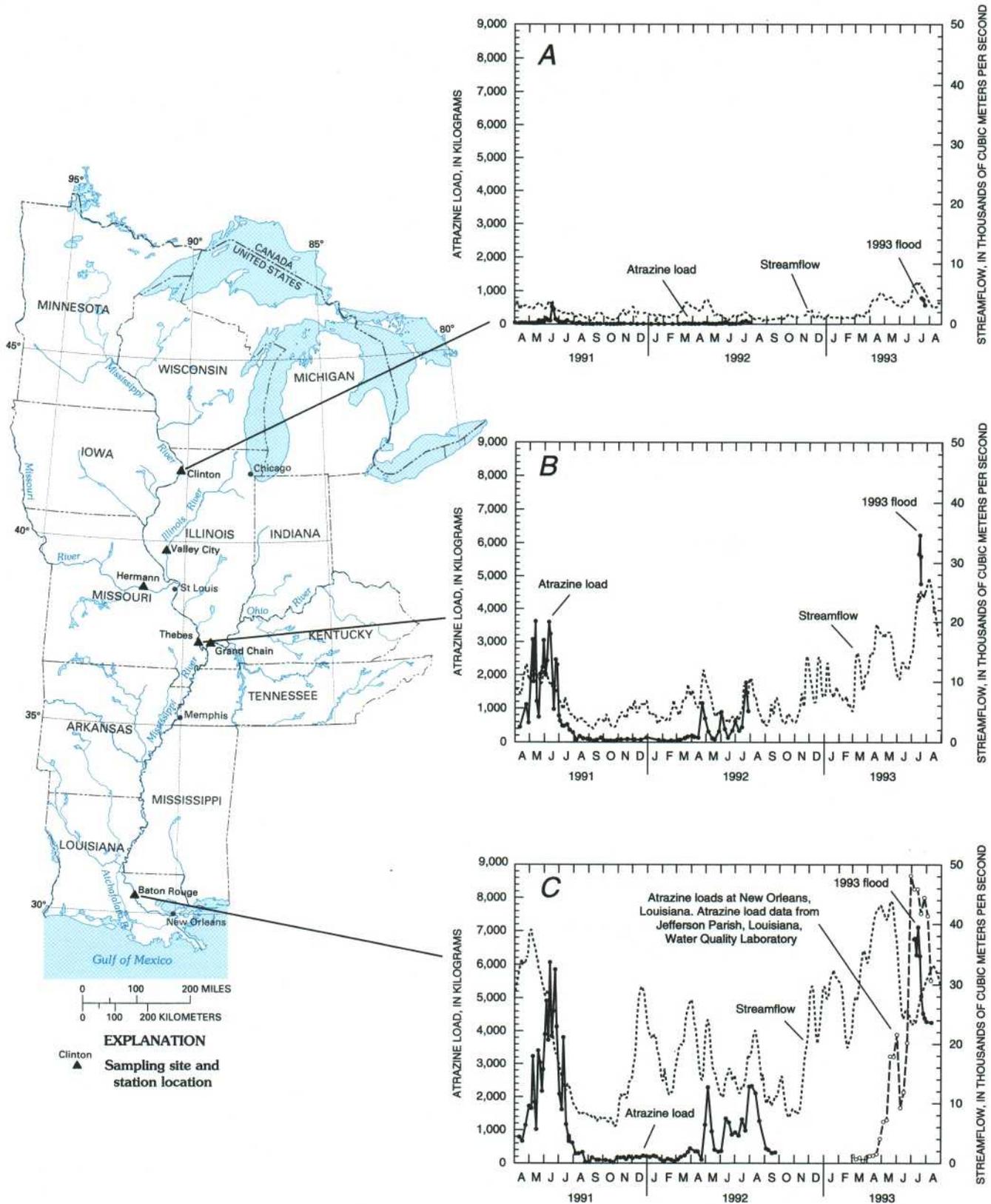


Figure 9. Streamflow and temporal distribution of daily load of atrazine at three sites on the Mississippi River from April 1991 through August 1993. A, Clinton, Iowa; B, Thebes, Illinois; C, Baton Rouge, Louisiana.

