DISTRIBUTION OF SELECTED HERBICIDES AND NITRATE IN THE MISSISSIPPI RIVER AND ITS MAJOR TRIBUTARIES, APRIL THROUGH JUNE 1991

By D.A. Goolsby, R.C. Coupe, and D.J. Markovchick

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CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
cubic foot per second (ft^3/s)	2.832×10^{-2}	cubic meter per second
foot (ft)	3.048×10^{-1}	meter
liter (L)	2.642×10^{-1}	gallon
microliter (µL)	2.642×10^{-7}	gallon
micrometer (µm)	3.937×10^{-5}	inch
mile	1.609	kilometer
millimeter (mm)	3.937×10^{-2}	inch
pound	4.536×10^{-1}	kilogram
square mile (mi^2)	2.590	square kilometer

To convert degrees Celsius (°C) to Fahrenheit (°F), use the following formula:

$$°F = 9/5(°C)+32.$$

Micrograms per liter (µg/L) is a unit expressing the concentration of a chemical constituent in solution as weight (micrograms) of solute per unit volume (liter) of water.

Milligrams per liter (mg/L) is a unit expressing the concentration of a chemical constituent in solution as weight (milligrams) of solute per unit volume (liter) of water; 1 mg/L equals 1,000 micrograms per liter (µg/L).

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ABSTRACT

One or more herbicides were detected in each of 146 water samples collected from 8 sites on the Mississippi River and its major tributaries in April, May, and June 1991. Atrazine was detected in every sample; median concentrations of atrazine ranged from 0.29 micrograms per liter in the Mississippi River at Clinton, Iowa, to 3.2 micrograms per liter in the White River at Hazelton, Ind. Concentrations of herbicides increased in early May in response to rainfall that occurred after herbicide application, and then began to decrease in early- to mid-June. The concentration of atrazine exceeded the maximum contaminant level for drinking water in the Missouri River at Hermann, Mo., throughout the month of June, and at two sites on the Mississippi River during parts of May and June. Alachlor exceeded the maximum contaminant level in a few samples collected from the smaller tributaries. Cyanazine, metolachlor, and simazine were also detected in many samples but concentrations did not exceed maximum contaminant levels or health advisory levels. The largest concentrations of nitrate-nitrogen were measured in the Illinois River and parts of the upper Mississippi River. None of the nitrate-nitrogen concentrations measured exceeded the maximum contaminant level.

Results from this study are consistent with the concept of an annual cycle of herbicide application followed by a series of flushing events during which herbicides are transported to streams by rainfall in late spring and summer. Herbicide concentrations decrease later in the year due to chemical and biological degradation, transport into streams, and other processes. During the flushing events, concentrations of some herbicides may exceed health based limits in streams throughout the upper midwestern United States, regardless of size, including the Mississippi River.

INTRODUCTION

More than 294 million pounds of herbicides are applied annually to cropland and pasture land in the midwestern United States (Gianessi and Puffer, 1990). Most of this amount is used to control weeds in the production of corn, soybeans, and sorghum. Regional-scale studies conducted by the U.S. Geological Survey during 1989 and 1990 (Thurman and others, 1991) indicate that these compounds are transported into streams each year during late spring and early summer, and ultimately discharge to the Ohio, Missouri, and Mississippi Rivers and the Gulf of Mexico. About 18 million people rely on the Ohio, Missouri, Mississippi, and numerous smaller rivers in the central United States for drinking-water supplies. At certain times of the year, herbicides and other agricultural chemicals, such as nitrate-nitrogen derived from fertilizer, may be present in these streams in concentrations that exceed health-based limits for drinking water.

Pesticide Use

Data reported by Gianessi and Puffer (1990) indicate that more than 294 million pounds of herbicides (active ingredients) were used annually during 1987-89 in agricultural crop production in 12 States that drain to the Mississippi River and its major tributaries (fig. 1, table 1). These States (Arkansas, Illinois, Indiana, Iowa, Kansas, Louisiana, Minnesota, Mississippi, Missouri, Nebraska, Ohio, and Wisconsin) account for most of the herbicide use in the Mississippi River basin. Herbicides used in these States account for about 60 percent of the total herbicide use for agriculture in the United States. Herbicides used in largest quantities are listed in table 2 along with selected physical and chemical properties, maximum contaminant levels (MCL) and health advisory (HA) levels for drinking water, and principal target crops. Herbicides with solubilities larger than about 30 mg/L, organic carbon partition coefficients (K_{oc}) smaller than 300-500, and soil half-lives greater than 21 days (table 2) are relatively mobile and persistent in the aquatic environment (Becker and others, 1989). Five herbicides (alachlor, atrazine, metolachlor, EPTC, and cyanazine) account for about 63 percent of the herbicides used in the 12-State area. They are used primarily on corn, soybeans, and sorghum.

Previous Studies

Studies conducted by the U.S. Geological Survey in 1989 and 1990 indicate that herbicides are flushed from cropland each spring and summer and are transported into streams tributary to the Missouri, Ohio, and Mississippi Rivers (Goolsby and others, 1991; Thurman and others, 1991). During May and June 1989, median concentrations of atrazine, alachlor, cyanazine, and metolachlor ranged from 1 to 3 µg/L in samples from streams draining hundreds to several thousand square miles; maximum concentrations for these four herbicides ranged from more than 10 for alachlor to more than 100 µg/L for atrazine (Thurman and others, 1991). Similar concentrations were measured in samples collected during May and June 1990 (Goolsby and others, 1991; Thurman and others, 1991). These studies also show that concentrations of herbicide that exceed MCLs can persist in streams for several months following application. For example, the concentration of atrazine in the West Fork Big Blue River in Nebraska (fig. 1) remained above the 3 µg/L MCL from early May until the end of August in 1990 (Thurman and others, 1991). A large increase in herbicide concentration in streams following application also has been documented in Iowa (Squillace and Engberg, 1988), Ohio (Baker and Richards, 1989), and Nebraska (Snow and Spalding, 1988).

Major rivers such as the Missouri, Ohio, and Mississippi are affected by the discharge of herbicides from tributary streams. Many water samples have been collected at points along the Mississippi River as part of U.S. Geological Survey research on sediment-related transport of organic substances in the river (Meade, 1989). Pereira and Rostad (1990) reported concentrations of dissolved atrazine and alachlor as large as about 1 µg/L in samples collected between St. Louis, Mo., and New Orleans, La., during May and June 1988. During mid-June 1990, atrazine concentrations in this same reach of the Mississippi River ranged from 3.0 to 4.5 µg/L (U.S. Geological Survey, unpublished data). Very recently, the Missouri River Public Water Supplies Association (Keck, 1991) reported sustained large concentrations of atrazine throughout the lower 500 miles of the Missouri River during May and June 1991. This study showed that at one site near St. Louis, Mo., in the lower reaches of the Missouri River, atrazine concentration exceeded

Figure 1.--Location of sampling sites.

Table 1.--*Amounts of principal herbicides used on crops in 12 States draining to the Mississippi River, 1987-89, in order of decreasing use (Source: Gianessi and Puffer, 1990)*

[--, no data; <, less than]

Herbicide	Amount used, in thousands of pounds of active ingredients per year											
	Ark.	Ill.	Ind.	Iowa	Kans.	La.	Minn.	Miss.	Mo.	Nebr.	Ohio	Wis.
Atrazine	568	8,708	5,309	7,102	5,560	1,110	2,235	290	3,964	15,457	3,929	4,336
Alachlor	560	7,689	7,638	9,898	1,844	722	4,547	229	2,759	3,691	5,428	3,185
Metolachlor	1,220	9,293	3,927	9,116	1,607	732	1,309	363	1,727	2,177	3,695	1,260
EPTC	5	1,703	350	7,971	867	241	7,664	19	769	1,020	312	1,015
Cyanazine	147	2,244	1,979	7,743	135	91	1,051	709	800	2,052	1,321	1,540
Trifluralin	1,126	3,066	973	4,481	948	802	2,566	1,512	1,850	671	446	82
2,4-D	561	1,033	432	1,146	2,152	741	1,064	340	1,352	488	251	242
Butylate	12	2,477	1,329	1,325	1,218	16	837	13	953	1,003	959	322
Bentazon	1,004	1,908	668	1,328	141	531	1,232	306	396	259	184	97
Pendimethalin	693	1,359	478	1,423	113	373	749	734	857	297	420	202
Propanil	1,166	--	--	--	--	751	--	704	219	--	--	--
Metribuzin	233	695	471	626	188	268	139	267	404	36	406	96
Glyphosate	237	202	113	153	203	228	645	601	325	104	725	149
MSMA	358	--	--	--	--	1,062	--	2,056	--	--	--	--
Propachlor	--	204	--	93	991	--	46	--	533	709	--	49
Molinate	1,458	--	--	--	--	563	--	196	19	--	--	--
Chloromben	--	180	89	1,336	188	16	935	<1	121	87	112	37
Simazine	<1	310	76	<1	45	3	<1	27	4	14	273	1

Table 2.--*Summary of data for principal herbicides used in 12 States draining to the Mississippi River*

[K_{oc}, organic-carbon partition coefficient; mg/L, milligrams per liter; µg/L, micrograms per liter; --, no data; *, none established]

Herbicide	1/ Annual use during 1987-89	2/ Solubility (mg/L)	2/ Soil half-life (days)	2/ K_{oc}	3/ Maximum contaminant level (µg/L)	4/ Lifetime health advisory (µg/L)	1/ Principal target crops
Atrazine	58,568	33	60	100	3	3	Corn, sorghum, sugar cane
Alachlor	48,190	240	15	170	2	*	Corn, soybeans, sorghum
Metolachlor	36,426	530	20	200	*	100	Corn, soybeans, sorghum
EPTC	21,936	375	30	280	*	*	Corn, hay
Cyanazine	19,812	170	14	190	*	10	Corn, cotton, sorghum
Trifluralin	18,523	0.3	60	7,000	*	2	Soybeans, cotton
2,4-D	9,802	6/	10	6/	70	70	Pasture, wheat, corn, hay
Butylate	10,464	46	12	126	*	350	Corn
Bentazon	8,054	230,000	20	35	*	20	Soybeans, rice
Pendimethalin	7,698	0.3	90	24,300	*	*	Soybeans, corn, cotton
Propanil	5,840	220	1	188	*	*	Rice
Metribuzin	3,829	1,220	30	41	*	200	Soybeans, hay, sugar cane
Glyphosate	3,690	900,000	47	24,000	700	700	Soybeans, corn, cotton, pasture
MSMA	3,476	--	--	--	*	*	Cotton
Propachlor	3,464	613	6	80	*	90	Sorghum, corn
Molinate	2,236	--	--	--			Rice
Chloromben	3,102	7/	14	7/	*	100	Soybeans
Simazine	755	6.2	75	138	5/ 1	1	Corn, seed crops, orchards

1/ Annual use in thousands of pounds of active ingredient, from Gianessi and Puffer (1990)
2/ Source: Becker and others (1989)
3/ Source: U.S. Environmental Protection Agency (1991a)
4/ Source: U.S. Environmental Protection Agency (1991b)
5/ Source: U.S. Environmental Protection Agency (1990)
6/ Solubilities: 2,4-D amine, 796,000 mg/L; 2,4-D ester, 1 mg/L; Koc: 2,4-D amine 20; 2,4-D ester 1,000
7/ pH dependent

the MCL of 3 µg/L 35 percent of the time between May 1 and July 28, 1991. A few samples had concentrations of alachlor that exceeded the MCL of 2 µg/L, but no samples exceeded the simazine MCL of 1 µg/L.

Results from these studies indicate that measurable quantities of herbicides enter the Ohio, Missouri, and Mississippi Rivers each year. Much of these herbicides ultimately discharge into the Gulf of Mexico. Little is known, however, about the temporal distribution, timing and annual mass transport, and duration of concentrations of herbicides above MCLs in these major rivers, or the predominant source areas for these herbicides.

