--Quality Assessment of Part of the Upper Mississippi River Basin, Minnesota and Wisconsin Id-Water Quality in an Agricultural Area of Sherburne County, Minnesota, 1998

**National Water-Quality Assessment Program** 

# Water-Quality Assessment of Upper Mississippi River Basin and Wisconsin—Ground-Wat Agricultural Area of Sherburn nesota, 1998

## Water-Resources Investigations Report 00–4107



# Water-Quality Assessment of Part of the Upper Mississippi River Basin, Minnesota and Wisconsin—Ground-Water Quality in an Agricultural Area of Sherburne County, Minnesota, 1998

By James F. Ruhl, Alison L. Fong, Paul E. Hanson, and William J. Andrews

Water-Resources Investigations Report 00–4107

**National Water-Quality Assessment Program U.S. Department of the Interior** Bruce Babbitt, Secretary

U.S. Geological Survey Charles G. Groat, Director Use of trade, product, or firm names in this report is for identification purposes only and does not constitute endorsement by the U.S. Government.

Mounds View, Minnesota, 2000

For additional information write to: District Chief U.S. Geological Survey, WRD 2280 Woodale Drive Mounds View MN 55112

Copies of this report can be purchased from: U.S. Geological Survey Branch of Information Services Box 25286 Federal Center Denver CO 80225

Information regarding the National Water-Quality Assessment Program (NAWQA) is available on the Internet via the World Wide Web. You may connect to the NAWQA Home Page using the Universal Resource Locator (URL) at http://wwwrvares.er.usgs.gov/nawqa/nawqa\_home.html You may also connect to the Upper Mississippi River Basin NAWQA Home Page at http://wwwmn.cr.usgs.gov/umis/index.html For more information on all USGS reports and products (including maps, images, and computerized data), call 1-888-ASK-USGS

Water-Resources Investigations Report 00-4107

## Foreword

The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth resources of the Nation and to provide information that will assist resource managers and policy makers at Federal, State, and local levels in making sound decisions. Assessment of water-quality conditions and trends is an important part of this overall mission.

One of the greatest challenges faced by water-resources scientists is acquiring reliable information that will guide the use and protection of the Nation's water resources. That challenge is being addressed by Federal, State, interstate, and local waterresource agencies and by many academic institutions. These organizations are collecting water-quality data for a host of purposes that include: compliance with permits and water-supply standards; development of remediation plans for a specific contamination problem; operational decisions on industrial, wastewater, or water-supply facilities; and research on factors that affect water quality. An additional need for water-quality information is to provide a basis on which regional and national-level policy decisions can be based. Wise decisions must be based on sound information. As a society we need to know whether certain types of water-quality problems are isolated or ubiquitous, whether there are significant differences in conditions among regions, whether the conditions are changing over time, and why these conditions change from place to place and over time. The information can be used to help determine the efficacy of existing water-quality policies and to help analysts determine the need for and likely consequences of new policies.

To address these needs, the Congress appropriated funds in 1986 for the USGS to begin a pilot program in seven project areas to develop and refine the National Water-Quality Assessment (NAWQA) Program. In 1991, the USGS began full implementation of the program. The NAWQA Program builds upon an existing base of water-quality studies of the USGS, as well as those of other Federal, State, and local agencies. The objectives of the NAWQA Program are to:

- Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.
- Describe how water quality is changing over time.
- Improve understanding of the primary natural and human factors that affect water-quality conditions.

This information will help support the development and evaluation of management, regulatory, and monitoring decisions by other Federal, State, and local agencies to protect, use, and enhance water resources.

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of 59 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 59 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

National synthesis of data analysis, based on aggregation of comparable information obtained from the study units, is a major

component of the program. This effort focuses on selected waterquality topics using nationally consistent information. Comparative studies will explain differences and similarities in observed water-quality conditions among study areas and will identify changes and trends and their causes. The first topics addressed by the national synthesis are pesticides, nutrients, volatile organic compounds, and aquatic biology. Discussions on these and other water-quality topics will be published in periodic summaries of the quality of the Nation's ground and surface water as the information becomes available.

This report is an element of the comprehensive body of information developed as part of the NAWQA Program. The program depends heavily on the advice, cooperation, and information from many Federal, State, interstate, Tribal, and local agencies and the public. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch Chief Hydrologist

## Contents

Abstract	1
Introduction	1
Purpose and scope	3
Previous investigations	3
Description of study area	4
Climate	4
Hydrogeologic setting	4
Land use and land cover	6
Population and water use	6
Methods of investigation	6
Acknowledgments	8
Sediment Characteristics	8
Ground-Water Quality	9
Physical and chemical properties	9
Ions and trace metals	9
Nutrients and organic carbon	11
Nitrogen isotope ratios	15
Pesticides	15
Volatile organic compounds	16
Tritium	18
Summary	21
References	22
Supplemental information	25

## Illustrations

Figures 1–3. Maps showing:	
1. Location of wells sampled for the agricultural land-use study of the Upper Mississippi River Basin study unit	2
2. Surficial geology of the agricultural land-use study area of the Upper Mississippi River Basin study unit	5
<ol> <li>Land use and land cover in the agricultural land-use study area of the Upper Mississippi River Basin study unit.</li> </ol>	6
Figure 4. Box plots showing field measurements of physical and chemical properties of ground-water samples from the sampled wells	10
Figure 5. Trilinear diagram showing ionic composition of ground-water samples from the sampled wells	12
Figures 6–7. Boxplots showing:	
6. Concentrations of dissolved ions and solids residue in ground-water samples from the sampled wells	13
7. Concentrations of dissolved nutrients and organic carbon in ground-water samples from the sampled wells	14
Figures 8-9. Bar charts showing:	
8. Frequencies of detection of pesticide compounds in ground-water sampled from the sampled wells.	18
<ol><li>Frequencies of detection of volatile organic compounds in ground-water sampled from the sampled wells.</li></ol>	20

## Tables

1. Reported ground-water withdrawals by land-use category for the study area, 1997	7
2. Laboratory analyses methods for measured water-quality constituents	8
3. Median and range of physical and chemical properties of sediment samples	9
4. Median, standard deviation, and range of physical and chemical properties for	
ground-water samples	11
5. Median, standard deviation, and range in concentrations of ions and trace metals for	
ground-water samples	13
6. Number of samples with reportable concentrations, method reporting limits, medians,	
standard deviation, and ranges in concentrations of nutrients and organic carbon for	
ground-water samples	14
7. Pesticide compounds analyzed for in ground-water samples by chemical group	16
8. Method reporting limits, number of samples with detectable concentrations, ranges, and	
maximum contaminant levels of pesticide compounds for ground-water samples	17
9. Volatile organic carbons analyzed for in ground-water samples by chemical group	19
10. Number of samples with detectable concentrations, method reporting limit, ranges, and	
maximum contaminant levels of volatile organic compounds for ground-water samples	20
11. Well construction data and site characteristics for sampled wells	26
12. Method reporting limits and concentration ranges of detected analytes in blanks and	
environmental samples	28
13. Method reporting limits, concentration, ranges, and mean percent recoveries for schedule 2010	
pesticide spikes	29
14. Method reporting limits, concentration, ranges, and mean percent recoveries for schedule 2051	
pesticide spikes	30
15. Method reporting limits, concentration, ranges, and mean percent recoveries for volatile	
organic carbon spikes and surrogates	31
16. Method reporting limits and concentrations of compounds in environmental and replicate	
samples that differed by greater than 5 percent	

## **Conversion Factors, Abbreviated Water-Quality Units, and Vertical Datum**

<u>Multiply</u>	<u>By</u>	<u>To obtain</u>
inch (in.)	2.5	centimeter
foot (ft)	.3048	meter
gallon per day (gal/d)	.003785	cubic meter per day
gallon per minute (gal/min)	.6309	cubic meter per second
square mile (mi <sup>2</sup> )	2.590	square kilometer
million gallons per day (Mgal/d	d) .04381	cubic meters per second
degrees Fahrenheit (°F)	$^{o}C = (^{o}F - 32)/1$	.8 degrees Celsius

Chemical concentrations of substances are given in metric units of milligrams per liter (mg/L) and micrograms per liter ( $\mu$ g/L). Milligrams and micrograms per liter express the concentration of the chemical constituent as a mass (mg or  $\mu$ g) per unit volume (L). One thousand micrograms per liter is equivalent to 1 milligram per liter.

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.

# Water-Quality Assessment of Part of the Upper Mississippi River Basin, Minnesota and Wisconsin—Ground-Water Quality in an Agricultural Area of Sherburne County, Minnesota, 1998

## by James F. Ruhl, Alison L. Fong, Paul E. Hanson, and William J. Andrews

#### ABSTRACT

The quality of shallow ground water in a 75-mi<sup>2</sup> agricultural area of the Anoka Sand Plain aquifer in central Minnesota is described as part of the National Water Quality Assessment (NAWQA) Program—a national-scale assessment of the quality of water resources within large study units in various hydrologic settings. Data were collected during 1998 from 29 wells completed in the aquifer, which predominantly consists of surficial glacial sand and gravel sediments.

The depth below land surface to the water table ranged from 3.3 to 44 ft (median of 15.5 ft). Ground water was of the calciummagnesium bicarbonate type. Ionic constituents also included sodium, sulfate, and chloride. Iron and manganese concentrations generally were not greater than their U.S. Environmental Protection Agency (USEPA) Secondary Maximum Contaminant Levels (300 and 50 µg/L, respectively).

About 38 percent of 29 samples had nitrate-N (nitrogen) concentrations greater than the USEPA Maximum Contaminant Level (MCL) of 10 mg/L. About 72 percent of the samples had nitrate-N concentrations greater than the presumed natural background level of 3 mg/L. The maximum nitrate-N concentration was 47 mg/L. The median nitrate-N concentration of 7.1 mg/L, although not greater than the MCL, exceeded the natural background level. Nitrogen isotope ratios indicate that the sources of nitrate were commercial fertilizer and soil organic matter. Con-

centrations of total dissolved phosphorus and orthophosphate were generally less than 1 mg/L.

About 86 percent of 29 samples had detectable concentrations of at least 1 of 13 pesticide compounds. The samples were analyzed for 83 pesticide compounds. Frequencies of detection of these compounds were: deethylatrazine—79 percent; atrazine— 76 percent; metolachlor—41 percent; metribuzin and bentazon— 21 percent; prometon—10 percent; tebuthiuron—7 percent; and alachlor, 2,6-diethylaniline, dicamba, dinoseb, malathion, and simazine—3 percent. The detected pesticide compounds had concentrations less than 1  $\mu$ g/L. Detected compounds with USEPA MCLs (atrazine, bentazon, alachlor, dinoseb, and simazine) had concentrations less than their respective MCLs.

About 50 percent of 20 samples analyzed for 86 volatile organic compounds (VOCs) had detectable concentrations of at least 1 of 7 VOCs. Frequencies of detection of these 7 VOCs were: 1,2,3,4-tetramethylbenzene—40 percent; and trichlorofluoromethane, styrene, chloromethane, benzene, methylbenzene, and trichloromethane—5 percent. The detected VOCs had concentrations less than 0.120  $\mu$ g/L. Detected VOCs with USEPA MCLs—styrene, benzene, methylbenzene, and trichloromethane—to concentrations 2–4 orders of magnitude less than their respective MCLs.

Tritium concentrations had a range of from 7.5 to 18.8 tritium units (TUs) and a median of 12.5 TUs. These concentrations indicate that the ground water predominantly recharged after testing of thermonuclear weapons during the early 1950's.

#### INTRODUCTION

In 1991, the U.S. Geological Survey (USGS) began full implementation of the National Water Quality Assessment (NAWQA) Program. Long-term goals of this program include description of the status and trends in the quality of large representative parts of the Nation's surface- and ground-water resources, and identification of the major natural and human-related factors that affect the quality of these resources and aquatic ecology. Nationally consistent data useful to scientists, policy makers, and water-resource managers are being collected under the NAWQA Program. Assessment of the water quality throughout the entire Nation is impractical; therefore, NAWQA studies take place within hydrologic systems called study units, which comprise river basins, aquifer systems, or both.

The Upper Mississippi River Basin (UMIS) NAWQA study unit encompasses an area of about  $47,000 \text{ mi}^2$  (fig. 1). This

area includes agricultural lands, forests, wetlands, and the Twin Cities metropolitan area (TCMA) of Minnesota, which includes Minneapolis, St. Paul and surrounding suburbs. Important water resources of the study unit include the entire drainage area of the Upper Mississippi River Basin, from its source at Lake Itasca to the outlet of Lake Pepin. Additionally, these resources include ground water in aquifers in bedrock and in sand and gravel.



Figure 1.--Location of wells sampled for the agricultural land-use study of the Upper Mississippi River Basin study unit.

The Upper Mississippi River, the headwaters of the largest river system in the Nation, is the source of water supply to major municipalities and is a vital part of the region's aquatic ecosystems. Bedrock and sand and gravel aquifers are important sources of water supply for municipalities, industries, individual households, and irrigation. Additionally, the sand and gravel aquifers are sources of recharge to underlying bedrock aquifers in some areas (Schoenberg, 1990; Stark and others, 1996).

Three land-use studies within the UMIS study unit were designed to determine the extent to which the quality of shallow ground water has been influenced by major land uses and land cover (Stark and others, 1999). One of these studies investigated an urban area in a residential/ commercial section of the TCMA (Andrews and others, 1998). Another one of these studies investigated a forested area in the northern part of the UMIS study unit (Fong, in press). The present study investigated an agricultural area in the central part of the UMIS study unit.

Each of the these three studies analyzed hydrogeologic and water-quality data collected from the uppermost aquifers of Pleistocene- and Holocene-age. These aquifers (hereinafter referred to as surficial aquifers) comprise sand- and gravel-sized sediments that are predominantly glacial outwash, and to a lesser extent, glacial ice-contact deposits and post-glacial terrace, eolian (wind-blown), and alluvial deposits. The Anoka Sand Plain aquifer, which covers about 1,700 mi<sup>2</sup> in parts of 11 counties in eastcentral Minnesota (Anderson, 1993), is the major surficial aquifer in the UMIS study unit (fig. 1).

Ground water in the surficial aquifers is susceptible to contamination because of relatively rapid transport time of contaminants from land surface to the water table due to a typically shallow water table and high permeability of unsaturated-zone materials (Landon and Delin, 1995). Sources of contaminants in the surficial aquifers include fertilizers and pesticides applied to lawns and croplands, manure in feedlots and earthen storage basins, septic-system effluent, road salts, and organic compounds from fuel products, cleaning agents, and solvents.

#### **Purpose and Scope**

The purpose of this report is to describe the quality of ground water in the Anoka Sand Plain aquifer within a selected agricultural area of the UMIS study unit. This approximately 75-mi<sup>2</sup> agricultural area (hereinafter referred to as the study area) is located northwest of the TCMA near the Mississippi River in Sherburne County (fig. 1). Although land use in the study area is predominantly row-crop agricultural, land use in portions of the study area are urban and residential.

A total of 29 observation wells completed in the Anoka Sand Plain aquifer were used as sources of water-quality and sediment data. Ground-water quality data are based on single samples collected during the spring or fall 1998. These data, therefore, represent a one-time assessment of ground-water quality conditions in the study area, but do not describe seasonal variation in ground-water quality that normally occurs in hydrogeologic settings such as the study area.