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, Louisiana¹									
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

¹Includes 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

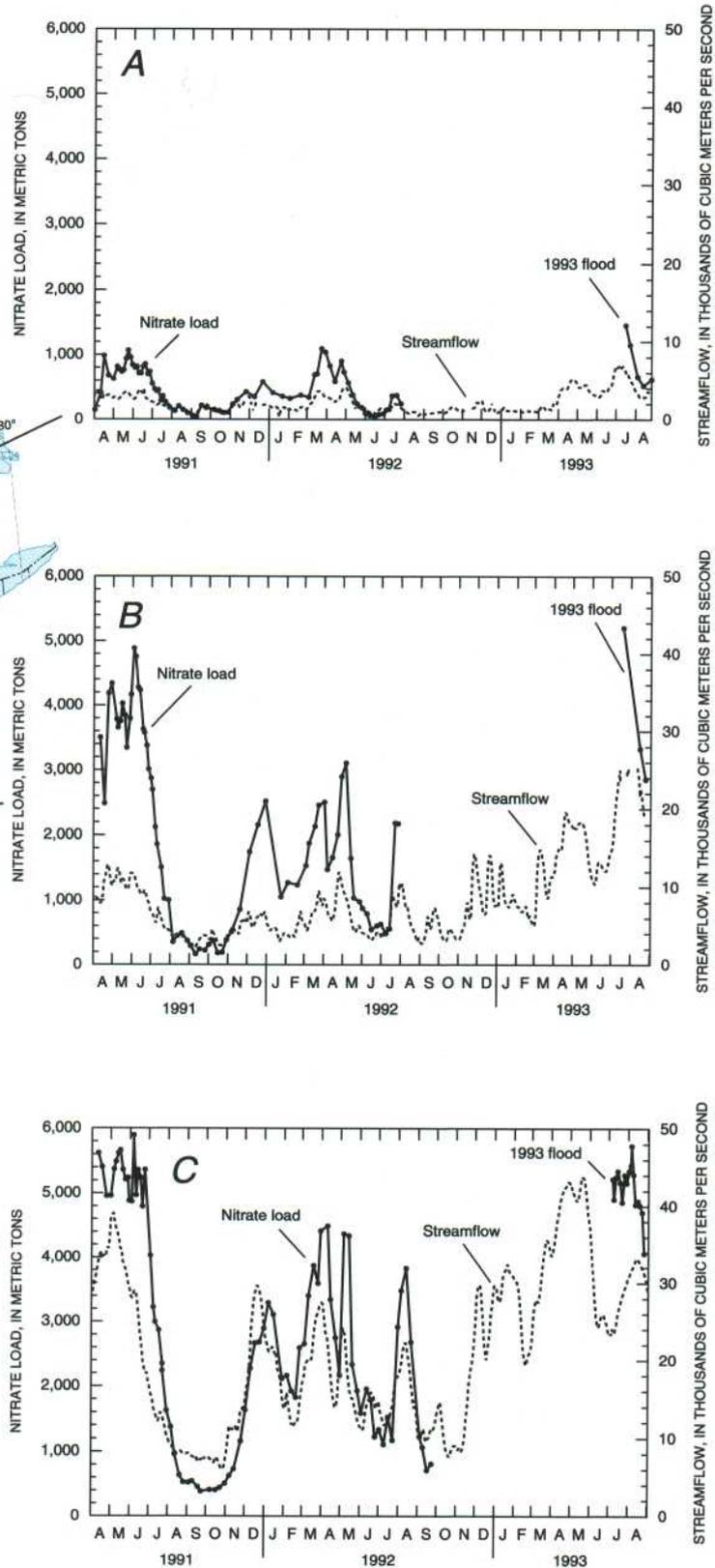
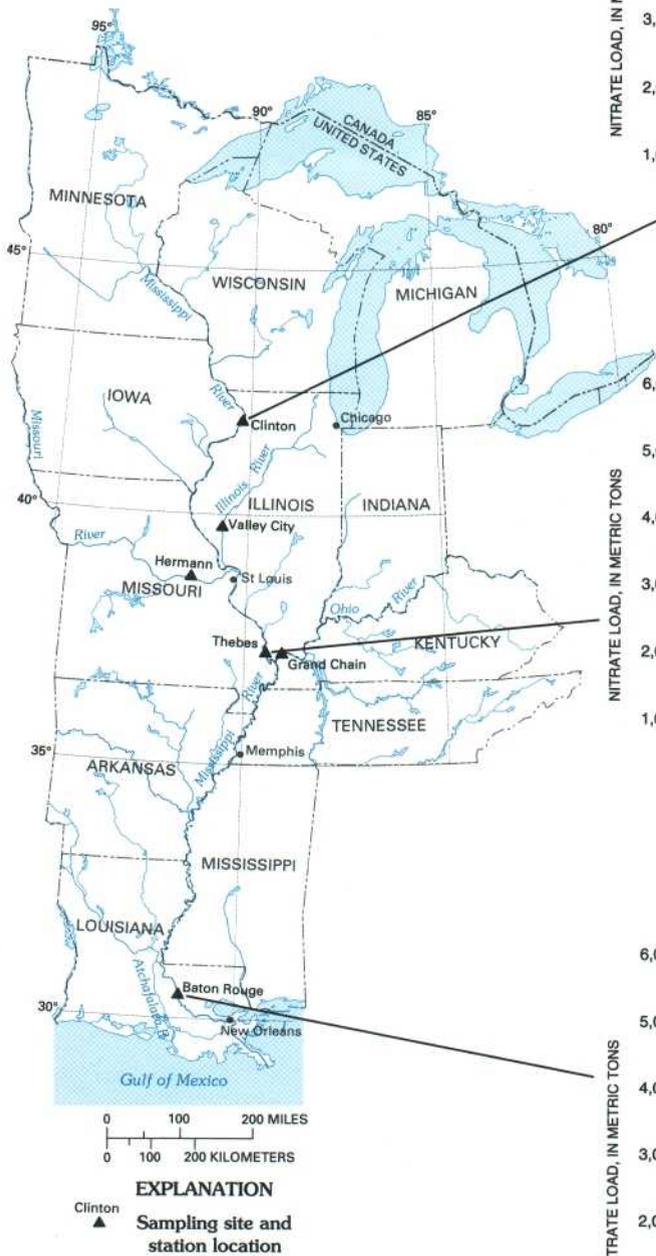