Objectives of This Study

In order to assist Federal and State agencies in determining if agricultural chemicals are present in concentrations that can affect water use in the Mississippi River system, the U.S. Geological Survey is presently (1991) conducting a study. Specific objectives of the study are to:

1. Determine the occurrence, temporal distribution, and annual mass transport of selected major insecticides, herbicides, herbicide metabolites, and inorganic nutrients in discharge from the Ohio, Missouri, and Mississippi Rivers and several smaller tributaries.

2. Determine the predominant source basins for insecticides, herbicides, and inorganic nutrients and estimate the fraction of the major agricultural chemicals applied throughout the Mississippi River basin that discharge to the Gulf of Mexico.

3. Determine the seasonality and timing of the transport of insecticides, herbicides, herbicide metabolites, nitrate, and orthophosphate.

4. Determine the duration of insecticide and herbicide concentrations greater than MCLs and HA levels for drinking water in the lower Ohio and Missouri Rivers and in the Mississippi River from the St. Louis area to New Orleans.

5. Test and implement a solid-phase-extraction gas chromatography/mass spectrometry analytical method that can be used to simultaneously analyze for several classes of pesticides including triazine, carbamate, and organophosphate compounds.

Purpose and Scope of this Report

Information obtained during the early phase of the study indicated that concentrations of some herbicides exceeded the drinking water MCLs or HAs in samples collected during May and June 1991. The purpose of this report is to document the methods used to collect and analyze the water samples and to describe the distributions of selected herbicides and nitrate-nitrogen at eight sampling sites on the Mississippi River and its major tributaries (fig. 1). The scope is limited to reporting information on the concentrations of five herbicides (atrazine, alachlor, cyanazine, metolachlor, and simazine) and nitrate-nitrogen in samples collected during April-June 1991.

After completion of the study in April 1992, all data and interpretation resulting from the study will be made available.

METHODS

Data Collection

This section provides a description of the sampling sites, the rationale for their selection, the sampling schedule, documentation of sample collection and sample analysis procedures, and a description of quality-assurance procedures for the study.

Description of Sampling Sites

The Mississippi River main stem is formed by the inflow from three major tributaries: the Missouri, the upper Mississippi, and the Ohio Rivers (fig. 1). Sampling sites were selected near the outflow of each of the three major rivers and on one or more large streams tributary to each of the three major rivers. The following is a brief description, by river basin, of each of the eight sampling sites. Their locations are shown on figure 1.

Upper Mississippi River Basin

1. Mississippi River at Clinton, Iowa (drainage area 85,600 square miles; mi^2): This site is the uppermost sampling site on the Mississippi River main stem. Samples from this site provide a measure of the agricultural chemical inputs from the upper basin States of northeastern Iowa, Minnesota and Wisconsin.

2. Illinois River at Valley City, Ill. (drainage area 26,742 mi^2): Samples from this site provide a measure of the inputs from a major tributary to the upper Mississippi River and an area of intensive row crop agriculture.

3. Mississippi River at Thebes, Ill. (drainage area 713,200 mi^2): Samples from this site provide a measure of all agricultural chemicals discharged from the upper Mississippi and Missouri River basins and represent essentially all of the Mississippi River discharge above the Ohio River. These samples indirectly (mathematically) provide an estimate of inputs from basins draining eastern Iowa and parts of Illinois below the Clinton sampling site.

Missouri River Basin

4. Platte River at Louisville, Nebr. (drainage area 85,800 mi^2): Samples from this site measure the inputs from a major tributary to the Missouri River. It drains an area of intensely irrigated agriculture in Nebraska.

5. Missouri River at Hermann, Mo. (drainage area 524,000 mi^2): This site is near the mouth of the Missouri River, and samples from the site provide a measure of agricultural chemical discharge to the Mississippi River from the entire Missouri River basin.

Ohio River Basin

6. White River near Hazleton, Ind. (drainage area 11,305 mi^2): This small basin drains an area of intensive agriculture in central and western Indiana. The White River discharges to the Wabash River, which in turn discharges to the Ohio River.

7. Ohio River near Grand Chain, Ill. (drainage area 203,100 mi^2): Samples from this site provide a measure of all inputs from the Ohio River basin to the Mississippi River.

Lower Mississippi River Basin

8. Mississippi River at Baton Rouge, La. (drainage area 1,125,000 mi^2): Measurements at this site and estimates of the Mississippi River diversions into the Atchafalaya River provide a measure of the total agricultural chemical discharge from the Mississippi River basin to the Gulf of Mexico. Discharge of agricultural chemicals into the Atchafalaya River, about 85 miles upstream from Baton Rouge (fig. 1), are estimated based on measurements of the quantity of water diverted to the Atchafalaya River and the concentrations of agricultural chemicals measured at Baton Rouge.

Sampling Schedule

Sample collection for this study began in early April 1991 and will continue for one year. Sample collection occurs about once per week, but is more frequent during late spring and summer when the concentrations of agricultural chemicals are expected to be largest and less frequent in the winter when concentrations of these chemicals are expected to be smallest. The sampling schedule is as follows:

April 1991	1 sample per week
May 6-July 15, 1991	2 samples per week (except Ohio River-- 1 sample per week)
July 15-October 30, 1991	1 sample per week
November 1991-February 1992	1 sample every two weeks
March, 1992	1 sample per week

The twice-weekly samples during May, June, and July will provide more intensive information on the concentrations and transport of agricultural chemicals during the "first-flush" events following application. Special efforts are made to distribute these samples over the discharge hydrograph to obtain the best estimates of mass transport.

Sample Collection and Processing Procedures

Samples are collected by equal-discharge-increment or equal-width-increment procedures (Edwards and Glysson, 1988) at all sites except the Mississippi River at Baton Rouge, La. Samples are collected in glass containers at five or more locations across the river at each sampling site using depth-integrating samplers and are composited in large glass or stainless steel containers. A Teflon cone splitter is then used to divide the composite sample into subsamples to be analyzed for the concentrations of dissolved herbicides and insecticides, dissolved nitrate, nitrite, and ammonia-nitrogen, dissolved orthophosphate, total organic plus ammonia-nitrogen, total phosphorus, and suspended sediment. This procedure provides a sample that is representative of the entire cross section of the river and makes it possible to compute loads of dissolved and suspended substances.

Previous work has indicated that dissolved solutes in the Mississippi River at Baton Rouge, La., are well mixed vertically and laterally (C.R. Demas, U.S. Geological Survey, Baton Rouge, La., oral commun., 1991). Therefore, to minimize sample-collection costs, samples collected at Baton Rouge are collected from the upper 20 feet of the water column at the end of a dock that extends about 150 feet from shore. As a quality-assurance measure, samples are periodically collected at several points across the river channel to verify that the river is well mixed. Samples for total organic plus ammonia-nitrogen, total phosphorus, and suspended sediment are not collected at this site.

In the present study, samples for herbicide and insecticide analysis are filtered through a 142-millimeter-diameter glass-fiber filter with a nominal pore size of 0.7 micrometer using aluminum or stainless steel-filter holders. Filtration is accomplished using either compressed nitrogen gas or pumps with ceramic and/or Teflon pump mechanisms. The filtrate is collected in pre-cleaned glass bottles.

Samples for nutrients (dissolved nitrogen and phosphorus compounds) are filtered through 0.45 micrometer membrane filters and preserved with mercuric chloride (40 mg/L). All herbicide, insecticide, and nutrient samples are chilled immediately after collection and are shipped to the U.S. Geological Survey's National Water Quality Laboratory (NWQL) in Arvada, Colo., for analysis.

On-Site Measurements and Streamflow

On-site measurements for specific conductance and pH are made on the composite mixture for each sample. Stream temperature is measured in situ. Except for the Baton Rouge, La., site, measurements of streamflow are obtained from stage-discharge relations at stations operated by the U.S. Geological Survey. Streamflow data for the Baton Rouge site are provided by the U.S. Army Corps of Engineers, New Orleans District; these data are for Tarberts Landing, about 80 miles upstream from Baton Rouge, but should closely represent the discharge at Baton Rouge. The U.S. Army Corps of Engineers also provides streamflow data for Mississippi River water that is diverted into the Atchafalaya River (fig. 1). The sum of the flow at Baton Rouge and the Atchafalaya diversion closely represents the total discharge from the Mississippi River basin above Baton Rouge.

Analytical Procedures

All water samples are analyzed at the NWQL in Arvada, Colo., for herbicides, insecticides, and nitrogen and phosphorus compounds. Analytical procedures used to analyze for herbicides and nitrate are briefly described below. Because results for insecticides and nutrient compounds other than nitrate are not presented in this report, analytical procedures for these compounds are not described.

Herbicides

Two analytical procedures are presently in use at the NWQL to analyze for the herbicides of interest in this study. These are a liquid-liquid extraction procedure using methylene chloride, and a solid-phase extraction procedure. The primary procedure used to obtain the data presented in this report is solid-phase extraction. A few samples were split and analyzed by both solid-phase extraction and liquid-liquid extraction.

Solid-Phase Extraction

This procedure is used for the isolation and analysis of triazine and other nitrogen-containing compounds. The procedure is described in detail by Sandstrom and others (in press), and is a modification of the procedure previously described by Thurman and others (1990). Approximately 100 milliliters of sample that has been filtered on-site through a 0.7-micrometer glass-fiber filter is pumped through a disposable C-18 solid-phase-extraction cartridge. Prior to extraction, a surrogate standard (terbuthylazine) is added to the sample to aid in determining the extraction efficiency and to aid in interpreting the analytical results. After extraction, the cartridges are dried with nitrogen gas and eluted with 1.8 milliliters of hexane-isopropanol (3:1) to remove the extracted compounds. The eluent is evaporated to about 100 microliters (μl) and herbicides are analyzed on a gas chromatograph equipped with a capillary column. Herbicides are identified and quantified with a mass spectrometer detector based on selected ion monitoring of the parent compound and two characteristic ions for each herbicide. Reporting limits for the five herbicides summarized in this report are 0.05 μg/L for alachlor, atrazine, metolachlor, and simazine, and 0.2 μg/L for cyanazine.

Liquid-Liquid Extraction

This is a long-established procedure for the analysis of triazine and other nitrogen-containing herbicides (Wershaw and others, 1987). The procedure is based on extraction of a 1-liter sample with methylene chloride. Extracts are analyzed on a gas chromatograph equipped with dual nitrogen-phosphorus detectors. This procedure is slightly less sensitive than the solid-phase extraction procedure, but has a long and well-documented history of use.

Nitrate-Nitrogen

Nitrate is determined by an automated colorimetric procedure. An aliquot of the sample is passed through a cadmium column on which nitrate is chemically reduced to nitrite (Fishman and Friedman, 1989). The resulting solution, which contains both the nitrite originally present in the sample plus the nitrite produced from the reduction of nitrate, is analyzed colorimetrically. A second part of the sample that does not pass through the cadmium column also is analyzed for nitrite. The concentration of nitrate in the sample is then calculated from the difference between these two determinations.

Quality-Assurance Procedures

Before collection of each sample, all sampling equipment is washed with a phosphate-free laboratory detergent, rinsed with tap water and distilled or deionized water, rinsed with a small amount of methanol and allowed to air dry. At the sampling site, all equipment (collection container, compositing container, cone splitter, pump mechanism, and filter) is rinsed with water from the stream. Glass-fiber filters and sample containers are baked at about 350 degrees Celsius to remove organic material. A field-equipment blank for pesticides is obtained with about every 10th sample. This sample consists of organic-free water that is processed through all of the sampling and filtration equipment. The sample is analyzed for the herbicides of interest. Sample collection and processing procedures used in the field are periodically reviewed for conformance with protocols established for the project.

