

Herbicides and Nitrate in Near-Surface Aquifers in the Midcontinental United States, 1991



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Cover photograph. A scene from northwest Iowa shows a common situation in the midcontinental United States in which agricultural land use occurs close to a well.

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By DANA W. KOLPIN, MICHAEL R. BURKART, and
E. MICHAEL THURMAN

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CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
<i>Length</i>		
foot (ft)	0.3048	meter
micrometer (µm)	0.0000394	inch
mile (mi)	1.609	kilometer
<i>Area</i>		
square mile (mi ²)	2.59	square kilometer
<i>Mass</i>		
pound	0.4536	kilogram
pound per square mile	0.1753	kilogram per square kilometer
ton per square mile (ton/mi ²)	0.3503	megagram per square kilometer
ton per year	0.9072	megagram per year

Milligram per liter (mg/L) is a unit expressing the concentration of a chemical constituent in solution as weight (milligram) of solute per unit volume (liter) of water.

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

Herbicides and Nitrate in Near-Surface Aquifers in the Midcontinental United States, 1991

By Dana W. Kolpin, Michael R. Burkart, and E. Michael Thurman

Abstract

The occurrence and distribution of selected herbicides, atrazine metabolites, and nitrate were determined for near-surface aquifers (within 50 feet of land surface) in the corn- and soybean-producing region of the midcontinental United States. The study region included all or parts of Illinois, Indiana, Iowa, Kansas, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, South Dakota, and Wisconsin. Water samples were collected during the spring and summer of 1991 from 303 wells completed in near-surface unconsolidated and near-surface bedrock aquifers. At least one herbicide or atrazine metabolite was detected in 24 percent of 579 water samples analyzed for herbicides, based on a reporting limit of 0.05 microgram per liter. However, no herbicide concentration exceeded the U.S. Environmental Protection Agency's maximum contaminant levels or health advisory levels for drinking water. The most frequently detected herbicide compound was desethylatrazine, an atrazine metabolite (18.1 percent), followed by atrazine (17.4 percent); deisopropylatrazine, an atrazine metabolite (5.7 percent); prometon (5.0 percent); metolachlor (2.7 percent); alachlor (1.7 percent); simazine (1.0 percent); metribuzin (1.0 percent); and cyanazine (0.7 percent). The herbicides ametryn, prometryn, propazine, and terbutryn were not detected during this study. Nitrate concentrations equal to or greater than 3.0 milligrams per liter (excess nitrate) were detected in 29 percent of the 599 nitrate analyses, and ammonium concentrations equal to or greater than 0.01 milligram per liter were detected in 78 percent of the 584 ammonium analyses. Nitrate concentrations equal to or

greater than the U.S. Environmental Protection Agency's maximum contaminant level for drinking water of 10 milligrams per liter were found in 6 percent of the samples.

The frequency of herbicide detection was, in part, affected by the analytical method's reporting limit. Results from this study show that the frequency of atrazine detection increases as the reporting limit decreases. Herbicide metabolite concentrations are critical to understanding the detection of herbicide residues. The frequency of detection of atrazine residue (atrazine + desethylatrazine + deisopropylatrazine) was 22.1 percent, which was more than the frequency of detection of atrazine alone (17.4 percent).

Prometon was detected more frequently than every other herbicide except atrazine. The prometon appears to be derived from areas of nonagricultural land use, such as golf courses and residential areas. Herbicides and excess nitrate were both rarely detected in the eastern part of the study region, even though this is an area of intense herbicide and nitrogen-fertilizer use.

Hydrogeologic factors, land use, agricultural practices, local features, and water chemistry were analyzed for possible relation to herbicide and excess-nitrate detections. Herbicides and excess nitrate were detected more frequently in near-surface unconsolidated aquifers than in near-surface bedrock aquifers. The depth to the top of the aquifer was inversely related to the frequency of detection of herbicides and excess nitrate. The proximity of streams to sampled wells also affected the frequency of herbicide detection. Significant seasonal differences were determined for the frequency of herbicide detection, but not for the frequency of excess nitrate.

INTRODUCTION

Crop yields in the United States have increased in recent decades largely because of the application of chemical nutrients to increase soil fertility and the use of pesticides to control competing vegetation and destructive insects. This intensive application of chemical nutrients and pesticides, particularly herbicides, has created concern and awareness of these compounds as a nonpoint source of contamination in the Nation's surface- and ground-water resources. Because it is an area of intense agriculture, the midcontinental United States has become a focus for research on agricultural chemical contamination in surface and ground water. Almost 60 percent of the pesticides (Gianessi and Puffer, 1990) and nitrogen fertilizers (U.S. Environmental Protection Agency, 1990) used in the United States are applied to cropland in 12 midcontinental States (table 1). The counties that have the greatest percentage of land receiving chemical treatment coincide with the corn- and soybean-producing region of the midcontinent (fig. 1).

In 1991, the U.S. Geological Survey (USGS) began a reconnaissance study of the distribution of herbicides and nitrogen compounds (nitrate plus nitrite, hereafter referred to as "nitrate") in ground water in the midcontinental region of the United States. This reconnaissance study is complementary to the National Pes-

ticide Survey (NPS; U.S. Environmental Protection Agency, 1992a) and the National Alachlor Well Water Survey (NAWWS; Holden and others, 1992), which are discussed in more detail in the "Previous Investigations" section of this report. The NPS and NAWWS were primarily designed to estimate the number of drinking water wells contaminated with herbicides and nitrate out of the total population of wells of interest. In contrast, the USGS reconnaissance was designed to determine the hydrogeologic, spatial, and seasonal distribution of herbicides and nitrate in a specified set of aquifers. Other objectives of this study were to (1) determine the statistical relations of herbicide and nitrate to natural and human factors, and (2) obtain data on herbicide and herbicide metabolite concentrations in ground water from geographic areas where few data existed. The USGS reconnaissance was carefully designed in terms of defining the specific population of aquifers, sample collection protocol, quality assurance program, and ancillary data collection (Kolpin and Burkart, 1991).

Purpose and Scope

This report summarizes the geographic and seasonal distributions of selected herbicides and nitrate detected in near-surface aquifers (top of aquifer less

Table 1. Summary of selected herbicide and nitrogen-fertilizer use on crops in the midcontinental United States, 1987–89

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

State	Herbicide use ¹ (10 ³ pounds of active ingredient per year)						Nitrogen fertilizer ² (10 ³ tons per year)
	Atrazine	Metolachlor	Alachlor	Metribuzin	Simazine	Cyanazine	
Illinois	8,504	8,083	7,960	562	309	3,071	988
Indiana	5,684	3,457	6,930	451	76	1,700	447
Iowa	5,584	8,475	6,440	296	<1	3,690	953
Kansas	4,702	2,199	1,930	54	45	206	568
Michigan	2,708	2,067	1,546	184	172	549	225
Minnesota	1,502	2,445	3,979	144	<1	2,808	573
Missouri	3,070	1,639	1,779	172	4	1,163	429
Nebraska	7,062	1,948	3,757	162	14	1,751	726
North Dakota	174	116	113	12	--	249	214
Ohio	3,846	4,005	3,674	712	273	1,580	326
South Dakota	488	965	1,891	41	73	316	200
Wisconsin	2,685	1,379	1,284	79	1	1,658	242
Total	46,009	36,778	41,283	2,869	968	18,741	5,891

¹Gianessi and Puffer (1990).

²U.S. Environmental Protection Agency (1990).

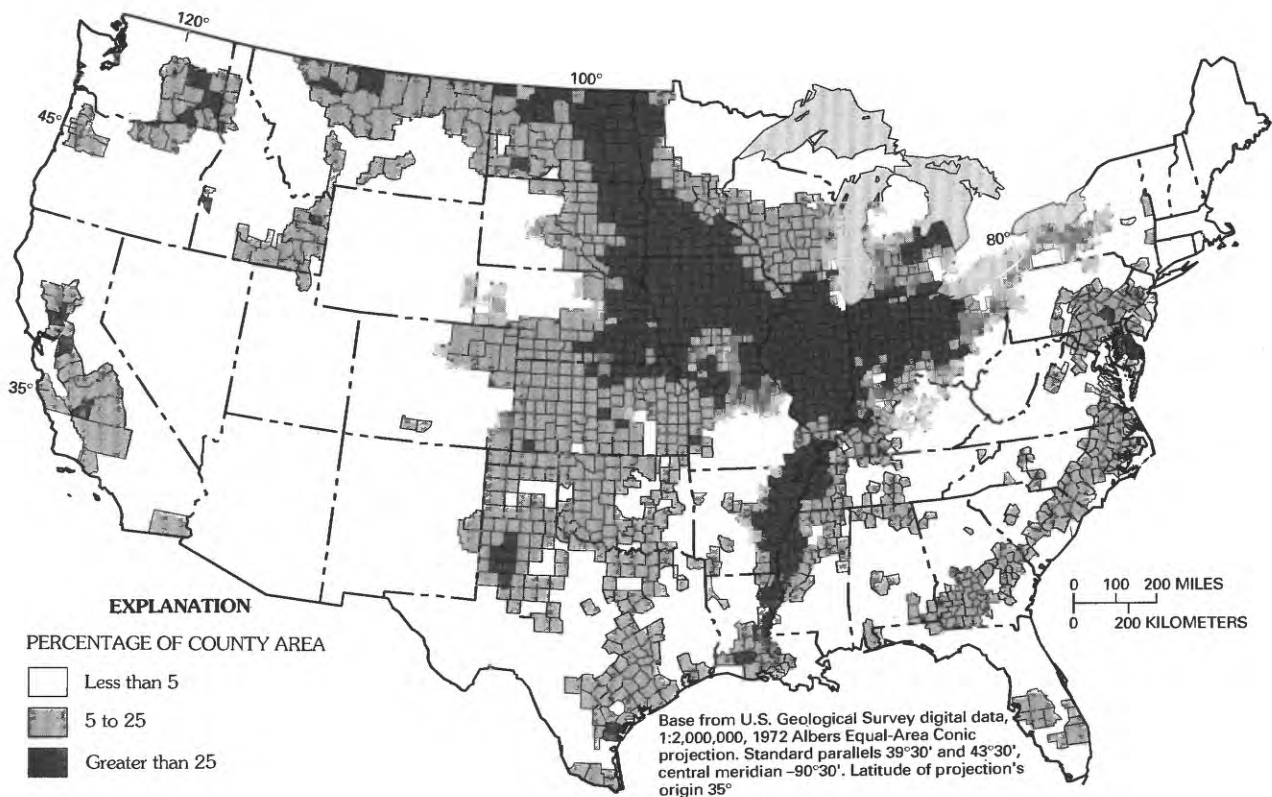


Figure 1. Percentage of area, by county, treated with herbicides to control weeds in crops in the contiguous United States (data from U.S. Bureau of the Census, 1989).

than 50 ft below land surface) in the midcontinental United States, and analyzes how these distributions are affected by hydrogeologic factors, land use, agricultural practices, local features, and water chemistry. The report discusses only near-surface aquifers of the midcontinent, as these are the aquifers most likely to be affected by applications of chemicals over large areas. It does not consider deeper aquifers or those in other regions.

Previous Investigations

Results of several statewide and national surveys of aquifers and wells have produced a variety of conclusions regarding the detection of herbicides in ground water (fig. 2). For example, the results for atrazine, a compound common to all of these surveys, show detections ranging from less than 1 percent to 47 percent. The differences among these surveys can be attributed to variations in laboratory reporting limits, aquifers of interest, wells of interest, well selection criteria, geography, time of collection, and objective of study. These differences make it difficult to combine

the surveys to assess the extent of herbicide contamination of aquifers in the midcontinent.

The recently completed NPS and NAWWS provide assessments of selected herbicides and nitrate in similar populations of drinking-water wells throughout the Nation. In the NPS, 1,349 public-supply and domestic wells were sampled between 1988 and 1990, and the samples were analyzed for pesticides, pesticide metabolites, and nitrate (U.S. Environmental Protection Agency, 1992a). The study estimated that water from 9.5 percent of the public-supply wells and 3.6 percent of the domestic wells in the Nation would contain one or more herbicides, and that water from 1.2 percent of the public-supply wells and 2.4 percent of the domestic wells would contain concentrations of nitrate that exceed the U.S. Environmental Protection Agency's maximum contaminant level of 10 mg/L. The estimates of herbicide occurrence from the NPS provide useful information at the national level against which regional results from other studies can be compared.

The NAWWS had a purpose and a design similar to those of the NPS. In the NAWWS (Holden and others, 1992), the specified population of wells to be studied consisted of all domestic wells located in counties where alachlor was sold in 1986. Because of this pop-

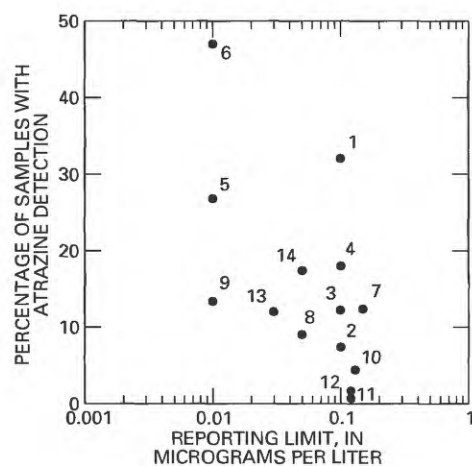


Figure 2. Frequency of atrazine detection compared to analytical reporting limits for selected studies in the midcontinental United States.

EXPLANATION				
Reference	Wells or aquifers of interest	States	Number of wells	Percent of atrazine detection
1 Chen and Druliner, 1987.	Irrigation, domestic, livestock	Nebr.	57	32.0
2 Stullken and others, 1987.	Irrigation, domestic, public supply, stock	Kans.	27	7.4
3 Breuer, 1988	Public supply	Iowa	849	12.2
4 Detroy and others, 1988.	Public supply	Iowa	355	18.0
5 Klaseus and others, 1988.	Public supply	Minn.	400	26.8
6 —do.—	Irrigation, domestic	Minn.	100	47.0
7 LeMasters and Doyle, 1989.	Dairy farm	Wisc.	534	12.4
8 Voelker, 1989	Public supply	Ill.	330	9.0
9 Exner and Spalding, 1990.	Irrigation, domestic, public supply, stock, observation	Nebr.	2260	13.4
10 Kross and others, 1990.	Domestic	Iowa	686	4.4
11 U.S. Environmental Protection Agency, 1992a.	Domestic	All	752	0.7
12 —do.—	Public supply	All	540	1.7
13 Holden and others, 1992.	Domestic wells, where alachlor sold	All	1430	12.0
14 This study	Near-surface aquifers	(¹)	303	17.4

¹ Illinois, Indiana, Iowa, Kansas, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, South Dakota, and Wisconsin.

ulation, the midcontinent was a large part of the study area. For this study, samples from 1,430 of the estimated 6 million domestic wells in the target area were analyzed for five herbicides (alachlor, atrazine, cyanazine, metolachlor, and simazine) between 1988 and 1989. Estimates from this study are that 12 percent of all domestic wells in the target area would have one or more of the five herbicides detected and that 4.9 percent would have concentrations of nitrate greater than 10 mg/L.

The NPS and the NAWWS are particularly important for understanding the extent to which drinking-water wells are contaminated with herbicides and nitrate nationally. Results of the NPS and the NAWWS can be compared with the USGS reconnaissance; however, these surveys were substantially different in study design, objective, aquifers of interest, and wells of interest.

Hydrogeology of the Study Region

The study region (fig. 3) includes approximately 467,000 mi² in all or parts of Illinois, Indiana, Iowa, Kansas, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, South Dakota, and Wisconsin. It

includes the contiguous counties where at least 25 percent of the cropland is in corn or soybean production (Gianessi and Puffer, 1988). In some counties of the study region, as much as 70 percent of the land surface is used for corn and soybean production. Consequently, ground water in the study region is expected to have the greatest potential to be affected by the application of herbicides and nitrogen fertilizer used for production of these two crops.

The USGS reconnaissance specifically targets the near-surface aquifers in the study region, which are defined as aquifers whose tops are within 50 ft of the land surface, regardless of whether the aquifer material is saturated or unsaturated. Depth to the top of the aquifer was used as a defining factor because preliminary research indicated that this depth may be an important hydrogeologic indicator of herbicide presence in aquifers (Kolpin and Burkart, 1989).

In this report, the near-surface aquifers of the study region are classified as either unconsolidated or bedrock. The distinction between these two types of aquifers is based on differences in lithology, well-completion methods, flow-system characteristics, and porosity. Both near-surface bedrock and unconsolidated aquifer classes are present discontinuously throughout the study region. Because many of these

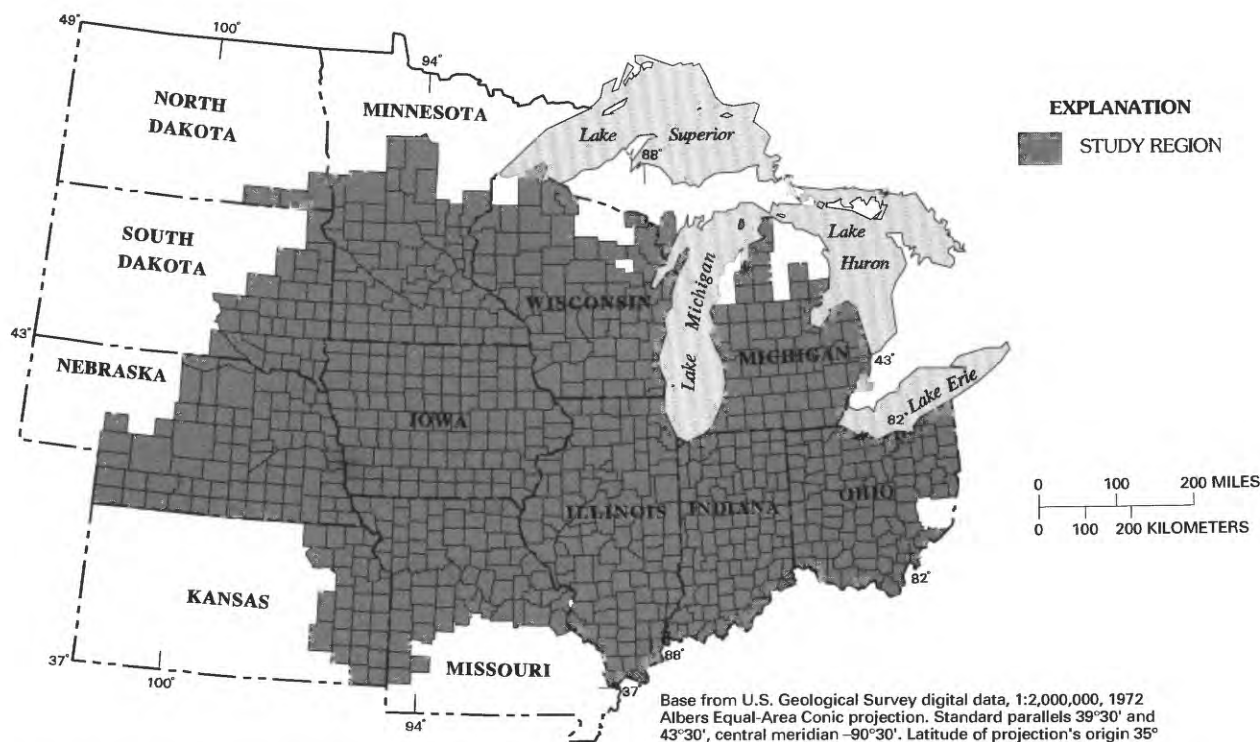


Figure 3. Study region in the midcontinental United States.

aquifers are at the land surface, they are the dominant parent material of the soils being farmed in many areas. They also are the most convenient, inexpensive ground-water resource to use for domestic and public water supplies.

