

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

By William J. Andrews, Alison L. Fong, Leigh Harrod¹, and Michael E. Dittes

**U.S. Geological Survey
Water-Resources Investigations Report 97-4248**

**Contribution from the
National Water-Quality Assessment Program**

**Mounds View, Minnesota
1998**

¹Hennepin County Soil and Water Conservation District

**U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, Secretary**

**U.S. GEOLOGICAL SURVEY
Thomas J. Casadevall, Acting Director**

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

For additional information
write to:

District Chief
U.S. Geological Survey
Water Resources Division
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
Denver, CO 80225-0286

Information regarding the National Water-Quality Assessment (NAWQA) Program 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

Information about the Upper Mississippi River Basin Project of the NAWQA Program is available on the World Wide Web at:

<http://wwwmn.cr.usgs.gov/umis/index.html>

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 water-resource 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 60 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 60 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 water-quality 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	2
Purpose and scope	2
Description of the urban study area	2
Climate	4
Hydrogeologic setting	4
Land use	4
Population and water use	8
Methods of drilling, sample collection, and data analysis	8
Acknowledgments	11
Sediment characteristics	11
Grain-size analysis and estimated saturated hydraulic conductivities	11
Organic- and inorganic-carbon content	13
pH	13
Ground-water quality	13
Physical parameters	13
Major ions	13
Nutrients and organic carbon	20
Trace metals	22
Mineral saturation	23
Pesticides	28
Volatile organic compounds	33
Tritium	40
Quality assurance/quality control	41
Effects of land use on ground-water quality	46
Summary and conclusions	50
References	51

Illustrations

Figures 1–5. Maps showing:

1. Location of the study unit and monitoring wells, and water-table altitude contours of the urban land use study area of the Upper Mississippi River National Water-Quality Assessment (NAWQA) study unit, June-July 1996	3
2. Dominant hydrologic soil class and organic matter content of generalized soil units in the urban land use study area	5
3. Surficial geology in the urban land use study area	6
4. Land use and land cover in the urban land use study area	7
5. Population density of the urban land use study area	9
6. Box plots showing field measurements of physical parameters in water samples from urban land use study wells	15

Illustrations—continued

7. Box plots showing concentrations of dissolved major ions in water samples from urban land use study wells16
8. Trilinear diagram of major ion concentrations in water samples from urban land use study wells19

Figures 9-10. Box plots showing:

9. Concentrations of dissolved nutrients and organic carbon in water samples from urban land use study wells21
10. Concentrations of detected dissolved trace metals in water samples from urban land use study wells24
11. Graphs showing concentrations of selected trace metals in relation to dissolved oxygen concentrations in water samples from urban land use study wells25
12. Box plots showing saturation indices of major minerals in water samples from urban land use study wells27
13. Map showing locations of wells with water samples having detectable and nondetectable concentrations of pesticides30
14. Bar chart showing frequencies of detection of pesticides in water samples from urban land use study wells31
15. Map showing locations of urban land use study area wells with water samples having detectable and nondetectable concentrations of volatile organic compounds35
16. Bar chart showing frequencies of detection of volatile organic compounds in water samples from urban land use study wells37

Tables

1. Estimated populations, projects populations, ground-water use, projected total ground-water use, number of wells completed in the surficial aquifer, and number of planned surficial-aquifer wells for cities in and adjacent to the urban study area using water from the surficial aquifer8
2. Laboratory analyses methods for measured water-quality constituents10
3. Saturated hydraulic conductivity (K) values calculated from grain-size distributions12
4. Organic- and inorganic-carbon contents and pH values of sediment samples14
5. Median values, standard deviations, and ranges of physical parameters in water samples from the 30 urban land use wells17
6. Median values, standard deviations, and ranges in concentrations of major ions dissolved in water samples from the 30 urban land use wells17
7. Number of samples with reportable concentrations, reporting limits, median concentrations, standard deviations, and ranges in concentrations of nutrients and organic carbon in water samples from the 30 urban land use wells20

Tables—continued

8. Number of samples with reportable concentrations, reporting limits, median concentrations, standard deviations, ranges in concentrations, and maximum contaminant levels of trace metals in water samples from the 30 urban land-use wells	23
9. Pesticide compounds analyzed in water samples, by chemical group	28
10. Reporting and detection limits, number of detections, ranges in concentrations, and maximum contaminant levels of pesticide compounds detected in water samples from the 30 urban land use wells and in 17 rainwater samples collected at Lake Harriet in southwest Minneapolis, April-August 1995	32
11. Volatile organic compounds analyzed in water samples, by chemical group	34
12. Detection limits, number of detections, ranges in concentrations, and maximum contaminant levels of volatile organic compounds detected in water samples from the 30 urban land use wells, ranges of volatile organic compound concentrations in air in downtown Minneapolis, and ranges of equilibrium volatile organic compound concentrations in rainwater.....	36
13. Tritium concentrations in water samples from selected monitoring wells.....	41
14. Reporting and detection limits and ranges in detected concentrations of analytes in blanks.....	42
15. Reporting limits, ranges in recovery percents, and mean recovery percents from Schedule 2010 pesticide spikes	44
16. Reporting limits, ranges in recovery percents, and mean recovery percents from Schedule 2051 pesticide spikes	45
17. Detection limits, ranges in recovery percents, and mean recovery percents from VOC field spikes ..	46
18. Reporting limits and ranges in concentrations of compounds with greater than 5 percent differences in replicate concentrations	46
19. Primary and secondary land uses and estimated population densities within a 500-meter radius of each well.....	48
20. Ground-water constituent concentrations with significant correlations to urban land use characteristics within 500 meters of the wells.....	49

Conversion Factors, Abbreviated Water-Quality Units, and Acronyms

<u>Multiply</u>	<u>By</u>	<u>To obtain</u>
inches (in.)	2.54	centimeters
inches per year (in./yr)	2.54	centimeters per year
feet (ft)	.3048	meters
feet per day (ft/d)	.3048	meters per day
square feet (ft ²)	0.0929	square meters
feet per mile (ft/mi)	.1927	meters per kilometer
feet per year (ft/yr)	.3048	meters per year
square miles (mi ²)	2.590	square kilometers
gallons per day (gal/d)	3.785	liters per day
million gallons per day (Mgal/d)	.04381	cubic meters per second
pounds (lb)	.4536	kilograms
pounds per square mile (lb/mi ²)	.1751	kilograms per square kilometer
degrees Fahrenheit (°F)	°C=(°F-32)/1.8	degrees Celsius (°C)

Chemical concentrations: Chemical concentrations of substances in water are given in metric units of milligrams per liter (mg/L) and micrograms per liter (µg/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as mass (milligrams) of solute per unit volume (liter) of water. Micrograms per liter is a unit expressing the concentration of chemical constituents in solution as mass (micrograms) of solute per unit volume (liter) of water. Micrograms per liter are equivalent to milligrams per liter divided by 1,000.

ATSDR--Agency for Toxic Substances and Disease Registry (an agency of the U.S. Department of Health and Human Services)

MCL--Maximum Contaminant Limit--health-based water-quality standard set by the USEPA

MPCA--Minnesota Pollution Control Agency

NADP/NTN--National Acidic Deposition Program/National Trends Network

NAWQA--National Water-Quality Assessment of the U.S. Geological Survey

TCMA--Twin Cities metropolitan area

UMIS--Upper Mississippi River Basin study unit of the National Water-Quality Assessment

USEPA--U.S. Environmental Protection Agency

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

By William J. Andrews, Alison L. Fong, Leigh Harrod¹, and M.E. Dittes

Abstract

In the spring of 1996, the Upper Mississippi River Basin Study Unit of the National Water-Quality Assessment Program drilled 30 shallow monitoring wells in a study area characterized by urban residential and commercial land uses. The monitoring wells were installed in sandy river-terrace deposits adjacent to the Mississippi River in Anoka and Hennepin Counties, Minnesota, in areas where urban development primarily occurred during the past 30 years.

Analyses of sediments collected during well drilling indicated that at most well sites the aquifer materials had relatively high hydraulic conductivities (ranging from 0.01 to 238 feet per day), and relatively low organic carbon contents (0.10 to 41 grams per kilogram), indicating a high susceptibility to leaching of fertilizers and organic substances used on the land surface. Sediment pH values, which can affect leaching of pesticides, were generally alkaline, ranging from 5.1 to 9.6.

Ground-water levels ranged from 2.39 to 23.14 feet below land surface, and indicated that shallow ground water flows primarily toward the Mississippi River. Dissolved-oxygen concentrations in water samples from the wells were generally less than 3 milligrams per liter (mg/L) and specific conductances were generally greater than 600 microsiemens per centimeter. Calcium, magnesium, sodium, bicarbonate, chloride, and sulfate were the primary dissolved constituents in the water samples. Sodium and chloride concentrations were generally greater than commonly reported in the region, probably due to leaching of sodium chloride applied to roads during the winter. Most trace-metal concentrations in ground-water samples were less than 10 micrograms per liter ($\mu\text{g/L}$), but concentrations of iron and manganese commonly exceeded Secondary Maximum Contaminant Levels set by the U.S. Environmental Protection Agency of 300 and 50 $\mu\text{g/L}$, respectively. Mineral saturation indices indicated that calcite, dolomite, and gypsum were slightly undersaturated in most water samples, and that quartz, and many oxides and hydroxides of iron and manganese were oversaturated in all of the water samples.

Concentrations of nitrate nitrogen, the primary nutrient of concern in ground water, ranged from less than 0.05 to 16 mg/L, with a median concentration of 1.4 mg/L. Dissolved phosphorus concentrations ranged from less than 0.01 to 1.5 mg/L in the water samples, with a median concentration of 0.02 mg/L. Water from one well was oversaturated with respect to hydroxyapatite, a phosphatic mineral used as a fertilizer.

Pesticide compounds were detected in water samples from 16 wells, but concentrations of those compounds were less than 1.0 $\mu\text{g/L}$. Prometon, an herbicide commonly used for right-of-way weed control, was detected in water samples from 10 of the wells. Atrazine, and its metabolite deethylatrazine, were detectable in water samples from 6 and 8 wells, respectively. Atrazine is commonly applied to land planted with corn and is detectable in rainfall and air samples in concentrations of less than 1 $\mu\text{g/L}$ in the urban land use study area. Other detected pesticide compounds, which are used in agriculture, right-of-way weed control, or lawn care included: tebuthiuron, EPTC, *p,p'*-DDE, metolachlor, simazine, bentazon, and bromacil.

Volatile organic compounds were detected in water samples from 26 wells, but the concentrations of most of those compounds were less than 1 $\mu\text{g/L}$. Carbon disulfide, which may be produced by bacteria in soils, was the most commonly detected volatile organic compound in water samples from the wells. Other detected volatile organic compounds included: methyl chloride, acetone, dichlorofluoromethane, tetrahydrofuran, trichlorofluoromethane, methyl iodide, 1,1-dichloroethane, chloroform, toluene, trichloroethane, trichloroethene, *cis*-1,2-dichloroethene, methylene chloride, bromodichloromethane, benzene, methylisobutylketone, ethyl ether, and tetrachloroethene.

¹ Hennepin County Soil and Water Conservation District

Tritium concentrations, analyzed in water samples from 15 of the 30 wells, indicated that shallow ground water has been recharged since the mid-1950's, and that shallow ground water should be affected by urban development that has taken place over the past 40 years.

Land uses in the urban land use study area affected the concentrations of some water-quality constituents. Concentrations of nitrate and chloride, and frequencies of detection of pesticides and of volatile organic compounds, were greater in water samples from the surficial sand and gravel aquifer underlying the urban land use study area than in water samples from similar aquifers from part of the Upper Mississippi River Basin National Water-Quality Assessment study unit. Land uses within 500-meter radii of each well were quantified by digitizing overlays of aerial photographs that were verified and updated in the field. Concentrations of magnesium and sulfate were greater in ground water beneath areas of denser residential development, which may be a natural artifact of better drainage and a deeper water table in those areas. Frequencies of detection of some pesticides and volatile organic compounds were greater in water from wells with greater proportions of industrial and transportation land uses. Ground water in areas with less dense residential development, mostly the more recently-developed areas, tended to have greater concentrations of agricultural herbicides and some nutrients—probably a relict of previous agricultural land use.

Introduction

In 1991, the USGS began full implementation of the NAWQA Program. Long-term goals of the NAWQA 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 anthropo-genic factors that affect the quality of the Nation's water resources. To meet these goals, nationally consistent data useful to policy makers, scientists, and managers are being collected and analyzed. Because assessment of the water quality in the entire Nation is impractical, major activities of the NAWQA Program take place within a set of hydrologic systems called study units, which comprise diverse hydrologic systems of river basins, aquifer systems, or both.

The UMIS study unit, which encompasses an area of about 47,000 mi² (fig. 1), includes the entire drainage area of the Upper Mississippi River Basin from the source at Lake Itasca to the outlet of Lake Pepin. The study unit includes areas of rich agricultural lands, forests, wetlands, prairies, and a major urban area. Water quality of the Upper Mississippi River, which contains the headwaters of the largest river system in the Nation, is of concern due to reliance on surface water by major municipalities in the basin and due to the necessity of good quality water to maintain the health of regional aquatic ecosystems. Ground water is the principal source of potable water to smaller municipalities and to domestic water systems in the study unit. In the urban land use study area (hereafter referred to as the urban study area) (fig. 1), there are two types of aquifers that are important sources of water supply-- bedrock aquifers in rocks of Paleozoic age and

a sand and gravel aquifer in deposits of Pleistocene age. Ground water in the uppermost of these aquifers, the unconfined sand and gravel aquifer, is susceptible to degradation from materials used at the land surface. This shallow aquifer is also the source of recharge to underlying bedrock aquifers (Schoenberg, 1990; Stark and others, 1996).

Purpose and Scope

The purpose of this report is to describe the quality of shallow ground water underlying an urban residential/commercial area developed primarily during the last 30 years in the TCMA of Minnesota. This report presents data from 30 shallow monitoring wells completed immediately below the water table in a surficial aquifer adjacent to the Mississippi River in the northwestern part of the TCMA (fig. 1). Ground water was sampled and analyzed for over 200 constituents, including physical parameters, major ions, nutrients, trace metals, pesticides, volatile organic compounds, and tritium (selected wells) in June and July 1996. Sediment samples (1-3 per hole drilled), collected with split-spoon samplers during drilling, were analyzed for pH, sediment-size distributions, and organic-carbon contents to assess the hydraulic conductivity of those sediments and the potential for leaching of organic compounds from the land surface.

