

Ground-Water Quality in Agricultural Areas, Anoka Sand Plain Aquifer, East-Central Minnesota, 1984-90

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Contents

Abstract	1
Introduction	2
Purpose and scope	2
Location and description of study area	2
Hydrogeology	2
Previous investigations.....	4
Methods of investigation.....	5
Ground-water-quality sampling and analysis	5
Sampling-well network	5
Sample collection	5
Sample analysis	7
Statistical methods	8
Well-numbering system	8
Acknowledgments	8
Ground-water quality, 1990	8
Inorganic constituents	8
Nutrients	10
Herbicides.....	14
Changes in ground-water quality, 1984-90.....	15
Summary	22
References.....	23

List of Illustrations

Figure 1-2. Maps showing:

1. Location of the Anoka Sand Plain and the Minnesota Management Systems Evaluation Area, Minnesota.....	3
2. Location of wells sampled in the Anoka Sand Plain aquifer, August through November 1990.....	6
3. Diagram showing well location and well-numbering system	9
4. Trilinear diagram showing the chemical character of ground water in the Anoka Sand Plain aquifer, August through November 1990.....	11
5. Box plots showing the statistical distribution of selected chemical constituents in the Anoka Sand Plain aquifer, August through November 1990.....	12
6-8. Maps showing:	
6. Concentrations of nitrite-plus-nitrate nitrogen in the Anoka Sand Plain aquifer, August through November 1990.....	13
7. Concentrations of atrazine in the Anoka Sand Plain aquifer, August through November 1990	16
8. Concentrations of de-ethylatrazine in the Anoka Sand Plain aquifer, August through November 1990	17

List of Illustrations—Continued

9-10. Graphs showing:

9. Relation of nitrite-plus-nitrate nitrogen and atrazine concentrations in the Anoka Sand Plain aquifer, August through November 1990	18
10. Monthly precipitation, water-level hydrographs, and concentrations of nitrite-plus-nitrate nitrogen for selected wells in the Anoka Sand Plain aquifer, 1984-90	20

Conversion Factors and Abbreviations

<u>Multiply</u>	<u>By</u>	<u>To obtain</u>
kilometer (km)	0.6214	mile
meter (m)	3.281	foot
meter per day (m/d)	3.281	foot per day
centimeter (cm)	.3937	inch
centimeter per day (cm/d)	.0328	foot per day
hectare (ha)	2.471	acre
liter (L)	.2642	gallon
liter per second (L/s)	15.85	gallon per minute
square kilometer (km ²)	.3861	square mile
<u>Temperature</u>		
degree Celsius (°C)	°F = 9/5 °C + 32	degree Fahrenheit (°F)

Sea level: In this report sea level refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

Chemical concentrations are given in milligrams per liter (mg/L) or micrograms per liter (µg/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter.

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Abstract

Ground-water quality in the Anoka Sand Plain aquifer was studied as part of the multiscale Management Systems Evaluation Area (MSEA) study by collecting water samples from shallow wells during August through November 1990. The sampling was conducted to: (1) aid in selection of the MSEA research area; (2) facilitate comparison of results at the MSEA research area to the regional scale; and (3) evaluate changes in ground-water quality in the Anoka Sand Plain aquifer since a previous study during 1984 through 1987. Samples were collected from 34 wells screened in the upper 6 meters of the surficial aquifer and located in cultivated agricultural areas. Water temperature, pH, specific conductance, and presence or absence of triazine herbicides were determined at all sites and samples from selected wells were analyzed for concentrations of dissolved oxygen, alkalinity, major cations and anions, nutrients, and selected herbicides and herbicide metabolites. The results of the study indicate that the water-quality of some shallow ground water in areas of predominantly agricultural land use has been affected by applications of nitrogen fertilizers and the herbicide atrazine.

Concentrations of nitrite plus nitrate nitrogen (nitrate-N) in 19 samples ranged from less than the detection limit of 0.1 to 21 milligrams per liter (mg/L) with a median of 10 mg/L. Concentrations of nitrate-N were not significantly correlated with depth below the water table or dissolved oxygen but were significantly correlated with concentrations of chloride. Concentrations of nitrate-N during 1990 were generally similar to concentrations measured during 1984 through 1987. Changes in concentrations of nitrate-N during 1984 through 1990 were likely related to variations in recharge or other site-specific factors.

Immunoassay analyses were used as screening tools to detect the presence of triazine herbicides. All samples in which triazine herbicides were detected by immunoassay, and selected samples in which triazine herbicides were not detected by immunoassay, were analyzed for selected herbicides and herbicide metabolites by gas chromatography/mass spectroscopy (GC/MS). There was an excellent correspondence between concentrations of triazine herbicides indicated by immunoassay and concentrations of atrazine measured by GC/MS, indicating that the immunoassay method was a valuable qualitative to semi-quantitative tool for evaluating the presence and approximate concentration of atrazine.

The combined results of immunoassay and GC/MS analyses indicate that atrazine was detected in 11 of the 34 wells with a median concentration less than the immunoassay detection limit of 0.1 micrograms per liter ($\mu\text{g/L}$). Atrazine was detected in 11 of the 17 samples analyzed by GC/MS at concentrations ranging from the detection limit of 0.05 to 0.81 $\mu\text{g/L}$ with a median of 0.09 $\mu\text{g/L}$. Atrazine metabolite de-ethylatrazine (DEA) was the most frequently detected herbicide or herbicide metabolite and generally was present at the greatest concentrations. There were detections of DEA in 13 of the 17 samples analyzed at concentrations ranging from the detection limit of 0.05 to 1.12 $\mu\text{g/L}$ with a median of 0.15 $\mu\text{g/L}$. Concentrations of DEA were significantly correlated with concentrations of calcium, magnesium, and specific conductance. The atrazine metabolite de-isopropylatrazine and the herbicide metolachlor both were detected in 1 of the 17 wells. The frequency of detection and the concentrations of atrazine in shallow ground water during 1990 were very similar to results of sampling conducted in 1984.

Concentrations of atrazine and DEA generally were greater near the water table and decreased or were not detected in deeper wells. All of the samples in which atrazine and DEA were detected also had increased (greater than 3 mg/L) nitrate-N concentrations. However, not all samples with increased concentrations of nitrate-N had detections of atrazine or DEA. This likely indicates either that there were sources of nitrate-N other than cultivated fields on which both atrazine and nitrogen were applied or that nitrate-N reached ground water more readily than atrazine or DEA.

Introduction

Sampling of ground-water quality in the Anoka Sand Plain aquifer was conducted during 1990 as part of the Minnesota Management Systems Evaluation Area (MSEA) study. The sampling was conducted to: (1) aid in selection of the MSEA research area; (2) facilitate comparison of results at the MSEA research area to the regional scale; and (3) evaluate changes in ground-water quality in the Anoka Sand Plain aquifer since a previous ground-water study conducted during 1984 through 1987 (Anderson, 1993).

In the Anoka Sand Plain, applications of fertilizers and herbicides are major sources of ground-water contamination (Anderson, 1993). Ground water in the surficial aquifer is susceptible to contamination because of the shallow depth of the water table below land surface, highly permeable aquifer material, and relatively high recharge rates that are characteristic of many sand-plain environments (Anderson, 1993; Komor and Anderson, 1993).

The Minnesota MSEA is one of five primary MSEA's in the Midwest corn belt (Delin and others, 1992). The Midwest corn belt was selected for intensive study because the majority of agricultural chemical use occurs in this area of the United States (Burkhart and others, 1990; Kolpin and others, 1993; Thurman and others, 1992). The MSEA's are located in different hydrogeologic and climatic settings (Hatfield and others, 1993). One of the objectives of the MSEA program is to evaluate the effects of agricultural management systems on water quality at multiple scales (Delin and others, 1992). The Minnesota MSEA is located within the Anoka Sand Plain in east-central Minnesota near the town of Princeton (fig. 1). Cooperative research at the Minnesota MSEA is being conducted primarily by the U.S. Geological Survey, the University of Minnesota Department of Soil Science, the U.S. Department of Agriculture—Agricultural Research Service, and the Minnesota Pollution Control Agency. The effects of improved and existing farming systems on ground-water quality are being evaluated at the Minnesota MSEA (Anderson and others, 1991; Delin and others, 1992; Landon and others, 1993).

Purpose and Scope

This report describes the results of reconnaissance sampling of ground-water quality in the Anoka Sand Plain aquifer during August through November 1990 and compares the results to those obtained in a previous study during 1984 through 1987 (Anderson, 1993). Water samples were collected from 34 wells screened in the upper 6 m of the Anoka Sand Plain aquifer (surficial

aquifer). The wells were located in areas of predominantly cultivated agricultural land use. The samples, therefore, represented shallow ground water in cultivated agricultural settings. The purpose of the sampling was to evaluate areal differences in ground-water quality in agricultural areas of the Anoka Sand Plain. Water samples also were collected from well nests at four locations to evaluate vertical differences in water-quality. This report emphasizes the distribution of nitrite plus nitrate nitrogen (nitrate-N) and herbicides in the Anoka Sand Plain aquifer.

Location and Description of Study Area

The Anoka Sand Plain forms an aquifer that has an areal extent of about 4,400 km² in parts of 11 counties in east-central Minnesota (fig. 1). The aquifer is used extensively for irrigation and domestic water supplies. Land use within the sand plain is predominantly agricultural with appreciable suburban and natural land use in some areas. Both irrigated and non-irrigated cultivation are present. The southeast corner of the Anoka Sand Plain (southern Anoka County, fig. 1) is part of the Minneapolis-St. Paul metropolitan area and is predominantly suburban. Water samples were not collected in suburban areas.

The surficial sand and gravel aquifer is susceptible to contamination from human activity at land surface. Agricultural chemicals (fertilizers and pesticides), manure from feedlots, lawn fertilizer, and septic-system effluent in suburban areas are potential sources of ground-water contamination in the Anoka Sand Plain aquifer.

Hydrogeology

The Anoka Sand Plain is composed of glacial deposits from several glacial advances and retreats during the Quaternary glaciation (Wright, 1972a, Wright, 1972b, and Wright and Ruhe, 1965). The sand plain was formed primarily by glacio-fluvial processes as glacial ice melted during the eastward diversion of the glacial Mississippi River around the Grantsburg sublobe of the Wisconsin glaciation (Cooper, 1935; Farnham, 1956). About 6 percent of the Anoka Sand Plain was re-worked by eolian processes (Cooper, 1935). Gray till deposited by the Grantsburg sublobe is present at the land surface on some topographic highs where outwash was not deposited. Underlying the surficial outwash is red till deposited by the Superior lobe of the Wisconsin glaciation (Cooper, 1935; Farnham, 1956). This glacial lobe expanded out of the Lake Superior Basin into the study area prior to the Grantsburg-sublobe advance.