Unconsolidated aquifers are composed of sand and gravel deposited by glacial meltwater streams or of alluvium deposited in and near modern stream channels. Meltwater, or outwash aquifers can cover extensive areas, as in Minnesota and Wisconsin, or form relatively local aquifers, as in many other parts of the study region. Alluvial aquifers, generally long and narrow because of their fluvial origin, are present throughout the study region. Unconsolidated aquifers have local flow systems with recharge and discharge areas relatively near each other. Many are at the land surface, providing the potential for direct recharge from the land surface over the entire aquifer. These aquifers provide major sources of water for a variety of uses.

Near-surface bedrock aquifers of the study region exist in areas where sandstone, limestone, or dolomite form the uppermost bedrock. In many places, these bedrock aquifers are of regional importance and have substantial recharge potential in areas where they are at or near the land surface. Unlike unconsolidated

aquifers, the potential area for direct recharge of bedrock aquifers is a small fraction of the areal extent of these aquifers. Some of these bedrock aquifers have a large amount of secondary porosity.

STUDY DESIGN AND METHODS

A work plan outlining the procedures for well selection, sample collection, and quality assurance was prepared to ensure the validity of collected data and of subsequent interpretations (Kolpin and Burkart, 1991). The well-selection process produced sampling sites that are geographically and hydrogeologically representative of near-surface aquifers in the corn- and soybean-producing region of the midcontinent. The sample-collection protocol ensured that water collected was representative of the aquifer at that site. The quality assurance program documented the accuracy of the data through tests of onsite-sampling and laboratory-analysis procedures.

Well Selection

Selected wells were distributed geographically and hydrogeologically by State, aquifer class, and rela-

tive depth within the aquifer. Each State was allocated a number of wells proportional to the area in corn and soybean production and to the area underlain by near-surface aquifers in the study region. Within each State, wells were distributed proportionally by aquifer class, based on the area of near-surface unconsolidated and near-surface bedrock aquifers. To obtain a vertical distribution of wells in each aquifer class, about 50 percent of the wells selected was completed in the upper half of the near-surface aquifers, and about 50 percent was completed in the lower half. Because the intent of the USGS reconnaissance was to obtain samples representative of the aquifers, wells were selected without regard to well type (public supply, domestic, observation, and so on).

To be selected, a well had to meet minimum requirements for hydrogeologic, land-use, and well-construction information. Wells were only selected if they were completed in a single near-surface aquifer, if at least 25 percent of the land in a 2-mi radius around the well had been planted in corn or soybeans during the previous growing season, and if the depth of the well was documented by a driller's or lithologic log. Well-selection procedures were designed to obtain an unbiased geographic distribution across the midcontinent. This was accomplished by randomly selecting counties in each State in the study region and initiating a search for wells near the center of each county. The first well identified that met the criteria for selection was designated as the primary well; any additional wells were designated as alternate wells. If no wells that met the selection criteria were found in a county, the search moved to the next randomly selected county until the number of wells allocated to the State was selected. A complete description of the criteria and procedures for well selection is presented by Kolpin and Burkart (1991).

Altogether, 303 wells were selected and sampled for the USGS reconnaissance. Of these selected wells, 151 were domestic wells, 92 were public supply, 34 were observation, and 26 were other types of wells (stock, irrigation, industrial, for example). Also, 198 were completed in near-surface unconsolidated aquifers and 105 were completed in near-surface bedrock aquifers. The well depths ranged from 8 to 750 ft below land surface; the median well depth was 70 ft.

Data Collection

All water samples were collected by USGS personnel trained in a variety of water-quality sampling procedures. The sampling equipment was constructed of materials that would not leach or adsorb organic

compounds. All wells were purged to chemical stability before water samples were collected to ensure that a representative sample was obtained. Chemical stability was reached when successive measurements of specific conductance, pH, and water temperature made at 5-minute intervals differed by less than allowable limits (Kolpin and Burkart, 1991). Water samples collected for herbicide analysis were filtered through a 1.0- μm glass-fiber filter into amber baked-glass bottles and immediately chilled. Water samples for nutrient analysis were filtered through a 0.45- μm acetate filter into opaque polyethylene bottles, preserved with mercuric chloride (40 mg/L), and immediately chilled. All collecting equipment was decontaminated between the collection of individual samples and at the end of the day to prevent cross-contamination between samples and wells.

Water samples were collected from 300 wells in March or April, which represented preplanting conditions. From these water samples, 299 herbicide, 300 nitrate, and 285 ammonium analyses were obtained. Water samples were collected from 299 wells in July or August, which represented postplanting conditions. From these water samples, 280 herbicide, 299 nitrate, and 299 ammonium analyses were obtained. Four wells sampled in March or April could not be resampled in July or August, but three substitute wells were used. Ancillary data on land use, such as land in pasture or urban residential, were estimated in broad percent classes (0, 1 to 25, 26 to 50, 51 to 75, and 76 to 100 percent) by visual inspection at each well. Local features, such as landfills and streams, that could affect water quality also were noted at the time of sampling. These ancillary data were summarized for three distances from the well: less than 100 ft, less than 0.25 mi, and between 0.25 and 2.0 mi. However, it is recognized that recharge to the aquifer in which a well is completed could take place more than 2 mi from the well. Topographic maps of the area and conversations with land and well owners facilitated the collection of the ancillary data. Activities involving the handling of herbicides at or near the well site also were recorded.

Laboratory Methods

Analyses for herbicides were done in the USGS Laboratory in Lawrence, Kans., by gas chromatography/mass spectrometry, using solid-phase extraction techniques described by Thurman and others (1990). Samples were analyzed for alachlor, ametryn, atrazine, cyanazine, metolachlor, metribuzin, prometon, prometryn, propazine, simazine, terbutryn, and the atrazine metabolites, desethylatrazine and deisopropylatrazine.

The laboratory reporting limit for all herbicides and atrazine metabolites was 0.05 µg/L. A detection of any of these compounds is defined as a concentration equal to or greater than the laboratory reporting limit.

Analyses for dissolved nitrogen and phosphorus compounds were done by the USGS National Water Quality Laboratory in Arvada, Colo., using an automated colorimetric procedure (Fishman and Friedman, 1989). The results of the analyses of nitrogen compounds were reported as nitrogen and included dissolved nitrite as nitrogen, dissolved nitrite plus nitrate as nitrogen, and dissolved ammonium as nitrogen. Phosphorus results included dissolved orthophosphate reported as phosphorus. Laboratory reporting limits were 0.01 mg/L for all compounds except nitrite plus nitrate, which was 0.05 mg/L. Because nitrite concentrations were negligible in all samples for this study, the concentration of nitrite plus nitrate is referred to as nitrate in this report.

Quality Assurance

A quality assurance program was used to determine the effect, if any, of field equipment and procedures on the herbicide and nitrate concentrations detected in the water samples. Field blanks, made from organic-free water, were submitted as herbicide and nutrient samples from 16 randomly predetermined sites, with at least one herbicide and one nutrient blank per State. Field blanks were subject to the same sample processing, handling, and equipment as the regular samples. Duplicate herbicide and nutrient samples were collected at 33 predetermined sites to determine the reproducibility of sample processing and analytical methods. Field duplicates were water samples collected along with the regular samples and processed as if they had been obtained at a unique site. Thirty blind spikes of known herbicide concentration were submitted to the laboratory. Concentrations of the herbicide spikes were 0.50, 1.0, or 2.0 µg/L.

The results of the herbicide field blanks showed no reportable concentrations of herbicides or atrazine metabolites. Only 3 of 16 nitrate field blanks contained reportable concentrations of nitrate, none of which exceeded 0.08 mg/L. Therefore, the field-equipment decontamination procedures were shown to be adequate to prevent cross-contamination of herbicides and nitrate between samples and wells.

The 33 herbicide field duplicates were each analyzed for 11 herbicides and 2 atrazine metabolites—a total of 429 determinations. In only six of these determinations did the concentration in the duplicate differ from that of the regular sample by more than 20 per-

cent. Of these six cases, four had herbicide or atrazine metabolite concentrations at or near the laboratory reporting limit of 0.05 µg/L. Only two nitrate field duplicates differed from the regular sample by more than 20 percent. The results from the field duplicates verify the reproducibility of sample processing and laboratory results.

Recoveries from herbicide blind spikes submitted during the preplanting sampling period had quartiles (25th, 50th, and 75th percentile) of 90, 100, and 112 percent. Blind spikes submitted during the postplanting sampling period had quartiles of 105, 118, and 141 percent. A careful examination of the herbicide results from both sampling periods showed that the higher recovery during the postplanting period did not affect the detection of herbicides but could have caused inflated readings in a few samples that had reported concentrations greater than 0.5 µg/L.

Statistical Methods

Nonparametric statistical methods were used to analyze the data collected. These methods were appropriate because the data were not normally distributed, and a large percentage of the data were censored; that is, many of the determinations found concentrations to be less than the reporting limit. Nonparametric statistics have the advantage of not being overly affected by outliers in the data because the ranks of the data are used in the statistics rather than the actual concentrations. The nonparametric statistical methods used included the Spearman's rank correlation, the Mann-Whitney rank sum test, and the Kruskal-Wallis test (Helsel and Hirsch, 1992). Spearman's rank correlation is a measure of the monotonic relation between two continuous variables. The Mann-Whitney test is the nonparametric equivalent of a two-sample t-test, in which medians of two groups of data are tested for the statistical significance of their difference, accounting for variability in each of the groups. The Kruskal-Wallis one-way analysis by ranks is an extension of the Mann-Whitney rank sum test that can test for differences in the medians of two or more groups.

A significance level of 0.05 was used for all statistical tests in this study. This acceptable probability of error ($p=0.05$) means that there is 1 chance in 20 that the statistical test reported a significant difference when one did not exist. Reporting the p -value associated with a test shows the level of certainty that a statistical difference exists. For example, a p -value of 0.01 corresponds to 1 chance in 100 that the test reported a statistical difference when one did not exist.

Thus, the smaller the *p*-value, the greater is the certainty that a reported statistical difference is real.

Contingency tables were used to measure the statistical association between factors that are grouped into categories of values. The following example illustrates the use of a 2×2 contingency table to measure the association of herbicide detection or nondetection with aquifer class (unconsolidated or bedrock).

	Unconsolidated aquifer	Bedrock aquifer
Herbicide detected	104 28.0%	35 16.8%
Herbicide not detected	267 72.0%	173 83.2%

This table results in four groups representing all possible combinations of the factors being compared. This example shows that 28.0 percent of the samples (104 of 371) from unconsolidated aquifers had herbicide or atrazine metabolites greater than or equal to the reporting limit of 0.05 µg/L. A statistical test is made to determine if the percent detections by aquifer class are significantly different. The bar charts for most of the figures included in this report are derived from the percentages calculated in the contingency tables.

OCCURRENCE OF HERBICIDES AND ATRAZINE METABOLITES

To determine the occurrence of herbicides and atrazine metabolites in water in near-surface aquifers of the midcontinent under both preplanting and postplanting conditions, 579 water samples from 303 wells were collected for analysis during 1991 (fig. 4); 299 of these samples were collected during March or April (preplanting), and 280 samples were collected during July or August (postplanting).

Herbicides or atrazine metabolites were detected in 24 percent of the 579 samples collected for analysis (table 2). A herbicide detection is defined as the presence of any herbicide or atrazine metabolite at a concentration equal to or greater than the analytical reporting limit of 0.05 µg/L. No herbicide concentration exceeded the U.S. Environmental Protection Agency's maximum contaminant level or health advisory level for drinking water (table 2). However, two samples had an atrazine residue (atrazine + desethylatrazine + deisopropylatrazine) that exceeded 3 µg/L.

The most frequently detected compound in the samples analyzed for herbicides and atrazine metabolites was desethylatrazine, which was detected in

18.1 percent of the samples. It was followed by atrazine (17.4 percent), deisopropylatrazine (5.7 percent), prometon (5.0 percent), metolachlor (2.7 percent), alachlor (1.7 percent), simazine (1.0 percent), metribuzin (1.0 percent), and cyanazine (0.7 percent) (table 2). The herbicides ametryn, prometryn, propazine, and terbutryn were not detected above reporting limits. Even among those concentrations that were above the analytical reporting limit, most were less than 0.5 µg/L (fig. 5), and only 11 concentrations (out of more than 7,500 determinations) exceeded 1.0 µg/L; however, a desethylatrazine concentration of 2.32 µg/L was the largest reported concentration of any compound (table 2).

A comparison of herbicide results from the USGS reconnaissance with the results from the NPS and the NAWWS shows a substantial difference in the frequency of herbicide detection. Estimates for the NPS indicated that water in 9.5 percent of public-supply and 3.6 percent of the domestic wells in the Nation would have contained one or more herbicides (U.S. Environmental Protection Agency, 1992a). The estimates for the NAWWS indicated that water in 12 percent of all domestic wells in the target area would have contained one or more herbicides (Holden and others, 1992). The USGS reconnaissance showed that water from 28.7 percent of the 303 wells sampled contained one or more herbicides or atrazine metabolites. The large difference in frequency of herbicide detection between the USGS reconnaissance and the NPS and NAWWS studies could be attributable to several factors. These include differences in well-selection methods, inclusion of atrazine metabolites in the USGS reconnaissance, and differences in analytical reporting limits. Wells sampled in the USGS reconnaissance were selected from near-surface aquifers in an area of intense row-crop agriculture. These aquifers are believed to be the ones most susceptible to nonpoint-source contamination. The detection of herbicides is more likely in these aquifers than in aquifers in nonagricultural areas or in deeper aquifers. This study also included analyses for two atrazine metabolites, one of which, desethylatrazine, was the most frequently detected compound. The NPS did analyze for desethylatrazine but had a much larger reporting limit (2.2 µg/L). Analyses for atrazine metabolites were not included in the NAWWS. Finally, the reporting limit for herbicides analyzed in the USGS reconnaissance was 0.05 µg/L. This is comparable to the reporting limit in the NAWWS (0.03 µg/L) but is less than one-half the reporting limit for the NPS (0.12 µg/L for atrazine) and could partially account for a larger frequency of herbicide detection than reported in the NPS. Thus,

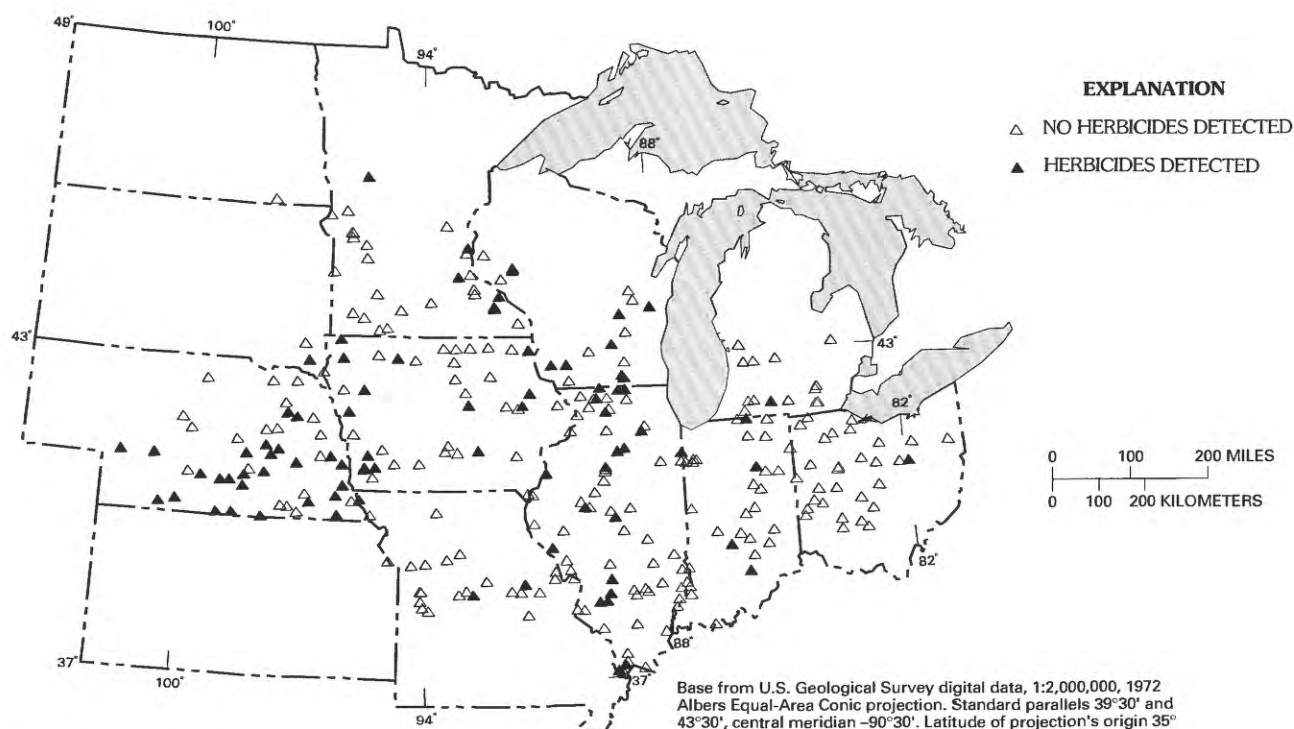


Figure 4. Location of sampled wells and herbicide detections.