Description of the Urban Study Area

Environmental setting variables that can influence ground-water quality include climate, hydro-geologic setting, land use and land cover, population, soils, and surface-water hydrology. Stark and others (1996)

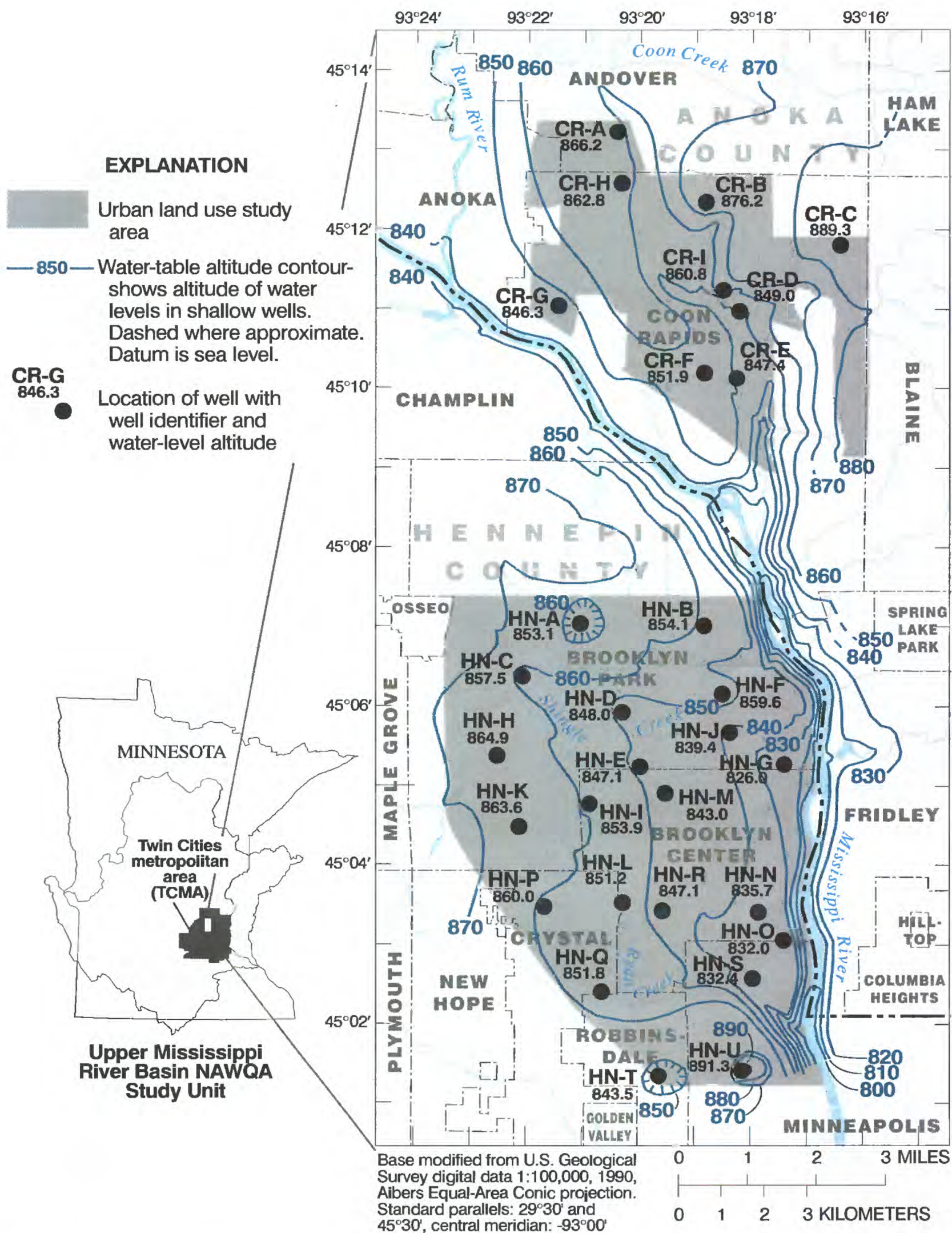


Figure 1.--Location of the monitoring wells, and water-table altitude contours of the urban land use study area of the Upper Mississippi River National Water-Quality Assessment (NAWQA) Study Unit, June-July 1996.

described those variables for the urban study area (fig. 1) and for the study unit.

Climate

Seasonal fluctuations in temperature and rainfall can affect the following: solubilities of volatile organic compounds (VOC's, which are used as fuels and solvents for a wide variety of products) in rainfall, volatilization of VOC's to the atmosphere, seasonal loadings of pesticides in rainfall, relative amounts of runoff and infiltration, and processes such as sorption and denitrification, which can affect the quality of ground water. Average monthly temperatures in the urban study area range from 11°F in January to 74°F in July (Minnesota State Climatologist, electronic commun., 1995). Average annual precipitation is between 28 and 30 in. in the urban study area (Minnesota State Climatologist, electronic commun., 1995). About three-fourths of the annual precipitation in the urban study area falls from May through September (Baker and others, 1979). Mean annual evaporation in the urban study area is approximately 36 in. (Farnsworth and others, 1982).

Hydrogeologic Setting

The presence and concentrations of many constituents in ground water are affected by the permeabilities and chemical compositions of soils and the unsaturated zone. Soils underlying the urban study area are generally porous, well-drained sandy soils of low slopes, with scattered occurrences of flat-lying, poorly drained peaty soils (Lueth, 1974; Chamberlain, 1977) (fig. 2). Relatively high permeabilities and low clay and organic matter contents of soils formed on sandy materials are conducive to leaching of many constituents from the land surface to ground water.

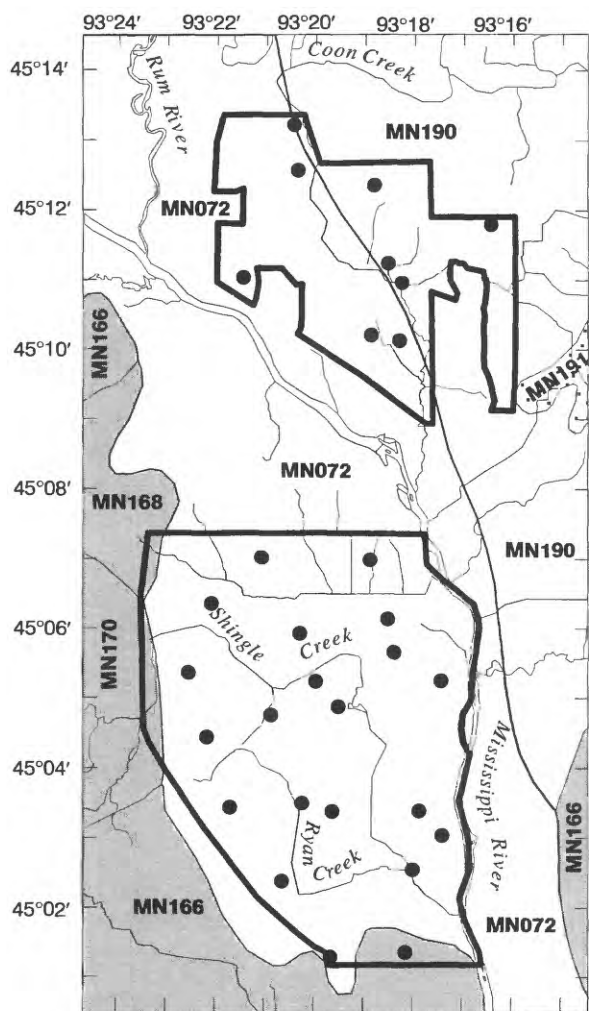
Beneath soils, the urban study area is mantled with less than 50 to greater than 400 ft of sand, gravel, and clay, which were deposited as river terraces or overbank deposits by melt water from the Des Moines glacial lobe during the Pleistocene Epoch (Norvitch, 1973; Bloomgren and others, 1989; Meyer and Hobbs, 1989; Anderson, 1993; Meyer, 1993). The terrace deposits (fig. 3) underlying the urban land use study area typically are comprised of brown to gray, coarse to fine, gravelly sand, with local clayey overbank deposits along streams. Pebbles, cobbles and sands in these deposits consist of mafic and felsic igneous and metamorphic minerals, dolomite, and quartz. Those sands and gravels

are commonly underlain by silty, sandy clays.

For most of the urban study area, estimates of relatively short transport times for water from the land surface to the water table indicate that the surficial sand and gravel aquifer is highly susceptible to contamination from activities conducted at the land surface (Piegat, 1989; Meyer, 1993). Seepage from the sand and gravel aquifer can also affect the quality of water in hydraulically connected rivers and bedrock aquifers in the urban study area. Ground water in the surficial aquifer flows toward the Mississippi River or tributaries of that river (Kanivetsky, 1989; Palen and others, 1989) (fig. 1). Helgesen and Lindholm (1977) estimated that recharge to the unconfined surficial aquifer in this area was 11 in./yr, based on analyses of hydrographs.

Land Use


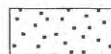




Land use and land cover in the urban study area (fig. 4) can have a great influence on the presence and distribution of constituents in ground water. Agricultural and residential areas can contribute nutrients and pesticides to ground water. Roadways and railroads can be substantial sources of sodium and chloride from deicing salt, herbicides, and VOC's emitted to the air and spilled on their surfaces. VOC's used by homeowners can be significant local sources of those compounds in ground water. Commercial and industrial activities may also discharge VOC's, metals, and other substances to the atmosphere or to the land surface in the course of their activities. Land uses in the urban study area are primarily residential, commercial, and transportation, with commercial land use being concentrated along major roadways. The urban study area was developed primarily from the 1960's to the 1990's. Ages of development are older toward the southern and eastern parts of the urban study area. Prior to residential and commercial development, the urban study area was characterized by row crops and truck farms, with wooded areas in the vicinity of wetlands. Agricultural land still exists (as of 1997) between the northern and southern portions of the urban study area, in northern Hennepin County. That area is being rapidly redeveloped for residential land use.

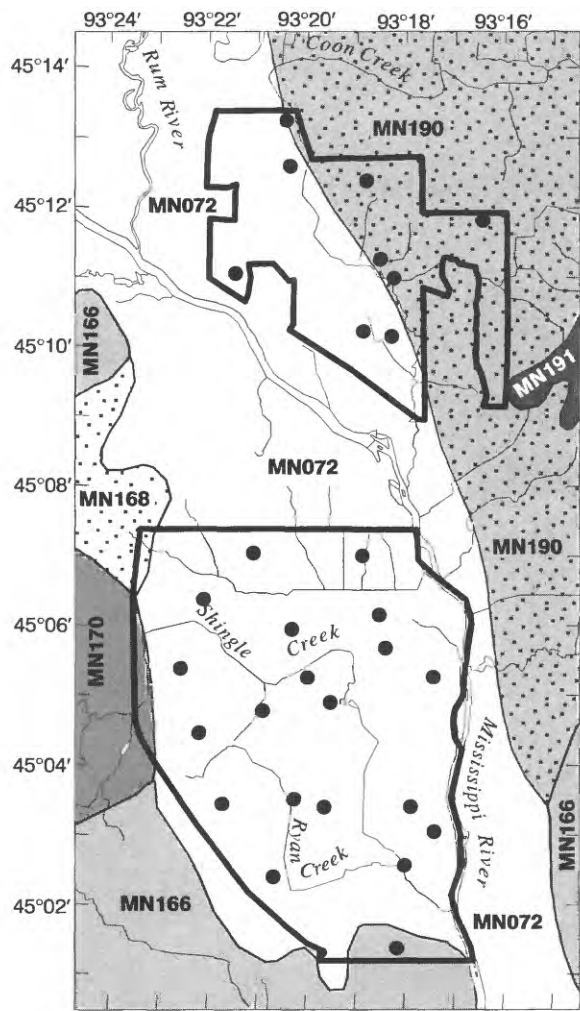


Base modified from U.S. Geological Survey digital data 1:100,000, 1990, Albers Equal-Area Conic projection. Standard parallels: 29°30' and 45°30', central meridian: -93°00'

EXPLANATION

Hydrologic class (infiltration rates):

-  High infiltration rates. Soils are deep, well drained to excessively drained sands gravels.
-  Well drained where soils are tiled/poorly drained where soils are not tiled.
-  Moderate infiltration rates. Deep and moderately deep, moderately well and well drained soils with moderately coarse textures.
-  Urban land use study area boundary
-  STATSGO map unit
-  Location of well



Base modified from U.S. Geological Survey digital data 1:100,000, 1990, Albers Equal-Area Conic projection. Standard parallels: 29°30' and 45°30', central meridian: -93°00'

EXPLANATION

Organic Matter content (in percent by weight):



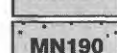


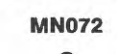



-  0.570 to 1.961
-  1.766 to 3.119
-  4.300 to 6.352
-  6.173 to 20.437
-  14.843 to 22.047
-  13.625 to 41.062
-  Urban land use study area boundary
-  STATSGO map unit
-  Location of well

Figure 2.--Dominant hydrologic soil class and organic matter content of generalized soil units in the urban land use study area (Data modified by David Wolock, U.S. Geological Survey, from State Soil Geographic (STATSGO) data base, 1994).

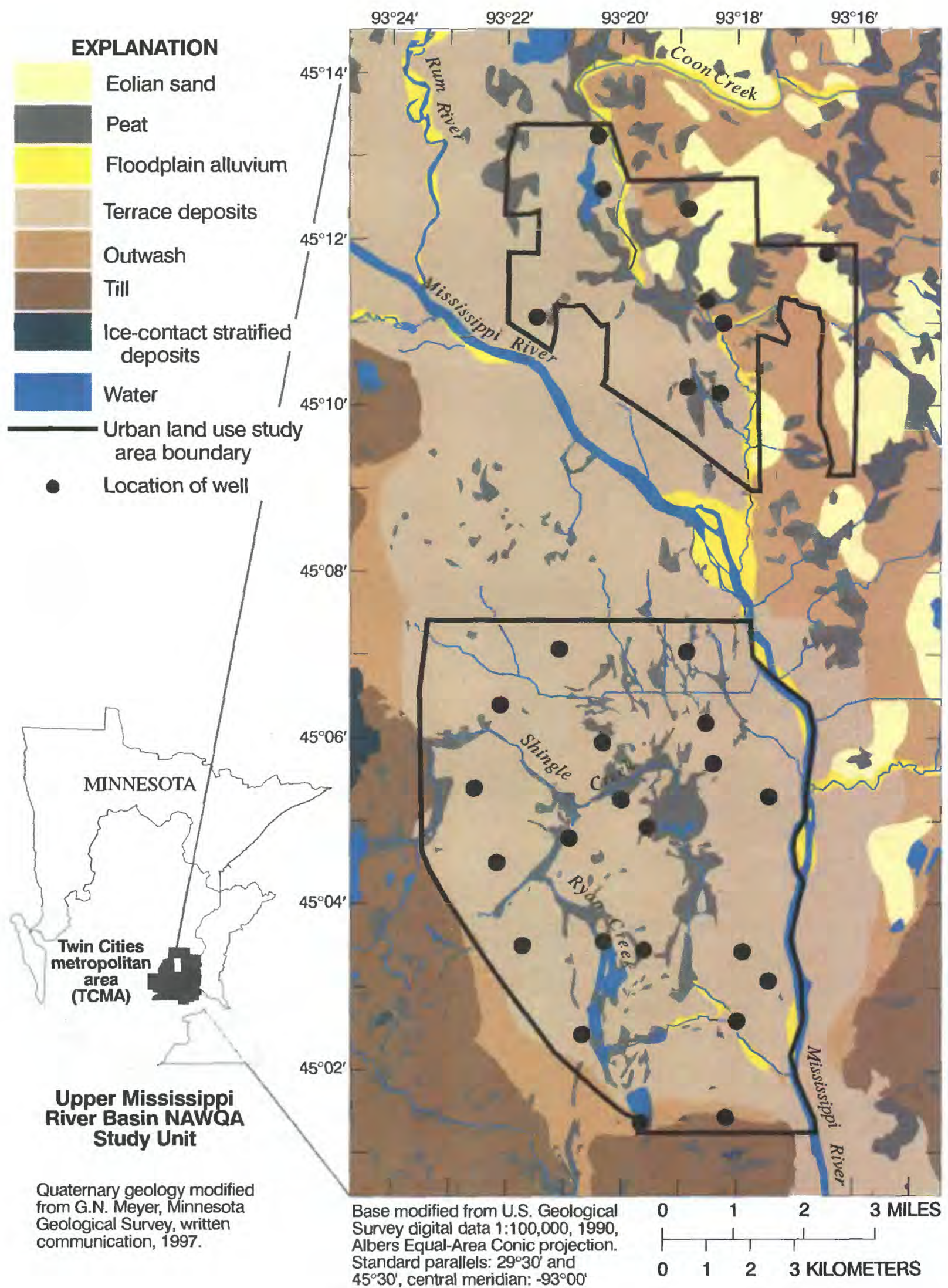


Figure 3.--Surficial geology in the urban land use study area.

