# SELECTED PAPERS ON AGRICULTURAL CHEMICALS IN WATER RESOURCES OF THE MIDCONTINENTAL UNITED STATES

Compiled by D.A. Goolsby, L.L. Boyer, and G.E. Mallard

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# INTRODUCTION

In 1989 the U.S. Geological Survey initiated a series of regional-scale studies to investigate the occurrence, geographic and temporal distribution, and transport of selected agricultural chemicals (pesticides and plant nutrients) in water resources of the midcontinental United States. The midcontinent was selected for these studies because it is the largest and most intensive agricultural region in the country. Consequently, the majority of all agricultural chemicals used in the United States are applied to crops in this region. The regional-scale studies are investigating agricultural chemicals in (1) streams whose drainage basins range in size from less than 100 square miles in area to the entire Mississippi River drainage basin, (2) selected reservoirs, (3) near-surface aquifers considered to be most susceptible to contamination, and (4) precipitation. Numerous papers resulting from these studies have been published in the scientific literature.

Because of the high interest in results that are being generated from these studies of agricultural chemicals in water resources of the midcontinent, six papers that represent several aspects of these studies have been compiled in this Open-File Report. This report is being released in order to make interpretations resulting from the studies available to Federal, State, and local agencies, and the private sector as quickly as possible. The first paper in this report presents a summary of information on the occurrence and distribution of pesticides and nitrate nitrogen in about 150 representative midwestern streams and in several large rivers such as the Ohio, Missouri, and Mississippi Rivers. The second paper describes the annual transport of selected herbicides and nitrate nitrogen in large midwestern rivers, including the relation between the amounts of these chemicals used annually in several river basins and the amounts transported annually in streamflow. The third paper presents the results of logistic regression models used to determine the relation between nitrate concentrations in 141 streams and several land-use factors.The fourth paper presents some preliminary results on the distribution and persistence of herbicides in 76 midwestern reservoirs. The fifth paper present some results from a reconnaissance conducted in 1991-92 to determine the occurrence and distribution of herbicides and nitrate in near-surface aquifers and to investigate statistical relations between the presence of herbicides and nitrate in ground water and various land-use factors. The sixth paper describes the temporal and geographic distribution of herbicides in precipitation (rain and snow) in the midwestern and northeastern United States, and the deposition patterns of the two most extensively used herbicides in the United States.

The information presented in this report should be useful in helping readers gain a general understanding of the occurrence and distribution of pesticides and nitrate nitrogen in water resources of the midcontinental United States. This research is being conducted as part of the U.S. Geological Survey's Toxic Substances Hydrology Program, National Water Quality Assessment Program, and National Research Program.

# CONTENTS

FIGURES

TABLES

**ANNUAL USE AND TRANSPORT OF AGRICULTURAL CHEMICALS IN THE MISSISSIPPI RIVER, 1991-92** *by* William A. Battaglin, Donald A. Goolsby, and Richard Coupe

FIGURES

TABLES

**RELATION OF NITRATE CONCENTRATIONS IN SURFACE WATER TO LAND USE IN THE UPPER-MIDWESTERN UNITED STATES, 1989-90** *by* David K. Mueller, Barbara C. Ruddy, and William A. Battaglin

FIGURES

TABLES

FIGURES

TABLES

**PESTICIDES IN NEAR-SURFACE AQUIFERS: RESULTS OF THE MIDCONTINENTAL UNITED STATES GROUND-WATER RECONNAISSANCE, 1991-92** *by* Dana W. Kolpin, Donald A. Goolsby, Diana S. Aga, Jana L. Iverson, and E. Michael Thurman

FIGURES

TABLES

**OCCURRENCE, DEPOSITION, AND LONG RANGE TRANSPORT OF HERBICIDES IN PRECIPITATION IN THE MIDWESTERN AND NORTHEASTERN UNITED STATES** *by* Donald A. Goolsby, E. Michael Thurman, Michael L. Pomes, Michael Meyer, and William A. Battaglin

FIGURES

TABLES

CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

| Multiply | By | To obtain |
|---|---|---|
| cubic foot per second ($ft^3/s$) | $2.832 \times 10^{-2}$ | cubic meter per second |
| foot (ft) | $3.048 \times 10^{-1}$ | meter |
| liter (L) | $2.642 \times 10^{-1}$ | gallon |
| microliter (µL) | $2.642 \times 10^{-7}$ | gallon |
| micrometer (µm) | $3.937 \times 10^{-5}$ | inch |
| mile | 1.609 | kilometer |
| millimeter (mm) | $3.937 \times 10^{-2}$ | inch |
| pound | $4.536 \times 10^{-1}$ | kilogram |
| square mile ($mi^2$) | 2.590 | square kilometer |
| acres | $4.047 \times 10^{3}$ | square meters ($m^2$) |
|  | $4.047 \times 10^{-1}$ | square hectometers ($hm^2$) |
|  | $4.047 \times 10^{-3}$ | square kilometers ($km^2$) |
| cubic feet ($ft^3$) | $2.447 \times 10^{3}$ | cubic meters ($m^3$) |
| tons (short) | $9.072 \times 10^{-1}$ | megagrams (Mg) or metric tons |

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To convert degrees Celsius ($^oC$) to Fahrenheit ($^oF$), use the following formula:
$^oF = 9/5(^oC)+32$.

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.

Use of trade names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

# OCCURRENCE, DISTRIBUTION AND TRANSPORT OF AGRICULTURAL CHEMICALS IN SURFACE WATERS OF THE MIDWESTERN UNITED STATES

**By Donald A. Goolsby and William A. Battaglin**

## ABSTRACT

Concentrations and mass transport of herbicides in streams throughout the midwestern United States follow an annual cycle. During storm runoff in May, June, and July, following herbicide application, a small fraction, generally less than 3 percent of the herbicide mass applied to cropland, is transported into streams. However, this mass is large enough to produce concentrations of some herbicides in excess of 3 micrograms per liter in the Mississippi River for a short period of time. Concentrations typically are an order of magnitude larger in tributary streams. Herbicide concentrations quickly decrease in mid to late summer, but some herbicides are detected at low concentrations year round, probably due to storage in surface-and ground-water reservoirs. Herbicide concentrations and mass transport measured in streams generally are related to the amounts of herbicides applied. Insecticides follow the same general pattern of occurrence and transport as herbicides, but they are less persistent, concentrations are lower, and peak concentrations occur later than herbicides. The cycle for nitrate-nitrogen differs from that of herbicides in that the highest concentrations and mass transport occur in the winter and spring. Low nitrate concentrations in the summer probably are due to increased use of nitrate by terrestrial and aquatic plants, and reduced leaching from soils to streams.

## INTRODUCTION

Chemical pesticides and nutrients are used extensively in the midwestern United States to increase production of agricultural crops. This region, which comprises much of the Mississippi River drainage basin (fig. 1), produces about 80 percent of the corn and soybeans grown in the country (Bureau of the Census, 1989). In producing these agricultural products, large amounts of pesticides, primarily herbicides, and nitrogen fertilizer are applied to cropland. It is estimated that more than 100,000 metric tons of pesticides and more than 6.3 million metric tons of nitrogen fertilizer were applied to cropland in the Mississippi River basin in 1991 (USDA, 1992; USEPA, 1990; Fletcher, J.J., West Virginia University, unpublished database, 1992). The estimated use of selected agricultural chemicals in the Mississippi River basin and several of its major tributary basins is given in table 1.

The intense use of soluble and mobile agricultural chemicals poses potential problems for nonpoint source contamination of streams and ground water throughout the Midwest. Previous studies have shown that runoff from fields immediately after application results in large concentrations of herbicides in surface water (Wauchope, 1978; Leonard, 1989; Wauchope, 1980). This finding has been documented in several small basin studies (Frank and others, 1982; Baker and Richards, 1989; Snow and Spalding, 1988; Wu and others, 1983), but except for one study (Pereira and Rostad, 1990) has not previously been investigated at a multi-state

Figure 1.--Location of sampling sites for Mississippi River study and temporal variability study.

Table 1.-- Estimated annual use of selected herbicides in the Mississippi River Basin and selected subbasins. (Source: Resources for the Future, 1987-89 Pesticide Data base, Gianessi and Puffer[3]) [Values in parenthesis are river basin drainage areas in square kilometers]

| | Chemical use in river basin upstream from specified site, in metric tons | | | | | | |
|---|---|---|---|---|---|---|---|
| Herbicide | Illinois at Valley City Ill. (69,300 km$^2$) | Platte at Louisville Nebr. (222,200 km$^2$) | Mississippi[a] above Missouri River (490,000 km$^2$) | Ohio at Grand Chain Ill. (526,000 km$^2$) | Missouri at Hermann Mo. (1,357,000 km$^2$) | Mississippi at Thebes, Ill. (1,847,000 km$^2$) | Mississippi at Baton Rouge, La. (2,914,000 km$^2$) |
| alachlor | 1,880 | 1,030 | 7,510 | 4,900 | 4,660 | 12,200 | 18,500 |
| atrazine | 1,960 | 1,600 | 7,110 | 5,060 | 6,280 | 13,400 | 20,600 |
| butylate | 715 | 559 | 2,250 | 2,030 | 1,900 | 4,160 | 6,650 |
| cyanazine | 715 | 464 | 4,240 | 1,440 | 1,970 | 6,210 | 8,170 |
| EPTC | 614 | 457 | 7,570 | 920 | 4,180 | 11,800 | 13,100 |
| metolachlor | 1,760 | 444 | 7,490 | 3,440 | 3,490 | 11,000 | 15,800 |
| metribuzin | 131 | 38 | 405 | 436 | 207 | 611 | 1,230 |
| simazine | 64 | 5 | 122 | 250 | 52 | 174 | 456 |
| trifluralin | 597 | 238 | 3,090 | 845 | 2,350 | 5,440 | 7,790 |

[a] Calculated from agricultural chemical use in the Mississippi River Basin above Thebes, Ill. (Fig. 1) minus use in the Missouri River Basin

scale to determine if herbicides and other agricultural chemicals cause contamination of surface water on a regional scale. During 1989-1992, the U.S. Geological Survey conducted several regional-scale studies to determine the occurrence, distribution, and transport of pesticides and nitrate in surface water in the midwestern United States. This paper presents a summary of those studies.

## REGIONAL-SCALE STUDIES

Three studies have recently been conducted in the midwest to investigate the occurrence and distribution of agricultural chemicals on a regional scale. These are: 1) a regional reconnaissance to determine the seasonal and geographic distribution of herbicides and nitrate in streams, 2) a study to determine the temporal variation of herbicides and nitrate in selected streams during storm runoff following application of agricultural chemicals and 3) a study of the occurrence, temporal variation, and transport of herbicides, insecticides, and nitrate in the Mississippi River and its major tributaries. Phosphorus and suspended sediment were also investigated in the Mississippi River study but are not included in this paper. Some results from these studies have been published previously (Thurman and others, 1991; Thurman and others, 1992; Goolsby and others, 1991a; Goolsby, and others, 1991b). The objectives and design of each of these studies are briefly described below.

### Regional Reconnaissance

A multi-state reconnaissance was conducted in 1989 to determine the seasonal and geographic distribution of herbicides and nitrate in 147 streams selected by a stratified random procedure (Thurman and others, 1991; Thurman and others, 1992; Goolsby and others 1991a, fig. 2). Drainage areas for the streams ranged from 260 $km^2$ to more than 160,000 $km^2$ and collectively totaled about 500,000 $km^2$ in the Midwest. The streams were sampled 3 times -- before planting (March - April), after planting during the first major storm runoff event (May - June), and in the fall during a period of low streamflow (October - November). All samples were filtered through glass fiber filters (1$\mu$m nominal pore size) at the time of collection to remove suspended material and were subsequently analyzed for triazine herbicides, by an immunoassay technique (Goolsby and others, 1990), and nitrate-nitrogen. Most samples were also analyzed for 11 herbicides and 2 atrazine metabolites by gas chromatography/ mass spectrometry (GC/MS) (Thurman and others, 1990). One-third of the streams were resampled in 1990 before planting and after planting during the first storm runoff event to confirm results obtained in 1989 (Goolsby and others, 1991a).

### Temporal Variability Study

Nine streams were sampled intensively from April through July 1990 to determine temporal variations in herbicide and nitrate concentrations during storm runoff following herbicide application (Thurman and others, 1992; Goolsby and others, 1991a, fig. 1). Samples were collected every few hours during storm runoff using automatic samplers and several times per week during periods of base flow. All samples were filtered through glass fiber filters (1$\mu$m nominal pore size) and analyzed for triazine herbicides by immunoaasay methods (Pomes and others, 1991), and nitrate. About one-fourth of the samples were also analyzed for 11 herbicides and 2 atrazine metabolites by GC/MS (Thurman and others, 1990). Two of the streams were

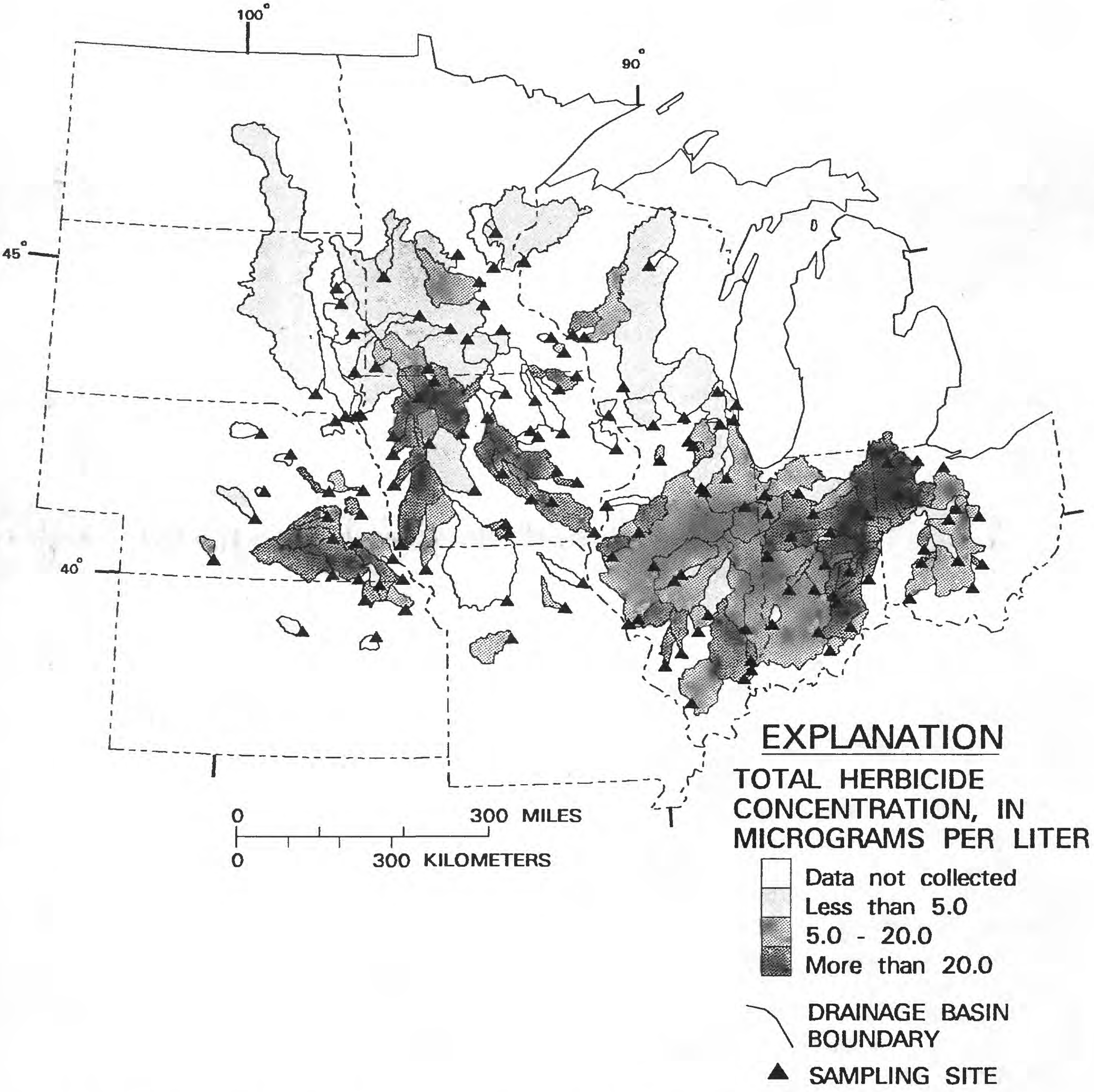

Figure 2.--Sampling sites for 1989 regional reconnaissance, and geographic distribution of total herbicide concentration measured by gas chromatography/mass spectrometry for the post-planting period displayed by drainage basin. Total herbicide concentration is the sum of all herbicides measured in each post-planting sample.

selected for further study during 1991. The West Fork Big Blue River in Nebraska and Sangamon River in Illinois (fig.1) were sampled intensively from April 1991 through March 1992 to provide information on annual mass transport of herbicides and nitrate. All herbicide samples from this phase of the study were analyzed by GC/MS (Thurman and others, 1990).

### Mississippi River Study

Three sites on the Mississippi River and 5 sites on major tributaries (fig.1) were sampled approximately once per week from April 1991 through March 1992 to determine the occurrence, temporal variation, and transport of herbicides, insecticides, nitrogen, and phosphorus in the Mississippi River and its major tributaries (Goolsby and others 1991b). Samples were filtered through glass fiber filters (0.7 µm nominal pore size) at the time of collection and subsequently were analyzed for 36 herbicides and insecticides by a combination of two analytical methods that used solid phase extraction and GC/MS. Method 1 (Sandstrom and others, 1991) included 12 herbicides and metabolites and had an analytical reporting limit of 0.05 µg/L (micrograms per liter) for all analytes except cyanazine, which had a reporting limit of 0.2 µg/L. Method 2 (Steven D. Zaugg, U.S. Geological Survey, written commun., 1992) provided analyses for 31 herbicides and insecticides, including 7 herbicides that were also analyzed by method 1. The analytical reporting limit for method 2 varied among analytes but ranged from 0.002 µg/L to 0.02 µg/L. Mass transport estimates of agricultural chemicals in the Mississippi River basin were obtained from chemical analyses and streamflow at each of the sampling locations. More complete details of study methods are given in Goolsby and others (1991b).

## OCCURRENCE AND GEOGRAPHIC DISTRIBUTION OF AGRICULTURAL CHEMICALS

### Pesticides

Herbicides were detected in nearly every sample collected as part of the regional-scale studies (tables 2 and 3). The herbicides detected most frequently were atrazine, desethylatrazine (an atrazine metabolite), alachlor, cyanazine, metolachlor, and simazine. Except for simazine, these are among the most heavily used herbicides in the Mississippi River basin (table 1). In the regional reconnaissance (fig. 2) atrazine, metolachlor, desethylatrazine, and alachlor were detected in 83 to 98 percent of 132 streams sampled during storm runoff after planting and application of herbicides in 1989 (table 1) and in 81 to 100 percent of 52 streams resampled during this same period of time in 1990 (Goolsby and others, 1991a). The widespread occurrence of herbicides in these streams (median drainage area about 2,000 $km^2$) indicates that most streams throughout the Midwest receive runoff during late spring and summer that contains appreciable quantities of herbicides. Further, the detection of atrazine in 76 percent of the streams sampled in fall of the year during low streamflow (table 2) and metolachlor and desethylatrazine in more than 40 percent of the streams, indicate that some heavily used herbicides can persist at low concentrations for long periods of time in surface water and ground water reservoirs that discharge to these streams (Thurman and others, 1992; Goolsby and others, 1991a). Flow from these streams maintains detectable concentrations of herbicides in large rivers such as the Ohio, Missouri, and Mississippi for much of the year.

Table 2.-- Summary of pesticide detections in streams in the midwestern United States during 1989-90, in percent of samples, arranged by overall frequency of detection.
[µg/L, micrograms per liter; n, number of samples analyzed; H, herbicide; M, metabolite]

| Pesticide[a] | Pesticide type | 1989 Pre-plant (n=55) | 1989 Post-plant (n=132) | 1989 Fall low-flow (n=145) | 1990 Pre-plant (n=52) | 1990 Post-plant (n=52) |
|---|---|---|---|---|---|---|
| atrazine | H | 91 | 98 | 76 | 96 | 100 |
| metolachlor | H | 34 | 83 | 44 | 67 | 96 |
| desethylatrazine | M | 54 | 86 | 47 | 86 | 98 |
| cyanazine | H | 5 | 63 | 0 | 8 | 81 |
| alachlor | H | 18 | 86 | 12 | 50 | 92 |
| simazine | H | 7 | 55 | 3 | 15 | 67 |
| metribuzin | H | 2 | 53 | 0 | 0 | 58 |
| prometon | H | 0 | 23 | 6 | 10 | 17 |
| desisopropylatrazine | M | 9 | 54 | 0 | 44 | 90 |
| prometryn | H | 0 | 0 | 0 | 0 | 0 |
| propazine | H | 0 | 40 | <1 | 0 | 65 |
| ametryn | H | 0 | 0 | 0 | 0 | 0 |
| terbutryn | H | 0 | 0 | 0 | 0 | 0 |

[a] Reporting limit is 0.05 µg/L for all pesticides except for cyanazine, which is 0.2 µg/L.

Table 3.-- Summary of pesticide detections in the Mississippi River and five large tributaries, April 1, 1991 through March 31, 1992, in percent of samples, arranged by overall frequency of detection.

[µg/L, micrograms per liter; n, minimum number of samples analyzed--n may be larger than the value shown for some pesticides; A, acaricide; H, herbicide; M, metabolite; I, insecticide; --, no analysis]

| | | | | | | | | ---------Mississippi River at--------- | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Pesticide[a] | Pesticide type | Reporting limit (µg/L) | White River (n=56) | Platte River (n=47) | Illinois River (n=45) | Missouri River (n=44) | Ohio River (n=35) | Clinton (n=44) | Thebes (n=45) | Baton[b] Rouge (n=65) |
| atrazine | H | 0.002 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 91 |
| metolachlor | H | .002 | 100 | 98 | 100 | 100 | 95 | 94 | 100 | 78 |
| desethylatrazine | M | .02 | 100 | 98 | 100 | 98 | 88 | 98 | 100 | 69 |
| cyanazine | H | .01 | 100 | 86 | 96 | 96 | 81 | 74 | 96 | 52 |
| alachlor | H | .002 | 90 | 86 | 94 | 96 | 70 | 85 | 100 | 48 |
| simazine | H | .002 | 100 | 90 | 92 | 86 | 93 | 72 | 90 | 31 |
| diazinon | I | .002 | 68 | 34 | 69 | 24 | 23 | 0 | 31 | -- |
| metribuzin | H | .005 | 55 | 29 | 44 | 36 | 12 | 17. | 43 | 14 |
| carbofuran | I | .002 | | 38 | 34 | 29 | 14 | 23 | 29 | -- |
| | | | | | | | | | | |
| trifluralin | H | .005 | 7 | 32 | 27 | 47 | 17 | 9 | 42 | -- |
| prometon | H | .002 | 60 | 8 | 48 | 12 | 7 | 7 | 10 | 12 |
| fonofos | I | .005 | 12 | 28 | 34 | 18 | 3 | 23 | 18 | -- |
| EPTC | H | .002 | 11 | 13 | 25 | 13 | 11 | 36 | 20 | -- |
| propachlor | H | .002 | 5 | 34 | 16 | 22 | 0 | 18 | 9 | -- |
| butylate | H | .002 | 23 | 15 | 16 | 11 | 23 | 0 | 9 | -- |
| desisopropylatrazine | M | .05 | 19 | 20 | 4 | 31 | 5 | 9 | 8 | 6 |
| carbaryl | I | .002 | 4 | 17 | 7 | 4 | 20 | 0 | 9 | -- |
| dieldrin | I | .02 | 2 | 0 | 23 | 13 | 0 | 2 | 16 | -- |
| pendimethalin | H | .01 | 0 | 11 | 2 | 11 | 3 | 2 | 7 | -- |
| | | | | | | | | | | |
| chlorpyrifos | I | .005 | 0 | 6 | 7 | 2 | 3 | 6 | 2 | -- |
| DDE | I | .005 | 2 | 4 | 2 | 9 | 9 | 0 | 2 | -- |
| prometryn | H | .05 | 0 | 2 | 0 | 2 | 2 | 0 | 2 | 5 |
| propazine | H | .05 | 2 | 2 | 2 | 4 | 0 | 0 | 2 | 0 |
| propagite | A | .01 | 2 | 0 | 0 | 4 | 0 | 2 | 0 | -- |
| malathion | I | .005 | 4 | 0 | 0 | 2 | 0 | 0 | 0 | -- |
| permethrin | I | .01 | 0 | 2 | 0 | 0 | 6 | 0 | 0 | -- |
| ametryn | H | .05 | 2 | 4 | 0 | 0 | 0 | 0 | 0 | 0 |
| terbufos | I | .02 | 0 | 2 | 2 | 0 | 0 | 0 | 0 | -- |
| linuron | H | .01 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | -- |
| methylparathion | I | .005 | 0 | 0 | 0 | 0 | 0 | 0 | 2 | -- |

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[a] Pesticides not detected; type and reporting limits in parenthesis: disulfoton(I, 0.02), ethoprop(I, .005), lindane(I, 0.005), azinphos-methyl(I, 0.01), parathion(I, 0.002), phorate(I, 0.02).

[b] Reporting limit is 0.05 µg/L for all pesticides except for cyanazine, which is 0.2 µg/L

The Mississippi River study has clearly demonstrated that many herbicides and insecticides are present at low concentrations in surface water in the Midwest. The analytical method used in this study was extremely sensitive. Quantitative reporting limits are as low as 0.002 µg/L for many analytes. This is about 25 times lower than for the method (Thurman and others, 1990) used in the regional reconnaissance. Of the 36 pesticides analyzed in this study, 28 were detected in one or more samples (table 3). Five herbicides (atrazine, metolachlor, cyanazine, alachlor, simazine) and desethylatrazine were detected in all samples collected at one or more of the 8 sites (fig. 1) sampled during a 1-year study period (table 3). For example, all of the above 6 compounds, except alachlor, were detected in every sample collected from the White River from April 1991 through March 1992. Three of the 6 compounds (atrazine, metolachlor, and desethylatrazine) were also detected in every sample from the Illinois River. These 6 compounds were detected at only slightly lower frequencies in large rivers such as the Ohio, Missouri, and Mississippi. Several other herbicides (metribuzin, trifluralin, prometon) and the insecticide, diazinon, were detected in about half the samples from some sites.

The most frequently detected herbicides occurred in the highest concentrations. Herbicide concentrations generally were higher in small streams sampled during the reconnaissance than in the large rivers sampled during the Mississippi River study. For example, the median concentration of atrazine measured in 132 streams during the post planting period of the regional reconnaissance was 3.8 µg/L and the median concentrations of alachlor cyanazine, and metolachlor were about 1 µg/L (fig.3). Maximum concentrations of these four herbicides ranged from about 50 µg/L to more than 100 µg/L (fig. 3). Concentrations of alachlor, atrazine, cyanazine and simazine in small streams exceeded maximum contaminant levels (MCL's) or health advisories (HA's) for drinking water established by the U.S. Environmental Protection Agency for short periods of time (U.S. Environmental Protection Agency, 1992). However, these high concentrations represent worst-case conditions, and as will be shown later, generally do not persist past mid-summer. Further, the MCL's and HA's for drinking water are based on average annual concentrations and not concentrations of short-duration.

The distribution of pesticide concentrations measured in the Mississippi River study are shown graphically in figure 4. For the purpose of this figure the minimum reporting limit (table 3) was assigned to all pesticide values less than the reporting limits. This figure is a composite representing all pesticides detected at all 8 sites sampled in the study (fig. 1) for a period of 1 year. Thus, the figure generally shows the annual distribution of pesticide concentrations for these 8 sites. The annual median concentration for atrazine is less than 0.5 µg/L, and the annual median for all other compounds generally is less than about 0.1 µg/L. Maximum concentrations at these 8 sites ranged from 5 µg/L to 11 µg/L for alachlor, atrazine, cyanazine, and metolachlor (fig. 4) or about one-tenth the maximum concentrations measured in the 1989 reconnaissance (fig. 3). Only alachlor, atrazine, and cyanazine had concentrations that occasionally exceeded MCL's or HA's for drinking water (2 µg/L for alachlor, 3 µg/L for atrazine, and 1 µg/L for cyanazine) (U.S. Environmental Protection Agency, 1992). These short-term exceedences of health based limits do not constitute a violation of drinking-water regulations.

Results from these studies show that high concentrations of several heavily used herbicides are present in streams throughout the Midwest following application to cropland. Figure 2

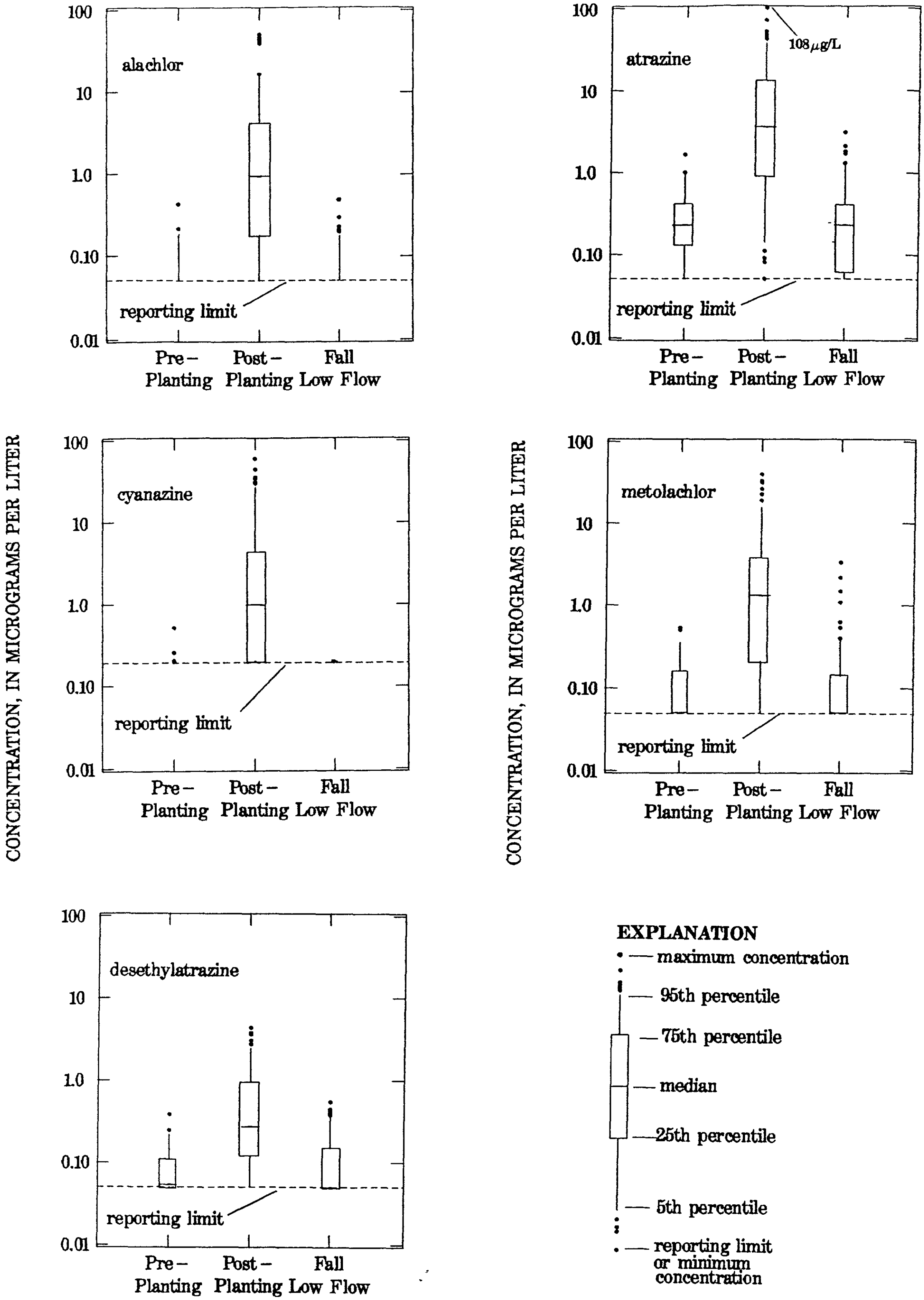
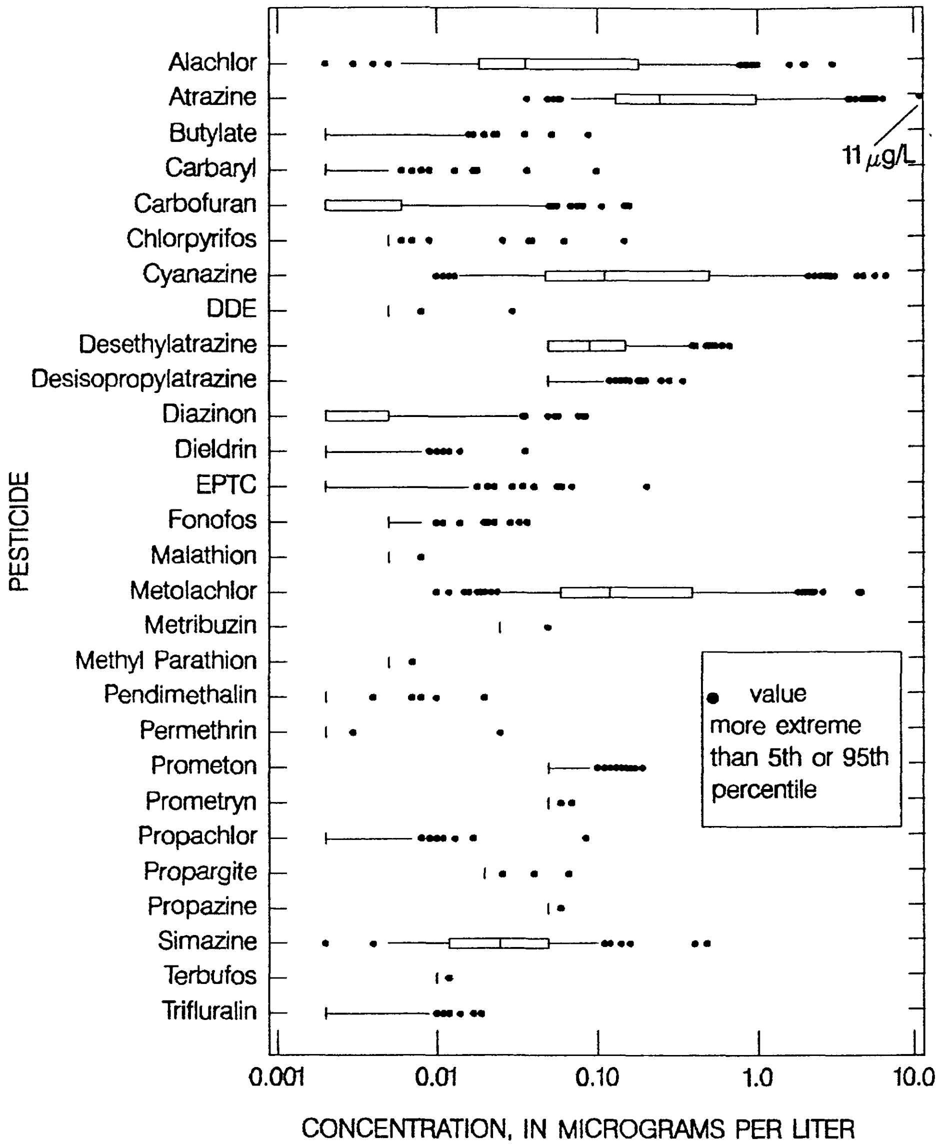


Figure 3.--Seasonal distribution in concentrations of selected herbicides in midwestern streams determined by 1989 regional reconnaissance.