Figure 10. Streamflow and temporal distribution of daily load of nitrate at three sites on the Mississippi River from April 1991 through August 1993. A, Clinton, Iowa; B, Thebes, Illinois; C, Baton Rouge, Louisiana.

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

¹Includes amounts of nitrate diverted from the Mississippi 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.

REFERENCES CITED

- Battaglin, W.A., Goolsby, D.A., and Coupe, R.H., 1993, Annual use and transport of agricultural chemicals in the Mississippi River, 1991–92, in Goolsby, D.A., and others, eds., Selected papers on agricultural chemicals in water resources of the Midcontinental United States: U.S. Geological Survey Open-File Report 93–418, p. 26–38.
- Becker, R. L., Herzfeld, D., Ostlie, K. R., and Stamm-Katovich, E. J., 1989, Pesticides—Surface runoff, leaching, and exposure concerns: Minneapolis, University of Minnesota, Minnesota Extension Service AG-BU-3911, 32 p.
- Fishman, M.J., and Friedman, L.C., 1989, Methods for the determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water Resources Investigations, book 5, chap. A1, 545 p.
- Gianessi, L.P., and Puffer, C.M., 1991, Herbicide use in the United States: Washington, D.C., Resources for the Future, December 1990 (revised April 1991), 128 p.
- Goolsby, D.A., and Battaglin, W.A., 1993, Occurrence, distribution, and transport of agricultural chemicals in surface waters of the Midwestern United States, in Goolsby, D.A., and others, eds., Selected papers on agricultural chemicals in water resources of the Midcontinental United States: U.S. Geological Survey Open-File Report 93–418, p. 1–24.
- Goolsby, D.A., Battaglin, W.A., Fallon, J.D., Aga, D.S., Kolpin, D.W., and Thurman, E.M., 1993, Persistence of herbicides in selected reservoirs in the Midwestern United States—Some preliminary results, in Goolsby, D.A., and others, eds., Selected papers on agricultural chemicals in water resources of Midcontinental United States: U.S. Geological Survey Open-File Report 93–418, p. 51–63.
- Goolsby, D.A., Coupe, R.H., and Markovchick, D.J., 1991, Distribution of selected herbicides and nitrate in the Mississippi River and its major tributaries, April through June 1991: U.S. Geological Survey Water-Resources Investigations Report 91–4163, 35 p.
- Goolsby, D.A., Thurman, E.M., Pomes, M.L., Meyer, M., and Battaglin, W.A., 1993, Occurrence, deposition, and long range transport of herbicides in precipitation in the Midwestern and Northeastern United States, in Goolsby, D.A., and others, eds., Selected papers on agricultural chemicals in water resources of the Midcontinental United States: U.S. Geological Survey Open-File Report 93–418, p. 75–87.