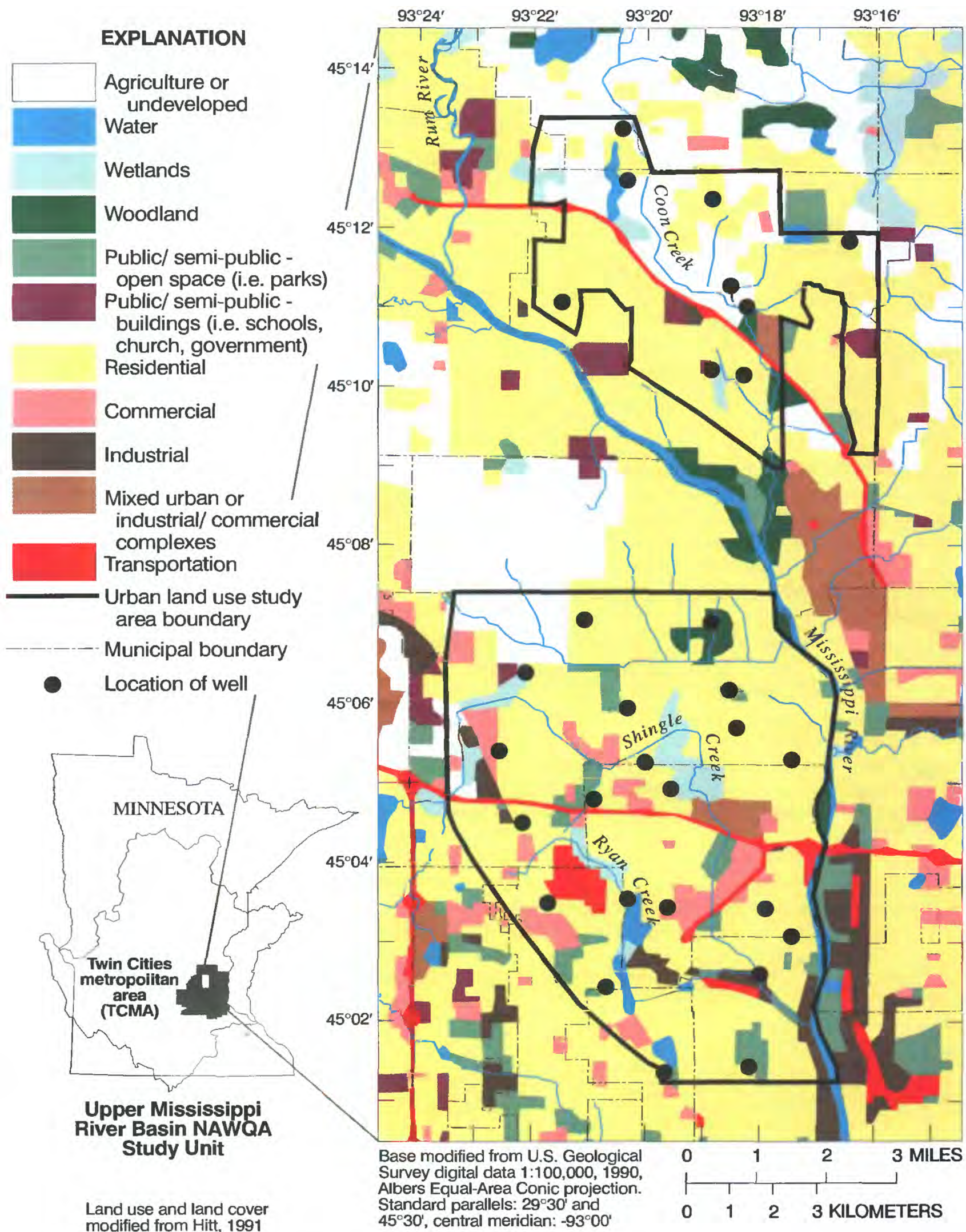


Figure 4.--Land use and land cover in the urban land use study area.

Population and Water Use

The estimated population of the urban study area in 1995 was about 148,000 (Gary Oberts, Twin Cities Metropolitan Council, written commun., 1997) (fig. 5). In 1996, public water supplies served all of the people in the urban study area with an average of approximately 19.5 Mgal/d; 83 percent of which was from ground water and 17 percent of which was from the Mississippi River (Gary Oberts, Twin Cities Metropolitan Council, written commun., 1997). The cities of Crystal and Minneapolis in Hennepin County (fig. 1) rely on treated water withdrawn from the Mississippi River near Fridley, Minnesota as their source of water supply. The cities of Brooklyn Center and Robbinsdale withdraw water from wells completed in a bedrock aquifer. The cities of Brooklyn Park and Coon Rapids in the urban study area and the adjacent cities of Anoka, Maple Grove, and Osseo withdraw ground water from wells completed in sand and gravel terrace deposits and in underlying bedrock aquifers for their water supplies. For cities in or adjacent to the urban study area, ground-water pumping capacity from municipal wells completed in the surficial aquifer was 61.3 Mgal/d as of 1995, although pumping from those wells may average about one-quarter of that amount. In addition to municipal wells, there are approximately 1,500 low-capacity domestic or lawn-irrigation wells in the urban study area (James Piegat, Hennepin Conservation District, written commun., 1997), which pump an estimated 75,000 gal/d from the surficial aquifer during summer months. As the population increases in the metropolitan area, the surficial aquifer will be

increasingly utilized for public water supplies. The greatest planned increase in pumping from the surficial aquifer is by the City of Maple Grove, which plans to increase pumping from the aquifer by 65 percent from 1995 to 2010 (table 1). Peak pumping by Maple Grove may ultimately approach 40 Mgal/d (Bonestroo, Rosene, Anderlik and Associates, 1995). Although Maple Grove is not located in the urban study area, it is situated on highly permeable glacial deposits directly northwest of the urban study area. Those deposits serve as a recharge area for the terrace deposits.

Methods of Drilling, Sample Collection, and Data Analysis

Drilling locations for monitoring wells installed for this study were selected based on well-selection criteria for NAWQA urban land-use studies specified by Squillace and Price (1996). Drilling locations were chosen based on a 30-well network established in a randomized areally distributed pattern over the urban study area using a site selection program described in Scott (1990).

The holes were drilled with 8-in. outer diameter hollow-stem steel augers. The wells were constructed of threaded 2-in. inner diameter by 10-ft long schedule 40 PVC (polyvinyl chloride) casing. The casings were connected to 0.010-in. slot size, 5-ft PVC screens tipped with flush-threaded PVC sandpoints. The tops of the

Table 1. Estimated populations, projected populations, ground-water use, projected total ground-water use, number of wells completed in the surficial aquifer, and number of planned surficial-aquifer wells for cities in and adjacent to the urban study area using water from the surficial aquifer (data from Gary Oberts, Metropolitan Council, written commun., 1997)
[-- unknown, Mgal/d; million gallons per day]

City	1995 estimated population	2010 projected population	1995 mean water use (average Mgal/d)	2010 projected mean water use [percent increase from 1995]	Number of surficial aquifer wells in 1995 [total capacity in Mgal/d]	Number of additional surficial aquifer wells planned [capacity in Mgal/d]
Anoka	17,460	18,200	2.6	2.8 [8]	1 [0.72]	1 [--]
Brooklyn Park	59,800	71,000	6.9	8.6 [25]	7 [23.8]	4 [--]
Coon Rapids	60,030	70,000	6.8	7.5 [10]	6 [8.42]	-- [--]
Maple Grove	44,380	58,500	5.7	9.4 [65]	9 [26.6]	5 [18.7]
Osseo	2,600	2,650	0.3	0.3 [0]	2 [1.8]	0 [0]
TOTAL	184,270	220,350	22.3	28.6 [28]	25 [61.3]	10 [--]

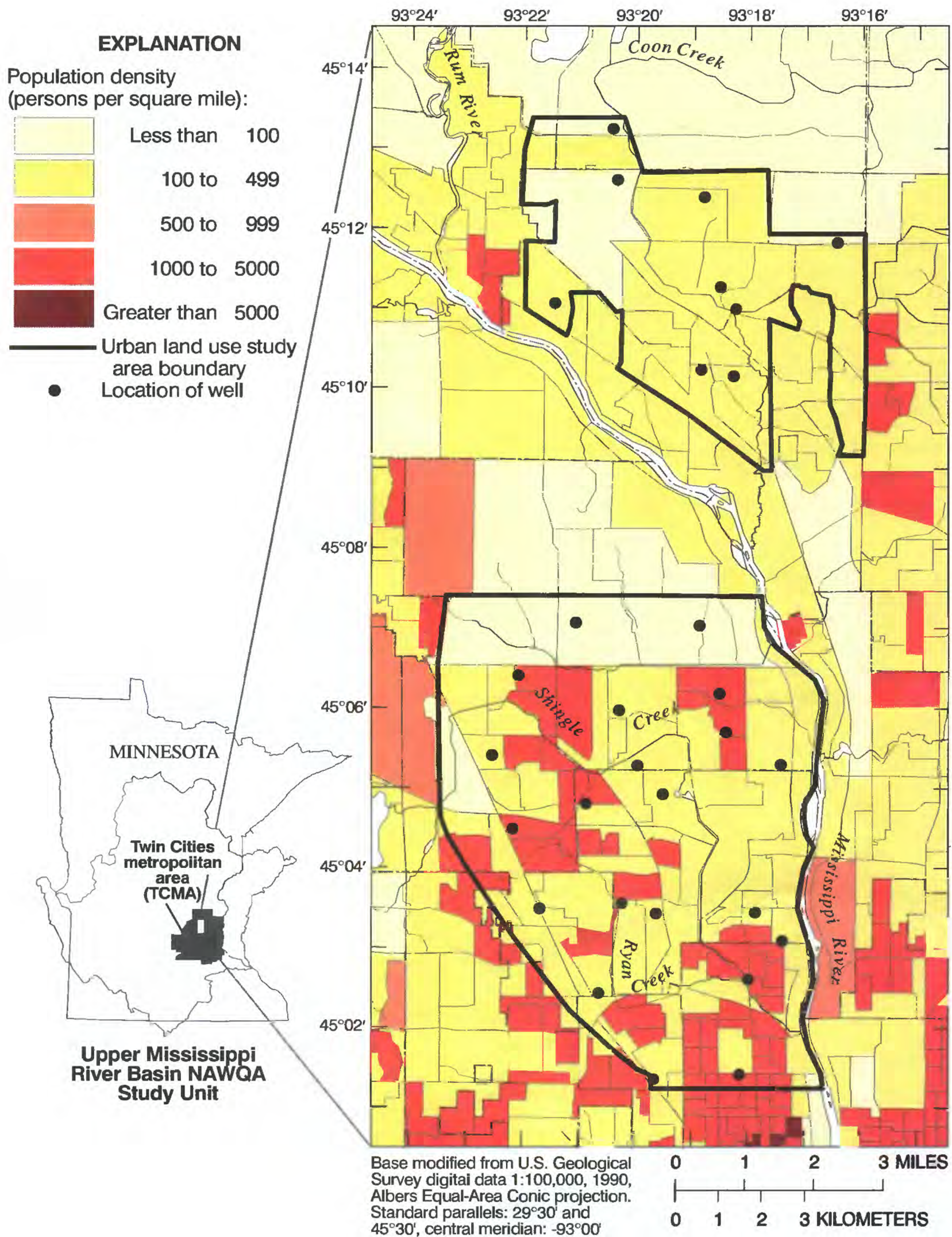


Figure 5.—Population density of the urban land use study area (Population data from U.S. Bureau of Census, 1991).

screens were generally placed 2 ft below the water table. Sand was allowed to collapse to within 2 ft of the tops of the well screens. In cases where natural sand collapse did not completely fill the borehole surrounding the screened interval, commercially-prepared washed sand was added to a level approximately 1 ft above the top of the well screen. The remaining annular space was grouted with bentonite slurry to within 2 ft of the land surface. The top 2 ft of the borehole was grouted with mortar to the land surface. Six-inch diameter schedule 40 steel protective casings with locking aluminium caps were set into the mortar and grout to a depth of 4 ft, with at least 2 ft left standing above land surface. All of the wells were constructed in accordance with Minnesota Department of Health regulations (Minnesota Department of Health, 1994) and in accordance to NAWQA program specifications for monitoring wells (Lapham and others, 1995). Wells were developed within 10 days of drilling by pumping with a centrifugal pump.

Water samples from the wells were analyzed for 240 compounds. Physical parameters, including air and water temperature, pH, specific conductance, turbidity, and alkalinity were measured in the field with instruments calibrated with standard solutions. Three to five standing volumes of water were pumped from the wells and stability of water chemistry was verified

through periodic measurements of temperature, pH, specific conductance, turbidity, and dissolved oxygen concentrations while purging the wells. Water samples were collected in a sealed system utilizing Teflon tubing and stainless steel fittings according to NAWQA protocols (Koterba and others, 1995). Water samples to be analyzed for VOC's, pesticides, nutrients, major ions, and trace metals were shipped to the USGS National Water Quality Laboratory in Arvada, Colorado where analyses were done according to USGS analytical protocols for analysis, quality assurance, and quality control (table 2).

Grain-size distributions were analyzed by sieving or by visual accumulation tube analysis (Guy, 1969) for sandy samples, and by pipette analysis (Guy, 1969) for clayey samples by the USGS sediment laboratory in Iowa City, Iowa. The purpose of grain-size analyses was to estimate hydraulic conductivities of the unsaturated and shallow saturated zone sediments at each well. Organic and inorganic carbon contents of sediment were analyzed by induction furnace, and a modification of the Van Slyke method (Wershaw and others, 1987) at the USGS National Water Quality Laboratory. pH values of sediment samples were measured 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.

Table 2. Laboratory analyses methods for measured water-quality constituents
[USGS, U.S. Geological Survey; VOC's, volatile organic compounds; DOC, dissolved organic carbon]

Constituent or constituent group	Analysis method	Reference
Major ions (USGS schedule 2750)	Atomic absorption spectrometry	Fishman and Friedman (1989)
Trace metals (USGS schedule 2703)	Atomic absorption spectrometry	Fishman and Friedman (1989)
Nutrients (USGS schedule 2752)	Colorimetry	Fishman and Friedman (1989)
VOC's (USGS custom method 9090)	Purge and trap capillary gas chromatography/mass spectrometry	Rose and Schroeder (1995)
Pesticides (USGS schedule 2010)	Gas chromatography/mass spectrometry	Zaugg and others (1995)
Pesticides (USGS schedule 2051)	Liquid chromatography with UV detection	Werner and others (1996)
DOC (USGS schedule 2085)	UV-promoted persulfate oxidation and infrared spectrometry	Brenton and Arnett (1993)
Tritium (USGS lab code 1565)	Electrolytic enrichment with gas counting	Ostlund and Dorsey (1975)

Water-quality data presented in this report were compared to quality-assurance samples (equipment and rinse-water blanks) to verify the efficacy of cleaning methods of sampling equipment and lack of cross-contamination between wells. Duplicate samples were collected from selected wells, and spiked samples were submitted for pesticides and VOC's.