Table 2. Frequency of herbicide and atrazine metabolite detection in preplanting and postplanting ground-water samples from the midcontinental United States, 1991

[µg/L, micrograms per liter; *, none established]

Compound	Frequency of detection ¹ (percent)			Maximum contaminant level ² (µg/L)	Health advisory level ³ (µg/L)	Maximum concentration (µg/L)
	Preplanting (299 analyses)	Postplanting (280 analyses)	All samples (579 analyses)			
Any herbicide or metabolite	20.4	27.8	24.0	*	*	2.32
Desethylatrazine	15.4	21.1	18.1	*	*	2.32
Atrazine	14.7	20.4	17.4	3.0	3.0	2.09
Deisopropylatrazine	4.0	7.5	5.7	*	*	.60
Prometon	4.0	6.1	5.0	*	*	.86
Metolachlor	3.0	2.5	2.7	*	100	1.46
Alachlor	2.3	1.1	1.7	2.0	*	1.05
Simazine7	1.4	1.0	⁴ 4.0	⁴ 4.0	.27
Metribuzin7	1.4	1.0	*	200	.57
Cyanazine3	1.1	.7	*	⁴ 1.0	.68

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

²U.S. Environmental Protection Agency (1991a).

³U.S. Environmental Protection Agency (1991b).

⁴U.S. Environmental Protection Agency (1992b).

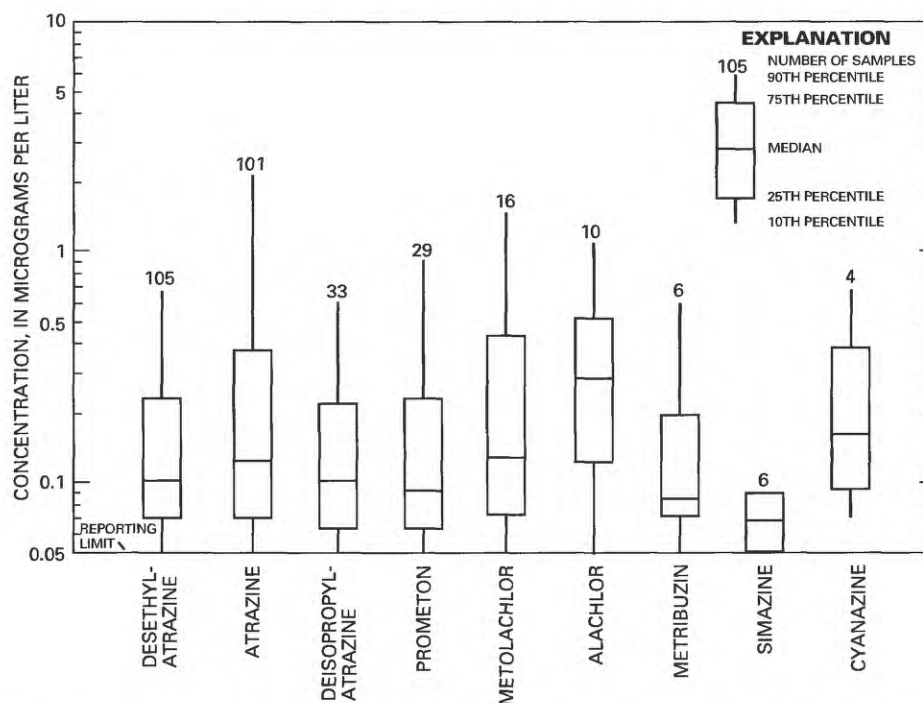


Figure 5. Measurable concentrations (equal to or greater than the analytical reporting limits) of herbicides and atrazine metabolites in ground-water samples from the midcontinental United States, 1991.

while the objectives of the three studies are complementary, direct comparisons of the results need to be made with a clear understanding of the differences between the studies.

In the USGS reconnaissance, any type of existing well completed in near-surface aquifers of the study region that met the selection criteria could potentially be selected for sampling. The selection procedure yielded 92 public-supply wells, 151 domestic wells, and 60 wells of other types. To determine if the multiple well types sampled in the study could have affected the herbicide results, 30 public-supply wells, 30 domestic wells, and 30 wells of other types were selected to obtain both a random and geographically representative distribution across the study region. A Kruskal-Wallis test indicated no significant difference ($p=0.20$) in the frequency of herbicide detection between the three sets of wells.

Data from the USGS reconnaissance indicate that the frequency of herbicide detection is, in part, a function of the analytical reporting limit. To illustrate this point, the data for atrazine detections were plotted as a function of several assumed reporting limits (fig. 6). The frequency of atrazine detections would have been decreased about 50 percent had the reporting

limit for atrazine been 0.1 µg/L instead of 0.05 µg/L. The data show an increase in frequencies of atrazine detection as the reporting limit decreases. At this rate of change, a reporting limit of 0.002 µg/L, which is now attainable for some analytical methods, could have produced at least three times the number of atrazine detections reported in this study. Similar trends in the relation between detection frequency and reporting limits probably exist for other compounds analyzed. The occurrence of herbicides and herbicide metabolites is important in tracking flow paths and transformation patterns in the hydrologic system because no natural background concentrations exist for these compounds. However, decreasing the analytical reporting limit would not change the current characterization of herbicide contamination in regard to human health.

Knowledge of herbicide metabolites is critical to understanding the detection, distribution, and fate of herbicides in the environment. Two biotic metabolites of atrazine, desethylatrazine and deisopropylatrazine, were analyzed in this study. By including these metabolites as indicators of atrazine, the frequency of atrazine-residue detection was 22.1 percent, compared to the frequency of atrazine detection alone of 17.4 percent at the analytical reporting limit of 0.05 µg/L. The

amount by which atrazine residue exceeds atrazine in frequency of detection increases disproportionately as the reporting limits decrease (fig. 6). It is likely that the detection frequencies for other herbicides would also increase if analyses for the metabolites of those herbicides were available. Consequently, if herbicide metabolites are not quantified, then the effects of herbicide use on ground-water quality could be substantially underestimated.

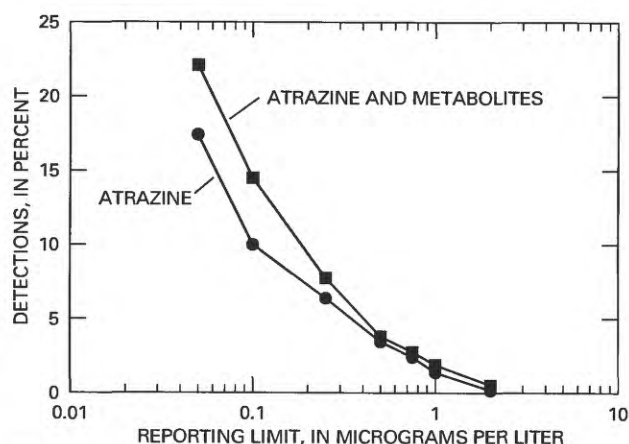


Figure 6. Relation between frequency of atrazine detection and atrazine reporting limits for 579 ground-water samples from the midcontinental United States, 1991.

It has been suggested (Adams and Thurman, 1991; Thurman and others, 1991) that the ratio of desethylatrazine to atrazine (DAR) can provide useful information on the source (point or nonpoint) of atrazine in ground water. Atrazine can be degraded by soil microorganisms to desethylatrazine and other metabolites. The fact that desethylatrazine was detected more frequently than deisopropylatrazine supports previous conclusions that de-ethylation is the preferred, and more stable, biotic degradation pathway (Geller, 1980; Adams and Thurman, 1991). The longer atrazine resides in the soil zone, the more of it is degraded and the larger the DAR value becomes in infiltrating water. As water moves below the soil zone, oxygen generally becomes scarce. In these anoxic conditions, the biotic degradation rates for atrazine are greatly decreased (Dhileepan and Schnoor, 1992). Thus, the more slowly infiltration through the soil occurs, the larger the DAR will become. On the other hand, rapid infiltration through porous soil, fractures, and macropores, and around poorly constructed wells will result in small values of DAR. Following a surface-water reconnaissance of Midwestern streams, Thurman and others (1992) reported DAR values generally less than 0.1 in streams shortly after herbicide application associated with planting, whereas DAR values generally were 0.3

or larger in the fall during base-flow conditions. The median DAR values obtained from the USGS ground-water reconnaissance for both sampling periods were about 0.7 (fig. 7). The DAR ranged from about 0.1 to 8.4. These results indicate that most of the atrazine detected in ground water during the USGS reconnaissance was derived from nonpoint sources and had infiltrated the soil slowly.

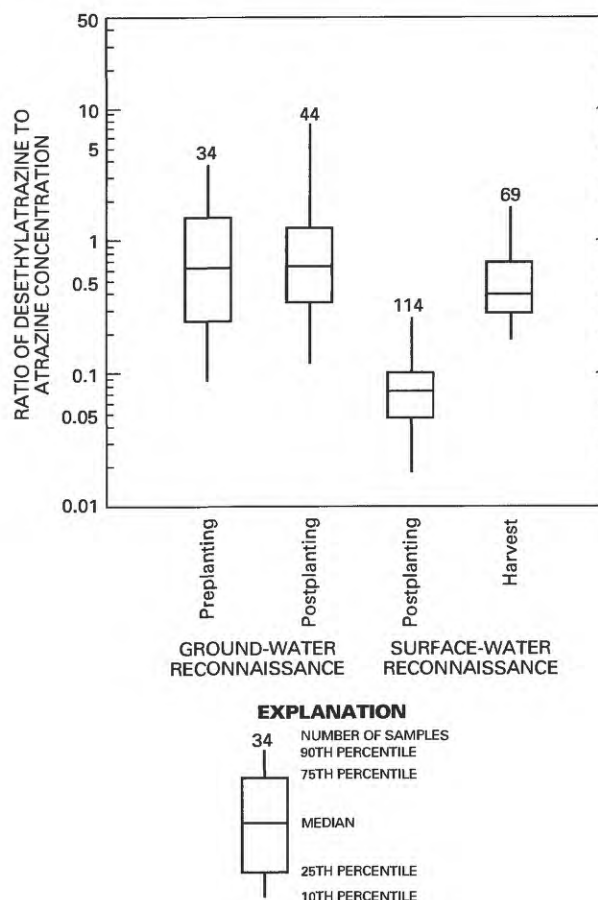


Figure 7. Desethylatrazine-to-atrazine ratios for ground-water samples (this study) and for surface-water samples (Thurman and others, 1992) from the midcontinental United States.

Spatial Distribution

Herbicides were not uniformly detected in near-surface aquifers throughout the study region (fig. 4). Greater detection frequencies were generally in the extreme western part and in a north-south corridor through the center of the study region. Herbicide detection was relatively uncommon in the eastern one-third of the study region, particularly when compared to areas in the extreme west. The reasons for these differences have not been determined.

A significant difference existed between the spatial distribution of herbicides in ground water compared to the distribution in streams in the midcontinent. The relatively small frequency (24 percent) and uneven distribution of herbicide detection in this study strongly contrasts with conditions in surface water within the study region (Goolsby and others, 1991; Thurman and others, 1992). Herbicides were detected in 98 percent of the 132 streams sampled after herbicide application. These two studies covered almost identical regions of the midcontinent, and samples were analyzed for the same set of herbicides and atrazine metabolites. These results indicate that surface water is more susceptible to contamination by herbicides than water in near-surface aquifers.

Atrazine and Atrazine Metabolites

Atrazine was detected in samples from 63 wells, and atrazine or atrazine metabolites were detected in samples from 78 wells at least once during either the preplanting or postplanting sampling. The distribution of atrazine residues (fig. 8) resembles the distribution of herbicide detection (fig. 4) because atrazine residues were the most frequently detected compounds. Atrazine, which has been the most heavily used herbicide in the Nation for much of the last 30 years, is used for selective weed control on corn and sorghum in the study region (U.S. Environmental Protection Agency, 1989). The estimated rates-of-use of atrazine, and the other herbicides discussed, are totals for all crops to which the herbicide was applied and are reported by county (Gianessi and Puffer, 1990). The rate-of-use categories shown in figure 8 and in subsequent figures represent the upper, middle, and lower one-third of the rates of use by county in the study region. The rates shown in these figures, in pounds per square mile, represent the total use in each county divided by the total land area of the county. Consequently, the rates shown are substantially less than those actually used to control weeds on crop land.

Although atrazine-residue detection generally corresponds to areas of heavy atrazine use, substantial areas of the midcontinent have inconsistent patterns of detection and use (fig. 8). Atrazine residues are rarely detected in the eastern one-third of the region, in spite of heavy atrazine use. In Iowa, total atrazine use has decreased recently because of an increase in the practice of post-emergent application (Iowa State University, 1991). This practice requires less active ingredient than the more common practice of pre-emergent application. The recent decrease in atrazine use in Iowa might not yet be reflected in the occurrence of atrazine residue in ground water in that State. Estimates from

previous years (Gianessi and Puffer, 1988, 1990) indicated atrazine use in Iowa had been as heavy as that in areas to the east and west.

Prometon

Prometon, a triazine compound, was the second most frequently detected parent herbicide compound in ground-water samples for the USGS reconnaissance. It was detected in 19 wells (two wells in Nebraska are too close to plot separately in figure 9) in either the pre-planting or postplanting samples and had a greater frequency of detection than other compounds, such as metolachlor and alachlor, that are used much more intensely in the midcontinent. Although the 19 wells in which prometon was detected are somewhat scattered across the study region, 12 are in Iowa or Nebraska (fig. 9). Because little is known about its general use and because of its nonselectivity in controlling most annual and many perennial broadleaf weeds and grasses (U.S. Environmental Protection Agency, 1989), prometon is apparently not used on crops in the midcontinent. However, 80 percent of the samples that had detectable prometon were from wells within 0.25 mi of urban residential land use or within 2 mi of a golf course, whereas only 36 percent of all other herbicide-bearing samples were from similarly situated wells. Among the 15 wells that were within 2 mi of a golf course and in which herbicides were detected, 8 contained prometon. These detection frequencies indicate that prometon in aquifers could result from commercial or urban residential use in recharge areas.

Other Herbicides

Herbicides other than atrazine and prometon were detected in samples from 12 or fewer wells. Because these other herbicides were so rarely detected, substantive statements about the relation of herbicide use to detection in near-surface aquifers are difficult to make.

Metolachlor was detected in samples from 12 wells (fig. 10). None of these wells were in the eastern one-third of the study region, even though this area had use rates similar to or greater than those in the west where most of the detections were made. Metolachlor is a pre-emergent selective-control herbicide (U.S. Environmental Protection Agency, 1989) and is the third most heavily used chemical to enhance corn and soybean production in the study region (table 1).

Although alachlor is the second most used herbicide in the study region (table 1), it was detected in samples from only six wells (fig. 11). Alachlor is used to control most annual grasses and some broadleaf

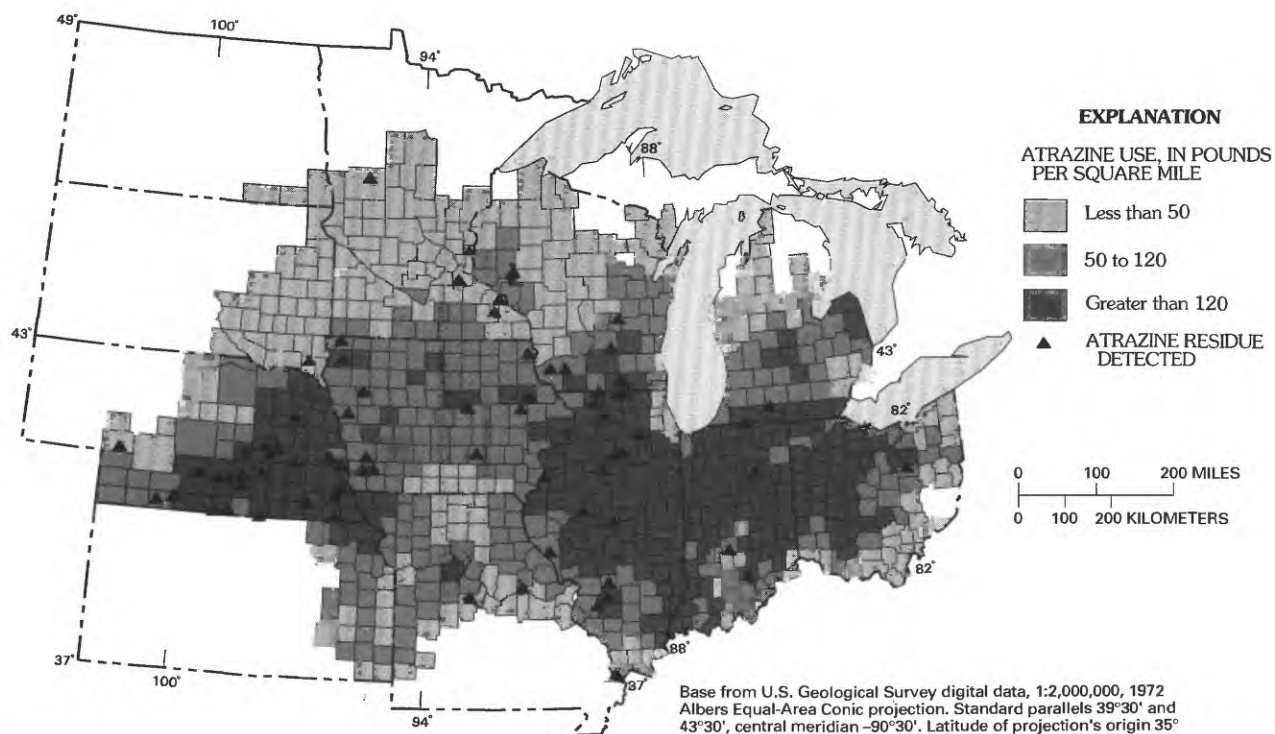


Figure 8. Spatial distribution of atrazine-residue detections in sampled wells and atrazine-use estimates by county (atrazine-use data from Gianessi and Puffer, 1990).



Figure 9. Spatial distribution of prometon detections in sampled wells.