Laboratory quality-assurance procedures include the determination of surrogate compound recoveries in each sample, blank, and laboratory reagent-water spikes. Blanks are used to verify that the glassware and reagents used in sample preparation are free of contamination. The surrogate added to each sample is used to monitor the extraction efficiency for each sample. Reagent-water spikes monitor extraction efficiencies for each analyte of interest. Spike data also are used to compile recovery statistics from which control limits can be established. Additional quality-assurance procedures include analysis of blind spike samples submitted from the field and analysis of split samples by both solid-phase extraction and liquid-liquid extraction.

ANALYTICAL RESULTS

Herbicides and Nitrate-Nitrogen

Analytical results for five herbicides, obtained by solid-phase extraction, and nitrate-nitrogen in samples collected during April, May, and June 1991 are listed in table 3 along with streamflow data and measurements of physical properties (temperature, pH, and specific conductance). The sampling sites are listed in downstream order in accordance with the streamflow-station numbering system of the U.S. Geological Survey. Results of analyses for herbicides and nitrate-nitrogen are statistically summarized in table 4. These results and their significance are discussed in subsequent sections of this report.

Quality-Assurance Samples

Results for herbicide recovery on reagent-water spikes are shown in table 5 for the solid-phase extraction and in table 6 for liquid-liquid extraction. Similar recoveries are obtained by both procedures. Atrazine recovery using solid-phase extraction ranged from 48 to 105 percent and averaged 88.5 percent. Similar recoveries were obtained for the other herbicides analyzed using this procedure. During May and June, 13 blind spikes in distilled water with concentrations ranging from 0.5 µg/L to 4.0 µg/L were analyzed using this procedure. Recoveries for the five herbicides of interest were within the range for the reagent-water spikes shown in table 5. For example, atrazine recovery ranged from 56 percent to 95 percent and averaged 82 percent

Table 3.--*Streamflow, physical property data, and results of analyses for herbicides and nitrate-nitrogen in samples collected during April, May, and June 1991*

[ft^3/s, cubic feet per second; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter; <, less than; --, no data]

Date	Time	Instantaneous streamflow (ft^3/s)	Temperature (°C)	pH	Specific conductance (µS/cm)	Nitrate-nitrogen (mg/L)	Alachlor (µg/L)	Atrazine (µg/L)	Cyanazine (µg/L)	Metolachlor (µg/L)	Simazine (µg/L)
03374100 - White River at Hazleton, Ind.											
May											
01	1000	14,100	17.5	7.9	436	2.09	<0.05	0.26	<0.02	0.19	<0.05
06	1115	11,900	17.5	8.0	444	1.60	<0.05	0.35	<0.02	0.16	0.07
09	1215	11,600	17.5	8.2	481	1.59	<0.05	0.42	0.20	0.20	0.06
13	1300	9,480	20.5	8.0	494	1.58	0.68	3.7	0.70	1.1	0.33
16	1130	8,010	23.5	8.2	568	1.18	0.08	0.91	0.60	0.35	0.12
20	1045	8,640	24.0	8.1	572	1.48	0.25	1.4	0.70	0.27	0.14
23	1100	9,980	24.5	8.0	537	2.16	1.3	3.4	1.40	1.5	0.30
28	1100	9,480	26.0	7.8	523	3.98	3.2	8.6	4.40	2.2	0.51
30	1200	8,400	27.5	7.9	540	3.07	2.1	9.2	2.80	3.3	0.72
June											
03	1200	7,750	28.5	7.9	511	3.05	0.88	8.2	2.10	2.8	0.58
06	1145	11,200	27.0	7.9	537	3.27	1.3	5.1	1.30	2.0	0.38
10	1200	6,520	26.5	--	522	2.89	1.2	5.5	2.00	2.2	0.70
13	1100	5,410	27.0	8.3	609	2.48	0.96	5.8	1.60	1.9	0.45
17	1200	4,950	27.5	8.3	581	1.28	0.30	3.2	0.87	0.89	0.17
20	1130	4,920	28.5	8.2	583	0.74	0.19	2.6	0.50	0.85	0.10
24	1215	4,370	27.5	8.3	577	0.86	0.27	2.7	0.60	0.98	0.16
27	1130	3,810	29.0	8.4	564	0.18	0.08	2.0	0.50	0.54	0.12

Table 3.--*Streamflow, physical property data, and results of analyses for herbicides and nitrate-nitrogen in samples collected during April, May, and June 1991*--Continued

Date	Time	Instantaneous streamflow (ft^3/s)	Tem-perature (°C)	pH	Specific con-ductance (µS/cm)	Nitrate-nitrogen (mg/L)	Alachlor (µg/L)	Atrazine (µg/L)	Cyanazine (µg/L)	Metolachlor (µg/L)	Simazine (µg/L)
03612500 - Ohio River at Dam 53 near Grand Chain, Ill.											
Apr.											
10	1200	407,000	15.5	8.5	150	0.98	<0.05	0.12	<0.20	0.09	0.06
18	1045	595,000	16.5	7.6	231	0.85	<0.05	0.15	<0.20	<0.05	<0.05
23	1110	565,000	16.0	7.3	236	1.09	<0.05	0.51	0.21	0.32	0.07
May											
01	1040	362,000	18.0	8.3	202	0.97	<0.05	0.18	<0.20	0.08	<0.05
07	1022	291,000	19.5	8.1	179	0.63	<0.05	0.23	<0.20	0.12	0.08
14	1045	340,000	20.5	8.5	170	0.70	<0.05	0.47	<0.20	0.10	0.16
21	1045	240,000	23.0	8.3	230	1.07	0.11	1.7	0.40	0.39	0.40
29	1030	504,000	24.0	7.8	170	0.61	0.05	0.54	0.20	0.10	0.05
June											
04	1135	214,000	26.5	7.6	290	0.97	0.24	1.6	0.50	0.35	0.12
11	1045	107,000	26.0	6.4	246	1.47	0.33	1.9	0.50	0.72	0.07
18	1040	137,000	27.0	5.6	197	0.96	0.40	2.1	0.70	0.95	0.12
25	0946	137,000	27.5	6.2	272	0.79	0.13	1.3	0.40	0.42	0.11

Table 3.--*Streamflow, physical property data, and results of analyses for herbicides and nitrate-nitrogen in samples collected during April, May, and June 1991*--Continued

Date	Time	Instantaneous streamflow (ft^3/s)	Temperature (°C)	pH	Specific conductance (µS/cm)	Nitrate-nitrogen (mg/L)	Alachlor (µg/L)	Atrazine (µg/L)	Cyanazine (µg/L)	Metolachlor (µg/L)	Simazine (µg/L)
05420500 - Mississippi River at Clinton, Iowa											
Apr.											
02	1040	127,000	8.0	7.5	305	0.55	<0.05	0.18	<0.20	<0.05	<0.05
11	1100	110,000	11.5	8.2	332	1.78	<0.05	0.15	<0.20	0.07	<0.05
16	1150	129,000	9.0	8.2	335	3.57	<0.05	0.17	<0.20	0.06	<0.05
23	1030	130,000	11.5	8.6	295	2.48	<0.05	0.17	<0.20	0.08	<0.05
May											
01	1150	117,000	14.0	8.5	366	2.58	0.06	0.15	<0.20	0.07	<0.05
07	1115	112,000	11.0	8.6	372	3.56	<0.05	0.17	<0.20	0.05	<0.05
10	1030	111,000	14.0	8.5	375	3.36	<0.05	0.13	<0.20	0.10	<0.05
14	1120	118,000	19.0	8.4	355	2.88	0.09	0.16	<0.20	0.12	<0.05
17	1045	132,000	20.5	8.7	355	2.67	0.06	0.12	<0.20	0.06	<0.05
21	1140	141,000	18.5	8.3	326	3.05	0.24	0.37	<0.20	0.25	0.06
24	1205	141,000	20.0	8.3	364	3.56	0.19	0.22	0.20	0.24	<0.05
28	1210	123,000	24.0	8.4	370	3.74	0.23	0.41	0.30	0.21	<0.05
31	1015	116,000	24.5	8.6	361	3.63	0.11	0.29	<0.20	0.16	0.05
June											
04	1300	113,000	23.5	8.4	338	3.47	0.48	0.78	0.30	0.36	0.11
07	1100	127,000	23.0	8.2	303	2.90	0.24	0.50	0.30	0.26	<0.05
10	1130	138,000	23.5	8.8	273	2.24	0.14	0.37	0.20	0.20	<0.05
13	1410	149,000	25.5	8.3	279	2.23	0.14	0.35	0.30	0.20	<0.05
17	1040	149,000	23.5	8.3	328	2.48	0.78	1.6	0.94	0.56	0.06
20	1345	128,000	26.0	8.2	362	3.18	0.85	1.6	0.82	0.72	0.06
24	1055	106,000	24.0	8.1	396	3.28	0.48	0.73	0.78	0.66	0.05
27	0915	96,900	25.0	8.3	425	3.79	0.54	0.66	1.20	0.87	<0.05

Table 3.--*Streamflow, physical property data, and results of analyses for herbicides and nitrate-nitrogen in samples collected during April, May, and June 1991*--Continued

Date	Time	Instantaneous streamflow (ft^3/s)	Temperature (°C)	pH	Specific conductance (µS/cm)	Nitrate-nitrogen (mg/L)	Alachlor (µg/L)	Atrazine (µg/L)	Cyanazine (µg/L)	Metolachlor (µg/L)	Simazine (µg/L)
05586100 - Illinois River at Valley City, Ill.											
Apr.											
05	1230	52,600	--	8.2	657	1.34	<0.05	0.18	<0.200	0.15	0.06
17	1330	42,700	--	7.0	670	5.33	0.62	2.4	1.30	1.5	<0.05
26	1000	53,700	14.5	6.9	631	6.23	0.14	0.96	0.700	0.92	<0.05
May											
03	1545	43,000	15.0	7.4	642	5.72	0.28	0.95	1.10	0.86	<0.05
08	1245	58,000	16.0	7.5	521	4.84	2.0	5.0	5.60	2.6	0.06
10	1100	57,800	23.0	6.8	516	5.23	3.0	6.3	2.90	4.4	0.14
17	1145	44,700	28.0	7.8	642	5.72	0.84	2.5	2.50	2.0	<0.05
19	1115	54,400	18.5	8.0	499	4.70	1.6	5.5	6.60	1.6	0.07
22	1715	50,100	21.5	7.5	495	6.38	0.92	3.4	2.90	2.1	0.05
29	1130	53,300	19.0	8.1	544	5.59	--	--	--	--	--
31	1045	64,800	25.0	8.1	468	4.60	0.97	4.9	2.50	2.0	0.07
June											
04	1215	55,200	28.0	7.9	585	5.67	0.85	4.6	2.70	2.1	0.09
06	1200	51,200	25.0	7.9	581	6.06	1.0	5.2	2.00	2.3	0.09
11	1345	40,300	25.0	7.9	627	5.69	0.84	4.7	1.80	2.0	0.14
14	1200	34,800	32.0	8.0	641	5.32	0.54	3.8	2.00	1.4	0.12
18	1130	29,800	29.5	8.1	651	4.60	0.36	2.1	0.900	0.78	0.07
20	1130	27,600	31.5	8.2	664	4.31	0.34	2.8	1.40	0.83	0.12
24	1130	17,100	13.0	7.9	661	3.34	0.17	2.4	1.40	0.63	0.09
27	1100	17,700	28.5	7.9	680	2.97	0.21	1.9	0.800	0.55	0.07

Table 3.--*Streamflow, physical property data, and results of analyses for herbicides and nitrate-nitrogen in samples collected during April, May, and June 1991*--Continued