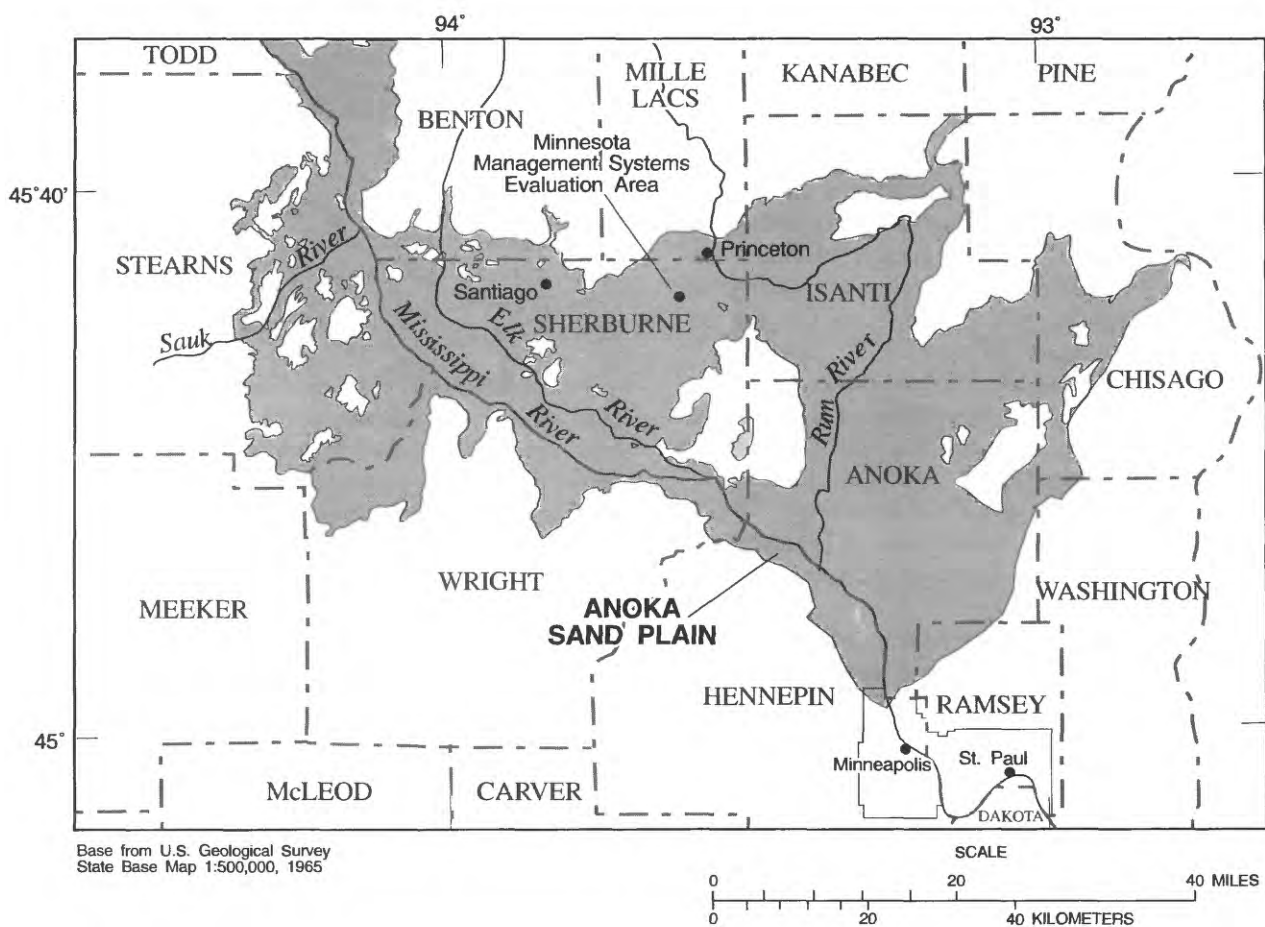


Figure 1.—Location of the Anoka Sand Plain and the Minnesota Management Systems Evaluation Area, Minnesota.

The outwash deposits are generally 5 to 35 m thick across the study area and consist of two units (Lindholm, 1980). The lower outwash unit is red sand of Superior lobe origin. It is discontinuous in the eastern two-thirds of the study area and is not present in the western one-third of the study area (Anderson, 1993). The upper outwash unit is gray sand of Grantsburg sublobe origin and is continuous across the study area. The outwash sediments generally consist of medium to coarse sand interlayered with clay, silt, silty sand, and gravel (Helgesen and Lindholm, 1977; Lindholm, 1980). Average mineralogical composition of the sediments at the Minnesota MSEA in the central part of the sand plain are 73 weight percent quartz, 14 weight percent plagioclase, 8 weight percent potassium feldspar, and 5 weight percent of carbonates, mica, montmorillonite, kaolinite, amphibole, and magnetite combined (Komor and Anderson, 1993).

Recharge to the Anoka Sand Plain aquifer is primarily from rain and snowmelt that percolates into the sandy soil and through the unsaturated zone to the water table (Lindholm, 1980). Most recharge generally occurs following spring snowmelt and spring rainfall. A second period of recharge generally occurs in the fall after the growing season but prior to freezing of the soil. Recharge averages about 20 cm per year (Lindholm, 1980). Most of the approximately 74 cm of mean annual precipitation is rainfall from May through September (Baker and Kuehnast, 1978). In irrigated fields, approximately 20 to 26 cm of irrigation water are added to corn crops during the growing season (U.S. Soil Conservation Service, 1976).

Water in the aquifer flows from areas of high hydraulic head toward areas of low hydraulic head and discharges to streams, lakes, and marshes. The water-table surface is generally a subdued reflection of the land surface topography (Lindholm, 1980; Palen and others, 1993). Ground-water withdrawal by pumping from wells also influences the ground-water flow paths (Lindholm, 1980).

Depths to the water table generally range from 0 to 10 m. Average annual fluctuation of the water table is about 60 cm (Anderson, 1993). Hydraulic gradients (vertical distance/horizontal distance) of shallow ground water generally are less than 2 m/km (Magner and others, 1990a). Saturated thickness typically ranges from 6 to 18 m. Hydraulic conductivity in sand and gravel deposits typically ranges from 30 to 150 m/day (Lindholm, 1980). About 20 percent of the Anoka Sand Plain aquifer is capable of yielding water to a well at a rate greater than about 30 L/s.

Previous Investigations

Reconnaissance studies of water resources that include parts of the Anoka Sand Plain are summarized by Ericson and others (1974), Lindholm and others (1974), and Helgesen and others (1975). Magner and others (1990a, 1990b) described hydrogeologic and land-use factors influencing water quality in predominantly agricultural study areas of less than 5 km² located within the Anoka Sand Plain in Stearns and Benton Counties.

Anderson (1993) collected samples from 100 wells in the Anoka Sand Plain aquifer during 1984 through 1987 to determine the effects of land use on the quality of ground water. Samples were collected from depths ranging from the water table to 30 m below the water table. Areal differences in water quality were evaluated with respect to the following major land-use types: natural-undeveloped, nonirrigated-cultivated, irrigated-cultivated, and residential. Analysis of 360 water samples indicated that the median concentrations of nitrate-N for areas of natural-undeveloped, nonirrigated-cultivated, irrigated-cultivated, and residential land use were 0.22, 2.0, 5.3, and 4.2 mg/L, respectively. Evaluation of vertical differences in water quality for 31 well clusters indicated that decreases in concentrations of nitrate-N with depth were statistically significant.

Komor and Anderson (1993) investigated the sources of nitrate-N in the Anoka Sand Plain aquifer using nitrogen isotopes. Nitrogen-isotope values of nitrate-N were measured in ground water from 51 wells in 1986-87 from the following five land-use settings: livestock feedlots, irrigated-cultivated fields, residential areas with septic systems, nonirrigated-cultivated fields, and natural-undeveloped areas. Nitrate-N concentrations and isotopic values indicated that nitrogen from commercial inorganic fertilizers was present in some ground water beneath all settings except the feedlots. Nitrate-N concentrations and isotopic values also indicated that nitrogen from animal waste was present in ground water beneath some feedlots, irrigated-cultivated fields that were fertilized with manure, and residential areas with septic systems. Nitrogen isotopic values of nitrate-N were found to increase with depth in many locations in the Anoka Sand Plain aquifer, possibly indicating progressive denitrification with depth or changes with depth in the proportions of nitrate-N from different sources.

Palen and others (1993) collected water samples from 43 wells in the Anoka Sand Plain aquifer from December 1990 to July 1991. The depth of the wells ranged from 16 to 100 m with a median depth of 35 m below land surface. Results were used to evaluate

recharge mechanisms and to verify the pollution sensitivity map developed during the study (Minnesota Department of Natural Resources, 1993). Some shallow wells were found to contain chloride, sulfate, and nitrate-N concentrations higher than typical background levels. Background levels of chloride, sulfate, and nitrate-N were interpreted to be less than 10 mg/L, less than 10 mg/L, and less than 2 mg/L, respectively.

Methods of Investigation

Ground-water-quality sampling and analysis

Water samples were collected from 34 wells in the Anoka Sand Plain aquifer from August 15 to November 1, 1990 (fig. 2). All but two of the wells were sampled from August 15 to September 13, 1990. Samples were collected from observation wells at the Minnesota MSEA on October 5 and on November 1, 1990.

Sampling-well network

Samples were collected from 31 observation wells and 3 domestic wells completed in the Anoka Sand Plain aquifer. Twenty-one of the observation wells were constructed of 5-cm diameter galvanized-steel casing with 90-cm-long galvanized screens. These wells were installed and sampled during a previous study of water quality during 1984 through 1987 (Anderson, 1993). Thus, 62 percent of the wells (21 of 34 wells) sampled in this study also were sampled during the 1984-87 study. Seven of the observation wells were constructed of 3.2-cm diameter galvanized-steel casing with 60-cm-long galvanized-steel screens. These wells were installed during previous hydrologic studies of the Anoka Sand Plain (Lindholm, 1980; Helgesen and Lindholm, 1977) but were not previously sampled for water quality. One of the observation wells was constructed of 5-cm diameter galvanized-steel casing with a 60-cm-long stainless-steel screen. This well was installed and sampled as part of a water-quality study conducted by the Minnesota Pollution Control Agency in Stearns County from 1987 to 1989 (Magner and others, 1990b). Two of the observation wells were constructed of 5-cm diameter galvanized-steel casing with 60-cm-long stainless-steel well screens and were installed at the Minnesota MSEA in October 1990. Well completion information was known for all wells except for two of the domestic wells. The bottom of the screen in all of the wells was within 6 m of the water table; the median depth of the bottom of the screen was 2.1 m below the water table. Four of the wells had screens that intersected the water table; the median depth of the top of the screen was 1.1 m below the water table.

Wells selected for sampling were chosen on the basis of the following criteria: (1) Wells were selected to obtain a distribution in the sand plain that was as even as possible; (2) Because the primary purpose of the MSEA study was to evaluate the effects of agricultural practices on ground-water quality, the wells selected were in rural areas where cultivated agriculture was the predominant land use. Wells in the southeastern part of sand plain were excluded because the Twin Cities metropolitan area (Hennepin, Ramsey, and Anoka Counties, fig. 1) encroaches on this area. Of the 34 wells sampled, 29 were immediately adjacent to or within a cultivated field. The remaining five wells were not immediately adjacent to cultivated fields but were in areas of predominantly cultivated-agricultural land use. Two of these wells were located on the edge of woodlands; (3) Because agricultural practices have the greatest effect on ground-water quality near the water table, only wells screened in the upper 6 m of the saturated zone were selected. While the main purpose of the study was to evaluate areal differences in ground-water-quality across the sand plain, samples also were collected from well nests at 4 locations to evaluate vertical differences in water quality. Each well nest consisted of two wells screened at different depths, generally with one well screened within 3 m of the water table and one well screened between 3 and 6 m below the water table; (4) Observation wells were selected in preference to domestic wells because they generally had more accurate geologic logs plus water-quality and water-level information. Because domestic wells generally were screened deeper in the aquifer, they were selected only in areas where observation wells were not present; (5) Wells were selected near potential locations for the MSEA study area.