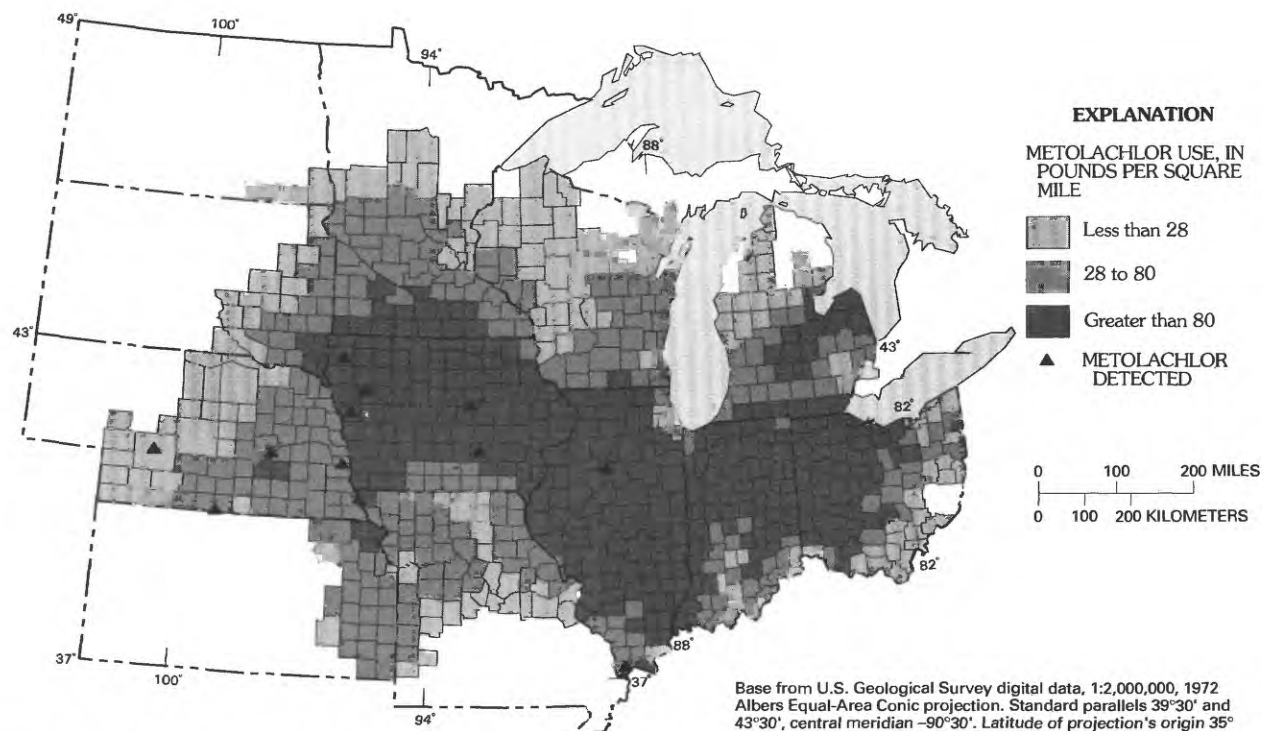


Figure 10. Spatial distribution of metolachlor detections in sampled wells and metolachlor-use estimates by county (metolachlor-use data from Gianessi and Puffer, 1990).

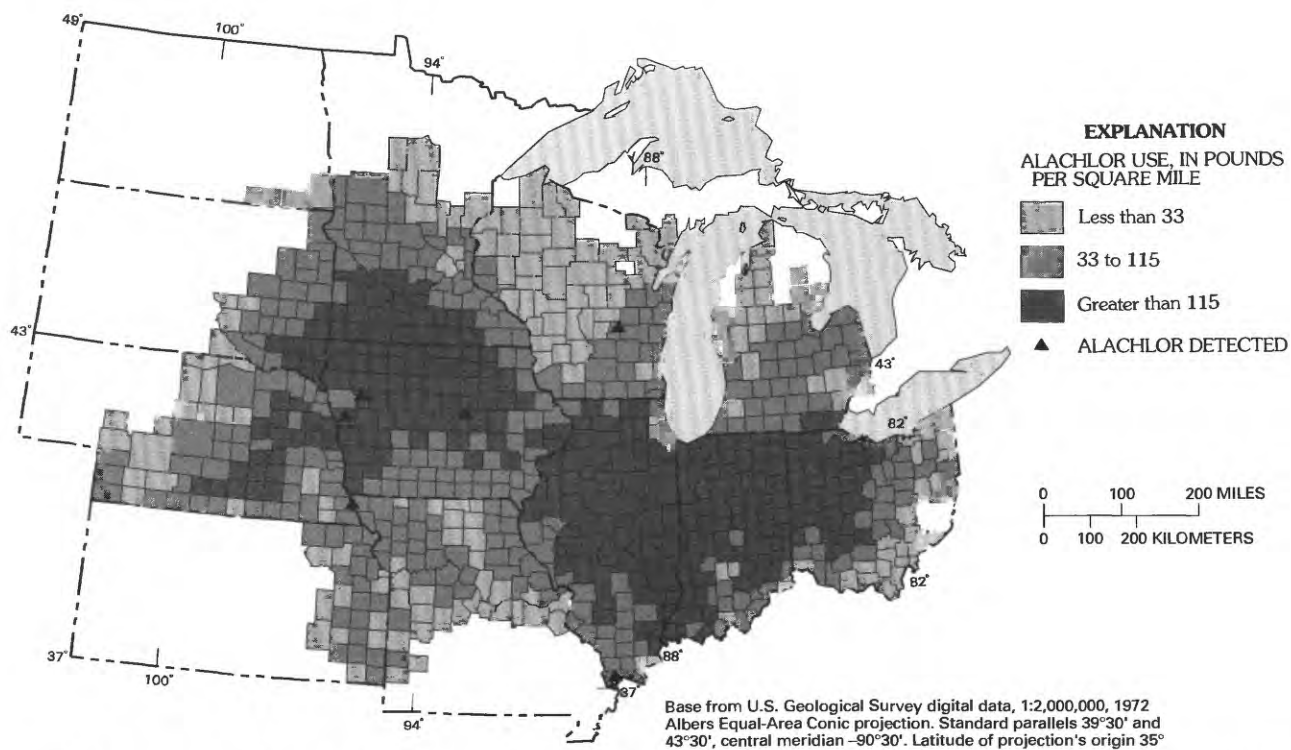


Figure 11. Spatial distribution of alachlor detections in sampled wells and alachlor-use estimates by county (alachlor-use data from Gianessi and Puffer, 1990).

weeds in the production of corn and soybeans in the study region (Meister, 1988). It can be used on fields on which crops are rotated because it leaves little or no residue in soil to affect crops the next year.

Simazine was detected in samples from five wells, all in areas of relatively light use (fig. 12). It is used to control annual grasses and broadleaf weeds in corn and in some fruit and berry production in the study region (U.S. Environmental Protection Agency, 1989). It is the least used of the herbicides examined in this study (table 1).

Metribuzin was detected in samples from four wells (fig. 13). These four wells are scattered across the study region and are too few to allow us to draw any conclusion regarding the geographic distribution of metribuzin. Metribuzin is a herbicide used to control a large number of grasses and broadleaf weeds in soybeans (U.S. Environmental Protection Agency, 1989). It is used much less than most other herbicides examined in this study (table 1).

Cyanazine was one of the least frequently detected herbicides during the USGS reconnaissance (table 2). Samples from only four wells contained this herbicide; three of the four wells were in Iowa (fig. 14), which has the largest rate of cyanazine use of any State in the Nation (Gianessi and Puffer, 1990). Cyanazine is used for pre- and post-emergence control of annual grasses and broadleaf weeds in corn production (U.S. Environmental Protection Agency, 1989).

Seasonal Distribution

The frequency of detection of herbicides and atrazine metabolites was significantly different in samples collected during preplanting and postplanting periods (fig. 15) ($p=0.04$; Mann-Whitney test). To determine if the seasonal difference in detection frequencies could have been caused by analytical variability, the nonquantifiable traces (concentration between 0.02 and 0.04 $\mu\text{g/L}$) of desethylatrazine and atrazine were examined. The examination indicated that the difference was not attributable to wells that tested nominally less than reporting limits in the preplanting period, and nominally greater than reporting limits in the postplanting period. In most of the wells in which a given herbicide was detectable only in the postplanting season, the increase in concentration was significant. The lack of well-specific information about ground-water flow paths prevents us from determining if the seasonal difference in detection frequency was caused by herbicides that were applied between the two sampling periods.

OCCURRENCE OF NITRATE AND AMMONIUM

In the USGS reconnaissance, 599 water samples were collected from 303 wells during 1991; 300 during March or April (preplanting period) and 299 during July or August (postplanting period). Nitrate analyses were obtained at all of these; ammonium analyses were obtained for 285 of the preplanting samples and for all 299 of the postplanting samples. The frequency of nitrate detection was much greater than that for herbicides. Because nitrate can be derived from natural and human sources (Madison and Brunett, 1985), a greater frequency of detection was expected for nitrate. The median nitrate concentration in the 599 samples was 0.17 mg/L, and the maximum concentration was 36.0 mg/L. For these same samples, 59 percent had nitrate concentrations greater than or equal to the reporting limit of 0.05 mg/L, and 29 percent were equal to or greater than 3.0 mg/L, a value suggested as a division between natural and human sources of nitrate (Madison and Brunett, 1985). Nitrate concentrations were equal to or greater than the maximum contaminant level of 10.0 mg/L in 6 percent of the 599 samples.

The frequent detection of ammonium in near-surface aquifers in the midcontinent was of importance because its occurrence in ground water is not well known (Korom, 1992). In 78 percent of the 584 samples analyzed, ammonium was present in concentrations equal to or greater than the reporting limit of 0.01 mg/L. In about 7 percent of the samples, ammonium concentrations were equal to or greater than 1.0 mg/L. The maximum ammonium concentration was 5.7 mg/L.

The nitrate results of the NPS and the NAWWS generally are similar to those of the USGS reconnaissance. According to the estimates in the NPS, water in 52 percent of the public-supply wells and 57 percent of the domestic wells in the Nation were expected to have nitrate concentrations that were equal to or greater than the 0.15 mg/L reporting limit, and 1.2 percent of the public-supply wells and 2.4 percent of the domestic wells in the Nation were expected to have nitrate concentrations greater than 10.0 mg/L nitrate (U.S. Environmental Protection Agency, 1992a). According to the estimates in the NAWWS, 52 percent of the wells were expected to have nitrate concentrations that were equal to or greater than the reporting limit of 0.10 mg/L, 24 percent equal to or greater than 3.0 mg/L, and 5 percent equal to or greater than 10 mg/L (Holden and others, 1992).

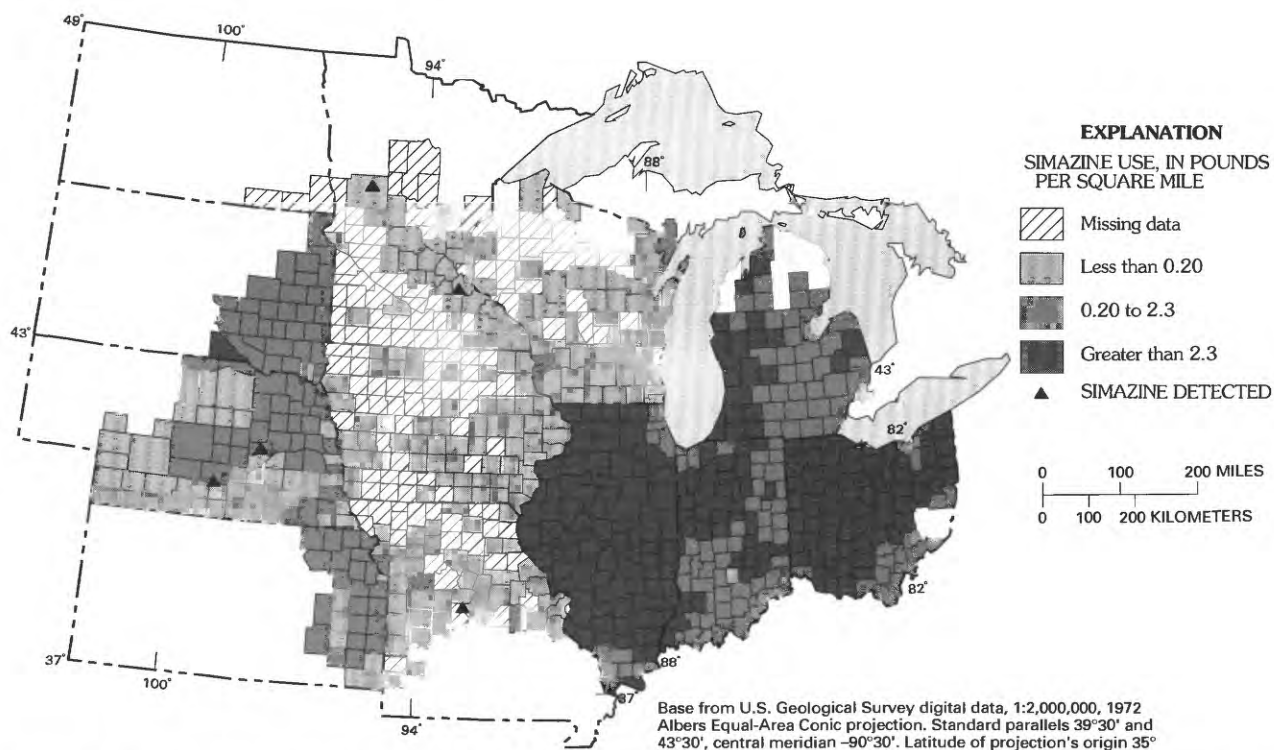


Figure 12. Spatial distribution of simazine detections in sampled wells and simazine-use estimates by county (simazine-use data from Gianessi and Puffer, 1990).

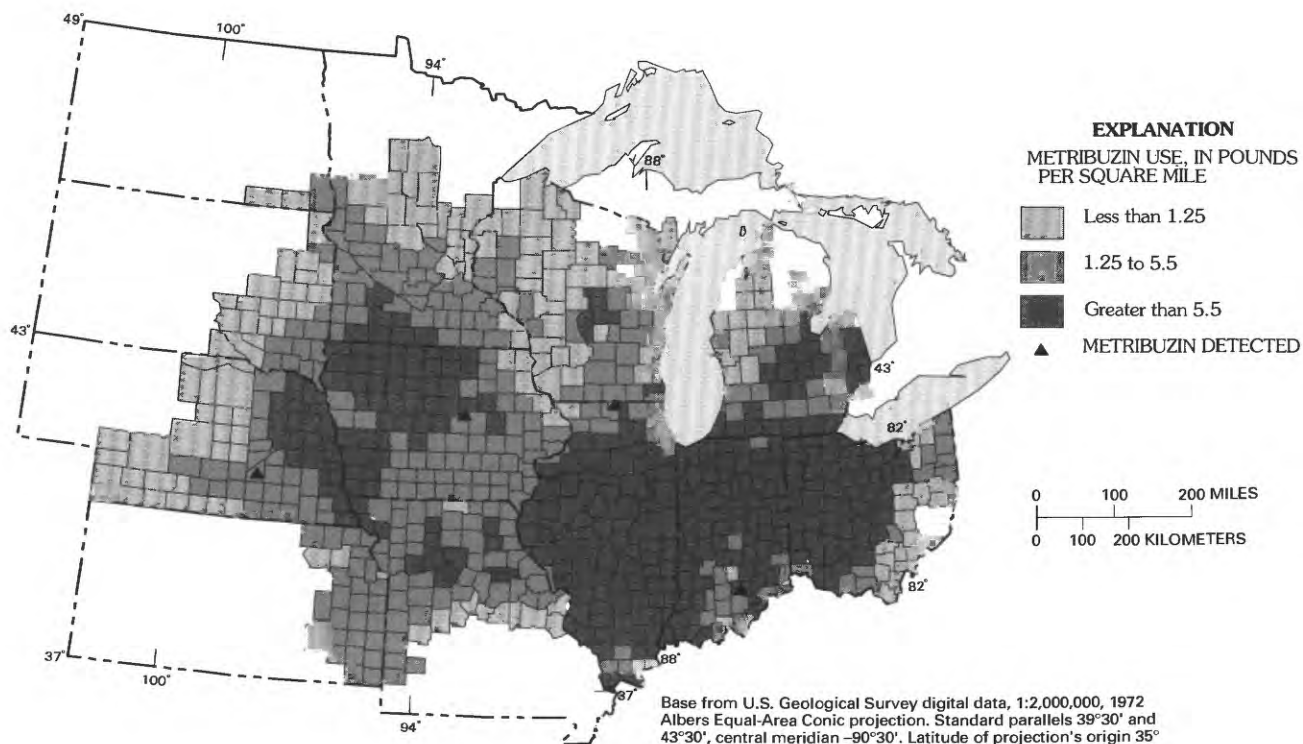


Figure 13. Spatial distribution of metribuzin detections in sampled wells and metribuzin-use estimates by county (metribuzin-use data from Gianessi and Puffer, 1990).