Date	Time	Instantaneous streamflow (ft^3/s)	Temperature (°C)	pH	Specific conductance (μS/cm)	Nitrate-nitrogen (mg/L)	Alachlor (μg/L)	Atrazine (μg/L)	Cyanazine (μg/L)	Metolachlor (μg/L)	Simazine (μg/L)
06805500 - Platte River at Louisville, Nebr.											
Apr.											
09	1250	4,800	--	8.7	635	0.16	0.10	0.25	<0.20	0.10	<0.05
16	1030	7,120	11.5	8.2	533	1.35	<0.05	0.37	<0.20	0.11	<0.05
24	1030	5,740	13.0	8.0	546	0.73	<0.05	0.06	<0.20	<0.05	<0.05
29	1000	5,430	11.0	8.8	595	0.29	0.14	0.66	<0.20	0.30	<0.05
May											
06	1115	8,870	10.0	8.4	470	0.68	0.27	1.3	0.38	0.47	<0.05
09	0940	7,910	18.0	8.3	588	0.97	0.14	0.81	0.20	0.21	0.09
13	1110	6,670	--	8.7	544	0.29	0.20	0.87	<0.20	0.21	<0.05
16	1130	5,600	23.0	8.9	483	<0.05	0.17	0.35	0.40	0.09	<0.05
21	0945	5,470	19.0	8.2	445	1.25	3.6	8.3	6.80	3.1	<0.05
24	0740	6,240	22.0	8.0	480	0.74	0.51	2.4	1.40	0.70	<0.05
29	1015	11,000	27.0	8.5	269	0.78	1.4	6.5	1.70	2.2	0.07
31	0735	8,460	24.0	7.5	555	1.27	2.1	6.8	7.00	2.6	0.06
June											
04	0800	20,400	24.0	6.3	437	1.27	1.7	5.7	3.70	1.9	0.06
07	1415	32,300	--	6.4	347	1.72	3.2	10	7.30	2.0	0.06
11	1045	12,800	23.0	6.1	491	1.25	0.80	5.4	2.00	1.3	<0.05
14	0750	19,400	22.0	6.4	360	1.26	0.99	4.7	1.90	1.4	0.05
18	0935	10,900	--	7.4	540	1.16	0.59	3.4	3.20	0.80	<0.05
21	1020	7,480	23.0	6.3	521	0.86	0.15	1.9	1.30	0.34	<0.05
24	1110	7,800	22.0	7.4	540	1.20	0.23	1.8	0.70	0.33	<0.05
27	1020	5,010	26.0	6.3	678	--	0.10	1.4	0.900	0.20	<0.050

Table 3.--*Streamflow, physical property data, and results of analyses for herbicides and nitrate-nitrogen in samples collected during April, May, and June 1991*--Continued

Date	Time	Instantaneous streamflow (ft^3/s)	Temperature (°C)	pH	Specific conductance (µS/cm)	Nitrate-nitrogen (mg/L)	Alachlor (µg/L)	Atrazine (µg/L)	Cyanazine (µg/L)	Metolachlor (µg/L)	Simazine (µg/L)
06934500 - Missouri River at Hermann, Mo.											
Apr.											
09	1331	41,400	--	8.2	570	1.68	0.07	0.37	<0.20	0.15	<0.05
16	1030	117,000	16.5	8.8	429	0.87	0.21	1.2	0.60	0.38	<0.05
24	1200	129,000	14.0	7.9	365	2.13	0.11	1.1	0.45	0.53	<0.05
May											
01	1130	128,000	17.5	8.0	502	2.45	0.26	1.6	0.70	0.79	<0.05
06	1100	149,000	16.5	7.6	361	1.63	0.33	2.6	1.50	1.0	<0.05
09	0930	142,000	16.5	7.9	375	1.55	0.47	3.2	0.80	0.77	0.09
13	1000	97,100	18.0	8.1	429	1.76	0.18	1.9	0.60	0.55	0.07
16	1020	127,000	21.5	8.1	370	1.36	0.17	1.8	0.50	0.43	<0.05
20	1000	84,300	22.0	7.9	515	2.06	0.19	1.7	0.70	0.48	<0.05
24	1000	84,000	23.0	8.1	549	2.20	0.68	2.7	2.10	1.4	<0.05
28	1030	111,000	24.0	7.9	406	1.80	0.57	2.9	1.60	1.3	<0.05
31	1040	105,000	25.5	8.2	430	1.80	0.42	3.2	2.00	1.1	<0.05
June											
03	1000	120,000	26.5	8.1	538	2.20	0.27	3.1	1.60	0.80	<0.05
06	1000	111,000	25.5	8.0	433	2.39	0.57	5.4	2.00	1.7	<0.05
11	1000	98,600	25.0	8.1	539	2.90	0.41	5.7	4.30	1.4	0.08
13	1000	84,100	26.0	8.2	458	2.59	0.92	5.7	4.70	1.7	0.06
21	1000	93,400	27.5	7.9	470	2.48	0.43	5.5	1.80	2.0	<0.05
25	1130	72,000	28.0	8.2	486	2.98	0.23	3.9	2.10	1.7	<0.05
27	1045	71,200	29.0	8.1	551	2.90	0.29	3.5	0.60	0.93	0.07

Table 3.--*Streamflow, physical property data, and results of analyses for herbicides and nitrate-nitrogen in samples collected during April, May, and June 1991*--Continued

Date	Time	Instantaneous streamflow (ft^3/s)	Temperature (°C)	pH	Specific conductance (µS/cm)	Nitrate-nitrogen (mg/L)	Alachlor (µg/L)	Atrazine (µg/L)	Cyanazine (µg/L)	Metolachlor (µg/L)	Simazine (µg/L)
07022000 - Mississippi River at Thebes, Ill.											
Apr.											
11	1500	285,000	14.5	7.8	489	5.02	0.31	0.64	<0.20	0.20	<0.05
18	1130	395,000	17.0	7.8	425	2.63	--	--	--	--	--
24	0930	475,000	13.5	7.8	408	3.75	0.21	1.0	0.52	0.52	<0.05
29	1230	379,000	16.5	7.9	454	4.75	0.12	0.63	0.40	0.31	<0.05
May											
07	1345	372,000	17.0	7.8	407	3.94	0.58	3.2	3.10	1.1	<0.05
09	0900	411,000	17.0	7.8	377	3.44	0.34	1.7	1.40	0.58	<0.05
13	1330	395,000	17.5	7.9	393	3.73	0.63	3.6	1.60	1.1	0.10
16	1200	370,000	20.0	7.9	482	4.33	0.31	1.3	1.00	0.69	<0.05
20	1430	378,000	23.5	7.8	434	4.13	0.13	0.80	0.50	0.24	<0.05
23	0916	340,000	22.0	7.7	433	3.96	0.59	2.4	2.30	0.75	<0.05
28	1300	390,000	25.5	8.2	468	4.08	0.65	2.4	2.80	1.4	<0.05
30	1330	406,000	25.0	8.0	422	4.10	0.77	3.0	2.50	1.7	<0.05
June											
03	1345	384,000	25.5	7.9	392	4.88	0.46	2.0	1.30	1.2	<0.05
06	1045	375,000	26.0	8.2	478	4.89	0.39	2.5	1.30	1.1	<0.05
10	1400	360,000	26.5	7.9	471	4.99	0.86	4.2	1.80	1.9	<0.05
13	1500	333,000	26.0	8.2	489	5.10	0.84	3.9	2.30	2.2	<0.05
18	1430	326,000	26.0	7.7	464	4.60	0.39	2.2	1.40	1.1	<0.05
20	1100	336,000	26.5	8.1	468	4.40	0.19	1.2	0.50	0.58	<0.05
24	1300	318,000	29.0	8.1	451	4.38	0.36	3.2	1.80	1.4	0.05
27	1400	300,000	27.0	8.2	434	4.30	0.85	3.3	0.06	1.8	0.080

Table 3.--*Streamflow, physical property data, and results of analyses for herbicides and nitrate-nitrogen in samples collected during April, May, and June 1991*--Continued

Date	Time	Daily mean streamflow (ft^3/s)	Temperature (°C)	pH	Specific conductance (µS/cm)	Nitrate-nitrogen (mg/L)	Alachlor (µg/L)	Atrazine (µg/L)	Cyanazine (µg/L)	Metolachlor (µg/L)	Simazine (µg/L)
07374000 - Mississippi River at Baton Rouge, La.											
Apr											
11	1430	882,000	16.5	7.9	366	1.99	<0.05	0.28	<0.20	0.12	<0.05
17	1415	972,000	18.0	7.8	306	1.88	<0.05	0.23	<0.20	0.10	<0.05
24	1045	1,020,000	18.0	7.8	293	1.69	<0.05	0.39	<0.20	0.13	<0.05
May											
01	1030	1,140,000	18.5	7.6	300	1.50	0.06	0.52	0.30	0.18	<0.05
06	0800	1,160,000	19.0	7.6	280	1.59	<0.05	0.49	0.20	0.18	<0.05
09	1030	1,170,000	19.0	7.6	277	1.70	0.13	1.0	0.21	0.31	0.10
13	0930	1,150,000	21.0	7.6	281	1.80	0.10	0.59	<0.20	0.23	0.08
16	1130	1,120,000	22.0	7.5	295	1.89	<0.05	0.34	0.20	0.14	<0.05
20	1330	1,050,000	22.5	--	291	1.89	0.13	1.2	0.90	0.38	<0.05
24	1315	1,020,000	23.0	7.7	294	1.89	0.14	1.1	0.60	0.40	<0.05
28	1255	965,000	24.5	7.8	311	2.00	0.07	0.83	0.30	0.36	<0.05
[1]30	1130	934,000	25.0	7.7	316	1.9	0.13	1.1	0.40	0.36	0.09
June											
[1]03	1045	869,000	26.0	7.7	336	2.0	0.18	1.6	0.90	0.48	0.08
[1]06	1300	870,000	27.0	7.7	353	2.4	0.34	2.0	1.10	0.71	0.08
[1]10	1315	856,000	26.5	7.7	307	2.0	0.23	1.5	0.80	0.67	0.05
[1]13	1400	809,000	27.0	7.8	338	2.3	0.29	2.6	1.20	0.97	0.11
17	1315	724,000	27.5	7.8	382	2.59	0.20	1.9	0.80	0.71	0.05
20	1415	641,000	28.0	8.0	403	2.60	0.30	2.5	0.88	0.87	0.07
24	1345	583,000	28.0	8.0	410	3.30	0.44	3.6	1.80	1.4	0.08
27	1400	574,000	28.0	8.0	409	<0.05	0.40	2.6	1.50	1.2	0.07

[1] Sample exceeded holding time for herbicide extraction and nitrate analysis.