Sample collection

Water samples were collected either by pumping with a peristaltic pump equipped with Teflon¹ tubing or by bailing with a Teflon bailer. A water level was measured in each observation well prior to well purging. At least 3 well volumes were purged from the well prior to sampling. Purging continued until measured field parameters were stable. The field parameters monitored before sampling included specific conductance, pH, dissolved oxygen (DO), and water temperature. Field parameters were considered approximately stable when the following criteria were met for at least 2 minutes: (1) a change in specific conductance of less than 3

¹ Use of brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey

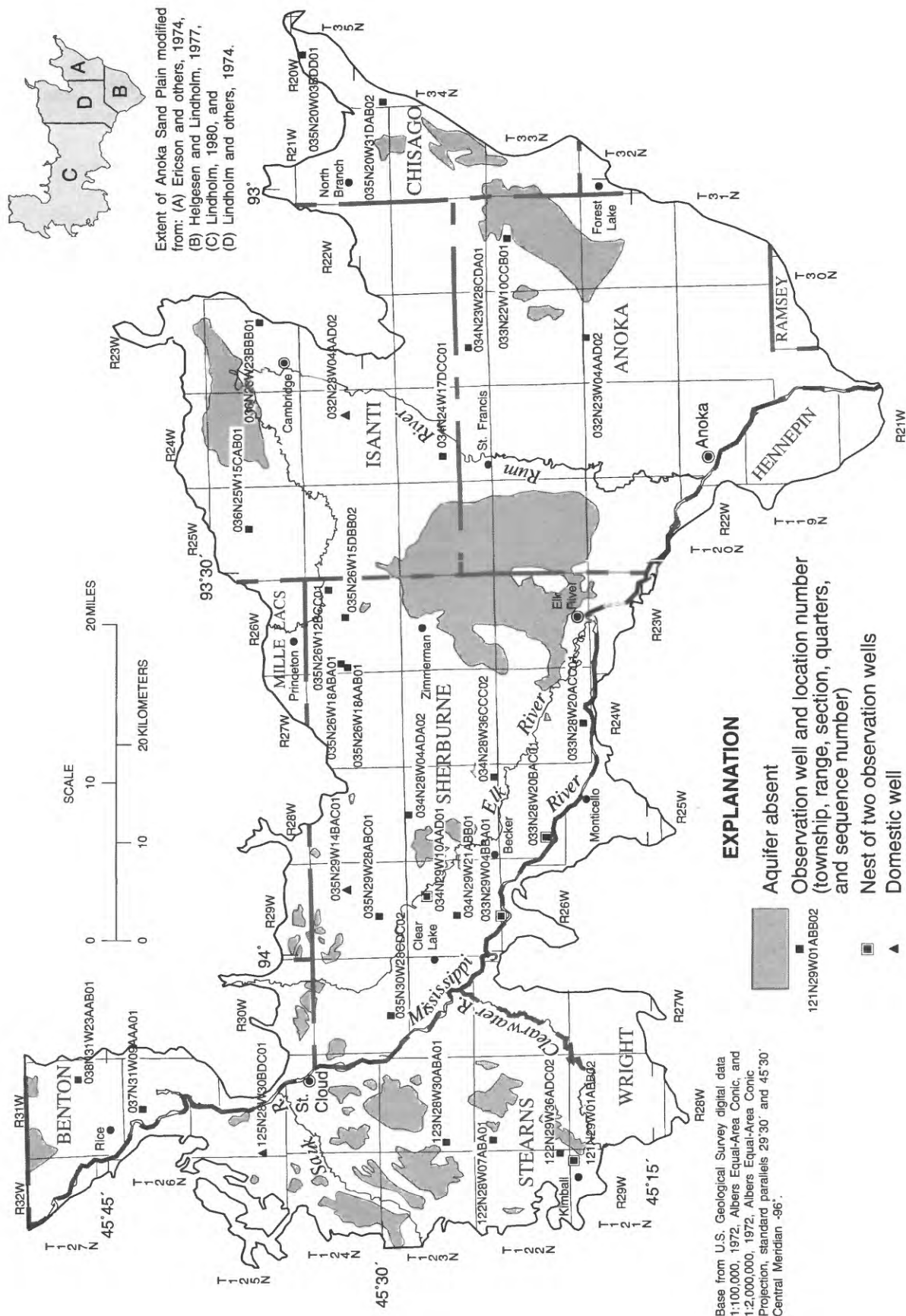


Figure 2.--Location of wells sampled in the Anoka Sand Plain aquifer, August through November 1990.

microsiemens per centimeter ($\mu\text{S}/\text{cm}$) per minute, (2) a change in pH of less than 0.02 units per minute, and (3) a change in DO of less than 0.1 mg/L per minute. A Hydrolab multiparameter monitoring system equipped with a flow-through chamber was used to monitor water temperature, specific conductance, pH, and DO during purging at 24 of the well sites. At the remaining 10 well sites, water temperature was measured with a thermometer, specific conductance was measured with a Beckman RB-5 meter, and pH was measured with a Radiometer meter with separate reference and glass pH electrodes. Instruments for measuring specific conductance and pH were calibrated daily with standards bracketing the range of values for water samples. Instruments for measuring DO were calibrated to the atmosphere daily. Alkalinity was determined for 24 samples by performing incremental titrations using a pH meter and 1.6-Normal sulfuric acid following the methods of Wells and others (1990). Alkalinity titrations were performed the same day the samples were collected.

Samples to be analyzed for inorganic constituents and nutrients were filtered through a 142-millimeter (mm)-diameter 0.45-micrometer (μm) cellulose nitrate filter. The filter and sample bottles were thoroughly rinsed with sample water before sample collection. Samples to be analyzed for cations were collected in 250 milliliter (mL) acid-rinsed polyethylene bottles and were acidified by adding 1 mL of concentrated nitric acid. One unfiltered, untreated sample and one filtered, untreated sample also were collected in 250 mL polyethylene bottles to be analyzed for other inorganic constituents. Nutrient samples were collected in opaque 250 mL polyethylene bottles and immediately preserved by adding 1 mL of mercuric chloride as a biocide. Samples to be analyzed for herbicides and herbicide metabolites were filtered through a 47-mm, 0.45- μm baked (at 450°C for 12 hours) glass-fiber filter in a stainless-steel filter holder and collected in baked 1 L amber glass bottles. All samples were placed in ice-filled coolers immediately after collection and preservation. Samples were stored in a refrigerator until they were sent to the analytical laboratory.

After sample collection, all sampling equipment was cleaned by thoroughly rinsing with organic-free deionized water and with methanol. The equipment was allowed to dry before further use.

Samples were collected and analyzed in triplicate at one well for quality assurance/quality control (QA/QC). An equipment blank using organic-free deionized water also was collected for QA/QC. These samples accounted for 15 percent of the total analyses.

Sample analysis

Water samples were tested for the presence of triazine herbicides with an immunoassay analysis kit manufactured by Immunosystems Inc. (Biddleford, Mass.) and a Dynatech MR250 portable microplate reader (Chantilly, Va.). The analytical procedures used in the immunoassay process are described by Thurman and others (1990). In brief, the adsorbance of standards having concentrations of 0.0, 0.1, 0.25, and 2.0 $\mu\text{g}/\text{L}$ atrazine were measured and compared to the adsorbance of water samples to evaluate whether triazine herbicides were present. The detection limit of the immunoassay analysis was 0.1 $\mu\text{g}/\text{L}$ for the triazine herbicides. The immunoassay analysis did not differentiate between various triazine compounds but was more sensitive to some triazine compounds than to others. For instance, the triazine immunoassay analysis is most sensitive to the presence of atrazine but has a very low sensitivity to atrazine metabolites de-ethylatrazine and de-isopropylatrazine. Three to eight analyses of all samples and standards were performed to verify the reproducibility of the results and to evaluate sensitivity of the measurements to environmental and instrument conditions. The results of the immunoassay analyses were used as one criterion in deciding which samples were to be analyzed for concentrations of major inorganic constituents, nutrients, and herbicides and herbicide metabolites.

A total of 17 environmental and 3 QA/QC samples were analyzed for dissolved major inorganic constituents (calcium, magnesium, sodium, potassium, silica, iron, manganese, chloride, sulfate, fluoride, and dissolved solids) and nutrients (ammonia nitrogen, ammonia plus organic nitrogen, nitrite-plus-nitrate nitrogen, total phosphorus, and orthophosphate) at the U.S. Geological Survey's National Water-Quality Laboratory in Arvada, Colo., using methods described in Fishman and Friedman (1989). Selected samples that had detections of triazine herbicides using the immunoassay test were analyzed. The remainder of the samples analyzed were selected to obtain the most comprehensive areal coverage of the sand plain.

A total of 17 environmental and 3 QA/QC samples were analyzed for herbicides and herbicide metabolites (atrazine, de-ethylatrazine (DEA), de-isopropylatrazine (DIA), alachlor, ametryn, metolachlor, simazine, propazine, cyanazine, metribuzin, prometryn, prometon, and terbutryn) at the U.S. Geological Survey's Organic Geochemistry Research Laboratory in Lawrence, Kans., using gas chromatography/mass spectroscopy (GC/MS) following methods described in Thurman and others (1992). All samples with detections of triazine herbicides (8 samples) by immunoassay analysis were

analyzed for herbicides and herbicide metabolites by GC/MS. An additional 9 samples in which triazine herbicides were not detected by immunoassay analysis also were analyzed by GC/MS.

Statistical methods

Relations between selected chemical constituents were evaluated using both parametric (Pearson) and nonparametric (Kendall) correlation tests (Helsel and Hirsch, 1992). Correlation coefficients provide a measure of the strength of association between two variables. A correlation between two variables, however, does not necessarily provide evidence of a causal relation between the two variables (Helsel and Hirsch, 1992). The Pearson correlation measures the linear association between two variables. Because the Pearson correlation is not resistant to outliers and assumes the data follow a normal distribution, all significant Pearson correlations were plotted graphically to verify that the data approximately met the requirements of the test. Kendall correlations were calculated as a comparison to the Pearson correlations. Results of the two correlation methods were generally similar. Correlation coefficients referred to in this report are Pearson coefficients (r). The correlation coefficient squared (r^2) indicates the proportion of variation in the y variable that can be attributed to a linear relationship between the x and y variables (Devore and Peck, 1986).

The attained significance level (p -value) was calculated and compared to a predetermined significance level ($\alpha = 0.01$) to determine when a correlation was statistically significant. The p -value is the probability of obtaining the computed test statistic when the null hypothesis (no correlation between variables) is true. The smaller the p -value, the less likely is the observed test statistic when the null hypothesis is true (Helsel and Hirsch, 1992). If the p -value was less than α the null hypothesis was rejected and the correlation was considered significant. Correlations were considered statistically significant only if p was less than α for both the Pearson and Kendall correlations. All statistics were determined using SAS statistical software (SAS Institute Inc., 1989).

Well-Numbering System

The system of numbering wells in this report is based on the U.S. Bureau of Land Management's system of land subdivision (township, range, and section). The system of numbering data-collection points is shown in figure 3. In this system, the first number of a location number indicates the township; the second, the range; and the third, the section in which the well is located.

Upper-case letters after the section number indicate the location within the section; the first letter denotes the 160-acre tract; the second, the 40-acre tract; and the third, the 10-acre tract; and so forth. Letters A, B, C, and D are assigned in a counterclockwise direction, beginning in the northeast corner of each tract. For example, the number 035N26W18ADC01 indicates the location of a well in the southwest 1/4 of the southeast 1/4 of the northeast 1/4 of section 18, range 26 west, township 35 north (fig. 3). The two-digit number at the end of the well number is a sequence number which indicates the relative depth of the well if there is a well nest present at that location. For instance, if the sequence number is 01 the well is the shallowest present at the site; a sequence number of 02 indicates the well is screened deeper in the aquifer.