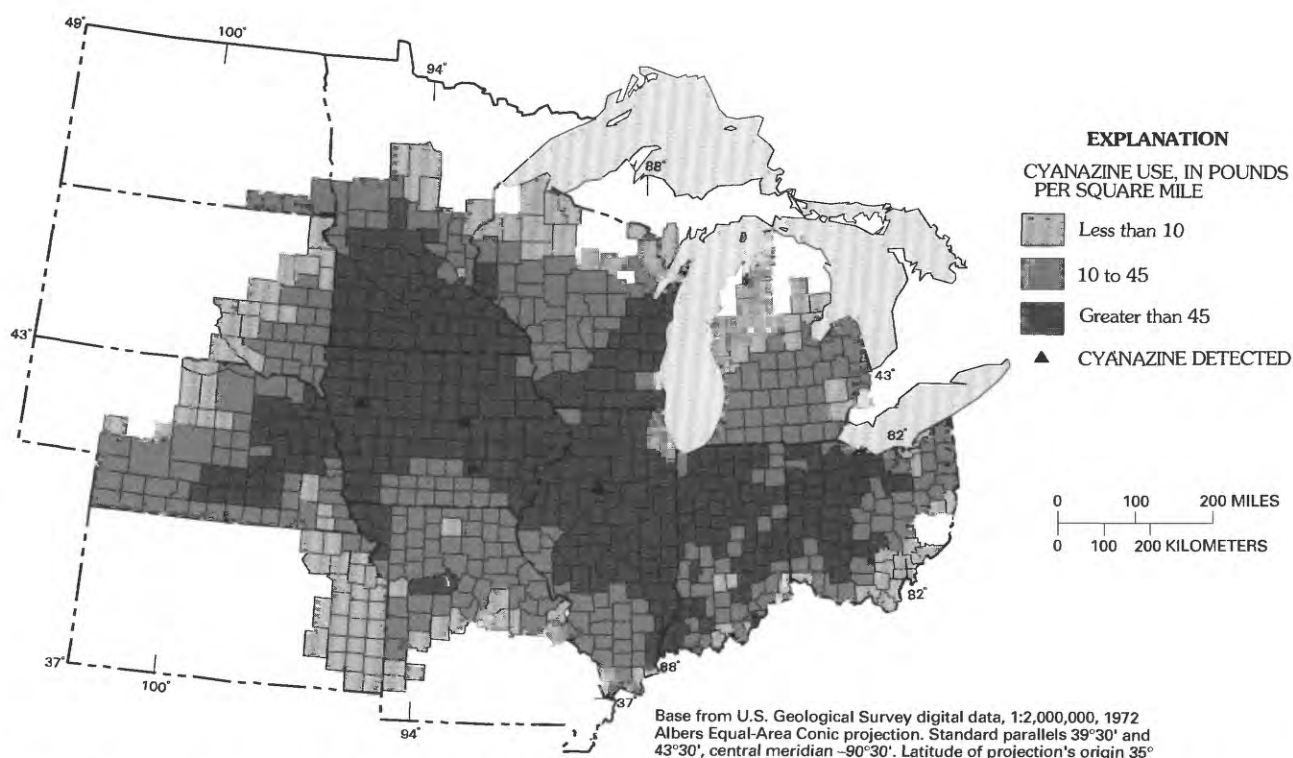


Figure 14. Spatial distribution of cyanazine detections in sampled wells and cyanazine-use estimates by county (cyanazine-use data from Gianessi and Puffer, 1990).

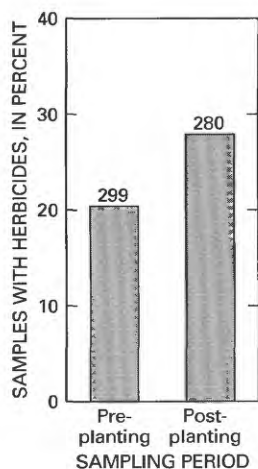


Figure 15. Frequency of herbicide and atrazine metabolite detection in preplanting and postplanting ground-water samples from the midcontinental United States, 1991. Total number of samples in category is shown above bar.

Spatial Distribution

Nitrate concentrations were not uniformly distributed in water in near-surface aquifers across the midcontinent. A comparison of the spatial distributions of nitrate concentrations and nitrogen-fertilizer use is shown in figure 16. Although the correlation between nitrate concentration and nitrogen-fertilizer

use is generally positive, the occurrence of large nitrate concentrations in samples from near-surface aquifers did not always conform to the pattern of intense use. Notable examples were in eastern Indiana, Michigan, and Ohio, where the nitrogen-fertilizer use generally was 7 tons/mi² or more, but most samples had a nitrate concentration less than the reporting limit (0.05 mg/L). Samples from wells in the eastern two-thirds of Iowa generally had nitrate concentrations less than 3.0 mg/L, even though most of the area had an estimated nitrogen-fertilizer use of more than 14 tons/mi².

The spatial distribution of ammonium (fig. 17) shows a general pattern opposite that of nitrate (fig. 16). Nitrate and ammonium concentrations were inversely related to each other in samples collected for this study because nitrate is the dominant nitrogen species under aerobic conditions and ammonium is the dominant nitrogen species under anaerobic conditions (Ceazan and others, 1989; Korom, 1992). This is reflected by a significant positive correlation for nitrate ($p < 0.001$; Spearman's rank correlation) and a significant negative correlation for ammonium ($p < 0.001$; Spearman's rank correlation) to dissolved-oxygen concentrations in water samples collected for the USGS

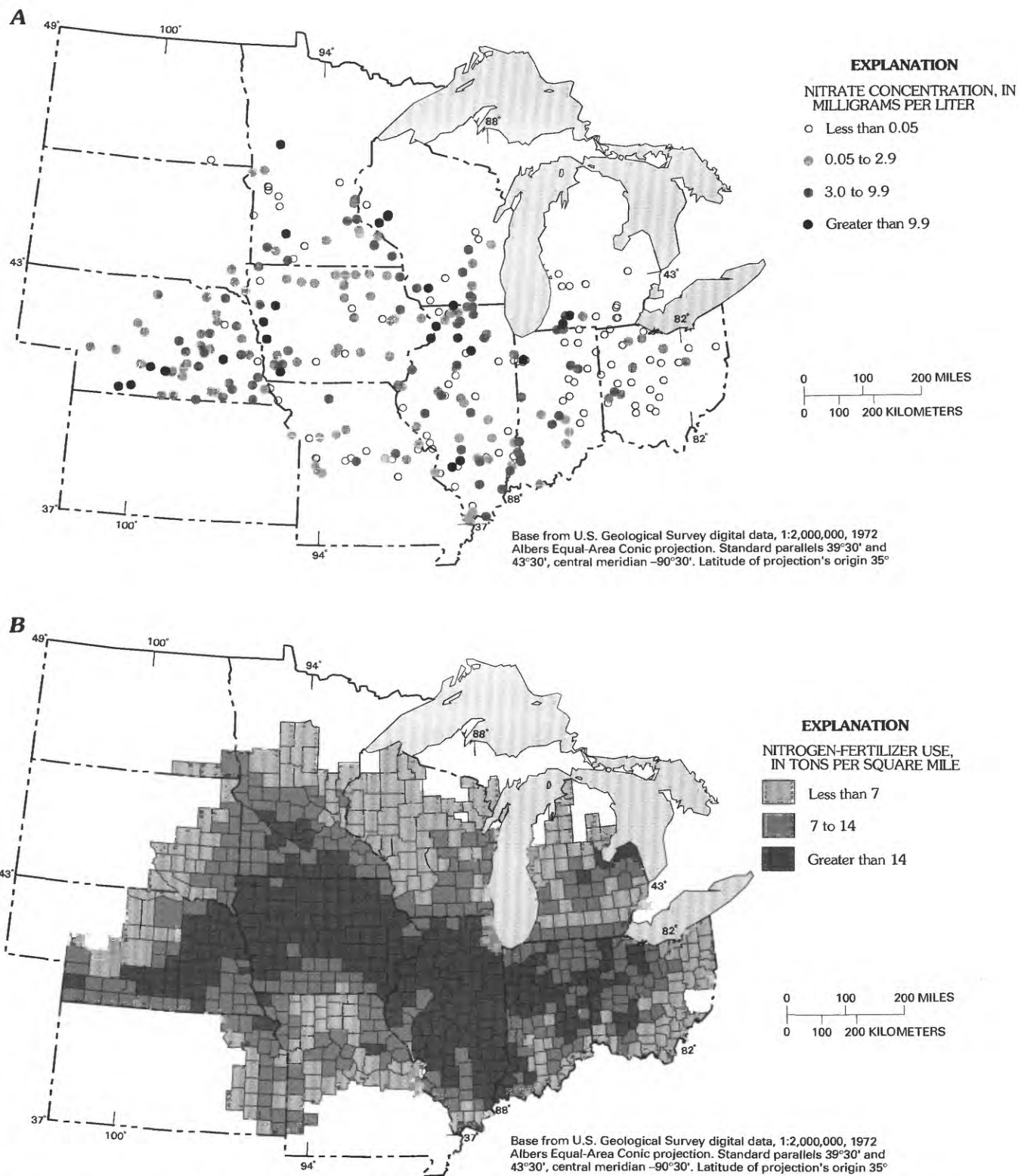


Figure 16. Spatial distribution of nitrate concentrations in ground-water samples from the midcontinental United States, 1991 (A) and estimated nitrogen-fertilizer use by county (B) (nitrogen-fertilizer use data from U.S. Environmental Protection Agency, 1990).

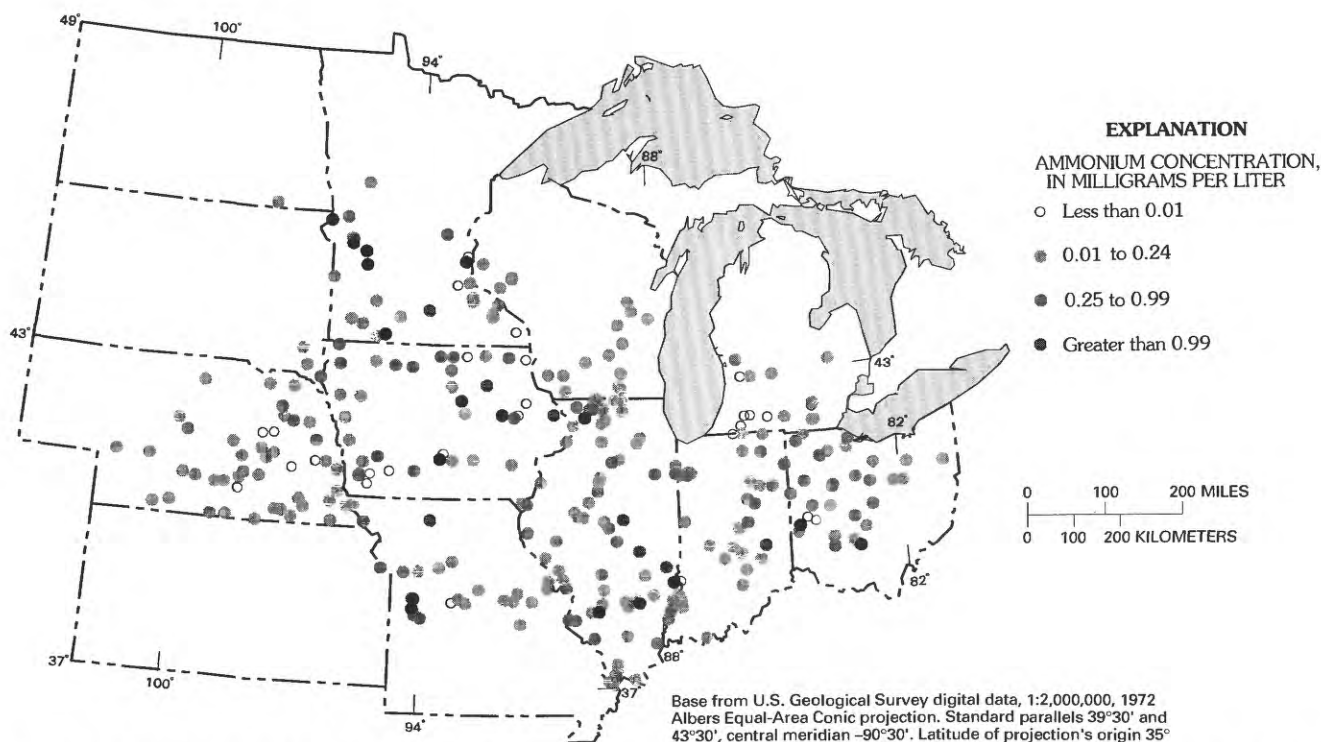


Figure 17. Spatial distribution of ammonium concentrations in ground-water samples from the midcontinental United States, 1991.

reconnaissance. Like nitrate, ammonium has natural and human sources and can be produced in an aquifer by anoxic decomposition of organic material or can be derived from the surface application of nitrogen fertilizer in the form of anhydrous ammonia. Anhydrous ammonia, a common form of nitrogen fertilizer applied in the midcontinent, constitutes 50 percent of the nitrogen-fertilizer use in the study region (U.S. Environmental Protection Agency, 1990). Ammonium is a readily adsorbed ion, binding tightly to soil particles, and thus has not been generally considered an important constituent in ground water.

Seasonal Distribution

There was no significant seasonal difference in nitrate concentrations ($p=0.89$; Mann-Whitney test) between the preplanting and postplanting samples in near-surface aquifers of the study region. The median nitrate concentration was 0.16 mg/L in preplanting and 0.20 mg/L in postplanting samples (fig. 18). There also was no significant seasonal difference (p values were greater than 0.05; Mann-Whitney tests) in nitrate con-

centration when the data were separated by aquifer class (unconsolidated and bedrock).

Samples from some individual wells did exhibit seasonal changes in nitrate concentration. Of the 296 wells from which preplanting and postplanting samples were available, 34 percent did not exceed the reporting limit of 0.05 mg/L, 28 percent showed no substantial change, 15 percent showed a substantial decrease, and 23 percent showed a substantial increase in nitrate concentration. A difference of at least 15 percent between the preplanting and postplanting samples for individual wells was used to define a substantial change in nitrate concentrations. Although nitrate concentrations had no significant seasonal trend in near-surface aquifers of the study region as a whole, clusters of wells had similar seasonal patterns in nitrate concentration (fig. 19).

The wells that have a seasonal change in nitrate concentration may also have a seasonal change in the frequency of herbicide detection. Of 24 wells in which a herbicide or atrazine metabolite was detected only in the postplanting samples, the median nitrate concentration increased from 2.85 to 4.45 mg/L. Of the 32 wells that had a 50 percent or greater increase in nitrate concentration between the preplanting and postplanting

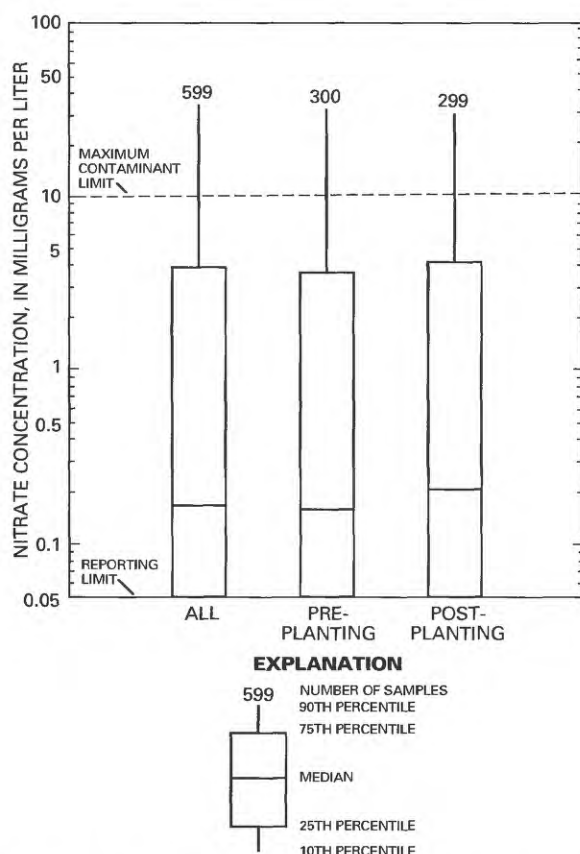


Figure 18. Nitrate concentrations in preplanting and postplanting ground-water samples from the midcontinental United States, 1991.

samples, the frequency of herbicide detection also increased from 12 to 28 percent.

FACTORS RELATED TO THE OCCURRENCE OF HERBICIDES

Numerous hydrogeologic, land-use, agricultural-practice, local-feature, and water-chemistry factors were statistically examined to determine possible relations to herbicide detections in the study region (table 3). Only those factors having the most significant relation to herbicide detection are discussed. A herbicide detection is defined as the presence of any herbicide or atrazine metabolite at a concentration equal to or greater than the analytical reporting limit of 0.05 µg/L, unless specifically noted. Relations between these factors and atrazine alone very closely approximate the relations presented for herbicide detections as a whole and, therefore, are not specifically discussed. The detection frequency of other individual herbicides was not sufficient for valid statistical analysis.

Hydrogeology

Multiple hydrogeologic factors were examined for possible relation to herbicide detections (table 3). Only the most significant of these factors are described here.

Aquifer Class

Herbicide detections were significantly ($p=0.002$; Mann-Whitney test) more frequent in water from unconsolidated aquifers than in that from bedrock aquifers. Herbicide was detected in 28 percent of the samples from unconsolidated aquifers but in only 17 percent of those from bedrock aquifers (fig. 20). Unconsolidated aquifers could be more susceptible to nonpoint-source contamination for a number of reasons, including their general unconfined nature and the relative proximity of wells in these aquifers to recharge sources. About 78 percent of the unconsolidated aquifers sampled were considered to be unconfined, compared to only 48 percent of the bedrock aquifers sampled. An aquifer that is confined in the vicinity of a properly constructed well should be isolated from herbicides being applied at the land surface immediately above it by a barrier of low-permeability materials. Most unconsolidated aquifers made up of alluvial sand and gravel deposits are relatively long and narrow compared to the bedrock aquifers sampled. Because of this aquifer geometry, the flow paths from surface-recharge areas to the wells generally should be substantially shorter for the unconsolidated aquifers than for the bedrock aquifers.