Table 4.--*Statistical summary of results in downstream order for five herbicides and nitrate-nitrogen in samples collected during April, May, and June 1991*

[>, greater than; MCL, maximum contaminant level; HA, health advisory level; µg/L, micrograms per liter; <, less than; mg/L, milligrams per liter; Note: MCLs are: alachlor-2 µg/L, atrazine-3 µg/L, simazine 1 µg/L; HAs are: cyanazine-10 µg/L, metolachlor-100 µg/L]

River (fig. 1)	Site (fig. 1)	Number of samples	Percent detections	Number of samples > MCL or HA	Concentration Median (µg/L)	Concentration Maximum (µg/L)	Number of samples	Percent detections	Number of samples > MCL or HA	Concentration Median (µg/L)	Concentration Maximum (µg/L)
		Alachlor					Atrazine				
White	Hazelton	17	82	2	0.30	3.2	17	100	9	3.2	9.2
Ohio	Grand Chain	12	50	0	<0.05	0.40	12	100	0	0.52	2.1
Mississippi	Clinton	21	71	0	0.14	0.85	21	100	0	0.29	1.6
Illinois	Valley City	18	94	1	0.73	3.0	18	100	9	3.1	6.3
Platte	Louisville	20	90	3	0.25	3.6	20	100	8	1.8	10
Missouri	Hermann	19	100	0	0.29	0.92	19	100	9	2.9	5.7
Mississippi	Thebes	19	100	0	0.39	0.86	19	100	6	2.4	4.2
Mississippi	Baton Rouge	20	75	0	0.13	0.44	20	100	1	1.1	3.6
		Cyanazine					Metolachlor				
White	Hazelton	17	88	0	0.7	4.4	17	100	0	0.98	3.3
Ohio	Grand Chain	12	58	0	0.2	0.7	12	92	0	0.22	0.95
Mississippi	Clinton	21	48	0	<0.2	1.2	21	95	0	0.20	0.87
Illinois	Valley City	18	94	0	1.9	6.6	18	100	0	1.5	4.4
Platte	Louisville	20	75	0	1.1	7.3	20	95	0	0.40	3.1
Missouri	Hermann	19	95	0	1.5	4.7	19	100	0	0.93	2.0
Mississippi	Thebes	19	95	0	1.4	3.1	19	100	0	1.1	2.2
Mississippi	Baton Rouge	20	80	0	0.5	1.8	20	100	0	0.37	1.4

Table 4.--*Statistical summary of results in downstream order for five herbicides and nitrate-nitrogen in samples collected during April, May, and June 1991*--Continued

River (fig. 1)	Site (fig. 1)	Number of samples	Percent detections	Number of samples > MCL or HA	Concentration Median (µg/L)	Concentration Maximum (µg/L)	Number of samples	Number of samples > MCL or HA	Concentration Median (mg/L)	Concentration Maximum (mg/L)
		Simazine					Nitrate-nitrogen			
White	Hazelton	17	94	0	0.17	0.72	17	0	1.60	3.98
Ohio	Grand Chain	12	83	0	0.08	0.40	12	0	0.96	1.47
Mississippi	Clinton	21	28	0	<0.05	0.11	21	0	3.05	3.79
Illinois	Valley City	18	78	0	0.07	0.14	19	0	5.32	6.38
Platte	Louisville	20	30	0	<0.05	0.09	19	0	0.97	1.72
Missouri	Hermann	19	26	0	<0.05	0.09	19	0	2.13	2.98
Mississippi	Thebes	19	16	0	<0.05	0.10	20	0	4.32	5.10
Mississippi	Baton Rouge	20	55	0	0.05	0.11	20	0	1.89	3.30

Table 5.--*Summary of recovery data for all reagent water spikes analyzed by solid-phase extraction during late May and June 1991*

[All compounds spiked at a concentration of 2.0 micrograms per liter; µg/L, micrograms per liter; %, percent]

	Alachlor	Atrazine	Cyanazine	Metolachlor	Simazine
Number of samples	30	30	30	30	30
Mean recovery (µg/L)	1.69	1.77	1.86	1.86	1.75
Range of recovery (µg/L)	0.86-2.18	0.94-2.10	1.14-2.5	0.94-2.24	0.96-2.06
Standard deviation	0.26	0.24	0.40	0.24	0.24
Relative standard deviation (%)	15.09	13.32	21.39	12.92	13.52
Mean recovery (%)	84.5	88.5	92.8	93.2	87.6

Table 6.--*Summary of recovery data for seven reagent water spikes analyzed by liquid-liquid extraction during late May and June 1991*

[µg/L, micrograms per liter; %, percent]

	Alachlor	Atrazine	Cyanazine	Metolachlor	Simazine
Amount added (µg/L)	0.84	0.74	0.80	0.83	0.76
Number of samples	7	7	7	7	7
Mean recovery (µg/L)	0.73	0.65	1.02	0.71	0.66
Range of recovery (µg/L)	0.66-0.85	0.56-0.74	0.88-1.21	0.62-0.80	0.54-0.76
Standard deviation (µg/L)	0.07	0.06	0.12	0.07	0.08
Relative standard deviation (%)	9.91	9.87	11.51	10.16	12.20
Mean recovery (%)	86.7	87.3	127.9	85.2	86.5

Results obtained from the analyses of nine samples that were split and analyzed by both solid-phase extraction and liquid-liquid extraction are shown in table 7. Similar results were obtained for alachlor, metolachlor, and simazine. However, solid-phase extraction gave lower results than did liquid-liquid extraction for atrazine and cyanazine at concentrations greater than about 2 μg/L. These results and the spike recoveries indicate that concentrations obtained for atrazine by solid-phase extraction may be slightly (10-20 percent) lower than concentrations actually present in the samples.

Herbicides were not detected in any of the 17 field-equipment blanks analyzed during April, May, and June. This provides assurance that samples were not contaminated during sample collection and processing.

Table 7.--*Results for split samples analyzed by solid-phase extraction and liquid-liquid extraction*

[all results in micrograms per liter; <, less than; SPE, solid-phase extraction; LLE, liquid-liquid extraction]

Collection	Alachlor		Atrazine		Cyanazine		Metolachlor		Simazine	
date	SPE	LLE	SPE	LLE	SPE	LLE	SPE	LLE	SPE	LLE
Illinois River at Valley City, Ill.										
5/22/91	[1]0.92	1.3	[1]3.4	7.0	[1]2.9	6.0	[1]2.1	3.0	[1]0.05	0.1
6/14/91	0.54	0.60	3.8	4.3	2.0	2.6	1.4	1.5	0.12	0.16
6/24/91	0.17	0.18	2.4	2.8	1.4	2.0	0.63	0.63	0.09	0.10
7/11/91	0.05	[1]<0.1	0.70	[1]0.34	0.3	0.2	0.12	0.1	0.06	[1]0.02
Platte River near Louisville, Nebr.										
5/21/91	[1]3.6	3.3	[1]8.3	12.8	[1]6.8	7.6	[1]3.1	3.3	[1]<0.05	0.06
5/29/91	1.4	1.1	6.5	8.1	1.7	1.2	2.2	1.6	0.07	0.07
6/4/91	1.7	1.6	5.7	9.0	3.7	8.7	1.9	1.5	0.06	0.09
6/7/91	3.2	3.9	10.0	13.2	7.3	10.9	2.0	1.8	0.06	0.1
7/8/91	<0.05	0.03	0.77	0.74	0.4	0.6	0.08	0.12	<0.05	0.02

[1] Sample had low surrogate recovery.

DISTRIBUTION OF HERBICIDES

Results obtained from the first 3 months of this study show that herbicides were present in the Mississippi River and several large tributaries (tables 3 and 4). Herbicide concentrations began to increase in early May in response to rainfall that occurred after herbicides were applied to cropland. The pattern of occurrence was similar to that reported by Thurman and others (1991) for streams throughout 10 midwestern States. They reported that large concentrations of herbicides are transported through the surface-water system in pulses each year during late spring and summer. Results from the present study show that these pulses reach the major rivers of the Midcontinent and can cause herbicide concentrations to exceed drinking-water regulations for periods of several weeks or longer.

Areal Distribution

One or more herbicides were detected in every water sample collected during April, May, and June 1991 (table 3). The distribution of alachlor, atrazine, cyanazine, and metolachlor concentrations are shown in boxplots in figures 2 and 3 for each of the 8 sampling sites. Lines extending to the bottom and top of each boxplot show the minimum and maximum concentrations measured at each site. The horizontal line near the middle of each boxplot shows the median concentration and the bottom and top of the rectangular portion of the boxplot represent the 25th and 75th percentiles, respectively. For example, the boxplot of atrazine for the Illinois River (fig. 2) shows that concentrations ranged from 0.18 µg/L to 6.3 µg/L with a median of 2.8 µg/L.

Atrazine was detected in every sample (146 samples) and had the largest concentrations of the herbicides measured (fig. 2, table 4). Median concentrations of atrazine ranged from 0.29 µg/L for the Mississippi River at Clinton to 3.2 µg/L for the White River (fig. 2). Cyanazine and metolachlor were detected in 78 and 98 percent of the samples, respectively. Median concentrations of cyanazine ranged from less than the reporting limit of 0.2 µg/L (fig. 3) in the Mississippi River at Clinton to 1.9 µg/L in the Illinois River. These two sampling sites also had the smallest median (0.20 µg/L) and largest median (1.5 µg/L) concentration of metolachlor, respectively. Overall, the concentrations of alachlor were somewhat lower than atrazine, cyanazine, and metolachlor. Median concentrations of alachlor ranged from less than 0.05 µg/L in the Ohio River to 0.73 µg/L in the Illinois River (table 4; fig. 2). Simazine was detected in less than one-half of the samples; its median concentration was less than the reporting limit of 0.05 µg/L. Alachlor, atrazine, cyanazine, and metolachlor are among the most extensively used herbicides in the 12-State area of the Mississippi River basin (table 2).

The largest concentrations of herbicides were measured in samples from the smaller tributaries--the White, Illinois, and Platte Rivers (figs. 2 and 3, table 4), probably because of the greater percentage of drainage area of the smaller basins that is in cropland and the more rapid response of these rivers to rainfall, which transports herbicides to the streams. For example, the concentration of atrazine exceeded 5 µg/L in about 25 percent of the samples collected from these tributaries, and the maximum atrazine concentration ranged from 6.3 to 10 µg/L (fig. 2).

The median concentration of atrazine measured in samples from the Missouri River at Hermann (fig. 2, table 4), 2.9 µg/L, was similar to median concentrations measured in samples from the smaller tributaries; the maximum atrazine concentration was 5.7 µg/L (table 4). A recent study of herbicides in the Missouri River by Keck (1991) indicates that the herbicides are derived largely from tributaries discharging to the Missouri River in Iowa, Kansas, Missouri, and Nebraska

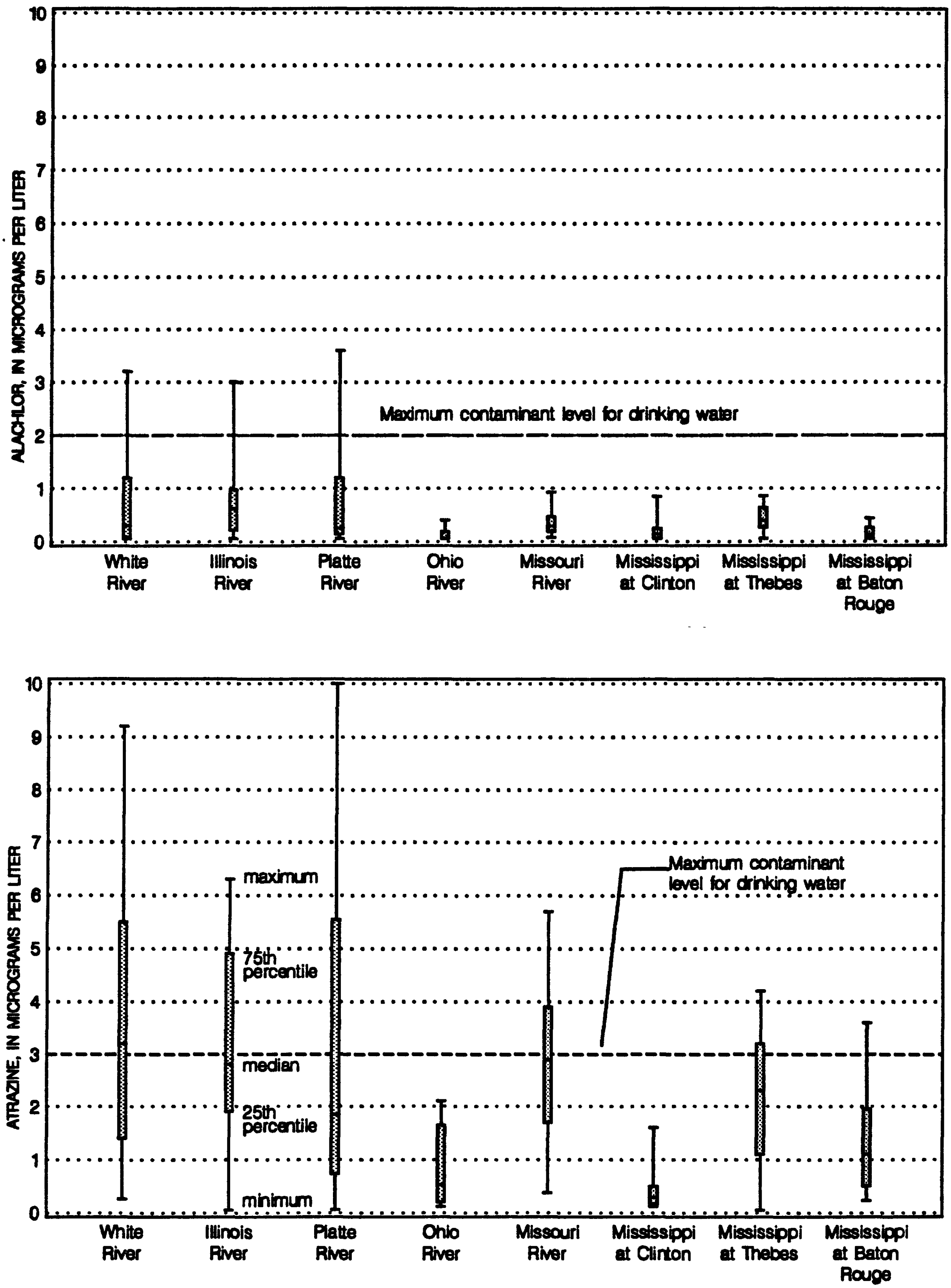

Figure 2.--Boxplots of alachlor and atrazine concentrations arranged by downstream order for samples collected in April, May, and June 1991.