## EXPLANATION

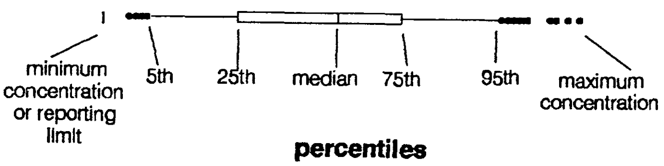


Figure 4.--Distribution of pesticide concentrations for three sites on the Mississippi River and five sites on major tributaries, April 1991 through March 1992.

postplanting storm runoff. Total herbicides is defined here as the sum of the concentrations of all 12 herbicides and metabolites measured in each reconnaissance sample. (table 2). The median total herbicide concentration in the 132 streams sampled was 8.7 µg/L. The median herbicide concentration was larger than 5 µg/L in two-thirds of the streams and larger than 20 µg/L in about one-third of the streams throughout the study area (fig. 2). All major herbicides measured as individual compounds (alachlor, atrazine, etc.) in the reconnaissance generally have the same geographic distribution pattern as total herbicides. However, results from the Mississippi River study indicate that certain pesticides are more common in some parts of the Midwest than in others. For example, diazinon and prometon are detected much more frequently in the White and Illinois Rivers than in other rivers sampled in this study (table 3). Trifluralin is detected most frequently in the Missouri River and in the Mississippi River at Thebes, Ill. (table 3) which is dominated by flow from the Missouri River, and propachlor is detected most frequently in the Platte River in Nebraska. These patterns of occurrence probably reflect the pesticide use on specific crops produced in these basins.

In general, the herbicides detected most frequently and in highest concentrations (alachlor, atrazine, cyanazine, metolachlor) are the ones used in largest quantities (table 1). However, there are exceptions, such as butylate, EPTC, and trifluralin which are heavily used but concentrations rarely, if ever, exceed 0.1 µg/L in the Mississippi River and its major tributaries (fig. 4). Factors such as soil half-life, soil-water partition coefficients, Henry's law constants, and methods of application have a large effect on the persistence and mobility of pesticides and consequently can have a major effect on the pesticide concentrations in surface water.

## Nitrate

Nitrate in streams is derived from many anthropogenic and natural sources including: chemical fertilizers, animal wastes, domestic sewage, legumes, mineralization of vegetation, and soil organic matter. Results from regional-scale studies in the Midwest provide information on the geographic distribution of nitrate in streams. Although these studies were not designed to identify specific sources of nitrate in streams, it appears that much of the nitrate is derived from agricultural-related activities. Nitrate concentrations (as nitrogen) measured in these studies are summarized in figure 5. Unlike herbicides, which occur in high concentrations throughout the study area (fig. 2), nitrate concentrations generally are much higher in streams in eastern Iowa, Illinois, Indiana, and Ohio than elsewhere in the study area. This difference was observed in all three regional-scale studies. For example, median nitrate concentrations measured in pre- and post-planting samples from streams in these 4 states during the regional reconnaissance (fig. 2) ranged from 2.8 to 5.8 mg/L. Median nitrate concentrations in streams sampled in all other states were 1.1 mg/L or less. This geographic difference is also illustrated by comparing the annual distribution of nitrate concentrations in two Illinois streams, the Sangamon and Illinois Rivers (fig. 5) with the distribution in two Nebraska streams, the West Fork Big Blue and Platte Rivers. These differences cannot be explained by differences in use of nitrogen fertilizer. It is hypothesized that the differences are caused by differences in soil type and characteristics, climatic factors, solute transport processes in ground water, and agricultural practices that occur across the area. Additional sources of nitrate in the eastern part of the Midwest, such as potentially more animal and domestic wastes may also, in part, contribute to observed geographic patterns.

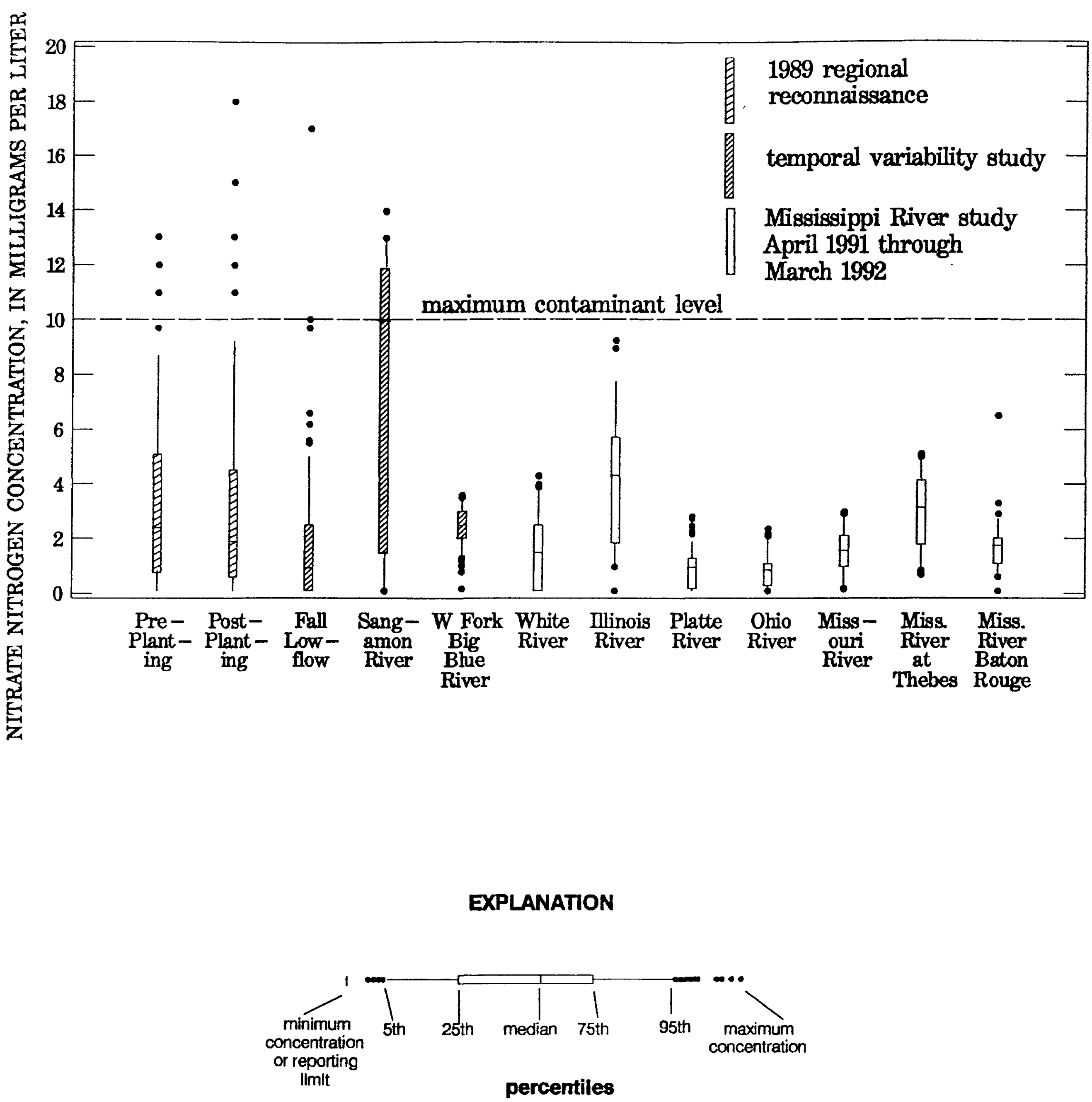


Figure 5.--Distribution of nitrate-nitrogen concentrations in streams determined by regional-scale studies.

# TEMPORAL DISTRIBUTION OF AGRICULTURAL CHEMICALS

## Pesticides

The most notable feature of all the regional-scale studies is the large increase in herbicide concentrations that occurs during storm runoff after herbicides are applied. Thurman and others (1991) referred to this feature as the "spring flush". During a short period after application, herbicides can be flushed from cropland and into streams of all sizes in response to rainfall. Median concentrations of alachlor, atrazine, cyanazine, and metolachlor measured during the regional reconnaissance increased about an order of magnitude during these rainfall events; maximum concentrations of these herbicides in some streams were as large as 50 to more than 100 μg/L (fig. 3). Concentrations decreased to about preplanting levels at the time of the fall sampling (fig. 3). Intensive sampling with automatic samplers during the temporal variability study showed that high concentrations of herbicides can occur during storm runoff for several weeks to several months following application (figs. 6a and 6b). Herbicide concentrations usually are highest during the first storms and decrease in subsequent storms. Between storms, as overland flow ceases and streamflow declines, herbicide concentrations tend to decrease and may approach pre-applications levels, only to sharply increase again during the next storm. Peak herbicide concentrations generally diminished with each successive runoff event. Herbicide concentrations in all nine basins studied during the temporal variability study in 1990 (fig. 1) showed the same pattern of response to storm runoff. Further study of the Sangamon River, Illinois, and West Fork Big Blue River, Nebraska in 1991, produced a pattern of results that was similar to those obtained in 1990 (fig. 6).

The Mississippi River study demonstrated that the same temporal pattern in herbicide concentrations observed in small streams also occurs in large rivers (figs. 7a-7c). However, concentrations change more slowly, peak concentrations are lower, and elevated concentrations are sustained for a longer period of time than in smaller streams. These differences can be attributed to the fact that these large rivers integrate the herbicide input from many smaller streams which may discharge herbicides on different time scales and in vastly different amounts.

Concentration hydrographs for several major herbicides and streamflow are shown in figures 7a, 7b and 7c for April 1991 through March 1992 for the Mississippi River at Thebes, Ill (drainage area 1,847,000 km$^2$). Considerable short-term variation in herbicide concentrations occured at this location because of variable streamflow and herbicide concentrations in three major upstream sources, the Missouri, Illinois, and upper Mississippi Rivers (fig. 2). The largest herbicide concentrations, greater than about 1 μg/L for atrazine, persist at this location from early May until early July 1991. It should be noted that the temporal variations in herbicide concentrations may be much different in another year with different rainfall patterns and streamflow conditions.

All of the regional-scale studies indicate that low concentrations of several herbicides persist year-round in many streams. The regional reconnaissance showed that three-fourth of the 145 streams sampled during a fall low-flow period contained atrazine at concentrations of 0.05 μg/L or larger (fig. 3), and nearly half had detectable concentrations of metalochlor and

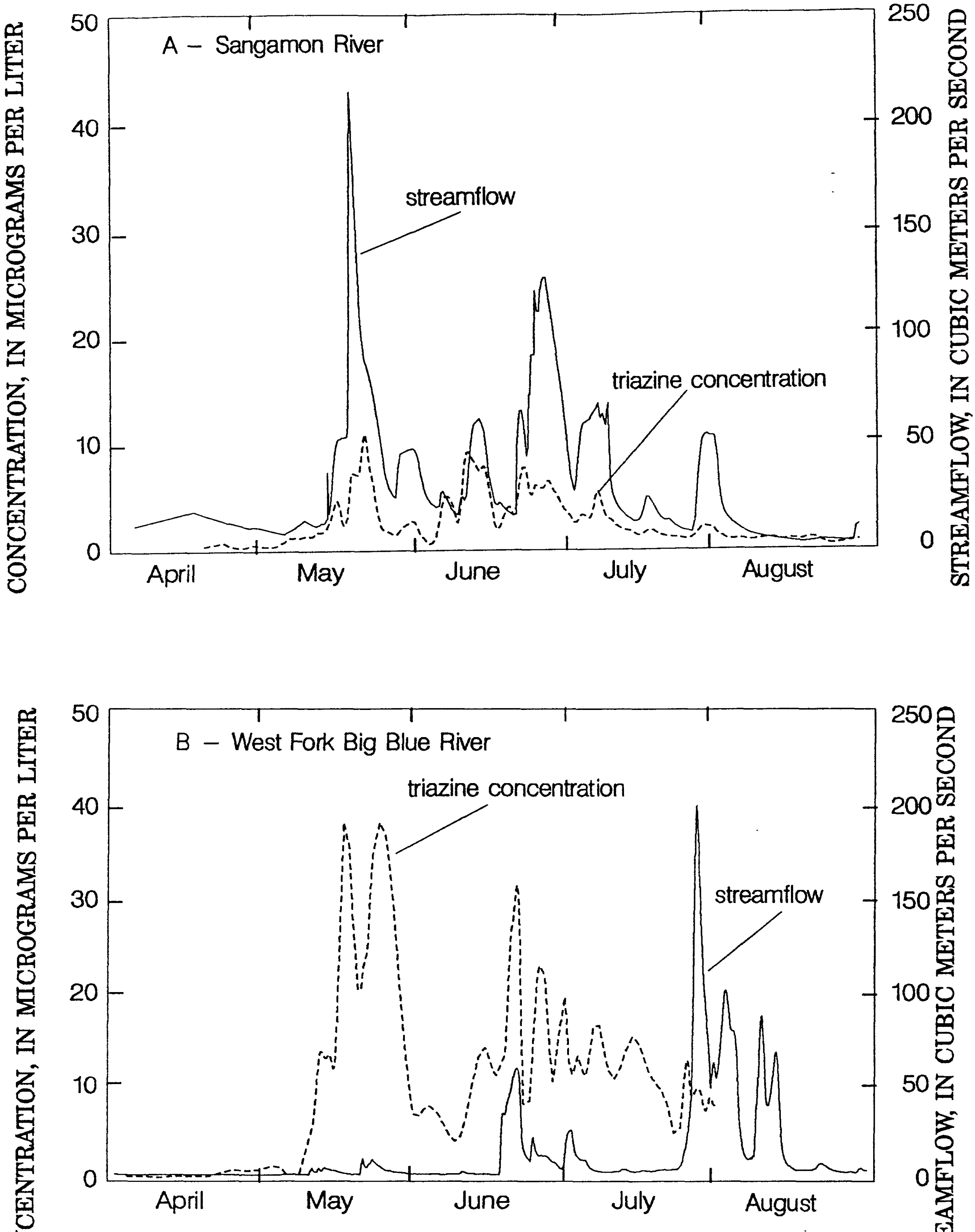


Figure 6.– –Streamflow and triazine herbicide concentrations determined by immunoassay analysis for the Sangamon River, Ill., and West Fork Big Blue River, Nebr., in 1990.

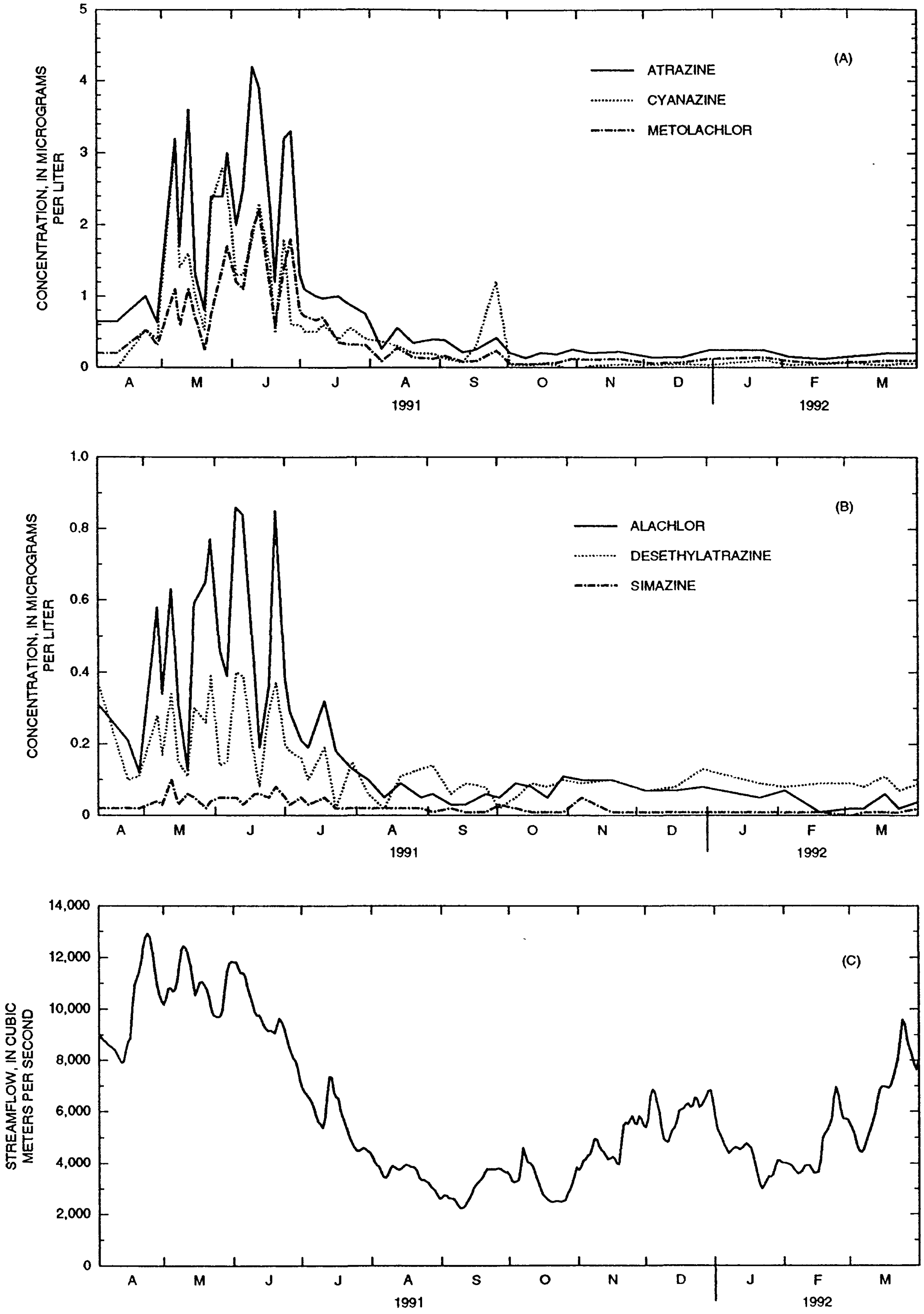


Figure 7. -- Temporal distribution of (A) atrazine, cyanazine, and metolachlor concentrations (B) alachlor,simazine, and desethylatrazine (an atrazine metabolite) concentrations, and (C) streamflow in the Mississippi River at Thebes, Illinois.

0.05 µg/L or larger (fig. 3), and nearly half had detectable concentrations of metalochlor and desethylatrazine. The Mississippi River study, with lower analytical reporting limits, showed that these three compounds as well as alachlor, cyanazine, and simazine were detectable in more than 90 percent of the samples collected at the Thebes, Ill. site during a 1-year period (figs. 7a and 7b, table 3). The year-round occurrence of these compounds indicates herbicides are stored in both surface-water and/or ground-water reservoirs (Squillace and Thurman, 1992) and are slowly being discharged into streams in quantities large enough to produce detectable concentrations all year long in the Mississippi River (figs. 7a and 7b). Desorption from suspended and streambed sediments is another possible source, but this seems less likely due to the solubility and sorption characteristics of these herbicides. Pesticides whose major route of dissipation is biodegradation by microbes may be more persistent in streams of low organic carbon content and in ground water than in soil because of low populations of microorganisms. Further, for pesticides with sufficiently long soil half-lives, two months for example, concentrations in the soil can remain high enough to produce detectable concentrations in runoff for many months after application.

### Nitrate

The temporal pattern in nitrate concentration was similar in all streams sampled. This pattern was strikingly different from the pattern observed for herbicides and indicates that processes in addition to those governing herbicide transport are important in controlling transport of nitrate to streams. Herbicides are generally applied to the soil surface and are transported primarily in overland flow after desorption from soil and sediment. Nitrate is a very soluble and mobile anion. It is transported in both overland flow and subsurface flow (Lucey and Goolsby, 1993). Nitrate concentrations were highest during late fall, winter, and spring and lowest during the summer (figs. 8a-8c). This pattern can probably be attributed to several factors, the most important of which may be the assimilation of nitrate by row crops and other terrestrial and aquatic plants which would reduce the amount of nitrate transported by streams during the summer growing season. Other factors that could result in lower nitrate concentrations during the summer would be decreased streamflow, decreased ground water discharge to streams, and greater evapotranspiration (ET) resulting in less leaching of nitrate to streams from the soil and unsaturated zone. ET and assimilation of nitrate by plants would be decreased and infiltration increased after the first frost or freezing temperatures in the fall, allowing larger quantities of nitrate to be leached from the soil and unsaturated zone and transported to streams as base flow.

## TRANSPORT OF AGRICULTURAL CHEMICALS

Major objectives of the Mississippi River study were to determine the predominant source areas for herbicides and nitrate and to estimate the mass transport of these chemicals from major tributaries into the Mississippi River and to the Gulf of Mexico for a 1-year period. Loads for each chemical of interest were calculated for each day using measured concentrations and daily mean streamflow. Concentrations were estimated by linear interpolations for days on which no samples were collected. The estimated daily loads were then summed to obtain an estimate of annual loads. Mass-transport estimates were made in this manner for all 8 sites in the study. Mass transport of herbicides and nitrate to the Gulf of Mexico was estimated from concentrations measured at Baton Rouge, La. and streamflow at Baton Rouge plus the

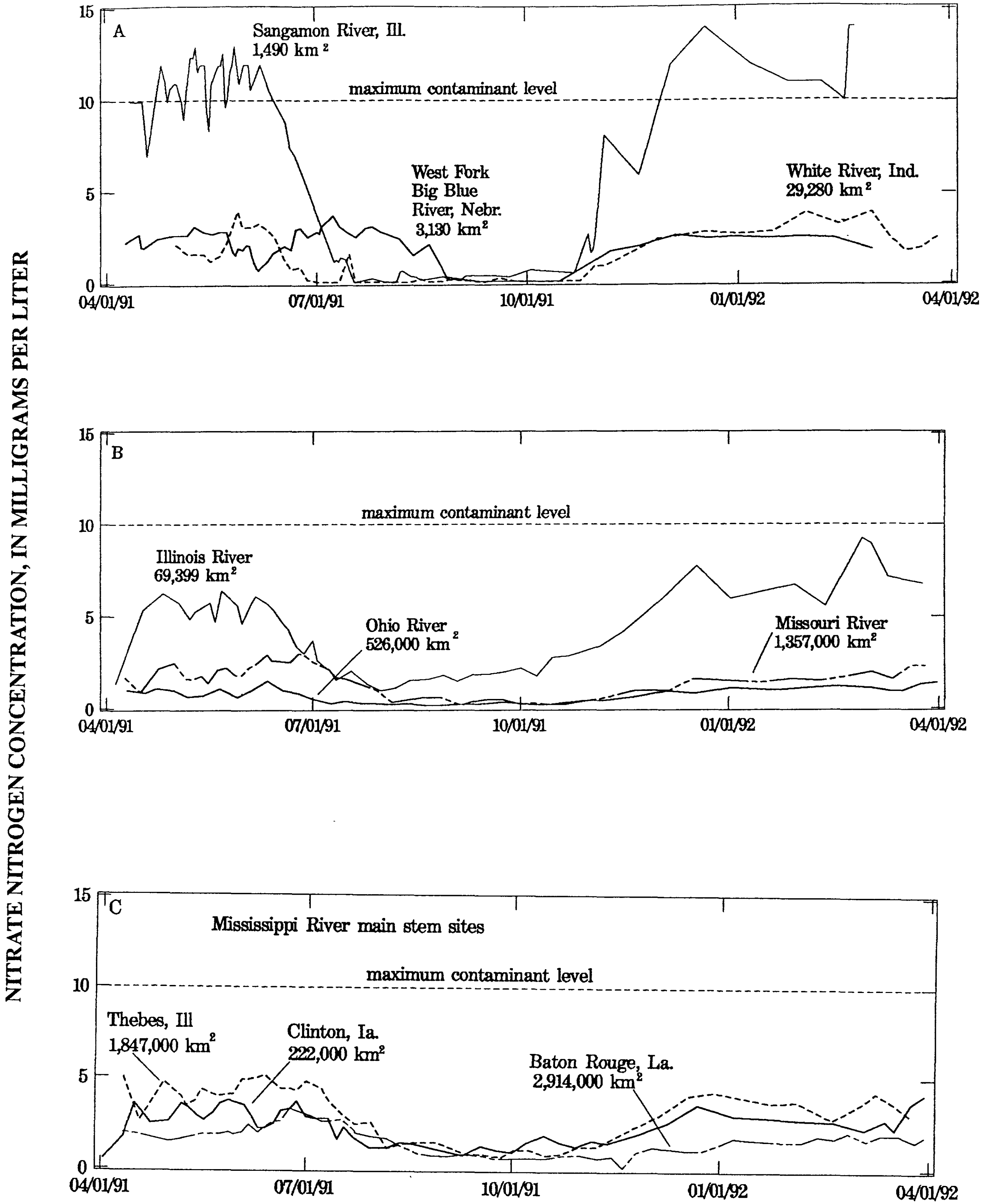


Figure 8.- -Temporal distribution in nitrate nitrogen concentrations for the Mississippi river and selected tributaries

streamflow diverted into the Atchafalaya River upstream from Baton Rouge (fig. 1). It should be noted that the analytical reporting limits for herbicide samples collected at Baton Rouge were higher (0.05 to 0.2 µg/L, see tables 2 and 3) than for samples collected at other sites (0.002 to 0.01 µg/L). This may have caused the herbicide annual mass transport at Baton Rouge to be underestimated by a small amount (less than 10 percent) in comparison to other sites in the basin.

Loads of herbicides and nitrate transported by the Mississippi River at several locations and by major tributaries during a 1-year period (April 1, 1991 through March 31, 1992) are given in table 4. Most of the herbicides and nitrate discharged into the Mississippi River originate in an area encompassed by the Ohio River basin and the Mississippi and Missouri basins above the Ohio River confluence (fig. 1). Except for atrazine and nitrate, there appears to be no significant inputs of most of these agricultural chemicals between the Ohio River confluence and Baton Rouge (table 4) a distance of about 1,160 river kilometers. The apparent decrease in loads for alachlor and simazine in this reach of the Mississippi River is due, in part, to a higher analytical reporting limit for samples collected at Baton Rouge (see table 2) and to degradation and sorption losses.

The predominant source area for most herbicides and nitrate discharged from the Mississippi River basin to the Gulf of Mexico is the upper Mississippi River basin. This area, which excludes the Ohio and Missouri River basins, constitutes about 22 percent of the Mississippi River drainage basin but contributes about one-half of the herbicides and about 59 percent of the nitrate transported by the Mississippi River (table 3). The area receives virtually all of the streamflow discharged from Iowa, Illinois, and Minnesota, which contain the most intensive crop-production areas in the basin. These three states apparently also are the source for much of the agricultural chemicals transported by the Mississippi River. The Ohio River basin is the source of about one-half the butylate and most of the simazine transported by the Mississippi River (table 3) and the Missouri River basin is the predominant source for trifluralin.

The rates and temporal distribution of agricultural chemical transport from the Mississippi River to the Gulf of Mexico is illustrated in figure 9 for 4 major herbicides used in the basin and in figure 10 for nitrate. Most of the herbicide transport during this 1-year study occured during May and June (fig. 9) or shortly after herbicide application. Maximum transport rates were about 5,000 kg per day for atrazine, about 3,000 kg per day for metolachlor, about 2,000 kg per day for cyanazine, and about 700 kg per day for alachlor. Other herbicides were transported at much lower rates. Although the annual mass transport appears to be large for several herbicides (table 4), it represents only a small fraction, generally less than 3 percent, of the herbicide mass applied (table 5). The mass of herbicides discharged from the Mississippi River basin as a percent of the mass applied for 1991 was 0.2% for alachlor, 0.8% for metolachlor, 1.6% for atrazine and cyanazine, and 2.7% for simazine. A similar fraction of the mass of these herbicides applied in the Illinois, Ohio, Platte, and Missouri River basins was discharged from these rivers (table 5).

About half of the annual mass transport of nitrate to the Gulf of Mexico occurred during April, May, and June. Mass transport rates during this period were 5,000 to 6,000 metric tons per day (fig. 10). Nitrate transport was lowest, about 500 metric tons per day, during late summer and fall when both nitrate concentrations and streamflow were lowest. The mass of

Table 4. Estimated loads of pesticides, in kilograms, and dissolved nitrate in metric tons transported by the Mississippi River and major tributaries, April 1991 through March 1992.

| Pesticide | Illinois River | Missouri River | Ohio River | Platte River | Mississippi River above Missouri River[1] | Mississippi River at Thebes, Ill[2] | Mississippi River below Ohio River[3] | Mississippi River at Baton Rouge, La[6] |
|---|---|---|---|---|---|---|---|---|
| alachlor | 8,790 | 7,870 | 4,970 | 2,350 | 35,000 | 42,900 | 47,900 | 33,700 |
| atrazine | 35,800 | 68,400 | 57,000 | 9,280 | 121,000 | 189,000 | 246,000 | 321,000 |
| desethylatrazine[4] | 4,170 | 6,380 | 12,500 | 858 | 23,000 | 29,400 | 41,900 | 41,500 |
| desisopropylatrazine[4] | 40 | 2,030 | 879 | 204 | 170 | 2,200 | 3,080 | 3,200 |
| atrazine sum [5] | 40,000 | 76,800 | 70,400 | 10,300 | 144,000 | 221,000 | 291,000 | 360,000 |
| butylate | 207 | 308 | 1,170 | 10 | 962 | 1,270 | 2,440 | --- |
| carbofuran | 357 | 1,190 | 301 | 175 | 1,810 | 3,000 | 3,300 | --- |
| carbaryl | 7 | 9 | 481 | 6 | 89 | 98 | 579 | --- |
| chlorpyrifos | 186 | 7 | 14 | 22 | 44 | 51 | 65 | --- |
| cyanazine | 19,800 | 31,300 | 13,400 | 5,910 | 81,700 | 113,000 | 126,000 | 127,000 |
| diazinon | 289 | 80 | 103 | 9 | 213 | 293 | 396 | --- |
| dieldrin | 33 | 350 | 0 | 0 | 0 | 125 | 125 | --- |
| EPTC | 516 | 105 | 130 | 8 | 826 | 931 | 1060 | --- |
| fonofos | 112 | 49 | 12 | 34 | 387 | 436 | 448 | --- |
| metolachlor | 18,900 | 24,700 | 20,200 | 2,470 | 62,500 | 87,200 | 107,000 | 123,000 |
| metribuzin | 600 | 1,420 | 545 | 160 | 3,090 | 4,510 | 5,060 | 6,810 |
| prometon | 514 | 433 | 822 | 29 | 767 | 1,200 | 2,020 | --- |
| propazine | 6 | 78 | 0 | 20 | 44 | 122 | 122 | --- |
| propachlor | 30 | 171 | 0 | 143 | 0 | 64 | 64 | --- |
| pendamethalin | 8 | 51 | 14 | 4 | 257 | 308 | 322 | --- |
| simazine | 864 | 1,090 | 9,370 | 114 | 3,250 | 4,340 | 13,700 | 12,500 |
| trifluralin | 48 | 248 | 101 | 26 | 158 | 406 | 507 | --- |
| Nitrate-nitrogen | 107,000 | 79,900 | 182,000 | 5,640 | 571,000 | 651,000 | 833,000 | 967,000 |

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[1] Calculated from load in Mississippi River at Thebes, Ill. minus load from Missouri River.