A significant seasonal difference in the frequency of herbicide detection between preplanting and postplanting samples existed for unconsolidated aquifers ($p=0.014$; Mann-Whitney test; fig. 20) but not for bedrock aquifers ($p=0.853$; Mann-Whitney test; fig. 20). The seasonal difference in samples from near-surface unconsolidated aquifers indicates that the wells completed in these aquifers probably are close to recharge sources, which would increase the likelihood of more rapid contamination following herbicide application. The desethylatrazine-atrazine ratio (DAR), an indirect measurement of residence time, provides further evidence that near-surface unconsolidated aquifers generally are closer to their recharge sources than near-surface bedrock aquifers. The median DAR for near-surface unconsolidated aquifers was 0.57, based on 55 values, whereas the median DAR for near-surface bedrock aquifers was 1.25, based on 23 values. The much smaller DAR for unconsolidated aquifers signifies that less biotic transformation of atrazine has taken place

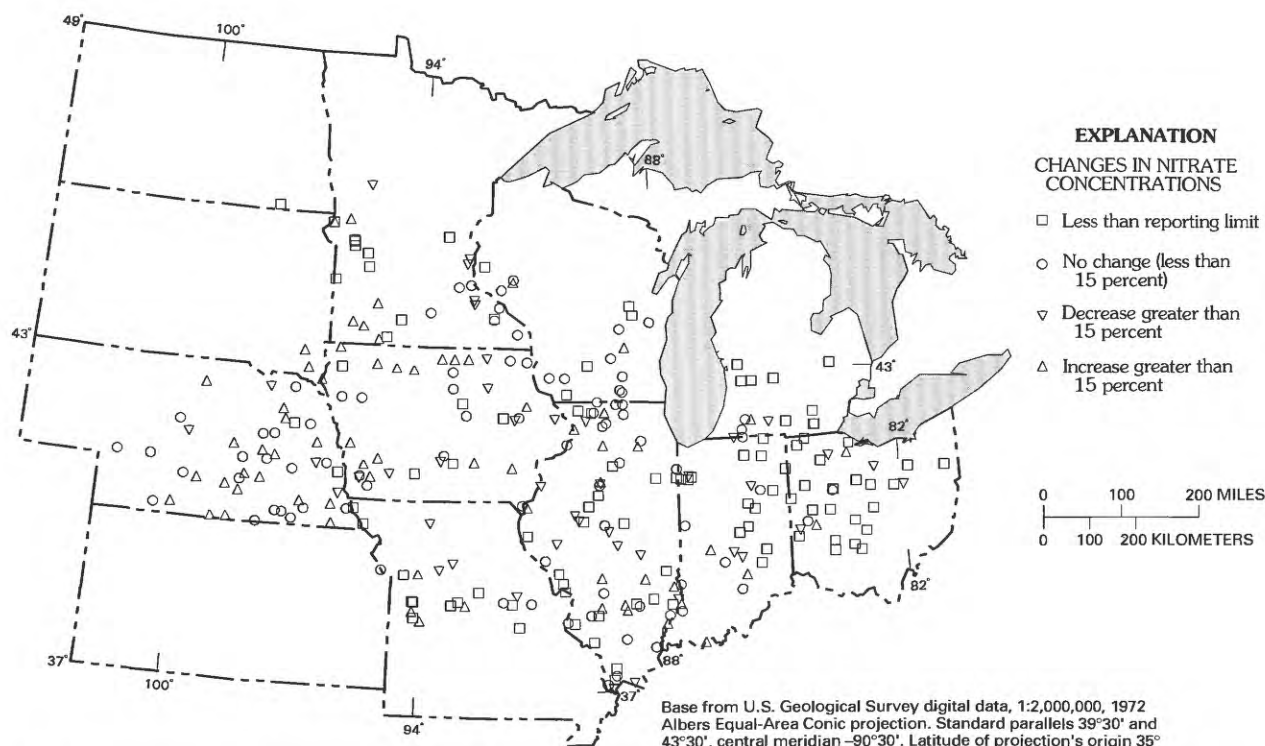


Figure 19. Differences in nitrate concentrations between the preplanting and postplanting ground-water samples from the midcontinental United States, 1991.

and indicates more rapid transport of atrazine from the recharge source.

Depth to the Top of the Aquifer

Depth to the top of the aquifer had the most significant ($p=0.009$; Spearman's rank correlation) relation to herbicide detection of the several depth factors examined. It is defined as the distance from land surface to the top of the aquifer material, regardless of whether the intervening material is saturated or unsaturated. Depth to the top of the aquifer is an important factor for predicting the potential for herbicide contamination. This factor indicates the proximity of an aquifer to recharge sources that could contain dissolved herbicides. The length of the recharge flow path in part determines the time available for transport, transformation, or sorption of herbicides, which is particularly important if much of the overlying material is in an unsaturated zone where aerobic and biotic degradation can occur.

In figure 21, the 0- to 10-ft interval for bedrock aquifers may not be adequately represented to indicate any relation, because only 21 samples were available. Otherwise, the depth intervals shown there had significantly different ($p=0.001$; Kruskal-Wallis test) and

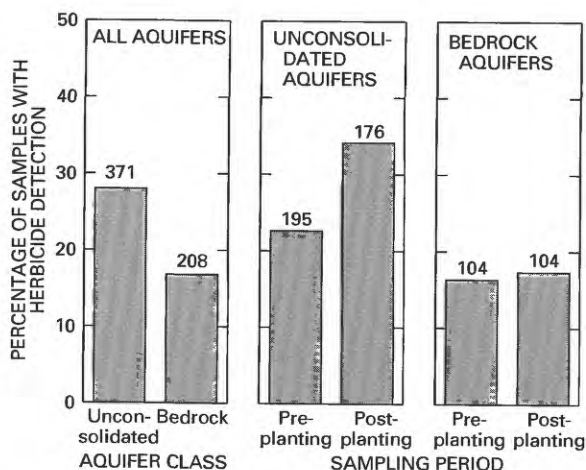


Figure 20. Relation of frequency of herbicide detection to aquifer class for preplanting and postplanting ground-water samples from the midcontinental United States, 1991. Total number of samples in category is shown above bar.

Table 3. Factors examined for their relation to herbicide and nitrate concentrations in ground-water samples from the midcontinental United States, 1991

[ft, feet; mi, miles]

Hydrogeology	Local features (within radial distances of less than 100 ft, less than 0.25 mi, and 0.25 to 2.0 mi)
<ul style="list-style-type: none"> Depth to the top of the aquifer material Aquifer class (unconsolidated or bedrock) Aquifer type (unconfined or confined) Hydrogeologic position of the well completion within the aquifer (upper half, lower half, both) Dominant type of material overlying the aquifer Depth of the well below land surface Depth to top of the open interval below land surface Depth to bottom of the open interval below land surface Depth of water level below land surface Topographic position of the well (flood plain, hillside) Primary use of the water (public supply, domestic) 	<ul style="list-style-type: none"> Chemical plant Waste disposal pond Landfill Golf course Flowing streams Irrigation canal Lake or pond Spring Mine, gravel pit, or quarry Farm building Abandoned well Grain elevator Feedlot Sinkhole
Land use and agricultural practices (within radial distances of less than 100 ft, 0.25 mi, and 2.0 mi)	Water chemistry
<ul style="list-style-type: none"> Urban residential Commercial Industrial Total corn and soybean production Irrigated corn and soybean production Orchards Other crop production Pasture Forest Wetlands Water Estimated county atrazine use 	<ul style="list-style-type: none"> Specific conductance pH Water temperature Dissolved oxygen Hydrogen sulfide odor Dissolved ammonium concentration (as nitrogen) Dissolved nitrite concentration (as nitrogen) Dissolved orthophosphate concentration (as phosphorus)

generally inverse relations to the frequency of herbicide detection. The frequency of herbicide detection differs substantially between the 21- to 30-ft and the 31- to 40-ft intervals, and this difference is seen in both classes of aquifers (fig. 21). However, there is no evidence to indicate that a depth of 30 ft to the top of the aquifer is a transition depth below which herbicide contamination potential is decreased. If herbicides and their metabolites persist without substantial transformation in ground-water flow systems, the frequencies of herbicide detection in more deeply buried aquifers could eventually increase with continued exposure to sources of herbicides.

Water Level and Well Depth

Previous studies have related water levels and well depths to herbicide contamination (Detroy and

others, 1988; Klaseus and others, 1988; U.S. Environmental Protection Agency, 1992a). In this study, however, the frequency of herbicide detection was not significantly different ($p=0.100$; Kruskal-Wallis test) between water-level intervals when samples from all wells were compared (fig. 22). The wells expected to have the strongest relation between water level and frequency of herbicide detection are those completed in unconfined, unconsolidated aquifers. However, even within this subset of wells, the frequency of herbicide detection was not significantly different ($p=0.192$; Kruskal-Wallis test) between water-level intervals (fig. 22). The quality of the water-level data for this reconnaissance may be insufficient to test the relation of frequency of herbicide detection to water level. For more than 80 percent of the wells, it was not possible to obtain a water-level measurement at the time of sampling, and so a water level was estimated. These esti-

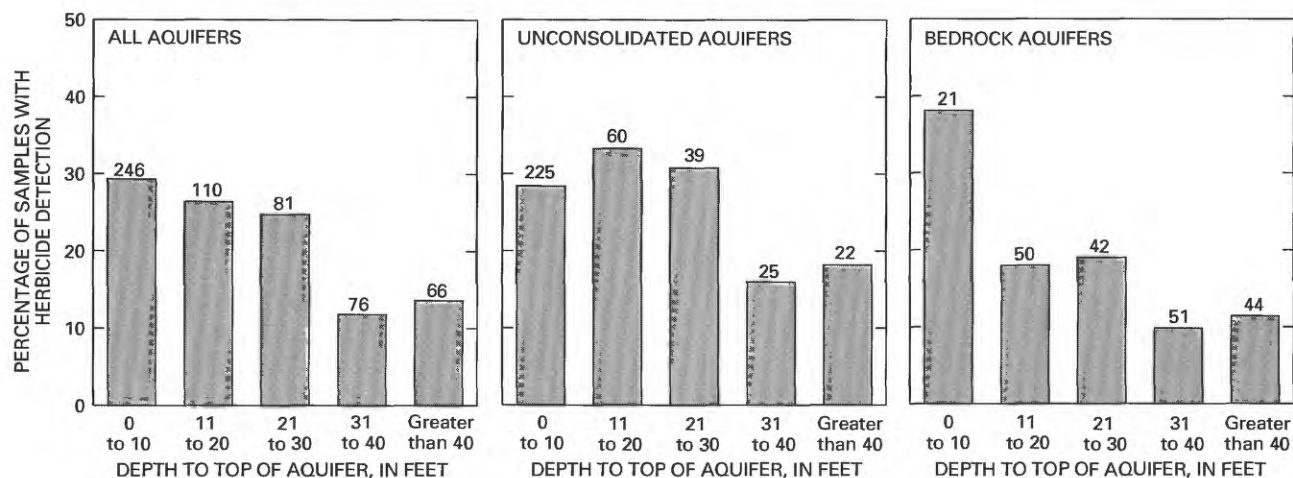


Figure 21. Relation of frequency of herbicide detection to depth to the top of the aquifer, midcontinental United States, 1991. Total number of samples in category is shown above bar.

mated water levels generally came from data collected at the time the well was drilled, which may not adequately reflect conditions at the time of sampling. In addition, the water level in a well is not necessarily a measure of water levels or water-table depth in the recharge areas where herbicides are introduced.

Only the deepest well-depth class, greater than or equal to 300 ft, had significantly fewer ($p=0.022$; Kruskal-Wallis test) herbicide detections than any other well-depth class. This comparison was made irrespective of aquifer class. There were no significant differences ($p>0.05$; Mann-Whitney test) in herbicide detection among other well-depth classes. The fact that only near-surface aquifers were examined for this study could have decreased the potential for determining a relation between well depth and herbicide detection; however, Holden and others (1992) reported no significant correlation of well depth to their herbicide results.

Land Use and Agricultural Practices

Land-use and agricultural-practice factors were examined to determine possible relations to herbicide detections (table 3). The factors were determined from onsite observations and were quantified for three radial distances from the sampled wells—less than 100 ft, less than 0.25 mi, and less than 2.0 mi.

The percentage of land in corn or soybean production within the three radial distances did not seem to be related to the frequency of herbicide detection in well water. Because of the large amount of herbicides used in corn and soybean production, a positive relation to the frequency of herbicide detection was expected, although the well-selection criteria for this study could have affected this relation. At least 25 percent of the land in a 2-mi radius from the wells was used for growing corn or soybeans during the previous

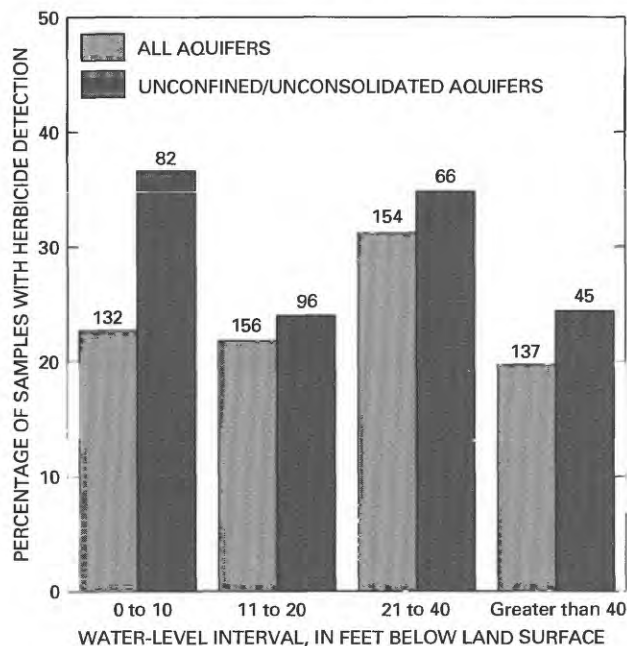


Figure 22. Relation of frequency of herbicide detection to water level in sampled wells, midcontinental United States, 1991. Total number of samples in category is shown above bar.

growing season, thus potentially affecting the water quality of all wells sampled. If the land use in a 2-mi radius around the well had been more distinctly separated into categories such as corn and soybeans, forest, and urban residential, the relation of corn and soybean production to the frequency of herbicide detection might have been more pronounced.

An agricultural practice that *was* related to the frequency of herbicide detection was crop irrigation ($p < 0.001$; Mann-Whitney test). Samples from wells located within 2 mi of irrigated crops had almost double the frequency of herbicide detection as samples from wells without nearby irrigation (fig. 23). Almost 95 percent of the wells near irrigated areas were completed in near-surface unconsolidated aquifers; irrigation water typically is derived from locally recharged aquifers. Under these conditions, irrigation could provide continuous leaching of chemicals from the unsaturated zone to the aquifer throughout the growing season. Moreover, the irrigation water itself may have pre-existing herbicide content. In the study region, the soils over aquifers where crops are irrigated generally have greater sand fractions than soils where crops are not irrigated because adequate soil drainage is necessary for irrigation to be used effectively. In these sandier soils, sorption is limited and the rate of recharge is rapid, resulting in a relatively large potential for contamination of aquifers with herbicides and their metabolites.

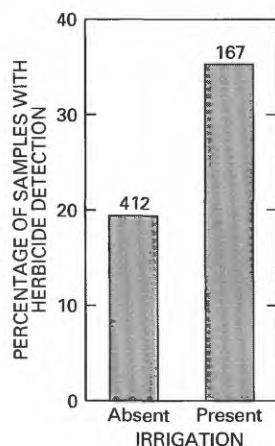


Figure 23. Relation of frequency of herbicide detection to the presence of irrigation within 2 miles of sampled wells, midcontinental United States, 1991. Total number of samples in category is shown above bar.

The percentage of forest land within 2 mi of the well was inversely related to the frequency of herbicide detection ($p = 0.001$; Kruskal-Wallis test; fig. 24). The most obvious explanation for this relation is that the herbicides of interest generally are not applied to forests, thus decreasing the potential source of these chemicals in the areas surrounding the wells.

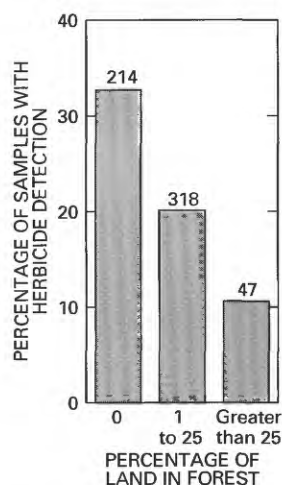


Figure 24. Relation of frequency of herbicide detection to the percentage of forest land within 2 miles of sampled wells, midcontinental United States, 1991. Total number of samples in category is shown above bar.

Atrazine was the only herbicide detected frequently enough to allow a valid statistical comparison of its detection in wells to the estimated rate-of-use in particular counties. The rate of atrazine use was estimated by dividing the total amount used in each county by the area of the county. Although the frequency of atrazine-residue detection appeared to generally increase with increasing atrazine-use class (fig. 25), there was no significant difference ($p = 0.308$; Kruskal-Wallis test) in atrazine-residue detection frequency between classes. Extensive atrazine use was expected to increase the amount of atrazine available for leaching in recharge areas, but this expectation was not met, particularly in the eastern part of the study region where atrazine use is very heavy but detections were few (fig. 8). Knowing the actual atrazine use near wells rather than the estimated use in the surrounding county could help us to better determine the relation of atrazine use to atrazine-residue detections in near-surface aquifers.

Local Features

A number of local features that could affect water quality were examined (table 3). The presence or absence of these features were documented in three categories based on their distances from a well; less than 100 ft, less than 0.25 mi, and 0.25 mi to 2.0 mi.

The proximity of a well to a stream was related to the frequency of herbicide detection (fig. 26). The frequency of herbicide detection doubled when a stream was within 100 ft of a well. About 48 percent of the 44 samples from wells within 100 ft of a stream had detectable herbicides, whereas only 22 percent of the 535 samples from wells that were not within 100 ft of a stream had a detectable herbicide. For the largest

distance category, 0 to 2.0 mi, there was no significant difference ($p=0.183$; Mann-Whitney test) in frequency of herbicide detection and the presence or absence of a stream.

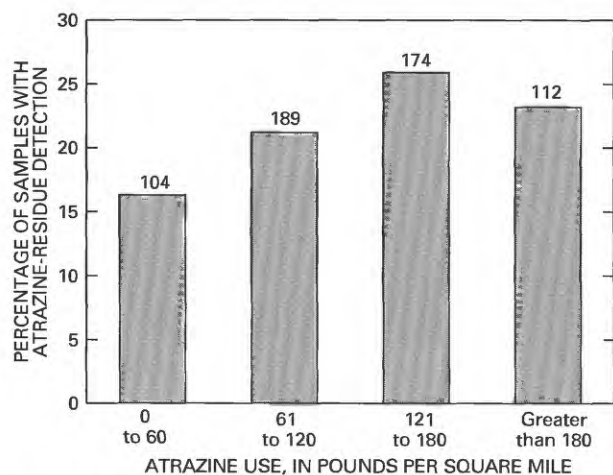


Figure 25. Relation of frequency of atrazine-residue detection in ground water to rate of atrazine use within county, midcontinental United States, 1991. Total number of samples in category is shown above bar.