#### **Previous Investigations**

Reconnaissance studies of water resources within river basins that include parts of the Anoka Sand Plain aquifer have been done by Ericson and others (1974), Lindholm and others (1974), Helgesen and others (1975), Helgesen and Lindholm (1977), and Lindholm (1980). Magner and others (1990a, 1990b) described hydrogeologic and land-use factors that influence ground-water quality in the Anoka Sand Plain aquifer.

Andrews and others (1998) conducted a UMIS NAWQA Program study of ground-water quality in an urban portion of the Anoka Sand Plain aquifer within the TCMA. Hydrogeologic and water-quality data were collected from 30 monitoring wells in that study. Concentrations of nitrate-N (nitrogen) ranged from less than 0.05 to 16 mg/L, with a median concentration of 1.4 mg/L.

Anderson (1993) studied the effects of land use on the quality of ground water based on data collected from 100 wells across the Anoka Sand Plain aquifer during 1984–87. The data were grouped and compared based on depth and local land use for the wells. The depths to the screened intervals of the wells ranged from the water table to about 100 ft deeper. Each of the wells was assigned to one of the following land-use types: natural-undeveloped, nonirrigated-cultivated, irrigated-cultivated, and residential. Analyses of 360 ground-water samples indicated that the median concentrations of nitrate-N for areas of natural-undeveloped, nonirrigated-cultivated, irrigatedcultivated, and residential land use were 0.22, 2.0, 5.3, and 4.2 mg/L, respectively.

Komor and Anderson (1993) investigated sources of nitrate-N in the Anoka Sand Plain aquifer from both concentra-tions and ratios of heavy  $({}^{15}N)$  to light  $({}^{14}N)$  nitrogen isotopes in ground-water samples from 51 wells during 1986-87. The sampled wells were grouped by the following land-use settings: livestock feedlots; irrigated-cultivated fields; residential areas with septic tanks; nonirrigated-cultivated fields; and naturalundeveloped areas. Results from this study indicated that nitrogen from commercial inorganic fertilizer was present in ground water from all settings except feedlots. Results of the study also indicated that nitrogen from livestock and human waste was present in ground water beneath some feedlots, irrigatedcultivated fields fertilized with manure, and residential areas with septic systems. Results of the study also suggested that denitrification increased with depth or that the proportions of nitrate-N from different sources changed with depth.

Palen and others (1993) collected ground-water samples from 43 wells in the Anoka Sand Plain aquifer during December 1990 to July 1991. The well depths ranged from about 16 to 100 ft with a median depth of 35 ft. Results of the study were used to evaluate recharge mechanisms and to verify the pollution sensitivity map developed during the study (Minnesota Department of Natural Resources, 1993). Ground-water samples from some shallow wells contained concentrations of chloride, sulfate, and nitrate-N greater than typical background levels-considered to be 10 mg/L, 10 mg / L, and 3 mg/L, respectively.

A reconnaissance study of groundwater quality in the Anoka Sand Plain aquifer was conducted during August through November 1990 under the Management Systems Evaluation Area (MSEA) Program (Landon and Delin, 1995). This study reported results of analyses of ground-water samples collected from 34 shallow wells at a research site located about 15 miles northeast of the study area described in this report. The study was done to: (1) aid in selection of the MSEA research site; (2) facilitate comparison of results at the MSEA research site to a regional scale; and (3) evaluate changes in ground-water quality in the Anoka Sand Plain aquifer since a previous study done during 1984-87 (Anderson, 1993). Results of this reconnaissance study indicated that concentrations of nitrite-plus-nitrate-N in 19 samples ranged from less than the detection limit of 0.100 to 21 mg/L, and had a median of 10 mg/L (Landon and Delin, 1995). Combined results of immunoassay and gas chromatography/mass spectrometry (GC/MS) analyses indicated that atrazine was detected in samples from 11 of the 34 wells. The median concentration of the atrazine determined by GC/MS was less than the immunoassay detection limit of 0.1  $\mu$ g/L. Deethylatrazine (DEA), the most frequently detected atrazine metabolite, was present at concentrations that ranged from less than the detection limit of 0.050 to 1.12 µg/L.

During the MSEA study, groundwater quality at the research site was monitored during 1991-95 (Landon and others, 1998). The objectives of this study were to: (1) describe the effects of three farming systems on ground-water quality; and (2) evaluate factors that affect ground-water quality and transport of agricultural chemicals. Concentrations of nitrate-N in the upper 3.28 ft of the saturated zone were greatest beneath two cropped areas with potato-sweet corn annual rotation (median concentrations of 22 and 23 mg/L) and were least beneath a field corn-soybean annual rotation (median concentration of 14 mg/L). The estimated proportion of applied nitrogen that reached ground water ranged from about 13 to 50 percent and averaged about 30 percent (Landon and others, 1998). Plant uptake appeared to account for most of the applied nitrogen.

Concentrations of atrazine plus the metabolites DEA and deisopropylatrazine (DIA) at the MSEA research site were significantly greater during 1994–95 than

during 1992-93 beneath all cropped areas in the upper 3.28 ft of the saturated zone. Concentrations of atrazine plus the metabolites during 1994-95 were greatest beneath the continuous corn (median of 1.07  $\mu$ g/L), intermediate beneath one cropped area with potato-sweet corn rotation (median of 0.37  $\mu$ g/L), and least beneath the other cropped areas with the potato-sweet corn rotation and field cornsoybean rotation and background areas (range of medians from 0.11 to 0.21  $\mu$ g/ L). Concentrations of atrazine plus the metabolites beneath the different cropped and background areas were similar during 1992-93. The proportion of applied atrazine, detected as atrazine or one of its metabolites, that reached ground water ranged from 0 to 1 percent and averaged about 0.37 percent. Nearly all of the applied atrazine and its metabolites underwent either adsorption or degradation in the soil.

## Description of the Study Area

Stark and others (1996) identified environmental variables that can influence the quality of ground and surface water in the UMIS study unit. These variables include climate, hydrogeologic setting, land use and land cover, population, soils, and surface-water hydrology. This report evaluates the relation of these variables to the quality of shallow ground water in the study area.

#### Climate

Climate affects water quality in many ways. Seasonal fluctuations in temperature affect solubilities of chemicals such as volatile organic compounds (VOCs) and pesticides in rainfall. Seasonal fluctuations in rainfall affect ground-water recharge, and thus loadings of these chemicals to shallow aquifers. Additionally, temperature fluctuations affect physical processes (volatilization of VOCs) and biochemical processes (oxidation of organic matter) in both ground and surface water.

Average monthly temperatures during 1961–90 for St. Cloud, Minnesota, located about 10 miles northwest of the study area, ranged from 8.1° F (Fahrenheit) in January to 70.1° F in July (Minnesota State Climatologist, electronic commun., 1999). Average annual precipitation during 1961–90 for St. Cloud was 27.43 inches (Minnesota State Climatologist, electronic commun., 1999). Approximately 80 percent of the annual precipitation occurs during May through October. Mean annual evaporation in the study area is approximately 38 inches (Farnsworth and others, 1982).

#### **Hydrogeologic Setting**

The study area is underlain by part of the Anoka Sand Plain aquifer, an unconfined (water-table), surficial aquifer. This aquifer is used extensively for irrigation and domestic water supplies. The aquifer is composed primarily of glacial outwash sediments from several glacial advances and retreats during the Quaternary glaciation (Wright, 1972a; Wright, 1972b; and Wright and Ruhe, 1965). In addition to the outwash deposits, the Anoka Sand Plain aquifer also includes glacial icecontact deposits and post-glacial alluvial and terrace deposits. The outwash sediments were deposited primarily by glaciofluvial 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). Gray till deposited by the Grantsburg sublobe is present at land surface on topographic high areas where outwash was not deposited. Underlying the outwash and gray till is red till deposited by the Superior lobe of the Wisconsin glaciation (Cooper, 1935; Farhnam, 1956). This glacial lobe expanded out of the Lake Superior Basin into the study area prior to the Grantsburg-sublobe advance. A small portion of the Anoka Sand Plain aquifer was reworked by eolian processes (Cooper, 1935). The portion of the Anoka Sand Plain aquifer that underlies the study area consists primarily of terrace deposits and, to a lesser extent, floodplain alluvium (fig. 2).

The deposits of the Anoka Sand Plain generally range in thickness from about 15 to 115 ft and consist of medium to coarse sand interbedded with thin layers of clay, silt, silty sand, and gravel (Helgesen and Lindholm, 1977; Lindholm, 1980). The mineralogical composition of sediments collected from these deposits at the MSEA research site east of the study area are 73 weight percent quartz, 14 weight percent plagioclase, 8 weight percent potassium feldspar, and less than 5 weight percent of carbonates, mica, montmorillonite, kaolinte, amphibole, and magnetite (Komor and Emerson, 1994).

Ground-water quality is influenced by the permeability and chemical composition of the overlying soils. Soil associations within the study area are predominantly Hubbard-Mosford and Zimmerman-Seelyeville and to a lesser extent Nebish-Braham-Stonelake (Bill Bronder, Natural Resource Conservation Service, written commun., 1999). These soils generally are well to excessively well drained, although portions of the Zimmerman-Seelyeville association are poorly drained. These soils have relatively high permeabilities and low clay and organic-matter contents. These soil characteristics are conducive to leaching of substances from the land surface to the water table.

In the study area, the depth below land surface to the water table ranged from 3.3 to 44 ft (median of 15.5 feet). The shallow depths make the aquifer vulnerable to land-surface sources of contamination. The aquifer typically ranges in saturated thickness from about 20 to 60 ft and in hydraulic conductivity from about 50 to as much as 1,000 ft/day (Anderson, 1993). Transmissivities range from about 5,000 to as much as 30,000 ft<sup>2</sup>/day (Lindholm, 1980). About 20 percent of the aquifer is capable of yielding water to a well at a rate of at least 475 gal/min (Anderson, 1993).

Recharge in the study area is from rain and snowmelt that percolates to the water table (Lindholm, 1980). Most recharge typically occurs soon after spring snowmelt and spring rainfall and before active plant growth. A second period of recharge typically occurs in the fall soon after the end of the growing season, but prior to soil freeze-up. The average annual recharge to sand plain aquifers in central Minnesota—an area that includes portions of the Anoka Sand Plain aquifer—was estimated to be about 8 inches per year (Lindholm, 1980).

Shallow ground water in the study area generally flows from topographically high to low areas and discharges to streams, lakes, and wetlands. Ground water also discharges to the atmosphere by evapotranspiration during the growing season where the depth below land surface to the water table is less than about 10 ft (Anderson, 1993). The water-table surface generally is a subdued reflection of topography (Lindholm, 1980; Palen and others, 1993). Ground-water withdrawals, attributable to pumping highcapacity wells, create cones of depression in the water table and thereby influence ground-water flow (Lindholm, 1980). Water-table gradients (vertical/horizontal distance of the water table) generally are less than 2 ft/1,000 ft (Magner and others, 1990a).



Figure 2.--Surficial geology of the agricultural land-use study area of the Upper Mississippi River Basin study unit.

#### Land Use and Land Cover

Land use and land cover in the study area is primarily agricultural and to a lesser extent urban, forest, and open water (fig. 3). The agricultural areas include both irrigated and nonirrigated croplands that are used to grow row crops such as potatoes, seed or field corn, and edible beans, and to a lesser extent, sweet corn and soybeans (Bill Bronder, Natural Resource Conservation Service, oral commun., 1999).

Land use in the study area influences the quality of shallow ground water. Agricultural areas are potential sources of nutrients and pesticides to the ground water. The residential areas, some of which are unsewered, have septic systems that treat domestic wastewater. These systems may release nutrients and chloride into ground water. Roadways can be sources of sodium and chloride from application of de-icing salts. Solvents, cleaning agents, and gasoline used by homeowners can be sources of VOCs in the ground water, particularly when these chemicals are not disposed of properly. Low-level concentrations of VOCs have been detected in ground-water samples collected from wells located in commercial and residential areas in the St. Cloud area (Minnesota Pollution Control Agency, 1999).

#### **Population and Water Use**

The total population in the study area, based on 1990 census data (U.S. Bureau of Census, 1991), was 18,569 people (this estimate includes Big Lake, which is just outside the study area). People who lived in unincorporated areas comprised slightly more than four-fifths of the total population. Based on data from the State Water Use Data System (SWUDS), total ground-water use in the study area during 1997 was 6,628.4 Mgal/ d (table 1). About 68 percent of this use was for irrigation (predominantly croplands and to a lesser extent golf courses, school grounds, and church yards). Withdrawals for municipal public supply accounted for about 5 percent of total use.

## Methods of Investigation

The site-selection criteria for the sampling locations are described in a previous NAWOA land-use study (Squillace and Price, 1996). The sites were selected to establish a 30-well network in a randomized, areally distributed pattern over the study area. This network was devised using a program described by Scott (1990). Twenty of the observation wells were installed by the USGS during 1997 (except for 1 well installed during 1998), 6 were existing monitoring wells, and 3 were existing domestic supply wells. One of the observation wells (ALUS-23) had to be abandoned; therefore, no data are presented for that well. The screen lengths for the 29 network wells are 5 ft for 20 wells, 10 ft for 5 wells, and 2 ft for 2 wells (the screen length is unknown for 2 wells). Data pertaining to the wells are



Figure 3.--Land use and land cover in the agricultural land-use study area of the Upper Mississippi River Basin study unit.

#### Table 1. Reported ground-water withdrawals by land use category for the study area,

1997

[Mgal/d, 1,000,000 gallons per day]

Water use category	Water withdrawals
Irrigation (croplands)	4,327.4
Irrigation (school grounds and church yards)	14.4
Irrigation (golf courses)	148.5
Power companies	271.0
Municipal public supply <sup>1</sup>	349.0
Industrial	2.5
Commercial	0.6
Rural domestic self supply <sup>2</sup>	1,515.0
listed in table 11 (Supplemental Informa- Ground-	water samples were col-

tion Section at the back of this report). The USGS-installed wells were drilled with 8-in. outer diameter, hollowstem steel augers. These wells were constructed of threaded 2-in. inside diameter, 10-ft long, schedule 40, polyvinyl chloride (PVC) flush-coupled casing, with 10slot PVC screens. The tops of the screens were placed about 2 ft below the water table. Native sand was allowed to collapse around the well screens up to the water table. In cases where native sand did not collapse to completely fill the annular space surrounding the screen, commercially prepared washed sand was used to fill the annular space to approximately 1 ft above the top of the screen. The portion of the annular space not filled with collapsed or added sand was filled with bentonite grout to within about 2 ft of land surface. The top 2 ft of the annular space was grouted with cement to land surface. Six-inch diameter schedule 40 steel protective casings with locking aluminum caps were set into the mortar and grout to a depth of 4 ft, with at least 2 ft left standing above land surface. These methods of construction comply with Minnesota Department of Health well code regulations (Minnesota Department of Health, 1994) and with NAWQA Program specifications for monitoring wells

(Lapham and others, 1995). The wells

lation with a centrifugal pump.

were developed within 10 days of instal-

lected for analyses during May and September 1998. Prior to collection of the samples, depths to water were measured in the wells, and then three to five standing volumes of water were pumped from the wells. During that time the chemical stability of the pumped water was monitored, based on periodic measurements of temperature, pH, specific conductance, turbidity, and dissolved oxygen concentration. After chemical stability was verified, final field measurements were made of temperature, pH, specific conductance, dissolved oxygen concentration, turbidity, and alkalinity. These measurements were made with instruments calibrated at the start of each sampling day with standard solutions. Ground-water samples were then collected, treated, and analyzed to determine concentrations of the dissolved phase of about 200 chemical constituents and isotopes. Analyzed constituents and isotopes included: (1) the ions calcium, magnesium, sodium, potassium, bicarbonate, sulfate, chloride, fluoride, bromide, and silica (expressed in mg/L); (2) the trace metals iron and manganese (expressed in  $\mu g/L$ ); (3) the nitrogen compounds nitrite, nitrate, ammonium, and ammonium- plus organic-N (reported as nitrogen and expressed in mg/L); (4) the phosphorus compounds total dissolved phosphorus and orthophosphate (expressed in mg/L); (5) dissolved organic carbon (DOC)

some of their metabolites (expressed in  $\mu g/L$ ); (7) VOCs (expressed in  $\mu g/L$ ); (8) the hydrogen isotope tritium (expressed as standard tritium units (TUs)); and (9) the nitrogen isotopic ratio ( ${}^{15}N/{}^{14}N$ ) (expressed as delta units ( $\delta {}^{15}N$ )).