[2] Above confluence with Ohio River.

[3] Below confluence with Ohio River; calculated from loads in Mississippi River at Thebes, Ill. plus load from Ohio River.

[4] Atrazine metabolite.

[5] Atrazine plus metabolites.

[6] Approximate transport from Mississippi River basin to Gulf of Mexico; includes diversion into Atchafalaya River.

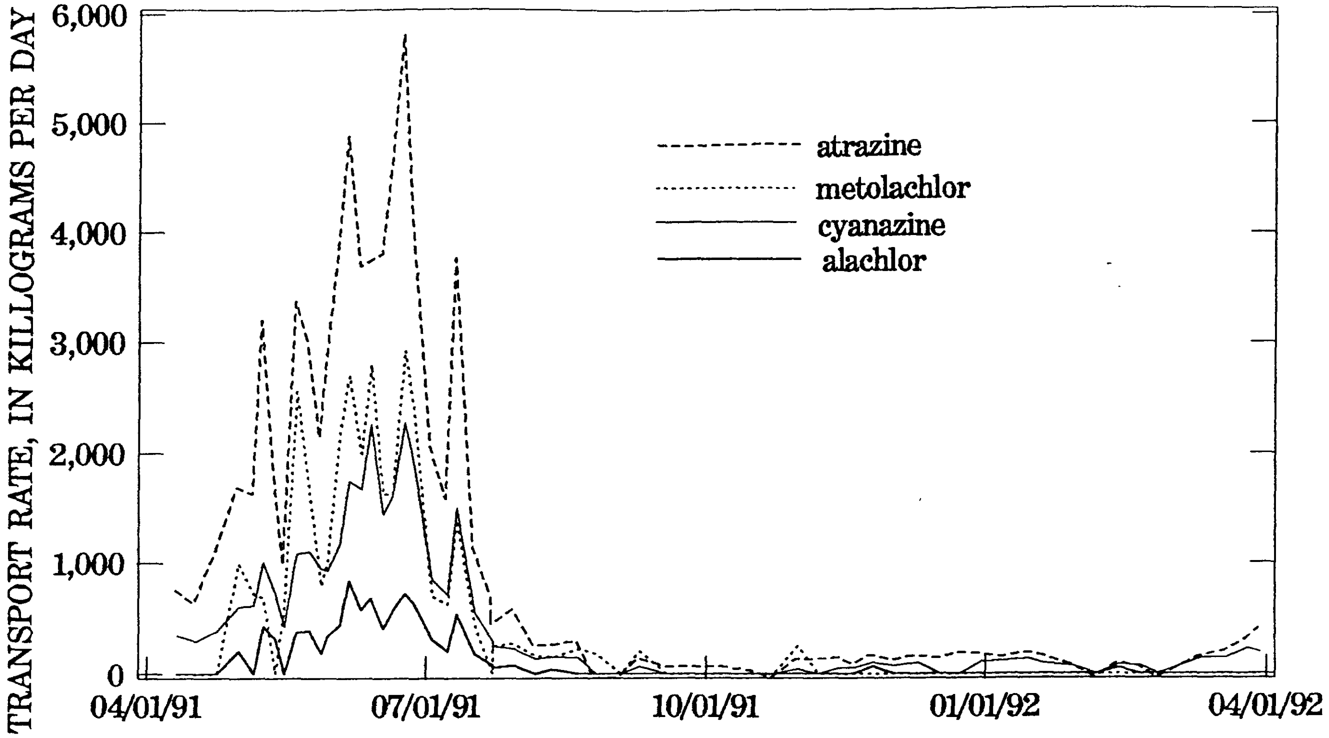

Figure 9.— —Transport rates of herbicides from the Mississippi River to the Gulf of Mexico (includes herbicides diverted into Atchafalaya River)

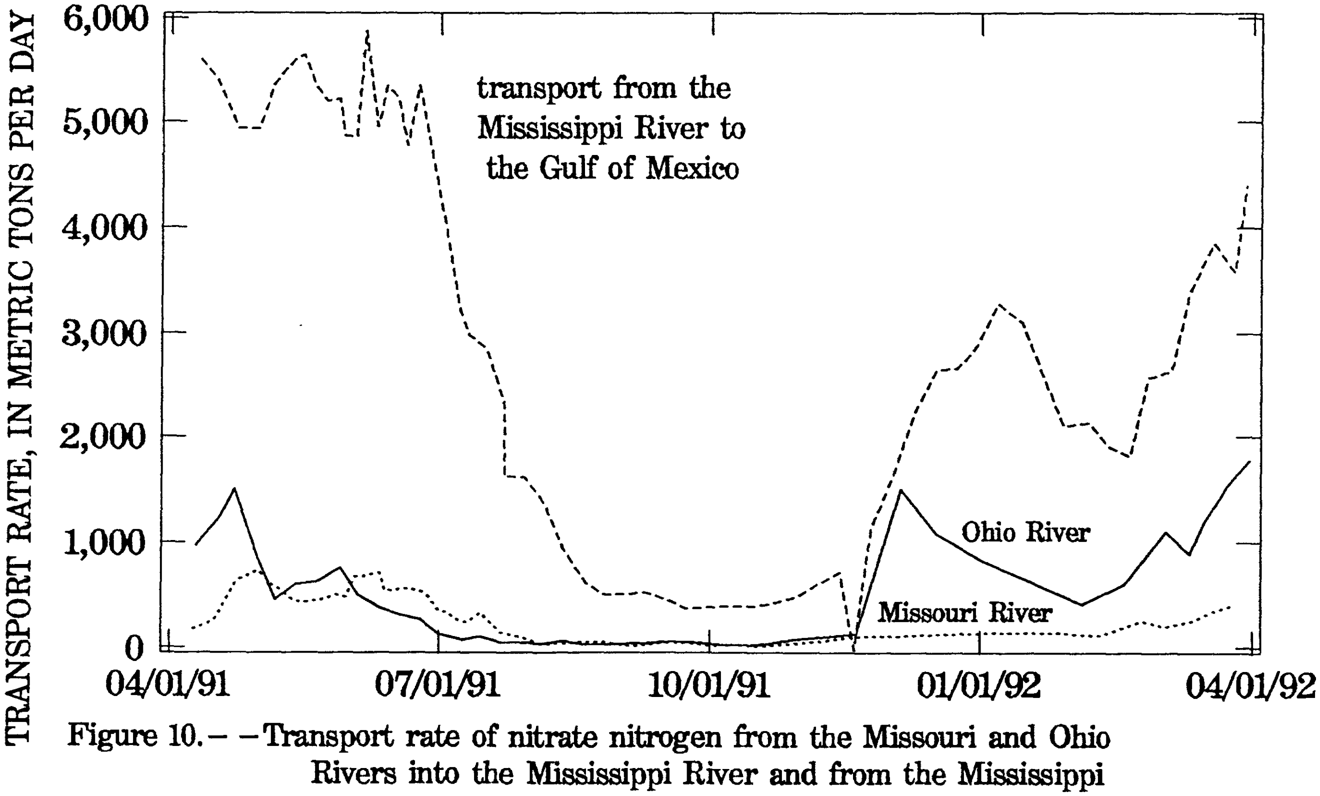

Figure 10.— —Transport rate of nitrate nitrogen from the Missouri and Ohio Rivers into the Mississippi River and from the Mississippi River into the Gulf of Mexico (includes nitrate diverted into the Atchafalaya River).

Table 5.--Estimated percentages of the amounts of agricultural chemicals used in the Mississippi River Basin that were transported out of the Basin in streamflow during April 1991 through March 1992.

[--, insufficient data; all estimates are in percent and calculated from data in Tables 1 and 4; values in parenthesis are river basin drainage areas in square kilometers]

| | River Basin | | | | | | |
|---|---|---|---|---|---|---|---|
| Agricultural Chemical | Illinois at Valley City Ill. (69,300$km^2$) | Platte at Louisville Nebr. (222,200$km^2$) | Mississippi[1] above Missouri River (490,000$km^2$) | Ohio at Grand Chain Ill. (526,000$km^2$) | Missouri at Hermann Mo. (1,357,000$km^2$) | Mississippi at Thebes, Ill. (1,847,000$km^2$) | Mississippi at Baton Rouge, La. (2,914,000$km^2$) |
| alachlor | 0.5 | 0.2 | 0.5 | 0.1 | 0.2 | 0.4 | 0.2 |
| atrazine | 1.8 | 0.6 | 1.7 | 1.1 | 1.1 | 1.4 | 1.6 |
| butylate | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | -- |
| cyanazine | 2.8 | 1.3 | 1.9 | 0.9 | 1.6 | 1.8 | 1.6 |
| EPTC | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | -- |
| metolachlor | 1.1 | 0.6 | 0.8 | 0.6 | 0.7 | 0.8 | 0.8 |
| metribuzin | 0.5 | 0.4 | 0.8 | 0.1 | 0.7 | 0.7 | 0.6 |
| simazine | 1.3 | 2.5 | 2.7 | 3.7 | 2.1 | 2.5 | 2.7 |
| trifluralin | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | -- |
| nitrogen-fertilizer | 23.8 | 1.3 | 26.9 | 16.1 | 4.1 | 16.1 | 15.4 |

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[1] Calculated from agricultural chemical use in the Mississippi River Basin above Thebes, Ill. (Fig. 1) minus use in the Missouri River Basin

nitrate discharged from the Mississippi River basin to the Gulf of Mexico in 1 year (967,000 metric tons, table 4) is equivalent to about 15 percent of the nitrogen fertilizer used on crops in the basin (table 5). However, it must be recognized that sources other than chemical fertilizer, such as animal wastes and legumes, also contribute to the nitrate load transported by the Mississippi River. Nitrate transport from the Upper Mississippi River basin, excluding the Missouri and Ohio basins, was equivalent to about 27 percent of the nitrogen fertilizer used in this area (table 5) and accounted for 59 percent of the nitrate discharged from the entire Mississippi River basin (table 4). The Missouri River and the Platte River, a major Missouri River tributary, had low transport rates for nitrate when compared to the other streams studied. The annual transport rates were equivalent to 4.1% of the nitrogen fertilizer use for the Missouri River basin and 1.3 percent of the nitrogen fertilizer use for the Platte River basin (table 5). Reasons for the significantly lower rate of transport in these basins are not fully understood, but they are believed to be related to soil type, climatic factors, unsaturated-zone ground water transport processes, and possibly lower population densities in the Missouri River basin.

## SUMMARY

Most streams throughout the midwestern United States contain water with high concentrations of herbicides for several weeks to several months following application. Concentrations generally are largest and may exceed MCL's or HA's for drinking water during the first runoff from storms after application. Concentrations decrease during later runoff. Maximum concentrations of heavily used herbicides such as alachlor, atrazine, cyanazine, and metolachlor range from 5 to 11 µg/L in large rivers such as the Mississippi, Missouri and Ohio, and from 50 to more than 100 µg/L in small tributaries. These generally are worst case conditions that do not persist past mid-summer. However, low concentrations (0.05 to 0.2 µg/L) of a few herbicides are detectable year-round in many streams due to storage and subsequent discharge from surface and ground water reservoirs. The total mass of herbicides discharged from the Mississippi River and its major tributaries from April 1991 through March 1992 represents a small fraction (< 0.1 percent to about 3 percent) of the amounts applied.

The temporal distribution pattern for nitrate concentrations is different from that of herbicides. Concentrations are lowest during the summer, and highest during late fall, winter and spring. This temporal pattern is believed to result from a combination of factors including assimilation of nitrate by aquatic and terrestrial plants, high ET rates, and reduced ground water and nitrate discharge to streams during the summer. Concentrations and mass transport of nitrate are considerably higher in streams draining eastern Iowa, Illinois, Indiana and Ohio than elsewhere in the Midwest. Nitrate concentrations may occasionally exceed drinking water standards in some of those streams. Differences in soils, climatic conditions, and subsurface solute transport may, in part, account for these geographic differences. The mass transport of nitrate from the Mississippi River to the Gulf of Mexico is equivalent to about 15 percent of the nitrogen fertilizer used in the basin. However, sources other than fertilizer also contribute to nitrate mass transport. Results from regional-scale studies indicate that processes in addition to those governing herbicide transport are important in controlling the transport of nitrate to streams. Nitrate transport appears to be by both surface runoff and ground-water discharge, whereas herbicides appear to be transported predominantly by surface runoff.

# REFERENCES

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, Blacksburg, Va., p. 103-120.

Bureau of the Census, 1989, Census of Agriculture, 1987, Final County File [machine readable data file], prepared by the Bureau of the Census, Washington, D.C.

Frank, R., Braun, H.E., Holdrinet, M.V., Sirons, G.J., Ripley, B.D., 1982, Agriculture and water quality in the Canadian Great Lakes basin: Pesticide use in 11 agricultural watersheds and presence in stream water, 1975-1977: Journal of Environmental Quality, v. 11, p. 497-505.

Gianessi, L.P., and Puffer, C.M., 1991, Herbicide use in the United States: Resources for the Future, 127 p.

Goolsby, D.A., Thurman, E.M., and Kolpin, D.W., 1991a, Geographic and temporal distribution of herbicides in surface waters in the upper midwestern United States, 1989-90: U.S. Geological Survey Water Resources Investigations Report 91-4034, p. 183-188.

Goolsby, D.A., Coupe, R.H., Markovchick, D.J., 1991b, 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., Clark, M.L., Pomes M.L., 1990, Immunoassay as a screening tool for triazine herbicides in streams: Comparison with gas chromatographic/mass spectrometric methods, *in* Immunoassays for Trace Chemical Analysis, Vanderlaan, M. Stanker, L.H., Watkins, B.E., Roberts, D.W., eds., Symposium Series 451, American Society, p. 86-99.

Leonard, R.A., 1989, Herbicides in surface water, *in* Environmental Chemistry of Herbicides, v. 1, CRC Press, Inc., Boca Raton, Fla., p. 45-88.

Lucey, K.J. and Goolsby, D.A., 1993, Effects of Short-Term Climatic Variations on Nitrate Concentrations in the Raccoon River, Iowa: Journal of Environmental Quality, v. 22, p. 38-46.

Pereira, W.E., and Rostad, C.E., 1990, Occurrence, distribution, 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.

Pomes, M.L., Thurman, E.M., and Goolsby, D.A., 1991, Comparison of microtiter-plate immunoassay (ELISA) and GC/MS for analysis of herbicides in storm-runoff samples, *in* G.E. Mallard and D.A. Aronson, eds., Proceedings of the U.S. Geological Survey Toxic Substances Hydrology Program Technical Meeting, Monterey, California, March 11-15, 1991: Water Resources Investigations Report 91-4034, p. 572-575.

Sandstrom, M.W., Wydoski, D.S., Schroeder, M.P., Zamboni, J.L., Foreman, W.T., 1991, Methods of analysis by the National Water Quality Laboratory: Determination of organonitrogen herbicides in water by solid phase extraction and capillary column gas chromatograph/mass spectrometry with selected ion monitoring: U.S. Geological Survey Open-File Report 91-519, 26 p.

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

Squillace, P.J., Thurman, E.M., 1992, Herbicide transport in rivers: Importance of hydrology and geochemistry in nonpoint-source contamination: Environmental Science and Technology, v. 26, p. 538-545.

Thurman, E.M., Goolsby, D.A., Meyer, M.T., 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.

Thurman, E.M., Goolsby, D.A., Meyer, M.T., Kolpin, D.W., 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.

Thurman, E.M., Meyer, M., Pomes, M., Perry, C.A., 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. Department of Agriculture, 1992, Agricultural Resources: Inputs Situation and Outlook, Economic Research Service publication AR-25, February 1992, 66 p.

U.S. Environmental Protection Agency, 1990, County-level fertilizer sales data: PM-2221, Washington D.C., Office of Policy, Planning, and Evaluation.

U.S. Environmental Protection Agency, 1992, Drinking Water Regulations and Health Advisories, U.S. EPA, Office of Water, 13 p.

Wauchope, R.D., 1978, The pesticide content of surface water draining from agricultural fields: A review: Journal of Environmental Quality, v. 7, p. 459-472.

Wu, T.L., Corell, D.L., and Remenapp, H.E.H., 1983, Herbicide runoff from experimental watersheds: Journal of Environmental Quality, v. 12, p. 330-336.

# ANNUAL USE AND TRANSPORT OF AGRICULTURAL CHEMICALS IN THE MISSISSIPPI RIVER, 1991-92

**By William A. Battaglin, Donald A. Goolsby and Richard H. Coupe**

## ABSTRACT

The presence of agricultural chemicals (herbicides, insecticides, and nutrients) in the Mississippi River and several tributaries follows an annual cycle. Herbicide concentrations are generally highest during periods of storm runoff following application in the spring and early summer. Nitrate concentrations are generally highest in the winter and spring and lower during the summer and fall.

Concentrations and mass transport of agricultural chemicals in rivers are generally related to the amounts of the chemicals used within the river drainage basins. A geographic information system (GIS) was used to analyze relations among county-level estimates of the mass of agricultural chemicals applied (kilograms of active ingredient applied per county) and the annual transport of dissolved chemicals in rivers. Relations were studied for the Mississippi River and several tributaries in the midwestern United States. County-level estimates of herbicide and nitrogen use were developed into a series of GIS data layers and used to estimate the mass of agricultural chemicals used annually within specific drainage basins. Analytical data from periodic water-quality sampling and daily streamflow data were used to estimate the mass of agricultural chemicals transported out of specific drainage basins by rivers. These data sets were used to develop statistical models for estimating annual transport of agricultural chemical as a percentage of estimated annual agricultural chemical use in the basins of the Mississippi River and several tributaries. Results indicated that, in 1991, estimated masses equivalent to about 15 percent of the commercial nitrogen fertilizer, 1.6 percent of the atrazine and cyanazine, 0.8 percent of metolachlor, and 0.2 percent of the alachlor applied in the drainage basins studied were transported out of the basins by rivers.

## INTRODUCTION

The U.S. Geological Survey presently (1993) is conducting studies to determine the distribution, transport, and persistence of selected agricultural chemicals (herbicides, insecticides, and inorganic nutrients) in the Mississippi River and several tributaries. Previous studies indicated that transport of agricultural chemicals in runoff to streams is seasonal; the largest contributions occur during periods of late spring and early summer runoff (Baker and Richards, 1990; Goolsby and others, 1991a; Thurman and others, 1991; Goolsby and others, 1991b; Thurman and others, 1992; Goolsby and Battaglin, in press). These studies also indicate that agricultural chemicals are present in surface waters in concentrations that exceed Federal health-based levels for drinking water at certain times of the year (U.S. Environmental Protection Agency, 1992). However, these high concentrations generally do not persist throughout the year, and the health-based levels are based on average annual concentrations, not concentrations of short-duration (Goolsby and Battaglin, in press).

The Mississippi River Basin contains some of the most productive cropland in the world (Spalding and Exner, 1991). Agricultural chemicals are used extensively in this region to increase yields of agricultural crops. In the Mississippi River Basin, an estimated 20,600 metric tons of atrazine, 18,500 metric tons of alachlor, 15,800 metric tons of metolachlor, 8,170 metric tons of cyanazine, and 6,263,000 metric tons of nitrogen fertilizer are used annually (Gianessi and Puffer, 1990; U.S. Environmental Protection Agency, 1990). Agricultural chemical use in the Mississippi River Basin accounts for more than one-half of the total use in the United States (Gianessi and Puffer, 1990; U.S. Environmental Protection Agency, 1990). Most of this agricultural chemical use is associated with the production of corn, soybeans, sorghum, and wheat.

Many agricultural chemicals are partially soluble in water and have the potential to leach to ground water or to run off to surface water. The presence of agricultural chemicals in surface waters of the midwestern United States is of concern because approximately 18 million people in the midwestern United States depend on the Ohio, Missouri, and Mississippi rivers and their tributaries for drinking-water supply (Howard Perlman, U. S. Geological Survey, written commun., 1991). Conventional water-treatment practices do not remove most of these agricultural chemicals, and costly alternative treatment methods, such as carbon filtration or denitrification, might be required to treat waters that do not meet health-based limits (U.S. Environmental Protection Agency, 1989; Adams and others, 1990; Madison and Brunett, 1985). An improved understanding of the spatial and temporal distribution agricultural chemicals in midwestern rivers is needed so that water-managers and suppliers can address the problems resulting from agricultural chemical contamination of water supplies.

The purposes of this paper are to (1) describe the methods used to estimate agricultural-chemical transport in the Mississippi River and several of its tributaries, and agricultural chemical use within the drainage basins associated with specific sampling points; and (2) present the results of simple statistical models that were used to estimate the annual dissolved transport of agricultural chemicals as a percentage of the estimated annual use of those chemicals. The results presented in this paper are for a particular year; the effects of climatic conditions and other factors that might change from year to year have on results are not addressed in this paper.

Eight large basins with drainage areas of 29,400 to 2,914,000 km$^2$ (fig. 1) were studied. The Mississippi River was sampled at three locations, and the Missouri, Ohio, Platte, Illinois, and White Rivers were each sampled at one location (fig. 1). All these river basins are predominantly within the corn and soybean producing region of the mid-continental United States.

## METHODS OF INVESTIGATION

Streamflow from the eight basins was sampled periodically from April 1991 through March 1992. Except for the Ohio River, all sites were sampled every 3 to 4 days during May through mid-July, once per week during the remainder of the summer and fall, and once every 2 weeks during winter. The Ohio River was sampled once per week, except during winter when samples were collected every 2 weeks (Goolsby and others, 1991b). Samples were collected by depth-width integrating methods (Edwards and Glysson, 1988) and composited in stainless steel or glass containers. Samples for pesticide analysis were filtered through 0.7–µm pore-diameter glass-fiber

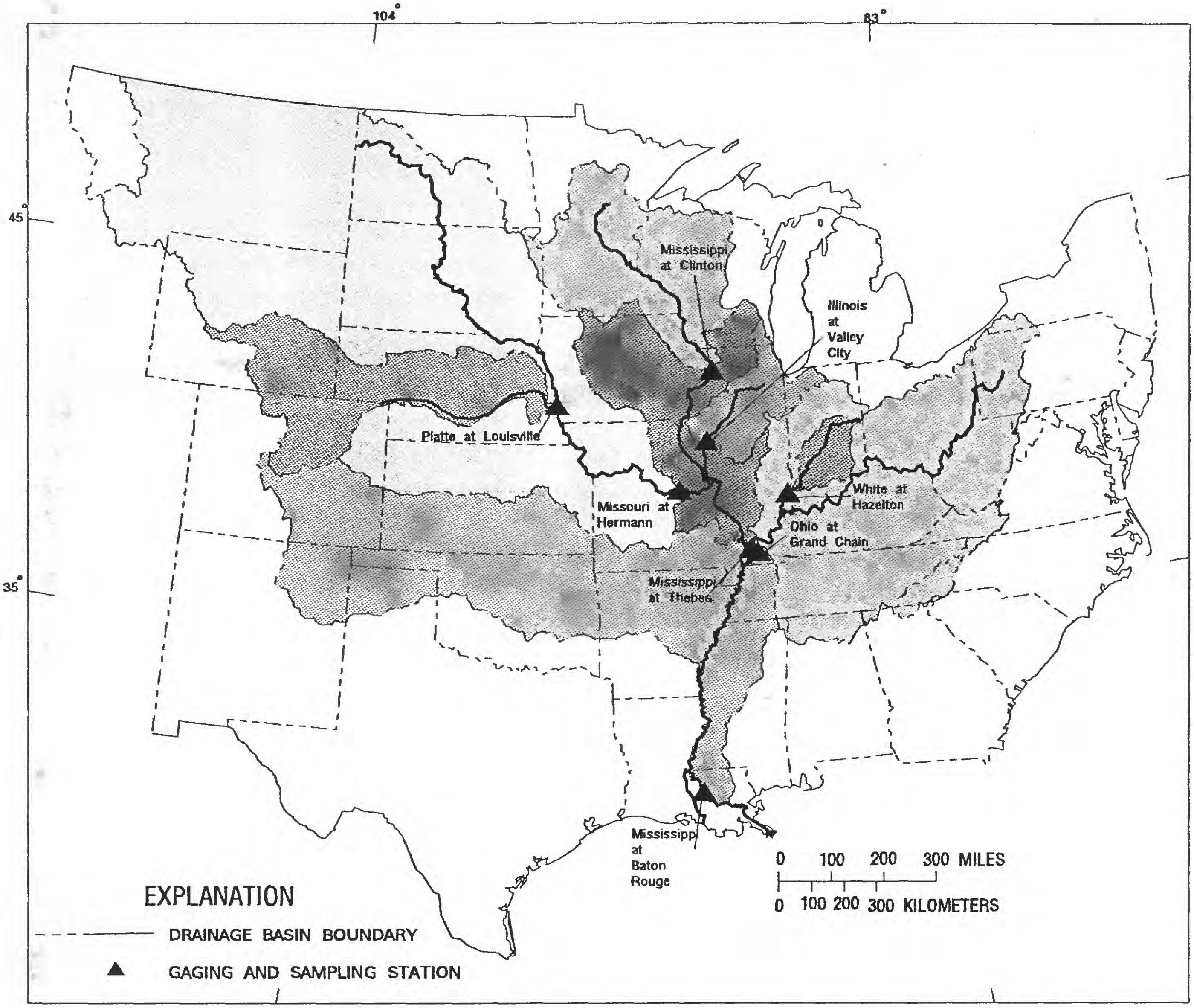


Figure 1.--Gaging and sampling station locations and associated drainage basins for the Mississippi River and several tributaries.

filters into pre-cleaned glass bottles. Samples for nitrate analysis were filtered through 0.45–μm-membrane filters.

All samples from the eight basins were analyzed for herbicides by gas chromatography/mass spectrometry (GC/MS) following solid-phase extraction on $C_{18}$ cartridges (Sandstrom and others, 1991). Nitrite and nitrite plus nitrate concentrations for all sites were determined by automated colorimetric procedures (Fishman and Friedman, 1989). Nitrate concentration was calculated as the difference in concentration resulting from these two analytical determinations.

Daily dissolved transport of atrazine, alachlor, cyanazine, metolachlor, and nitrate as nitrogen was calculated for the eight basins as the product of measured or estimated daily concentrations and daily mean streamflow. Concentrations were estimated by linear interpolation on days when no samples were collected. The estimated daily transport was accumulated for the period April 1, 1991 to March 31, 1992, to obtain estimates of annual transport.

County-level herbicide use estimates were constructed by Gianessi and Puffer (1991) by --

(1) compiling statistics by State and by crop, on percentage of acres treated with a given herbicide and average annual application rate of the herbicide from surveys sent to Extension Service weed scientists in 1989 and 1987;
(2) augmenting survey data with published surveys and reports from specific States (U.S. Department of Agriculture, 1989);
(3) establishing herbicide-use profiles, by State and by crop, containing the percentage of acres treated and average annual applications rates;
(4) multiplying county-level crop acreage estimates from the 1987 Census of Agriculture (Bureau of the Census, 1989) by percentage of acres treated and average annual application rates to get herbicide use estimates; and
(5) tabulating use of active ingredient of herbicides used by crop and by county.

The total use of individual herbicides on all crops for each county was calculated prior to entering the herbicide-use estimates into the GIS.

County-level nitrogen fertilizer sales for the 1991 fertilizer year (July 1, 1990 through June 30, 1991), were estimated (Gerald Fletcher, West Virginia University, written commun., 1992; U.S. Environmental Protection Agency, 1990). The fertilizer-sales estimates are reported as tons of actual nutrient (inorganic nitrogen, phosphate, and potash). The fertilizer sales estimates do not account for the use of manure. County-level nitrogen-fertilizer sales estimates were constructed by --

(1) compiling annual State fertilizer-sales data reported as tonnages to the National Fertilizer and Environmental Research Center of the Tennessee Valley Authority;
(2) calculating the ratio of expenditures on commercial fertilizers by county to expenditures on commercial fertilizers by State from the 1987 Census of Agriculture (Bureau of the Census, 1989); and
(3) computing annual county-level fertilizer sales, in tons, by multiplying estimates of annual State sales by the ratio of county expenditures to State expenditures.

The county-level estimates of nitrogen-fertilizer sales in tons of actual nutrient were entered directly into the GIS.

An area-weighted transfer algorithm was programed in the GIS and used to generate estimates of the masses of agricultural chemicals used within the drainage basins studied. The transfer algorithm accounts for cases where both the entire county is within a drainage basin, and where only a portion of a county is within a drainage basin. In the latter case, the value of the attribute being transferred is weighted by the ratio of the area of the county within the basin to the total county area. For example, if 25 percent of county X falls within basin Y, and atrazine use is estimated to have been 4,000 kg in county X, then 1,000 kg of atrazine from county X is transferred to basin Y.

## USE AND TRANSPORT OF AGRICULTURAL CHEMICALS

Graphs of concentration for atrazine, alachlor, cyanazine, metolachlor, and nitrate in water samples collected at the sampling site on the Mississippi River at Thebes, Ill., (fig. 2) show the temporal patterns in agricultural-chemical concentrations that were observed at all eight sampling sites. The spring-flush phenomenon previously reported by Thurman and others (1991) is readily apparent. In the Mississippi River, concentrations change more slowly, peak concentrations are lower, and elevated concentrations are sustained for a longer period of time than they are in smaller streams. These differences can be attributed to the fact that these large rivers integrate the agricultural-chemical input from many smaller streams. The year-round occurrence of herbicides, such as atrazine, in the Mississippi River indicates that some agricultural chemicals are stored and subsequently released from surface-water and ground-water reservoirs (Goolsby and Battaglin, in press; Squillace and Thurman, 1992).

The estimates of annual agricultural chemical transport (table 1) represent only transport of dissolved chemicals. Earlier research by Pereira and Rostad (1990) indicated that 99.5 percent of the atrazine, cyanazine and metolachlor was in the dissolved phase and less than 0.5 percent was in the suspended phase in the lower Mississippi River. Squillace and Thurman (1992) estimated that 1 percent or less of the total atrazine was present in the suspended phase in samples from the Cedar River in Iowa. The estimates of annual transport of agricultural chemicals in the Mississippi River are similar to those reported by Goolsby and others (1991) but significantly larger than those reported by Pereira and others (1989).