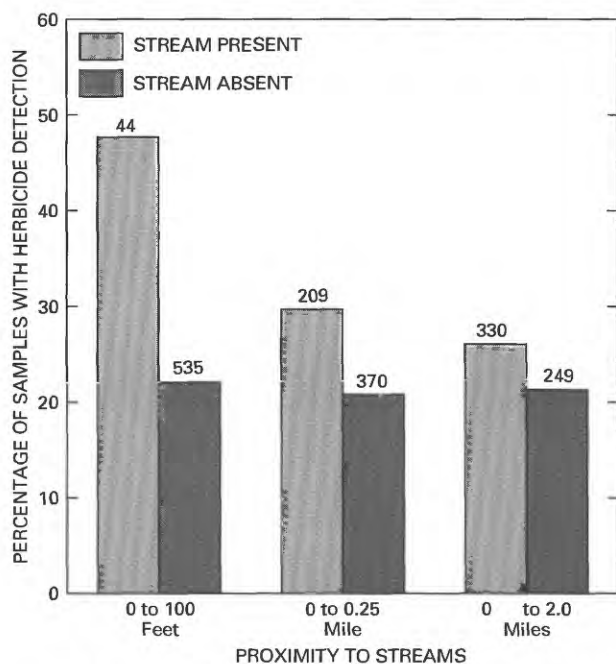


Figure 26. Relation of frequency of herbicide detection to proximity of sampled wells to a stream, midcontinental United States, 1991. Total number of samples in category is shown above bar.

The greater frequency of herbicide detection near streams could result from a hydraulic gradient

from the streams to the near-surface aquifers, which could be either natural or induced by pumping, or from the convergence of flow paths near discharge areas along the streams. Because more than 80 percent of the wells within 100 ft of a stream were completed in unconsolidated aquifers, it is possible that the natural gradient toward the stream could be reversed during pumping, which would result in recharge of the aquifer by stream water. Because streams in the midcontinent have been documented as having larger frequencies of detection and larger concentrations of herbicides than ground water, the recharge to the aquifer from stream-flow could be a source of herbicide contamination (Liszewski and Squillace, 1991). Another possible explanation for the increase in herbicide detections close to streams is that a stream could be a discharge location for multiple ground-water flow paths. Integrating the flow from many areas increases the likelihood of herbicide detection.

Water Chemistry

Water-chemistry factors examined for this study included field measurements of specific conductance, pH, water temperature, and dissolved oxygen and laboratory analyses of nutrients (table 3). The frequency of herbicide detection was positively related to nitrate ($p<0.001$; Kruskal-Wallis test) and dissolved-oxygen concentrations ($p<0.001$; Kruskal-Wallis test) and inversely related to ammonium concentrations ($p<0.001$; Kruskal-Wallis test) (fig. 27). These three factors are not independent of each other. Oxygen tends to be consumed through biotic and abiotic processes at varying rates as water travels from zones of recharge. In the absence of oxygen in the ground-water flow system, nitrate becomes the energy source for the growth of bacteria. Consequently, nitrate should be the dominant nitrogen species in oxidizing conditions, and ammonium should be the dominant nitrogen species in reducing conditions. This conclusion is supported by the data for this study, which show that nitrate was positively related and ammonium was inversely related to dissolved-oxygen concentrations. Thus, dissolved-oxygen, nitrate, and ammonium concentrations do not necessarily have a causative relation to herbicide detection but rather may simply indicate proximity to recharge areas. Samples from wells near recharge areas would generally have larger dissolved-oxygen concentrations and potentially larger nitrate concentrations than samples from wells more distant from recharge areas.

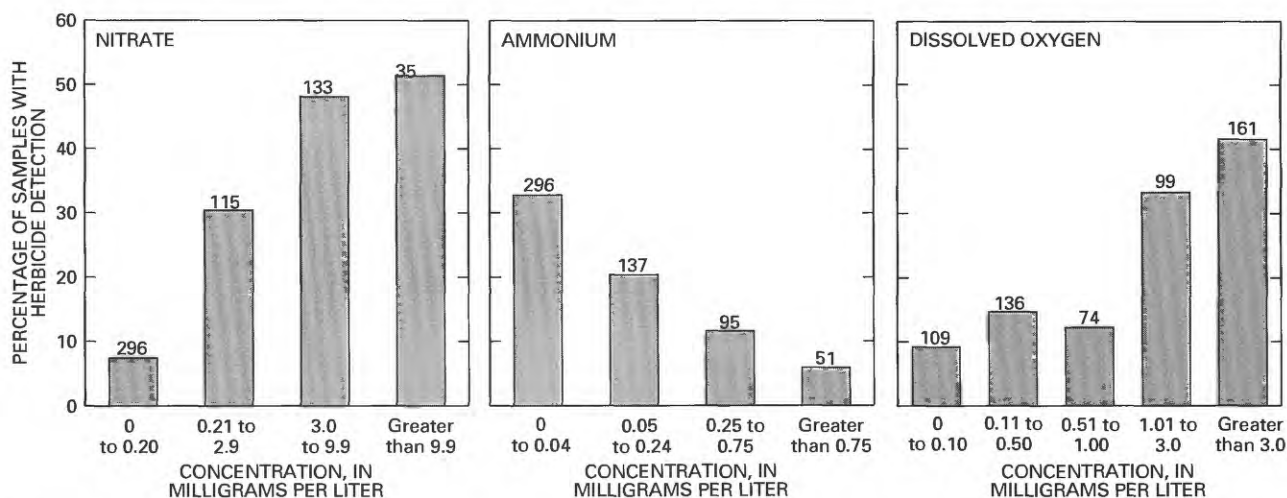


Figure 27. Relation of frequency of herbicide detection to concentrations of nitrate, ammonium, and dissolved oxygen in ground-water samples from the midcontinental United States, 1991. Total number of samples in category is shown above bar.

FACTORS RELATED TO THE OCCURRENCE OF NITRATE

Many hydrogeologic, land-use, agricultural-practice, local-feature, and water-chemistry factors were statistically examined to determine possible relation to nitrate in near-surface aquifers (table 3). Only those factors having the most significant relation to nitrate are described here. The frequency of nitrate concentration equal to or greater than 3.0 mg/L (hereafter referred to as excess nitrate) was used to determine related factors.

The largest artificial source of nitrate in near-surface aquifers in the midcontinent is the agricultural application of nitrogen fertilizers (Hallberg, 1989). Because herbicides and nitrogen fertilizers are both applied to soils, they represent diffuse, nonpoint sources. Consequently, the detection frequency of herbicides and excess nitrate may have similar relations to the factors examined.

Hydrogeology

Multiple hydrogeologic factors were examined to determine possible relation to the frequency of excess-nitrate detection (table 3). Aquifer class and depth to the top of the aquifer were most significantly related to excess nitrate.

Aquifer Class

Samples from unconsolidated aquifers had a significantly larger ($p < 0.001$; Mann-Whitney test) frequency of excess nitrate than samples from bedrock aquifers (fig. 28). The median nitrate concentration was 0.94 mg/L for unconsolidated aquifers and less than 0.05 mg/L for bedrock aquifers. This difference in the frequency of excess nitrate indicates that unconsolidated near-surface aquifers are more susceptible to nitrate contamination than bedrock near-surface aquifers. The susceptibility difference could be the result of factors not directly measured for this study. For example, recharge rates are likely to be faster and ground-water flow paths shorter in unconsolidated aquifers than in bedrock aquifers. Also, fewer unconsolidated aquifers than bedrock aquifers sampled in this study were considered to be confined at the well site. Aquifers that are confined are generally less susceptible to contamination from agricultural application of chemicals because of the presence of overlying low-permeability units.

Depth to the Top of the Aquifer

A significant inverse relation ($p < 0.05$; Kruskal-Wallis test) exists between depth to the top of the aquifer and the frequency of excess nitrate; aquifers at shallower depth generally have greater frequencies of excess nitrate than those at greater depth (fig. 29). Depth to the top of the aquifer gives a general indication of proximity to a recharge source. The greater the

depth to the top of an aquifer, the longer the flow paths and the more time there is for loss of nitrate through transformation processes. When the samples were separated by aquifer class, differences in the relation of excess nitrate to depth to the top of the aquifer were evident; there was no significant relation ($p=0.605$; Kruskal-Wallis test) for samples from unconsolidated aquifers but a very strong relation ($p<0.001$; Kruskal-Wallis test) for samples from bedrock aquifers (fig. 29). Perhaps the unconsolidated aquifers would also have shown some relation between these variables if greater aquifers depths had been included. Unconsolidated aquifers generally are more susceptible to contamination by surface sources of nitrate because they generally are unconfined and receive more recharge from local sources than bedrock aquifers.

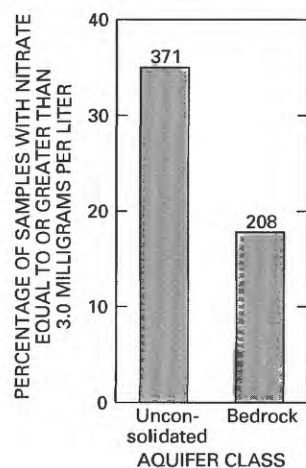


Figure 28. Relation of frequency of excess nitrate to aquifer class, midcontinental United States, 1991. Total number of samples in category is shown above bar.

Water Level and Well Depth

The frequency of excess nitrate was significantly different ($p=0.001$; Kruskal-Wallis test) between classes of water levels when all wells were compared (fig. 30). However, this difference can be attributed entirely to the 21- to 40-ft water-level interval. There was no significant difference between the remaining three classes of water levels ($p=0.561$; Kruskal-Wallis test). The wells expected to have the strongest relation between water level and frequency of excess nitrate are those completed in unconfined, unconsolidated aquifers. For this group of wells, the frequency of excess nitrate was significantly smaller ($p<0.001$) for water-level intervals less than or equal to 20 ft below land surface than for those at greater depths (fig. 30). Thus, it appears that denitrification could be occurring in water levels closer to the land surface. Denitrification takes place under anaerobic conditions when oxygen

becomes depleted and NO_3^- becomes the electron acceptor. Denitrification also requires the presence of sufficient organic carbon as an energy source for the bacteria. The dissolved-oxygen concentrations measured in samples from the wells completed in unconfined, unconsolidated aquifers provide evidence that proper conditions could exist for denitrification to take place. The median dissolved-oxygen concentration in samples from water-level intervals less than or equal to 20 ft deep was 0.7 mg/L, whereas the median concentration in samples from deeper water-level intervals was 2.7 mg/L. However, no information is available on the organic carbon content of the water or aquifer material of the aquifers sampled.

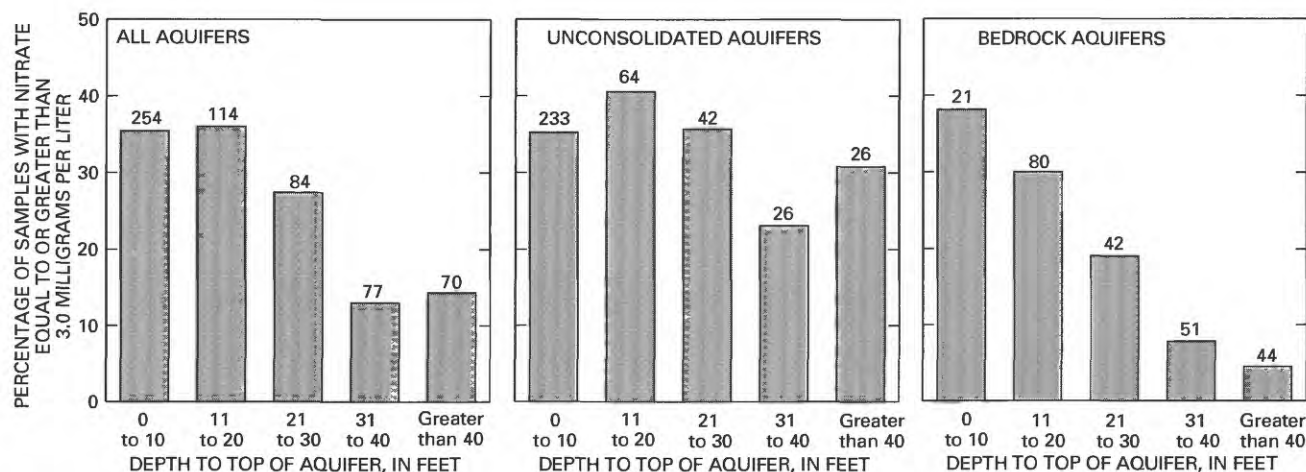


Figure 29. Relation of frequency of excess nitrate to depth to the top of the aquifer, midcontinental United States, 1991. Total number of samples in category is shown above bar.

Previous studies have indicated an inverse relation between nitrate concentration and well depth (Detroy and others, 1988; Hallberg, 1989). The results from this study also indicated a weak but significant inverse relation ($p=0.008$; Spearman's rank correlation) between nitrate concentration and well depth. An examination of the frequency of excess nitrate by classes of well depth did not indicate a clear inverse pattern until well depths exceeded 300 ft (fig. 31). The comparisons were made irrespective of aquifer class (unconsolidated and bedrock). The fact that only near-surface aquifers were examined for this study could have decreased the potential relation of well depth to excess nitrate.

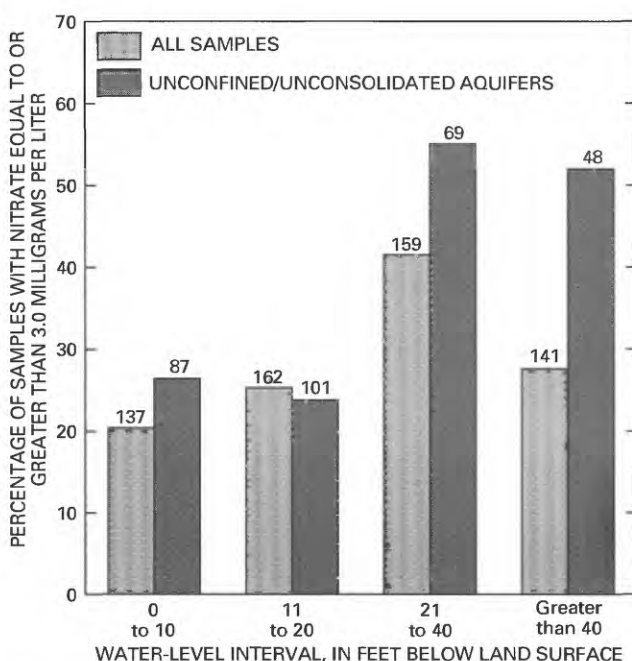


Figure 30. Relation of frequency of excess nitrate to water level in sampled wells, midcontinental United States, 1991. Total number of samples in category is shown above bar.

Land Use and Agricultural Practices

Multiple land-use and agricultural-practice factors were examined to determine possible relation to frequency of excess nitrate (table 3). Categories of land use were estimated within broad percentage ranges (0, 1 to 25, 26 to 50, 51 to 75, and 76 to 100 percent) from onsite observations. Estimates were made for land use within three radial distances from the sampled wells; less than 100 ft, less than 0.25 mi, and less than 2.0 mi.

Samples from wells that had 25 percent or less of the surrounding land in corn or soybean production

within a 2-mi radius had significantly smaller frequencies of excess nitrate than samples from wells that had substantially more than 25 percent of the surrounding land in corn or soybean production (fig. 32). This difference in the frequency of excess nitrate detection can be explained both by a larger mass of source material (nitrogen fertilizer) available and by a larger potential for ground-water recharge areas to have nitrogen fertilizer directly applied. The area in corn and soybean production is directly proportional to the amount of nitrogen fertilizer applied.

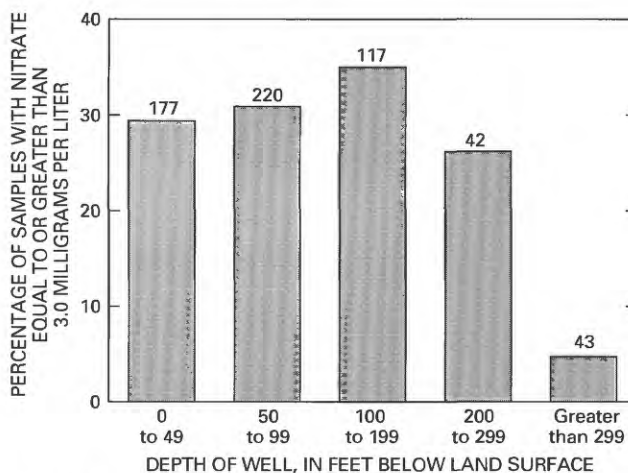


Figure 31. Relation of frequency of excess nitrate to depth of sampled wells, midcontinental United States, 1991. Total number of samples in category is shown above bar.

Irrigation also was related to the frequency of excess nitrate. The frequency of excess nitrate was significantly larger ($p<0.001$; Mann-Whitney test) where irrigation was used within 2 mi of a well than where no irrigation was used (fig. 32). Irrigation could provide a more continuous source of water than precipitation and, thereby, a continuous potential for leaching nitrate from the unsaturated zone to the aquifer. Also, many areas in the midcontinent that require irrigation tend to have sandier soils with large infiltration rates, which increases the potential for contamination of near-surface aquifers.

The percentage of land in forest and pasture within 2 mi of a well was inversely related ($p=0.003$; Kruskal-Wallis test) to the detection of excess nitrate (fig. 32). One explanation is that with more land in forest and pasture, less land can be used for corn and soybean production; therefore, less nitrogen fertilizer is used.

Wells that were close to urban-residential areas had a significantly ($p<0.05$; Mann-Whitney test) larger frequency of samples with excess nitrate than wells that were not. For example, where no urban-residential

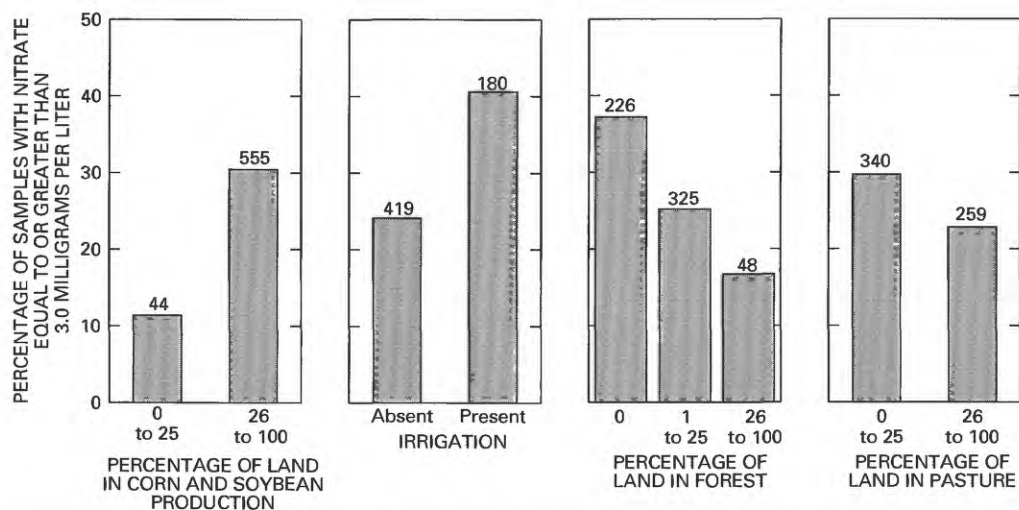


Figure 32. Relation of frequency of excess nitrate to the percentage of selected land-use characteristics within 2 miles of a sampled well, midcontinental United States, 1991. Total number of samples in category is shown above bar.

land use was present 100 ft from the well, 24.6 percent of the samples had excess nitrate, but where urban-residential land use was present, 44 percent of the samples had excess nitrate. Possible explanations for the difference in the frequency of excess nitrate include lawn fertilizers used in urban-residential areas, which become an additional nitrogen source to the aquifers. Also, the presence of residential areas increases the likelihood of other urban nitrogen sources such as sewage effluents, grain elevators, chemical storage facilities, and chemical dealerships that store and sell nitrogen fertilizers.