Water samples were collected under conditions that prevented exposure to the atmosphere using a sealed system of Teflon tubing and stainless steel fittings specified in NAWQA protocols (Koterba and others, 1995). Water samples analyzed for ions, trace metals, nutrients, DOC, pesticides and their metabolites, VOCs, and nitrogen isotopes were shipped overnight to the USGS National Water Quality Laboratory (NWQL) in Arvada, Colorado, where the samples were analyzed according to USGS analytical protocols for analysis, quality assurance, and quality control (table 2). Tritium analyses were done according to USGS analytical protocols at a USGS laboratory in Reston, Virginia.

In some cases concentrations of constituents are reported as estimated (E). In most cases estimated concentrations are less than the constituent's Method Reporting Limit (MRL). MRLs are the smallest concentrations of constituents that can be reliably cited by the NWQL with an acceptable degree of confidence. Although concentrations of constituents less than its MRL can be detected, the reliability of the reported concentrations have a lower degree of confidence rela-

(expressed in mg/L); (6) pesticides and

tive to reported concentrations greater than its MRL.

Quality-assurance/quality-control (QA/QC) samples were analyzed to estimate bias and variability and to verify that contamination of environmental samples did not result from: (1) cleaning of equipment; (2) collection and processing of samples; and (3) handling and transport of samples. Details and results of the QA/ QC samples are shown in tables 12–16 (Supplemental Information Section at the back of this report.

Sediment samples were collected at variable depths with a 2-ft-long splitspoon core barrel during drilling of 19 of the 20 USGS-installed wells. Unsaturated-zone samples were collected below the upper soil horizons at depths of 3 to 6.5 ft below land surface; saturated-zone samples were collected at depths of 7.5 to 46.5 ft below land surface. The samples were analyzed for grain-size distribution at the USGS sediment laboratory in Iowa City, Iowa using methods described by Guy (1969). Hydraulic conductivity was estimated from the sediment grain-size distribution using Hazen's equation (Freeze and Cherry, 1979):

$$K = A(d_{10})^2$$

In this equation K is hydraulic conductivity, A is a coefficient, and  $d_{10}$  is the effective grain-size diameter at which 10 percent of the particles by weight are finer and 90 percent are coarser (Freeze and Cherry, 1979).

Organic and inorganic carbon contents of sediment samples were analyzed by induction furnace and a modification of the Van Slyke method (Wershaw and others, 1987) at the USGS NWQL. The pH of sediment samples was determined in the field by mixing sediment samples with deionized water on a 1:1 weight basis and measuring the pH of the resulting solution with a portable pH meter.

#### Acknowledgments

The authors express appreciation to the land owners who granted permission to the U.S. Geological Survey for access to, and in some cases installation of, wells on their property. The authors express appreciation to Steve Bluhm of Northern States Power Company and Michael Goebel of the City of Big Lake for their willingness to grant permission to the U.S. Geological Survey to install and sample three of the observation wells used in this study.

## SEDIMENT CHARACTERISTICS

Grain-size distribution is important because it affects hydraulic conductivity of the sediments, and thereby the rapidity that leachate reaches the water table. The organic carbon content is important because it affects the sorptive capacity of the sediments, and thereby the capacity of soil materials to retard leachate, particu-

larly organic compounds in pesticides and VOCs, from reaching the water table. The organic carbon content may also be important because it is sometimes a substrate for bacteria that reduce nitrate and sulfate in ground and soil water. The inorganic carbon content indicates the presence of carbonate minerals, which can affect pH buffering (capacity for neutralizing acid) and major-ion chemistry of ground water in contact with these minerals. The pH may affect degradation and transport of organic compounds. Acidic organic compounds are likely to be sorbed in alkaline sediments; basic organic compounds are likely to be sorbed in acidic sediments.

Grain-size analyses of both unsaturated-zone and saturated-zone sediment samples indicated an identical median hydraulic conductivity of 102 ft/d (table 3). Due to layering of sand and clay in these sediments, the vertical hydraulic conductivity may be as much as five orders of magnitude less than the horizontal hydraulic conductivity (Schoenberg, 1990). Similar organic-carbon content in the unsaturated-zone and saturated-zone sediments indicated that sorption of organic contaminant substances would not be expected to differ appreciably between the two zones. Greater inorganic carbon contents in the saturated-zone sediments than in the unsaturated-zone sediments indicated that carbonate minerals were leached by recharge that percolated

Table 2. Laboratory analyses methods for measured water-quality constituents.

Constituent or constituent group	Analysis Method	Reference
Ions (USGS schedule 2750)	Atomic absorption spectrometric	Fishman and Fried- man (1989)
Nutrients (USGS schedule 2752)	Colorimetric, cadmium reduction-diazotization, automated-segmented flow; ion- exchange chromatographic; colorimetric, distillation-nesslerization; colorimetric, block digester-salicylate-hypochlorite, automated-segmented flow; colorimetric, phosphomolybdate	Fishman and Fried- man (1989)
VOCs (USGS schedule 2020)	Purge and trap capillary gas chromatography/mass spectrometery	Connor and others (1998)
Pesticides (USGS schedule 2010)	Solid-phase extraction technology using a C-18 cartridge and gas chromatography/mass spectrometry	Zaugg and others (1995)
Pesticides (USGS schedule 2051)	Solid-phase extraction technology using a Carbopak-B cartridge and high perfor- mance liquid chromatography with UV detection	Werner and others (1996)
DOC (USGS schedule 2085)	UV-promoted persulfate oxidation and infrared spectrometry 15	Brenton and Arnett (1993)

through soils to the water table. The greater pH values of the saturated-zone sediments relative to the unsaturated-zone sediments indicated increased buffering by carbonate minerals.

## **GROUND-WATER QUALITY**

The quality of the ground water was evaluated in terms of sources of constituents and drinking-water criteria established by the U.S. Environmental Protection Agency (USEPA). These criteria are Secondary Maximum Contaminant Levels (SMCLs), which are unenforceable guidelines regarding taste, odor, color, and other properties of water that affect its suitability for drinking and general household usage; and Maximum Contaminant Levels (MCLs), which are health-based drinking water standards that set maximum permissible levels for contaminants in water delivered to users of public water systems.

## Physical and Chemical Properties

The median field pH of 7.5 (fig. 4, table 4), which was slightly alkaline (>7.00), was within the SMCL range from 6.5 to 8.5 (U.S. Environmental Protection Agency, 1996). The alkaline pH values probably resulted from buffering of the ground water caused by dissolution of carbonate minerals in the sands (Anderson, 1993). Specific conductance, which is the capacity of water to conduct electrical current, is generally proportional to the dissolved solids concentration. The specific conductance (field) had a range of from 224 to 1,070  $\mu$ S/cm at 25<sup>o</sup> C and a median of 558 µS/cm at 25<sup>o</sup> C (fig. 4, table 4). The alkalinity, which is an indicator of buffering capacity, is commonly reported as an equivalent amount of calcium carbonate. The range in alkalinity

was from 61 to 283 mg/L as CaCO<sub>3</sub>, and the median was 178 mg/L as CaCO<sub>3</sub>. Although drinking-water criteria for alkalinity have not been established, recommended limits for alkalinity of industrial process waters range from 30 to 250 mg/L as CaCO<sub>3</sub> (Todd, 1980). Thus, the alkalinity of the ground water was generally suitable for industrial uses.

Hardness, which is directly related to calcium and magnesium ion concentrations, is an indicator of how readily water forms insoluble residues with soaps and scale deposits in boilers and pipes. Hardness is calculated by multiplying the sum of milliequivalents per liter of calcium and magnesium by 50 and is expressed in mg/L of CaCO<sub>3</sub> (Hem, 1985). Hardness ranged from 72 to 468 mg/L as CaCO<sub>3</sub> and had a median of 249 mg/L as CaCO<sub>3</sub> (table 4). Based on the hardness scale of Durfor and Becker (1964), most ground water was "very hard" (greater than 180 mg/L as CaCO<sub>3</sub>). Turbidity, which is inversely related to water clarity and directly related to suspended particulate matter, had a median value of 3.9 nephelometric turbidity units (NTUs) (fig.4, table 4).

The dissolved oxygen concentration in ground water indicates the redox condition of the water—an important factor that can affect biochemical processes such as denitrification. (The absence of measurable dissolved oxygen favors denitrification (Freeze and Cherry, 1979)). Most ground water contains little or no dissolved oxygen. Shallow ground water in surficial, sandy aquifers that constitutes recent recharge, however, typically does contain detectable concentrations. The dissolved oxygen concentrations observed in the present study—a range from <0.1 to 11.2 mg/L and a median of 4.9 mg/L (fig. 4, table 4)—are representative of these settings.

### lons and Trace Metals

A trilinear plot of the relative proportions of dissolved ions (based on milliequivalents per liter) in the groundwater samples indicates calcium-magnesium bicarbonate type water (fig. 5) with small amounts of sodium, sulfate, and chloride. Other ions present in the samples included (in descending order of median concentration) silica, potassium, fluoride, and bromide (fig. 6, table 5). Anderson (1993) reported a similar ionic composition in his earlier, broader study of the Anoka Sand Plain aquifer.

Water with a dissolved solids concentration that ranges from 1,000 to 3,000 mg/L is considered to be slightly saline (Hem, 1985). Ground water in the study area had a dissolved solids concentration that ranged from 140 to 610 mg/L with a median of 309 mg/L. These concentrations, which indicate fresh water, generally were within the SMCL of 500 mg/L (U.S. Environmental Protection Agency, 1996).

The median calcium concentration was 67 mg/L (fig. 6, table 5). Sources of this ion were primarily from dissolution of soluble carbonate minerals such as calcite and dolomite, and secondarily from dissolution of silicate minerals such as feldspar, pyroxene, and amphibole. Rainwater was a minor source of calcium-the mean annual concentration during 1997 was 0.18 mg/L, which was determined at a National Atmospheric Deposition Program (NADP) site about 50 miles northwest of the study area (fig. 1) (National Atmospheric Deposition Program/ National Trends Network, electronic commun., 1999). Relatively low concentrations of calcium (less than 50 mg/L) in

 Table 3. Median and range of physical and chemical properties of sediment samples.

 [ft/d, feet per day; g/kg, grams per kilogram]

Physical and chemical properties	Unsaturated zone sediments		Saturated zon	e sediments
	Median	Range	Median	Range
Hydraulic conductivity (ft/d)	102	48–238	102	5–192
Organic carbon content (g/kg)	2.3	0.70–5.9	2.7	0.20–6



Figure 4.--Field measurements of physical and chemical properties of ground-water samples from the sampled wells.

ground-water samples from several of the wells may have resulted from ion exchange with sodium or potassium on clay-particle surfaces in the unsaturated zone.

The median concentration of magnesium was 20 mg/L (fig. 6, table 5). Magnesium concentrations generally were less, by a factor of about three, than calcium concentrations. Magnesium is present in limestones and dolomites, ferromagnesian minerals (such as olivine, pyroxenes, amphiboles, and biotite) and minerals (such as chlorite and serpentine) in metamorphic rocks (Hem, 1985). Rainwater, which had a mean annual concentration during 1997 of 0.03 mg/L (National Atmospheric Deposition Program/National Trends Network, electronic commun., 1999), was not an important source.

The median concentrations of sodium and potassium were 4.4 and 1.3 mg/L, respectively (fig. 6, table 5). A potentially important source of sodium, and to a lesser extent of potassium, were de-icing salts applied onto roadways during winter. Another potential source of potassium may have been application to croplands of potash fertilizer, which contains potassium chloride. The maximum sodium concentration of 66 mg/L did not exceed the SMCL of 250 mg/L (U.S. Environmental Protection Agency, 1996). The maximum potassium concentration was 7.3 mg/L (potassium does not have an SMCL). The mean annual concentrations of sodium and potassium in rainwater were 0.035 and 0.026 mg/L, respectively (National Atmospheric Deposition Program/National Trends Network, electronic commun., 1999)—amounts too small for rainwater to be a significant source of these constituents.

Bicarbonate is an important indicator of water quality because this ion typically is the most important determinant of alkalinity. The median bicarbonate concentration was 217 mg/L (fig. 6, table 5). This ion is formed from dissociation of one hydrogen ion proton from carbonic acid, which forms when gaseous carbon dioxide dissolves in water. Bicarbonate, rather than carbonic acid, is the predominant form of dissolved carbon dioxide in water that has a pH within the normal range of 6–9 (Hem, 1985).

Sulfate concentrations, which were similar to chloride concentrations, ranged from 2.3 to 61 mg/L and had a median concentration of 20 mg/L (fig. 6, table 5). No ground-water sample had a sulfate concentration that exceeded the SMCL of 250 mg/L (U.S. Environmental Protection Agency, 1996). Water with a sulfate concentration that exceeds its SMCL may be unsuitable for some industrial uses. Sulfate is the most common form of dissolved sulfur in oxygenated natural waters. Potential sources of sulfur in natural waters include atmospheric emissions from combustion of fossil fuels, volcanic eruptions, and smelting of ores (Hem, 1985). Other sources of sulfur in natural waters include dissolution of metallic sulfide minerals, which contain reduced forms of sulfur, in igneous and sedimentary rocks. Additionally, dissolution of the mineral gypsum may release sulfate into natural waters (Hem, 1985). Rainwater, which had a mean annual concentration of Table 4. Median, standard deviation, and range of physical and chemical properties for ground-water samples. [µS/cm, microsiemens per centimeter; mg/L, milligrams per liter; NTU, nephelometric turbidity unit; SMCL, Secondary Maximum Contaminant Level; —, no value]

Physical and chemical properties	Units	Median	Standard deviation	Range	SMCL
Water temperature (field)	°C	11	2.5	7.0–18	_
pH (field)	pH units	Ъ	.30	6.6–8.2	6.5 - 8.5
pH (lab)	pH units	77	.20	7.0–8.1	6.5 - 8.5
Specific conductance (field)	μS/cm at 25 <sup>O</sup> C	558	207	224–1,070	_
Specific conductance (lab)	μS/cm at 25 <sup>O</sup> C	518	181	224–923	_
Turbidity (field)	NTU	39	8.8	.60–46	

0.75 mg/L (National Atmospheric Deposition Program/National Trends Network, electronic commun., 1999), was not an important source.