Graphics showing the relative intensity of agricultural-chemical use were created to help visualize the spatial distribution of agricultural chemical use across the United States. Examples of the herbicide and nitrogen-fertilizer use data are shown in figure 3. For these examples, county-level estimates of atrazine use, in kilograms, or nitrogen-fertilizer use, in metric tons, have been divided by county land area. A statistical distribution was used to select six class intervals for the graphic displays of agricultural chemical use. The empty (white) class represents counties where data on agricultural-chemical use are missing or zero. The first shaded class (lightest grey) represents use data that are greater than zero and as large as the 25th percentile of the data, the second grey-shaded class represents use data that are greater than the 25th percentile and as large as the median of the data, the third grey-shaded class represents use data that are greater than the median and as large as the 75th percentile of the data, the fourth grey-shaded class represents use

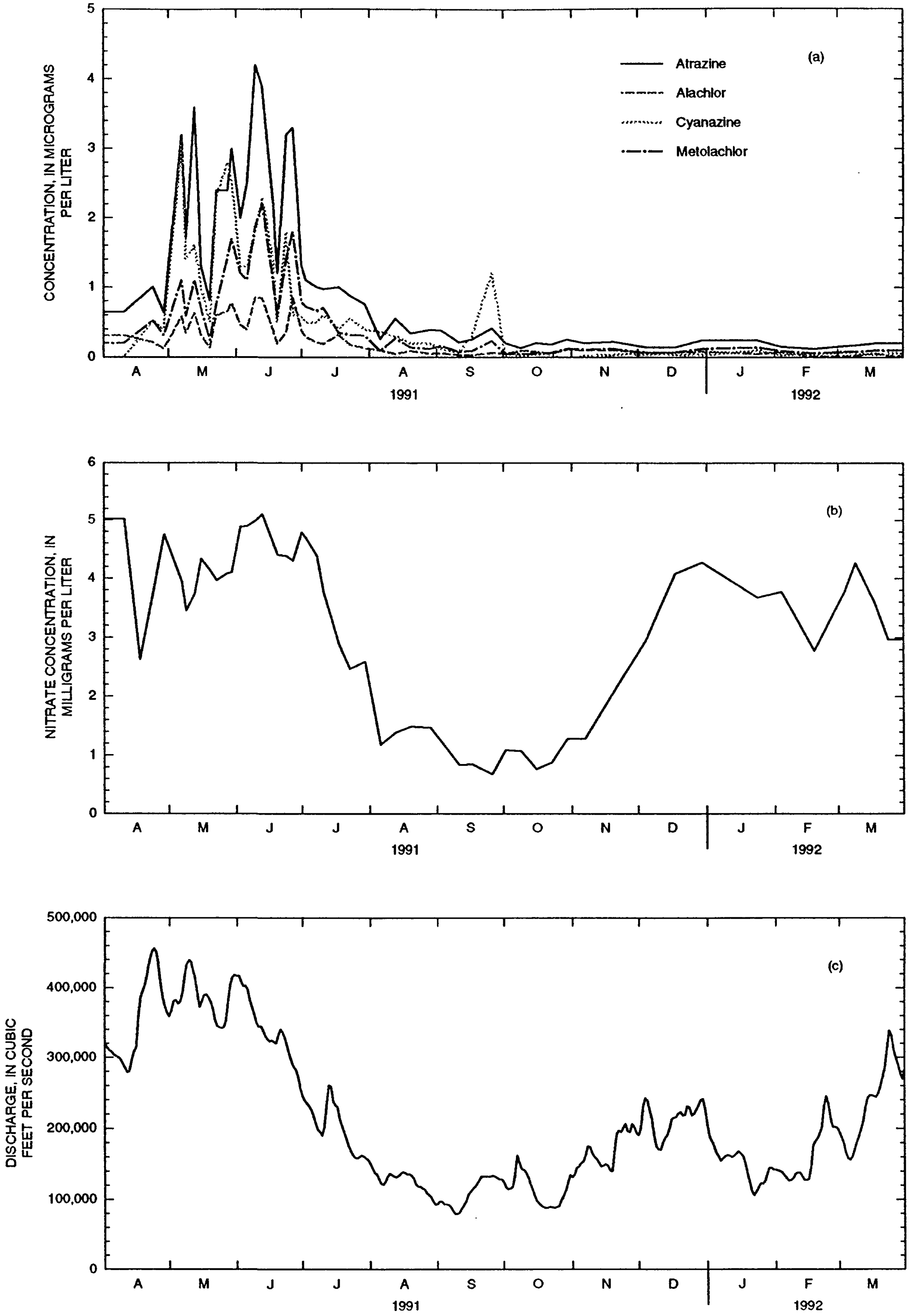


FIGURE 2. -- TEMPORAL DISTRIBUTION OF (A) HERBICIDES: ATRAZINE, ALACHLOR, CYANAZINE, AND METOLACHLOR CONCENTRATIONS (B) NITROGEN CONCENTRATION, AND (C) DISCHARGE IN THE MISSISSIPPI RIVER AT THEBES, ILLINOIS

Table 1.--Estimated transport of atrazine, alachlor, cyanazine, metolachlor, and nitrate in metric tons, by the Mississippi River and several tributaries, April 1991 through March 1992

| Sampling station name | Estimated transport | | | | |
|---|---|---|---|---|---|
| | Atrazine | Alachlor | Cyanazine | Metolachlor | Nitrate |
| Mississippi at Baton Rouge, La. | 321. | 33.7 | 127. | 123. | 967,000 |
| Mississippi at Thebes, Ill. | 189. | 42.9 | 113. | 87.2 | 651,000 |
| Missouri River at Hermann, Mo. | 68.4 | 7.87 | 31.3 | 24.7 | 79,900 |
| Ohio River at Grand Chain, Ill. | 57.0 | 4.97 | 13.4 | 20.2 | 182,000 |
| Mississippi River at Clinton, Iowa | 15.1 | 5.64 | 8.94 | 8.10 | 157,000 |
| Platte River at Louisville, Nebr. | 9.28 | 2.35 | 5.91 | 2.47 | 5,640 |
| Illinois River at Valley City, Ill. | 35.8 | 8.79 | 19.8 | 18.9 | 107,000 |
| White River at Hazelton, In. | 5.68 | 1.04 | 1.71 | 2.11 | 11,500 |

Table 2.--Estimated annual application of atrazine, alachlor, cyanazine, metolachlor, and nitrogen as commercial fertilizer in metric tons, in the Mississippi and several tributary basins

| Sampling station name | Upstream drainage area in square kilometers | Estimated application, in metric tons | | | | |
|---|---|---|---|---|---|---|
| | | Atrazine | Alachlor | Cyanazine | Metolachlor | Nitrogen |
| Mississippi at Baton Rouge, La. | 2,914,000 | 20,600 | 18,500 | 8,170 | 15,800 | 6,263,000 |
| Mississippi at Thebes, Ill. | 1,847,000 | 13,400 | 12,200 | 6,210 | 11,000 | 4,055,000 |
| Missouri River at Hermann, Mo. | 1,357,000 | 6,280 | 4,660 | 1,970 | 3,490 | 1,930,000 |
| Ohio River at Grand Chain, Ill. | 526,000 | 5,060 | 4,900 | 1,440 | 3,440 | 1,133,000 |
| Mississippi River at Clinton, Iowa | 222,000 | 1,440 | 2,040 | 1,590 | 1,630 | 607,000 |
| Platte River at Louisville, Nebr. | 222,000 | 1,600 | 1,030 | 464 | 444 | 425,000 |
| Illinois River at Valley City, Ill. | 69,000 | 1,960 | 1,880 | 715 | 1,760 | 450,000 |
| White River at Hazelton, In. | 29,000 | 711 | 851 | 214 | 424 | 143,000 |

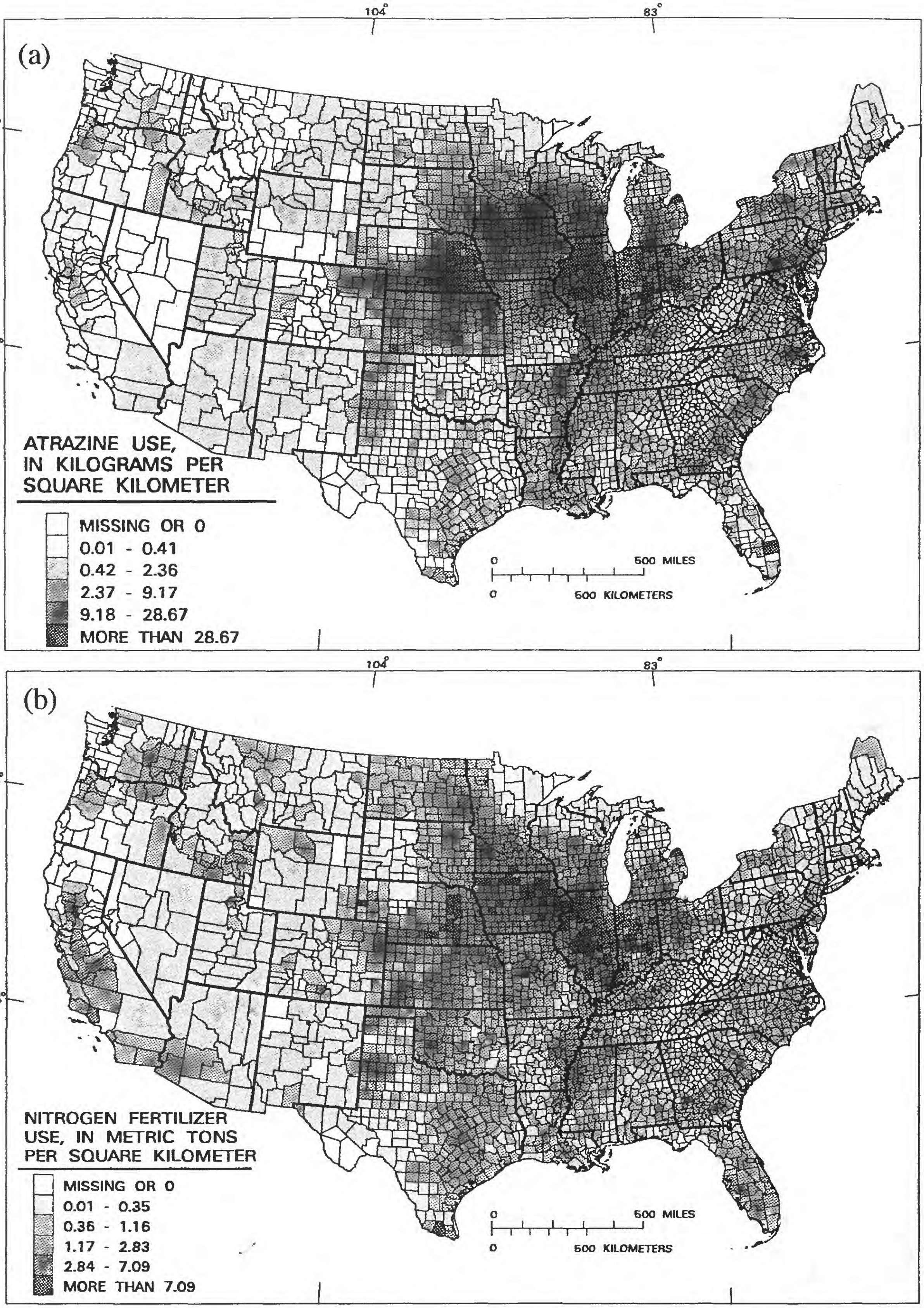


Figure 3.--Estimated county-level: (a) atrazine use; (b) nitrogen fertilizer use, July 1, 1990 to June 30, 1991

data that are greater than the 75th percentile and as large as the 75th percentile plus two standard deviations of the data, and the fifth grey-shaded class represents use data that are greater than the 75th percentile plus two standard deviations.

Linear regressions were used to investigate relations between estimates of agricultural chemical transport (table 1) and use (table 2), and to estimate transport of agricultural chemicals as a percentage of estimated annual agricultural-chemical use. For the Mississippi River and several tributaries, significant relations ($p < 0.05$) were determined when estimates of annual transport were regressed with estimates of annual use for atrazine, alachlor, cyanazine, metolachlor, and nitrate as N (table 3).The regressions with alachlor and nitrate do not appear to fit well at the smaller values of transport and use (fig. 4). However, there are other sources of nitrogen besides chemical fertilizers, such as domestic and animal wastes, legumes, and natural sources that are not accounted for in the use term of the nitrate regression equation.

Values for the Pearsons product-moment correlation coefficient (Davis, 1986), multiple R-square, P(F) value, and slope of the regression line for the regressions equations are given in table 3. Both agricultural-chemical transport and use are highly correlated to basin area, which could inflate the goodness of fit statistics in table 3. Also, the Mississippi River at Baton Rouge site has a strong influence on all of the regressions because this site represents the largest drainage area (fig. 4).

Estimates of annual agricultural chemical transport as a percentage of estimated annual use for the eight drainage basins are shown in table 4. The results in tables 3 and 4 indicate that, on an annual basis, estimated masses equivalent to about 15 percent of the commercial fertilizer, 1.6 percent of the atrazine and cyanazine, 0.8 percent of metolachlor, and 0.2 of the alachlor used in large drainage basins in the midwestern United States are transported out of the basins by rivers. However, table 4 indicates that there is significant basin-to-basin variability in the estimates of transport as a percentage of use. The maximum values of all herbicide transport as a percentage of use are for the Illinois River. The estimates of chemical transport as a percentage of estimated annual use for cyanazine are likely to be to smaller than those listed in table 4, since cyanazine use estimates were constructed using 1989 data, and the manufacturer of cyanazine reports a 24.3 percent increase in cyanazine sales between 1989 and 1991 (Patti Tillotson, DuPont Agricultural Products, written commun., 1993).

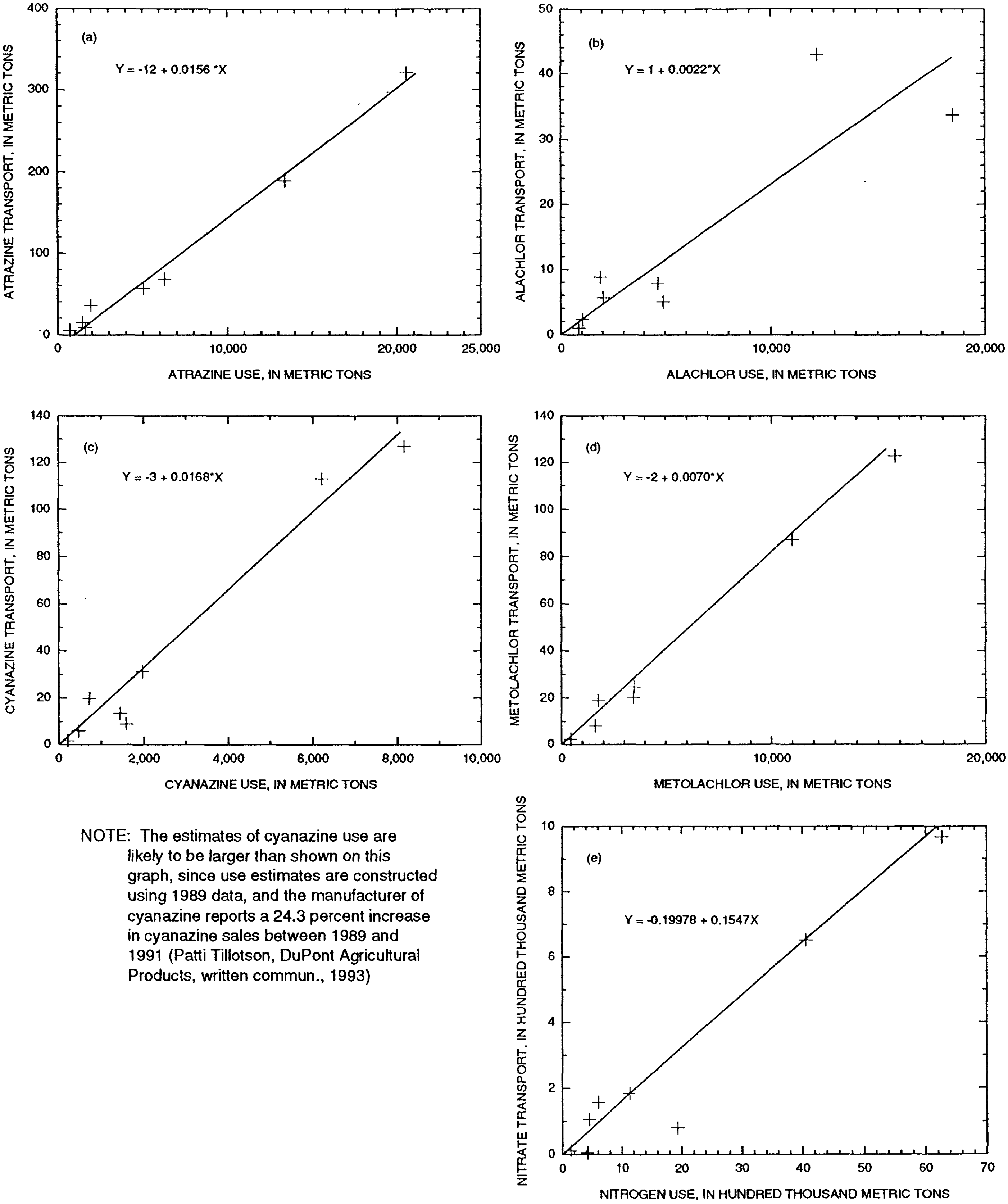
Previous investigations have demonstrated a relation between herbicide use and time-weighted mean herbicide concentrations (Baker and Richards, 1990) and between herbicide use and transport (Hall and others, 1972; Squillace and Thurman, 1992). Wauchope (1978) summarized the results of several studies investigating the loss (transport from field to stream) of herbicides from agricultural areas and proposed numbers representing expected herbicide losses as a percentage of use that could be useful for water-quality planning for large regions. The results from this study can be compared with results from these other studies. Hall and others (1972) estimated atrazine transport in runoff water was 2 percent of the amount applied at the recommended rate. Squillace and Thurman (1992) estimated that 1.5 to 5 percent of the atrazine applied was transported from the Cedar River basin in 1984. Wauchope (1978) estimated that 2 to 5 percent of herbicides applied as wettable powders (includes atrazine and cyanazine) and 1 percent of other herbicides (including alachlor), were lost in runoff. The results of the present

Table 3.-- Goodness of fit statistics for regression relations of agricultural chemical transport, April 1991 through March 1992, with annual use

| | Atrazine | Alachlor | Cyanazine | Metolachlor | Nitrate |
|---|---|---|---|---|---|
| Pearson product-moment correlation coefficient | 0.994 | 0.889 | 0.983 | 0.997 | 0.968 |
| Multiple R-square | 0.989 | 0.790 | 0.967 | 0.994 | 0.936 |
| P(F)-value | 0.0000 | 0.0032 | 0.0000 | 0.0000 | 0.0001 |
| Slope of regression line | 1.56 | 0.22 | 1.68 | 0.79 | 15.47 |

Table 4.--Estimated transport, April 1991 through March 1992, as a percentage of use for atrazine, alachlor, cyanazine, metolachlor, and nitrate, in the Mississippi River and several tributaries

| Sampling | Estimated transport as a percentage of use | | | | |
|---|---|---|---|---|---|
| station same | Atrazine | Alachlor | Cyanazine | Metolachlor | Nitrate |
| Mississippi at Baton Rouge, La. | 1.56 | 0.18 | 1.55 | 0.78 | 15.44 |
| Mississippi at Thebes, Ill. | 1.41 | 0.35 | 1.82 | 0.79 | 16.05 |
| Missouri River at Hermann, Mo. | 1.09 | 0.17 | 1.59 | 0.71 | 4.14 |
| Ohio River at Grand Chain, Ill. | 1.13 | 0.10 | 0.93 | 0.59 | 16.06 |
| Mississippi River at Clinton, Iowa | 1.05 | 0.28 | 0.56 | 0.50 | 25.86 |
| Platte River at Louisville, Nebr. | 0.58 | 0.23 | 1.27 | 0.57 | 1.33 |
| Illinois River at Valley City, Ill. | 1.83 | 0.47 | 2.77 | 1.07 | 23.78 |
| White River at Hazelton, In. | 0.80 | 0.12 | 0.80 | 0.50 | 8.04 |
| Value from regression of transport with use, all basins | 1.56 | 0.22 | 1.68 | 0.79 | 15.47 |



NOTE: The estimates of cyanazine use are likely to be larger than shown on this graph, since use estimates are constructed using 1989 data, and the manufacturer of cyanazine reports a 24.3 percent increase in cyanazine sales between 1989 and 1991 (Patti Tillotson, DuPont Agricultural Products, written commun., 1993)

Figure 4. -- Graphs showing agricultural chemical transport as a function of use in the Mississippi River and several tributaries for: (a) atrazine, (b) alachlor, (c) cyanazine, (d) metolachlor, and (e) nitrate

study indicate slightly smaller loss of herbicides than estimated by Wauchope (1978) and Hall and others (1972). The difference could be the result of basin-to-basin variability, climatic conditions particular to the year of study, or changing agricultural management systems (including changes in application method and rate); However, the difference is likely to be a function of the area studied and the design of the experiments. The experiments summarized by Wauchope (1978) were mostly field-scale studies with study plots less than 2 ha, not basin-scale studies as used in the present study. In the study by Hall and others (1972), field runoff was maximized by experimental design and plot construction.

Estimates of nitrogen transport as a percentage of nitrogen use calculated for this study (table 4) are well within the range of values (1.5 to 64 percent) observed during 1979-90, but are somewhat lower than the reported long-term average (24.7 percent) in a small basin in Iowa (Lucey and Goolsby, 1993). In their review of nitrate contamination in the United States, Spalding and Exner (1991) indicated that nitrate in surface water is more of a problem in the Northeast, where runoff is high, and in the Midwest, where tile drainage contributes to surface-water flow, and less of a problem in the High Plains States. Results from this study also indicate that annual nitrogen transport, as a percentage of nitrogen use, is greater in the Ohio and Illinois river basins than for the Platte and Missouri river basins (table 4).

Possible causes of variations in nitrate transport from east to west include differences in agricultural practices, population density, climatic conditions, and surficial materials. These possible causes need to be tested in future studies. The strength of the relations between agricultural chemical use and agricultural chemical transport (table 3) indicates that rates of chemical use could be as important in determining regional vulnerability to surface-water contamination as other hydrogeological factors, such as aquifer type, soil type, and agricultural management systems.

## SUMMARY

Estimates of agricultural chemical use compiled using a GIS and estimates of agricultural chemical transport calculated from periodic water-quality sampling and daily mean stream flow data were compared using linear regression models for the Mississippi River and several of its tributaries in the midwestern United States. Results indicated that, during April 1991 thorough March 1992, estimated masses equivalent to about 15 percent of the commercial fertilizer, 1.6 percent of the atrazine and cyanazine, 0.8 percent of metolachlor, and 0.2 of the alachlor used in the basins were transported in the dissolved phase out of the basins by rivers.

# REFERENCES

Adams, C.D., Randtke, S.J., Thurman, E.M., and Hulsey, R.A., 1990, Atrazine and its degradation products in soil and ground water, and the effectiveness of water-treatment processes for their removal, in Proceedings from the 40th annual University of Kansas Environmental Engineering Conference, February 7, 1990, 24 p.

Baker, David B., and Richards, R. Peter, 1990, Transport of soluble pesticides through drainage networks in large agricultural river basins *in* Kurtz, David A.,ed., Long Range Transport of Pesticides: Lewis Publishers, Inc., Chelsea, Michigan, p. 241-270.

Bureau of the Census, 1989, Census of Agriculture, 1987, Final County File [machine-readable data file], prepared by the Bureau of the Census, Washington, D.C.

Davis, John C., 1986, Statistics and Data Analysis in Geology: John Wiley & Sons, Inc., New York, 646 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, Leonard P. and Puffer, Cynthia, 1990 (revised 1991), Herbicide use in the United States: Washington, D.C., Resources for the Future, December 1990 (Revised April 1991). 128 p.

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

Goolsby, D. A., Coupe, R.H., and Markovchick, D. J., 1991b, 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., and Battaglin, W. A., in press, Occurrence and distribution of pesticides in rivers of the midwestern United States, *in* Leng, M.L., ed., Regulation of Agrochemical Environmental Fate in the Nineties: Chelsea, Michigan, Lewis Publishers.

Hall, J.K., Pawlus, M., and Higgins, E.R., 1972, Losses of atrazine in runoff water and soil sediment: Journal of Environmental Quality, v. 1, no. 2, p. 172-176.

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.

Madison, R.J., and Brunett, J.O., 1985, Overview of the occurrence of nitrate in ground water of the United States, in National Water Summary 1984 - Water-Quality Issues: U.S. Geological Survey Water-Supply Paper 2275, p. 93-105.

Pereira, W.E., Rostad, C.E., and Leiker, T.J., 1989, Preliminary assessment of the fate and transport of synthetic organic agrochemicals in the lower Mississippi River and its tributaries, *in* G.E. Mallard and S.E. Ragone, eds., Proceedings of the U.S. Geological Survey Toxic Substances Hydrology Program Technical Meeting, Phoenix, AZ, September 26-30, 1998: U.S. Geological Survey Water-Resources Investigations Report 88-4220, p. 453-464.

Pereira, Wilfred E., and Rostad, Colleen E., 1990, Occurrence, distribution, and transport of herbicides and their degradation products in the lower Mississippi River and its tributaries: Environmental Science and Technology, v. 24, no. 9, p. 1400-1406.

Sandstrom, M.W., Wydoski, D.S., Schroeder, M.P., Zamboni, J.L., and Foreman, W.T., 1991, 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, 26 p.

Spalding, R.F., and Exner, M.E., 1991, Nitrate contamination in the contiguous United States, *in* Bogardi, I. and Kuzelka, R.D.,[ed.], Nitrate Contamination, NATO ASI series, v. G 30, Springer-Verlag, Berlin, p. 13-48.

Squillace, Paul J., and Thurman, E.M., 1992, Herbicide transport in rivers: Importance of hydrology and geochemistry in nonpoint-source contamination: Environmental Science and Technology, v. 26, no. 3, p. 538-545.

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.

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

Thurman, E.M., Goolsby, D.A., Meyer, M.T., Mills, M.S., Pomes, M.L., and Kolpin, D.W., 1992, A reconnaissance study of herbicides and their metabolites in surface water of the Midwestern United States using Immunoassay and Gas Chromatography/Mass Spectrometry: Journal of Environmental Science and Technology, v. 26, no. 12, p. 2440-2447.

U.S. Department of Agriculture, 1989, Agricultural Resources, Situation and Outlook Report. Economic Research Service, February, Washington, D.C.

U.S. Environmental Protection Agency, 1989, Drinking Water Health Advisory: Pesticides: Office of Drinking Water Health Advisories: Chelsea, Michigan, Lewis Publishers, Inc., 819 p.

U.S. Environmental Protection Agency, 1990, County-level fertilizer sales data: Office of Policy, Planning, and Evaluation (pm-221).

U.S. Environmental Protection Agency, 1992, Drinking Water Regulations and Health Advisories; Office of Water, 13 p.

Wauchope, R. D., 1978, The pesticide content of surface water draining from agricultural fields - a review: Journal of Environmental Quality, 1978, v. 7, n. 4, p. 459-472.

# RELATION OF NITRATE CONCENTRATIONS IN SURFACE WATER TO LAND USE IN THE UPPER-MIDWESTERN UNITED STATES, 1989-90

By David K. Mueller, Barbara C. Ruddy, and William A. Battaglin

## ABSTRACT

As part of a study on contamination from agricultural chemicals, nitrate data were collected during several synoptic surveys at a large number of surface-water sites in 10 Midwestern states during 1989-90. These data were analyzed using logistic regression to relate discrete categories of nitrate concentrations to land use in the drainage basins upstream from the sampling sites. The nitrate data were divided into three categories representing background concentrations, elevated concentrations, and concentrations that exceeded the U.S. Environmental Protection Agency maximum contaminant level for drinking water. Land-use data were derived from spatial-digital data available from several sources in national data bases. The explanatory variables selected for the best-fit model were percentile of streamflow at the time of sampling, acreage of the basin in corn, acreage in soybeans, density of cattle, and population density. All these variables have qualitative relations to nitrate sources, mobilization, or transport. Classification of nitrate categories from this model was 80 percent accurate in comparison to observed categories. The accuracy of the model was better for classification into categories that represented lower concentrations; however, incorrect classifications were not biased either high or low. Results from this study indicate that land-use data can be useful in analyses of water-quality conditions in large regions and that logistic regression is a valuable technique for use in such analyses.

## INTRODUCTION

Large quantities of agricultural chemicals, including herbicides and nitrogen fertilizers are applied each year to farmland in the upper-midwestern United States. These applications, in conjunction with the moderately large solubility and mobility of some herbicides and nitrate, creates the possibility for substantial contamination of surface and ground water. In 1989, the U.S. Geological Survey (USGS) began a regional study of herbicides and nitrate in surface waters of a 10-State area (fig. 1). Synoptic sampling surveys were conducted in the spring and summer of 1989 and 1990 and in the fall of 1989. Analysis of regional synoptic data is an important aspect of several programs within the USGS, including the National Water Quality Assessment Program (NAWQA) and the Toxic Substances Hydrology Program. The results of herbicide analyses from these samples have been presented previously (Goolsby and others, 1991; Thurman and others, 1991).

This paper presents results of the nitrate-data analysis -- specifically, the concept that nitrate concentrations in the synoptic samples are related to land-use data derived from large-scale geographic data bases. Also, statistical models that can be used to estimate nitrate concentrations from land-use data are evaluated.

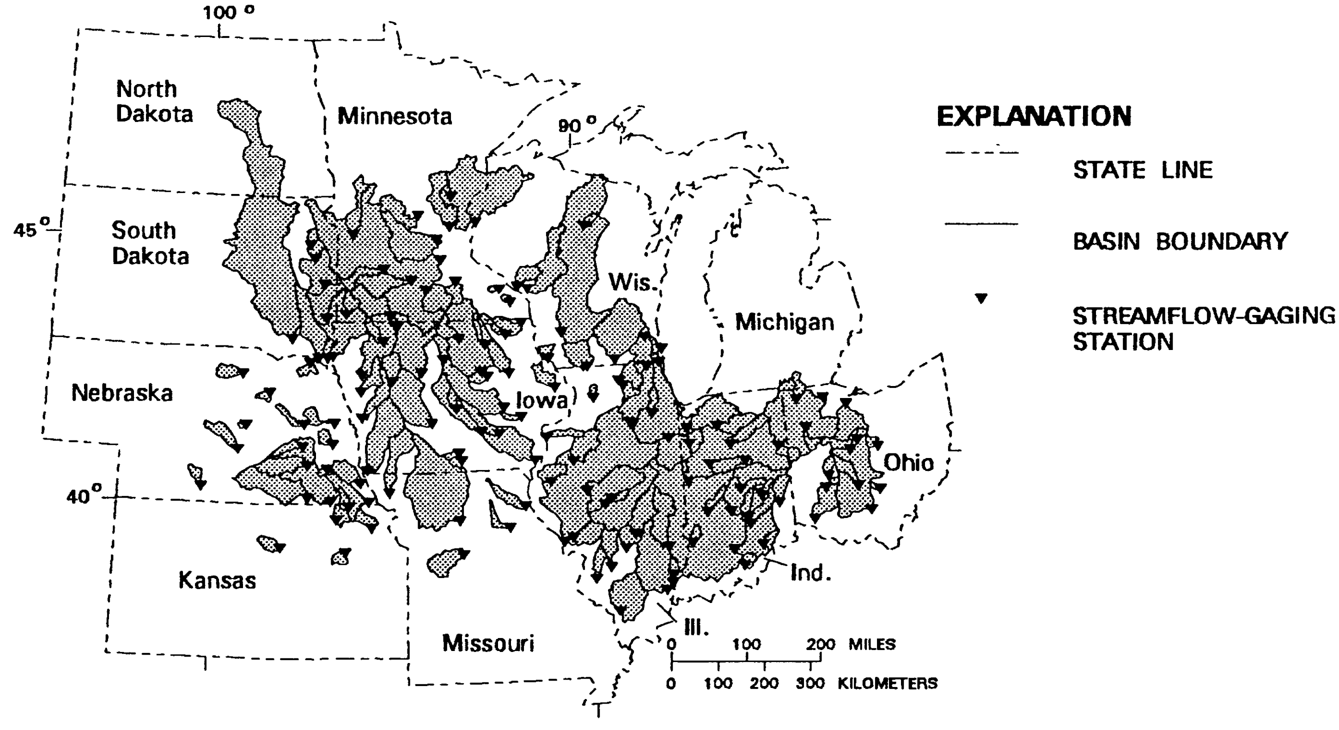


Figure 1. Location of selected stream-sampling sites and upstream drainage basins in the upper midwestern United States.

## SOURCE OF DATA

Surface-water samples were collected at 141 sites in Illinois, Indiana, Iowa, Kansas, Minnesota, Missouri, Ohio, Nebraska, South Dakota, and Wisconsin (fig. 1). Sampling sites were selected to be proportional to corn production in each State (D.A. Goolsby, U.S. Geological Survey, written commun., 1989, 1990). Within States, site selection was based on geographic distribution and drainage-basin area. Most sites were located at existing USGS streamflow-gaging stations.

Samples were collected three times in 1989: (1) spring (March-May), before the application of herbicides, but not necessarily prior to application of nitrogen fertilizers; (2) summer (May-July), during the first major runoff event after application of herbicides; and (3) fall (October-November), after the first killing frost. Samples were analyzed for selected herbicides and for dissolved nitrite plus nitrate (hereinafter referred to as nitrate). Field measurements of temperature, pH, and specific conductance were made and streamflow was either measured or derived from a rating curve.

Fifty sites were resampled during the spring and summer of 1990. Selection of these sites was based on ranking the samples collected during the summer of 1989 according to the total herbicide concentration. The sampling sites were divided into three equal groups. Twenty-five sampling sites were randomly selected from the group that contained the highest concentrations; 13 sampling sites were randomly selected from the middle group; and 12 sampling sites were randomly selected from the group that contained the lowest concentrations. Two additional sampling sites were selected in northeast Iowa from basins that were not sampled in the summer of 1989 because of drought.

Geographic data for the study area were obtained from several sources. Agricultural data, including land use, crop types, and livestock, were collected for the 1987 Census of Agriculture (U.S. Bureau of Census, 1989). Data on nitrogen fertilizer sales during 1989 and 1990 were obtained from the U.S. Environmental Protection Agency (USEPA) (1990). Although these data are for sales, they were considered to represent fertilizer application as well. Population data were collected for the 1990 Census of Population and Housing (U.S. Bureau of Census, 1990). All data were retrieved from Geographic Information System (GIS) data bases, stored as 1:2,000,000-scale digital maps of the conterminous United States. The agricultural and fertilizer data were stored by county. The population data were stored by census geographic units (block groups).

Digital data extracted from these sources were used to compute values for the drainage basin upstream from each surface-water sampling site. A computerized GIS procedure was used to areally weight the extracted data and sum it by basin. When basins were nested (a large basin can contain several smaller basins), the data for the smaller basins were summed to derive the information for the large basin.

The final step in development of the data was to convert the basin data to units that were independent of basin size. For the geographic data, this conversion was done by dividing the data values by basin area. Streamflow at the time of sampling was converted to a percentile value on the basis of the flow-duration relation for daily streamflow at the site. Percentile of flow has been shown to be preferable to actual streamflow in making comparisons among basins of different sizes and, consequently, different flow regimes (D.R. Helsel, U.S. Geological Survey, written commun., 1993). Daily streamflow records were not available for five sampling sites; therefore, flow percentiles could not be computed and those basins were omitted from subsequent analyses. Also, one basin was omitted because no samples were collected during the spring or summer sampling periods in either 1989 or 1990. The resultant data set contained values for 135 basins, having drainage areas that ranged from 89 to about 19,000 $mi^2$ (square miles). The variables in this data set are listed in table 1.