Acknowledgments

The authors express appreciation to the following persons and agencies for allowing the installation of monitoring wells on their properties, and for their interest in the project: Mr. Thomas Redman of the Anoka-Hennepin Independent School District #11, Mr. and Mrs. Delroy Rucks, Mr. Lowell Lewbeck of the City of Coon Rapids Parks Department, Mr. William Ottensmann of the City of Coon Rapids Public Works Department, Mr. Ronald Cox of the Anoka County Parks Department, Mr. and Mrs. Ted Speiss, Mr. John Awalt Jr. of the Church of the Epiphany, Mr. and Mrs. Tony Taylor, Mr. George Hoffman, Mr. Jonathan Watson of the City of Brooklyn Park Engineering Department, Mr. and Mrs. Daniel Strum, Mr. Marl Ramsey of Anoka-Hennepin Independent School District #279, Mr. and Mrs. Brian L. Benson, Mr. and Mrs. Mark Curwick, Mr. and Mrs. David N. Knapp, Mr. and Mrs. Ernest Gottlich, Mr. and Mrs. Raymond Beach, Mr. Scott Brink of the City of Brooklyn Center Engineering Department, Mr. and Mrs. Jerome F. Johnson, Mrs. Colleen Kopet, Mr. and Mrs. Stanley Larson, Mrs. Audrey Yates, Mr. Jeffrey Lee and the members of the Park Board of the Minneapolis Parks Department, and Ms. Maria D'Andrea of the City of Robbinsdale Engineering Department.

The authors also thank Dr. James Piegat of the Hennepin Conservation District, Mr. Bart Biernat of the Anoka County Community Health and Environmental Services Department, and staff of the Minnesota Geological Survey for their assistance in evaluating land uses, age of development, area geology, and significant local features of the urban study area. The authors express appreciation to Mr. Arvid Gutzwiller of the Anoka County Highway Department, Mr. Wayne Jude of Northern States Power Company, Mr. Wayne Matsumoto and Mr. Joe Levernier of the Hennepin County Public Works Department, and Mr. Glen Dunkin of the Burlington Northern Railroad for sharing information about herbicide applications to right-of-ways. The authors are also grateful to Mr. Gary Eckhardt of the Minnesota Pollution Control Agency for supplying data from analysis of VOC's from their

sampling station in downtown Minneapolis and to Dr. Don Goolsby and Mr. Greg Stratton of the U.S. Geological Survey for supplying pesticide-concentration data from rainfall samples collected at Lake Harriet. Appreciation is also extended to Michael Menheer of the U.S. Geological Survey, who determined spike recovery percentages, and to Paul Hanson of the U.S. Geological Survey, who created many of the illustrations in this report.

Sediment Characteristics

Sediment samples were collected during well drilling with a 2-ft long split-spoon core barrel sampler from the unsaturated zone beneath soils and from the first few feet of the saturated zone. Samples were analyzed for particle-size distribution, organic- and inorganic-carbon content, and pH, to evaluate the likelihood of substances leaching from the land surface.

Grain-Size Analysis and Estimated Saturated Hydraulic Conductivities

Hydraulic conductivity values were estimated from sediment grain-size distributions using Hazen's equation (Freeze and Cherry, 1979):

$$K = A(d_{10})^2 \quad (1)$$

in which K is hydraulic conductivity (in centimeters per second), A equals 1.0 centimeters per second per millimeters squared (cm/s/mm²), and d₁₀ is the grain-size diameter (in millimeters) at which 10 percent of the particles by weight are finer and 90 percent are coarser (Freeze and Cherry, 1979). Estimated hydraulic conductivity values were relatively great and ranged from 0.01 to 238 ft/d (table 3). Due to layering of sand grains and morphology of clay layers in the sands, vertical hydraulic conductivities in the sand and gravel aquifer may be as much as five orders of magnitude less than horizontal hydraulic conductivities (Schoenberg, 1990). The median estimated hydraulic conductivity of about 58 ft/d and an average hydraulic gradient of 10 ft/mi (0.0019) (fig. 1) indicate that ground water may flow through these sands horizontally at a velocity of about 0.44 ft/d or 161 ft/yr.

Table 3. Saturated hydraulic conductivity (K) values calculated from grain-size distributions
[--, sample not collected]

Well	Sampling depth interval (feet)	Estimated K value (feet per day)	Estimated K value (centimeters per second)
CR-A	3-5 ¹ , 18-20 ¹	31, 52	0.011, .018
CR-B	4-5, 24-26	18, 44	0.0064, 0.016
CR-C ¹	3-5 ¹ , --	48, --	0.017, --
CR-D	3-5, 8-10	48, 125	0.017, 0.044
CR-E	3-5, 14-16	113, 73	0.040, 0.026
CR-F	5-7, 16-18	73, 64	0.026, 0.023
CR-G	4-5, 5-6, 10-12	57, 52, 48	0.020, 0.018, 0.017
CR-H	3-5, 19-21	25, 34	0.0086, 0.012
CR-I	7-9, 13-15	52, 18	0.018, 0.0064
HN-A	4-6, 14-16	82, 48	0.029, 0.017
HN-B	4-6, 12-14	16, 34	0.0055, 0.012
HN-C	4-6, 20-22	85, 20	0.030, 0.0072
HN-D	3-5 ¹ , 18-20 ¹	52, 150	0.018, 0.053
HN-E	3-5, 18-20	144, 163	0.051, 0.058
HN-F	3-5, 12-14	20, 192	0.0072, 0.068
HN-G	4-5, 34-35	22, 48	0.0077, 0.017
HN-H	3-4, 12-14	48, 177	0.017, 0.063
HN-I	3-5, 14-16	28, 125	0.010, 0.044
HN-J	3-5 ¹ , 13-15 ¹	108, 82	0.038, 0.029
HN-K	3-5, 20-22	23, 82	0.0083, 0.029
HN-L	3-5, --	48, --	0.017, --
HN-M	3-5 ¹ , --	184, --	0.065, --
HN-N	3-5 ¹ , 3-5 ¹ , 13-15 ¹	100, 192	0.035, .068
HN-O	3-5 ¹ , 25-27	102, 0.01	0.036, .000005
HN-P	3-5 ¹ , 13-15 ¹	66, 82	0.023, .029
HN-Q	4-6, 24-26 ¹	12, 82	0.0041, .029
HN-R	3-5 ¹ , --	44, --	0.016, --
HN-S	--, 13-15 ¹	--, 238	--, 0.084
HN-T	3-5 ¹ , 13-15 ¹	22, 7	0.0077, 0.003
HN-U	3-5, 18-20	0.03, 0.1	0.000009, 0.00004
Medians	Unsaturated zone, saturated zone	48, 68	0.017, 0.024

¹ Indicates sieved sample, other finer-grained samples were analyzed by visual accumulation tube.

Organic- and Inorganic-Carbon Content

Organic carbon in sediments can affect the amounts of organic compounds, such as pesticides and VOC's, that can leach from the land surface to ground water. Organic carbon may also provide substrate for bacteria that can reduce nitrate and sulfate in ground water or in soil water. Organic-carbon contents ranged from less than 0.1 to 41 grams per kilogram (g/kg) (median of 1.7 g/kg) immediately beneath soils and from 0.4 to 14 g/kg (median of 1.8 g/kg) in sediments at the top of the saturated zone (table 4). The relatively low organic-carbon content of sediment (fig. 2) (Nelson and Sommers, 1982) indicates that organic compounds that flow past soil with more organic carbon could readily seep through the unsaturated zone to the water table in the vicinity of most of the wells. Inorganic carbon content primarily indicates the presence of carbonate minerals, which can buffer pH and affect major-ion chemistry of water samples. Inorganic carbon concentrations generally were greater in deeper sediment samples, suggesting leaching of those minerals below soils as water seeps from the land surface.

pH

The acidity of sediments overlying the water table can affect the degradation and transport of organic compounds from the land surface to the saturated zone. Acidic organic compounds are more likely to be sorbed in alkaline sediments and basic organic compounds are more likely to be sorbed in acidic sediments. pH values of sediment samples had a wider range than those measured in ground water, ranging from 5.1 to 9.6 (table 4). pH values of sediments in the vicinity of the water table generally were greater than those beneath soils, probably due to buffering by carbonate minerals dissolved as water percolates through the unsaturated zone.

Ground-Water Quality

Ground-water-quality analytes summarized in this report include: physical parameters, major ions, nutrients, trace metals, pesticides, volatile organic compounds, and tritium.

Physical Parameters

Physical parameters measured in the wells include: depth to water, temperature, pH, specific conductance,

dissolved oxygen concentration, turbidity, and alkalinity. The depth of the water table below the land surface was generally less than 20 ft. Water-table altitude contours (fig. 1) indicate that ground water underlying the urban study area flows primarily toward the Mississippi River. Alkaline pH values, and large values of specific conductances and alkalinity (table 5, fig. 6) were due in part to buffering by dissolution of carbonate minerals in the sands. Anderson (1993) reported somewhat lesser median specific conductances and greater alkalinities in water samples from more than 29 wells sampled in residential areas of the Anoka Sand Plain, a 1,400-mi² area covered by glacial outwash with primarily agricultural land use northwest of the urban study area. Most dissolved oxygen concentrations were less than 1 mg/L, indicating that reduction processes such as denitrification, sulfate reduction, and reduction of metallic oxides may occur in shallow ground water.

Major Ions

Major ions analyzed in water samples included calcium, magnesium, sodium, potassium, chloride, fluoride, bromide, sulfate, and silica. Hardness, an important water-quality characteristic to most water users, was calculated from the concentrations of calcium and magnesium in the water samples.

Calcium concentrations were greater than most of the major ions (table 6, fig. 7). Calcium, which occurs only in the divalent (Ca⁺²) oxidation state, occurs in ground water primarily through dissolution of the relatively soluble carbonate minerals calcite and dolomite, and secondarily through dissolution of the silicate minerals feldspar, pyroxene, and amphibole. Although the terrace deposits were primarily composed of quartz sands, sources of calcium, including fragments and clasts of igneous rocks and of dolomite, were abundant in auger cuttings and core samples. The median calcium concentration (110 mg/L) was greater than that reported in water sampled in residential areas of the Anoka Sand Plain (72 mg/L) by Anderson (1993). Rainfall is a minor source of calcium through entrainment of terrestrial dust in the atmosphere--calcium concentrations in rainfall in the vicinity of the urban study area in 1995 were typically less than 0.5 mg/L, (National Atmospheric Deposition Program/National Trends Network, electronic commun., 1997). Relatively low concentrations of calcium (less than 50 mg/L) in water from several of the wells may be associated with ion exchange with sodium or potassium on clay-particle surfaces in the unsaturated zone or in the surficial aquifer.

Table 4. Organic- and inorganic-carbon contents and pH values of sediment samples
[g/kg, grams per kilogram; --, not analyzed]

Well	Sampling depth interval (feet)	Organic-carbon content (g/kg)	Inorganic-carbon content (g/kg)	pH
CR-A	3-5, 18-20	1.0, 0.4	0.1, 0.1	7.4, 7.5
CR-B	4-5, 24-26	0.8, 1.1	0.1, 5.5	6.0, 8.6
CR-C	3-5, --	0.1, --	0.1, --	5.1
CR-D	3-5, 8-10	4.6, 6.7	0.1, 0.1	7.0, 6.8
CR-E	3-5, 14-16	0.6, 1.0	0.1, 1.0	5.1, 8.5
CR-F	5-7, 16-18	41, 2.0	1.6, 11.	7.3, 8.0
CR-G	4, 6, 10-12	5.3, 14, 0.4	0.1, 0.1, 0.1	6.5, 6.4, 8.0
CR-H	3-5, 19-21	2.7, 0.5	1.6, 0.6	7.6, 8.3
CR-I	7-9, 13-15	0.3, 2.0	0.1, 12	7.6, 9.6
HN-A	4-6, 14-16	4.8, 2.4	8.2, 5.5	8.9, 8.4
HN-B	4-6, 20-22	1.7, 1.0	5.2, 3.7	7.9, 9.3
HN-C	4-6, 20-22	0.32, 6.0	0.1, 19	5.4, 9.3
HN-D	3-5, 18-20	2.5, 6.2	0.1, 9.8	7.6, 8.3
HN-E	3-5, 18-20	0.3, 1.5	0.1, 8.4	7.0, 8.2
HN-F	3-5, 12-14	6.0, 0.5	17, 1.2	7.3, 8.1
HN-G	4-5, 34-35	2.0, 0.9	17, 4.9	7.8, 8.6
HN-H	3-4, 12-14	15, 14	0.6, 9.3	8.3, 8.0
HN-I	3-5, 14-16	0.87, 0.80	0.1, 8.3	6.4, 9.2
HN-J	3-5, 13-15	0.20, 2.5	0.2, 4.9	6.3, 7.4
HN-K	3-5, 20-22	0.20, 2.9	0.1, 9.1	7.0, 7.9
HN-L	3-5	19	0.1	7.7
HN-M	3-5	0.3	0.1	7.1
HN-N	3-5, 13-15	1.8, 3.3	2.0, 9.7	7.8, 7.8
HN-O	3-5, 25-27	<0.1, 5.0	0.3, 17	7.3, 8.6
HN-P	3-5, 13-15	0.2, 1.9	0.1, 4.6	6.4, 7.9
HN-Q	4-6, 24-26	1.8, 1.7	0.1, 6.6	7.4, 8.2
HN-R	3-5	1.4	0.1	6.5
HN-S	13-15	1.5	0.7	8.3
HN-T	3-5, 13-15	2.0, 2.2	10, 9.8	7.9, 7.8
HN-U	3-5, 18-20	3.9, 0.7	0.1, 0.1	6.5, 7.6
Medians	Unsaturated zone, saturated zone	1.7, 1.8	0.1, 5.5	7.3, 8.2