The median chloride concentration was 17 mg/L (fig. 6, table 5). None of the chloride concentrations, which ranged from 1.1 to 88 mg/L, exceeded the SMCL of 250 mg/L (U.S. Environmental Protection Agency, 1996). Water with a chloride concentration that exceeds its SMCL may have a salty taste. A potential source of chloride, as with sodium, may have been de-icing salts. Another potentially important source may have been application to croplands of potash fertilizer, which contains potassium chloride. Rainwater, which had a mean annual chloride concentration of 0.06 mg/L (National Atmospheric Deposition Program/National Trends Network, electronic commun., 1999), was not an important source.

Fluoride and bromide were present in the ground-water samples in trace amounts (median concentrations of 0.13 and 0.04 mg/L, respectively, fig. 6, table 5). Fluoride concentrations commonly were less than the laboratory reporting limit of 0.10 mg/L and in all cases less than the USEPA (1996) established SMCL of 2 mg/L. Trace amounts of fluoride are added to drinking water to harden tooth enamel and to reduce the incidence of dental caries. The purpose of the SMCL for fluoride is to protect against mottling of tooth enamel. Bromide had a median concentration of 0.04 mg/L and a range from less than the laboratory reporting limit of 0.01 to 0.14 mg/L (fig. 6,

table 5). Bromide is similar in chemical behavior to chloride, but is much less abundant in natural waters (Hem, 1985). In addition to naturally-occurring bromide, bromide may also be derived from ethylene dibromide (a widely used gasoline additive), and from fumigants and fire-retardant agents.

The term "silica", which is silicon dioxide (SiO<sub>2</sub>), is commonly used to refer to silicon in natural waters, but the actual form is silicon hydroxide (Si(OH)<sub>4</sub>). The ionic form of silicon (Si<sup>+4</sup>) bonds with oxygen to form tetrahedral crystalline units (SiO<sub>4</sub><sup>-4</sup>) that constitute silicate mineral components of many igneous and metamorphic rocks. Quartz, which consists of crystalline silicon dioxide, is an abundant mineral in the sands and gravels of the surficial aquifers. Silica ranged in concentration from 7.8 to 25 mg/L, with a median concentration of 15 mg/L (fig. 6, table 5).

Trace metals that were analyzed in the ground-water samples were iron and manganese. Iron concentrations ranged from <10 to 5,000 µg/L with a median of  $<10 \,\mu$ g/L, and in some cases exceeded the USEPA established SMCL of 300 µg/L (fig. 6, table 5). Iron in water at concentrations greater than its SMCL can cause staining of plumbing fixtures and laundry. Natural sources of iron include minerals such as ferrous sulfides and oxides and siderite. Iron also is present in decaying plant material and humic compounds in soils (Hem, 1985). Manganese concentrations ranged from <4.0 to 387 µg/L with a median of  $<4.0 \,\mu\text{g/L}$ , and in some cases

exceeded the USEPA established SMCL of 50  $\mu$ g/L. Manganese in water at concentrations greater than its SMCL degrades water quality for reasons similar to those for iron. Natural sources of manganese include olivine, pyroxene, and amphibole minerals. Additionally, small amounts of manganese substitute for calcium in calcite and dolomite minerals.

#### Nutrients and Organic Carbon

The primary nutrients of concern in ground water are nitrate and orthophosphate. Nitrate-N concentrations typically are reported as the sum of nitrite- plus nitrate-N concentrations. Nitrite is an unstable compound typically detected in low concentrations, consequently nitriteplus nitrate-N concentrations commonly are about the same as nitrate-N concentrations. Results from this study validate that assumption-the median concentration of nitrite (<0.01 mg/L) was very small relative to the median concentration of nitriteplus nitrate-N (7.1 mg/L) (fig. 7, table 6). In this report, therefore, the concentration of nitrite- plus nitrate-N concentrations are considered to be equivalent to the concentrations of nitrate-N.

Consumption of drinking water with nitrate-N concentrations that exceed the MCL of 10 mg/L (U.S. Environmental Protection Agency, 1996) have been associated with "blue-baby" syndrome (methemoglobinemia), increased rates of stomach cancer, birth defects, miscarriage, and leukemia (Forman and others, 1985; National Research Council, 1985; Fan and others, 1987). Ground water with large concentrations of nitrate-N and



#### PERCENTAGE REACTING VALUES

Figure 5.--Ionic composition of ground-water samples from the sampled wells.

orthophosphate that discharges to surface water may lead to eutrophication, a condition of nutrient enrichment in lakes and rivers that typically results in increased growth of certain kinds of aquatic vegetation, particularly algae. These conditions typically result in depletion of oxygen, reduced clarity, and a rise in the temperature of the water, possibly resulting in fish kills.

The ammonium form of nitrogen, which can be released from minerals, animal wastes, and fertilizers into soil and shallow ground water, is oxidized (nitrified) under aerobic conditions to form nitrate. Nitrate is a mobile ion that commonly leaches from land-surface sources into shallow ground water, particularly where the unsaturated zone materials are permeable, such as in the study area. Rainwater may also be a source of nitrate in soil and ground water. The mean annual nitrate-N concentration in rainwater near the study area was 1.19 mg/L during 1997 (National Atmospheric Deposition Program/National Trends Network, electronic commun., 1999). Nitrate can be removed from ground water by denitrification and assimilation. Denitrification, which reduces nitrate to gases such as nitrous oxide or dinitrogen, is accomplished by bacteria. Assimilation, which is the uptake of dissolved nitrate into living matter, is a biochemical process that occurs in plant roots or bacteria.

Nitrate-N concentrations ranged from <0.05 to 47 mg/L (fig. 7, table 6). About 38 percent of samples had nitrate-N concentrations greater than the U.S. Environ-



Figure 6.--Concentrations of dissolved ions and solids residue in ground-water samples from the sampled wells.

mental Protection Agency (1996) MCL of 10 mg/L, and about 72 percent of samples had nitrate-N concentrations greater than the presumed background level of 3 mg/L (Madison and Brunett, 1984). The median nitrate-N concentration was 7.1 mg/L, which was less than the MCL but greater

than the presumed natural background level (fig. 7, table 6). The median concentration of nitrate-N, therefore, implies nitrogen contamination from non-natural sources, such as nitrogen-based fertilizers, animals wastes, and septic-system leachate. Anderson (1993) reported a slightly smaller median nitrate-N concentration (5.3 mg/L) for irrigated land-use settings overlying the Anoka Sand Plain aquifer. Ammonium and ammonium- plus organic-nitrogen, which typically sorb to organic matter and clay particles, were present at lesser concentrations (medians

Table 5. Medians, standard deviation, and range in concentrations of ions and trace metals for ground-water samples. [All concentrations in milligrams per liter unless otherwise indicated; <, less than;  $\mu$ g/L, micrograms per liter; SMCL, Secondary Maximum

Contaminant Level; ---, no value]

Constituent	Median	Standard deviation	Range	SMCL
Calcium	67	27	22–130	
Magnesium	20	7.9	4.2–37	_
Sodium	4.4	13.1	2.3–66	_
Potassium	1.3	1.3	.28–7.3	_
Bicarbonate	217	63	74–345	_
Sulfate	20	16	2.3–61	250
Chloride	17	18	1.1-88	250
Fluoride	.13	.04	<.10–.19	2
Bromide	.04	.04	<.0114	_



Figure 7.--Concentrations of dissolved nutrients and organic carbon in ground-water samples from the sampled wells.

of 0.04 and <0.01 mg/L, respectively) (fig. 7, table 6).

Total phosphorus concentrations had a range of <0.01 to 0.12 mg/L and a median of 0.02 mg/L (fig. 7, table 6). Orthophosphate concentrations had a range of from <0.01 to 0.12 mg/L and a median of 0.02 mg/L. Orthophosphate concentrations were generally similar to total phosphorus concentrations, indicating the predominance of that form of phosphorus. Concentrations of phosphorus compounds—both total dissolved and orthophosphate—commonly were one or more orders of magnitude less than nitrate-N concentrations.

Sources of phosphorus include minerals in igneous and sedimentary rocks, animal wastes, and detergents containing phosphorus (Hem, 1985). Orthophosphate, the final dissociation product of phosphoric acid, is one of many chemical forms in which phosphorus occurs in natural waters. Phosphorus commonly is taken up by plant roots, and also is sorbed to organic matter and soil particles in both unsaturated- and saturated-zone sediments.

DOC was detected in ground-water samples at concentrations that ranged

Table 6. Number of samples with reportable concentrations, method reporting limits, medians, standard deviation, and ranges in concentrations of nutrients and organic carbon for ground-water samples.

[All concentrations in milligrams per liter; MRL, Method Reporting Limit; MCL, Maximum Contaminant Level; <, less than; ---, no value]

Constituent	Number of samples with reportable concentrations	MRL	Median	Standard deviation	Range	MCL
Nitrite- + nitrate-N	27	005	7.1	12.4	<0.05– 47	10
Nitrite-N	11	01	<.0 1	.03	<.01– .15	
Ammonium-N	27	02	.04	.06	<.02– .31	_

from 0.40 to 9.1 mg/L (fig. 7, table 6). The median concentration was 0.85 mg/L. Although not a nutrient, DOC may undergo oxidation and thereby release nutrients and reduce the dissolved oxygen concentration.

### Nitrogen Isotope Ratios

Ratios of nitrogen isotopes in ground water have been investigated as qualitative indicators of nitrate sources (Gormly and Spalding, 1979; Kreitler and Browning, 1983; Flipse and Bonner, 1985; Heaton, 1986; Kaplan and Magaritz, 1986; Wells and Krothe, 1989; Komor and Anderson, 1993; and Ruhl, 1995). These ratios ( $\delta^{15}$ N) are expressed as ‰ (delta units in parts per thousand). The ratios, which are a function of the ratios of heavy ( $^{15}$ N) to light ( $^{14}$ N) nitrogen isotopes in sample-water nitrogen and in atmospheric nitrogen, are defined by the following expression:

 $\delta^{15}N = \{ \ [ \ (^{15}N/^{14}N) \ sample-water-N / (^{15}N/^{14}N) \ atmospheric-N] - 1 \ \} \ x \ 1,000 \ \%.$ 

A positive  $\delta^{15}$ N value indicates that the heavy <sup>15</sup>N isotope is more abundant in sample-water nitrogen than in atmospheric nitrogen, and a negative  $\delta^{15}$ N indicates that the heavy <sup>15</sup>N is less abundant in sample-water nitrogen than in atmospheric nitrogen.

The interpretation of nitrogen isotope data is based on differences in the expected ranges of  $\delta^{15}N$  values for nitrate-N derived from three principal sources. These expected ranges and sources are: (1) from -4 to 4 ‰ for commercial fertilizer; (2) from >4 to 9 ‰ for soil organic matter; and (3) from >9 to 22 ‰ for animal waste (Heaton, 1986). Although increases in the  $\delta^{15}$ N value of nitrate-N may result from fractionation attributable to denitrification (Hauck and others, 1972; Bremner and Tabatabai, 1973; Edwards, 1973; Meints and others, 1975; and Broadbent and others, 1980), this potential source of error was not considered important in this study because of the presence of detectable amounts of dissolved oxygen in the ground-water samples. The range and median  $\delta^{15}$ N values were from 0.1 to 10.5 ‰ and 3.5 ‰. These results suggest that the nitrate-N in the ground-water samples were mostly

derived from commercial fertilizer and naturally occurring soil organic matter, and perhaps rarely derived from animal waste.

## Pesticides

Pesticides are compounds used to kill selected plants and insects. Pesticides are mostly applied to croplands and to a lesser extent lawns, gardens, golf courses, and right-of-ways in urban areas. A total of 83 pesticide compounds, which consisted of commonly used pesticides and their metabolites, were analyzed in the 29 ground-water samples (table 7). About 86 percent of samples had detectable concentrations of at least one of 13 pesticide compounds (table 8). None of the detected pesticide compounds were present at concentrations that exceeded 1 µg/L, and none of these compounds with established MCLs (atrazine-3.0 µg/L, alachlor-2.0 µg/L, dinoseb-7.0  $\mu$ g/L, and simazine—4.0  $\mu$ g/L) were present at concentrations that exceeded their respective MCL.

Many factors affect leaching of pesticides into ground water. These factors include methods and timing of application, cultivation and irrigation practices, and soil characteristics-such as hydraulic conductivity, cation exchange capacity, and organic carbon content (Rao and Alley, 1993). Chemical and physical characteristics of the pesticides, such as organic-carbon sorption coefficient, solubility, acidity, and oxidation and hydrolysis half-life, may also affect leaching. Pesticides typically are formulated so as not to leach below the soil zone. Pesticides also may sorb to organic carbon and clay minerals or degrade by abiotic and biotic processes within the soil (Rao and Alley, 1993). Pesticides are more likely to be sorbed in less permeable soils with abundant organic carbon. Alkaline pesticide compounds are more likely to be sorbed in acidic soils; the opposite is true for acidic pesticide compounds.

DEA, a metabolite formed from biologically mediated degradation of atrazine, was the most frequently detected pesticide compound (23 samples, 79 percent detection frequency) (fig. 8, table 8). The detectable concentrations of DEA ranged from E 0.002 to E 0.149  $\mu$ g/L. Atrazine, a triazine herbicide, was the second most detected pesticide compound (22 samples, 76 percent detection frequency). Detectable concentrations of atrazine ranged from E 0.004 to 0.275  $\mu$ g/L. Anderson (1993) reported a slightly greater concentration (maximum concentration of 1.7  $\mu$ g/L determined for 18 samples), but a smaller detection frequency (44 percent), across the Anoka Sand Plain aquifer.

Atrazine is a moderately persistent triazine herbicide used to control annual grasses in cornfields (Winkelmann and Klaine, 1991). Atrazine has been one of the most widely detected herbicides in surficial aquifers in the UMIS study unit (Fallon and others, 1997). Atrazine, because of its basic pH, sorbs to acidic soil particles (Weber, 1994). Atrazine, which is a possible carcinogen, has a MCL of 3 µg/L (U.S. Environmental Protection Agency, 1996). Potential herbicidal, toxic, and carcinogenic effects were not evaluated for DEA, which has no established MCL.

Metolachlor, a chloroacetanilide compound, was detected in 12 samples (detection frequency of 41 percent) (fig. 8, table 8). Detectable concentrations ranged from E 0.003 to 0.199  $\mu$ g/L (table 8). Metolachlor is used as a pre-emergent herbicide for corn, soybeans, grain sorghum, and potatoes (Sine, 1993). This pesticide has relatively low solubility in water, moderate volatility, and a relatively low sorption coefficient to organic carbon. This pesticide, which is considered a possible human carcinogen, has a lifetime health advisory limit in drinking water of 70 µg/L (U.S. Environmental Protection Agency, 1996). Degradation of metolachlor, which has a half-life of 40 days, is primarily attributable to soil fungi (Weber, 1994).