Acknowledgments

Property owners are thanked for their cooperation and the use of their wells for collecting water samples. Appreciation also is extended to the Soil and Water Conservation Districts of Sherburne and Stearns Counties for assistance in well selection. Appreciation is extended to Chuck Regan, Minnesota Pollution Control Agency, for input on data analysis. Appreciation is extended to Joe Magner, Minnesota Pollution Control Agency, for advice concerning sampling of wells. Appreciation is extended to John Hines, Minnesota Department of Agriculture, for supplying preliminary ground-water quality data which aided in the well selection process.

Ground-Water Quality, 1990

The results of reconnaissance sampling of ground-water quality in the Anoka Sand Plain aquifer during August through November 1990 are described in the sections below.

Inorganic Constituents

Of the 17 samples analyzed for cations and anions, 12 were calcium-bicarbonate type waters (fig. 4). A calcium-bicarbonate type water is a sample in which calcium is more than 60 percent (in milliequivalents) of the total cations and bicarbonate is more than 60 percent (in milliequivalents) of the total anions. If no single cation (or cation grouping, fig. 4) is more than 60 percent of the total cations then the water is of mixed type with respect to cations and similarly with anions. Three samples were calcium-mixed-bicarbonate-chloride and nitrate-N type waters (fig. 4). One sample (033N22W10CCB01) was a mixed-calcium-magnesium-chloride and nitrate-N type water (fig. 4).

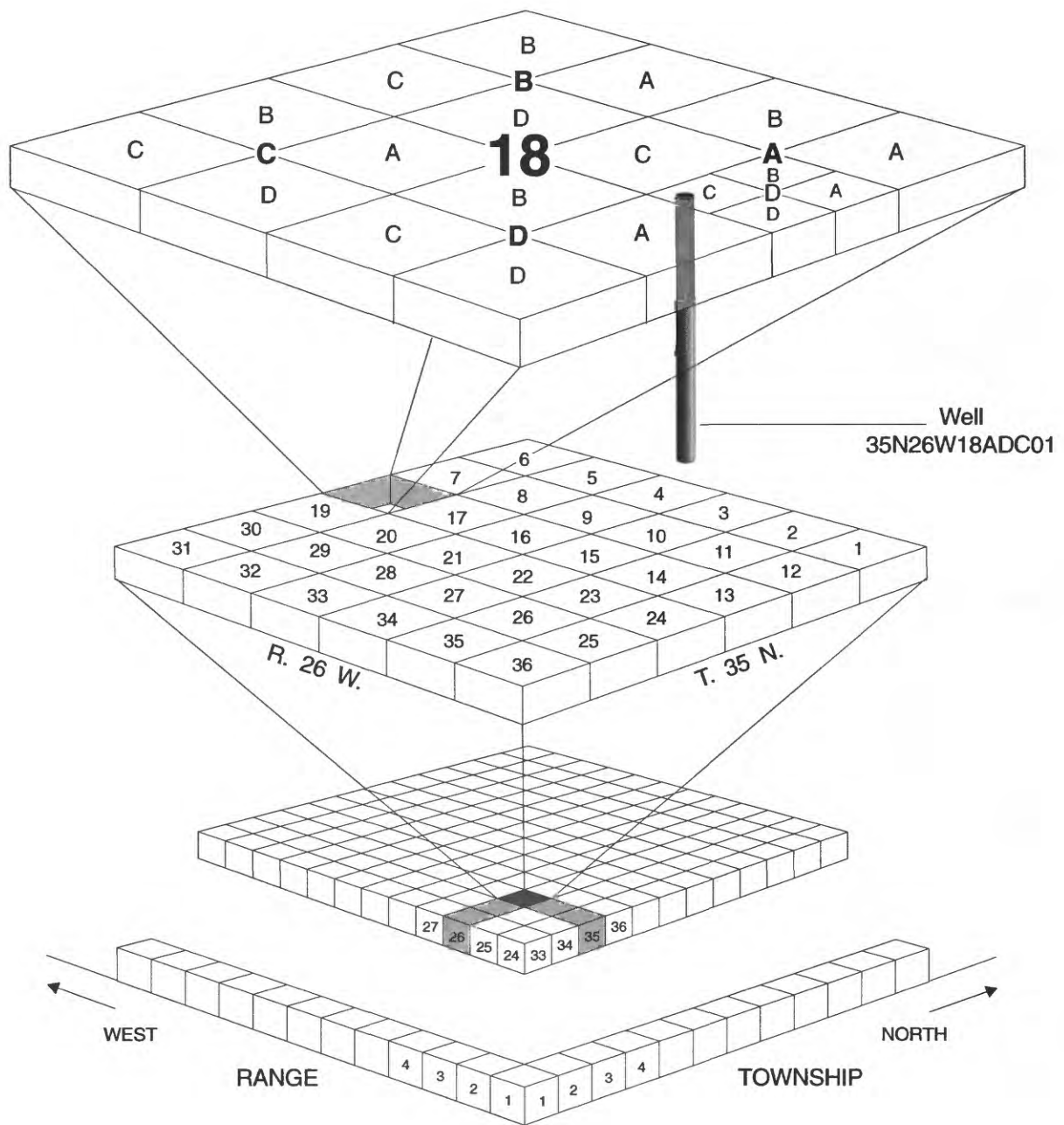


Figure 3.—Well location and well-numbering system.

This sample was collected from a well on the edge of a corn field. One sample collected from a domestic well (125N28W30BDC01), was a mixed-sodium-calcium-bicarbonate type water (sodium was 56 percent of total cations) (fig. 4). This result is anomalous for ground water near the water table in an outwash aquifer. Because the history of this well was not known, it cannot be conclusively determined whether this sample represents contaminated or treated ground water or whether a natural process produces sodium-bicarbonate water at this location. However, the well owner indicated that the water was not softened or treated. Most of the samples plotted in one of two distinct clusters on the anion portion of the trilinear diagram (fig. 4). Differences in the major-ion chemistry of these two groups of samples were related to the abundance of chloride and nitrate-N even though all of these samples had bicarbonate as the most abundant anion. Total hardness (calcium plus magnesium) ranged from 54 to 410 mg/L as calcium carbonate, with a median concentration of 290 mg/L, indicating that much of the shallow ground water in the Anoka Sand Plain aquifer can be classified as very hard (more than 180 mg/L as calcium carbonate) (Hem, 1992).

Concentrations of DO ranged from 1.2 to 8.1 mg/L with a median of 5.4 mg/L (fig. 5). Thus, all of the ground-water samples were oxygenated. Concentrations of DO did not decrease systematically with depth below the water table, as observed in other studies (Postma and others, 1991). However, this lack of correlation with depth below the water table likely resulted from all samples being collected from the upper few meters of the aquifer. This part of the aquifer likely is influenced by frequent influxes of oxygenated recharge water.

Statistical analyses indicated significant correlations between calcium and magnesium concentrations ($r = 0.97$, $p = 0.0001$). Concentrations of these constituents also were significantly correlated with concentrations of bicarbonate ($r=0.87$, $p=0.0001$ for calcium; $r = 0.83$, $p=0.0001$ for magnesium). Concentrations of magnesium were significantly correlated with concentrations of chloride ($r=0.68$, $p=0.0026$) but concentrations of calcium were not. Concentrations of calcium and magnesium were not significantly correlated with concentrations of nitrate-N or sulfate, the other major anions.

As would be expected, there were significant correlations between specific conductance and the major dissolved ions calcium ($r=0.96$, $p=0.0001$), magnesium ($r=0.96$, $p=0.0001$), and bicarbonate (0.82 , $p=0.0001$). Specific conductance also was significantly correlated with concentrations of chloride ($r=0.70$, $p=0.0019$) but was not significantly correlated with other major inorganic constituents.

Depth of the well screen below the water table was not significantly correlated with concentrations of any major inorganic constituent in the upper 6 m of the saturated zone from which the samples were collected. Similarly, well depth below land surface was not significantly correlated with concentrations of any major inorganic constituent.

Nutrients

The median concentration of nitrate-N in this study was identical to the U.S. Environmental Protection Agency's (USEPA) Maximum Contaminant Level (MCL) of 10 mg/L for nitrate nitrogen (fig. 5) (U.S. Environmental Protection Agency, 1986). Concentrations of nitrate-N equaled or exceeded the MCL in 10 of the 19 samples analyzed (fig. 6). Concentrations of nitrate-N ranged from less than the detection limit of 0.1 to 21 mg/L. Results of previous studies have indicated that concentrations of nitrate-N greater than 3 mg/L reflect the effects of anthropogenic activities (Fedkiw, 1991; Anderson, 1993). Of the 19 samples analyzed for nitrate-N, 14 had concentrations greater than 3 mg/L.

Nitrate-N was the predominant nutrient in all of the water samples except one. Median concentrations of ammonia nitrogen and ammonia plus organic nitrogen were 0.03 and 0.70 mg/L, respectively (fig. 5). Subtracting concentrations of ammonia nitrogen from concentrations of ammonia plus organic nitrogen indicates that organic nitrogen was the second most abundant nitrogen species present. Both of these constituents were present in all but one of the samples analyzed. Concentrations of total phosphorus and orthophosphate were above the detection limit of 0.01 mg/L in 3 and 4 of the samples analyzed, respectively, and had median concentrations less than the detection limit.

Concentrations of nitrate-N were not correlated with depth below the water table ($r=0.03$, $p=0.9134$), in contrast to the results of Anderson (1993). Concentrations of nitrate-N in wells screened less than 3 m below the water table ranged from less than the detection limit of 0.1 mg/L to 20 mg/L with a median of 10 mg/L. By comparison, concentrations of nitrate-N in wells screened 3 m to 6 m below the water table ranged from 0.2 to 21 mg/L with a median of 12 mg/L.