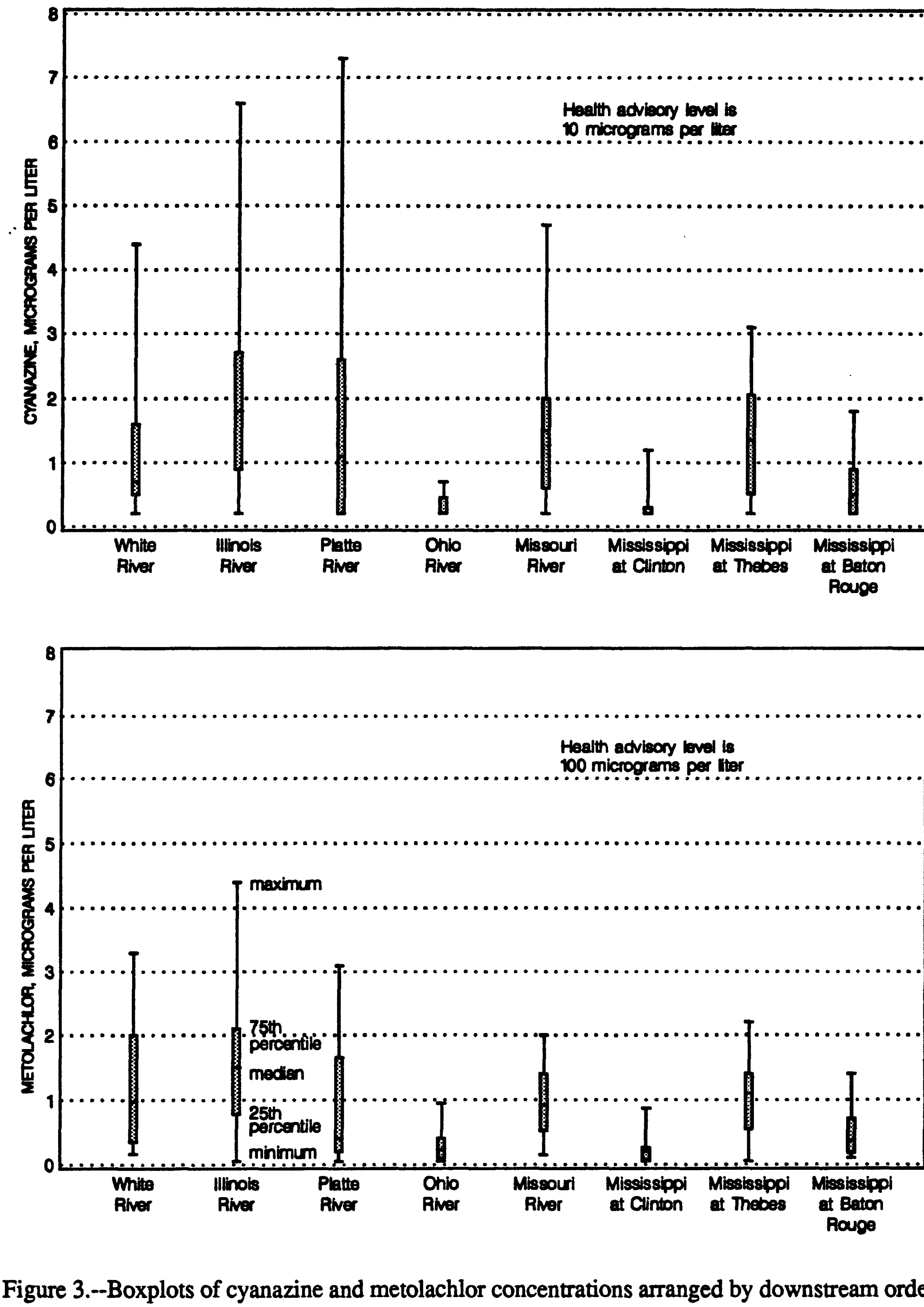

Figure 3.--Boxplots of cyanazine and metolachlor concentrations arranged by downstream order for samples collected in April, May, and June 1991.

Herbicide concentrations larger than 1 μg/L were measured in many samples from the Mississippi River at the Thebes site (fig. 1). For example, the median concentration of atrazine was 2.3 μg/L (table 4), and about 25 percent of the samples had concentrations larger than 3.2 μg/L (fig. 2). Median concentrations of cyanazine and metolachlor exceeded 1 μg/L. These concentrations reflect the inflow from the Missouri River and inflow from the Illinois River and other rivers draining from Iowa and Illinois downstream from the Clinton sampling site. As shown in a later section of this report (Atrazine Loads and Source Areas), the inputs from streams draining from Iowa and Illinois are larger than those from the Missouri River basin.

Herbicide concentrations generally were smallest in the Ohio River and in the Mississippi River at Clinton, Iowa, the most upstream sampling site (figs. 2 and 3). Median concentrations were about 0.5 μg/L or less and the maximum concentration for any herbicide measured at these two sites was 2.1 μg/L for atrazine in the Ohio River. This probably reflects the lower overall intensity of herbicide use in these drainage areas. Herbicides concentrations in excess of 20 μg/L have been documented in drainage to the Ohio River from the States of Indiana and Ohio (Thurman and others, 1991). However, streamflow entering the Ohio River from Kentucky and Tennessee, where herbicide use is much less than in the other Ststes, results in dilution and decreases the overall concentration of herbicides measured in the Ohio River at the Grand Chain, Ill., sampling site.

Temporal Distribution

The temporal distribution was similar for all herbicides. When the concentration of atrazine increased or decreased, so did the concentrations of the other herbicides. The rank correlation coefficient between atrazine and alachlor, cyanazine, and metolachlor was highly significant ($p < 0.001$) for each of the eight sites. Thus, the temporal pattern for atrazine shown in figures 4-6 generally is indicative of the patterns (but not absolute concentrations) of the other herbicides measured. The temporal distribution for atrazine in the smaller tributaries--the White, Illinois, and Platte Rivers--is shown in figure 4. The distributions for atrazine in the major tributaries--the Missouri and Ohio Rivers--and in the Mississippi River main stem are shown in figures 5 and 6.

Herbicide concentrations in the smaller tributaries began to increase in early- to mid-May (fig. 4) following herbicide application and subsequent rainfall. Herbicide concentrations generally were largest between early May and early June, and began to decrease in mid-June. A smaller and more gradual increase in herbicide concentrations occurred in the Missouri and Ohio Rivers (fig. 5). The largest concentrations of herbicides in the Missouri River occurred a little later than in the tributaries. The atrazine concentrations measured in the Missouri River at Hermann (fig. 5) were very similar to concentrations reported by Keck (1991, p. 20) for a site at St. Louis, 60 to 70 miles farther downstream.

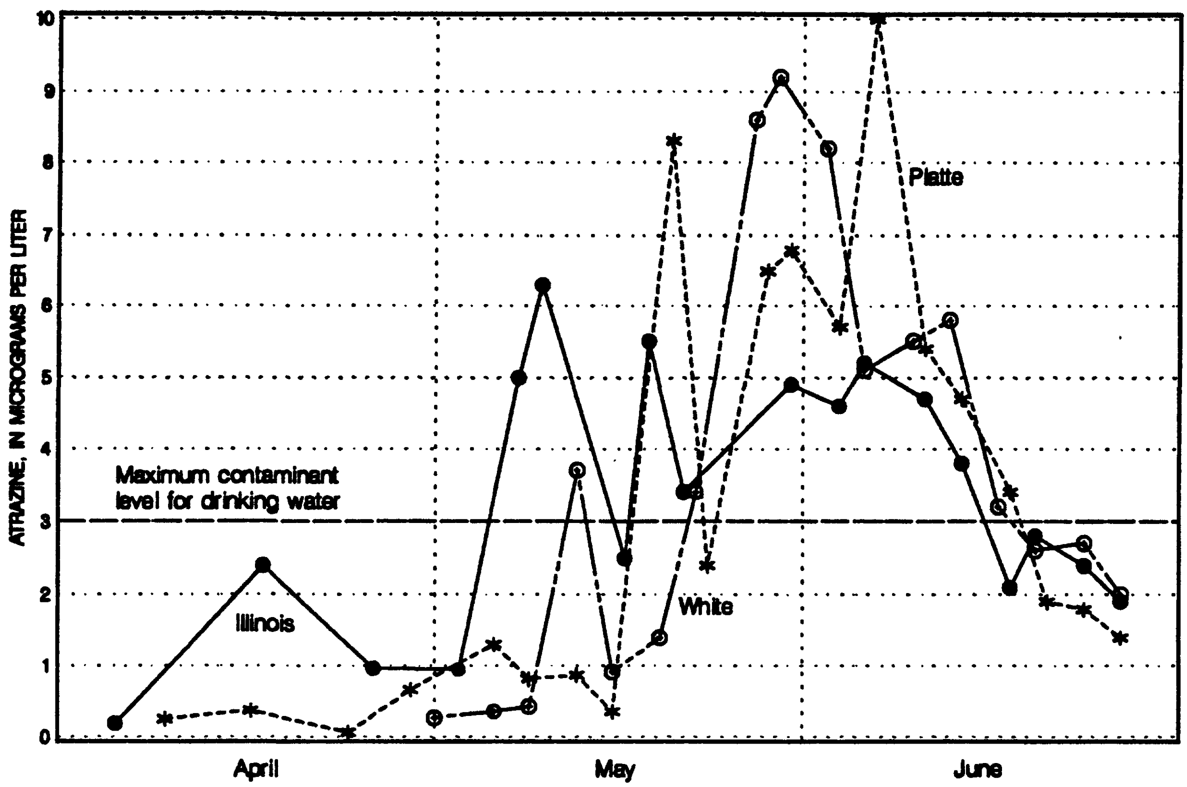

Figure 4.--Time-series plots of atrazine concentrations in the Illinois River at Valley City, Ill., Platte River at Louisville, Nebr., and White River at Hazelton, Ind., April through June 1991.