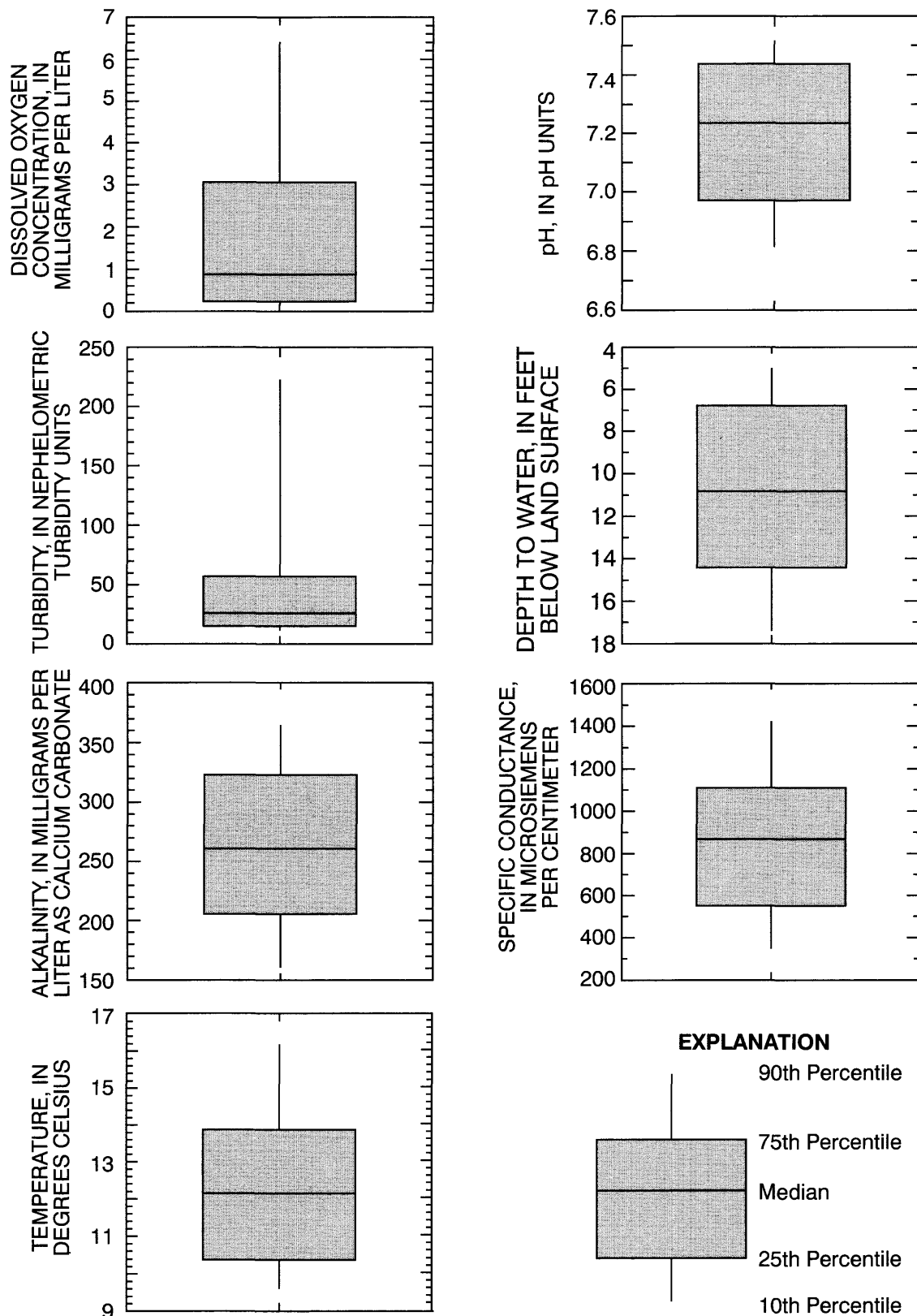
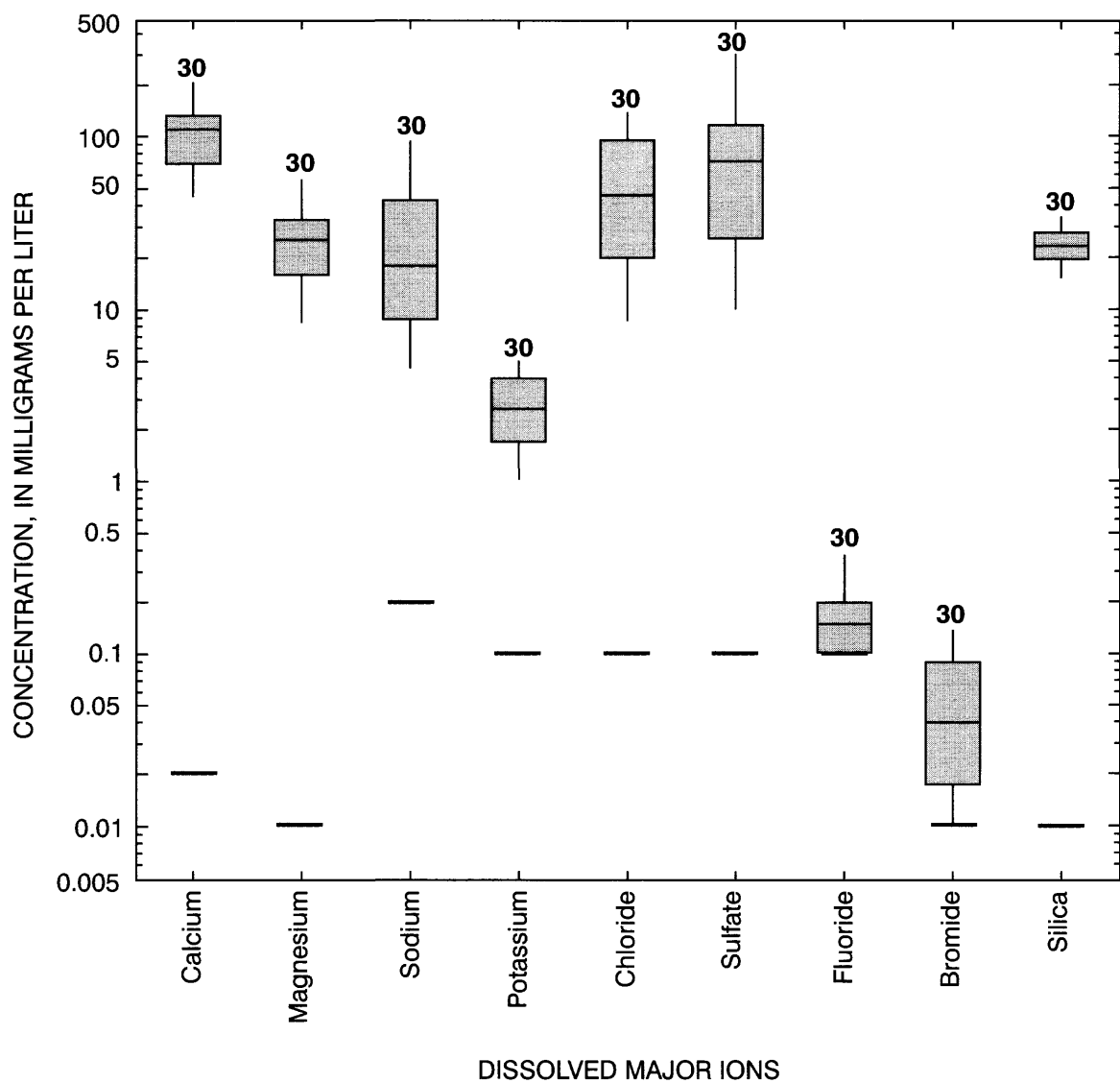


Figure 6.--Field measurements of physical parameters in water samples from urban land use study wells.



EXPLANATION

30=Number of Samples

90th Percentile

75th Percentile

Median

25th Percentile

10th Percentile

— Reporting Limit

Figure 7.--Concentrations of dissolved major ions in water samples from urban land use study wells.

Table 5. Median values, standard deviations, and ranges of physical parameters in water samples from the 30 urban land use wells

[°C, degrees Celsius; $\mu\text{S}/\text{cm}$, microsiemens per centimeter; mg/L , milligrams per liter; NTU, nephelometric turbidity unit]

Physical parameter	Units	Median	Standard deviation	Range
Depth to water table	feet below land surface	10.83	4.8	2.39–23.14
Water temperature	°C	12.2	2.8	8.9–18.7
pH	pH units	7.24	0.3	6.55–7.87
Specific conductance	$\mu\text{S}/\text{cm}$ at 25°C	870	450	150–2,450
Dissolved oxygen concentration	mg/L	0.87	2.3	0.09–7.5
Turbidity	NTU	26	170	4.7–720
Alkalinity	mg/L as CaCO_3	261	101	18.3–539

Table 6. Median values, standard deviations, and ranges in concentrations of major ions dissolved in water samples from the 30 urban land use wells

[Concentrations in milligrams per liter]

Constituent	Median	Standard deviation	Range
Calcium	110	55	15–240
Magnesium	26	15	3.6–69
Hardness, as CaCO_3	380	190	52–880
Sodium	18	49	3.6–230
Potassium	2.6	4.5	0.4–26
Chloride	46	74	4.3–370
Fluoride	0.15	0.09	<0.1–0.4
Bromide	0.04	0.05	<0.1–0.18
Sulfate	72	120	8.6–520
Silica	24	6.4	14–38

Magnesium concentrations were generally less, by a factor of four, than calcium concentrations (table 6, fig. 7). Magnesium is a major constituent in ferromagnesian minerals such as olivine, pyroxenes, amphiboles, and biotite; in metamorphic minerals such as chlorite and serpentine, and as mineral concretions in limestones and dolomites (Hem, 1985). The median concentration of magnesium (26 mg/L) was somewhat greater than that reported by Anderson (1993) (21 mg/L) from wells sampled in residential areas of the Anoka Sand Plain. As with calcium, low concentrations of magnesium are deposited in rainfall in the vicinity of the urban study area (typically less than 0.1 mg/L in 1995) (National Atmospheric Deposition Program/National Trends Network, electronic commun., 1997). With calcium, magnesium contributes to hardness of water. Hardness, an indicator of water's ability to form insoluble residues with soaps and to form scale in boilers and pipes, is

calculated by multiplying the sum of milliequivalents per liter of calcium and magnesium by 50, and is expressed in mg/L of CaCO_3 (Hem, 1985). By the hardness scale of Durfor and Becker (1964), most of the water samples were "very hard" (greater than 180 mg/L as CaCO_3) (table 6).

Sodium concentrations were somewhat greater (ranging from 3.6 to greater than 230 mg/L (table 6, fig. 7)) than those reported by Anderson (1993) in water samples from wells in residential portions of the Anoka Sand Plain (a median concentration of 13 mg/L). None of the samples exceeded the secondary MCL of 250 mg/L , established by the USEPA because of the relation between sodium consumption and hypertension. Secondary MCL's are unenforceable Federal guidelines regarding taste, odor, color, and other effects of drinking water (U.S. Environmental Protection Agency, 1996). The most likely source of elevated concentrations of

sodium in water in the urban study area is leaching of salts applied to deice roadways during the winter. Sodium chloride is the primary compound used for roadway deicing in the urban study area, generally being applied in 5-15 percent mixtures with sand (Wayne Matsumoto, Hennepin County Public Works Department, oral commun., 1997; Arvid Gutzwiller, Anoka County Highway Department, written commun., 1997). Rainfall is also a minor contributor of sodium to ground water--sodium concentrations were less than 0.1 mg/L in rainfall sampled in the vicinity of the urban study area in 1995 (National Atmospheric Deposition Program/National Trends Network, electronic commun., 1997).

As with sodium, chloride concentrations were greater than commonly reported in the urban study area, ranging from 4.3 to greater than 370 mg/L (table 6, fig. 7). In contrast, chloride concentrations in water sampled from 992 wells completed in unconfined sand and gravel aquifers in part of the UMIS study unit generally ranged from 1-50 mg/L (Stark and others, 1996). Anderson (1993) also reported a substantially lesser median chloride concentration in water samples from wells (26 mg/L) in residential areas of the Anoka Sand Plain. Rainwater is a minor source of chloride, with less than 0.1 mg/L being detected in rainfall in the vicinity of the urban study area in 1995 (National Atmospheric Deposition Program/National Trends Network, electronic commun., 1997). Probable sources of elevated concentrations of chloride in the urban study area include sodium chloride applied to deice highways in the winter and potassium chloride (KCl) fertilizers applied to lawns during the summer. Only one water sample, from well HN-T, located a few meters downgradient from a 4-lane highway, had a chloride concentration exceeding the secondary MCL of 250 mg/L set by the USEPA.

Sulfate concentrations were somewhat greater than chloride concentrations, ranging from 8.6 to 520 mg/L (table 6, fig. 7). Anderson (1993) reported a substantially lesser median sulfate concentration (20 mg/L) in water samples from wells in residential areas of the Anoka Sand Plain. The secondary MCL of 250 mg/L for sulfate (U.S. Environmental Protection Agency, 1996) was exceeded in water from four wells (HN-A, HN-B, HN-C, and HN-F) (table 6, fig. 1). Sulfate (SO_4^{2-}) is the most common form of sulfur dissolved in oxygenated natural waters. In anoxic systems, bacteria consume oxygen from sulfate anions, converting them to the relatively toxic hydrogen sulfide (H_2S) gas. Sulfur is widely distributed in reduced form as metallic sulfide minerals in igneous and sedimentary

rocks and as sulfate in the mineral gypsum (Hem, 1985). Other significant sources of sulfur include atmospheric emissions from volcanoes, combustion of fossil fuels, and smelting of ores (Hem, 1985). Rainfall is a relatively minor contributor of sulfate in the urban study area--sulfate concentrations in rainfall in 1995 were at or below 1 mg/L in the vicinity of the urban study area in 1995 (National Atmospheric Deposition Program/National Trends Network, electronic commun., 1997).

Trilinear diagrams show relative proportions of major ions dissolved in water. A trilinear diagram of major ion concentrations (fig. 8) indicates that water composition in most of the surficial aquifer in the urban study area is dominated by calcium, magnesium, and bicarbonate, but the composition is dominated by sodium and chloride in water from some of the wells (fig. 8).

Fluoride concentrations were less than the laboratory reporting limit of 0.1 mg/L in water samples from 10 of the wells and concentrations in samples from the other wells were less than 0.5 mg/L (table 6, fig. 7). The median concentration of fluoride in water samples from wells sampled in residential portions of the Anoka Sand Plain (0.1 mg/L) reported by Anderson (1993) was similar to that in water samples from the 30 urban study area wells. Although trace amounts of fluoride are added to drinking water to harden tooth enamel and reduce the incidence of dental caries, the USEPA has established a secondary MCL of 2 mg/L for fluoride due to mottling of tooth enamel at greater concentrations (U.S. Environmental Protection Agency, 1996). None of the fluoride concentrations exceeded the secondary MCL.

Bromide concentrations were less than 0.2 mg/L in all of the water samples (table 6, fig. 7). Bromide is similar in chemical behavior to chloride, but is much less abundant in natural waters (Hem, 1985). Bromide concentrations in rainwater and snow range from 0.005 to 0.15 mg/L (Fuge, 1973). 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.