Metribuzin and bentazon were each detected in 6 samples (detection frequency of 21 percent) (fig. 8, table 8). Metribuzin is a herbicide used to control broadleaf weeds and annual grasses in crops such as potatoes and tomatoes. The half-life of metribuzin varies with soil type from 90 to 115 days. Detectable concentrations of metribuzin ranged from 0.014 to 0.142  $\mu$ g/L. Anderson (1993) reported a maximum concentration of 0.200  $\mu$ g/L and a detection frequency of 11 percent. Bentazon is used for post-

Triazines	Organophospho- rus	Organochlorines	Carbamates	Dinitroaniline	Carboxylic Acids
atrazine	malathion	P,P'-DDE	butylate	benfluralin	2,4-DB
deethylatrazine	parathion	dieldrin	carbaryl	trifluralin	2,4-D
simazine	phorate	chlorothalonil	aldicarb	pendimethalin	chloramben
cyanazine	disulfoton	bromoxynil	aldicarb-sulfone	ethalfluralin	MCPA
metribuzin	methylparathion	НСН-а	aldicarb-sulfoxide		picloram
prometon	methyl-azinphos	НСН-ү	molinate	Aminosulfonyl	dichlorprop
	ethoprop		triallate	bentazon	МСРВ
Pyrethroid	terbufos	Amides	carbofuran	oryzalin	trichlopyr
cis-permethrin	fonofos	napropamide	methomyl	Hydroxy Acid	dicamba
		propachlor	oxamyl	terbacil	acifluorfen
Phenyl Ureas	Phospho- rothiotes	pronamide	EPTC	bromacil	
diuron	diazinon	propanil	thiobencarb	DNOC	Other

Table 7. Pesticide compounds analyzed for in ground-water samples by chemical group

emergent control of broadleaf weeds on land planted in alfalfa, cereal grains, clover, corn, grasses, sorghum, and soybeans (Sine, 1993). Bentazon has moderate solubility in water, low volatility, a low sorption coefficient to organic carbon, and a relatively short soil half-life of 20 days (Weber, 1994). Detectable concentrations of bentazon ranged from 0.060 to 0.810  $\mu$ g/L, much less than its MCL of 20  $\mu$ g/L (U.S. Environmental Protection Agency, 1996).

Prometon was detected in 3 samples (detection frequency of 10 percent) (fig. 8, table 8) at concentrations that ranged from E 0.007 to 0.023  $\mu$ g/L (table 8). This pesticide is a nonselective, long-lasting, pre- and post-emergent herbicide used to control perennial broadleaf weeds and grasses on right-of-ways (Sine, 1993). No MCL has been established for prometon, but the USEPA (1996) has established a lifetime health advisory level for drinking water of 100  $\mu$ g/L, which was not exceeded in any samples. Prometon, which has a basic pH, degrades relatively slowly in soils—the estimated half-life is 200–500 days (Rao and Alley, 1993; Weber, 1994).

Tebuthiuron was detected in 2 samples (detection frequency of 7 percent) (fig. 8, table 8) at concentrations of 0.035 and 0.077  $\mu$ g/L (table 8). This herbicide commonly is used on road right-of-ways. This pesticide also has a basic pH like prometon and atrazine, but has a greater solubility and a lesser sorption coefficient than either of those two compounds (Weber, 1994). Tebuthiuron has a relatively long half-life of 360 days (Weber, 1994). A lifetime health advisory level of 500  $\mu$ g/L has been established for tebuthiuron in drinking water (U.S. Environmental Protection Agency, 1996).

Each of the following pesticide compounds were detected in a single sample (a detection frequency of 3 percent): alachlor; 2,6-diethylaniline; dicamba; dinoseb; malathion; and simazine (fig. 8, table 8). The concentrations of these pesticide compounds were 0.029, 0.001, E 0.008, 0.010, 0.006, and 0.011  $\mu$ g/L, respectively. Alachlor is a chloroacetanilide applied as a pre-emergent or early post-emergent herbicide to control annual grasses and broadleaf weeds in croplands used to grow corn and beans. 2,6-Diethylaniline is a metabolite of alachlor. Dicamba is a carboxylic acid applied as a pre-emergent and post-emergent herbicide to control annual and perennial broadleaf weeds in croplands used to grow grains. Dinoseb is a hydroxy acid used as a post-emergent herbicide to control weeds in croplands used to grow beans and potatoes. Malathion is an organophosphate used as an insecticide to control insects that attack vegetables, fruits, and field crops. Simazine is a triazine herbicide commonly applied to corn. Like atrazine, simazine has a basic pH that results in sorption to acidic soil particles (Weber, 1994). In neutral soils, simazine has a half-life of 90 days (Weber, 1994).

## Volatile Organic Compounds

Ground-water samples from 20 of the wells were analyzed to determine concentrations of 86 VOCs (table 9). VOCs are carbon-containing compounds that readily evaporate at atmospheric temperature and pressure. VOCs are present in many commercial chemical products that

linuron		Acetanilides	methiocarb	dinoseb	dacthal
fenuron	Chloroacetanil- ides	acetochlor	propoxur	Pyridazinone	dacthal, mono acid
fluometuron	metolachlor	Benzonitriles	propham	chlorpyrifos	diethylanaline
tebuthiuron	alachlor	dichlobenil	3-hydroxy-carbo- furan		norflurazon
neburon	-		pebulate		chlopyralid
	Sulfite Ester				2,4,5-T
	propargite				silvex

Table 7. Pesticide compounds analyzed for in ground-water samples by chemical group



Figure 8.--Frequencies of detection of pesticide compounds in ground-water sampled from the sampled wells.

include: gasoline, paints, adhesives, solvents, wood preservatives, dry-cleaning agents, pesticides, cosmetics, correction fluids, and refrigerants. When these chemicals are released as free product at or near land surface from improper disposal, spills, and container leaks, these chemicals may then enter the ground water and become sources of contamination. These chemicals also may enter the ground water from atmospheric deposition and rainfall.

About 50 percent of the samples had a detectable concentration of at least one of the following seven VOCs: 1,2,3,4-tetramethylbenzene, trichlorofluoromethane, styrene, chloromethane, benzene, methylbenzene, and trichloromethane (fig.9, table 10). The other 79 VOCs were not detected in any samples. 1,2,3,4-Tetramethylbenzene was detected in 8 samples (a detection frequency of 40 percent). The detected VOCs had concentrations less than or equal to 0.120  $\mu$ g/L. Detected VOCs with USEPA MCLs, which were styrene (100  $\mu$ g/L), benzene (5.0  $\mu$ g/L), methylbenzene (1,000  $\mu$ g/L), and trichloromethane ( $100 \mu g/L$ —based on the total concentration of 4 trihalomethane compounds (trichloromethane, dibromochloromethane, bromodichloromethane, and tribromomethane)), had concentrations that were 2–4 orders of magnitude less than their respective MCLs.

Detectable concentrations of 1,2,3,4tetramethylbenzene in 8 samples (detection frequency of 40 percent) (fig. 9) ranged from E 0.029 to E 0.062  $\mu$ g/L (table 10). This VOC is an odorless, colorless liquid that typically indicates contamination from hydrocarbon fuel products. Neither a lifetime health advisory level nor a MCL for this VOC in drinking water has been established by the USEPA.

Trichlorofluoromethane was detected in one sample at a concentration of E  $0.032 \mu g/L$  (table 10). This VOC is a chlorofluorocarbon that is used in the manufacture of aerosol sprays, commercial refrigerants, cleaning compounds, solvents, and fire retardants (Verschueren, 1983). Production of this compound was banned in the United States since January 1, 1995.

Styrene was detected in one sample at a concentration of E 0.029  $\mu$ g/L (table 10). Styrene is used in the production of polystyrene and as an insulator. Styrene both volatilizes from and biodegrades in natural waters. The half life of styrene is estimated to be about 3 hours (Verschueren, 1983).

Chloromethane was detected in one sample at a concentration of E 0.099  $\mu$ g/L (table 10). Chloromethane is used in the production of silicones, tetraethyl lead, synthetic rubber, methyl cellulose, refrigerants, methylene chloride, chloroform, carbon tetrachloride, and fumigants (Verschueren, 1983). Chloromethane also is used as a low-temperature solvent, a component of medicines, a fluid in thermostatic equipment, an extractant, a propellant, and a component of herbicides. This VOC has been reported to be present in cigarette smoke in parts-perthousand concentrations (Verschueren, 1983). The USEPA (1996) has determined that chloromethane is a possible

## Table 8. Method reporting limits, number of samples with detectable concentrations, ranges, and maximum contaminant levels of pesticide compounds for ground-water samples.

[All concentrations in micrograms per liter; MRL, Method Reporting Limit; MCL, Maximum Contaminant Level; E, estimated; <, less than]

Pesticide compound	MRL	Number of samples with detectable concentration	Range or values of detectable concentrations	MCL
Deethylatrazine	0.002	23	E 0.002– E .149	
Atrazine	.001	22	E .004–.275	3.0
Metolachlor	.002	12	E .003–.199	
Metribuzin	.004	6	.014–.142	
Bentazon	.014	6	.060–.810	<sup>1</sup> 20
Prometon	.018	3	E .007–.023	
Tebuthiuron	.010	2	.035–.077	
Alachlor	.002	1	.029	2.0
2,6-Diethylaniline	.003	1	.001	
Dicamba	.035	1	E .008	
Dinoseb	.035	1	.010	7.0
Malathion	.005	1	.006	
Simazine	.005	1	.011	4.0

human carcinogen and has established a lifetime health advisory level in drinking water of 3,000  $\mu$ g/L, which was not exceeded in any of the samples. Low concentrations of chloromethane may have been attributable to reactions between naturally-occurring organic matter in the water samples and the drops of 50 percent hydrochloric acid used to preserve the samples analyzed for VOCs. Thus it is possible that the single detection of this VOC may have been an artifact of the sample preservation procedure rather than a reflection of ambient environmental conditions.

Benzene was detected in one sample at a concentration of  $0.120 \ \mu g/L$  (table 10). Benzene is used in the production of detergents, pesticides, plastics and resins, synthetic rubber, aviation fuel and gasoline, pharmaceuticals, dyes, explosives, polychlorinated biphenyls, flavors and perfumes, paints and coatings, and photographic chemicals (Verschueren, 1983). Benzene released into the environment is most commonly linked to the storage, dispensation, and combustion of gasoline (Verschueren, 1983). Benzene harms human health by damaging the immune system and increasing the risk of leukemia and birth defects (Verschueren, 1983).

Methylbenzene was detected in one sample at a concentration of  $0.083 \ \mu g/L$ (table 10). Methylbenzene can be emitted by petroleum refining and coal tar distillation and is used in the manufacture of benzene derivatives, saccharin, medicines, dyes, perfumes, explosives, detergent, gasoline, asphalt, solvents for paints, resins, rubber, lacquer thinners, and adhesive solvents (Verschueren, 1983).

Trichloromethane, also known as chloroform, was detected in one sample at a concentration of E 0.020  $\mu$ g/L (table 10). Trichloromethane is a probable human carcinogen that can damage the central nervous system, liver, and kidneys (U.S. Environmental Protection Agency, 1996). Primary sources of trichloromethane include pulp and paper mills, pharmaceutical plants, chemical plants, sewage treatment plants, and water utilities (Verschueren, 1983). Minor sources of trichloromethane include automobile exhaust, pesticides, tobacco smoke, decomposition of trichloroethene, and combustion of plastics (Verschueren, 1983).

#### Tritium

Tritium is an isotope of hydrogen, usually occurring in water molecules, that breaks down to deuterium through emission of a beta particle. Tritium decays rapidly, with a half-life of 12.43 years. Tritium is naturally produced in the atmosphere by interactions between cosmicray-produced neutrons and nitrogen (Freeze and Cherry, 1979). Anthropogenic sources of tritium include detonations of thermonuclear weapons that mainly occurred during the early 1950's. Prior to that time tritium concentrations in rainwater were less than 10 TUs (1 TU =one tritium atom/1,018 hydrogen atoms) (Drever, 1988). During the 1960's tritium concentrations in rainwater increased to more than 5,000 TUs (Plummer and others, 1993). The current (1997) annual average tritium concentration in rainwater in Minnesota is about 10 TUs, although the seasonal variation ranges from approximately 5 to 20 TUs (James Walsh, Minnesota Department of Health, written commun., 1997).

Table 9. Volatile organic compounds analyzed for in ground-water samples by chemical group

Alkanes	Alkenes	Alkyl Benzenes
1,1,1-trichloroethane / methyl chloro- form	chloroethene / vinyl chloride	(1-methylethyl) benzene / isopropyl- benzene
bromomethane / methyl bromide	bromoethene	ethylbenzene
chloromethane / methyl chloride	trichloroethene	<i>n</i> -propylbenzene
chloroethane	hexachlorobutadiene	<i>n</i> -butylbenzene
dichloromethane /methylene chloride	tetrachloroethene	methylbenzene / toluene
1,1,1,2-tetrachloroethane	cis-1,2-dichloroethene	1,3-dimethylbenzene and 1,4-dimethylbenzene / <i>m</i> - and <i>p</i> -xylene
dibromomethane	trans-1,2-dichlorethene	1,2-dimethylbenzene / o-xylene
1,1-dichloroethane	cis-1,3-dichloropropene	2-ethyltoluene / o-ethyltoluene
1,2-dichloroethane	trans-1,3-dichloropropene	1-isopropyl-4-methylbenzene / p-iso- propyl-toluene
1,2-dichloropropane	3-chloro-1-propene	(1,1-dimethylethyl) benzene / <i>tert</i> -butyl-benzene
1,1,2,2-tetrachloroethane	1,1-dichloropropene	(1-methylpropyl) benzene / <i>sec</i> -butyl- benzene
1,2-dibromo-3-chloropropane	trans-1,4-dichloro-2-butene	1,2,3-trimethylbenzene
1,2,3-trichloropropane	1,1-dichloroethene	1,2,4-trimethylbenzene
1,2-dibromoethane	Halogenated Aromatics	1,3,5-trimethylbenzene
1,1,2-trichloroethane	1,2,3-trichlorobenzene	1,2,3,4-tetramethylbenzene / prehnitene
1,1,1,2,2,2-hexachloroethane	1,2-dichlorobenzene	1,2,3,5-tetramethylbenzene / isodurene
bromochloromethane	1,3-dichlorobenzene	Ethers and other oxygenated com- pounds
2,2-dichloropropane	1,4-dichlorobenzene	methyl tert-butyl ether / MTBE
1,3-dichloropropane	chlorobenzene	diethyl ether / ethyl ether
iodomethane / methyl iodide	1,2,4-trichlorobenzene	diisopropyl ether
tetrachloromethane / carbon tetrachlo- ride / CFC-10	bromobenzene	<i>tert</i> -amyl methyl ether / <i>t</i> -pentyl meth- ylether
trichlorofluoromethane / CFC-11	1-chloro-2-methylbenzene / <i>o</i> -chloro-toluene	ethyl <i>tert</i> -butyl ether / <i>t</i> -butyl ethyl ether
dichlorodifluoromethane / CFC-12	1-chloro-4-methylbenzene / <i>p</i> -chloro-toluene	tetrahydrofuran

The concentration of tritium in ground water depends on the time of recharge. After correcting historical tritium concentrations in precipitation for radioactive decay to 1997, concentrations of tritium in ground water can be used to estimate the time of recharge. Ground water with tritium concentrations less than 0.8 TUs is considered to have recharged prior to testing of thermonuclear weapons during the early 1950's, and ground water with tritium concentrations that range from 0.8 to 5 TUs is considered to have recharged both prior to, during, and after the testing—in other words, recharge derived from each time period that mixed with each other. Ground water with tritium concentrations that range from greater than 5 to 10 TUs could reflect either mixing of pre-and post-1950's recharge or reflect recent precipi-

1,1,2-trichloro-1,2,2-trifluoroethane / Freon 113		acetone
bromodichloromethane	Aromatic Hydrocarbons	2-hexanone
tribromomethane / bromoform	benzene	2-butanone / methyl ethyl ketone
dibromochloromethane	naphthalene	4-methyl-2-pentanone / methyl isobu- tyl ketone
trichloromethane / chloroform	ethenylbenzene / styrene	Others
		carbon disulfide
		2-propenenitrile / acrylonitrile
		2-propenal / acrolein
		methyl acrylonitrile
		methyl methacrylate
		ethyl methacrylate
		methyl acrylate



ground-water samples from the sampled wells.

tation with seasonally low tritium values. Ground water with tritium concentrations greater than 10 TUs is considered to have recharged after the testing of thermonuclear weapons.