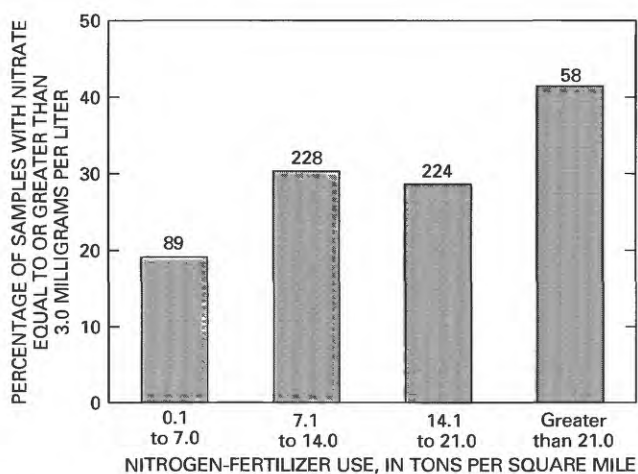


Figure 33. Relation of frequency of excess nitrate in sampled wells to the rate of nitrogen-fertilizer use within county, midcontinental United States, 1991. Total number of samples in category is shown above bar.

The rate of nitrogen-fertilizer use was estimated for each county in which a well was located by dividing the total amount used by the county area. The estimated rate had a significant positive ($p=0.033$; Kruskal-Wallis test) relation to excess nitrate. In general, as the nitrogen-fertilizer-use rate increased, the frequency of samples that had excess nitrate also increased (fig. 33). However, there were parts of the study region where this relation was not as strong, particularly the eastern one-third of the study region and north-central Iowa. These areas had frequencies of excess nitrate much smaller than would be expected based on their relatively large nitrogen-fertilizer-use rates. Understanding of the relation of nitrogen-fertilizer-use rate to nitrate in near-surface aquifers could be improved with more detailed data on the rate of nitrogen-fertilizer use in specific ground-water recharge areas and the hydrogeology of near-surface aquifers in these areas.

Ammonium was detected (fig. 17) in smaller concentrations but more frequently than nitrate. In ground water, ammonium can be derived from three sources—reduction of nitrate, application of nitrogen fertilizers in the form of anhydrous ammonia or ammonium nitrate, and breakdown of organic matter in the aquifer (Kross and others, 1990). Total inorganic nitrogen in ground water (nitrate + nitrite + ammonium) was used to determine if, by including ammonium concentrations, the relation to nitrogen-fertilizer-use rate was more significant than that for just nitrate. There was a significant relation of total inorganic nitrogen to nitrogen-fertilizer-use rate ($p<0.001$; Spearman's rank cor-

relation). The rank correlation coefficient was larger, and more significant, for total inorganic nitrogen than that for nitrate alone ($p=0.007$; Spearman's rank correlation). These findings indicate that ammonium needs to be considered to better understand the relation of nitrogen-fertilizer use to nitrogen detection in near-surface aquifers. Additional study is needed to determine whether ammonium is being formed in situ or is being transported to aquifers from sources where it is applied as fertilizer.

Local Features

A number of local features that could affect water quality were examined (table 3). The presence or absence of these features was documented in three radial distances from a well; less than 100 ft, less than 0.25 mi, and 0.25 mi to 2.0 mi.

The frequency of excess nitrate was significantly larger ($p<0.001$; Mann-Whitney test) in samples from wells within 2 mi of a chemical plant than in samples from wells more distant (fig. 34). As defined for this study, a chemical plant included a variety of facilities, such as grain elevators, chemical dealers, and anhydrous ammonia storage facilities. There were not enough samples from wells within 100 ft or 0.25 mi of a chemical plant to determine if there was a relation to excess nitrate.

The frequency of excess nitrate was also significantly larger ($p=0.006$; Mann-Whitney test) in samples from wells within 2 mi of a golf course than in samples from wells more distant (fig. 34). There were not enough samples from wells within 100 ft or 0.25 mi of

a golf course to determine any relation. Golf courses commonly use nitrogen fertilizer and irrigation, practices also common for corn and soybean production.

The frequency of excess nitrate was significantly smaller for wells that were close to feedlots than for wells that were not (fig. 34; $p=0.019$, 0.001, and 0.021, respectively, for wells within 100 ft, 0.25 mi, and 2 mi of a feedlot; Mann-Whitney test). Information about the number or kind of animals at feedlots was not available. This inverse relation of the presence of feedlots to the frequency of excess nitrate occurrence was not expected because animal manure has been documented as a source of nitrate in ground water (Madison and Brunett, 1985). The presence of feedlots might increase the organic matter content of the material through which water travels. This increased organic matter should decrease the dissolved-oxygen concentration, thereby increasing the potential for the reduction of nitrate to ammonium (Korom, 1992). Samples from the wells near feedlots showed a marginally significant decrease in dissolved-oxygen concentrations, compared to those from other wells ($p=0.053$, 0.086, and 0.068, respectively, for wells within 100 ft, 0.25 mi, and 2 mi of a feedlot; Mann-Whitney test). However, a significant increase in ammonium concentration ($p=0.002$; Mann-Whitney test) was shown only by samples from within 0.25 mi from feedlots. Because ground-water flow paths at the sampled wells are unknown, it cannot be determined how many of the feedlots are in aquifer-recharge areas or upgradient from wells sampled.

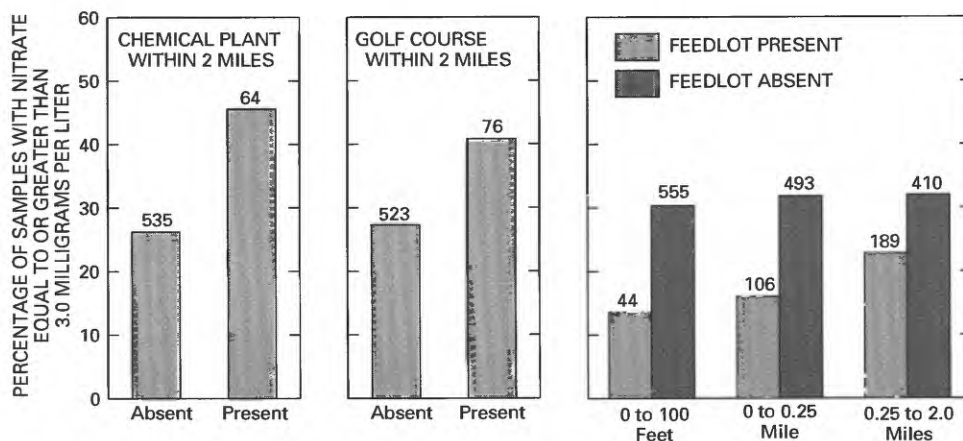


Figure 34. Relation of frequency of excess nitrate in sampled wells to the presence of chemical plants, golf courses, and feedlots; midcontinental United States, 1991. Total number of samples in category is shown above bar.

Water Chemistry

The water-chemistry factors examined include field measurements of specific conductance, pH, water temperature, and dissolved oxygen and laboratory analysis of nitrite (as nitrogen), ammonium, and dissolved orthophosphate (as phosphorus) (table 3). These factors had some of the most significant relations to nitrate of all factors examined.

The frequency of excess nitrate had a strong inverse relation ($p < 0.001$; Kruskal-Wallis test) to ammonium concentration. In general, the greater the ammonium concentration, the smaller the frequency of excess nitrate (fig. 35). Because nitrate is the dominant nitrogen species in oxidizing conditions and ammo-

num is the dominant nitrogen species in reducing conditions (Korom, 1992), this inverse relation was expected. Also, dissolved-oxygen concentration had a direct relation to the frequency of excess nitrate (fig. 35) and an inverse relation to ammonium concentration. Furthermore, nitrate concentrations greater than the 0.05 mg/L reporting limit were rarely found in samples from wells that contained hydrogen sulfide, indicating a strongly reducing environment, and none of these samples contained excess nitrate. However, where hydrogen sulfide was not present, 31.5 percent of the samples had excess nitrate.

Excess nitrate had a significant positive relation ($p < 0.001$; Kruskal-Wallis test) to dissolved-orthophosphate concentration (fig. 35). A potential source of dissolved orthophosphate in ground water is

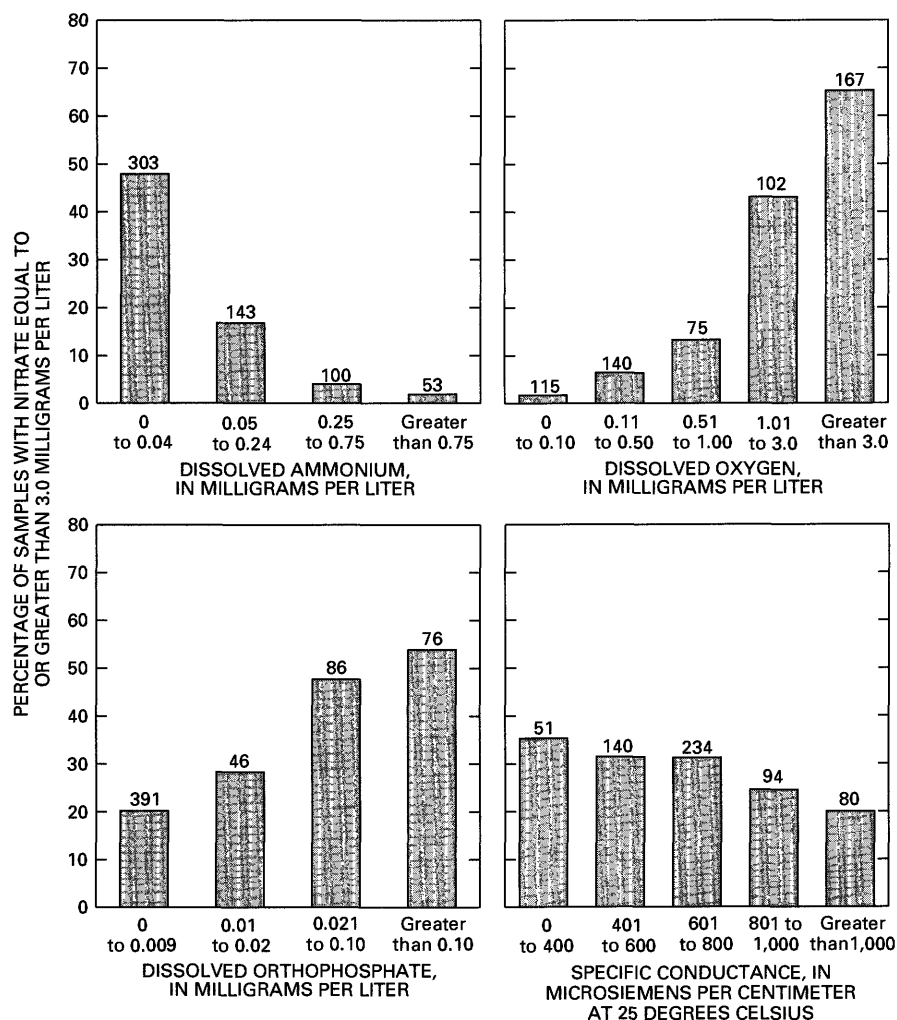


Figure 35. Relation of frequency of excess nitrate in sampled wells to selected chemical characteristics of sampled water, midcontinental United States, 1991. Total number of samples in category is shown above bar.

the application of chemical fertilizers. Nitrate and dissolved orthophosphate differ in their adsorption and rates of transport. Nitrate is soluble and very mobile, but orthophosphate is more readily adsorbed to sediment and aquifer matrix and, thus, is not as readily transported by ground water. Dissolved-orthophosphate detection in ground water could indicate rapid recharge rates, or short flow paths, or both. When dissolved orthophosphate is detected in ground water, it is very likely that nitrate also will be detected.

Specific conductance had a significant inverse relation ($p < 0.001$; Kruskal-Wallis test) with frequency of excess nitrate (fig. 35). Specific conductance, an indirect measure of dissolved-solids concentration, generally increases with water residence time and distance of flow through aquifers as minerals are dissolved. Consequently, parts of aquifers in which the water has large values of specific conductance and small frequencies of excess nitrate are interpreted to be more distant from recharge and, consequently, from nitrogen sources than parts of aquifers in which the water has smaller values of specific conductance and larger frequencies of excess nitrate.

SUMMARY AND CONCLUSIONS

The detection and distribution of selected herbicides, atrazine metabolites, nitrate, and ammonium were determined for water in near-surface aquifers in the midcontinental United States. Water samples were collected during preplanting and postplanting periods in 1991 from 303 wells completed in unconsolidated and bedrock aquifers in Illinois, Indiana, Iowa, Kansas, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, South Dakota, and Wisconsin. The maximum depth to the top of the aquifers was about 50 ft below land surface.

At least one herbicide or atrazine metabolite was detected in 24 percent of 579 samples collected for herbicide analysis, based on a laboratory reporting limit of 0.05 $\mu\text{g/L}$. No herbicide concentrations exceeded any of the U.S. Environmental Protection Agency's maximum contaminant levels or health advisory levels. The most frequently detected compound was desethylatrazine (18.1 percent) followed by atrazine (17.4 percent), deisopropylatrazine (5.7 percent), prometon (5.0 percent), metolachlor (2.7 percent), alachlor (1.7 percent), simazine (1.0 percent), metribuzin (1.0 percent), and cyanazine (0.7 percent). Nitrate concentrations were equal to or greater than 3.0 mg/L (excess nitrate) in 29 percent of the 599 samples, and ammonium concentrations were equal to or greater than 0.01 mg/L in 78 percent of the 584 samples. The maximum contaminant level for nitrate in drinking water of 10 mg/L was

equaled or exceeded in 6 percent of the samples analyzed. Prometon was the second most frequently detected herbicide parent compound, although little information is available on its use in the study region. Prometon is apparently not used on crops in the study region but rather on land such as golf courses and urban residences.

Analysis of parent compounds alone is insufficient to determine fully the effects of herbicide use on ground-water quality. Desethylatrazine and deisopropylatrazine were the first and third most frequently detected compounds. The frequency of atrazine-residue detection (atrazine + desethylatrazine + deisopropylatrazine) was 22.1 percent, which was greater than the frequency of atrazine detection alone (17.4 percent).

The frequency of herbicide detection is, in part, a function of the laboratory reporting limits. For example, results from this study show that decreasing the atrazine reporting limit from 0.1 to 0.05 $\mu\text{g/L}$ increases the frequency at which atrazine is detected by about 50 percent. It was estimated that an additional threefold increase in the frequency of atrazine detections could result if the reporting limit could be further decreased 0.002 $\mu\text{g/L}$.

The geographic distribution of herbicides and excess nitrate is nonuniform in near-surface aquifers of the study region. These contaminants were detected most frequently in the extreme western part of the study region, less frequently in the central part, and relatively infrequently in the eastern part. The infrequent detections in the eastern part of the study region are unexpected because of the intense herbicide and nitrogen-fertilizer use. Hydrogeologic characteristics of the eastern part of the study region generally are similar to those for the study region as a whole. Consequently, factors other than those examined in this study could affect herbicide detection and excess-nitrate occurrence in this area.

The frequency of herbicide detections was significantly larger in the postplanting season samples than in the preplanting samples from unconsolidated aquifers. Seasonal variations in the frequency of herbicide detection in the unconsolidated aquifers could be the result of relatively rapid recharge. One sample obtained during the summer might maximize the detection frequency, but multiple samples in an annual cycle need to be obtained to determine possible seasonal fluctuations in the detection frequency and concentration of herbicides.

Many hydrogeologic, land-use, agricultural-practice, local-feature, and water-chemistry factors were used in a statistical analysis to determine relations to herbicide detection and to excess-nitrate occurrence.

Unconsolidated aquifers were more susceptible to herbicide and excess-nitrate contamination than were bedrock aquifers. This difference could be a result of the relatively short flow paths from recharge areas to wells within many of the unconsolidated aquifers. The geometry and hydrology of alluvial aquifers limits the distance between recharge areas and wells, whereas the greater lateral extent of bedrock aquifers creates the potential for increased diversity of chemical use in recharge areas, longer flow paths from recharge areas to wells, and greater opportunity for dispersion of contaminants.

The depth to the top of the aquifer was inversely related to the frequency of herbicide detection and excess-nitrate occurrence. This factor was used as an indirect measure of the flow-path length that, in part, determines the amount of time available for the transportation, transformation, or adsorption of chemicals. Inverse relations existed between the frequency of herbicide detection and the depth to the top of the aquifer for samples from both unconsolidated and bedrock aquifers. However, excess nitrate was inversely related to the depth to the top of the aquifer only in bedrock aquifers. Unconsolidated aquifers generally are unconfined and receive more recharge from local sources than bedrock aquifers, which could account for the more uniform contamination by excess nitrate in the unconsolidated aquifers. Many decades of nitrogen-fertilizer use could extend the nitrate contamination to greater depths in particularly susceptible aquifers where dissolved oxygen is present.

The frequency of herbicide detection was related to the proximity of wells to streams. The frequency of detection in samples where a stream was within 100 ft of the well was more than double that for samples where a stream was not within 100 ft. The larger frequency of herbicide detection in samples from wells near streams could be the result of several factors, including a natural or induced hydraulic gradient from streams to aquifers or a convergence of flow paths that discharge to streams.

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