Silica concentrations ranged from 14 to 38 mg/L in water samples (table 6, fig. 7). The median silica concentration in water samples from wells in residential areas of the Anoka Sand Plain reported by Anderson (1993) was less than (18 mg/L) in water samples from the 30 urban study area wells (24 mg/L). Silicon forms strong bonds with oxygen, commonly forming SiO_4^{4-} tetrahedra as building blocks of many igneous and metamorphic minerals. SiO_2 , the mineral quartz, is an

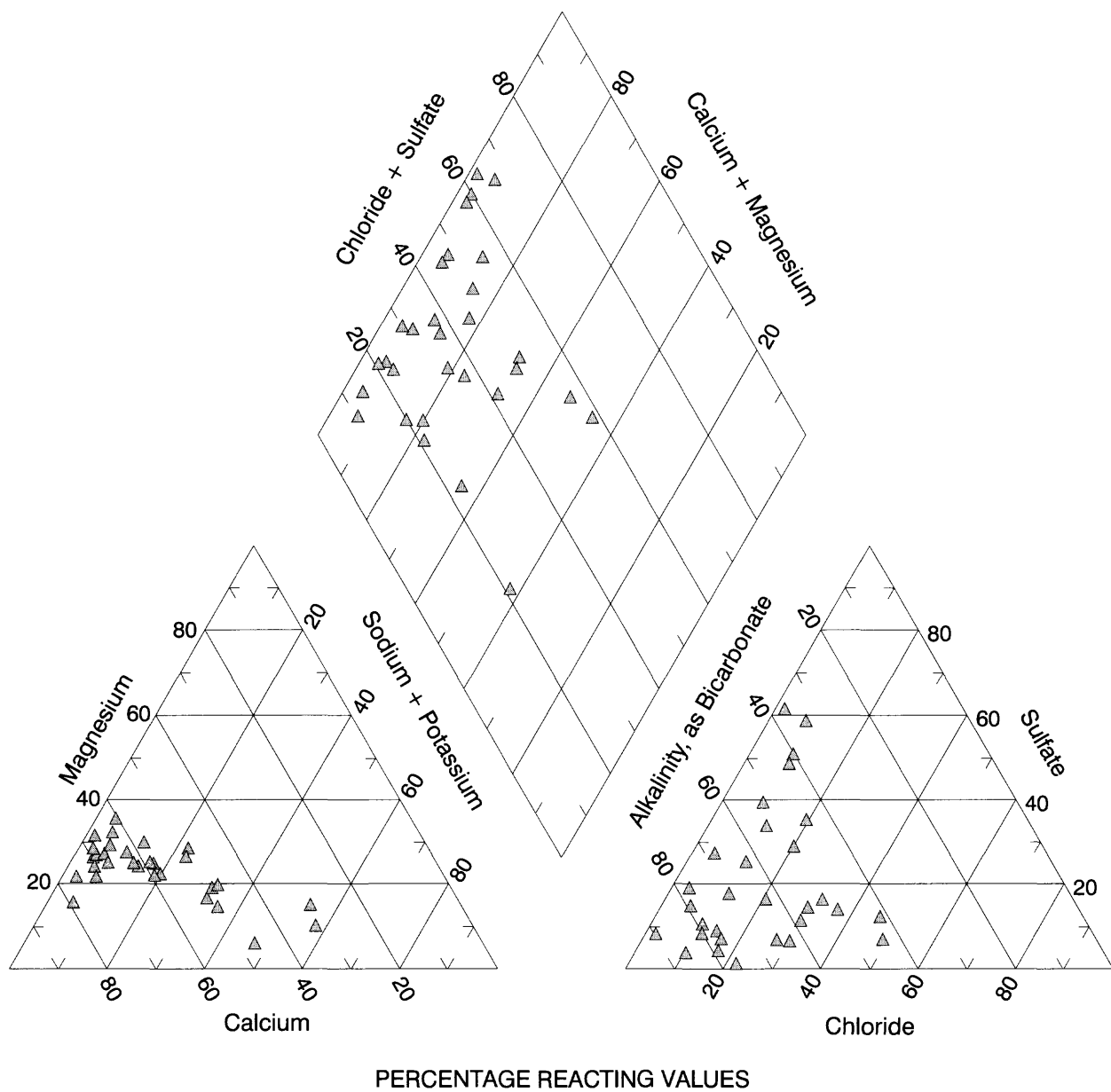


Figure 8.--Trilinear diagram of major ion concentrations in water samples from urban land use study wells (expressed as milliequivalents per liter).

important constituent in igneous rocks and sandstones, and is the predominant mineral in the surficial aquifer in which the wells were completed.

Nutrients and Organic Carbon

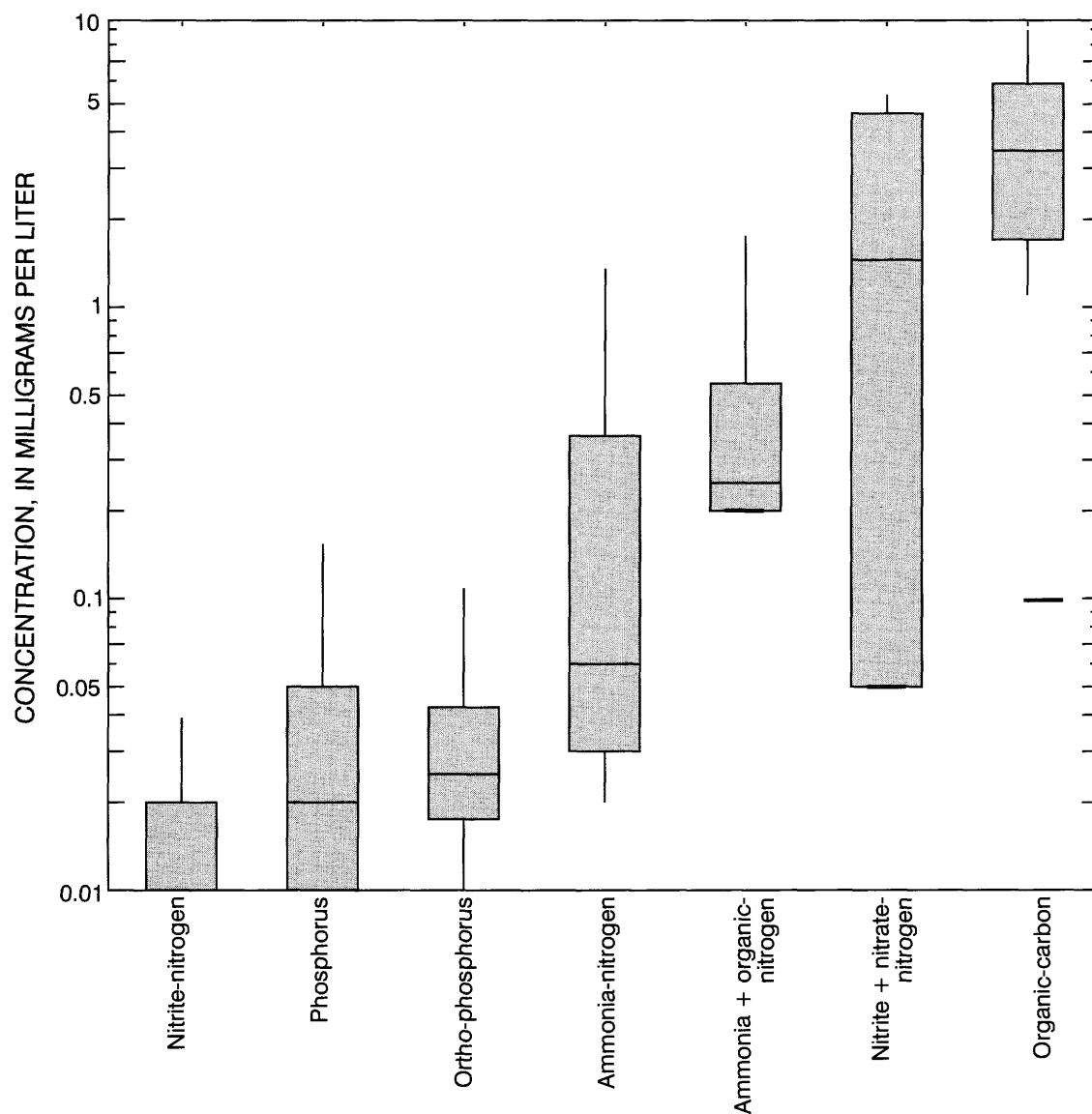
The primary nutrients of concern in ground water are nitrate (NO_3^-) and phosphorus. Nitrate is typically reported as the sum of nitrite plus nitrate as nitrogen. Because nitrite (NO_2^-) is usually detected in low concentrations, nitrite plus nitrate essentially is equal to the concentration of nitrate, so will be referred to in this report as “nitrate”. Elevated concentrations of nitrate in drinking water (exceeding the USEPA MCL of 10 mg/L as nitrogen) have been associated with “blue-baby” syndrome (methemoglobinemia), and with increased rates of stomach cancer, birth defects, miscarriage, and leukemia (Dorsch and others, 1984; Forman and others, 1985; Fan and others, 1987; National Research Council, 1985). Nitrate and phosphorus in ground water discharged to surface water can also lead to eutrophication in lakes and rivers, which can kill fish and other aquatic species.

Most nitrate concentrations were less than 3 mg/L (table 7, fig. 9). The USEPA MCL for nitrate was exceeded in water from only one of the wells (CR-B) (fig. 1). Stark and others (1996) reported a similar range of nitrate concentrations in water from wells completed in unconfined sand and gravel aquifers in part of the UMIS study unit, but much of that area is overlain by agricultural land use, which probably would have greater nitrogen loadings than the residential/commercial land uses of the urban study

area. Anderson (1993) reported greater median nitrate concentrations in water samples from wells in each of the following settings--residential (4.2 mg/L), irrigated agricultural (5.3 mg/L), and nonirrigated agricultural (2.0 mg/L) in the Anoka Sand Plain. Nitrate in ground water is principally derived from the following sources: nitrate-mineral deposits (which do not occur in the urban study area), animal wastes, soils, and fertilizers. Most nitrate is oxidized (nitrified) in soils from the ammonia form of nitrogen (NH_4^+), which is leached from animal wastes, soils, and fertilizers. Rainwater can be another important source of nitrate to soils and ground water. Nitrate concentrations in rainfall in the vicinity of the urban study area ranged from 1.0 - 1.5 mg/L in 1995 (National Atmospheric Deposition Program/National Trends Network, electronic commun., 1997). Nitrate concentrations exceeding 3 mg/L commonly indicate contamination by non-natural sources (Madison and Brunett, 1984). Nitrate can be removed from water by the processes of denitrification and assimilation. Denitrification, which reduces nitrate to gases such as nitrous oxide (N_2O) or dinitrogen (N_2), is accomplished by bacteria or reduced forms of metals in oxygen-depleted water. Assimilation is the uptake of nitrate and other nutrients by plant roots or by biota such as algae and bacteria. Nitrite is an unstable intermediate product of nitrification, which does not commonly occur in substantial concentrations in ground water (table 7, fig. 9). Because organic and ammonia forms of nitrogen tend to sorb to organic matter or to clay particles, concentrations of these constituents in water samples were relatively low (table 7, fig. 9).

Table 7. Number of samples with reportable concentrations, reporting limits, median concentrations, standard deviations, and ranges in concentrations of nutrients and organic carbon in water samples from the 30 urban land use wells
[Concentrations in milligrams per liter]

Constituent	Number of samples with reportable concentrations	Reporting limit	Median	Standard deviation	Range
Nitrate + nitrite-nitrogen	21	0.05	1.4	3.4	<0.05–16
Nitrite-nitrogen	13	0.01	<0.01	0.02	<0.01–0.07
Ammonia + organic nitrogen	17	0.2	0.25	0.58	<0.2–2.0
Ammonia-nitrogen	30	0.01	0.06	0.48	0.02–1.6
Phosphorus	16	0.01	0.02	0.28	<0.01–1.5
Orthophosphorus	25	0.01	0.025	0.09	<0.01–0.5
Organic carbon	30	0.1	3.4	2.9	1.0–9.6



DISSOLVED NUTRIENTS

EXPLANATION

30=Number of Samples

90th Percentile

75th Percentile

Median

25th Percentile

10th Percentile

— Reporting Limit

Figure 9.--Concentrations of dissolved nutrients and organic carbon in water samples from urban land use study wells.

Phosphorus concentrations ranged from less than 0.01 to 1.5 mg/L; most concentrations were below 0.5 mg/L (table 7, fig. 9). Phosphorus tends to be taken up by plant roots, and is also sorbed to organic matter or to metallic oxides in soils, and to minerals in the unsaturated and saturated zones. Because of sorption to organic and inorganic fractions in soils and sediments, phosphorus concentrations are commonly one or more orders of magnitude less than nitrate concentrations. Sources of phosphorus include minerals in igneous and sedimentary rocks, animal wastes, and detergents containing phosphorus (Hem, 1985). Orthophosphorus is one of many chemical forms in which phosphorus occurs in natural waters and is the form of phosphorus preferentially taken up by plants and algae. Orthophosphorus concentrations were generally similar to dissolved phosphorus (all species) concentrations, indicating the predominance of that form of phosphorus in shallow ground water in the urban study area.

Dissolved organic carbon was detected in water samples from all of the wells (table 7, fig. 9). Although not a nutrient, organic carbon concentrations in water can affect dissolved oxygen concentrations, which can affect what species of nutrients are present in water. Anderson (1993) reported a lesser median concentration of dissolved organic carbon (1.2 mg/L) in water samples from residential areas of the Anoka Sand Plain.

Trace Metals

Trace metals analyzed in water samples included: manganese, barium, iron, nickel, chromium, zinc, aluminum, copper, molybdenum, cobalt, uranium, selenium, arsenic, antimony, silver, lead, cadmium, and beryllium. Although they are semi-metallic elements, arsenic, and antimony are referred to as trace metals in this report. The predominant metals dissolved in ground-water samples were iron and manganese (table 8).

The median concentration of manganese (440 µg/L) was the greatest of all of the trace metals (table 8, fig. 10). Anderson (1993) reported a lesser median concentration of 7 µg/L in water samples from wells in residential areas of the Anoka Sand Plain. Because of the tendency for black manganese oxide stains to form on laundry and plumbing fixtures, the USEPA has set a secondary MCL of 50 µg/L for manganese (U.S. Environmental Protection Agency, 1996). Water samples from 22 of the wells in the urban study area had manganese concentrations exceeding the secondary MCL. Manganese is a minor constituent in olivine,

pyroxenes, and amphiboles and small amounts of manganese commonly substitute for calcium in calcite and dolomite (Hem, 1985). Fragments of most of those minerals were observed in surficial aquifer sediments into which the wells were installed. As with most metals, manganese concentrations were greater in samples with lesser dissolved oxygen concentrations (fig. 11a), due to the propensity of metals to form low-solubility oxides and hydroxides.

The median concentration of barium was the second greatest (91 µg/L) of the trace metals analyzed and was detectable in water samples from all of the wells (table 8, fig. 10). Barium is commonly associated with the relatively insoluble sulfate mineral barite (BaSO₄), and is also a common constituent in metallic oxides and hydroxides (Hem, 1985). The MCL for barium of 2,000 µg/L (U.S. Environmental Protection Agency, 1996) was not exceeded in any of the water samples.

Although the median concentration of iron (63 µg/L) was less than that for barium, iron was detected in the greatest concentration of any of the trace metals (table 8, fig. 10). Anderson (1993) reported a lesser median iron concentration of 10 µg/L in water samples from wells in residential areas of the Anoka Sand Plain. Potential sources of iron in ground water include the minerals pyroxene, amphibole, biotite, magnetite, and olivine in igneous rocks; and ferrous polysulfides, siderite, or ferric oxides or oxyhydroxide minerals in sedimentary rocks and unconsolidated sediments (Hem, 1985). Iron is also present in organic wastes and in decaying plant debris and humic compounds in soils (Hem, 1985). Oxygen in water tends to oxidize ferrous iron (Fe⁺²) to ferric iron (Fe⁺³), with which it combines to form relatively insoluble ferric hydroxides (Hem, 1985), so dissolved iron concentrations were greater in samples with lesser dissolved oxygen concentrations (fig. 11b). Because iron oxyhydroxide compounds stain laundry and plumbing fixtures, the USEPA has established a secondary MCL of 0.3 mg/L (300 µg/L) for iron (U.S. Environmental Protection Agency, 1996), which was exceeded in water samples from 11 of the wells.