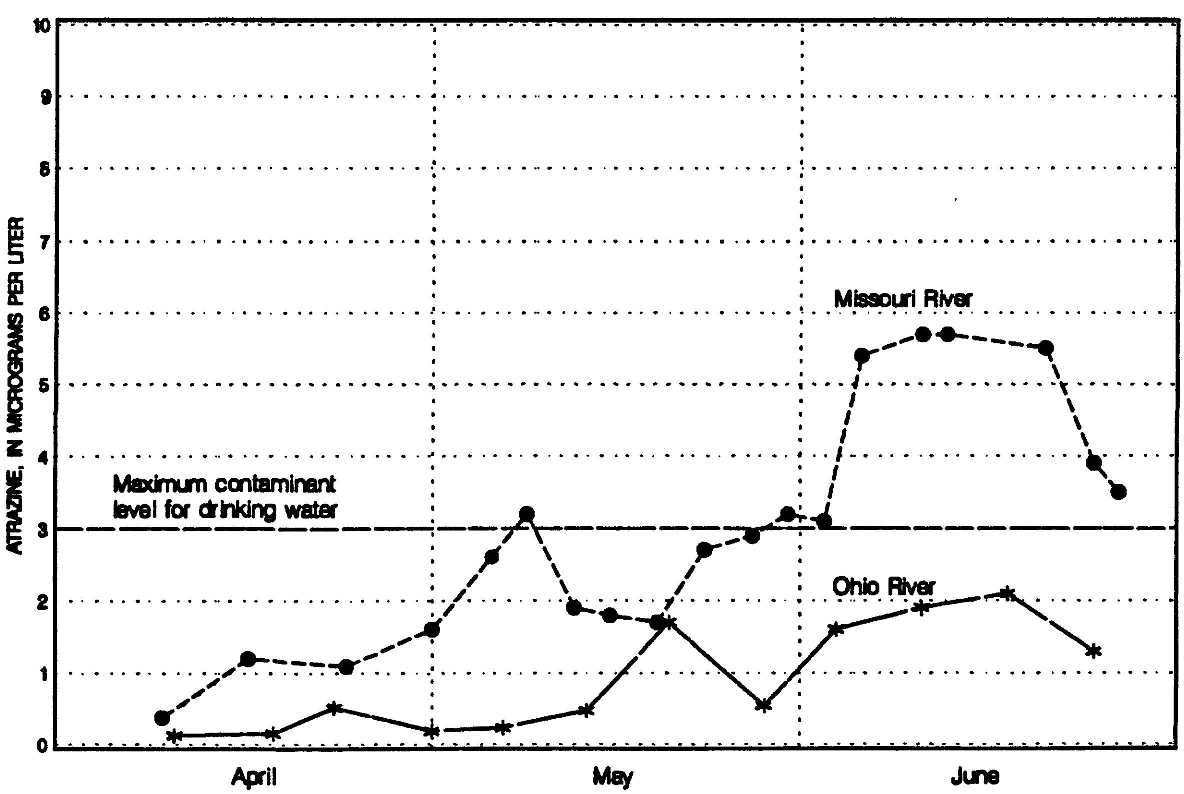

Figure 5.--Time-series plots of atrazine concentrations in the Missouri River at Hermann, Mo., and the Ohio River at Grand Chain, Ill., April through June 1991.

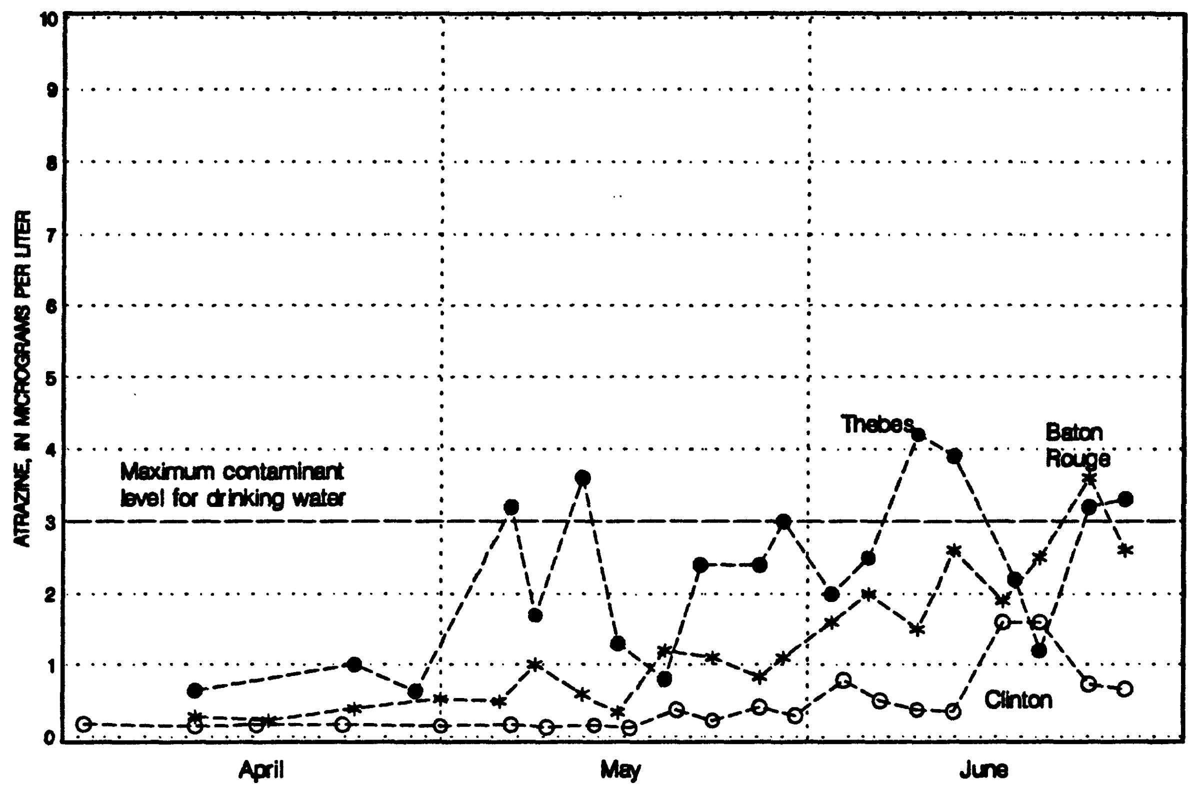

Figure 6.--Time-series plots of atrazine concentrations in the Mississippi River at Clinton, Iowa, Thebes, Ill., and Baton Rouge, La., April through June 1991.

An even smaller and more gradual increase in herbicide concentrations was measured on the Mississippi River main stem at the Thebes and Baton Rouge sites (fig. 6) than was measured on most tributaries. The increase in concentration at the Thebes site results from inflow to the Mississippi River from the Missouri River and streams draining from Iowa and Illinois. The concentrations at Baton Rouge result from inflow from the entire upper Mississippi River basin as measured by the Thebes site, inflow from the Ohio River, and to a small extent inflow from tributaries that enter the Mississippi below the Ohio River. The peak concentrations at Baton Rouge occurred 10 to 14 days later than at Thebes (fig. 6), which is the approximate travel time for this reach of the river (about 760 river miles).

Generally, the concentrations of herbicides began to decrease by mid-June, which is consistent with findings reported by Thurman and others (1991). It is also consistent with the concept of an annual cycle of increasing herbicide concentrations in streams after application and a subsequent decrease in concentrations as a result of chemical and biological degradation, sorption, transport in storm runoff, volatilization, and other processes.

Relation to Maximum Contaminant Levels

About 18 million people in the Ohio, Missouri, and Mississippi River basin receive drinking water from surface-water sources (U.S. Geological Survey, Water Use Data System). Many of these sources are reservoirs and streams that are tributaries to these three major rivers. In addition, a number of cities withdraw water directly from the Ohio, Missouri, and Mississippi Rivers for public supply. These cities include: Cincinnati, Ohio, Evansville, Ind., and Louisville, Ky., on the Ohio River; Omaha, Nebr., Kansas City, Mo., and St. Louis, Mo., on the Missouri River; and Minneapolis/St. Paul, Minn., Cape Gireadeu, Mo., and much of New Orleans, La., on the Mississippi River. The concentrations of herbicides in these rivers are therefore of interest to the suppliers and consumers of surface water throughout the entire Mississippi River basin.

Of the five herbicides studied, only two, atrazine and alachlor, occasionally were present in concentrations that exceeded the MCLs for drinking water established by the U.S. Environmental Protection Agency (1990, 1991a). The results in this report are for untreated river water whereas MCLs apply to water supplied to the user after treatment. However, conventional treatment processes generally do not remove these herbicides. Atrazine exceeded the MCL of 3 µg/L in 27 percent of the samples collected during these 3 months, and alachlor exceeded the MCL of 2 µg/L in 4 percent of the samples. On the basis of the 146 samples analyzed, atrazine exceeded the MCL from about mid-May to mid-June in the smaller tributaries (fig. 4), and for all of June in the Missouri River at Hermann (fig. 5). Atrazine also exceeded the MCL in the Mississippi River at Thebes during parts of May and June, and in one sample collected at Baton Rouge in late June (fig. 6). Alachlor only exceeded the MCL in 6 samples, all of which were collected from the three smaller tributaries (fig. 2) during mid- to late-May (table 3).

Atrazine Loads and Source Areas

One of the objectives of this study is to determine the mass of each major herbicide transported in 1 year (April 1991-April 1992) into the Mississippi River from each of the principal tributaries, the mass transported to the Gulf of Mexico, and the principal source areas for the herbicides. This objective cannot be achieved with only 3 months of data. However, it is possible to determine the principal source areas, estimate the relative contribution from each, and estimate the loads transported during this 3-month period. This was accomplished for atrazine based on loads estimated by the following approach.

Loads were calculated for each day on which samples were collected using atrazine concentration and streamflow data (table 3). An average daily atrazine load was then estimated for each month by averaging the loads calculated from the samples collected that month. Generally, there were about four samples per month for April and seven or eight samples per month for May and June, except for the Ohio River which only had four samples per month for the entire period. The average daily load (pounds per day) for atrazine was then multiplied by the number of days in the month to obtain an estimate of the total load for each month (pounds). Loads for each month were summed to obtain the total atrazine mass transport for the 3-month period. Mass-transport estimates were made using this method for each site on the main stem of the Mississippi River, and the Missouri and Ohio Rivers. In addition, an estimate was obtained for the atrazine load entering the Mississippi River from Iowa and Illinois between the Clinton, Iowa, site and the Missouri River (fig. 1). This estimate was obtained by subtracting the atrazine load for the Clinton site and the atrazine load for the Missouri River basin from the load calculated at the Thebes site. The mass transport of atrazine from the Mississippi River basin to the Gulf of Mexico was estimated from measurements of concentration at the Baton Rouge site and the flow at Baton Rouge plus the flow diverted into the Atchafalaya River. The results of these calculations are given in the following table for the period April-June 1991. Because the solid-phase extraction analytical procedure did not give 100 percent recovery of atrazine (see section of this report on quality assurance samples), and because no correction was made to account for incomplete recovery, the actual loads may be 10 to 20 percent larger than reported here.

Source area (see fig. 1)	Drainage area (mi^2)	Atrazine (pounds)	[1]Atrazine (percent)
Mississippi basin above Clinton	85,600	24,900	4.8
Mississippi basin, Clinton to Missouri River	103,600	189,700	36.7
Missouri River basin	524,000	131,600	25.4
Ohio River basin	203,100	95,500	18.5
Undetermined	208,700	75,300	14.6
[2]Total discharge from Mississippi basin	1,125,000	517,000	100.0

[1] Percent of atrazine contributed to the total atrazine discharge from the Mississippi River basin.
[2] Flow at Baton Rouge plus flow diverted into Atchafalaya River.

Keck (1991) estimated the monthly loads of atrazine discharged from the Missouri River for May, June, and July 1991. The results for May and June are similar to results obtained in this study.

	Atrazine load, in pounds	
	Keck (1991)	This study
May 1991	40,262	44,800
June 1991	56,884	70,700
Total	97,146	115,500

Estimates obtained from this study for April, May, and June indicate that the area between the Clinton sampling site and the Missouri River contributes the largest percentage of atrazine (36.7 percent) to the Mississippi River. This area includes the Illinois River and numerous smaller rivers that discharge into the Mississippi River from Iowa and Illinois. The second largest source area is the Missouri River basin (25.4 percent), followed by the Ohio River basin (18.5 percent). The mass of atrazine discharged from the Mississippi River basin to the Gulf of Mexico during April, May, and June 1991 (517,000 pounds) is within the range reported by Pereira and

Rostad (1990). They reported an annual transport (converted from metric units) of 231,000 pounds in 1988 and 945,000 pounds in 1989. Their calculations were based on fewer samples than are available from the present study but were for the entire year. The atrazine discharge from the basin during April-June 1991 represents about 0.9 percent of the atrazine applied in the 12-State area (tables 1 and 2). The atrazine discharge from the Mississippi River basin for a 1-year period, obviously, will be somewhat larger than values for April-June.