**Table 1.** Variables (attributes) included in the final data set

[mg/L, milligrams per liter; acre/$mi^2$, acres per square mile; number/$mi^2$, number per square mile; ton N/$mi^2$, tons nitrogen per square mile]

| Variable (attribute) | Units | Minimum | Median | Maximum |
|---|---|---|---|---|
| Dissolved nitrite plus nitrate, as nitrogen | mg/L | < 0.1 | 2.5 | 19 |
| Percentile of flow | none | .5 | 67.5 | 99.5 |
| Total harvested cropland | acre/$mi^2$ | 57.1 | 345 | 480 |
| Acreage in corn, including silage | acre/$mi^2$ | 3.06 | 149 | 267 |
| Acreage in soybeans | acre/$mi^2$ | .51 | 126 | 239 |
| Acreage in grain (wheat, oats, and rye) | acre/$mi^2$ | 1.69 | 15.9 | 192 |
| Acreage in hay | acre/$mi^2$ | 4.25 | 25.4 | 158 |
| Pastureland, including pastured woodland | acre/$mi^2$ | 6.04 | 49.4 | 397 |
| Woodland, not pastured | acre/$mi^2$ | 1.09 | 11.3 | 75.5 |
| Cattle | number/$mi^2$ | 5.09 | 55.3 | 176 |
| Hogs | number/$mi^2$ | .99 | 98.3 | 448 |
| Poultry (chickens and turkeys) | number/$mi^2$ | .05 | 32.3 | 6,280 |
| Fertilizer application | ton N/$mi^2$ | 1.38 | 14.3 | 27.2 |
| Population density | number/$mi^2$ | 1.58 | 32.8 | 1,960 |

## STATISTICAL METHODS

The initial attempt to relate nitrate concentrations at each site to land use in the upstream drainage basin was made by using multiple linear regression (MLR). However, no satisfactory MLR models were identified. Logistic regression was selected as an alternative method. Logistic regression commonly is used when the response variable is discrete or categorical, rather than continuous (Helsel and Hirsch, 1992, p. 393). The logistic regression model is similar to the MLR model in that a set of explanatory variables is used to estimate the value of a response variable. The response variable in logistic regression is the log of the odds ratio, p/(1-p), where p is the probability of a data value being in one of the possible categories (Helsel and Hirsch, 1992, p. 395-396). The logistic regression equation is

$$\log\left(\frac{p}{1-p}\right) = b_0 + \boldsymbol{bX}, \tag{1}$$

where

$b_0$ = the intercept,
$X$ = the vector of $k$ explanatory variables, and
$\boldsymbol{b}$ = the vector of slope coefficients for each explanatory variable, so that $\boldsymbol{bX} = b_1X_1 + b_2X_2 + \ldots + b_kX_k$.

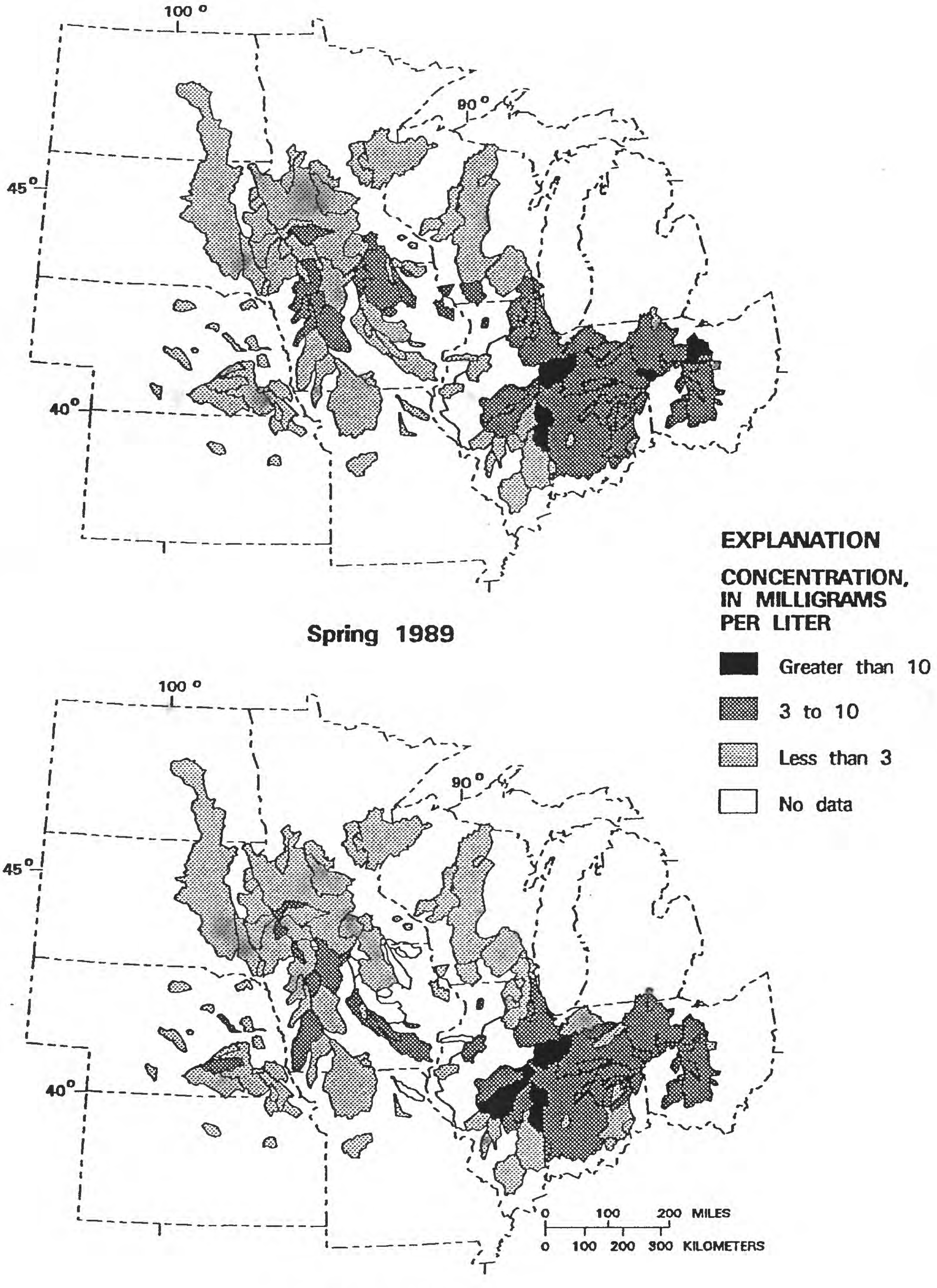
The slope coefficients are fit to the categorical data by the method of maximum likelihood (Helsel and Hirsch, 1992, p. 397). This method optimizes the likelihood that the observed data will be estimated from a given set of slope coefficients.

To create a discrete variable, observed concentrations of nitrate (as nitrogen) in each sample were divided into three categories: less than 3 mg/L, 3 to 10 mg/L, and greater than 10 mg/L. A total of 359 samples from the 135 sites during four synoptic sampling periods (spring and summer, 1989 and 1990) were included in this data set. More than one-half of the observations (192) were in the first category, which was considered to include background concentrations of nitrate in the study area. Observations in the second category (138) were considered elevated but were less than the USEPA maximum contaminant level (MCL) of 10 mg/L for drinking water (U.S. Environmental Protection Agency, 1986). Observations in the third category (29) exceeded the MCL. The categorized nitrate data for samples collected during the spring and summer of 1989 are shown in figure 2.

Best-fit logistic regression models were selected to estimate nitrate concentrations from land-use data by using a stepwise procedure. Explanatory variables were added to the model in order of significance, if the significance level (p-value) of the slope coefficient was less than or equal to 0.15. As variables were added, previously entered variables could be removed if their p-values increased to greater than 0.20.

To decrease the possibility of collinearity (cross correlation among the independent variables), the list of explanatory variables used in model fitting was restricted. Fertilizer application and total cropland were strongly correlated with corn and soybean acreage; therefore, fitting procedures were applied to two sets of explanatory variables: one set included fertilizer and total cropland data, and the other included corn and soybean acreage data. All the other explanatory variables listed in table 1 were included in both sets. Slope coefficients were determined separately for spring and summer data. Separate coefficients also were determined for classification between the low (concentrations less than 3 mg/L) and medium (3 to 10 mg/L) nitrate categories and between the medium and high (greater than 10 mg/L) categories. Overall, four sets of coefficients were determined using the same selected group of explanatory variables. A model consisted of the selected variables and the four sets of coefficients.

Models were compared on the basis of their capability to classify nitrate concentrations correctly. First, the model was used to estimate the probabilities of nitrate concentrations being in a particular category for each sample. Estimated probabilities were computed for the same data set



Spring 1989

Summer 1989

Figure 2. Geographic distribution of concentrations of dissolved nitrite plus nitrate as nitrogen, in selected streams in the upper-midwestern United States, displayed by drainage basin, for samples collected during the spring and summer 1989.

used to fit the model. The classified category was selected to be the one with the maximum probability. The accuracy of the model was determined by comparing the classified category to the observed category.

## RESULTS AND DISCUSSION

Two best-fit models were selected -- one from each set of explanatory variables. For the variable set that included fertilizer and total-cropland data but no data on individual crop types, the selected explanatory variables were percentile of flow, fertilizer application, and population density. The logistic regression fit to these explanatory variables is referred to as model 1 in this paper. Comparisons of nitrate categories estimated by model 1 to observed nitrate concentrations are listed in table 2. The overall accuracy of the model is determined by the total percentage of correct classifications. For model 1, 73 percent of the classifications were correct. However, only 34 percent of the observations greater than 10 mg/L were correctly classified. Also, model 1 might be biased because most of the incorrect classifications were low. Model 2 was fitted by use of the set of explanatory variables that included crop types, but not fertilizer application or total cropland. The selected explanatory variables from this set were percentile of flow, acreage in corn, acreage in soybeans, cattle, and population density. Accuracy results for model 2 also are listed in table 2.

**Table 2.** Observed nitrate categories and category classifications from the logistic regression models

[mg/L, milligrams per liter; - -, not applicable]

| Category (mg/L) | Observed | Classified correct | | Classified low | | Classified high | |
|---|---|---|---|---|---|---|---|
| | | Number | Percent | Number | Percent | Number | Percent |
| | | Model 1 (percentile of flow, fertilizer application, and population density) | | | | | |
| < 3 | 192 | 164 | 85 | - - | - - | 28 | 15 |
| 3 - 10 | 138 | 87 | 63 | 42 | 30 | 9 | 7 |
| > 10 | 29 | 10 | 34 | 19 | 66 | - - | - - |
| Total | 359 | 261 | 73 | 61 | 17 | 37 | 10 |
| | | Model 2 (percentile of flow, acreage in corn, acreage in soybeans, cattle, and population density) | | | | | |
| < 3 | 192 | 166 | 86 | - - | - - | 26 | 14 |
| 3 - 10 | 138 | 104 | 75 | 27 | 20 | 7 | 5 |
| > 10 | 29 | 16 | 55 | 13 | 45 | - - | - - |
| Total | 359 | 286 | 80 | 40 | 11 | 33 | 9 |

The overall accuracy of correct classifications was 80 percent, which is a slight improvement over that of model 1. Most of this improvement was attributed to better accuracy in classifying the higher concentrations. Classifications from model 2 were correct for 75 percent of the observed nitrate concentrations in the medium (3 to 10 mg/L) category and for 55 percent of the observed nitrate concentrations in the high (greater than 10 mg/L) category. This accuracy is a substantial improvement over model 1. Also, the incorrect classifications were about evenly distributed between high and low values, so model 2 does not seem to be biased.

The spatial distribution of the classification accuracy using model 2 for data from the spring and summer of 1989 is shown in figure 3. Incorrect classifications, both low and high, are distributed in a relatively uniform pattern throughout the study area. This result indicates that the model classifications are not geographically biased. Therefore, the accuracy of the model does not seem to depend on correlation of the explanatory variables with regional geography. In general, model 2, which is based on crop-type data, is superior to model 1, which is based on fertilizer data. Model 2 also is reasonably accurate in categorizing nitrate concentrations in the outflow from a variety of basins on a regional and seasonal scale. Model classifications do not seem to be biased in either magnitude or geographic distribution. These results lead to two primary conclusions. First, the level of nitrate contamination in midwestern streams is most strongly related to streamflow and to several characteristics of the upstream basin, including the areal extent of corn and soybean production, the density of cattle, and the population density. This list seems logical because each variable has a qualitative relation to nitrate. Streamflow results from basin runoff, which provides the mechanism for mobilization and transport of nitrate. In the model, as the percentile of flow increases, the probability increases that nitrate concentration will be in a higher category. Corn and soybeans are the major crops in the region, and their extent in the basin logically should be related to the use of all fertilizers, including commercial fertilizers and manure. Cattle also could be related to fertilizer use because they are a primary source of manure. Perhaps if data were available on actual fertilizer application, rather than only on fertilizer sales, a better model based on fertilizer instead of crop-type and livestock data could be developed. Population density is related to outflow from sewage-treatment plants, which generally are point sources of nitrate or of ammonia (a nitrogen species that can readily oxidize to nitrate). Even in rural areas, population density likely is related to nitrate contamination from septic system leachate.

A second conclusion is that an adequate model can be developed by relating synoptic water-quality data to regionally derived geographic data. All the explanatory variables in the model were retrieved from large GIS data bases that had, at best, a county-scale resolution. Yet these data were adequate to classify 80 percent of the observed nitrate concentrations correctly in outflow from a variety of basins.

The implication of these conclusions is that land-use data can be used to analyze water-quality conditions within large regions. Reasonable models can be developed for relating water quality to land use. These models can be adequate, even if the land-use data are extracted from large-scale data bases. Refinement of the models might be possible by collecting more precise land-use data in the basins upstream from sampling sites. More precise explanatory data could improve the accuracy of model classifications. The models could be used to identify other basins in the region where surface-water contamination might be a problem. Models from different regions could be compared to identify similarities and differences in the land-use factors that affect water quality in the regions. Logistic regression is a valuable technique for the development of these models.

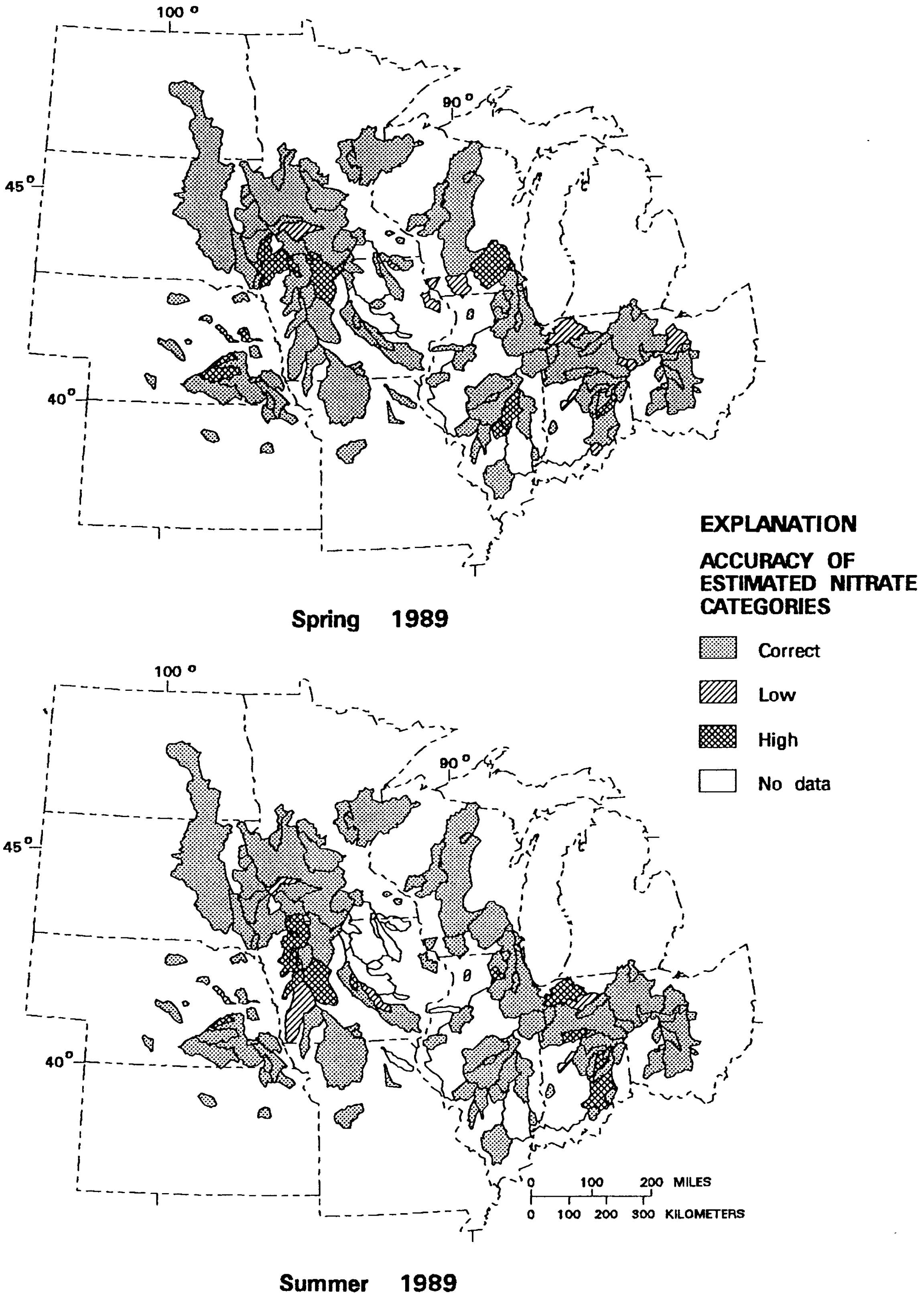


Figure 3. Accuracy of nitrate-concentration categories estimated from logistic model 2 based on comparison to concentrations in samples collected during the spring and summer of 1989.

# REFERENCES

Goolsby, D.A., Thurman, E.M., and Kolpin, D.W., 1991, Geographic and temporal distribution of herbicides in surface waters of the upper Midwestern United States, 1989-90, *in* Mallard, G.E., and Aronson, D.A., eds., U.S. Geological Survey Toxic Substances Hydrology Program--Proceedings of the technical meeting, Monterey, California, March 11-15, 1991: U.S. Geological Survey Water-Resources Investigations Report 91-4034, p. 183-188.

Helsel, D.R., and Hirsch, R.M., 1992, Statistical methods in water resources: New York, Elsevier, 522 p.

Thurman, E.M., Goolsby, D.A., Meyer, M.T., and Kolpin, D.W., 1991, Herbicides in surface waters of the Midwestern United States--The effects of spring flush: Environmental Science and Technology, v. 25, no. 10, p. 1794-1796.

U.S. Environmental Protection Agency, 1986, Quality criteria for water--1986: EPA 440/5-86-001, Washington D.C., Office of Water Regulation and Standards, unnumbered pages.

U.S. Environmental Protection Agency, 1990, County-level fertilizer sales data: PM-2221, Washington D.C., Office of Policy, Planning, and Evaluation.

U.S. Department of Commerce, Bureau of the Census, 1989, Census of agriculture, 1987--Final county file: Washington, D.C., Data Users Services Division.

U.S. Department of Commerce, Bureau of the Census, 1990, Census of population and housing, 1990: Washington, D.C., Data Users Services Division.

# PERSISTENCE OF HERBICIDES IN SELECTED RESERVOIRS IN THE MIDWESTERN UNITED STATES: SOME PRELIMINARY RESULTS

By Donald A. Goolsby, William A. Battaglin, James D. Fallon, Diana S. Aga,
Dana W. Kolpin, and E. Michael Thurman

## ABSTRACT

Preliminary results from a study of herbicides in 76 midwestern reservoirs show that some herbicides and metabolites of atrazine and alachlor are detected more frequently throughout the year in reservoirs than in streams. Except for a short period after application to cropland, herbicide concentrations also are generally higher in reservoirs than in streams. Herbicides or their metabolites were detected in 82 to 92 percent of the reservoirs sampled during four periods from late April through early November 1992. Atrazine was detected most frequently and in highest concentrations, followed by an alachlor metabolite (alachlor ethanesulfonic acid), and two atrazine metabolites (desethylatrazine and deisopropylatrazine). The longer persistence of some herbicides and metabolites in reservoirs than streams is attributed to longer half lives for these compounds in the water column than in the soil where concentrations of organic matter and microorganisms are much higher and contribute to rapid biodegradation of herbicides. A second contributing factor is long-term storage of water in reservoirs that originates as spring and summer storm runoff from cropland and which contains high concentrations of herbicides.

## INTRODUCTION

Reservoirs are an important part of hydrologic systems in the Midwestern United States. According to data compiled by Ruddy and others (1990), about 440 large reservoirs (normal storage capacity greater than 5,000 acre-feet) in 11 upper Midwestern States discharge streamflow to the Mississippi River by way of tributaries. The primary function of these reservoirs is to impound surface water for many uses, including flood control, hydropower, recreation, and aquatic life habitat. These large reservoirs and numerous smaller reservoirs also can serve as sources of drinking water for public supplies. In addition to storing surface water, reservoirs also can store undesirable substances such as sediment and toxic chemicals including pesticides. Most of the sediment entering reservoirs is permanently trapped and deposited on the bottom of the reservoir. However, chemicals such as soluble herbicides generally remain in the water column and are stored only temporarily until they are flushed from the reservoir or removed from solution by biotic and abiotic processes.

Storage of herbicides is a potential problem in reservoirs that receive drainage from agricultural areas in the upper Midwest. Recent studies by the U.S. Geological Survey (USGS) (Thurman and others, 1991, 1992; Goolsby and others, 1991) have shown that most streams in the upper Midwest contain herbicides at some time during the year. Large quantities of herbicides are flushed from agricultural fields each spring and summer during rainfall following application of herbicides. Median concentrations of the herbicides atrazine, alachlor, cyanazine, and metolachlor in streams increased by at least an order of magnitude from March and April 1989 to May and June 1989. For example, the median concentrations of herbicides in Midwestern streams, in 1989, ranged from less than 0.3 μg/L before planting to as much as

3 µg/L after planting, and the maximum concentrations in a few streams reached 100 µg/L (Thurman and others 1991). During late spring and early summer, concentrations of atrazine can exceed the U.S. Environmental Protection Agency's maximum contaminant level (MCL) for drinking water of 3 µg/L for several weeks to several months in both small streams and large rivers, such as the Mississippi River.

Because reservoirs collect and store water, they can be affected by storm runoff that contains large concentrations of herbicides for a much longer period of time than the streams that supply the reservoirs (Stamer and Zelt, 1992). This can substantially affect the water quality of streams downstream from reservoirs. The length of time that reservoirs discharge water with elevated concentrations of herbicides depends on a number of factors including residence time of water in the reservoir, timing of inflow to the reservoir, land use and herbicide use in the contributing drainage area, and the timing and intensity of rainfall. Unregulated streams exhibit the flush effect (Thurman and others, 1991), which can produce high concentrations of herbicides for short periods of time. In contrast, peak concentrations of herbicides in streams regulated by reservoirs are much lower, but elevated concentrations (near or above MCLs) can persist for much longer periods of time. Stamer and Zelt (1992) have shown that atrazine concentrations in Perry Lake, Kans., remained near or above the MCL of 3 µg/L from March 1989 through October 1989 and above 1µg/L through February 1990, whereas atrazine concentrations in the principal tributary to Perry Lake exceeded the MCL for only a few months in late spring. However, atrazine concentrations in some of the samples from tributaries exceeded 10 µg/L during this period and much of the water in Perry Lake was replaced with containing these atrazine concentrations. Because little additional inflow to Perry Lake occurred after early summer, this "herbicide rich" water was stored in the reservoir until the next spring, when the cycle was repeated.

The process of storage and attenuation of herbicides documented in Perry Lake likely occurs in most other Midwestern reservoirs to greater or lesser degree depending on physical and hydrologic characteristics of the reservoirs and land use in the reservoir drainage basin. Atrazine concentrations in mid-winter samples during 1990-92 from several large reservoirs in Illinois, Iowa, Kansas, and Missouri are listed in table 1. Water samples from many of these reservoirs had atrazine concentrations of at least 2 µg/L during this time, which likely reflected the storage of herbicide-laden inflow originating from the "spring flush." In general, it appears that the larger the volume-to-drainage area ratio of the reservoir, the greater the atrazine concentration.

The way in which unregulated streams in the Midwest respond to the seasonal application of herbicides has been documented (Thurman and others, 1992; Goolsby and others, 1991). However, the temporal distribution of herbicides in streams regulated by reservoirs has not been examined. In addition, the process(es) by which physical, hydrologic, and land use characteristics of reservoirs and their contributing drainage areas interact to affect herbicide concentrations in the outflows from reservoirs has not been studied. In order to develop an understanding of these processes in reservoirs, a study was begun as part of the USGS's Toxic Substances Hydrology Program in April 1992. The study is still in progress at the present time (May 1993). The purpose of this paper is to describe the study plan and to summarize some of the preliminary study results.

## Table 1.—Atrazine concentrations in water samples from selected midwestern reservoirs during winter months, 1990-92

[Vol/DA, volume to drainage area ratio; acre-ft, acre-feet; GC, gas chromatography; ELISA, immunoassay; µg/L, micrograms per liter, --, no data]

| Reservoir | Sample date | Vol/DA (acre-ft/acre) | Atrazine concentration by GC (µg/L) | Atrazine concentration by ELISA (µg/L) |
|---|---|---|---|---|
| Illinois | | | | |
| Carlyle Lake outflow | 1- 3-92 | 0.14 | -- | 2.3 |
| Lake Decatur outflow | 1- 8-92 | .05 | -- | .2 |
| Rend Lake Spillway | 1- 2-92 | .59 | -- | .6 |
| Lake Shelbyville outflow | 1- 8-92 | .31 | -- | 1.1 |
| Lake Springfield at Sugar Creek | 1-30-92 | .34 | -- | 2.5 |
| Lake Springfield at Spaulding Dam | 1-30-92 | .34 | -- | 4.0 |
| Iowa | | | | |
| Coralville Lake | 2-21-92 | 0.01 | -- | .2 |
| Corydon Reservoir | winter, 1992 | -- | -- | 10 |
| Rathbun Reservoir | --12-90 | .58 | 3.7 | -- |
| Rathbun Reservoir | 2-20-92 | .58 | -- | 2.8 |
| Red Rock Reservoir | 2-12-92 | .01 | -- | .2 |
| Saylorville Lake | 2-12-92 | .02 | -- | .1 |
| Kansas | | | | |
| Perry Lake | 2- 3-91 | .34 | 3.9 | -- |
| Missouri | | | | |
| Long Branch Reservoir | --12-90 | .50 | 2.0 | -- |
| Smithville Reservoir | --12-90 | 1.06 | 3.6 | -- |

# STUDY AREA AND PLAN OF INVESTIGATION

The study area (fig. 1) was defined as all hydrologic units in parts of 11 states (Illinois, Indiana, Iowa, Kansas, Minnesota, Missouri, Nebraska, North Dakota, Ohio, South Dakota, and Wisconsin) that drain to the Ohio, Upper Mississippi, and Lower Missouri Rivers. This area comprises about 450,000 $mi^2$ and is virtually the same area covered by the 1989-90 reconnaissance for herbicides in streams (Thurman and others, 1991; 1992).

The primary objectives of the study are to (1) determine the occurrence and temporal distribution of selected herbicides and herbicide metabolites in the outflow from selected reservoirs in the upper Midwest, and (2) determine if the persistence of large concentrations (greater than about 1 µg/L) of herbicides in reservoir outflow can be quantified on the basis of reservoir and drainage-basin characteristics, hydrology, land use, herbicide use, and climate. Some specific hypotheses to be tested are--

1. Herbicides will be detected in Midwestern reservoirs for a longer period of time than in unregulated streams, but peak concentrations will be lower in the reservoirs than in these streams.
2. The duration of herbicide concentrations in reservoir outflow above a threshold value can be explained (statistical model) by reservoir and drainage-basin characteristics, land use, herbicide use, rainfall (intensity, timing and amount), and stability (half-lives) of individual herbicides. Consequently, the probability that a herbicide such as atrazine will persist in a reservoir all year above a specified concentration can be predicted.
3. The occurrence and concentrations of herbicides and herbicide metabolites in the anoxic hypolimnia of reservoirs during summer stratification differ from those in the aerobic epilimnia.

Reservoirs for study were selected from the reservoir data base compiled by Ruddy and others (1990). The principal criterion for selection of reservoirs was that data on reservoir volume and reservoir discharge must be obtainable so that the residence time of water in the reservoir and the timing of outflow can be determined. In addition, the reservoir outflow must be accessible for sampling. The reservoir data base was screened to determine which reservoirs met these criteria. As a result of this screening, 74 of the 440 reservoirs in the reservoir data base were selected for sampling. Two additional reservoirs, Lakes Monona and Waubesa in Wisconsin, which form a chain of reservoirs receiving outflow from Lake Mendota, also were selected. These three reservoirs will be treated as a single unit. Locations of these 76 reservoirs are shown in figure 1.

The outflow from each reservoir was sampled six times (approximately bimonthly) from April 1992 through March 1993, and a seventh time in mid-summer 1993. Samples are collected near the centroid of flow or other outflow point by methods that provide a representative sample of dissolved herbicides and nutrients in the outflow from the reservoir. During August 1992, herbicide samples, dissolved oxygen profiles, and temperature profiles were collected near the deepest point in 19 selected reservoirs to examine the effect, if any, of chemical stratification on herbicide concentrations. Herbicide samples were collected near the surface and near the bottom of each reservoir.

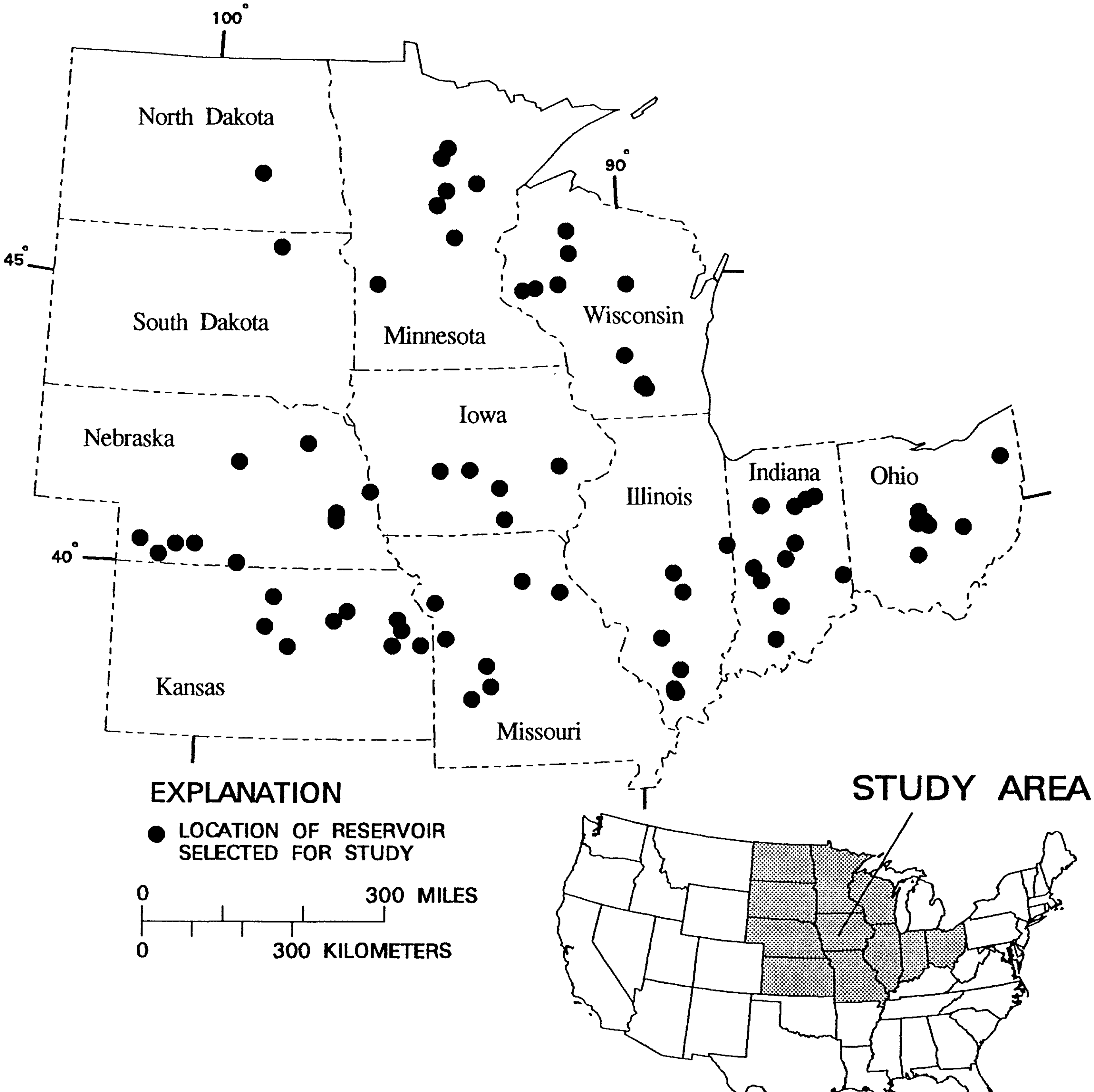


Figure 1.--Location of study area and selected reservoirs.