Tritium concentrations ranged from 7.5 to 18.8 TUs and had a median of 12.5 TUs. Thus, the ground water appears to have been recharged predominantly during the period after the testing of thermonuclear weapons during the early 1950's. Although the tritium values from 7.5 to 10 TUs are in the range that could indicate mixing of pre- and post-1950's recharge, these results more likely reflect recharge of modern precipitation with seasonally low tritium values. Given the hydrogeologic setting of sampling in a surficial, water-table, sand-plain aquifer with about 8 in. of annual recharge, a reasonable interpretation of the tritium results is that the reported concentrations are due to seasonal recharge of modern precipitation with temporary low tritium rather than to mixing of pre- and post-1950's recharge near the water table.

Table 10. Number of samples with detectable concentrations, method reporting limits, ranges, and maximum contaminant levels of volatile organic compounds for ground-water samples

[All concentrations in micrograms per liter; E, estimated; <, less than]

Volatile organic compound	Number of samples with detectable concentrations	Method reporting limit	Range or values of detectable concentrations	Maximum contaminant level
1,2,3,4, Tetramthylbenzene	8	0.230	E. 0.029–E.62	none
Trichdlorofluoromethane	1	.090	E032	none
Styrene	1	.042	E .029	100
Chloromethane	1	.250	E .099	none
Benzene	1	.100	.120	5.0

#### **SUMMARY**

The USGS studied the quality of shallow ground water in part of the Anoka Sand Plain aquifer as part of the NAWQA Program—a national-scale assessment of the quality of water resources within large study units in various hydrologic settings. The study was done during 1998 in a representative, 75-mi<sup>2</sup> agricultural area of the aquifer, an unconfined, surficial sand and gravel unit that extends across central Minnesota. Ground water in the aquifer is particularly vulnerable to contamination because of the relatively shallow depths to the water table and the high permeability of the soils and underlying unsaturated materials.

Split-spoon samples of sediments were collected at variable depths below land surface during the installation of 19 observation wells. Grain-size distributions of the sediment samples were determined and used to estimate hydraulic conductivity. Estimated hydraulic conductivities ranged from 48 to 238 ft/d for unsaturated-zone samples, and from 5 to 192 ft/d for saturated-zone samples. The median hydraulic conductivity was 102 ft/d for both unsaturated and saturated-zone samples.

The depth below land surface to the water table ranged from 3.3 to 44 ft (median of 15.5 ft). Respective ranges and medians of field-measured physical and chemical properties of ground-water samples were: (1) 6.6–8.2, and 7.5 for pH; (2) 224–1,070  $\mu$ S/cm, and 558  $\mu$ S/cm for specific conductance; (3) <0.10–11.2 mg/L, and 4.9 mg/L for dissolved oxygen; (4) 61–283 mg/L as CaCO<sub>3</sub>, and 178 mg/L as CaCO<sub>3</sub> for alkalinity; and (5) 72–468 mg/L as CaCO<sub>3</sub> for hardness.

Ground water was of the calcium-magnesium bicarbonate type. The median concentrations of calcium, magnesium, and bicarbonate in ground-water samples were 67, 20, and 217 mg/L, respectively. Sodium, chloride, and sulfate also were present in samples, but at smaller concentrations (median concentrations were 4.4, 17, and 20 mg/L, respectively). The median iron concentration was <10  $\mu$ g/L, but individual concentrations were as great as 5,000  $\mu$ g/L; the median manganese concentration was <4  $\mu$ g/L, but individual concentrations were as great as 387  $\mu$ g/L. Both iron and manganese, therefore, in some cases exceeded their respective USEPA SMCLs of 300 and 50  $\mu$ g/L.

About 38 percent of 29 samples had nitrate-N concentrations greater than the USEPA MCL of 10 mg/L, and about 72 percent of the samples had nitrate-N concentrations greater than the presumed natural background level of 3 mg/L. The median nitrate-N concentration of 7.1 mg/L, although not greater than the MCL, was greater than the natural background level. Dissolved phosphorus concentrations ranged from <0.01 to 0.12 mg/L. Orthophosphate had concentrations that were similar to that for dissolved phosphorus. Nitrogen isotope ratios determined for the ground-water samples indicate that the sources of nitrate-N in the sample water were predominantly commercial nitrogen-based fertilizer and soil organic matter. The ratios did not indicate that animal waste was an important source of the nitrate-N in most samples.

Of the 83 pesticide compounds that were analyzed in 29 ground-water samples, at least 1 of 13 compounds were detected in about 86 percent of the samples. The detected pesticide compounds were present at concentrations less than 1  $\mu$ g/L. Four detected pesticide compounds (atrazine, alachlor, dinoseb, and simazine) with established MCLs were present at concentrations that were less than their respective MCLs.

DEA, an atrazine metabolite, was the most frequently detected pesticide compound (23 samples, detection frequency of 79 percent) at concentrations that ranged from E 0.002 to E 0.149 µg/L. Atrazine was the second most frequently-detected pesticide compound (22 samples, detection frequency of 76 percent) at concentrations of E 0.004 to E 0.275 µg/L. Metolachlor was detected in 12 samples (detection frequency of 41 percent) at concentrations of E 0.003 to 0.199 µg/L. Metribuzin and bentazon were each detected in 6 samples (detection frequency of 21 percent). The detectable concentrations of metribuzin and bentazon ranged from 0.014 to 0.142  $\mu$ g/L and from 0.060 to 0.810 µg /L, respectively. The herbicides prometon and tebuthiuron were detected in 3 and in 2 samples, respectively (detection frequencies of 10 and 7 percent, respectively). Alachlor, 2,6diethylaniline, dicamba, dinoseb, malathion, and simazine were each detected in 1 sample (detection frequency of 3 percent) at concentrations of 0.029, 0.001, E 0.008, 0.010, 0.006, and 0.011 µg/L, respectively.

Of 86 VOCs analyzed for in 20 ground-water samples, at least 1 of 7 VOCs were detected in about 50 percent of the samples. None of the detected VOCs had concentrations greater than 0.120 µg/L. The frequencies of detection of the VOCs were: 1,2,3,4-tetramethylbenzene—8 samples (detection frequency of 40 percent); and trichlorofluoromethane, styrene, chloromethane, benzene, methylbenzene, and trichloromethane—1 sample each (detection frequency of 5 percent). Detected VOCs with USEPA MCLs, which are styrene (100 µg/L), benzene (5.0 µg/L), methylbenzene (1,000 µg/L), and trichloromethane (100 µg/L—based on the total concentration of 4 trihalomethane compounds), had concentrations that were 2–4 orders of magnitude less than their respective MCLs.

Ground-water samples from the 29 monitoring wells had tritium concentrations that had a range of from 7.5 to 18.8 TUs and a median of 12.5 TUs. These concentrations indicate that the ground water predominantly consisted of recharge that postdated testing of thermonuclear weapons during the early 1950's.

## REFERENCES

- Anderson, H.W., 1993, Effects of agricultural and residential land use on ground-water quality, Anoka Sand Plain aquifer, east-central Minnesota: U.S. Geological Survey Water-Resources Investigations Report 93– 4074, 62 p.
- Andrews, W.J., Fong, A.L., Harrod, L., and Dittes, M.E., 1998, Water-quality assessment of part of the Upper Mississippi River Basin, Minnesota and Wisconsin—Ground-water quality in an urban part of the Twin Cities metropolitan area, Minnesota, 1996: U.S. Geological Survey Water-Resources Investigations Report 97– 4248, 54 p.
- Bremner, J.M., and Tabatabai, M.A., 1973, Nitrogen-15 enrichment of soils and soil-derived nitrate: Journal of Environmental Quality, v. 2, no. 3, p. 363–365.
- Brenton, R.W., and Arnett, T.L., 1993, Methods of analysis by the U.S.
  Geological Survey National Water-Quality Laboratory—Determination of dissolved organic carbon by UVpromoted persulfate oxidation and infrared spectrometry: U.S. Geological Survey Open-File Report 92– 480, 12 p.
- Broadbent, F.E., Rauschkolb, R.S., Lewis, K.A., and Chang, G.Y., 1980, Spatial variability of nitrogen-15 in some virgin and cultivated soils: Soil Science Society of America Journal, v. 44, p. 524–527.
- Connor, B.F., Rose, D.L., Noriega, M.C., Murtagh, L.K., and Abney, S.R., 1998, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of 86 volatile organic compounds in water by gas chromatography/mass spectrometry, including detections less than reporting limits: U.S. Geological Survey Open-File Report 97–829, 78 p.
- Cooper, W.S., 1935, History of the Upper Mississippi River in Late Wisconsin and post-glacial time: Minnesota Geological Survey Bulletin 26, 116 p.

- Drever, J.I., 1988, The geochemistry of natural waters, 2nd ed.: Englewood Cliffs, N. J., Prentice-Hall, p. 379.
- Durfor, C.N., and Becker, E., 1964, Public water supplies of the 100 largest cities in the United States, 1962:U.S. Geological Survey Water-Supply Paper 1812, 364 p.
- Edwards, A.P., 1973, Isotopic tracer techniques for identification of sources of nitrate pollution: Journal of Environmental Quality, v. 2, no. 3, p. 382–387.
- Ericson, D.W., Lindholm, G.F., and Helgesen, J.O., 1974, Water resources of the Rum River watershed, central Minnesota: U.S. Geological Survey Hydrologic Investigations Atlas HA-509, 3 sheets.
- Fallon, J.D., Fong, A.L., and Andrews,
  W.J., 1997, Water-quality assessment of part of the Upper Mississippi River Basin, Minnesota and Wisconsin—Pesticides in streams, streambed sediment, and ground water, 1974–94: U.S. Geological Survey Water-Resources Investigations Report 97–4141, 53 p.
- Fan, A.M., Wilhite, C.C., and Book, S.A., 1987, Evaluation of the nitrate drinking water standard with reference to infant methemoglobinemia and potential reproductive toxicity: Regulatory Toxicology and Pharmacology, v. 7, p. 135–137.
- Farnham, R.S., 1956, Geology of the Anoka Sand Plain, *in* Wright, H.E., assoc. ed., The Geological Society of America, Glacial geology, eastern Minnesota: Field Trip No. 3, p. 53– 64.
- Farnsworth, D.K., Thompson, E.S., and Peck, E.L., 1982, Annual free water surface (FWS) evaporation from shallow lakes, 1956–70, map 3 of evaporation atlas for the contiguous 48 United States: National Oceanic and Atmospheric Administration Technical Report NWS 33, scale 1:4,800,000.
- Fishman, M.J., and Friedman, L.C., eds., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p.

- Flipse, W.J., Jr., and Bonner, F.T., 1985, Nitrogen-isotope ratios of nitrate in ground water under fertilized fields, Long Island, New York: Ground Water, v. 23., no. 1, p. 59–67.
- Fong, A.L., in press, Water-quality assessment of the Upper Mississippi River Basin, Minnesota and Wisconsin—Ground-water quality in three different land-use areas, 1996–98: U.S. Geological Survey Water-Resources Investigations Report 00– 4131.
- Forman, D., Al-Dabbagh, S., and Doll, R., 1985, Nitrates, nitrites, and gastric cancer in Great Britain: Nature, v. 313, p. 620–625.
- Freeze, R.A., and Cherry, J.A., 1979, Groundwater: Prentice-Hall, Inc., Englewood Cliffs, N. J., 604 p.
- Gormly, J.R., and Spalding, R.F., 1979, Sources and concentrations of nitrate nitrogen in ground water of the Central Platte Region, Nebraska: Ground Water, v. 17, no. 3, p. 291–301.
- Guy, H.P., 1969, Laboratory theory and methods for sediment analysis: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. C1, 58 p.
- Hauck, R.D., Bartholomew, W.V., Bremner, J.M., Broadbent, F.E., Cheng,
  H.H., Edwards, A.P., Deeney, D.R.,
  Legg, J.O., Olsen, S.R., and Porter,
  L.K., 1972, Use of variations in natural nitrogen isotope abundance for
  environmental studies—A questionable approach: Science, v. 177, p.
  453–454.
- Heaton, T.H.E., 1986, Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere—A review: Chemical Geology, v. 59, p. 87–102.
- Helgesen, J.O., Ericson, D.W., and Lindholm, G.F., 1975, Water resources of the Mississippi and Sauk Rivers watershed, central Minnesota: U.S. Geological Survey Hydrologic Investigations Atlas HA-534, 3 sheets.
- Helgesen, J.O., and Lindholm, G.F., 1977, Geology and water-supply potential of the Anoka Sand-Plain aquifer, Minnesota: Minnesota Department of Natural Resources, Technical Paper No. 6, 17 p.

- Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water: U.S. Geological Survey Water-Supply Paper 2254, 3rd ed., 263 p.
- Hitt, K.J., 1996, Digital map file of major land uses in the United States: U.S. Geological Survey, Reston, Va., scale 1:7,500,000.
- Kaplan, I.R., and Magaritz, M., 1986, A nitrogen-isotope study of the sources of nitrate contamination in ground water of the Pleistocene coastal plain aquifer, Israel: Water Research, v. 20, p. 131–153.
- Komor, S.C., and Anderson, H.W., Jr., 1993, Nitrogen isotopes as indicators of nitrate sources in Minnesota sandplain aquifers: Ground Water, v. 31, no. 2, p. 260–270.
- Komor, S.C., and Emerson, D.G., 1994, Movement of water, solutes, and stable isotopes in the unsaturated zones of two sand plains in the upper Midwest: Water Resources Research, v. 30, no. 2, p. 253–267.
- Koterba, M.T., Wilde, F.D., and Lapham, W.W., 1995, Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program—Collection and documentation of water-quality samples and related data: U.S. Geological Survey Open-File Report 95–399, 113 p.
- Kreitler, C.W., and Browning, L.A., 1983, Nitrogen-isotope analysis of groundwater nitrate in carbonate aquifers— Natural sources versus human pollution: Journal of Hydrology, v. 61, p. 285–301.
- Landon, M.K., and Delin, G.N., 1995, Ground-water quality in agricultural areas, Anoka Sand Plain aquifer, east-central Minnesota, 1984–90: U.S. Geological Survey Water-Resources Investigations Report 95– 4024, 25 p.
- Landon, M.K., Delin, G.N., Lamb, J.A., Anderson, J.L., and Dowdy, R.H., 1998, Effects of farming systems on ground-water quality at the management systems evaluation area near Princeton, Minnesota, 1991–95: U.S. Geological Survey Water-Resources Investigations Report 98–4128, 51 p.