Concentrations of nitrate-N were determined in samples collected from three well nests where one well was screened less than 3 m below the water table (shallow) and one well was screened between 3 and 6 m below the water table (deep). In two of the three well nests (121N29W01ABB, 033N28W20BAC)

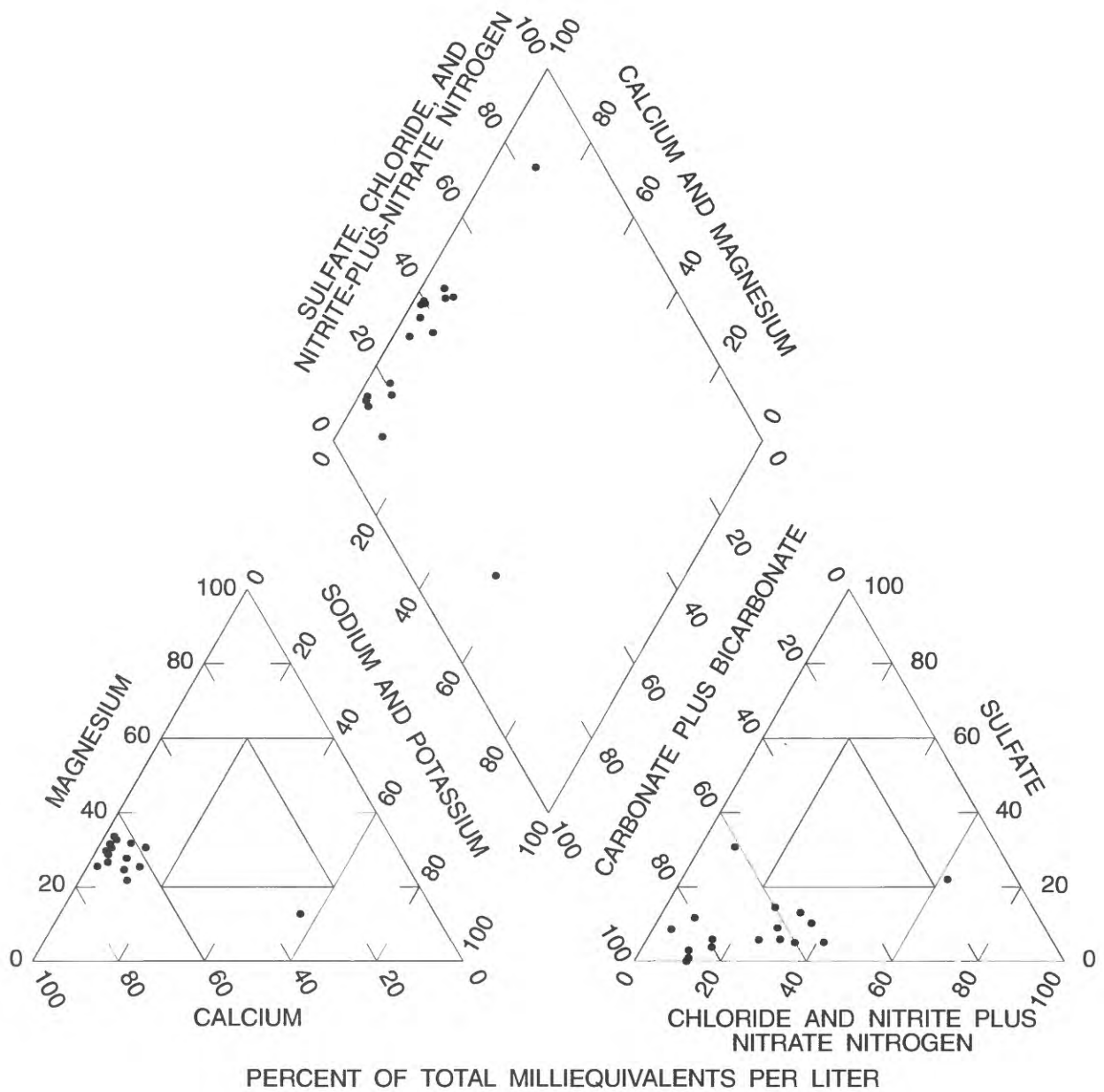


Figure 4.--Trilinear diagram showing the chemical character of ground water in the Anoka Sand Plain aquifer, August through November 1990.

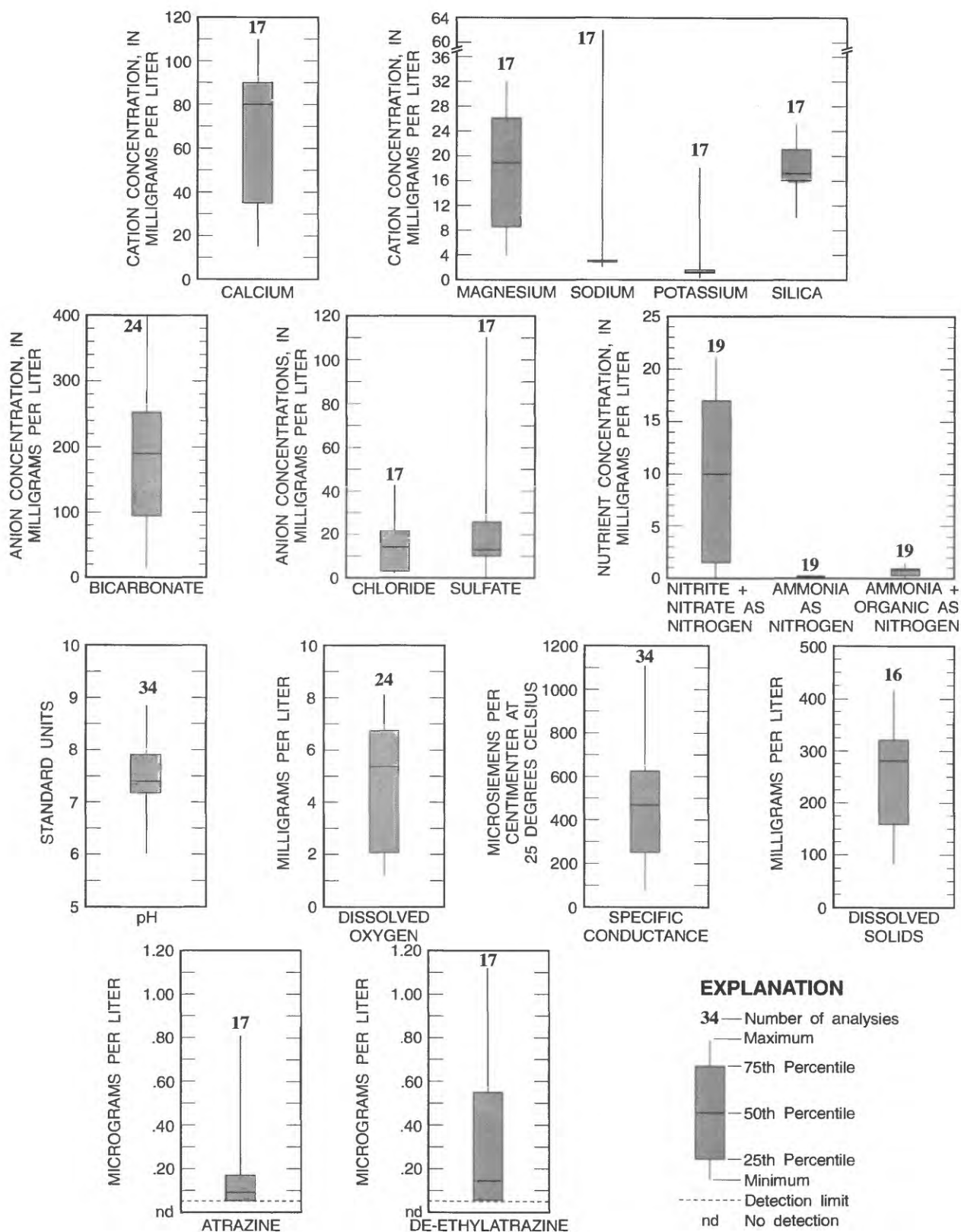


Figure 5.—Statistical distribution of selected chemical constituents in the Anoka Sand Plain aquifer, August through November 1990.

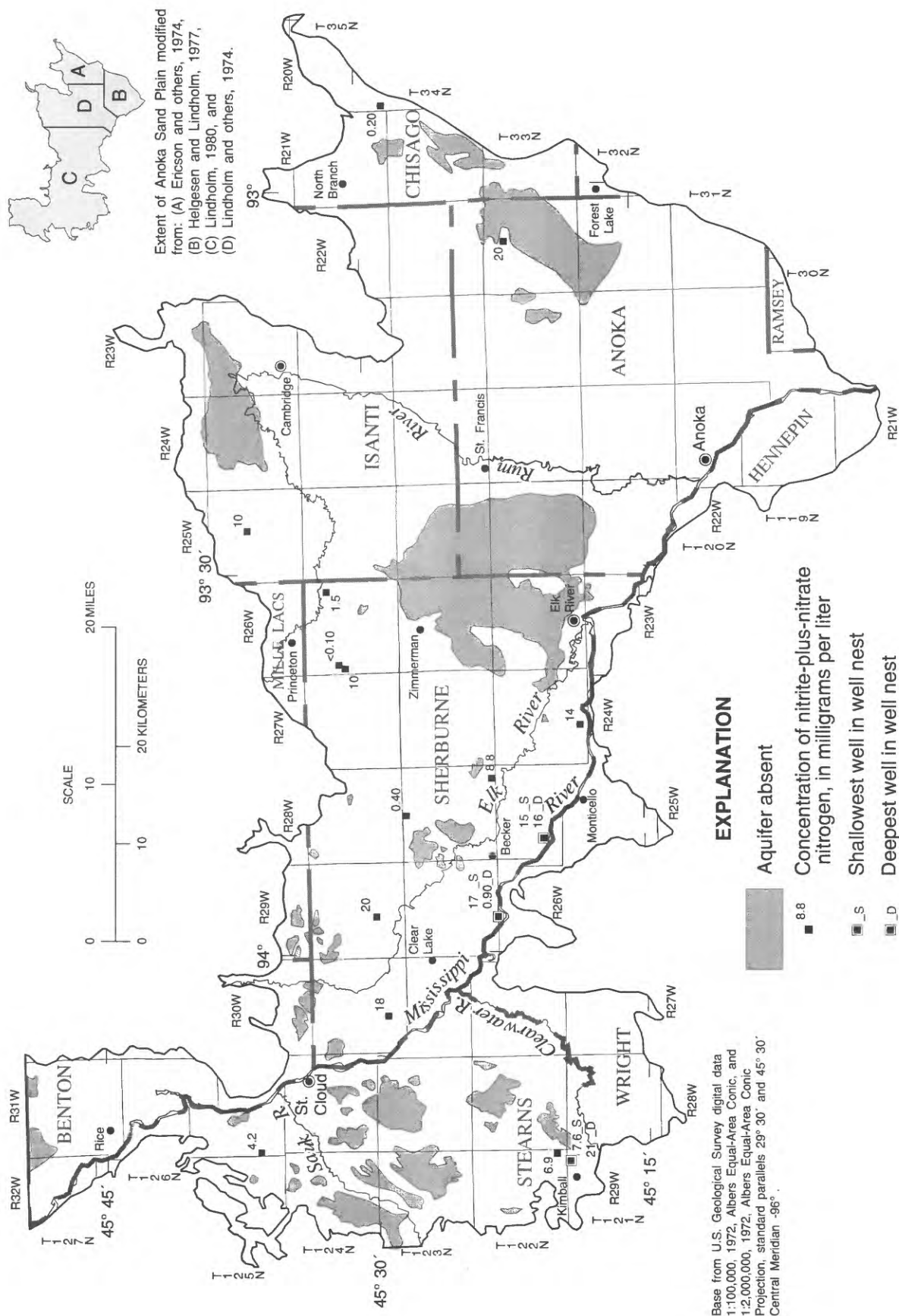


Figure 6.--Concentrations of nitrite-plus-nitrate nitrogen in the Anoka Sand Plain aquifer, August through November 1990.

concentrations of nitrate-N were greater in the deep well than in the shallow well (fig. 6). In the other well nest (033N29W04BBA), concentrations of nitrate-N were greater in the shallow well than in the deep well (fig. 6).

One reason why nitrate-N concentrations do not decrease uniformly with depth may be that denitrification, or dissimilatory nitrate reduction, is not taking place between 3 and 6 m below the water table as it would under more reducing conditions at greater depth below the water table (Postma and others, 1991). Ground water in the upper 6 m of the aquifer was oxygenated and concentrations of DO did not decrease systematically with depth. In addition, concentrations of nitrate-N were not correlated with concentrations of DO ($r=0.10$, $p=0.7559$). Thus, there was no evidence that oxygen or nitrate-N reduction reactions were occurring or that the ground water became more reducing with depth in the upper 6 m of the aquifer. This result is similar to that of Komor and Anderson (1993) who found that variations in nitrate-N concentrations and changes in nitrogen isotopic composition of nitrate-N with depth were not supportive of denitrification in more than half of the well pairs sampled.