All samples are analyzed for 11 herbicides (alachlor, atrazine, ametryn, cyanazine, metolachlor, metribuzin, propazine, prometon, prometryn, simazine, and terbutryn) and at least 5 herbicide metabolites (desethylatrazine, desisopropylatrazine, deethylcyanazine, cyanazine amide, and deethylcyanazine amide) by gas chromatography/mass spectrometry (GC/MS). A metabolite of alachlor, [(2,6-diethylphenyl)(methoxymethyl) amino-2-oxoethane sulfonic acid], (ESA) is analyzed by immunoassay following isolation on $C_{18}$ cartridges (Diana S. Aga, U.S. Geological Survey, written commun., 1993). Selected ESA samples are confirmed by high-performance liquid chromatography. Samples are also analyzed for nitrite, nitrate, ammonia, orthophosphate, and silica.

Ancillary data including land use, herbicide use, rainfall, and reservoir characteristics, are obtained from the following sources and stored in a geographic information system (GIS):

| Data Type | Source |
|---|---|
| Land Use | 1987 Census of Agriculture data. |
| Herbicide Use | Gianessi and Puffer, 1990. |
| Rainfall | National Weather Service. |
| Reservoir characteristics | U.S. Geological Survey and Corps of Engineers data bases. |

## PRELIMINARY RESULTS AND DISCUSSION

Analytical results from samples collected during the first four sampling periods, during April through November 1992 indicate that a number of herbicides and/or their metabolites, are present in many Midwestern reservoirs for long periods of time. The four sampling periods include pre-planting (late April-early May), post-planting (late June-early July), late summer (late August-mid-September), and fall (mid October-early November). Herbicides were detected in 82 to 92 percent of the 76 reservoirs during all four sampling periods. Four compounds (atrazine, desethylatrazine, desisopropylatrazine, and metolachlor) were detected in more than half the reservoirs during the fall (October-November sampling; table 2), whereas only atrazine was detected in more than one half the streams sampled in the fall of 1989 (table 2). One of the most notable differences between the occurrence of herbicides in reservoirs and streams is the much higher frequency of detection of cyanazine and desisopropylatrazine in reservoirs. A possible explanation (hypothesis) for this observation is that these two compounds are much more stable in the water column of lake and streams than in soil, where organic matter and microorganisms promote rapid biodegradation. Consequently, late spring and summer runoff can flush large amounts of these two compounds into reservoirs, where they can persist in the water column for long periods of time. Neither cyanazine nor desisopropylatrazine was detected in streams during the fall (table 2) because these compounds are no longer present in significant amounts on the agricultural fields where they were applied. This hypothesis points to the need for data on the half-lives of herbicides and insecticides in water. Virtually all available data on the half lives of herbicides are for soils. Water-column-half lives are particularly important with regard to the persistence of herbicides in reservoirs, lakes, and estuarine systems.

The spatial distribution of the detections of herbicides and metabolites in the 76 reservoirs is shown in figures 2 and 3 for the four sampling periods. These figures also show which reservoirs contained herbicides in concentrations that exceeded MCL's and/or health advisories

Table 2. - Herbicides analyzed and percent detections in Midwestern reservoirs during 1992, and in Midwestern streams during 1989.

[µg/L, micrograms per liter; ESA, ethanesulfonic acid metabolite of alachlor;; --, no data <, less than; N, number of samples]

| | | Percentage of detections greater than reporting limit : | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 76 Midwestern reservoirs in 1992 | | | | Midwestern streams in 1989 | | |
| Herbicide | Reporting limit (µg/L) | late April-mid-May | late June-early July | late August-early September | late October-early November | pre-application (N=55) | post-application (N=132) | fall low-flow (N=145) |
| alachlor | 0.05 | 36 | 48 | 26 | 16 | 18 | 86 | 12 |
| ametryn | .05 | 0 | 1 | 3 | 1 | 0 | 0 | 0 |
| atrazine | .05 | 72 | 92 | 86 | 80 | 91 | 98 | 76 |
| cyanazine | .05 | 49 | 65 | 56 | 46 | -- | -- | -- |
| | [1]0.2 | 25 | 40 | 33 | 26 | 5 | 63 | 0 |
| desethyl-atrazine | .05 | 63 | 78 | 74 | 70 | 54 | 86 | 47 |
| desisopropyl-atrazine | .05 | 58 | 70 | 63 | 62 | 9 | 54 | 0 |
| metolachlor | .05 | 46 | 62 | 52 | 51 | 34 | 83 | 44 |
| metribuzin | .05 | 12 | 9 | 5 | 0 | 2 | 53 | 0 |
| prometon | .05 | 5 | 14 | 15 | 14 | 0 | 23 | 6 |
| propazine | .05 | 2 | 10 | 5 | 1 | 0 | 40 | <1 |
| ESA | .1 | 72 | 79 | 77 | 64 | -- | -- | -- |

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[1] Reporting limit for Midwestern streams in 1989 was 0.2 µg/L. Percent detections for both reporting limits are given for data from 76 Midwestern reservoirs.

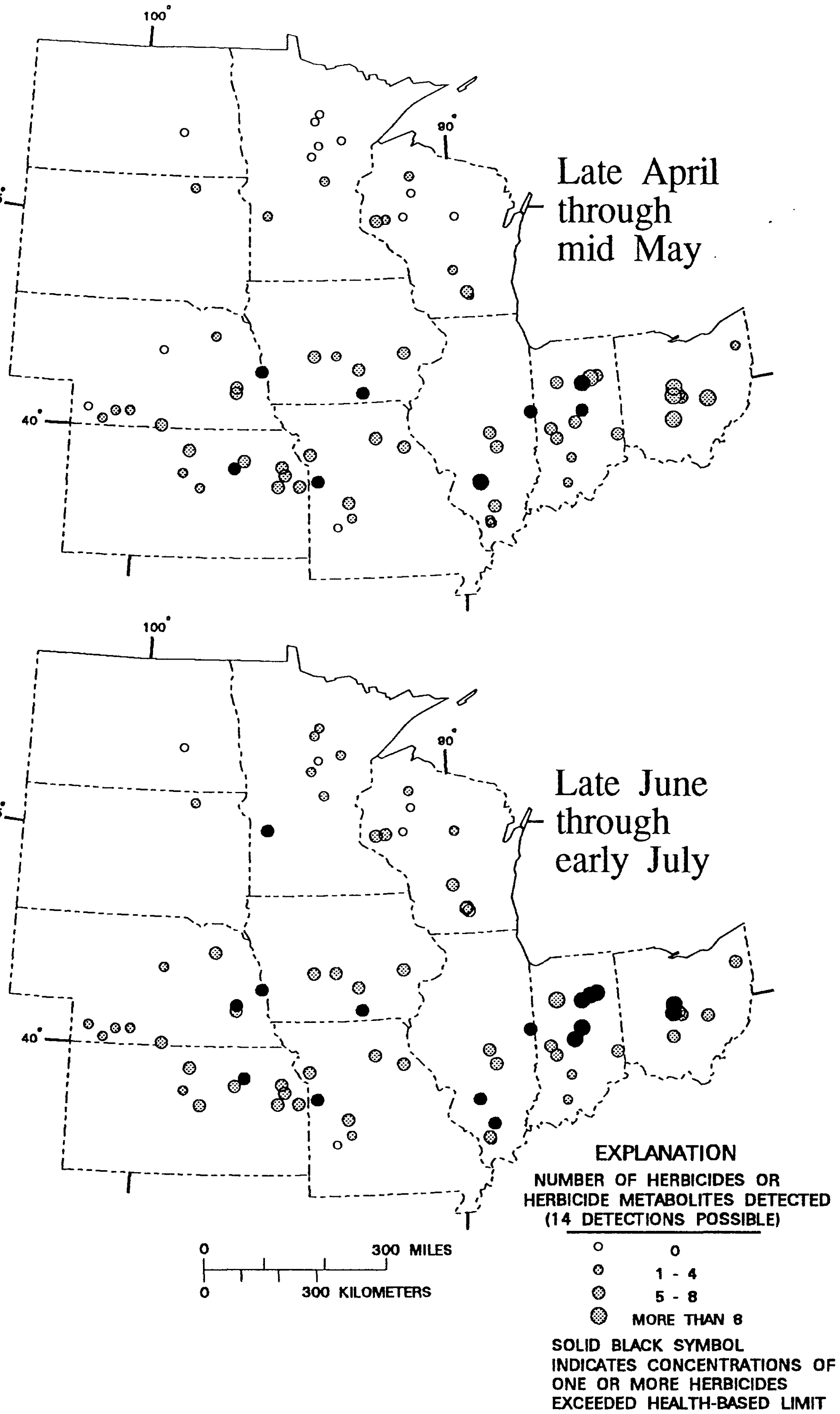

Figure 2.--Generalized distribution of herbicide detections in Midwestern reservoirs and reservoirs in which concentrations of one or more herbicides exceeded a U.S. Environmental Protection Agency maximum contaminant level or health-advisory level for drinking water during late April through mid May and late June through early July, 1992.

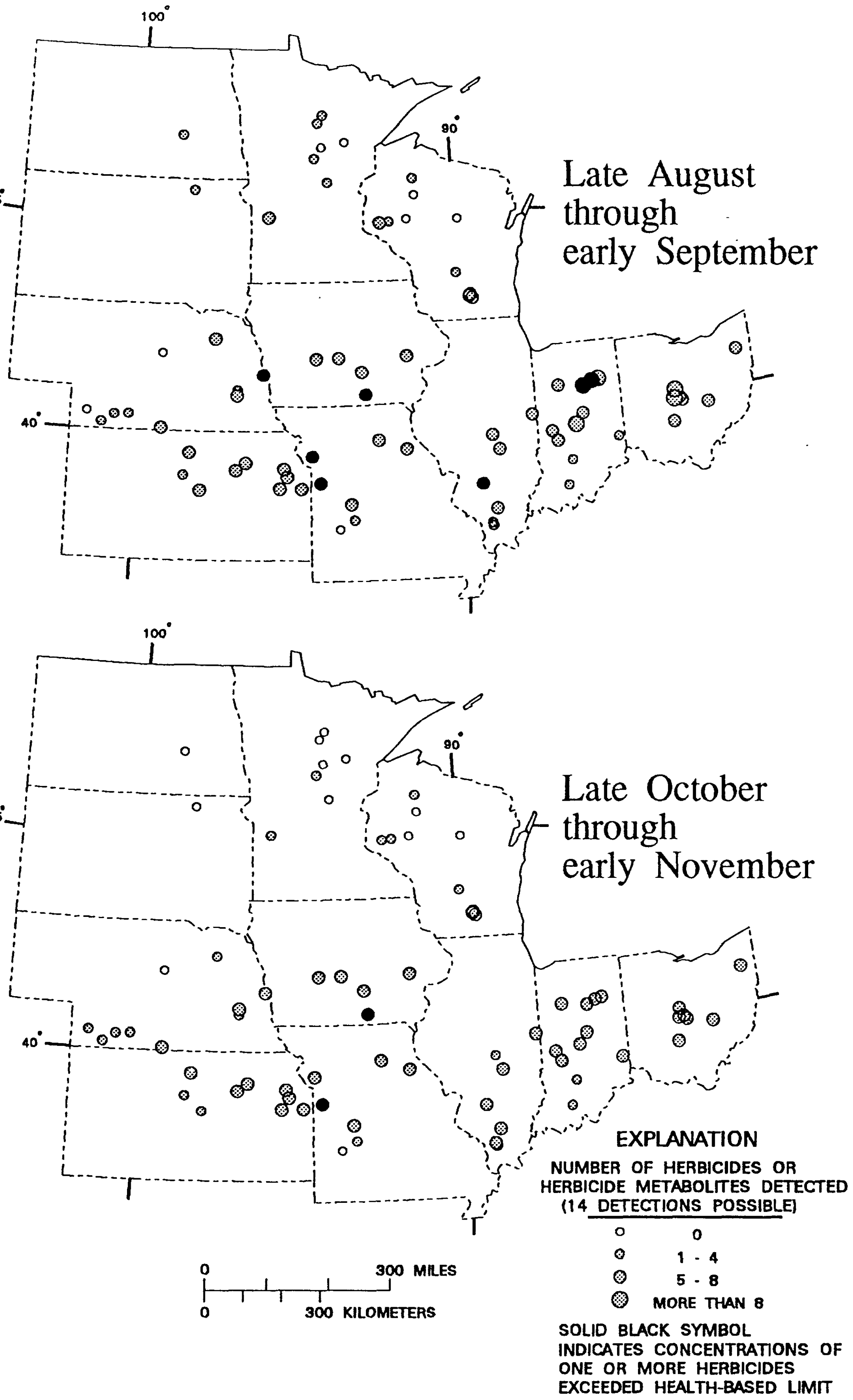

Figure 3.--Generalized distribution of herbicide detections in Midwestern reservoirs and reservoirs in which concentrations of one or more herbicides exceeded a U.S. Environmental Protection Agency maximum contaminant level or health-advisory level for drinking water during late August through early September and late October through early November, 1992.

(HA's) for drinking water. MCL's apply to average annual concentrations and are legally enforceable under the 1986 Safe Drinking Water Act, whereas HA's are not enforceable. Exceedence of MCL's or HA's is of concern because many Midwestern reservoirs are used for public water supply. Concentrations of one or more herbicides exceeded MCL's or HA's in 8 reservoirs during the first sampling period, in 16 reservoirs during the second sampling period (fig. 2), in 7 reservoirs in the third sampling period, and in 2 reservoirs during the fourth sampling period (fig. 3). More herbicides and metabolites were detected in reservoirs in areas where use of herbicides is most intense--that is, the area from eastern Kansas and Nebraska to Ohio (figs. 2 and 3).

One of the most significant findings from this study to date is the abundance and persistence of herbicide metabolites in reservoirs. Data are presently available from this study on two metabolites of atrazine (desethylatrazine and desisopropylatrazine) and one metabolite of alachlor, ethanesulfonic acid (ESA). The occurrence of atrazine metabolites in streams and their use as indicators of surface-water/ground-water interaction has been reported previously by Thurman and others (1991, 1992). The presence of ESA in ground water was recently reported by Baker and others (1993) and Kolpin and others (1993). However, the present reservoir study is believed to be the first systematic effort to investigate ESA in surface water. The frequency of detection was greatest for atrazine, followed by three metabolites, ESA, desethylatrazine, and desisopropylatrazine in the 76 reservoirs during the four sampling periods (table 2). The overall median concentrations of these four compounds followed the same order. Cyanazine, metolachlor, and alachlor were fifth, sixth, and seventh, respectively with respect to frequency of detection and median concentration. Previous studies have shown that the herbicide, alachlor is not very persistent in streams (Thurman and others, 1991, 1992; Goolsby and others, 1991) or in ground water (Kolpin and others, 1993). However, this does not appear to be the case for one of its metabolites, ESA, which apparently is both mobile and relatively persistent (stable) in surface water.

The temporal distribution of atrazine, alachlor, and three metabolites during the four reservoir sampling periods is shown in figure 4. Also shown for comparison purposes is the temporal distribution of these compounds (except ESA) during the 1989 reconnaissance of Midwestern streams (Thurman and others 1991, 1992). These results indicate that concentrations of atrazine and its metabolites in streams shortly after herbicide application are higher than in reservoirs. However, at other times of the year, concentrations are somewhat higher in the reservoirs, particularly concentrations of the two metabolites of atrazine. Desisopropylatrazine was detected infrequently in streams prior to application and not at all in the fall of the year (fig. 4). In contrast, this metabolite of atrazine was detected in 58 to 70 percent of all samples collected during the four reservoir-sampling periods. As hypothesized previously, the reason for this large difference in frequency of detection is probably the short half life for desisopropylatrazine in soil combined with its much longer half life in the water column, and long-term storage of this compound in the water mass within reservoirs.

With regard to alachlor there appears to be little difference between concentrations in streams and reservoirs except shortly after application when concentrations in streams are higher (fig. 4). Alachlor disappears rather quickly in streamflow and in reservoirs, consistent with data reported for Perry Lake in Kansas (Stamer and others, 1993). ESA appears to be a major soil

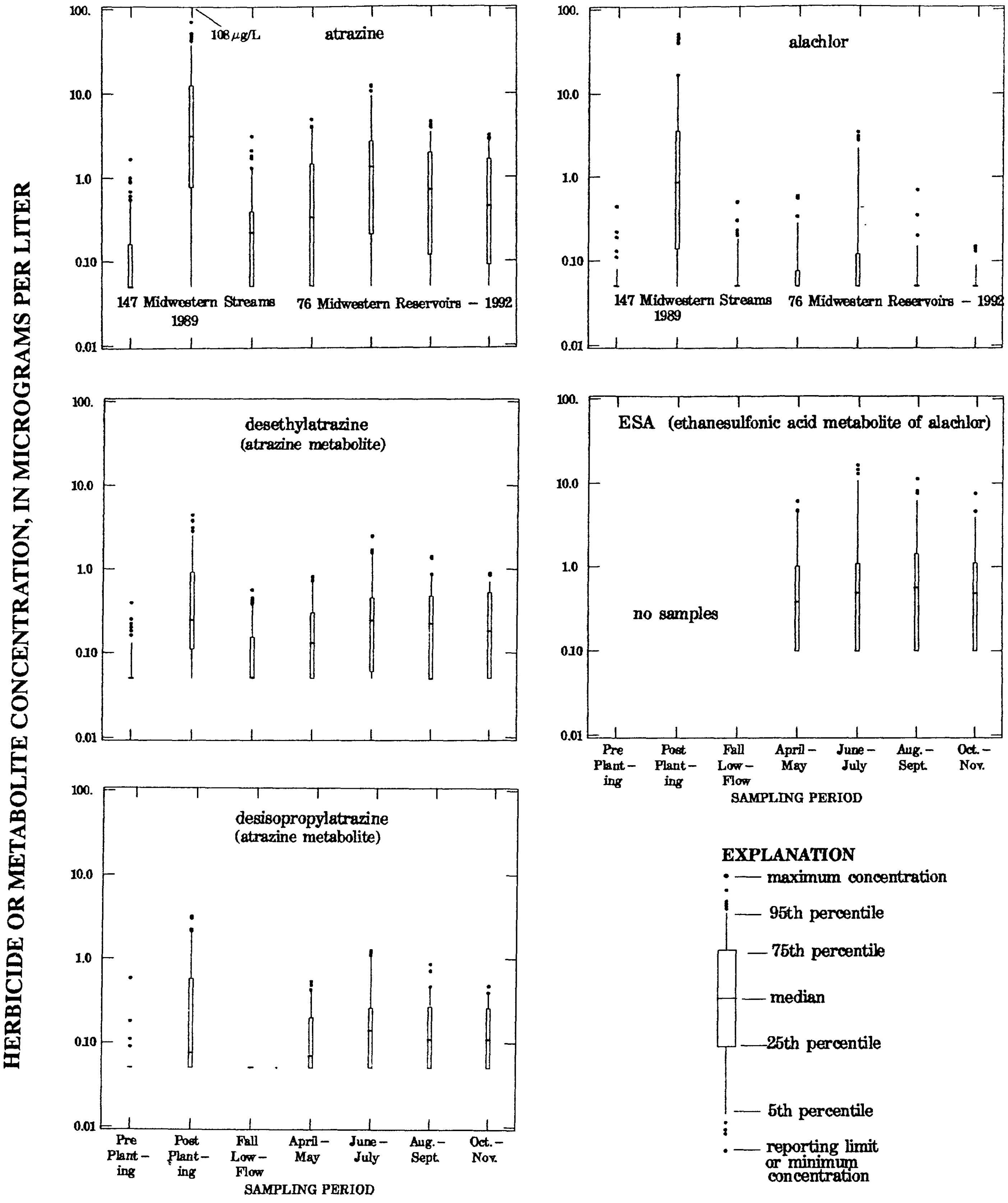

Figure 4.--Temporal distribution of atrazine, alachlor, and three metabolites in midwestern reservoirs during 1992 and in midwestern streams during 1989

metabolite of alachlor (Baker and others, 1993); however, it is not known whether significant degradation of alachlor to ESA occurs in the water column of streams and reservoirs. The ESA concentrations in reservoirs were similar during all four sampling periods (fig. 4).

Data on herbicide and nutrient concentrations, reservoir inflow and outflow (residence time), rainfall-patterns, pesticide use and land use will be available upon the completion of this study.

# REFERENCES

Baker, D.B., Bushway, R.J., Adams, S.A., and Macomber, C., 1993, Immunoassay screens for alachlor in rural wells: false positives and an alachlor soil metabolite: Environmental Science and Technology, no. 3, p. 562-564.

Gianessi, L.P., and Puffer, C.M., 1990, Herbicide use in the United States: Washington, D.C., Resources for the Future, [Inc.], Quality of the Environment Division, 127 p. [Revised 1991].

Goolsby, D.A., Coupe, R.H., and Markovchick, 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.

Kolpin, D.W., Burkart, M.R., and Thurman, E.M., in press, Herbicides and nitrate in near-surface aquifers of the Mid-Continent United States: U.S. Geological Survey Water Supply Paper 2413.

Kolpin, D.W., Goolsby, D.A., Aga, D.S., and Iverson, J.L., 1993, Agricultural chemicals in near-surface aquifers: Results of the 1991-92 Midcontinent ground water reconnaissance, *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. 64-75.

Ruddy, B.C., Hitt, K.J., and Kerie, J., 1990, Summary of selected characteristics of large reservoirs in the United States and Puerto Rico, 1988: U.S. Geological Survey Open-File Report 90-163, 295 p.

Stamer, J.K. and Zelt, R.B., 1992, Distribution of atrazine and similar nitrogen-containing herbicides in the lower Kansas River basin, U.S. Geological Survey Yearbook Fiscal Year 1991, U.S. Government Printing Office, Washington, D.C., p. 76-79.

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 spring flush: Journal of Environmental Science and Technology, v. 25, no. 10, p. 1794-1796.

Thurman, E.M., Goolsby, D.A., Meyer, M.T., and Kolpin, D.W., 1992, A reconnaissance study of herbicides and their metabolites in surface water in the midwestern United States using immunoassay and gas chromatography/mass spectrometry: Environmental Science and Technology, v. 26, no. 12, p. 2440-2447.

# PESTICIDES IN NEAR-SURFACE AQUIFERS: RESULTS OF THE MIDCONTINENTAL UNITED STATES GROUND-WATER RECONNAISSANCE, 1991-92

**By Dana W. Kolpin, Donald A. Goolsby, Diana S. Aga, Jana L. Iverson, and E. Michael Thurman**

## ABSTRACT

Selected pesticides and metabolites were examined in near-surface aquifers in the corn- and soybean- producing region of the midcontinental United States to determine their hydrogeologic, spatial, and seasonal distribution. At least one herbicide or atrazine metabolite was detected in 28.4 percent of the 303 wells sampled during the spring and late summer of 1991. During 1991, deethylatrazine was the most frequently detected compound followed by atrazine, deisopropylatrazine, and prometon. No herbicide concentration exceeded the U.S. Environmental Protection Agency's maximum contaminant levels for drinking water. During 1991, the highest frequency of herbicide detection was in the western part of the study region and lowest frequency of detection was in the eastern part of the study region. Unconsolidated aquifers were found to be more susceptible to herbicide contamination than bedrock aquifers on the basis of results of the 1991 study. During the summer of 1992, additional water samples were collected from 101 wells to examine the occurrence of agricultural chemicals not analyzed during the previous year. Water from 62 percent of the resampled wells had detectable concentrations of either a pesticide or pesticide metabolite; 27 different compounds were detected. During the 1992 study, five of the six most frequently detected compounds were herbicide metabolites.

## INTRODUCTION

Almost 60 percent of the pesticides (Gianessi and Puffer, 1990) and fertilizers (U.S. Environmental Protection Agency, 1990) used in the United States are applied in the Midcontinent to enhance crop yields. Because of the potential for these contaminants to affect the quality of water resources, the Midcontinent has become a focus for research on agricultural-chemical contamination in all parts of the environment including streams, reservoirs, ground water, and rainfall. In 1991, the U.S. Geological Survey (USGS) through its Toxics Substances Hydrology Program, began a ground-water-reconnaissance of agricultural-chemical contamination in aquifers located within 15 m of the land surface (near-surface) in the midcontinental United States. Near-surface aquifers represent hydrogeologic settings that have the greatest potential for herbicide contamination. The objectives of this reconnaissance are to (1) determine the hydrogeologic, spatial, and seasonal distribution of agricultural chemicals in near-surface aquifers of the midcontinent; (2) determine statistical relations between the occurrence of agricultural chemicals and selected human and natural factors; and (3) collect data on pesticides and their metabolites in ground water from geographic areas where few data previously were available. Because of questions generated by results of the 1991 sampling, additional data were collected during July and August of 1992. The major objective of the additional sampling was to investigate why reportable herbicide concentrations were not measured in more than 70 percent of the near-surface aquifers sampled in 1991. Possible explanations include the following: The wells sampled produce "old" water, which would not be expected to contain herbicides; herbicides are present in many of these aquifers but at concentrations below the reporting limits available during the 1991 study; herbicides are present but are compounds that were not examined during 1991; and the herbicide metabolites might be more persistent and mobile than their parent compounds and are present in the aquifers sampled. To help test these hypotheses, the number of compounds analyzed for during 1992 was increased and included additional herbicides and selected metabolites, insecticides and selected metabolites, detergents, volatile organic compounds, and surfactants. Only the results for pesticides and pesticide metabolites are discussed here.

This paper describes results of a regional reconnaissance of selected agricultural chemicals in near-surface aquifers that was conducted during 1991, and some initial results from the continued investigation of agricultural chemicals in near-surface aquifers conducted during 1992. A comprehensive discussion of the data and interpretive results derived from the 1991 reconnaissance study is presented elsewhere (Kolpin and others, in press; Kolpin and others, 1993).

## STUDY DESIGN AND METHODS

Wells sampled during 1991 (fig. 1) were selected to ensure that sites were geographically and hydrogeologically representative of near-surface aquifers in the corn- and soybean-producing region of the Midcontinent. The wells were distributed geographically by State and hydrogeologically by aquifer class (unconsolidated as opposed to bedrock) and relative depth within the aquifer. A work plan outlining the design and plan for well selection, sample-collection protocol, and quality assurance was prepared to ensure the validity of collected data (Kolpin and Burkart, 1991). Most of the wells selected were sampled twice during 1991. A total of 299 herbicide analyses were obtained during March or April (preplanting); and 290 herbicide analyses were obtained during July or August (postplanting). Ancillary data on land use and other features near the wells were collected at the time of sampling.

In 1992, 101 wells were sampled during July or August after the application of pesticides. These wells were distributed geographically by State and hydrogeologically by aquifer class. This approach resulted in a widespread distribution of sampling sites across the Midcontinent (fig. 1).

All samples were collected by USGS personnel using equipment constructed of materials, such as glass and stainless steel, that would not leach or adsorb organic compounds. Decontamination procedures were implemented to prevent cross-contamination between wells and samples (Kolpin and Burkart, 1991). Wells were purged before sampling until pH, water temperature, and specific conductance stabilized. A quality-assurance program using a series of field blanks, field duplicates, and spikes verified effectiveness of the sampling protocol and the analytical procedures.

All samples collected during 1991 were analyzed for 11 herbicides and 2 atrazine metabolites by gas chromatography/mass spectrometry (GC/MS) (Thurman and others, 1990).

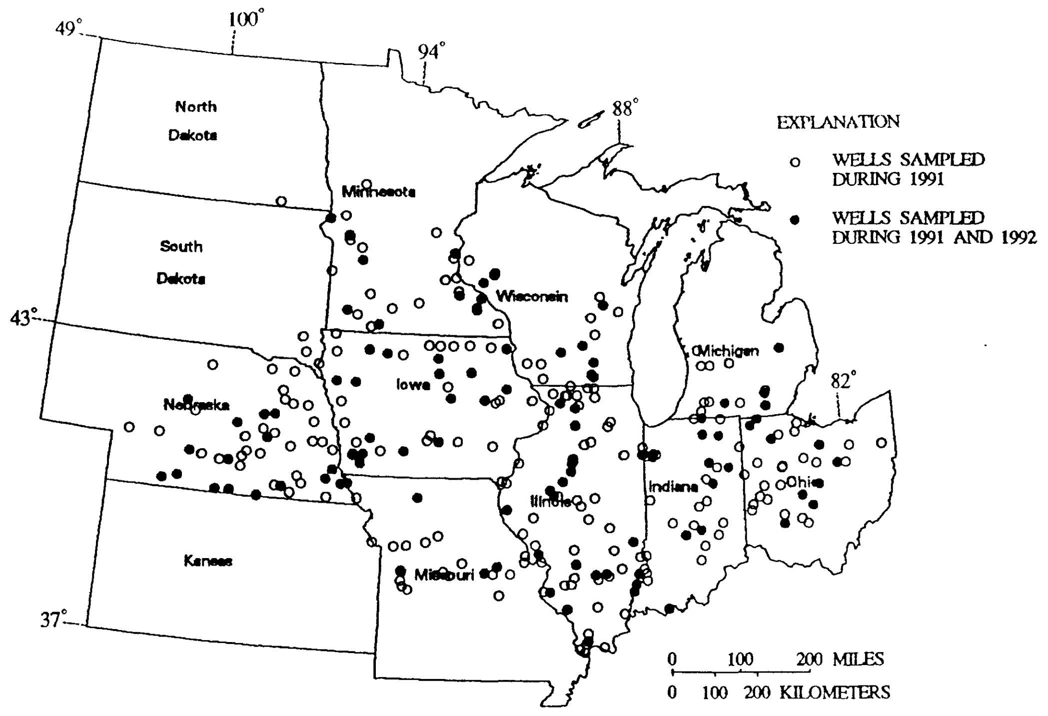

Figure 1. Location of wells sampled during 1991 and 1992.

This method had an analytical reporting limit of 0.05 μg/L. For the samples collected during 1992, several additional analytical methods also were used including a 1-liter solid-phase extraction GC/MS method (Steven D. Zaugg, U.S. Geological Survey, written commun., 1993). This method analyzed for 47 pesticides at reporting limits as low as 0.001 μg/L. A total of 45 samples collected during 1992 were analyzed for chlorophenoxy acid herbicides (2,4-D for example) and DCPA. The selection of these 45 samples was biased toward wells with herbicides detected during 1991. Sixty-six samples were analyzed for an ethanesulfonate alachlor metabolite (ESA) (Diana S. Aga, U.S. Geological Survey, written commun., 1993). The selection of these 66 samples also was biased toward wells with herbicides detected during 1991.

## RESULTS AND DISCUSSION

### 1991 Sampling

Herbicides or atrazine metabolites were detected in 28.4 percent of the wells sampled during the two collection periods in 1991 (table 1), but no concentrations exceeded U.S. Environmental Protection Agency (USEPA) maximum contaminant levels (MCL) for drinking water. The relatively low frequency of herbicide detection in near-surface aquifers strongly contrasts with conditions observed in streams for this same region; herbicides were detected in nearly all of the streams sampled, and some of the concentrations exceeded an MCL (Thurman and others, 1992). Herbicides were not distributed uniformly in near-surface aquifers across the study region (fig. 2). The highest frequency of detection was observed in the extreme western part of the region; the lowest frequency of detection was observed in the eastern third of the region.