- Lapham, W.W., Wilde, F.D., and Koterba, M.T., 1995, Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program—Selection, installation, and documentation of wells and collection of related data: U.S. Geological Survey Open-File Report 95– 398, 69 p.
- Lindholm, G.F., 1980, Ground-water appraisal of sand plains in Benton, Sherburne, Stearns, and Wright Counties, central Minnesota: U.S. Geological Survey Water-Resources Investigations Report 80–1285, 103 p.
- Lindholm, G.F., Farrell, D.F., and Helgesen, J.O., 1974, Water resources of the Crow River watershed, southcentral Minnesota: U.S. Geological Survey Hydrologic Investigations Atlas HA-528, 3 sheets.
- Madison, R.J., and Brunett, J.O., 1984, Overview of the occurrence of nitrate in ground water of the United States, *in* National Water Summary, 1984: U.S. Geological Survey Water-Supply Paper 2275, p. 93–105.
- Magner, J.A., Wall, D.B., and Wilson, N.E.,1990a, Agricultural and lake influences on water quality in outwash aquifers in the School Section Lake area of Stearns County, Minnesota: Minnesota Pollution Control Agency, Water Quality Division, 129 p.
- 1990b, Factors relating to nitrate contaminated wells in an agricultural/residential area of Benton County, Minnesota: Minnesota Pollution Control Agency, Water Quality Division, 165 p.
- Meints, V.W., Boone, L.V., and Kurtz, L.T., 1975, Natural 15N abundance in soil, leaves, and grain as influenced by long-term additions of fertilizer N at several rates: Journal of Environmental Quality, v. 4 no. 4, p. 486–490.
- Menheer, M.A., and Brigham, M.E., 1997, Ground-water sampling methods and quality-control data for the Red River of the North Basin, Minnesota, North Dakota, and South Dakota, 1993–95: U.S. Geological Survey Water-Resources Investigations Report 96–4317, 34 p.

- Meyer, G.N., and Patterson, C.J., 1999, Surficial geology of the Anoka 30 x 60 minute quadrangle, Minnesota: Minnesota Miscellaneous Map M-97, 1:100,000, 1 plate.
- Minnesota Department of Health, 1994, Rules Handbook—A guide to Minnesota Rules, Chapter 4725.6450, Wells and Borings, August, 1994: Minnesota Department of Health, St. Paul, p. 393–401.
- Minnesota Department of Natural Resources, 1993, Regional Hydrogeologic Assessment, Anoka Sand Plain, Anoka, Chisago, Isanti, and Sherburne Counties, Minnesota, Regional Hydrogeologic Assessment RHA-1: Minnesota Department of Natural Resources, Division of Waters, 3 plates.
- Minnesota Pollution Control Agency, 1999, Effects of land use on ground water quality—1998 results, prepared by Ground Water Monitoring and Assessment Program, 46 p.
- Minnesota State Climatologist, electronic communication, 6/1/1999, URL at http://climate.umn.edu/doc/historical.htm.
- National Atmospheric Deposition Program/National Trends Network, electronic communication, 6/1/1999, URL at http://nadp.sws.uiuc.edu/.
- National Research Council, 1985, The health effects of nitrate, nitrite, and N-nitroso compounds: Washington, D.C., National Academy of Press, 723 p.
- Ostlund, H.G., and Dorsey, H.G., 1975, Rapid electrolytic enrichment of hydrogen gas proportional counting of tritium: International Conference on Low Radioactivity Measurement and Applications, High Tatras, Czechoslovakia, October 1975 [Proceedings], 6 p.
- Palen, B.M., Kanivetsky, R., and Christopher, R.A., 1993, Water-table hydrogeology, *in* Regional Hydrogeologic Assessment, Anoka Sand Plain, Anoka, Chisago, Isanti, and Sherburne Counties, Minnesota:
  Regional Hydrogeologic Assessment RHA-1, 1 plate.
- Plummer, L.N., Michel, R.L., Thurman, E.M., and Glynn, P.D., 1993, Environmental tracers for age-dating

young ground water, *in* Alley, W.M., ed., Regional ground-water quality: New York, Van Nostrand Reinhold, p. 255–294.

- Rao, P.S.C., and Alley, W.M., 1993, Pesticides, *in* Alley, W.M., ed., Regional ground-water quality: New York, Van Nostrand Reinhold, p. 345–382.
- Ruhl, J.F., 1995, Presence, distribution, and potential sources of nitrate and selected pesticides in the surficial aquifer along the Straight River in north-central Minnesota, 1992–93: U.S. Geological Survey Water-Resources Investigations Report 95– 4151, 24 p.
- Schoenberg, M.E., 1990, Effects of present and projected ground-water withdrawals on the Twin Cities aquifer system, Minnesota: U.S. Geological Survey Water-Resources Investigations Report 90–4001, 165 p.
- Scott, J.C., 1990, Computerized stratified random site-selection approaches for design of a ground-water-quality sampling network: U.S. Geological Survey Water-Resources Investigations Report 90–4101, 109 p.
- Sine, C., ed., 1993, Farm chemical handbook '93: Willoughby, Ohio, Meister Publishing Company, variously paged.
- Solley, W.B., Pierce, R.R., and Perlman, H.A., 1995, Estimated use of water in the United States in 1995: U.S. Geological Survey Circular 1200, 71 p.
- Squillace, P.J., and Price, C.V., 1996, Urban land-use study plan for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 96–217, 19 p.
- Stark, J.R., Andrews, W.J., Fallon, J.D., Fong, A.L., Goldstein, R.M., Hanson, P.E., Kroening, S.E., and Lee, K.E., 1996, Water-quality assessment of part of the Upper Mississippi River Basin, Minnesota and Wisconsin—Environmental setting and study design: U.S. Geological Survey Water-Resources Investigations Report 96–4098, 62 p.
- Stark, J.R., Fallon, J.D., Fong, A.L., Goldstein, R.M., Hanson, P.E., Kroening, S.E., and Lee, K.E., 1999, Water-quality assessment of part of

the Upper Mississippi River Basin, Minnesota and Wisconsin—Design and implementation of water-quality studies, 1995–98: U.S. Geological Survey Water-Resources Investigations Report 99–4135, 85 p.

- Todd, D.K., 1980, Groundwater Hydrology: New York, John Wiley & Sons, Inc., 2nd ed., 535 p.
- U.S. Bureau of Census, 1991, Census of Population and Housing, 1990: P.L. (Public Law) 94–171, data from CD ROM (Minnesota), Washington, D.C.
- U.S. Environmental Protection Agency, 1996, Drinking water regulations and health advisories: U.S. Environmental Protection Agency, Office of Water, EPA 822-B-96-002, October 1996, 9 p.
- Verschueren, Karel, 1983, Handbook of environmental data on organic chemicals: New York, Van Nostrand Reinhold, 1310 p.
- Weber, J.B., 1994, Properties and behavior of pesticides in soil, *in* Honeycutt, R.C, and Schabacker, D.J., eds., Mechanisms of pesticide movement into ground water: Boca Raton, Fla., Lewis Publishers, p. 15–41.
- Wells, E.R., and Krothe, N.C., 1989, Seasonal fluctuation in  $\delta^{15}$ N of groundwater nitrate in a mantled karst aquifer due to macropore transport of fertilizer-derived nitrate: Journal of Hydrology, v. 112, p. 191–201.
- Werner, S.L., Burkhardt, M.R., and DeRusseau, S.N., 1996, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of pesticides in water by Carbopak-B solid-phase extraction and high-performance liquid chromatography: U.S. Geological Survey Open-File Report 96– 216, 42 p.
- Wershaw, R.L., Fishman, M.J., Grabbe, R.R., and Lowe, L.E., 1987, Methods for the determination of organic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A3, 80 p.
- Winkelmann, D.A., and Klaine, S.J., 1991, Atrazine metabolite behavior in soil-core microcosms—Forma-

tion, disappearance, and bound residues, *in* Somasundarum, L., and Coats, J.R., eds., Pesticide transformation products—Fate and significance in the environment: American Chemical Society, Symposium Series 59, Washington, D.C., p. 75– 92.

- Wright, H.E., Jr., 1972a, Physiography of Minnesota, *in* Sims, P.K., and Morey, G.B., eds., Geology of Minnesota— A centennial volume: Minnesota Geological Survey, p. 561–578.
- \_\_\_\_\_, 1972b, Quaternary history of Minnesota, *in* Sims, P.K., and Morey, G.B., eds., Geology of Minnesota— A centennial volume: Minnesota Geological Survey, p. 515–546.
- Wright, H.E., Jr., and Ruhe, R.V., 1965,
  Glaciation of Minnesota and Iowa, *in*Wright, H.E., Jr., and Frey, D.G.,
  eds.: The Quaternary of the United
  States, Princeton, N.J., Princeton
  University Press, p. 29–41.
- Zaugg, S.D., Sandstrom, M.W., Smith, S.G., and Fehlberg, K.M., 1995, Methods of analysis by the National Water Quality Laboratory—Determination of pesticides in water by C-18 solid-phase extraction and capillary column gas chromatography/ mass spectrometry with selected-ion monitoring: U.S. Geological Survey Open-File Report 95–181, 60 p.

# **Supplemental Information**

## **TABULATION OF WELL DATA**

Table 11.	Well con	struction	data and	site	charact	eristics	for	sampled	wells	[NA,	not a	applicat	ble]
								1		•		11	

Local well identifier number (shown in figure 1)	Site identifier	Minnesot a unique well number	County	Latitud e	Longitud e	Alti- tude of land sur- face above sea level (feet)	Date of constructio n	Wel l dept h (fee t)	Depth to bottom of casing (feet)
ALUS-1	4524080935530 01	582131	Sher- burne	45°24'0 8"	093°55'3 0"	975	09/16/97	31. 5	26.5
ALUS-2	4524280935916 01	582132	Sher- burne	45°24'2 8"	093°59'1 6"	960	09/17/97	20. 5	15.5
ALUS-3	4525450935710 02	371006	Sher- burne	45°25'4 5"	093°57'1 0"	985	10/21/76	36. 2	34.2
ALUS-4	4526100935530 01	582133	Sher- burne	45°26'1 0"	093°55'3 0"	975	09/18/97	11.5	6.5
ALUS-5	4527200935522 02	NA	Sher- burne	45°27'2 0"	093°55'2 2"	970	10/11/83	25	23
ALUS-6	4527110935655 01	582134	Sher- burne	45°27'1 1"	093°56'5 5"	975	09/18/97	14. 5	9.5
ALUS-7	4526090935530 01	582135	Sher- burne	45°26'3 2"	093°55'1 8"	975	09/18/97	15. 5	10.5
ALUS-8	4525430935448 01	482926	Sher- burne	45°25'4 3"	093°54'4 8"	980	04/21/92	57	53
ALUS-9	4524080935529 01	NA	Sher- burne	45°24'4 3"	093°54'0 8"	975	NA	28	NA
ALUS-10	4523240935416 01	517548	Sher- burne	45°23'2 4"	093°54'1 6"	971	04/01/93	34	24
ALUS-11	4522290935258 01	NA	Sher- burne	45°22'2 9"	093°52'5 8"	963	08/26/81	60	40
ALUS-12	4519530934849 01	582149	Sher- burne	45°19'5 3"	093°48'4 9"	950	09/11/97	43	38
ALUS-13	4520300935114 03	612777	Sher- burne	45°20'3 0"	093°51'1 4"	929	07/10/98	22. 5	17.5
ALUS-14	4521110935234 01	582051	Sher- burne	45°21'1 1"	093°52'3 4"	950	09/17/97	34	24
ALUS-15	4522100935237 01	493038	Sher- burne	45°22'1 0"	093°52'3 7"	960	09/06/91	37	27

Table 11. Well construction data and site characteristics for	r sampled wells	[NA, not applicable]
---	-----------------	----------------------

Local well identifier number (shown in figure 1)	Site identifier	Minnesot a unique well number	County	Latitud e	Longitud e	Alti- tude of land sur- face above sea level (feet)	Date of constructio n	Wel l dept h (fee t)	Depth to bottom of casing (feet)
ALUS-16	4523350935043 01	NA	Sher- burne	45°24'0 0"	093°51'0 7"	955	1978	23	NA
ALUS-17	4523350935045 01	582136	Sher- burne	45°23'3 5"	093°50'4 5"	960	09/15/97	18	13
ALUS-18	4522150934810 01	582137	Sher- burne	45°22'1 5"	093°48'1 0"	955	09/16/97	26	21
ALUS-19	4520400934631 01	582138	Sher- burne	45°20'4 0"	093°46'3 1"	940	09/12/97	24. 2	19.2
ALUS-20	4519570934832 01	582139	Sher- burne	45°19'5 7"	093°48'3 2"	940	09/12/97	49	44
ALUS-21	4519240934746 01	582140	Sher- burne	45°19'2 4"	093°47'4 6"	945	09/11/97	35	30
ALUS-22	4518110934456 01	582141	Sher- burne	45°18'1 1"	093°44'5 6"	930	09/10/97	19	14
ALUS-23	4517550934339 01	582142	Wright	45°17'5 5"	093°43'3 9"	920	09/10/97	25	15
ALUS-24	4518350934004 01	582143	Sher- burne	45°18'3 5"	093°40'0 4"	920	09/08/97	11.8	6.8
ALUS-25	4518220934132 01	582144	Sher- burne	45°18'2 2"	093°41'0 8"	920	09/08/97	30	25
ALUS-26	4519150934639 01	475151	Sher- burne	45°19'1 5"	093°46'3 9"	944	05/16/91	28. 2	18.2
ALUS-27	4519210934451 01	582145	Sher- burne	45°19'2 1"	093°44'5 1"	930	09/10/97	8	3
ALUS-28	4520070934130 01	582146	Sher- burne	45°20'0 7"	093°41'3 0"	930	09/09/97	16	11
ALUS-29	4517300934230 01	582147	Sher- burne	45°20'1 0"	093°42'3 0"	930	09/09/97	15	10
ALUS-30	4520360934237 01	582148	Sher- burne	45°20'3 6"	093°42'3 7"	930	09/09/97	9	4

Compound (units)	Method reporting limit	Field/equipment blanks	Trip blanks	Source-solution blanks	Range or values of detectable concentrations in environmental samples
Calcium (mg/L)	0.020	0.059–.17	na	na	22–130
Magnesium (mg/L)	.040	.009–.02	na	na	4.2–37
Iron (µg/L)	10	< 10–14	na	na	<10–5,000
Dissolved organic carbon (mg/ L)	.10	.20	na	na	0.40–9.1
Trichloromethane (µg/L)	.052	E 0.029	nd	nd	E .020
Methylbenzene (µg/L)	.050	E .044	E 0.020	nd	E .083

Table 12. Method reporting limits and concentration ranges of detected analytes in blanks and environmental samples. [na, not analyzed; nd, not detected; E, low-level detection with estimated concentration; <, less than]

## QUALITY-ASSURANCE/ QUALITY-CONTROL

Nine quality-assurance/quality-control (QA/QC) samples were collected and analyzed in accordance with NAWQA protocols (Koterba and others, 1995). These samples included: (1) three field/ equipment blanks; (2) one trip blank; (3) one source-solution blank; (4) two replicates; and (5) two spikes (and a replicate spike in addition to each regular spike).