The trace metals nickel, chromium, zinc, aluminum, copper, and molybdenum were detectable in water samples from most of the monitoring wells, generally at concentrations near reporting limits of 1 µg/L and none of the detected concentrations of these metals exceeded MCL's (table 8, fig. 10). Those metals may be partly attributed to the stainless steel pump used to sample the wells, stainless steel fittings in the water-sampling system, and the aluminum foil used to wrap the pump after each cleaning. Similar concentrations of these trace

Table 8. Number of samples with reportable concentrations, reporting limits, median concentrations, standard deviations, ranges in concentrations, and maximum contaminant levels of trace metals in water samples from the 30 urban land-use wells
[Concentrations in micrograms per liter]

Trace metal	Number of samples with reportable concentrations	Reporting limit	Median	Standard deviation	Range	Maximum contaminant level
Manganese	29	1	440	750	<1–2,700	50 ¹
Barium	30	1	91	69	38–290	2,000
Iron	30	3	63	5,400	3–26,000	300 ¹
Nickel	30	1	9.0	4.6	2–21	100
Chromium	28	1	6.0	3.2	<1–17	100
Zinc	30	1	5.5	12	1–52	5,000 ¹
Aluminum	30	1	5.0	23	3–97	none
Copper	23	1	2.0	2.6	<1–11	1,000 ¹
Molybdenum	24	1	2.0	3.2	<1–18	none
Cobalt	13	1	0.79	0.9	<1–4	none
Uranium	14	1	<1	2.8	<1–13	20
Arsenic	15	1	<1	62	<1–340	50
Selenium	5	1	<1	0.6	<1–2	50
Antimony	2	1	<1	0.2	<1–2	6
Silver	2 ²	1	<1	0	<1	none
Lead	0	1	<1	0	<1	<1
Cadmium	0	1	<1	0	<1	5
Beryllium	0	1	<1	0	<1	4

¹Secondary MCL.

²Interference prevented quantification of silver concentrations in two samples.

metals were detected in equipment blanks and ground-water samples collected with the same equipment, as described in Menheer and Brigham (1997). Greater purge volumes when sampling wells, as opposed to collecting blanks, may reduce metal concentrations from the sampling equipment in ground-water samples.

Water samples from most or all of the monitoring wells did not have detectable concentrations of the trace metals cobalt, uranium, selenium, arsenic, antimony, silver, lead, cadmium, and beryllium. As with iron and manganese, concentrations of cobalt and uranium were strongly related to dissolved oxygen concentrations (figs. 11a and 11b). With the exception of arsenic, none of the detected concentrations of those trace metals exceeded MCL's. The MCL for arsenic was exceeded in the water sample from one well--CR-D (fig. 1) (340 µg/L). A duplicate sample from that well confirmed the arsenic concentration. Sources of arsenic in the

environment include naturally occurring sulfide minerals such as arsenopyrite, chemical disposal sites, metal smelting, combustion of fossil fuels, paints, dyes, rat poisons, wood preservatives, and pesticide compounds (Agency for Toxic Substances and Disease Registry, electronic commun., 1997). Arsenic is both a systemic poison and a carcinogen (Agency for Toxic Substances and Disease Registry, electronic commun., 1997). Although lead was widely dispersed in urban air during the last 50 years through the combustion of gasoline containing tetraethyl lead, lead is relatively immobile in soils and generally does not leach to ground water in detectable concentrations.

Mineral Saturation

Saturation indices (SI's) of minerals in ground water can indicate minerals present in aquifers and minerals

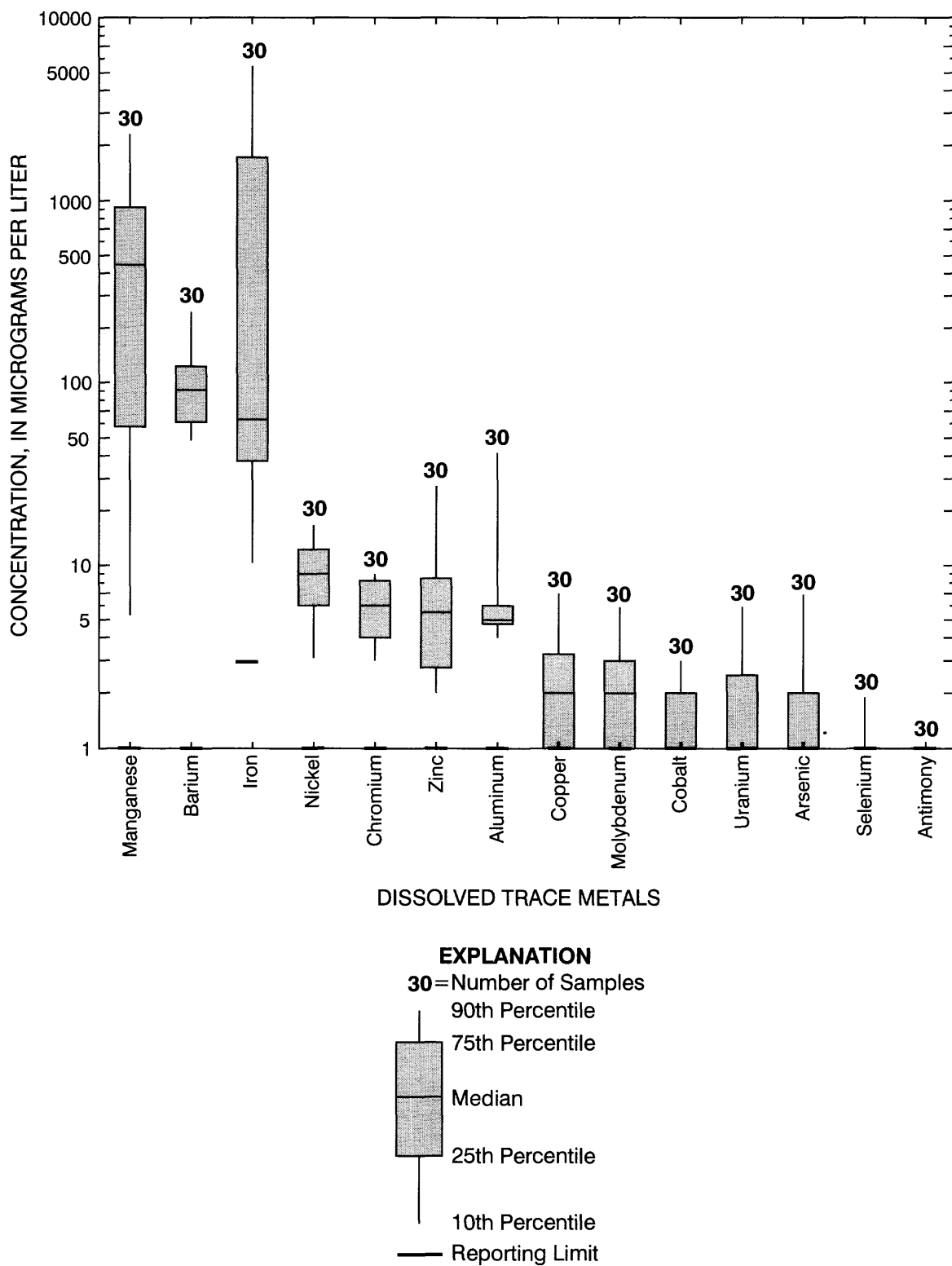


Figure 10.--Concentrations of detected dissolved trace metals in water samples from urban land use study wells.

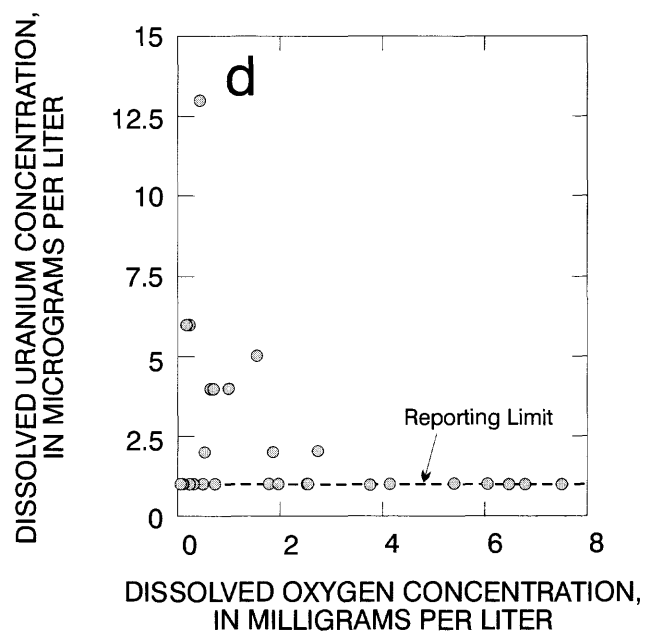
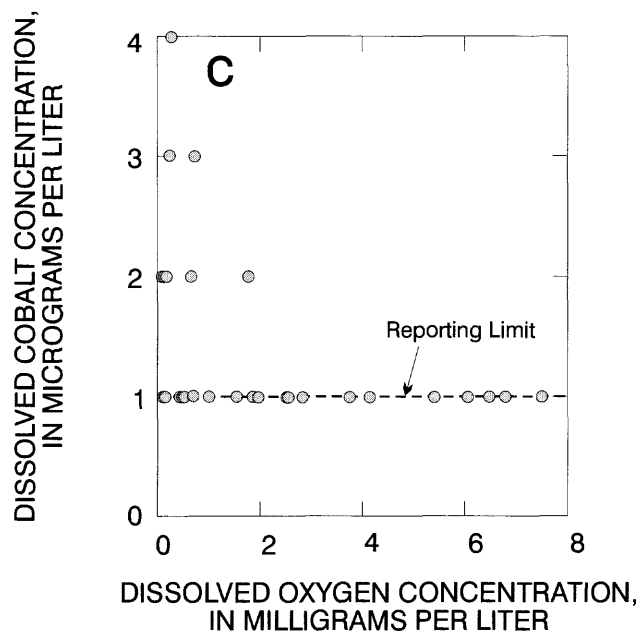
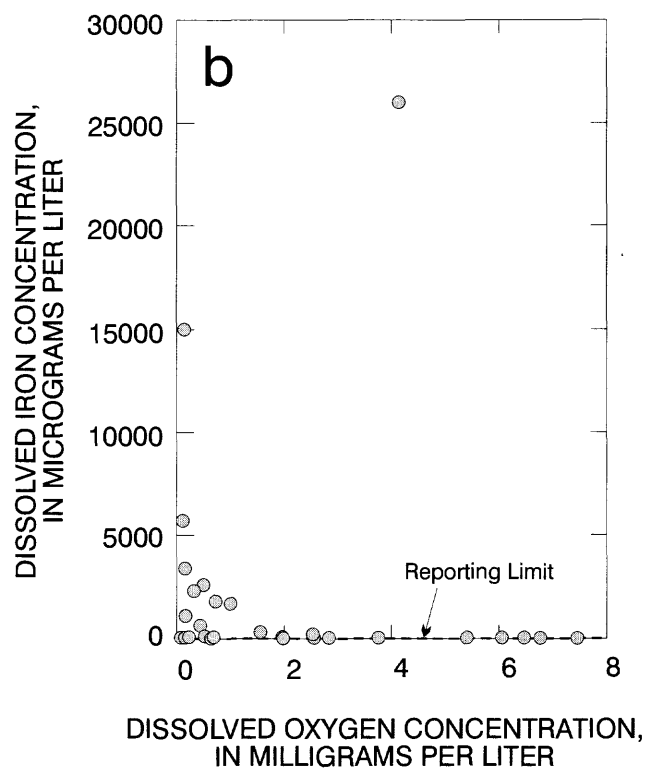
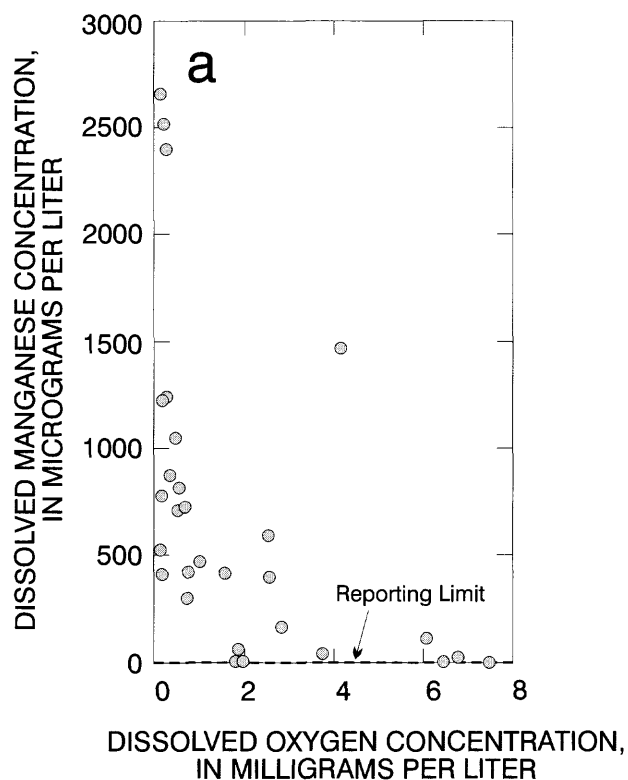


Figure 11.--Concentrations of selected trace metals in relation to dissolved oxygen concentrations in water samples from urban land use study wells.

which may precipitate in aquifers or in water-supply systems. SI's are calculated by the following equation:

$$SI = K_a / K_{eq} \quad (2)$$

where

K_a is equal to the product of the activities of reaction products divided by the product of the activities of reactants (both raised to the powers of their quotients in the reaction equation), and

K_{eq} is the product of the activities of reaction products divided by the products of the reactants (both raised to the powers of their quotients) at equilibrium.

SI's equal to zero indicate that a solution is saturated with a mineral's components, SI's less than zero indicate undersaturation, and SI's greater than zero indicate oversaturation of a mineral. Ground water may be oversaturated with a mineral's components without that mineral forming and precipitating due to high activation energies required for mineral formation or to lack of reaction due to mineral constituents being bound to colloidal particles. SI's of major minerals were calculated using the PHREEQC program (Parkhurst, 1995). Water-quality constituent concentrations input to the PHREEQC program included: pH, temperature, dissolved oxygen, alkalinity (as bicarbonate), calcium, magnesium, sodium, potassium, sulfate, chloride, nitrate plus nitrite nitrogen, nitrite nitrogen, ammonia nitrogen, phosphorus, iron, manganese, aluminum, copper, zinc, barium, and silica.

Hydroxide and oxide minerals of iron and manganese, including hematite (Fe_2O_3), goethite ($FeO(OH)$), pyrolusite (MnO_2), and manganite ($MnO(OH)$) were oversaturated in water samples from all of the wells, indicating that users of water from this aquifer will almost certainly have problems with precipitation and staining by those minerals in plumbing systems, unless the water is pretreated to remove those minerals. Another manganese oxide compound, hausmannite (Mn_3O_4), was oversaturated in water samples from 28 of the wells. Sources of iron and manganese may be ferruginous minerals transported by glaciers from the "Iron Range" in the northern part of Minnesota or from the Pierre Shale in the western part of the state. Another metallic hydroxide, gibbsite ($Al(OH)_3$), was oversaturated in water samples from all of the wells (fig. 12), but the aluminum causing that oversaturation may be due to materials used during sampling.