Data on herbicide metabolites are important to understand fully the occurrence, distribution, and fate of herbicides in the environment. The most frequently detected herbicide compound in

**Table 1.** Frequency of herbicide and atrazine- metabolite detection in water from wells sampled during the spring and summer of 1991

[%, percent; N, number of wells sampled; µg/L, micrograms per liter]

| Compound | % detection[1] (N=303) | Maximum concentration (µg/L) |
|---|---|---|
| Any herbicide or metabolite | 28.4 | 2.32 |
| Deethylatrazine | 21.4 | 2.32 |
| Atrazine | 20.8 | 2.09 |
| Deisopropylatrazine | 7.6 | 1.17 |
| Prometon | 6.3 | 0.86 |
| Metolachlor | 4.0 | 1.46 |
| Alachlor | 2.0 | 1.05 |
| Simazine | 1.6 | 0.27 |
| Metribuzin | 1.3 | 0.57 |
| Cyanazine | 1.3 | 0.68 |

[1] Analytical reporting limit for all compounds is 0.05 µg/L

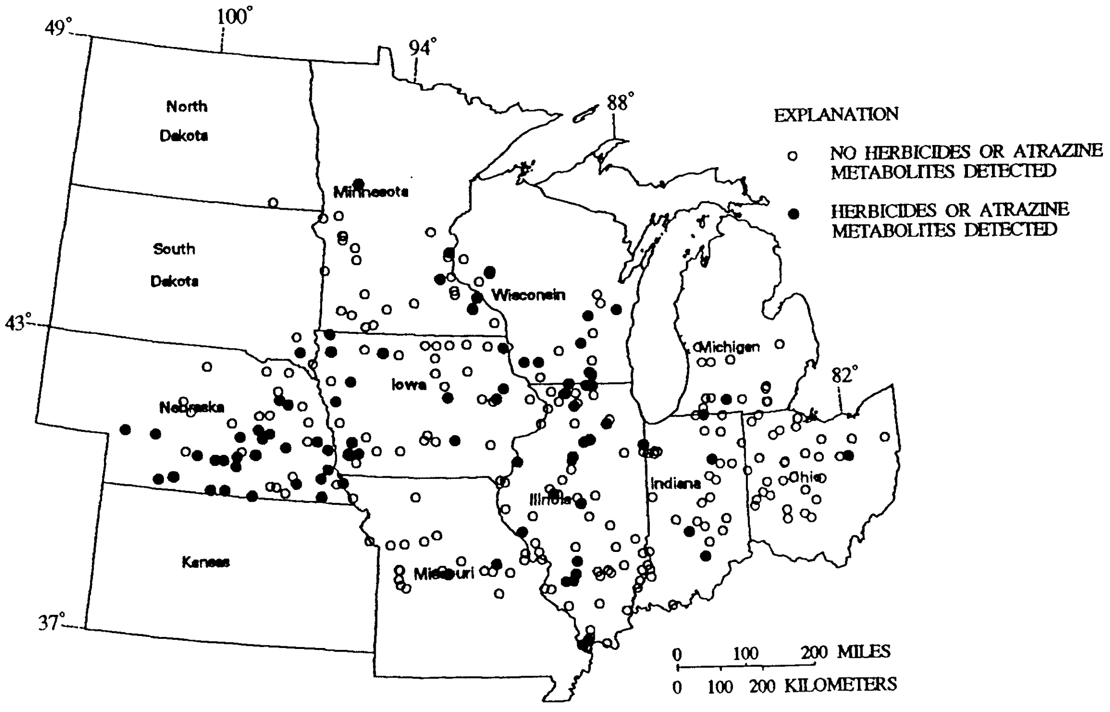

Figure 2. Spatial distribution of herbicide or atrazine metabolite detections in wells sampled during 1991 (reporting limit of 0.05 micrograms per liter for all compounds).

water from wells sampled during the 1991 study was deethylatrazine (table 1). The frequency of atrazine-residue detection (atrazine plus deethylatrazine plus deisopropylatrazine) was 25.7 percent, whereas the frequency of atrazine detection alone was 20.8 percent. It is likely that the frequency of detection for other herbicide residues also would be larger if analyses for the metabolites of those herbicides were available. Consequently, if herbicide metabolites are not quantified, the effects of herbicide usage on the quality of water resources could be substantially underestimated.

The deethylatrazine-to-atrazine ratio (DAR) in water can provide information on the residence time of atrazine in the unsaturated zone (Thurman and others, 1992). Atrazine can be degraded by soil microorganisms to deethylatrazine and other metabolites. Below the soil zone, the effects of decreased amounts of available oxygen, reduced microbial activity, and reduced amounts of organic carbon combine to greatly reduce the biodegradation rates for atrazine (Dhileepan and Schnoor, 1992). Thus, slow infiltration through the soil results in larger DAR values than does rapid infiltration. Thurman and others (1992) reported DAR values in midwestern streams during 1989-90 generally were less than 0.1 during periods of spring runoff shortly after herbicide application but generally were 0.4 or larger in the fall during base-flow conditions. The median DAR value obtained from the 1991 ground-water reconnaissance (Kolpin and others, 1993a) was about 0.7 (fig. 3).

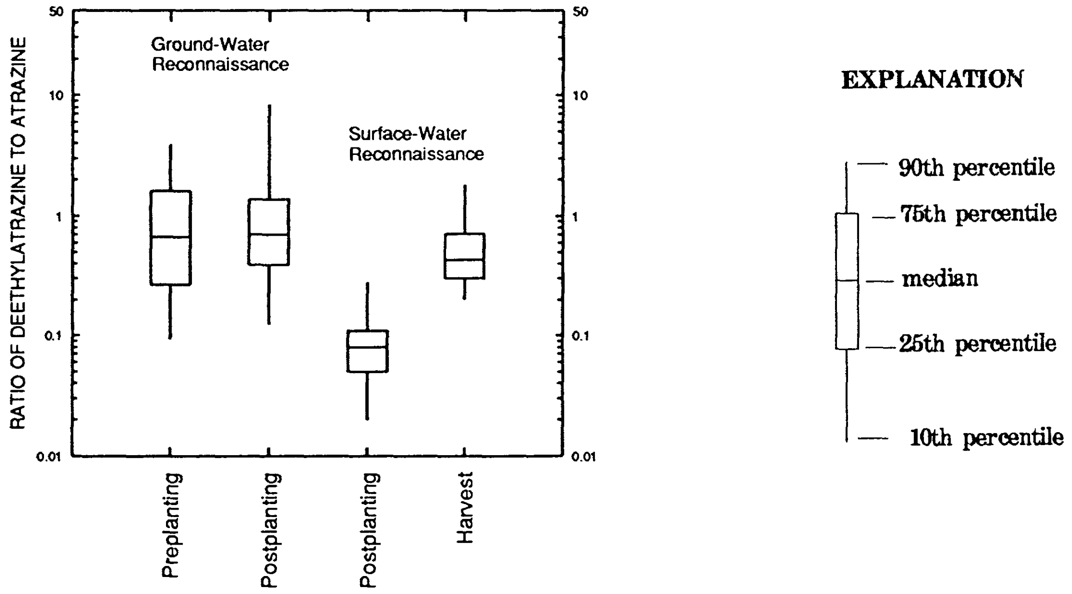

Figure 3. Deethylatrazine-to-atrazine ratios from wells sampled during 1991 and for the surface water reconnaissance during 1989-90 (Thurman and others, 1992).

The frequency of herbicide detection in water from near-surface aquifers was significantly larger (p = 0.002; Mann-Whitney test) in unconsolidated aquifers (28 percent) than in bedrock aquifers (17 percent). Unconsolidated aquifers might be more susceptible to herbicide contamination than bedrock aquifers for several reasons. First, most of the unconsolidated aquifers sampled, being alluvial in origin, have a long and narrow planar geometry; accordingly, paths of ground-water flow from recharge areas are much shorter than ground-water flow paths in the more laterally extensive bedrock aquifers sampled for this study. Second, there is a general absence of low-permeability material overlying the unconsolidated aquifers. About 78 percent of the unconsolidated aquifers sampled, but only 48 percent of the bedrock aquifers sampled, were under unconfined conditions. An aquifer that is confined in the vicinity of a properly constructed well is effectively isolated from the downward percolation of herbicides that might be applied near that well. Two lines of evidence support the conclusion that the unconsolidated aquifers are unconfined more often than bedrock aquifers and contain mostly local paths of ground-water flow. First, a significant difference in the frequency of herbicide detection between preplanting (22.6 percent) and postplanting (34.1 percent) sampling periods was found only in water samples from unconsolidated aquifers. Differences in water quality during such a short time would be expected only in aquifers that are recharged rapidly or that are located a short distance from its recharge area. Second, the median DAR was 0.57 for water samples from unconsolidated aquifers and 1.25 for water samples from bedrock aquifers. Because the DAR can indicate residence time in the unsaturated zone, the comparatively small DAR for unconsolidated aquifers again indicate that the recharge rates were generally more rapid than for the bedrock aquifers sampled.

The frequency of herbicide detection differed significantly (p = 0.001; Kruskal-Wallis test) among intervals of depth to the top of the aquifer material (0 to 3 m, 28.4 percent; 3 to 6 m, 29.9 percent; 6 to 9 m, 23.9 percent; 9 to 12 m, 16.9 percent; and greater than 12 m, 11.1 percent). In general, the greater the depth to the top of the aquifer material, the smaller the frequency of herbicide detection. This vertical distance from land surface to the top of the aquifer material gives a general indication of the proximity of an aquifer to recharge source. The greater this distance, the greater the opportunity for processes such as transport, transformation, or sorption of chemicals to take place.

The percentage of land in corn or soybean production within a 3.2-km radius surrounding the wells did not appear to affect the frequency of herbicide detection. Although this lack of an association was unexpected, it could have been affected by either the selection criteria for this study, which required at least 25 percent of the land in a 3.2-km radius surrounding the wells be in corn or soybean production in the 1990 growing season, or that many herbicides being used in the Midcontinent and their respective metabolites were not analyzed during the 1991 study.

The frequency of herbicide detection was related to crop irrigation. Water samples from wells located within 3.2 km of irrigated crops had almost double (35 percent) the frequency of herbicide detection than was observed in water samples from wells without nearby irrigation (19 percent). Almost 95 percent of the wells near irrigated areas were in unconsolidated aquifers, where some of the irrigation water typically recharges locally to aquifers. Under these conditions, irrigation could result in continuous leaching of chemicals to the aquifer throughout the irrigation season.

The frequency of herbicide detection was related to the proximity of a well to a stream. The frequency of herbicide detection in water samples from wells within 30 m of a well was more than double (48 percent) that observed in water samples from wells with no stream nearby (22 percent). This difference can result from a hydrologic connection between aquifers and streams due to either natural or induced hydraulic gradients or a convergence of ground-water flow paths where ground water discharges to streams. Frequencies of detection and concentrations of herbicides are much larger in streams than in aquifers in the Midcontinent (Thurman and others, 1992). Thus, recharge to an aquifer by a stream could be a source of herbicide contamination to the aquifer (Squillace and others, 1993).

## 1992 Sampling

Herbicides, herbicide metabolites, or insecticides (table 2) were detected in water samples from 62 percent of the wells resampled during 1992. Most of these detections were at concentrations of less than 0.5 µg/L; some concentrations were in the parts per trillion range. No concentration exceeded a USEPA MCL for drinking water. Although concentrations of some of these compounds can be very low, even trace amounts can be important in identifying flow paths and transformation patterns in the hydrologic system, because these compounds are not present in the environment under natural conditions. The frequency of herbicide detection was much larger in 1992 than in 1991 because more herbicides and herbicide metabolites were analyzed (40 in 1992 as opposed to 13 in 1991); 20 insecticides were included in the suite of compounds analyzed; analytical reporting limits for many compounds were about an order of magnitude lower for the 1992 study than for the 1991 study; and the sample selection for some of the herbicides and herbicide metabolites analyzed for the 1992 study was biased toward wells where these compounds were detected during 1991.

A preliminary analysis of results indicates that the detections of pesticides in the 1992 study were much more evenly distributed across the Midcontinent (fig. 4) than determined from the 1991 sampling (fig. 2). In particular, spatial patterns of detections in the eastern part of the study region were similar to those in other parts of the region, in contrast to results from the 1991 study. The greater frequency of detection in the eastern part of the study region can be attributed to the lowered reporting limits for atrazine and simazine and to the analysis of alachlor metabolites. Spatial patterns of detections across the Midcontinent are apparent when specific compounds are examined. For example, more than 50 percent of the insecticide detections were in Nebraska and more than 60 percent of the simazine detections were in Ohio.

Data obtained from the 1992 sampling reinforces the importance of metabolite information to understand fully the occurrence, distribution, and fate of pesticides in the environment. Of the six most frequently detected pesticide compounds during 1992, five were herbicide metabolites (table 2). In addition to alachlor, two alachlor metabolites also were detected: 2,6-diethylanaline and ESA. ESA recently has been identified as a relatively persistent and mobile compound (Baker and others, 1993). Analytical results on alachlor and the two aforementioned metabolites were available from 66 samples. Of these samples, only about 8 percent contained detectable concentrations of alachlor; however, 21 percent contained detectable levels of 2,6-diethylanaline and 47 percent contained ESA. The detection frequency of alachlor-residue (alachlor plus 2,6-diethylanaline plus ESA) was 53 percent, or more than 5 times the detection frequency of the

**Table 2.** Frequency of pesticide and pesticide metabolite detections in water from wells sampled during 1992, Midcontinental United States

[μg/L, micrograms per liter; ESA, alachlor metabolite]

| Compound | percent detection | Number of samples[1] | Maximum concentration (μg/L) | Reporting limit (μg/L)[2] | Action/use[3] |
|---|---|---|---|---|---|
| Any pesticide or metabolite | 62.0 | 100 | | | |
| ESA | 47.0 | 66 | 4.95 | 0.100 | Herbicide metabolite (alachlor) |
| Atrazine | 43.0 | 100 | 1.03 | .005 | Selective herbicide: corn, sorghum |
| Deethylatrazine | 31.0 | 100 | 1.79 | .015 | Herbicide metabolite (atrazine) |
| Deisopropylatrazine | 18.2 | 66 | .28 | .050 | Herbicide metabolite (atrazine) |
| 2,6-Diethylanaline | 16.0 | 94 | .022 | .003 | Herbicide metabolite (alachlor) |
| DCPA | 15.6 | 45 | 2.22 | .010 | Herbicide metabolite (dacthal) |
| Simazine | 13.0 | 100 | .077 | .005 | Selective herb:icide corn, |
| Metolachlor | 11.0 | 100 | .76 | .002 | Selective herbicide: corn, sorghum, soybeans |
| Prometon | 9.0 | 100 | 1.35 | .010 | Nonselective herbicide |
| 2,4-D | 6.7 | 45 | .89 | .010 | Selective herbicide:c orn, sorghum, pasture |
| P,P' DDE | 6.4 | 94 | .03 | .006 | Insecticide metabolite (DDT) |
| Alachlor | 5.0 | 100 | .99 | .002 | Preemergent herbicide: corn, soybeans |
| Dicamba | 4.4 | 45 | .01 | .010 | Herbicide |
| Picloram | 4.4 | 45 | .03 | .010 | Systemic herbicide: deep-rooted plants |
| Chlorpyrifos | 4.2 | 94 | .024 | .004 | Insecticide: corn, soybeans |
| Ethalfluralin | 3.2 | 94 | .014 | .004 | Selective preemergence herbicide: soybeans |
| Cyanazine | 3.0 | 100 | .02 | .008 | Selective herbicide: corn |
| 2,4,5-T | 2.2 | 45 | .02 | .010 | Discontinued herbicide |
| EPTC | 2.1 | 94 | .003 | .002 | Selective herbicide: corn |
| Trifluralin | 2.1 | 94 | .016 | .003 | Selective preemergence herbicide: soybeans |
| Triallate | 2.1 | 94 | .007 | .001 | Selective preemergence herbicide: wheat |
| Benfluralin | 1.1 | 94 | .018 | .004 | Herbicide: alfalfa, clover |
| Napropamide | 1.1 | 94 | .008 | .003 | Selective herbicide: orchards, tobacco |
| Pendimethalin | 1.1 | 94 | .01 | .008 | Selective herbicide: corn, soybeans |
| Propachlor | 1.1 | 94 | .002 | .007 | Herbicide |
| Tebuthiuron | 1.1 | 94 | .05 | .010 | Herbicide: noncropland areas, rangeland |
| Metribuzin | 1.0 | 100 | .05 | .005 | Herbicide: soybeans |

[1] When sample size is less than 94, the frequency of detection for that compound may be affected by the biased sample selection toward wells that had a herbicide detection during 1991

[2] Reporting limits of compounds not detected: alpha BHC (0.002), ametryn (0.05), bentazon (0.10), butylate (0.002),carbaryl (0.01), carbofuran (0.01), 2.4-DP (0.01), dacthal (0.002), diazinon (0.002), dieldrin (0.002), dimethoate (0.02), disulfoton (0.017), ethoprop (0.003), fonofos (0.003), linuron (0.01), malathion (0.005), methyl parathion (0.008), methyl azinphos (0.005), molinate (.004), parathion (0.005), pebulate (0.005), permethrin (0.01), phorate (0.003), prometryn (0.05), pronamide (0.004), propargite (0.02), propanil (0.005), propazine (0.05), silvex (0.01), terbacil (0.01), terbufos (0.013), terbutryn (0.05), thiobencarb (0.002)

[3] modified from Meister (1992)

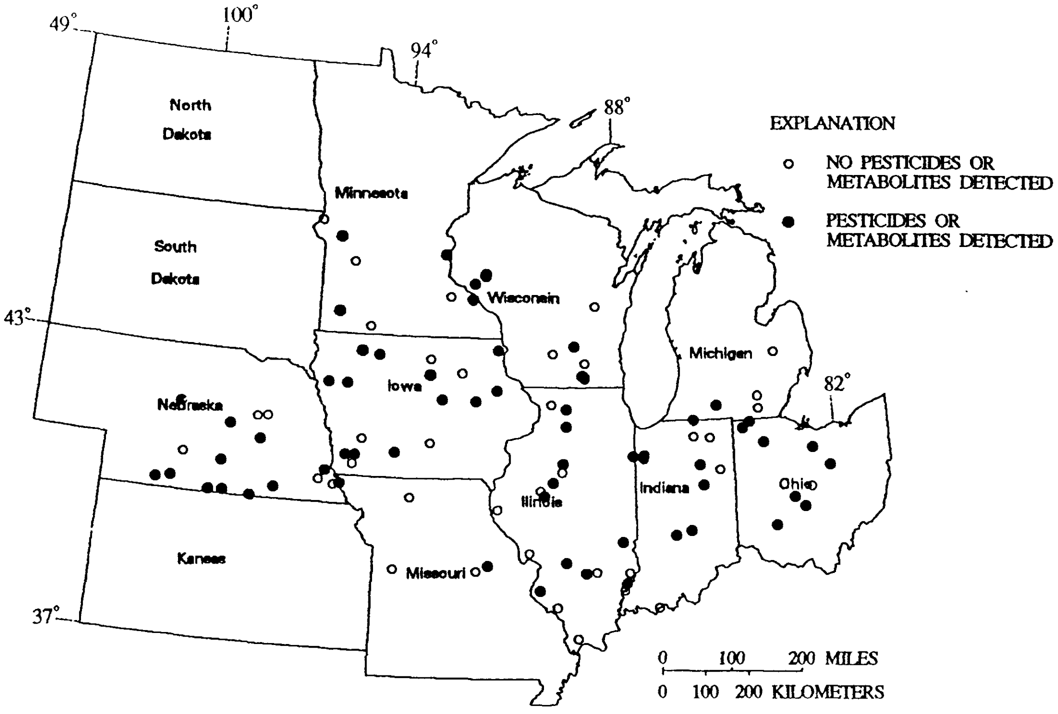

Figure 4. Spatial distribution of pesticide or metabolite detections in water from wells sampled during 1992 (reporting limits of 0.001 to 0.1 micrograms per liter for compounds analyzed).

parent compound alone. Although no alachlor concentrations exceeded the USEPA MCL of 2.0 μg/L, 4.5 percent of alachlor-residue concentrations exceeded 2.0 μg/L, and 15 percent exceeded 1.0 μg/L. These results show how the affects of pesticides on the quality of water resources can be substantially underestimated without data on metabolites.

## SUMMARY

Herbicides or herbicide metabolites were detected in water samples from 28.4 percent of wells sampled in near-surface aquifers of the Midcontinent during 1991. During 1991, deethylatrazine was the most frequently detected compound followed by atrazine, deisopropylatrazine, and prometon. The highest frequency of detection was observed in the extreme western part of the region; the lowest frequency of detection was observed in the eastern third of the region. Unconsolidated aquifers were more susceptible to herbicide contamination than the bedrock aquifers sampled because of their general long and narrow planar geometry and the general absence of overlying confining units. The frequency of herbicide detection was inversely related to the depth to the top of the aquifer material. The greater this depth, the greater the opportunity for processes such as transport, transformation, and sorption of chemicals to occur. The frequency of herbicide detection almost doubled when crops were irrigated within 3.2 km of the well. The frequency of herbicide detection more than doubled when a well was within 30 m of a stream, possibly because of either natural or induced hydraulic gradients or from a convergence of ground-water flow paths near a stream.

During 1992, a pesticide or pesticide metabolite was detected in 62 percent of the 101 wells resampled. The greater frequency of detection during 1992 was caused by an increased number of herbicides and herbicide metabolites analyzed, inclusion of insecticides in the suite of compounds analyzed, analytical reporting limits for many compounds that were lower (about an order of magnitude) in 1992 than in 1991, and biasing the sample selection for some of the herbicides analyzed toward wells in which herbicides were detected during 1991. Herbicide detections in the 1992 study were much more evenly distributed across the region than in the 1991 study, probably because of the low reporting limits of atrazine and simazine and the analysis of alachlor metabolites.

Data on herbicide metabolites are important for a full understanding of the occurrence, distribution, and fate of herbicides in the environment. During 1991, the most frequently detected compound was deethylatrazine, and the frequency of atrazine-residue detection was greater than the frequency of atrazine detection alone. During the 1992 resampling, five of the six most frequently detected compounds were herbicide metabolites. The frequency of alachlor-residue detection was more than five times the frequency of alachlor detection alone. These results show how the affects of pesticides on the quality of water resources can be substantially underestimated without data on metabolites.

# REFERENCES

Baker, D.B., Bushway, R.J., Adams, S.A., and Macomber, Carol, 1993, Immunoassay screens for alachlor in rural wells: False positives and an alachlor soil metabolite: Environmental Science and Technology, v. 27, no. 3, p 562-564.

Dhileepan, N.R., and Schnoor, J.L., 1992, Effect of two electron acceptors on atrazine mineralization rates in soil: Environmental Science and Technology, v. 26, no. 11, p. 2298-2300.

Gianessi, L.P., and Puffer, C.M., 1990, Herbicide use in the United States: Washington, D.C., Resources for the Future, [Inc.], Quality of the Environment Division, 127 p. [revised 1991]

Kolpin, D.W., and Burkart, M.R., 1991, Work plan for regional reconnaissance for selected herbicides and nitrate in ground water of the mid-continental United States, 1991: U.S. Geological Survey Open-File Report 91-59, 18 p.

Kolpin, D.W., Burkart, M.R., and Thurman, E.M., in press, Herbicides and nitrate in near-surface aquifers in the midcontinental United States, 1991: U.S. Geological Survey Water-Supply Paper 2413.

Kolpin, D.W., Burkart, M.R., and Thurman, E.M., 1993, Hydrogeologic, water-quality, and land-use data for the reconnaissance for herbicides and nitrate in near-surface aquifers of the midcontinental United States, 1991: U.S. Geological Survey Open-File Report 93-114, 61 p.

Meister, R. T., editor, 1992, Farm Chemicals Handbook 1992: Willoughby, Ohio, Meister Publishing Company, 794 p.

Squillace, P.J., Thurman, E.M., and Furlong, E.T., in press, Ground water as a nonpoint source of atrazine and deethylatrazine in a river during base-flow conditions: Water Resources Research, vol 29, no. 6, p. 1719-1729.

Thurman, E.M., Meyer, Michael, Pomes, Michael, Perry, C.E., and Schwap, A.P., 1990, enzyme-linked immunosorbent assay compared with gas chromatography/mass spectrometry for the determination of triazine herbicides in water: Analytical Chemistry, v. 62, no. 18, p. 2043-2048.

Thurman, E.M., Goolsby, D.A., Meyer, M.T., Mills, M.S., Pomes, M.L., and Kolpin, D.W., 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.

U.S. Environmental Protection Agency, 1990, County-level fertilizer sales data: Washington, D.C., Office of Policy Planning and Evaluation, September 1990, computer disk.

# OCCURRENCE, DEPOSITION, AND LONG RANGE TRANSPORT OF HERBICIDES IN PRECIPITATION IN THE MIDWESTERN AND NORTHEASTERN UNITED STATES

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

## ABSTRACT

Herbicides were detected in precipitation throughout the midwestern and northeastern United States during late spring and summer of 1990 and 1991. During May and June atrazine, alachlor, or both were detected in 60 to 75 percent of weekly accumulations of precipitation collected at 81 sampling sites in 23 States. Atrazine or alachlor were detected in at least one sample from all States, including samples from remote wilderness areas such as Isle Royale in northern Lake Superior. During the remainder of the year, herbicides generally were detected in weekly samples at less than about 20 percent of the sites. Atrazine was the most frequently detected herbicide, followed by alachlor, desethylatrazine, and metolachlor. Herbicide concentrations and frequency of detection were much higher in the Midwest than elsewhere. Precipitation-weighted herbicide concentrations for mid-April through mid-July typically were 0.2 to 0.4 µg/L (micrograms per liter) in the Midwest and weighted concentrations as large as 0.9 µg/L were present at a few sites. Concentrations of 1 to 3 µg/L were measured in a few individual samples representing small amounts of precipitation. Deposition rates for both atrazine and alachlor ranged from more than 200 ($\mu g/m^2$)/yr (micrograms per square meter per year) at a few sites in the Midwest to less than 10 ($\mu g/m^2$)/yr in the Northeast. These amounts represent less than 1 percent of the atrazine and alachlor applied annually to crops. The geographic pattern of herbicide deposition provides evidence for long-range atmospheric transport.

## INTRODUCTION

Current agricultural practices in the United States require extensive use of herbicides for economical production of corn, soybeans, sorghum, and other row crops. Data compiled by Gianessi and Puffer (1991) show that about two-thirds of the 285 million kg of herbicides used annually in the United States (Aspelin and others, 1992) are used in crop production in the Midwestern United States, and principally in the Mississippi River drainage basin. As a consequence, the Midwest is the major source area for transport of herbicides into streams and ground water in the midcontinent as well as to the atmosphere. Most herbicides are relatively soluble but significant amounts (a few percent of the amounts applied) can be transported into streams (Baker and Richards, 1989; Goolsby and others 1991; Thurman and others, 1992) and ground water (Hallberg, 1989; Holden and others, 1992; Kolpin and others, in press). Previous research has also shown that herbicides and other organic compounds can be transported into the atmosphere by various processes. In the atmosphere, these compounds can be dispersed by air currents and redeposited on the land surface, lakes, and streams by rainfall, snow, and dry deposition, often at considerable distances from their origin. For example, the transport of chlorinated insecticides and polychlorinated biphenyls (PCB's) into the Great Lakes is believed to be largely from the atmospheric sources (Eisenreich and others, 1981). Herbicides have been reported in fog (Glotfelty and others, 1987) and rainfall in the midwestern United States (Capel and others, 1991; Nations and Hallberg, 1992; Richards and others, 1987; Williams and others 1992), eastern United States (Glotfelty and others, 1990; Wu, 1981), and in Europe (Buser, 1990; Trevisan, 1993). In spite of these studies, relatively little is known on a regional or multistate scale about deposition patterns of herbicides in precipitation and the magnitude of herbicide deposition in precipitation in comparison to quantities applied to cropland or to surface-runoff losses.

In order to learn more about herbicides in precipitation, a study was conducted during 1990 and 1991 to determine the occurrence and distribution of herbicides in precipitation (rain and snow) for a large part of the United States, including much of the Mississippi River basin where most of the herbicides are used. The study was conducted as part of the Toxic Substances Hydrology Program and was mass oriented in that it attempted to determine the mass deposited in precipitation over nearly one-quarter of the United States for the two most heavily used herbicides in the country, --atrazine and alachlor (Gianessi and Puffer, 1991). Specific objectives of the study were to (1) determine the occurrence and temporal distribution of several major herbicides in precipitation, (2) estimate the amounts of atrazine and alachlor deposited in precipitation annually in individual States and over a large part of the conterminous United States, (3) relate annual deposition of atrazine and alachlor to amounts applied annually, and (4) compare annual herbicide deposition in precipitation within the Mississippi River basin to the estimated annual amount transported out of the basin in streamflow. A summary of results from this study is presented in this paper.

## DESCRIPTION OF STUDY AREA AND DATA COLLECTION METHODS

The study area for this investigation encompassed 26 States (fig. 1). It includes States in the upper Midwest where the use of herbicides, such as atrazine and alachlor, is most intense, and States eastward to the Atlantic Ocean and northward to the Canadian border that potentially may receive atmospheric deposition of herbicides applied in the Midwest. Precipitation samples were obtained from the study area through the cooperation and assistance of the National Atmospheric Deposition Program / National Trends Network (NADP/NTN), Fort Collins, Colo., and the Illinois State Water Survey, Champaign, Ill. The National Atmospheric Deposition Program (1992) operates a network of about 200 sites nationwide to monitor the status and trends in acid deposition. Weekly accumulations of precipitation (rain and snow) were obtained at 81 NADP/NTN sampling sites located in 23 States within the 26-State study area (fig. 1). In addition, five NADP/NTN sites in high-elevation areas along the Rocky Mountains (fig. 1) and in Alaska (not shown on fig. 1) were sampled to provide background data on herbicides in precipitation at sites far from the study area. A complete description of each sampling site is given in a directory of precipitation monitoring sites (National Atmospheric Deposition Program, 1986). Collection of samples began in March 1990 and continued through September 1991--a period of 19 months.

Each NADP/NTN monitoring site is equipped with an Aerochem Metrics Wet/Dry collector to collect precipitation and a separate Belfort 5-780 Universal Rain Gage to make an independent measurement of precipitation amount. The wet/dry collectors are equipped with two 13-liter polyethylene buckets that alternately collect wet or dry deposition. The "wet side" bucket is covered with a tight fitting lid until precipitation begins, at which time a heated sensor opens the

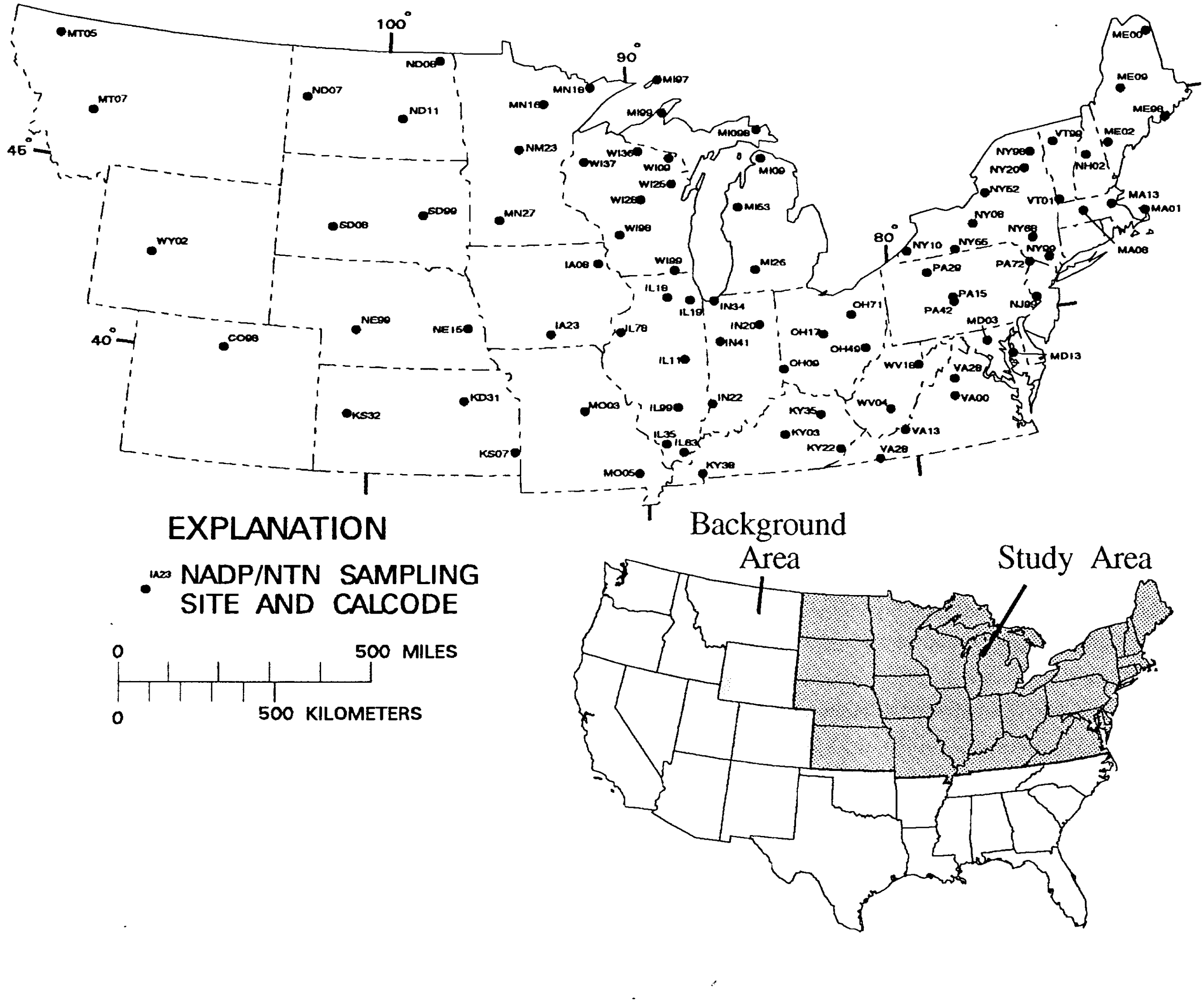

Figure 1.--Location of study area, background area, and National Atmospheric Deposition/National Trends Network (NADP/NTN) sampling sites.

lid to allow collection of wet deposition. When precipitation ceases, the sensor closes the lid until the next precipitation event. Precipitation is accumulated in this manner for a period of 1 week. Each Tuesday, regardless of whether precipitation has occurred the previous week, a site operator removes the "wet side" bucket, seals it with a polyethylene lid, and sends it to the Central Analytical Laboratories (CAL) operated by the Illinois State Water Survey in Champaign, Ill. for analysis. For the 86 NADP/NTN sites used in this study, a subsample was obtained from the polyethylene buckets upon receipt at the CAL. The subsample, consisting of 10 to 125 mL (milliliters), depending on the amount of precipitation collected, was transferred to a 125-mL baked glass bottle, chilled, and sent to the U.S. Geological Survey's laboratory in Lawrence, Kans., for herbicide analysis. Buckets from sites where no precipitation occurred were leached for 24 hours with 50 mL of distilled water, which then was used as a system blank. Subsamples of these blanks were provided by the CAL for herbicide analysis. Only herbicides deposited in precipitation (rain and snow) were analyzed in this study. No samples of dry deposition were analyzed.