- Iowa Agricultural Statistics, 1993, Iowa crops and weather: Des Moines, Iowa Agricultural Statistics, v. 93, no.16, 1 p.
- Kent, R.A., Pauli, B.D., Trotter, D.M., and Gareau, J., 1991, Canadian water quality guidelines for metolachlor: Ottawa, Environment Canada, Scientific Series 184, 34 p.
- Lucey, K.J., and Goolsby, D.A., 1993, Effects of climatic variations over 11 years on nitrate-nitrogen concentrations in the Raccoon River, Iowa: *Journal of Environmental Quality*, v. 22, p. 38–46.
- Meyer, M.T., Mills, M.S., and Thurman, E.M., 1993, Automated solid-phase extraction of herbicides from water for gas chromatography/mass spectrometry analysis: *Journal of Chromatography*, v. 629, p. 55–59.
- Parrett, Charles, Melcher, N.B. and James, R.W., Jr., 1993, Flood discharges in the upper Mississippi River Basin, in *Floods in the upper Mississippi River Basin, 1993*: U.S. Geological Survey Circular 1120–A, 14 p.
- Pauli, B.D., Kent, R.A., and Wong M.P., 1990, Canadian water quality guidelines for metribuzin: Ottawa, Environment Canada, Scientific Series 179, 44 p.
- Pauli, B.D., Kent, R.A., and Wong, M.P., 1991a, Canadian water quality guidelines for cyanazine: Ottawa, Environment Canada, Scientific Series 180, 26 p.
- Pauli, B.D., Kent, R.A., and Wong, M.P., 1991b, Canadian water quality guidelines for simazine: Ottawa, Environment Canada, Scientific Series 187, 29 p.
- Squillace, P.J., Thurman, E.M., and Furlong, E.T., 1993, Groundwater as a nonpoint source of atrazine and deethylatrazine in a river during base flow conditions: *Water Resources Research*, v. 29, no. 6, p. 1719–1729.
- Thurman, E.M., Meyer, M.T., Pomes, M. L., Perry, C.E., and Schwab, A.P., 1990, Enzyme-linked immunosorbent assay compared with gas chromatography/mass spectrometry for the determination of herbicides in water: *Analytical Chemistry*, v. 62, p. 2043–2048.
- Thurman, E.M., Goolsby, D.A., Meyer, M.T., and Kolpin, D.W., 1991, Herbicides in surface waters of the Midwestern United States—The effect of spring flush: *Environmental Science and Technology*, v. 25, p. 1794–1796.
- _____ 1992, A reconnaissance study of herbicides and their metabolites in surface water of the Midwestern United States using immunoassay and gas chromatography/mass spectrometry: *Environmental Science and Technology*, v. 26, no. 12, p. 2440–2447.
- Tierney, D.P., 1992, A review of historical surface water monitoring for atrazine in the Mississippi, Missouri, and Ohio Rivers, 1975–1991: Greensboro, N.C., Ciba Geigy Corporation, Technical Report 6–92, 69 p.
- Trotter, D.M., Baril, A., Wong, M.P., and Kent, R.A., 1990, Canadian water quality guidelines for atrazine: Ottawa, Environment Canada, Scientific Series 168, 106 p.
- U.S. Department of Agriculture, 1992, Agricultural resources—Situation and outlook report: U.S. Department of Agriculture, Economic Research Service, AR–25, 66 p.
- _____ 1993, Agricultural resources—Situation and outlook report: U.S. Department of Agriculture, Economic Research Service, AR–30, p. 42–45.
- U.S. Department of Commerce, 1989, Census of agriculture, 1987—Final county file: U.S. Department of Commerce, Bureau of Census, [machine-readable data file].
- U.S. Environmental Protection Agency, 1988, Methods for the determination of organic compounds in drinking water: U.S. Environmental Protection Agency, EPA-600/4-88/039, p. 109–141.
- _____ 1990, County-level fertilizer sales data: U.S. Environmental Protection Agency, Office of Policy, Planning, and Evaluation, PM–221.
- _____ 1992, Drinking Water Regulations and Health Advisories, U.S. Environmental Protection Agency, Office of Water, 13 p.
- Wahl, K.L., Vining, K.C., and Wiche, G.J., 1993, Precipitation in the Upper Mississippi River Basin, January 1 through July 31, 1993, in *Floods in the upper Mississippi River Basin, 1993*: U.S. Geological Survey Circular 1120–B, 10 p.
- Wong, M.P., and Kent, R.A., 1988, Developing Canadian water quality pesticide guidelines for the protection of aquatic life: *Water Pollution Control Research Journal of Canada*, v. 23, no. 4, p. 500–509.