DISTRIBUTION OF NITRATE-NITROGEN

The distribution of nitrate-nitrogen concentrations at the eight sampling sites is shown in figure 7. Concentrations were largest in the Illinois River and two Mississippi River main-stem sites--Clinton and Thebes. These results indicate that the major influx of nitrate-nitrogen to the Mississippi River is from Iowa, Illinois, and possibly Minnesota and Wisconsin. The maximum nitrate-nitrogen concentration measured in any sample was 6.4 mg/L in the Illinois River. Unlike the temporal distribution pattern for herbicides, nitrate-nitrogen showed very little response to rainfall, except in the smaller tributaries (table 3). None of the samples had nitrate-nitrogen concentrations in excess of the 10 mg/L MCL.

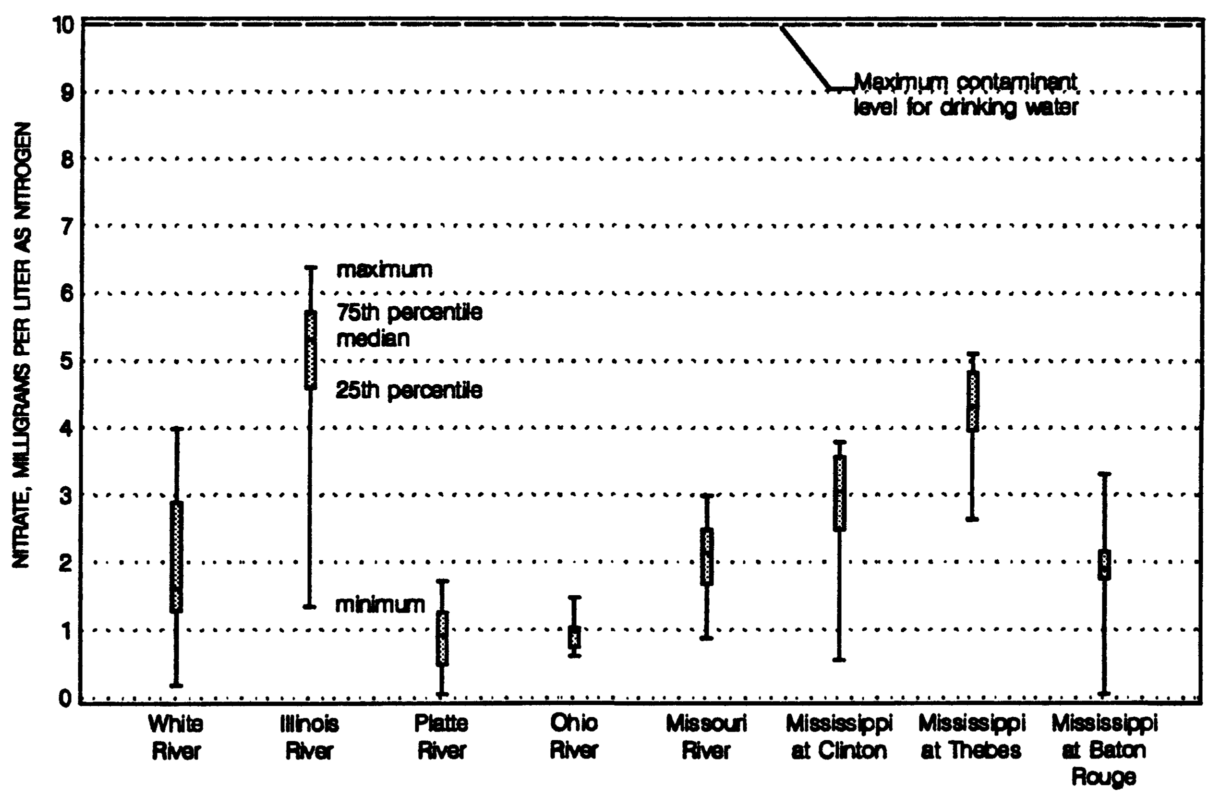

Figure 7.--Boxplots of nitrate-nitrogen concentrations arranged by downstream order for samples collected in April, May, and June 1991.

SUMMARY

The U.S. Geological Survey is presently (1991) conducting a study to determine the distribution, transport, and persistence of herbicides, insecticides, and inorganic nutrients in the Mississippi River and several major tributaries. The study began in April 1991, and will continue for 1 year. Results obtained for April, May, and June 1991 showed the presence of herbicides in the Mississippi and Missouri Rivers and several smaller tributaries. These early findings prompted the preparation of this report in order to make the sampling methods and results available.

Water samples were collected once or twice a week from three sites on the main stem of the Mississippi River, and from sites on the Ohio River, the Missouri River, and three smaller tributaries. One or more herbicides were detected in every sample (146) collected in April, May, and June. Atrazine was detected most frequently (100 percent of samples), followed by cyanazine, metolachlor, alachlor, and simazine. The median concentration of atrazine ranged from 0.29 μg/L in the Mississippi River at Clinton to 3.2 μg/L in the White River. The range in median concentrations for other herbicides were: cyanazine, <0.2 to 1.9 μg/L; metolachlor, 0.20 to 1.5 μg/L; alachlor, <0.05 to 0.73 μg/L; and simazine, <0.05 to 0.17 μg/L. The largest herbicide concentrations occurred in the smaller tributaries--White River in Indiana, Illinois River, and the Platte River.

Herbicide concentrations began to increase in early- to mid-May in response to rainfall after herbicides were applied to cropland. Maximum concentrations measured for atrazine were 6.3 to 10 μg/L for the smaller tributaries, and 3.7 to 5.7 μg/L in samples from the lower Mississippi and Missouri Rivers. Maximum concentrations measured for cyanazine, metolachlor, and alachlor were 7.3, 4.4, and 3.6 μg/L, respectively. These concentrations persisted for several weeks and began to decrease in early to mid-June.

Two herbicides, atrazine and alachlor, occasionally exceeded maximum contaminant levels for drinking water. Atrazine exceeded the MCL in 27 percent of the samples and alachlor in 4 percent of the samples. Atrazine exceeded the 3 μg/L MCL in samples from the smaller tributaries from mid-May to mid-June, and in samples from the lower Missouri during all of June. Atrazine also exceeded the MCL in samples from the Mississippi River at Thebes, Ill., during part of May and part of June. Atrazine exceeded the MCL in 1 sample collected from the Mississippi River at Baton Rouge, La. Alachlor exceeded the 2 μg/L MCL in a few samples, but only in the smaller tributaries.

Mass-transport calculations were made for atrazine to determine the predominant source area. These calculations indicate that about 37 percent of the atrazine discharged from the Mississippi River into the Gulf of Mexico entered the river from streams draining Iowa and Illinois. The second largest source area was the Missouri River basin, which contributed about 25 percent of the atrazine. The atrazine discharged from the Mississippi River basin during April, May, and June 1991 was estimated to be 517,000 pounds and was equal to about 0.9 percent of the amount applied in 12 major crop-producing States that drain to the Mississippi River.

Nitrate-nitrogen concentrations in the smaller tributaries increased slightly in response to rainfall, but did not have the same response that was observed for herbicides. The maximum concentration measured in any sample was 6.4 mg/L in a sample from the Illinois River. The maximum concentrations measured on the Mississippi River main stem were 3.8 mg/L at Clinton, Iowa, and 5.1 mg/L at Thebes, Ill. Nitrate concentration did not exceed the MCL in any sample. A major source for nitrate-nitrogen in the upper Mississippi appears to be discharge from streams in Iowa and Illinois.

REFERENCES CITED

Baker, D.B., and Richards, R.P., 1989, Herbicide concentration patterns in rivers draining intensively cultivated farmlands of northwestern Ohio, *in* Pesticides in the Terrestrial and Aquatic Environments, Proceedings of a National Research Conference, May 11-12, 1989, Blacksburg, Va., p. 103-120.

Becker, R.L., Hergfeld, D., Ostlie, K.R., and Stamm-Katovich, E.J., 1989, Pesticides: Surface runoff, leaching, and exposure concerns: University of Minnesota Extension Service publication AG-BU-3911, 32 p.

Edwards, T.K, and Glysson, G.D., 1988, Field methods for measurement of fluvial sediment: U.S. Geological Survey Open-File Report 86-53, 118 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., 1990, Herbicide use in the United States: Washington, D.C., Resources for the Future, December 1990, 127 p.

Goolsby, D.A., Thurman, E.M., and Kolpin, D.W., 1991, Herbicides in streams: Midwestern United States, *in* Irrigation and Drainage, Proceedings of the 1991 American Society of Civil Engineers Conference, Honolulu, Hi., July 22-26, 1991, p. 17-23.

Keck, Paul, 1991, Missouri River Public Water Supplies Association: 1991 Missouri River Monitoring Study, September 19, 1991: St. Louis, Mo., St. Louis County Water Company, 40 p.

Meade, R.H., 1989, Sediment-transported pollutants in the Mississippi River: U.S. Geological Survey Yearbook 1988, p. 20-23.

Pereira, W.E., and Rostad, C.E., 1990, Occurrence, distributions, and transport of herbicides and their degradation products in the lower Mississippi River and its tributaries: Environmental Science and Technology, v. 24, p. 1400-1406.

Sandstrom, M.W., Wydoski, D.S., Schroeder, M.P., Zamboni, J.L., and Foreman, W.T., (in press), Methods of analysis by the National Water Quality Laboratory: Determination of organonitrogen herbicides in water by solid phase extraction and capillary column gas chromatography/mass spectrometry with selected ion monitoring: U.S. Geological Survey Open-File Report 91-519.

Snow, D.D., and Spalding, R.F., 1988, Soluble pesticide levels in the Platte River basin of Nebraska in the Platte River basin of Nebraska, *in* Agricultural Impacts on Ground Water--A Conference, Des Moines, Ia., 1988, p. 211-233.

Squillace, P.J., and Engberg, R.A., 1988, Surface-water quality of the Cedar River basin, Iowa, with an emphasis on the occurrence and transport of herbicides, May 1984 through November 1985: U.S. Geological Survey Water-Resources Investigations Report 88-4060, 82 p.

Thurman, E.M., Goolsby, D.A., Meyer, M.T., and Kolpin, D.W., 1991, Herbicides in surface water of the midwestern United States: The effect of the spring flush: Journal of Environmental Science and Technology, v. 25, no. 10, p. 1794-96.

Thurman, E.M., Meyer, M., Pomes, M., Perry, C.E., and Schwab, A.P., 1990, Enzyme-linked immunosorbent assay compared with GC/MS for the determination of herbicides in water: Analytical Chemistry, v. 62, p. 2043-2048.

U.S. Environmental Protection Agency, 1990, National primary and secondary drinking water regulations, proposed rule: U.S. Federal Register, 40CFR, parts 141, 142, and 143, v. 55, no. 143, July 25, 1990, p. 30370-73.

_______ 1991a, National primary drinking water regulations, final rule: U.S. Federal Register, 40CFR, parts 141, 142, and 143, v. 56, no. 20, January 30, 1991, p. 3526-94.

_______ 1991b, Drinking water regulations and health advisories: U.S. Environmental Protection Agency, Office of Drinking Water, April 1991, 11 p.

Wershaw, R.L., Fishman, M.J., Grabbe, R.R., and Lowe, L.E., eds., 1987, Methods for the determination of organic substances in water and fluvial sediments: U. S. Geological Survey Techniques of Water Resources-Investigations, book 5, chap. A3, 80 p.