Field/equipment blanks consisted of water that was free of inorganic and organic compounds. These blanks were processed in the field and treated and processed in the same manner and with the same equipment as the environmental samples. These blanks were analyzed to verify that contamination of samples did not occur because of: (1) cleaning of equipment; (2) collection and processing of samples; and (3) handling and transport of samples. Two field/equipment blanks were analyzed for nutrients, ions, DOC, and pesticides, and one field/equipment blank was analyzed for VOCs.

Trip blanks consisted of vials of water free of VOCs stored in the sampling vehicle during a specified period of time. These blanks were processed at the USGS office in Mounds View, Minnesota to identify potential contamination from storage, transport, and handling. A source-solution blank was prepared by filling sample bottles directly with VOCfree blank water without contact with any of the sampling equipment used to treat environmental samples. Analyses of this blank indicated if the specially prepared blank water was actually free of VOCs.

Replicate samples consist of environmental water collected in addition to the regular environmental samples. These replicates are analyzed for the same chemical constituents as the regular environmental samples. One of the replicates was analyzed for nutrients, ions, DOC, and pesticides; the other replicate was analyzed for VOCs. Analyses of the replicates indicated if sample variability was attributable to sample collection by USGS field technicians and to handling and processing at the NWQL.

Two spiked samples were analyzed to test for bias resulting from interference by chemical constituents other than the analytes of interest or from degradation of the analytes of interest. The spiked sam-

 Table 12. Method reporting limits and concentration ranges of detected analytes in blanks and environmental samples. [na, not analyzed; nd, not detected; E, low-level detection with estimated concentration; <, less than]</td>

Dichloromethane (µg/L)	.38	17	nd	nd	nd
M/P Xylene (µg/L)	.060	E .020	nd	nd	nd

Table 13. Method reporting limits, concentrations, ranges and mean percent recoveries for schedule 2010 pesticide spikes  $[\mu g/L, micrograms per liter; <, less than]$ 

Pesticide Compound	Method reporting limit ( $\mu$ g/L)	Recovery (percent)	Mean percent recovery
2,6-Diethylaniline	<0.003	84.8-85.5	85.1
Acetochlor	<.002	95.4–98.1	96.8
Alachlor	<.002	92.8–96.3	94.6
Alpha Bhc	<.002	87.1–107	97.1
Atrazine	<.001	86.5–90.1	88.3
Benfluralin	<.002	82.2–109	95.5
Butylate	<.002	91–108	99.5
Carbaryl	<.003	76.2–146	111
Carbofuran	<.003	87.1–114.2	100.6
Chlorpyrifos	<.004	81–107	94
Cyanazine	<.004	95.4–102	98.6
Dcpa	<.002	42.1-84.4	63.2
Deethylatrazine	<.002	56.4-60	58.2
Diazinon	<.002	81.2-103	91.9
Dieldrin	<.001	91.9–107	99.5
Disulfoton	<.017	61.4–69.6	65.5
Eptc	<.002	84.8–91	87.9
Ethalfluralin	<.004	82.8 - 134	108
Ethoprop	<.003	81.3–93.7	87.5
Fonofos	<.003	82.6-86.8	84.7
Lindane	<.004	84.7–104	94.6
Linuron	<.002	47–99.9	73.5
Malathion	<.005	83–96.3	89.6
Methyl Azinphos	<.001	102–208	155
Methyl Parathion	<.006	92.8–93.7	93.2
Metolachlor	<.002	91–110	100
Metribuzin	<.004	84.7–97.2	91
Molinate	<.004	91–92.8	91.9
Napropamide	<.003	97.2–122	110
P,p' Dde	<.006	73.9–90.1	82
Parathion	<.004	87.4–131	109.3
Pebulate	<.004	92.8–92.8	92.8
Pendimethalin	<.004	91–125	108
Permethrin	<.005	57.7–63.6	60.7

Pesticide Compound	Method reporting limit ( $\mu$ g/L)	Recovery (percent)	Mean percent recovery	
Phorate	<.002	73.1–77.9	75.5	
Prometon	<.018	86.8–94.6	90.7	
Pronamide	<.003	89.2–99	94.1	
Propachlor	<.007	98.1–104	101	
Propanil	<.004	83.6–97.2	90.4	
Propargite	<.013	78.6–85	81.8	
Simazine	<.005	86.8–87.1	87	
Tebuthiuron	<.010	86.6–107.9	97.3	
Terbacil	<.007	64.8–91	77.9	
Terbufos	<.013	79.9–89.2	84.6	
Thiobencarb	<.002	93.7–96.3	95	
Triallate	<.001	78.9–92.8	85.8	
Trifluralin	<.002 83.5–114		98.8	
Surrogates				
Diazinon	nd	104–121	112	
нсн-а	nd	102–112	108	
Terbuthylazine	nd	86.5–107	95.1	

# Table 14. Method reporting limits, concentrations, ranges, and mean percent recoveries for schedule 2051 pesticide spikes [<, less than]

Pesticide compound	Method reporting limit (µg/ L)	Recovery (percent)	
2,4,5-t	<0.035	55.5	
2,4-d	<0.150	45.1	
2,4-db	<.240	47.9	
Acifluorfen	<.035	54.5	
Aldicarb	<.550	22.8	
Aldicarb sulfone	<.100	4.7	
Aldicarb sulfoxide	<.021	61.7	
Bentazon	<.014	34.2	
Bromacil	<.035	63.9	
Bromoxynil	<.035	49.4	
Carbaryl	<.008	86.5	
Carbofuran	<.120	78	
3-hydroxy-carbofuran	<.014	88.4	
Chloramben	<.420	72.4	
Chlorothalonil	<.480	50.9	
Clopyralid	<.230	3.8	
Dacthal mono-acid	<.017	55.3	
Dicamba	<.035	40.8	
Dichlobenil	<1.20	47	
Dichloroprop	<.032	49.4	
Dinoseb	<.035	49.4	
Diuron	<.020	76.9	
Dnoc	<.420	46.5	
Fenuron	<.013	83.6	
Fluometuron	<.035	83.7	
Linuron	<.018	79	
Мсра	<.170	44.2	
Мсрb	<.140	64.9	
Methiocarb	<.026	78	

Pesticide compound	Method reporting limit (µg/ L)	Recovery (percent)
Methomyl	<.017	73.3
Neburon	<.015	76.1
Norflurazon	<.024	81.8
Oryzalin	<.310	69.6
Oxamyl	<.018	73.3
Picloram	<.050	4.7
Propham	<0.035	76.1
Propoxur	<.035	125
Silvex	<.021	53.2
Triclopyr	<.250	48.9
Surrogate		
BDMC	nd	87

# Table 15. Method reporting limits, concentrations, ranges, and mean percent recoveries for volatile organic compounds spikes and surrogates.

[<, less than; nd, not determined]

Volatile organic compound	Method reporting limit ( $\mu$ g/L)	hod reporting limit (µg/L) Recovery (percent)		
Dibromomethane	<0.050 65.0-69.2		67.1	
Bromodichloromethane	<.048	55.4-66.0	60.7	
Tetrachloromethane	<.088	29.6–47.9	38.7	
1,2-Dichloroethane	<.130	61.5–69.8	65.7	
Bromoform	<.100	66.6–69.9	68.3	
Dibromochloromethane	<.180	59.4–67.2	63.3	
Trichloromethane	<.052	46.4–61.8	54.1	
Methylbenzene	<.050	44.0–58.2	51.1	
Benzene	<.100	39.6–54.4	47.0	
Acrylonitrile	<1.20	92.5–95.0	93.8	
Chlorobenzene	<.028	46.0–56.8	51.4	
Chloroethane	<.120	31.2–46.4	38.8	
Ethylbenzene	<.030	39.2–53.2	46.2	
Hexachloroethane	<.360	39.4–52.2	45.8	
Bromomethane	<.150	32.4-48.0	40.2	
Chloromethane	<.250	32.0–47.3	39.7	
Methylene chloride	<.380	48.9-63.2	56.1	
Tetrachloroethene	<.100	36.2–54.2	45.2	
Trichlorofluoromethane	<.090	26.9–45.4	36.2	
1,1-Dichloroethane	<.066	42.6-60.6	51.6	
1,1-Dichloroethene	<.044	28.4-45.8	37.1	
1,1,1-Trichloroethane	<.032	33.8–52.6	43.2	
1,1,2-Trichloroethane	<.064	70.7–74.7	72.7	
1,1,2,2-Tetrachloroethane	<.130	78.5-80.0	79.2	
1,2-Dichlorobenzene	<.048	57.0-65.0	61.0	
1,2-Dichloropropane	<.068	51.3-64.4	57.9	
trans-1,2-Dichloroethene	<.032	36.4–55.6	46.0	
1,2,4-Trichlorobenzene	<.190	56.3-62.1	59.2	
1,3-Dichlorobenzene	<.054	49.8–59.0	54.4	
1,4-Dichlorobenzene	<.050	49.6–58.8	54.2	
Dichlorodifluoromethane	<.140	26.0–38.0	32.0	
Napthalene	<.250	71.2–73.2	72.2	

Table 15. Method reporting limits, concentrations, ranges, and mean percent recoveries for volatile organic compounds spikes and surrogates.—Continued

Volatile organic compound	Method reporting limit ( $\mu$ g/L)	thod reporting limit ( $\mu$ g/L) Recovery (percent)	
trans-1,3-Dichloropropene	<.130 58.2–64.0		61.1
cis-1,3-Dichloropropene	<.090	51.0-61.0	56.0
Vinyl chloride	<.110	27.4–44.2	35.8
Trichloroethene	<.038	38.2–56.6	47.4
Hexachlorobutadiene	<.140	40.9–55.6	48.2
Methyl acrylate	<1.40	81.3-83.3	82.3
1,2,3,4-Tetramethylbenzene (preh- nitene)	<.230	57.4–66.0	61.7
1,2,3,5-Tetramethylbenzene	<.200	47.5–56.7	52.1
Bromochloromethane	<.100	58.8–96.0	77.4
Ethyl-t-butyl ether (ETBE)	<.054	58.8–66.0	62.4
tert-Pentyl methyl ether (TAME)	<.110	60.9–65.9	63.4
trans-1,4-Dichloro-2-butene	<.700	89.3–90.6	89.9
Ethyl methacrylate	<.280	70.0–73.9	72.0
Carbon disulfide	<.370	30.0–48.4	39.2
cis-1,2-Dichloroethene	<.038	44.0–58.0	51.0
2-Hexanone	<.700	80.7–84.0	82.3
Styrene	<.042	50.4-62.0	56.2
o-Xylene	<.060	45.5–57.5	51.5
1,1-Dichloropropene	<.026	33.4–53.8	43.6
2,2-Dichloropropane	<.078	31.5–48.0	39.8
1,3-Dichloropropane	<.120	65.1–71.3	68.2
2-Ethyl toluene	<.100	41.8–54.2	48.0
1,2,3-Trimethylbenzene	<.120	55.4–67.3	61.3
1,2,4-Trimethylbenzene	<.056	46.0–59.0	52.5
Isopropylbenzene	<.032	38.2–52.8	45.5
n-Propylbenzene	<.042	37.6–50.2	43.9
1,3,5-Trimethylbenzene	<.044	43.2–56.0	49.6
2-Chlorotoluene	<.042	44.6–56.4	50.5
4-Chlorotoluene	<.056	46.0–58.0	52.0
Vinyl bromide	<.044	27.3–32.2	29.8
n-Butylbenzene	<.190	34.4–47.1	40.7
sec-Butylbenzene	<.048	35.0–50.8	42.9

Volatile organic compound	Method reporting limit (µg/L) Recovery (percent)		Mean percent recovery	
tert-Butylbenzene	<.100 38.8–52.3		45.6	
p-Isopropyltoluene	<.110	39.3–52.8	46.0	
Methyl iodide	<.210	47.5–67.5	57.5	
1,2,3-Trichloropropane	<.160	72.5–73.0	72.8	
1,1,1,2-Tetrachloroethane	<.044	50.2–59.8	55.0	
1,2,3-Trichlorobenzene	<.270	61.1–65.6	63.3	
1,2-Dibromoethane	<.036	67.6–75.2	71.4	
1,1,2-Trichloro-1,2,2-trifluoroethane	<.032	25.8–45.0	35.4	
Methyl-tertiary-butyl ether (MTBE)	<.170	61.5–67.5	64.5	
3-Chloropropene	<.200	34.0–52.2	43.1	
4-Methyl-2-pentanone	<.370	81.9-82.2	82.0	
Acetone	<5.00	83.3-84.3	83.8	
Bromobenzene	<.036	51.6-62.2	56.9	
Diethyl ether	<.170	61.2–70.6	65.9	
Di-isopropyl ether	<.098	54.1-64.0	59.1	
Methyl acrylonitrile	<.570	77.2–79.7	78.4	
2-Butanone	<1.60	91.5–95.2	93.3	
Methyl methacrylate	<.350	80.6-82.6	81.6	
Tetrahydrofuran	<9.00	80.0-83.0	81.5	
1,2-Dibromo-3-chloropropane	<.210	74.3–74.3	74.3	
m- and p-Xylene	<.060	41.8–56.1	49.0	
Surrogates				
Ethane 12DICL	nd	94–113	106	
Methylbenzene D8	nd	96–102	100	
Benzene 14BRFL	nd	96–103	100	

# Table 16. Method reporting limits and concentrations of compounds in environmental and replicate samples that differed by greater than 5 percent

Compound (unit)	Method reporting limit	Environmental sample concentration	Replicate sample concentration	Percent difference in concentrations between environmental and replicate samples	Absolute difference in concentrations between environmental and replicate samples
<sup>1</sup> Ammonium- + organic-nitrogen (mg/ L)	0.10	0.91	0.82	11.1	0.09
<sup>1</sup> Sulfate (mg/L)	.10	4.7	4.2	10.6	.50
<sup>1</sup> Flouride (mg/L)	.10	0.14	.12	14.3	.02
<sup>2</sup> Methylbenzene ( $\mu$ g/L)	.050	<.050	E .031	_	—
<sup>2</sup> 1,2,3,4-Tetramethyl-benzene ( $\mu$ g/L)	.230	E .037	E .033	10.8	.004
<sup>2</sup> Isodurene ( $\mu$ g/L)	.200	<.200	E .007	_	—
<sup>2</sup> 1,2,4-Trimethyl-benzene ( $\mu$ g/L)	.056	<.056	E .008	_	

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

<sup>1</sup> Sample collected from observation well ALUS-18.

<sup>2</sup> Sample collected from observation well ALUS-1.