Another possible explanation for the absence of a uniform decrease in nitrate-N concentrations with depth may be that two wells in a well nest may not intercept ground-water flow paths originating from the same source area (Komor and Anderson, 1993). Because ground-water flow paths in sand plain aquifers are subhorizontal, deep and shallow wells in nested well pairs likely intercept different flow paths rather than two points along a single flow path. Differences in nitrate-N concentrations between a deep and shallow well in a well pair may then reflect different source areas of nitrate-N (Komor and Anderson, 1993).

Because Anderson (1993) sampled 100 wells and 29 well nests compared to 17 wells and 3 well nests in this study, his conclusion of a strong correlation between increasing depth below the water table and decreasing nitrate-N concentrations is statistically more valid. However, comparison of the 1990 data to that of Anderson (1993) illustrates that decreasing nitrate-N concentrations with depth in the upper 6 m of the saturated zone does not occur at all times or at all locations. This result is similar to that of Komor and Anderson (1993) who found both increases and decreases in nitrate-N concentrations with depth in 21 nested well pairs.

Concentrations of nitrate-N were significantly correlated with concentrations of chloride ($r=0.63$, $p=0.0065$). Similar correlations between concentrations of nitrate-N and chloride have been noted in other

studies (Hamilton and others, 1993; Landon and others, 1993), reflecting that nitrate-N and chloride frequently have the same sources such as agricultural applications or septic systems. Concentrations of nitrate-N also were significantly correlated with concentrations of organic plus ammonia plus organic nitrogen ($r=0.73$, $p=0.0010$). Concentrations of nitrate-N were not significantly correlated with any other inorganic constituents or nutrients.

Herbicides

Triazine herbicides were detected by immunoassay analysis in 8 of the 34 water samples. The detection limit of the immunoassay analysis was $0.1 \mu\text{g/L}$. Samples in which the immunoassay analysis indicated triazine herbicides were present also were analyzed by GC/MS for quantitative confirmation. Nine samples in which triazines were not detected by the immunoassay analysis also were analyzed by GC/MS. Samples in which triazine herbicides were not detected by the immunoassay analysis and that were not analyzed by GC/MS were treated as no detections for atrazine. Because the immunoassay analysis has a very low sensitivity to DEA and DIA, immunoassay analysis was not considered to be a reliable test for presence or absence of these herbicide metabolites.

Atrazine was detected in 11 of the 17 samples analyzed by GC/MS (11 of the total of 34 wells sampled, 32 percent) (fig. 7). Concentrations ranged from the detection limit of 0.05 to $0.81 \mu\text{g/L}$ with a median of $0.09 \mu\text{g/L}$. There were no detections of atrazine above the USEPA MCL of $3 \mu\text{g/L}$ (U.S. Environmental Protection Agency, 1986). The combined results of immunoassay and GC/MS analyses indicated that atrazine was detected in 11 of the 34 samples with a median concentration less than the immunoassay detection limit of $0.1 \mu\text{g/L}$. The most commonly detected herbicide or herbicide metabolite in ground water was DEA. The presence of DEA as the predominant metabolite in ground water is consistent with results of other studies of atrazine metabolites in ground water (Denver and Sandstrom, 1991; Thurman and others, 1992, 1993; Landon and others, 1993) and with results of studies of atrazine degradation in soils (Mills and Thurman, 1994). There were detections of DEA in 13 of the 17 samples analyzed by GC/MS (fig. 8). Concentrations ranged from the detection limit of 0.05 to $1.12 \mu\text{g/L}$ with a median of $0.15 \mu\text{g/L}$. There was a detection of DIA in only 1 of the 17 samples at a concentration of $0.06 \mu\text{g/L}$, just above the detection limit. Therefore, the median concentration of DIA was less than the detection limit of $0.05 \mu\text{g/L}$. Metolachlor also was detected in only 1 of the 17 samples at a

concentration of 0.45 µg/L. Therefore, the median concentration of metolachlor was less than the detection limit of 0.05 µg/L. There were no detections of the other herbicides analyzed for by GC/MS (alachlor, ametryn, simazine, propazine, cyanazine, metribuzin, prometryn, prometon, and terbutryn).

The DEA to atrazine ratio (DAR) was calculated for the 17 samples analyzed by GC/MS. Other studies (Thurman and others, 1992, 1993) demonstrated that the DAR can be a useful tool for evaluating the history and pathways of atrazine. Because degradation of atrazine into DEA mostly takes place in the unsaturated zone, DAR values of less than 1.0 indicate rapid transport of atrazine to ground water (Thurman and others, 1993). Values of DAR for the 11 samples that contained detectable atrazine and DEA ranged from 0.5 to 7.0. Only one well (035N20W03BDD01) had a DAR of less than 1.0. The median DAR value was 2.0. These DAR values are typical of values determined in agriculturally impacted ground water elsewhere in the Midwest (Thurman and others, 1992; Kolpin and others, 1993).

Concentrations of atrazine were determined in samples collected from four well nests where one well was screened less than 3 m below the water table (shallow) and one well was screened between 3 and 6 m below the water table (deep). In three well pairs atrazine was detected in the shallow well but not in the deep well (fig. 7). In one well nest (033N28W20BAC01) atrazine was detected at a greater concentration (0.57 µg/L) in the shallow well than in the deep well (0.09 µg/L). Samples also were analyzed for DEA in one of the well nests (033N28W20BAC01). Similarly, DEA was detected at a greater concentration in the shallow well (0.66 µg/L) than in the deep well (0.18 µg/L) (fig. 8). Greater concentrations of atrazine and DEA near the water table is consistent with leaching of atrazine and metabolites from land-surface applications.

Samples in which atrazine was detected had concentrations of nitrate-N that ranged from 7.6 to 20 mg/L with a median concentration of 16 mg/L (fig. 9). Thus, all wells in which atrazine was detected had increased (greater than 3 mg/L) concentrations of nitrate-N. Similarly, in samples in which DEA was detected, concentrations of nitrate-N ranged from 4.2 to 20 mg/L with a median of 13 mg/L. However, not all wells with increased concentrations of nitrate-N had detections of atrazine or DEA. This result likely indicates either that there were sources of nitrate-N other than cultivated fields on which both atrazine and nitrogen were applied or that nitrate-N has reached ground water more readily than atrazine or DEA. These samples in which nitrate-N, but not atrazine, was

present is the reason for the lack of a significant correlation ($r=0.42$, $p=0.1381$) between these two constituents, even though concentrations of the two constituents are generally positively correlated (fig. 9). There were similar relations between concentrations of atrazine and chloride, DEA and nitrate-N, and DEA and chloride.

Concentrations of atrazine were significantly correlated with concentrations of DEA ($r=0.84$, $p=0.0001$). Concentrations of DEA were significantly correlated with specific conductance ($r=0.62$, $p=0.0080$), calcium ($r=0.76$, $p=0.0023$), and magnesium ($r=0.81$, $p=0.0008$). These results indicate that for samples in which concentrations of some major inorganic constituents and total dissolved solids (specific conductance) were greater, concentrations of DEA also were greater. This result possibly may indicate that greater concentrations of major inorganic ions are present in ground water affected by agriculture. Concentrations of atrazine and DEA were not correlated with any other constituents or with depth below land surface or the water table.

There was an excellent correspondence ($r=0.84$) between the immunoassay and GC/MS results, indicating the immunoassay analysis was a valid test for presence of triazine herbicides. There were no samples in which atrazine was detected by GC/MS at concentrations greater than the immunoassay detection limit of 0.1 µg/L for which the presence of triazines was not also indicated by immunoassay. Numerous replicate analyses indicated that the immunoassay results were reproducible. The immunoassay method generally overestimated concentrations of atrazine. One reason for this may be that the immunoassay analysis detects all triazine herbicides rather than specifically detecting atrazine. Thus, other triazine herbicides in the samples, such as DEA, may have resulted in the immunoassay concentration exceeding the GC/MS concentration of atrazine. However, for the purposes of this study, the immunoassay analysis was clearly a valuable qualitative to semi-quantitative tool for evaluating the presence and approximate concentration of atrazine.

Changes in Ground-Water Quality, 1984-90

Concentrations of inorganic constituents and nutrients measured in this study were generally within the ranges of concentrations measured in ground water samples collected from 100 wells across the Anoka Sand Plain in 1984 (Anderson, 1993). Differences in water quality between this study and that of Anderson (1993) primarily were due to the fact that only shallow

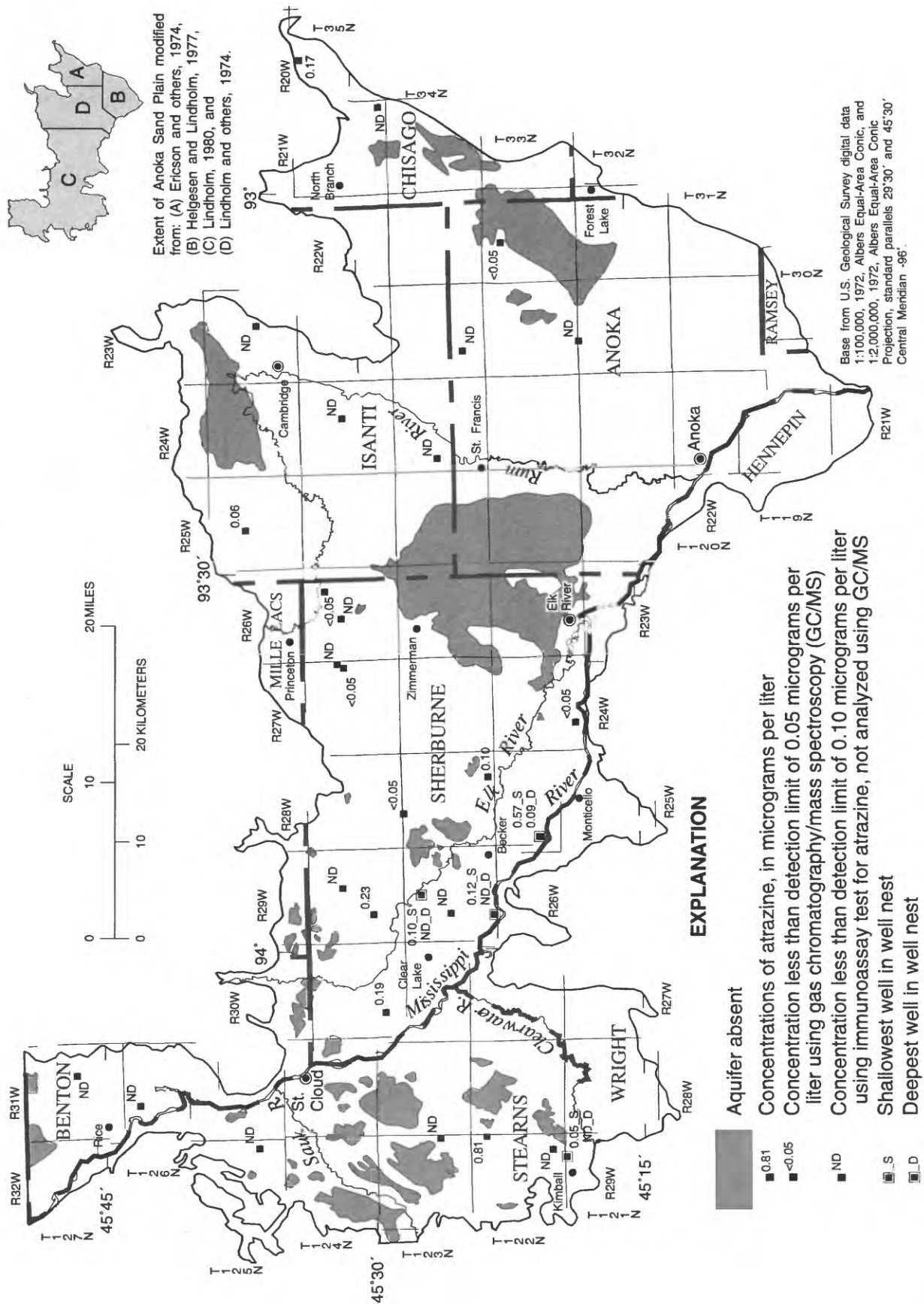


Figure 7.--Concentrations of atrazine in the Anoka Sand Plain aquifer, August through November 1990.