All precipitation samples were analyzed by enzyme-linked immunosorbent assay (ELISA) for both alachlor and atrazine. The reporting limits for ELISA were 0.1 μg/L for atrazine and 0.2 μg/L for alachlor. Samples in which herbicides were detected and that had a sample volume of at least 60 mL were confirmed by gas chromatography/mass spectrometry (GC/MS). Analysis of samples with less than 60 mL were not confirmed. About 10 percent of all samples that were found to contain no herbicides by ELISA also were analyzed by GC/MS. These samples were chosen randomly from all negative samples. An exception to the above procedure occurred during the first few months of the study when 20 percent of all samples with 60 mL or more of water were randomly selected for GC/MS analysis regardless of whether herbicides were detected by ELISA. Of about 6,000 samples analyzed by ELISA during the study, more than 2,200 were confirmed by GC/MS analysis. Included in the 6,000 samples were about 1,200 samples analyzed by ELISA and 400 samples analyzed by GC/MS that were used for quality-assurance (QA) purposes.

Samples for ELISA analysis were analyzed in duplicate (Pomes and others, 1991) using microtiter plates. Concentrations were determined with a microtiter plate reader and calibration curves were developed from four standard solutions of known atrazine or alachlor concentration that ranged from 0 to 5 μg/L. Samples were analyzed in duplicate and the results averaged. Standards were analyzed in triplicate or quadruplicate. GC/MS samples were analyzed by an automated procedure (Thurman and others, 1990) following solid-phase extraction of samples on $C_{18}$ cartridges. Samples were analyzed for 11 parent herbicides: alachlor, ametryn, atrazine, cyanazine, metolachlor, metribuzin, prometon, prometryn, propazine, simazine, and terbutryn, and two metabolites of atrazine--desethylatrazine and deisopropylatrazine.

Several experiments conducted on the NADP/NTN plastic collection buckets over periods of 3 weeks confirmed that no significant sorption, degradation, or other losses of the major herbicides studied occurred in the buckets. However, the buckets contributed a compound with a GC/MS peak that interfered with the identification of deisopropylatrazine in some of the samples.

Linear-regression equations, given below, were developed from more than 2,200 samples analyzed for atrazine and alachlor by both ELISA and GC/MS. Because of slight changes in methodology and differing batches of ELISA kits, regression results were improved by developing separate equations for samples collected in 1990 and 1991.

1990: atrazine = -0.01 + 0.70 ELISA. $R^2 = 0.94$; standard error of estimate = 0.09 µg/L.
1991: atrazine = 0.00 + 0.80 ELISA. $R^2 = 0.78$; standard. error of estimate = 0.10 µg/L.
1990: alachlor = 0.00 + 0.64 ELISA. $R^2 = 0.76$; standard. error of estimate = 0.08 µg/L.
1991: alachlor = 0.00 + 0.84 ELISA. $R^2 = 0.86$; standard. error of estimate = 0.09 µg/L.

These equations were used to estimate concentrations of atrazine and alachlor in about 3,700 samples (including quality assurance samples) analyzed only by ELISA. The measured or estimated concentrations and precipitation amounts were then used to calculate weekly deposition of these two herbicides at each sampling site which were expressed as micrograms per square meter (µg/m$^2$) per week.

## RESULTS AND DISCUSSION

Ten of the 13 herbicides and metabolites analyzed in this study were detected in precipitation samples from the 81 sampling sites in the study area (table 1). Atrazine and alachlor were detected (at concentrations of 0.1 to 0.2 µg/L or greater) by ELISA in 26.2 percent and 9.0 percent of the samples, respectively. These two herbicides were detected (at concentrations of 0.05 µg/L or greater) in 33.9 and 21.5 percent, respectively, of the samples selected for analysis by GC/MS. However, it should be stated that this is a biased result since the samples for GC/MS analysis were previously screened by ELISA for the presence or absence of herbicides. Consequently these results are not typical of the frequency of occurrence of these herbicides in the 6,000 samples collected during the period of this study. Desethylatrazine was the third most frequently detected compound in the ELISA-screened samples (19.5 percent), followed by metolachlor (14.9 percent), and cyanazine (8.1 percent). Five other herbicides and metabolites (table 1) were detected in 3 percent or fewer of the samples. Only about 1 percent of the samples had herbicide concentrations exceeding 1 µg/L. Because of the proximity of some sampling sites to cropland, the possibility of spray drift cannot be ruled out as a possible source for some of the high concentrations. Atrazine and alachlor were detected in concentrations near the analytical reporting limit (see table 1) in a small number of samples from sites located in the background area (fig 1.).

The spatial pattern of occurrence and temporal distribution of atrazine and alachlor in precipitation is similar to the pattern observed in streams throughout the Midwest (Goolsby and others, 1991; Thurman and others, 1992). The frequency at which these two herbicides were detected each week at sampling sites throughout the study area (fig. 1) began to increase in mid-April following application of herbicides to cropland, and peaked in mid-June or early July (fig. 2). During this period, atrazine was detected each week at 60 to 75 percent of the sites sampled and alachlor was detected at 30 to 40 percent of the sites. During the remainder of the year, these herbicides generally were detected at less than about 20 percent of the sites sampled. Samples were not collected at all sites each week because of periods of no precipitation (fig. 2). Atrazine and alachlor were detected most frequently at sites in the Midwest, but at least one sample (confirmed by GC/MS) from all 23 States with sampling sites had detectable concentrations of one or both herbicides. These sites included sites in areas remote from cropland such as Maine and Isle Royale in northern Lake Superior. The processes by which these and other herbicides are transported into the atmosphere include volatilization (primarily from moist soils),

Table 1. Statistical summary of herbicide concentrations measured in precipitation samples from 81 National Atmospheric Program/National Trends Network sites during March 1990 through September 1991 [µg/L, micrograms per liter; <, less than; not detected: ametryn, prometryn, terbutryn]

| Herbicide | Reporting limit µg/L | Number of samples | Percent detections | Concentration, in µg/L, for indicated percentiles | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | 50 (median) | 75 | 90 | 95 | 99 | 100 (maximum) |
| ELISA[1] Analysis (all samples) | | | | | | | | | |
| atrazine | 0.1 | 4,762 | 26.2 | <0.10 | 0.10 | 0.26 | 0.47 | 1.3 | 16 |
| alachlor | 0.2 | 4,764 | 9.0 | <.2 | <.2 | <.2 | .34 | 1.3 | 16 |
| GC/MS[2] Analysis (samples pre-screened by ELISA) | | | | | | | | | |
| atrazine | 0.05 | 1,848 | 33.9 | <.05 | .09 | .25 | .45 | 1.1 | 10.9 |
| alachlor | .05 | 1,849 | 21.5 | <.05 | <.05 | .13 | .29 | .97 | 3.2 |
| desethylatrazine | .05 | 1,849 | 19.5 | <.05 | <.05 | .10 | .16 | .40 | .75 |
| metolachlor | .05 | 1,849 | 14.9 | <.05 | <.05 | .09 | .18 | .68 | 3.0 |
| cyanazine | .05 | 1,849 | 8.1 | <.05 | <.05 | <.05 | .08 | .29 | 2.0 |
| deisopropylatrazine | .05 | 1,849 | 3.0 | <.05 | <.05 | <.05 | <.05 | .18 | 1.2 |
| simazine | .05 | 1,849 | 1.6 | <.05 | <.05 | <.05 | <.05 | .07 | 1.5 |
| metribuzin | .05 | 1,849 | .7 | <.05 | <.05 | <.05 | <.05 | <.05 | .18 |
| prometon | .05 | 1,849 | .5 | <.05 | <.05 | <.05 | <.05 | <.05 | .20 |
| propazine | .05 | 1,849 | .1 | <.05 | <.05 | <.05 | <.05 | <.05 | .12 |

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[1] ELISA, enzyme-linked immunosorbent assay.

[2] GC/MS, gas chromatography/mass spectrometry.

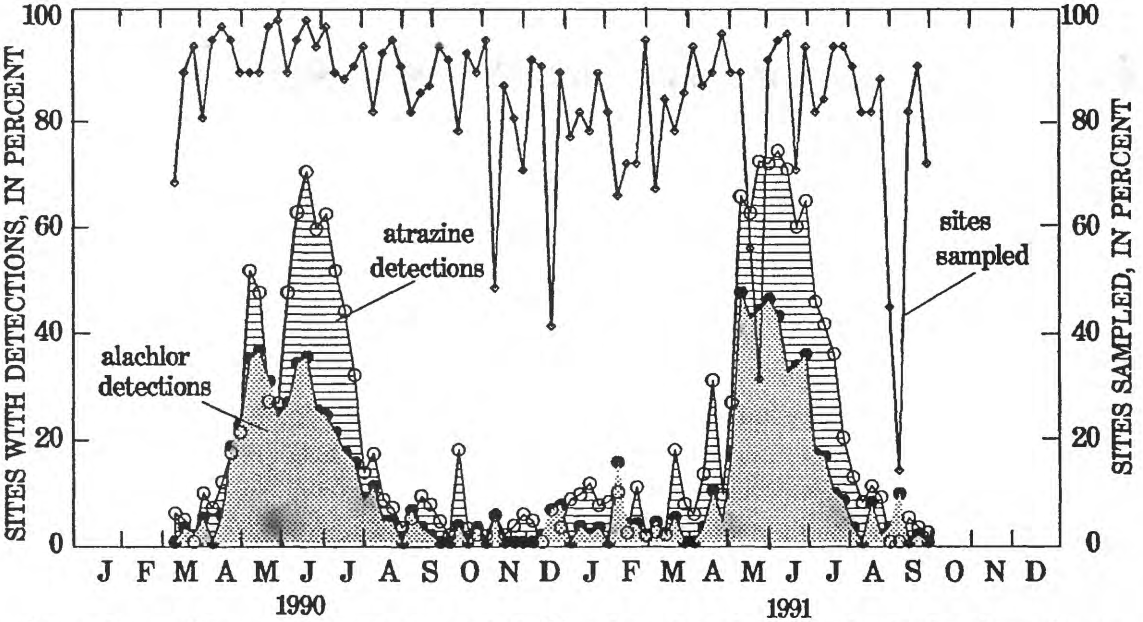

Figure 2.— — Frequency of atrazine and alachlor detections, by week, for 81 sites in study area (midwestern and northeastern United States). Includes detections by immunoassay and gas chromatography / mass spectrometry. Immunoassay reporting limits are 0.1 and 0.2 micrograms per liter respectively for atrazine and alachlor and 0.05 micrograms per liter for gas chromatography— mass spectrometry.

attachment to soil and dust particles that are blown into the atmosphere, and spray drift during application. Of these processes, volatilization is believed to be predominant (Tierney, 1993). Atrazine is about 10 times less volatile than alachlor and has a longer soil half-life (about 60 days) than alachlor (about 15 days). Consequently, it volatilizes into the atmosphere at a slower rate and is available for volatilization from the soil for a longer period of time than is alachlor. Because of these properties, atrazine is present in precipitation for a longer time than is alachlor (fig. 2).

Atrazine and alachlor concentrations were highest and detections were most frequent at sites in the Midwest (fig. 3) where these herbicides are used most extensively. Concentrations as high as 3 µg/L were detected in individual samples at some sites. In areas where the use of atrazine and alachlor are similar such as Iowa, Illinois, and Indiana, alachlor concentrations generally were higher than atrazine concentrations (fig. 3), in part, because of the greater volatility of alachlor relative to that of atrazine. In remote areas such as Maine and parts of Michigan, herbicide concentrations were very low and detections were infrequent (fig. 3). The highest herbicide concentrations tended to occur during small precipitation events after herbicide application, because the first part of a precipitation event flushes most of the herbicides from the atmosphere (Capel, 1991). Subsequent precipitation dilutes the concentrations from the earlier precipitation. Therefore, it is difficult to make meaningful comparisons of herbicide concentrations among sites or over time on the basis of individual weekly samples. A better comparison can be made with precipitation-weighted concentrations, which are calculated by summing the product of precipitation amounts and herbicide concentrations over a period of time, such as 3 months, and dividing by the total amount of precipitation. Precipitation-weighted concentrations of atrazine and alachlor calculated for a 13-week period from mid-April through mid-July 1991 are shown in figure 4; the map was constructed using a geographic information system (GIS). Precipitation-weighted concentrations of 0.2 to 0.4 µg/L are typical throughout the Midwest and weighted concentrations of 0.4 to 0.9 µg/L were detected at sites in Iowa, Illinois, and Indiana. The spatial pattern of weighted concentrations reflects the intensity of use of these two herbicides. It also provides tentative evidence for long-range atmospheric transport of herbicides.

The estimated masses of atrazine and alachlor deposited in precipitation during January through September 1991 are shown in figure 5. The deposition rates range from more than 200 $\mu g/m^2$ for both herbicides at a few sites in the Midwest to less than 10 $\mu g/m^2$ in the Northeast. Most of the deposition occurs during April through July. The deposition patterns are somewhat similar for the two herbicides, except in the western part of the study area (Nebraska and Kansas) where alachlor deposition is considerably less than atrazine deposition, reflecting the different usage patterns of these herbicides. The total mass of herbicides deposited in precipitation over the entire study area during 1991 is estimated to be 140,000 kg for atrazine and 82,000 kg for alachlor. These amounts represent about 0.6 and 0.4 percent of the atrazine and alachlor applied to cropland in the study area. These percentages are smaller than volatilization losses reported in the literature (Taylor and Glotfelty, 1988). There are many possible reasons for the relatively small measured amounts including dry deposition of herbicides between precipitation events, photochemical degradation of herbicides in the atmosphere, especially atrazine (Gates and others, 1991; Pelizzetti and others, 1990), atmospheric transport of herbicides beyond the study area, and inadequate analytical detection limits, especially for the ELISA methods.

The amount of atrazine deposited annually in precipitation appears to be somewhat smaller

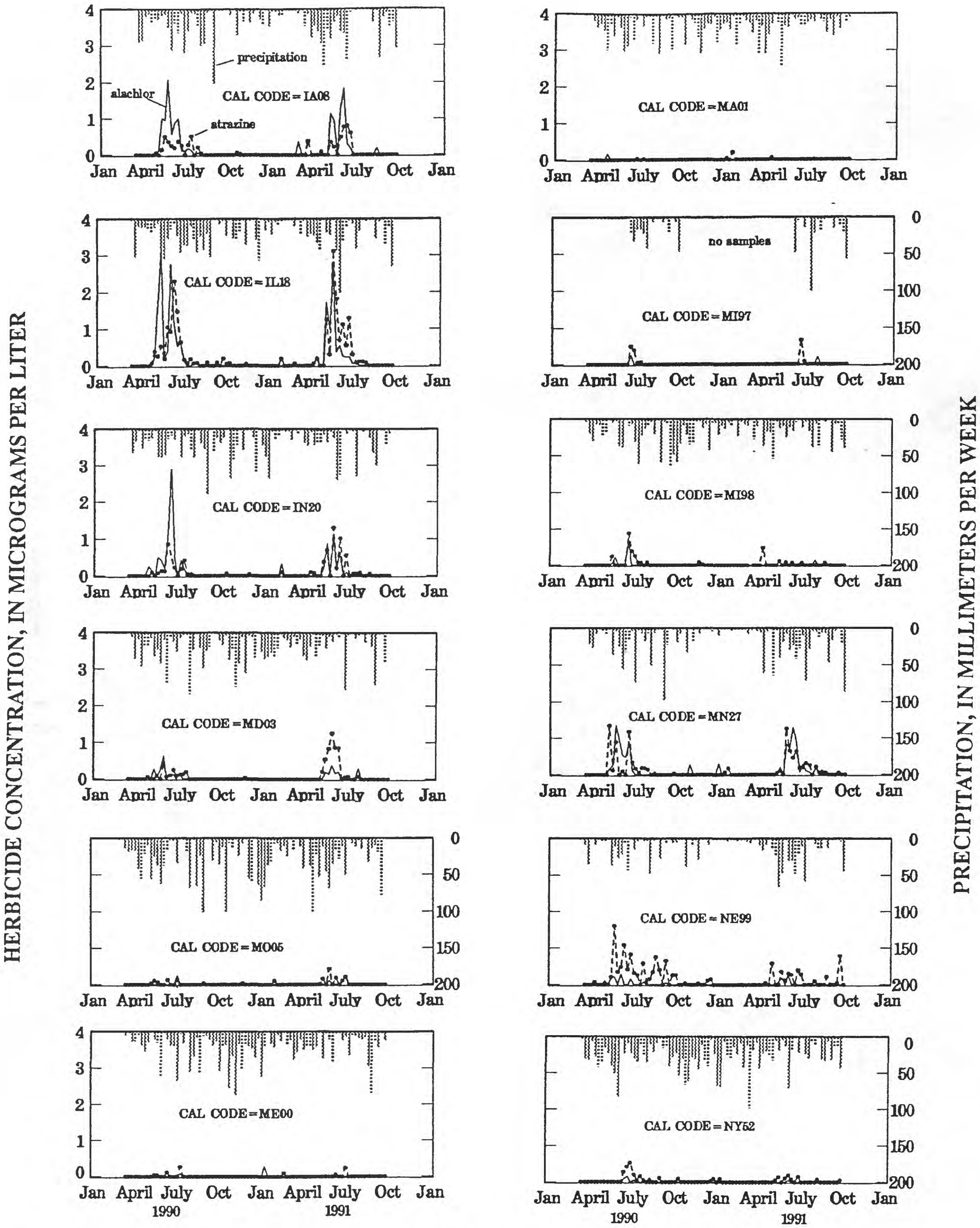

Figure 3. Atrazine and alachlor concentrations in precipitation, and precipitation amounts, March 1990 through September 1991 for selected atmospheric deposition sites in the midwestern and northeastern United States. (some herbicide concentrations estimated from Immunoassay-GC/MS regression equations; site locations shown in figure 1.)

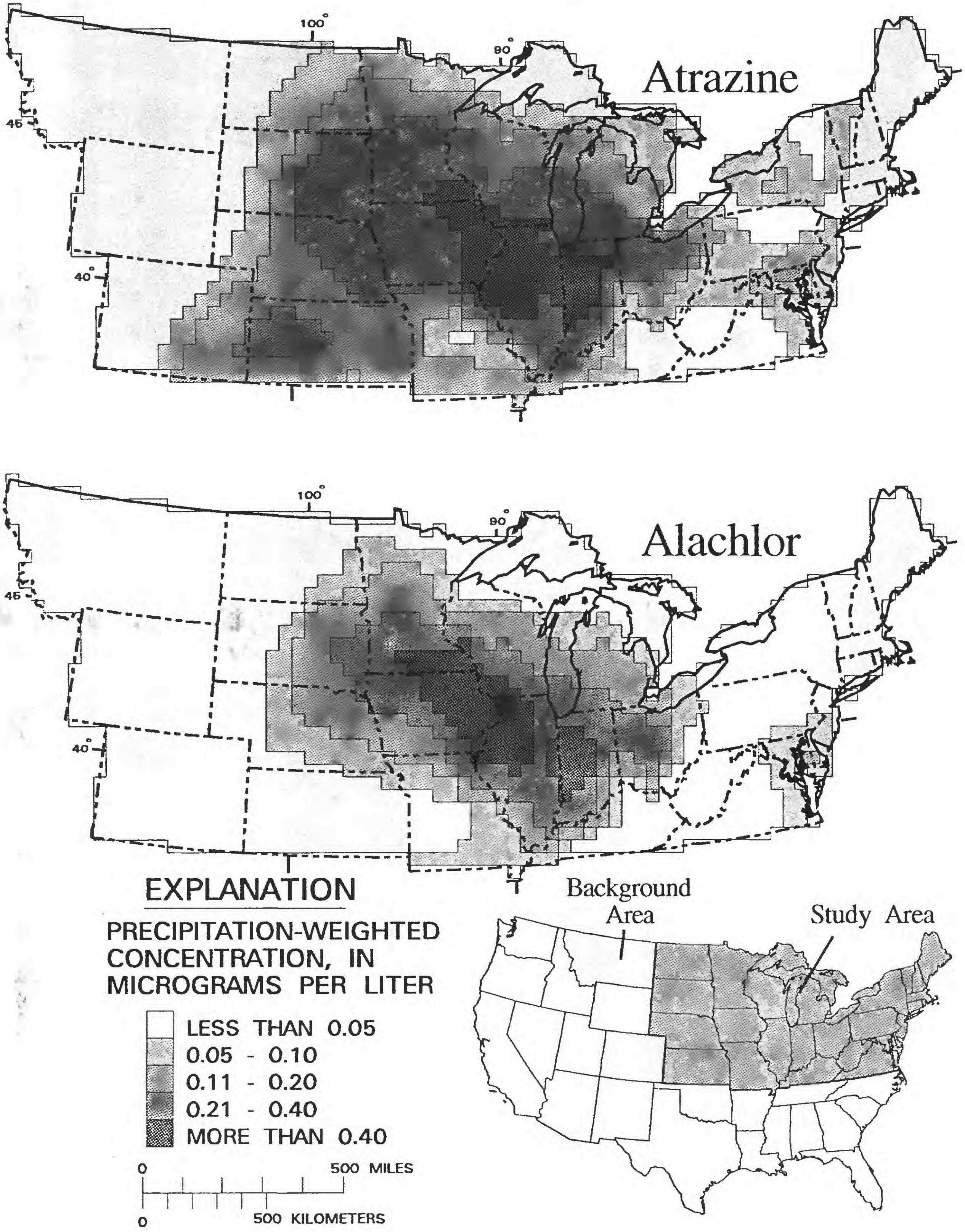

Figure 4.--Precipitation-weighted concentrations of atrazine and alachlor throughout the midwestern and northeastern United States, April 16 through July 16, 1991.

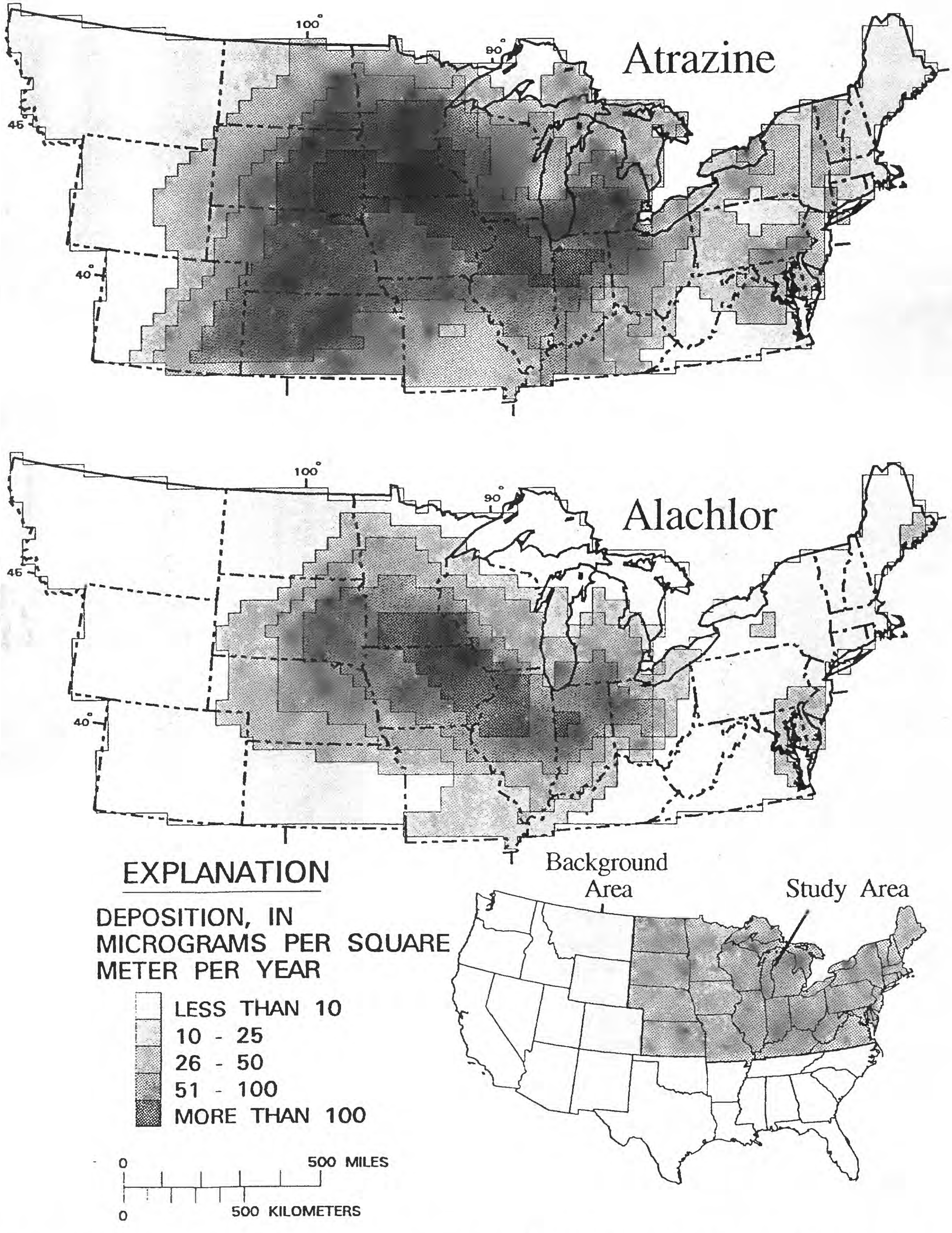

Figure 5.--Estimated deposition of atrazine and alachlor in precipitation throughout the midwestern and northeastern United States, January through September 1991.

than the amount transported to streams in surface runoff, whereas the annual deposition of alachlor appears to be somewhat larger than the amount transported in surface runoff. For example, in a recent study (Battaglin and others, 1993) estimated that 321,000 kg of atrazine and 33,700 kg of alachlor were discharged from the Mississippi River basin to the Gulf of Mexico in streamflow during a 1-year period, while the amounts of these herbicides used in the basin were approximately equal. In comparison, it is estimated from this study that about 110,000 kg of atrazine and 68,000 kg of alachlor are deposited annually on the Mississippi River basin in precipitation. These quantities could be considerably larger if the amounts of dryfall were known. These results indicate that more alachlor is deposited through precipitation in the Mississippi River basin than is transported out of the basin in streamflow, whereas the opposite relation could be true for atrazine.

## SUMMARY

Results from this study indicate that significant amounts of atrazine and alachlor are lost through volatilization and that these losses can be comparable to losses transported in surface runoff. Because of its comparatively higher volatility and shorter soil half-life, considerably more alachlor appears to volatilize than is transported by surface-runoff losses. Additional unmeasured amounts of herbicides were likely present in dry deposition. Further research is needed to determine the relative amounts of herbicides, insecticides, and other organic compounds, including photochemical degradation products, deposited in wet and dry deposition. Several other extensively used herbicides such as 2,4-D, EPTC, and trifluralin are considerably more volatile than atrazine and alachlor and might be present in atmospheric deposition in substantial amounts.

# REFERENCES

Aspelin, A.L., Grube, A.H., and Toria, R., 1992, Pesticide industry sales and usage, 1990 and 1990 and 1991 market estimates: U.S. Environmental Protection Agency, Washington, D.C., 37 p.

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.

Battaglin, W.A., Goolsby, D.A., and Coupe, R.H., 1993, Occurrence and annual 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.

Buser, Hans-Rudolf, 1990, Atrazine and other s-triazine herbicides in lake and in rain in Switzerland: Environmental Science and Technology, v. 24, no. 7, p. 1049-1058.

Capel, P.D., 1991, Wet deposition of herbicides in Minnesota, *in* Mallard, G.E., and Aronson, D.A., eds., U.S. Geological Survey Toxics Substances Hydrology Program: Proceedings of technical meeting, Monterey, California, March 11-15, 1991: Water Resources Investigations Report 91-4034, p. 334-337.

Eisenreich, S.J., Looney, B.B. and Thornton, J.D., 1981, Airborne organic contaminants in the Great Lakes ecosystem: Environmental Science and Technology, v. 15, no. 1, p. 30-38.

Gates, P.M., Foreman, W.T., DeGiacomo, W.G., and Anderson, L.G., 1991, Estimates of gas-phase photolysis for atrazine, simazine, alachlor, and metolachlor from effective absorption cross-section measurements, *in* Mallard, G.E., and Aronson, D.A., eds., U.S. Geological Survey Toxics Substances Hydrology Program: Proceedings of technical meeting, Monterey, California, March 11-15, 1993: Water-Resources Investigations Report 91-4034, p. 219-222.

Gianissi, L.P., and Puffer, C.M., 1991, Herbicide use in the United States: Resources for the Future, 127 p.

Glotfelty, D.E., Williams, G.H., Freeman, H.P., and Leech, M.M., 1990, Regional atmospheric transport and deposition of pesticides in Maryland, *in* Kurtz, D.L., ed., Long range transport of pesticides: Chelsea, Michigan, Lewis Publishers, p. 199-221.

Glotfelty, D.E., Seiber, J.N., and Lilijahl, L.A., 1987, Pesticides in fog: Nature, v. 325, p. 602-605.

Goolsby, D.A., Coupe, R.H., and Markovchick, D.J.,1991, Distribution of selected herbicides 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.

Hallberg, G.R., 1989, Pesticide pollution of groundwater in the humid United States: Agriculture, Ecosystems and Environment, v. 26, p. 299-367.

Holden, L.R., Graham, J.A., Whitmore, R.W., Alexander, W.J., Pratt, R.W., Liddle, S.K., and Piper, L.L., 1992, Results of the National Alachlor Well Water Survey: Environmental Science and Technology, v. 26, no.5, p. 935-943.

Kolpin, D.W., Burkart, M.R., and Thurman, E.M., in press, Herbicides and nitrate in near-surface aquifers in the mid-continental United States, 1991: U.S. Geological Survey Water Supply Paper 2413.

National Atmospheric Deposition Program, 1986, Directory of precipitation monitoring sites: National Resource Ecology Laboratory, Colorado State University, Fort Collins, Colo., v. 2.

National Atmospheric Deposition Program, 1992, NADP/NTN annual data summary, precipitation chemistry in the United States, 1991: National Resource Ecology Laboratory, Colorado State University, Fort Collins, Colo., 475 p.

Nations, B.K., and Hallberg, G.R., 1992, Pesticides in Iowa precipitation: Journal of Environmental Quality: v. 21, p. 486-92.

Pelizzetti, Ezio, Maurino, Valter, Minero, Claudio, Carlin, Vilma, Pramauro, Edmondo, Zerbinati, Orfeo, and Tosato, M.L., 1990, Photocatalytic degradation of atrazine and other s-triazine herbicides: Environmental Science and Technology, v. 24, p. 1559-1565.

Pomes, M.L., Thurman, E.M., and Goolsby, D.A., 1991, Comparison of microtitre-plate, enzyme-linked immunosorbent assay (ELISA) and gas chromatography/mass spectrometry (GC/MS) for analysis of herbicides in storm runoff samples, *in* Mallard, G.E., and Aronson, D.A., eds., U.S. Geological Survey Toxic Substances Hydrology Program: Proceedings of technical meeting, Monterey, California, March 11-15, 1991: Water Resources Investigations Report 91-4034, p. 572-575.

Richards, P.R., Kramer, J.W., Baker, D.B., and Kreiger, K.A., 1987, Pesticides in rainwater in the northeastern United States: Nature, v. 327, p. 129-131.

Taylor, A.W. and Glotfelty, D.E., 1988, Evaporation from soils and crops, *in* Grover, R., ed.,: Environmental chemistry of herbicides, v. 1, Boca Raton, Fla., CRC Press, p. 89-129.

Tierney, D.P., 1993, Biological assessment of atrazine and metolachlor in rainfall: Technical Paper 1-1993, Ciba-Geigy Corporation, Greensboro, N.C., 16 p.

Thurman, E.M., Goolsby, D.A., Meyer, M.T., and Kolpin, D.W., 1992, A reconnaissance study of herbicides and their metabolites in surface water of the Midwestern United States

Trevisan, M., Montepiani, C., Ragozza, L., Bartoletti, C., Ioannilli, E., and Del Re, A.A.M., 1993, Pesticides in rainfall and air in Italy: Environmental Pollution, v. 80, p. 31-39.

Williams, A.L., Sweet, C.W., and Peters, Cathy, 1992, Herbicide concentrations in air and rain: *in* Proceedings of the 85th Annual Meeting and Exhibition of the Air and Waste Management Association, 1992, p. 2-12.

Wu, T.L., 1981, Atrazine residues in estuarine water and the areal deposition of atrazine into Rhode River, Maryland: Water, Air, and Soil Pollution, v. 15, p. 173-184.