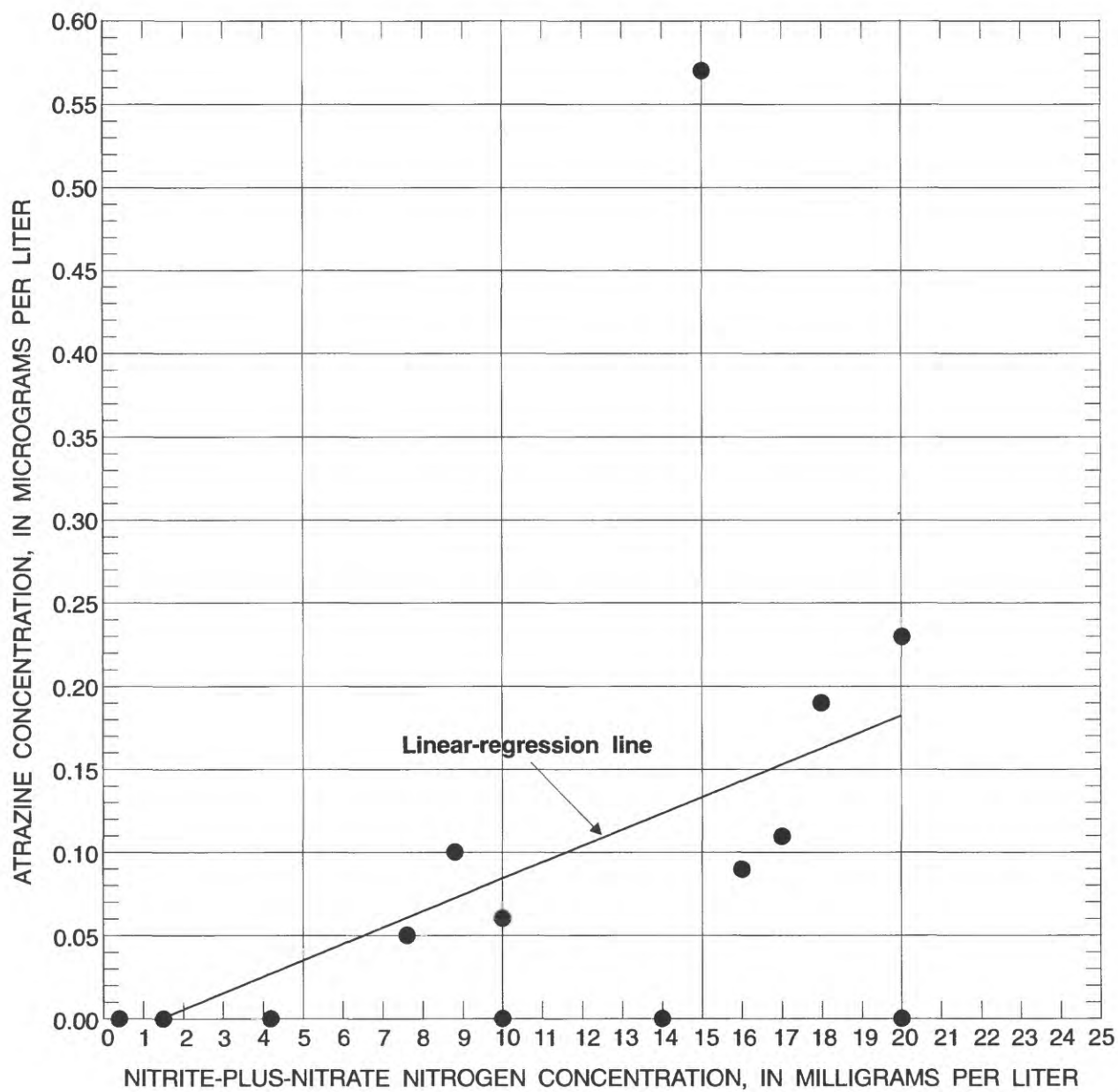


Figure 9.--Relation of nitrite-plus-nitrate nitrogen and atrazine concentrations in the Anoka Sand Plain aquifer, August through November 1990.

ground water in agriculturally impacted settings was sampled in this study whereas ground water from depths up to 30 m below the water table and from many different land-use settings were sampled by Anderson (1993).

The median concentration of nitrate-N of 10 mg/L in this study was considerably greater than the median concentration of 2.8 mg/L measured in 1984 (Anderson, 1993). However, the 100 wells sampled by Anderson (1993) were located in residential and natural-undeveloped areas, as well as areas of agricultural-cultivated land use. The median concentration of nitrate-N in nonirrigated-cultivated settings (97 samples) and in irrigated-cultivated settings (129 samples) during 1984 through 1987 were 2.0 and 5.3 mg/L, respectively (Anderson, 1993). These medians were less than the median nitrate-N concentration of 10 mg/L determined in this study likely because deeper wells were sampled by Anderson (1993).

To better evaluate changes in nitrate-N concentrations in the Anoka Sand Plain during 1984 through 1990, concentrations measured during 1984 through 1987 were compared to concentrations measured during 1990 for 11 wells. Each of the wells was sampled 3 to 8 times during 1984 through 1987 and once during 1990.

Concentrations of nitrate-N during 1990 were within the range of variation in concentrations measured during 1984 through 1987 in 10 of the 11 wells. Concentrations of nitrate-N were less than 5 mg/L throughout the period of record in 4 of these 10 wells, such as well 035N20W31DAB02 (fig. 10). Variations in the concentrations of nitrate-N over the period of record were minor (less than 3 mg/L) in these 4 wells and there was no consistent trend of increasing or decreasing concentrations. Nitrate-N concentrations were generally greater than 8 mg/L throughout the period of record and showed large variations seasonally in the remaining 6 of the 10 wells, such as wells 033N27W33ACC01 and 033N22W10CCB01 (fig. 10). The concentrations of nitrate-N in these 6 wells varied by as much as a factor of 5 over the period of record (fig. 10). Greater temporal variations were observed for shallow wells than for deep wells with the greatest concentrations generally occurring in 1984 or 1985. These high nitrate-N concentrations probably were related to above-normal precipitation and greater amounts of recharge occurring during these years (Anderson, 1993) (fig. 10). Nitrate-N concentrations declined from their peak values in 1984 or 1985 to lower concentrations in 1986 or 1987 in 5 of these 6 wells. Comparing concentrations in the summer of 1986

to those in the summer of 1990, concentrations increased by more than 3 mg/L in 2 wells, did not change by more than 3 mg/L in 2 wells, and decreased by more than 3 mg/L in 2 wells.

Of the 11 wells for which historical comparisons were made, concentrations of nitrate-N in 1990 were greater than concentrations measured during 1984 through 1987 only in well 035N30W28CDC02 (fig. 10). There was a substantial increase in the concentration of nitrate-N in this well, from less than 3 mg/L during 1984 through 1987 to 18 mg/L in 1990 (fig. 10).

Overall, concentrations of nitrate-N were similar during 1990 as compared to 1984 through 1987. Changes in nitrate-N concentrations over this period likely are related, in part, to differences in ground-water recharge. In addition, other site-specific factors, including variability in local farming practices, mixing of ground-water flow paths from different source areas, and spatial and temporal variability in nitrate-N-consuming reactions, contribute to the temporal variability of nitrate-N concentrations. This seasonal to yearly variability in concentrations is of greater magnitude than any apparent long-term trends in nitrate-N concentrations. Because nitrate-N concentrations can vary considerably over time intervals shorter than the sampling interval of this study, trends in nitrate-N concentrations are not definitive. Concentrations measured once or twice during the year may be related to short-term variations and not necessarily represent the average concentration for that year. Thus, evaluation of temporal trends in concentrations based upon 4 to 9 measurements over a 7 year period should be done with the awareness that concentrations actually may be more variable than the limited data indicate.

Anderson (1993) collected samples from 18 wells in areas of cultivated land use in 1984 and analyzed them for herbicides by GC/MS with a detection limit of 0.1 µg/L. Atrazine was detected in 8 of the 18 wells (44 percent) with a median concentration less than the detection limit of 0.1 µg/L, a 75th-percentile concentration of 0.1 µg/L, and a maximum concentration of 1.7 µg/L. This distribution is similar to results of this study (fig. 5). Of the 18 samples analyzed for herbicides by Anderson (1993), cyanazine was detected in 6 samples, alachlor in 3 samples, simazine in 2 samples, metribuzin in 2 samples, and cyprazine in 1 sample. In comparison, the herbicides cyanazine, alachlor, simazine, and metribuzin were analyzed for but not detected in the 17 samples collected in this study. It is not known whether the decrease in detections of these herbicides is related to changes in herbicide usage or cropping practices.

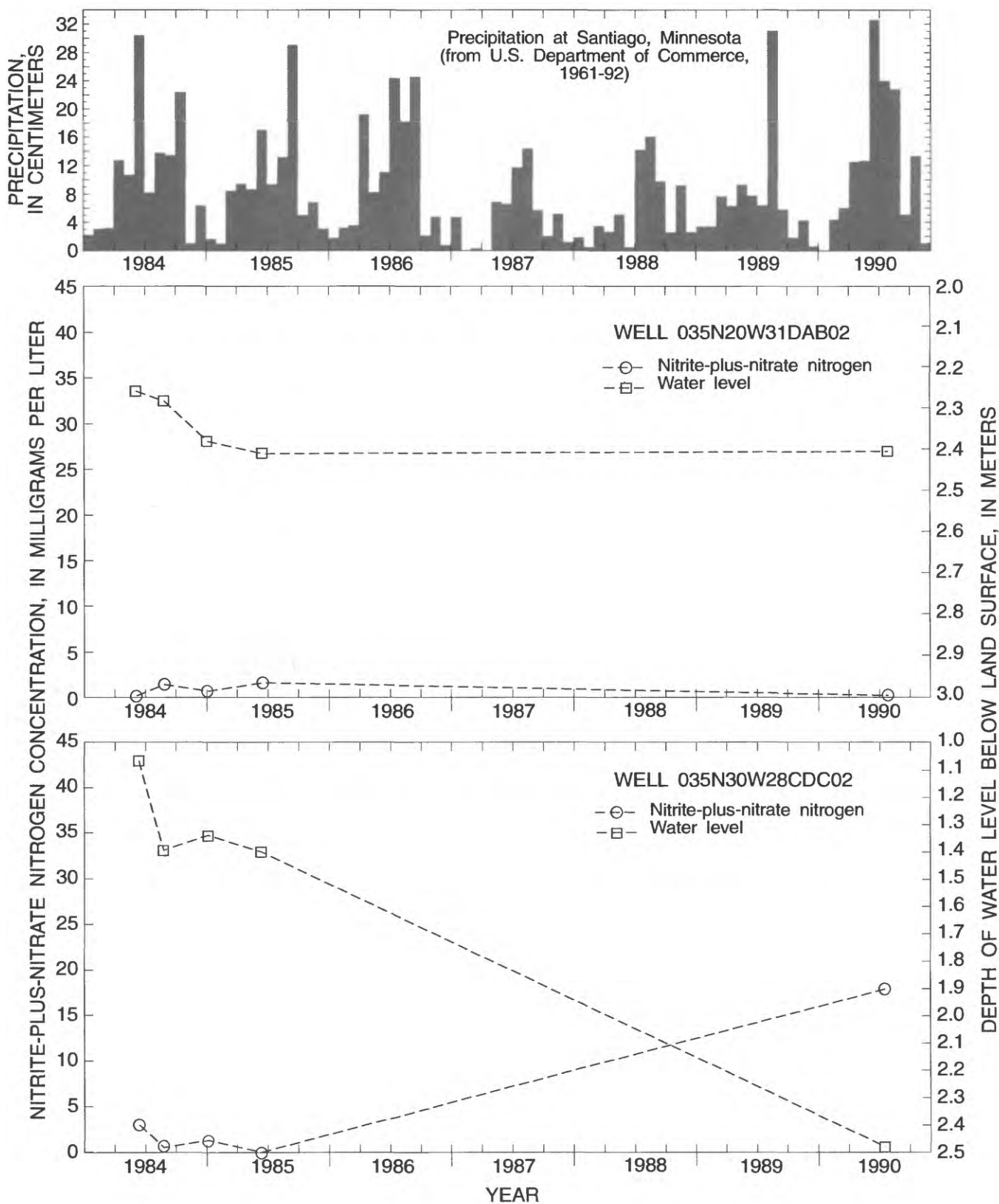
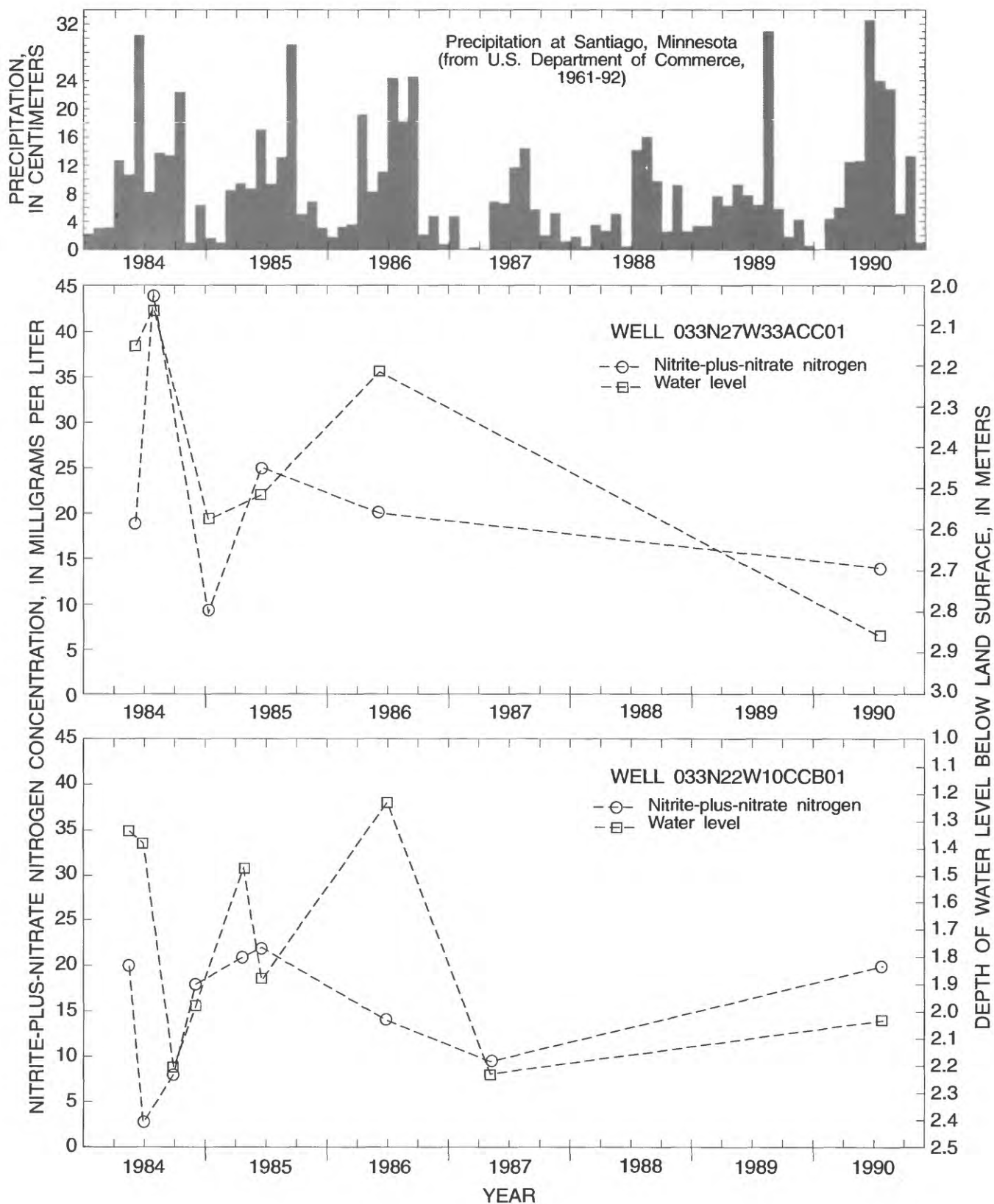


Figure 10.--Monthly precipitation, water-level hydrographs, and concentrations of



nitrite-plus-nitrate nitrogen for selected wells in the Anoka Sand Plain aquifer, 1984-90.

Eleven wells analyzed for concentrations of herbicides in 1984 (Anderson, 1993) also were analyzed in this study. Atrazine was not detected in either 1984 or 1990 in 5 wells. In the other 6 wells, atrazine concentrations did not change in one well, increased more than 0.3 µg/L in one well, decreased more than 0.3 µg/L in 2 wells, and decreased less than 0.1 µg/L in 2 wells. Comparison of the data indicate that atrazine concentrations generally did not change substantially between 1984 and 1990. Because concentrations of DEA were not determined in 1984, a comparison could not be made for this compound.

Summary

Ground-water quality in the Anoka Sand Plain aquifer was studied as part of the multiscale Management Systems Evaluation Area (MSEA) study, by collecting water samples from shallow wells during August through November 1990. The sampling was conducted to: (1) aid in selection of the MSEA research area; (2) facilitate comparison of results at the MSEA research area to the regional scale; and (3) evaluate changes in ground-water quality in the Anoka Sand Plain aquifer since a previous study during 1984 through 1987. Samples were collected from 34 wells screened in the upper 6 m of the surficial aquifer in cultivated agricultural settings. The results of the study indicate that the water-quality of some shallow ground water in areas of predominantly agricultural land use has been affected by applications of nitrogen fertilizers and the herbicide atrazine.

Immunoassay tests were used as a screening tool for the presence of triazine herbicides. All samples in which triazine herbicides were detected and selected samples in which triazine herbicides were not detected were sent to laboratories for further analysis. Nineteen samples were analyzed for nutrients, 17 samples were analyzed for major cations and anions, and 17 samples were analyzed for selected herbicides and herbicide metabolites using gas chromatography/mass spectroscopy (GC/MS).

Most ground water was of the calcium-bicarbonate type. All ground water samples also had detectable dissolved oxygen (DO), indicating oxidizing conditions. Concentrations of DO did not decrease systematically with depth below the water table. Concentrations of nitrate-N ranged from less than the detection limit of 0.1 to 21 mg/L with a median concentration of 10 mg/L. Concentrations of nitrate-N generally were unrelated to depth below the water table. Concentrations of nitrate-N also were not correlated with concentrations of DO. Thus, there was no evidence that oxygen or nitrate-N

reduction reactions were occurring or that the ground water became more reducing with depth in the upper 6 m of the aquifer. Because most of the samples were collected in the oxidized upper few meters of the aquifer, this lack of correlation between nitrate-N concentrations and depth may indicate that denitrification or dissimilatory nitrate reduction occur only at greater depths in the aquifer. Concentrations of nitrate-N were significantly correlated with concentrations of chloride which likely indicates that nitrate-N and chloride originate from the same sources such as agricultural applications.

The combined results of immunoassay and GC/MS analyses indicate that atrazine was detected in 11 of the 34 wells with a median concentration less than the immunoassay detection limit of 0.1 µg/L. Atrazine was detected in 11 of the 17 samples analyzed by GC/MS at concentrations ranging from the detection limit of 0.05 µg/L to 0.81 µg/L with a median of 0.09 µg/L. Atrazine metabolite de-ethylatrazine (DEA) was the most frequently detected herbicide or herbicide metabolite and generally was present at the greatest concentrations. This result is consistent with results of other studies of atrazine metabolites in ground water and reflects that DEA is the predominant product of atrazine degradation in soils. There were detections of DEA in 13 of the 17 samples at concentrations ranging from the detection limit of 0.05 µg/L to 1.12 µg/L with a median of 0.15 µg/L. Concentrations of DEA were significantly correlated with concentrations of calcium, magnesium, and specific conductance, possibly indicating that greater concentrations of major inorganic ions occur in ground water affected by agriculture. The atrazine metabolite de-isopropylatrazine and the herbicide metolachlor both were detected in 1 of the 17 samples. There was an excellent correspondence ($r=0.84$) between the immunoassay concentrations for triazine herbicides and GC/MS concentrations of atrazine, indicating that the immunoassay analysis was a good qualitative to semi-quantitative screening tool for evaluating the presence of atrazine.

Concentrations of atrazine and DEA were generally greater near the water table and decreased or were not detected at greater depths. All of the samples in which atrazine and DEA were detected also had increased nitrate-N concentrations (greater than 3 mg/L). However, not all wells with increased concentrations of nitrate-N had detectable atrazine or DEA. This likely indicates either that there were sources of nitrate-N other than cultivated fields on which both atrazine and nitrogen were applied or that nitrate-N has reached ground water more readily than atrazine or DEA.

The DEA to atrazine ratio (DAR) ranged from 0.5 to 7.0. Because degradation of atrazine mostly takes place in the unsaturated zone, DAR values of less than 1.0 indicate rapid transport of atrazine to ground water. Only one well had a DAR of less than 1.0 and the median DAR value was 2.0, which is similar to values determined in ground water elsewhere in the midwest.

Differences in median concentrations of nitrate-N determined by this study and a previous study during 1984 through 1987 likely are primarily due to differences in study design and the depths of wells sampled. Concentrations measured in this study were greater primarily because samples were collected from shallower depths below the water table exclusively in agricultural-cultivated settings. Concentrations of nitrate-N in ground water during 1990 were similar to concentrations measured during 1984 through 1987. Changes in concentrations of nitrate-N over this period appeared to be more strongly related to seasonal or annual variations in recharge or other site-specific factors than to any long-term trends in concentrations. Other site-specific factors include variability in local farming practices, mixing of ground-water flow paths from different source areas, and spatial and temporal variability in nitrate-N-consuming reactions.

The frequency of detection and the concentrations of atrazine in shallow ground water during 1990 were very similar to results of sampling in 1984. However, there were no detections of cyanazine, alachlor, simazine, or metribuzin in 1990 whereas these compounds were detected in 1984. It is not known whether the decrease in detections of these herbicides is related to changes in herbicide usage or cropping practices.

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