The phyllosilicate minerals calcium-montmorillonite ($Ca_{0.165}Al_{2.33}Si_{3.67}O_{10}(OH)_2$), illite ($K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$), muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$), and kaolinite ($Al_2Si_2O_5(OH)_4$), which were oversaturated in water samples from all of the wells (fig. 12), are probably present in the terrace deposits comprising the aquifer, which contain clay lenses and disseminated clays. Additional oversaturated phyllosilicate minerals included chlorite ($(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2(Mg,Fe)_3(OH)_6$) and talc ($Mg_3Si_4O_{10}(OH)_2$) in water samples from wells HN-B, and from HN-B and HN-O, respectively. Both of those wells are completed in silty, fine sand lenses in clayey overbank deposits.

Quartz (SiO_2) was the only tectosilicate mineral that was oversaturated in water samples from all of the wells (fig. 12). Chalcedony (cryptocrystalline quartz) was oversaturated in water samples from 12 wells. Quartz sand is the primary constituent of the terrace deposits underlying the urban study area. Dissolution of quartz sand would lead to the slight oversaturation of quartz and chalcedony. Orthoclase ($KAlSi_3O_8$) was oversaturated in water samples from three wells and was nearly saturated in water samples from most of the wells (fig. 12). Orthoclase is a common constituent in granitic sands and gravels and was observed in the split-spoon samples and cuttings from many of the wells.

The carbonate minerals calcite ($CaCO_3$), rhodochrosite ($MnCO_3$), aragonite ($CaCO_3$), and dolomite ($CaMg(CO_3)_2$) were oversaturated in water samples from 18, 17, 9, and 8 wells, respectively. In many of the water samples, the SI's for these minerals were negative numbers near zero, indicating slight under-saturation. Dolomite and calcite are present in underlying bedrock aquifers, and particles of dolomite were commonly observed in auger cuttings.

Additional oversaturated minerals included barite ($BaSO_4$) (in water samples from 15 wells), the phosphatic mineral hydroxyapatite ($Ca_5(PO_4)_3OH$) (in a sample from well HN-D), and the hydroxysulfate minerals jarosite ($KFe_3(SO_4)_2(OH)_6$) and alunite ($KAl_3(SO_4)_2(OH)_6$) in water samples from eight and two wells, respectively (fig. 12). Those minerals were substantially undersaturated in most of the samples. Barite is probably a minor source of sulfate to ground water in the urban study area because it is relatively insoluble and, on a molar basis, barium concentrations are about two orders of magnitude less than sulfate concentrations. Barite is an evaporitic mineral that may have been transported by Des Moines lobe glaciers from

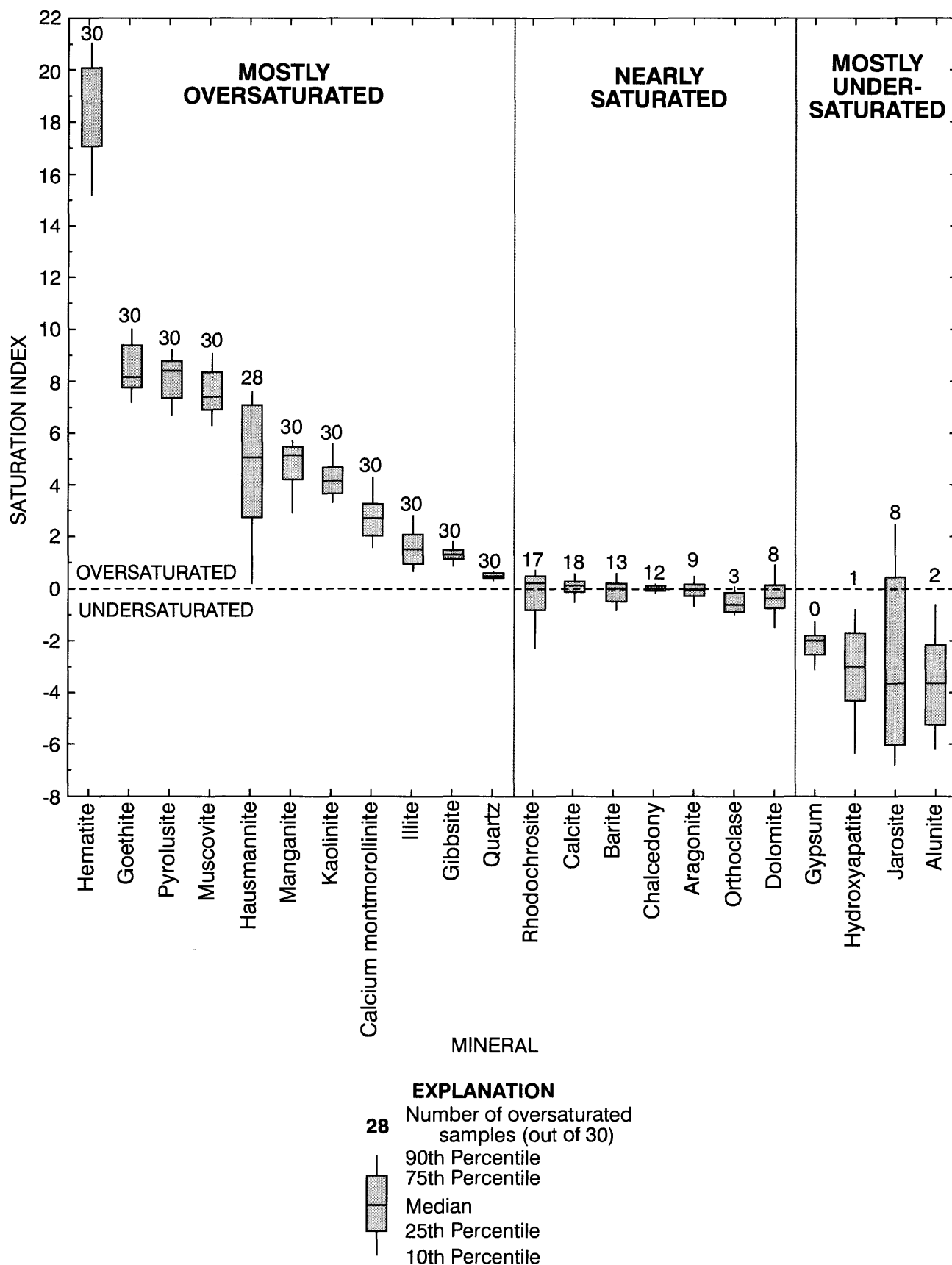


Figure 12.--Saturation indices of major minerals in water samples from urban land use study wells.

the northwest to the urban study area. Additional minerals that were overestimated in water samples from some wells included hydroxyapatite, which is a common accessory constituent in igneous, sedimentary, and metamorphic rocks and has also been used as a fertilizer (Hurlbut and Klein, 1977). Jarosite is a secondary mineral commonly occurring as crusts and coatings on ferruginous ores (Hurlbut and Klein, 1977). Alunite is formed by the reaction between sulfuric acid solutions and rocks containing orthoclase (Hurlbut and Klein, 1977), a common accessory mineral in the granitic gravels and sands of the surficial aquifer. Gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$) was slightly undersaturated in all of the samples (fig. 12).

Pesticides

Pesticides are compounds primarily used to kill weeds or insect pests. Many of the most commonly-applied

classes of pesticides were analyzed in ground-water samples (table 9). The majority of pesticide applications are to cropland, but applications of these compounds may also be substantial to lawns, gardens, golf courses, and right-of-ways in urban areas. Leaching of pesticides to ground water is affected in part by application practices including rates, times, and methods of application; by formulations of applied pesticides; by cultivation methods; and by the use of irrigation water (Rao and Alley, 1993). Chemical and physical characteristics of pesticides such as organic-carbon sorption coefficients, solubilities, acidities, and oxidation and hydrolysis half-lives can also affect leaching of pesticides to ground water. Most pesticides are designed to stay in the soil zone--many are prone to sorb to organic carbon and clay minerals in soils, are degraded by abiotic and biotic processes in soils and the unsaturated zone, and have relatively low solubilities in water (Rao and Alley, 1993).

Table 9. Pesticide compounds analyzed in water samples, by chemical group

<u>Triazines</u>	<u>Organophosphorus</u>	<u>Organochlorines</u>	<u>Carbamates</u>	<u>Dinitroaniline</u>	<u>Carboxylic</u>
Atrazine	Malathion	<i>p,p'</i> -DDE	Butylate	Benfluralin	2,4-DB
Deethylatrazine	Parathion	Dieldrin	Carbaryl	Trifluralin	2,4-D
Simazine	Phorate	Chlorothalonil	Aldicarb	Pendimethalin	Chloramben
Cyanazine	Malathion	Bromoxynil	Aldicarb-sulfone	Ethalfuralin	MCPA
Metribuzin	Disulfoton	α -HCH	Aldicarb-sulfoxide	<u>Aminosulfonyl</u>	Picloram
Prometon	Methyl parathion	γ -HCH	Molinate	Bentazon	Dichlorprop
Terbuthylazine	Azinphos-methyl	<u>Amides</u>	Triallate	Oryzalin	DCPA
<u>Pyrethroid</u>	Ethoprop	Napropamide	Carbofuran	<u>Hydroxy Acid</u>	MCPB
Esfenvalerate	Terbufos	Propachlor	Methomyl	Terbacil	Trichlopyr
Permethrin	Fonofos	Pronamide	Oxamyl	Bromacil	Dicamba
<u>Phenyl Ureas</u>	<u>Phosphorothiotates</u>	Propanil	EPTC	DNOC	Acifluorfen
Diuron	Diazinon	<u>Acetanilides</u>	Thiobencarb	Dinoseb	<u>Other</u>
Linuron	<u>Chloroacetanilides</u>	Acetochlor	Methiocarb	<u>Pyridazinone</u>	Dacthal
Fenuron	Metolachlor	<u>Benzonitriles</u>	Propoxur	Chlorpyrifos	Chlordane
Fluometuron	Alachlor	Dichlobenil	Propham		Chlopyralid
Linuron	2,6-Diethylalanine		3-hydroxy-carbofuran		1-naphthol
Tebuthiuron	<u>Sulfite Ester</u>		Pebulate		2,4,5-T
Neburon	Propargite				Silvex

Some of the most commonly sold pesticides for use on lawns, gardens and golf courses (not all of which were analyzed in water samples) include: glyphosate, 2,4-D, dacthal, diazinon, and carbaryl. Pesticides applied to roadways in the urban study area include picloram, 2,4-D, glyphosate, simazine, clopyralid, prometon, and imazapyr, and glufosinate-ammonium (Joe Levernier, Hennepin County Public Works Dept., oral commun., 1997; Arvid Gutzwiller, Anoka County Highway Dept., oral commun., 1997; and Robert Wiyk, Minnesota Dept. of Transportation, written commun., 1997). Powerline right-of-ways in the urban study area were not sprayed with herbicides in many years, but a spraying program was reinstituted in 1996 in which glyphosate and picloram were sprayed on mowed areas, and triclopyr, picloram and glyphosate were sprayed on brushy areas along major powerline right-of-ways (Wayne Jude, Northern States Power Co., oral commun., 1997). Along railway right-of-ways, diuron and imazapyr are the primary herbicides used to control weed growth (Glen Dunkin, Burlington Northern Railway Co., oral commun., 1997). Because much of the urban study area was previously used for agriculture, relict concentrations of agricultural pesticides may also be detectable in ground water in areas that have been recently redeveloped to residential or commercial land uses. Pesticides may also be deposited to the land surface at great distances from application locations by atmospheric deposition of pesticides volatilized during and after application (Spencer and Cliath, 1990; Majewski and Capel, 1995).

Soil and unsaturated-zone properties including hydraulic conductivity, organic-carbon content, pH, and cation-exchange capacity may affect leaching of a pesticide compound to ground water. Pesticides are more likely to be sorbed to less permeable soils with greater organic-carbon contents. There are variable effects on pesticide leaching in relation to soil pH values--alkaline compounds are more likely to be sorbed in acidic soils and the contrary is true for acidic compounds. Although there are relations between soil and sediment characteristics and likelihood of pesticides to leach to ground water, there were no significant correlations between pesticide detections and estimated permeabilities, organic carbon contents, and pH values of sediment samples collected during well drilling. Correlations between those constituents were tested with Kendall-tau values (Kendall, 1975). The level of significance of the test was alpha values less than or equal to 0.05.

Water samples from 16 of the wells had detectable concentrations of one or more pesticides (fig. 13). That

frequency of detection is somewhat less than those reported by the USGS for sand and gravel aquifers in part of the UMIS study unit (Fallon, 1997). Prometon was the most frequently detected pesticide, occurring in detectable concentrations in water samples from 10 wells (CR-A, CR-D, CR-F, HN-D, HN-M, HN-P, HN-Q, HN-R, HN-S, and HN-T) (table 10, fig. 14). Prometon is a nonselective, long-lasting, pre- and post-emergent herbicide used to control perennial broadleaf weeds and grasses on right-of-ways (Sine, 1993). There is no MCL established for prometon, but the USEPA has established a lifetime health advisory level of 100 µg/L for drinking water (U.S. Environmental Protection Agency, 1996), which was not exceeded in any of the water samples. Prometon is relatively slow to degrade in soils, with an estimated half-life of 200-500 days (Rao and Alley, 1993; Weber, 1994). Prometon, a methoxy-s-triazine, is moderately basic, meaning that it has a tendency to protonate and sorb to acidic soils (Weber, 1994). Prometon has a relatively low sorption coefficient to organic carbon in soils, making it more likely to leach to ground water (Weber, 1994). There were no significant correlations between detection of prometon and soil properties, such as estimated hydraulic conductivity, organic-carbon content, and pH. Prometon use in 1996 by the Minnesota Department of Transportation was only four gallons per year in the metropolitan area (Robert Wiyk, Minnesota Dept. of Transportation, written commun., 1997). The widespread detection of prometon in ground water, its occurrence in rainwater in very low concentrations for only a short period in the spring of 1995 at Lake Harriet in southwest Minneapolis (table 10), and the long half-life of prometon indicate that detectable concentrations of that herbicide may be relicts of local applications made in the past or that there may be additional users of this compound in the urban study area.

Atrazine and its metabolite (break-down product) deethylatrazine were detected in water samples from six wells (CR-A, HN-H, HN-M, HN-P, HN-Q, HN-S) and eight wells (CR-A, HN-H, HN-K, HN-L, HN-M, HN-P, HN-Q, HN-S), respectively (fig. 14). Atrazine is a moderately persistent triazine herbicide used to control annual grasses in cornfields (Winkelman and Klaine, 1991). Atrazine has been the most widely detected herbicide in ground water in sand and gravel aquifers in part of the UMIS study unit (Fallon, 1997). Being an alkaline pesticide like prometon, atrazine is also more likely to sorb to acidic soils (Weber, 1994), but atrazine concentrations in water samples and pH values of soil samples were not significantly correlated. Atrazine is less volatile and less soluble in water than prometon (Weber, 1994). Average atrazine application rates in

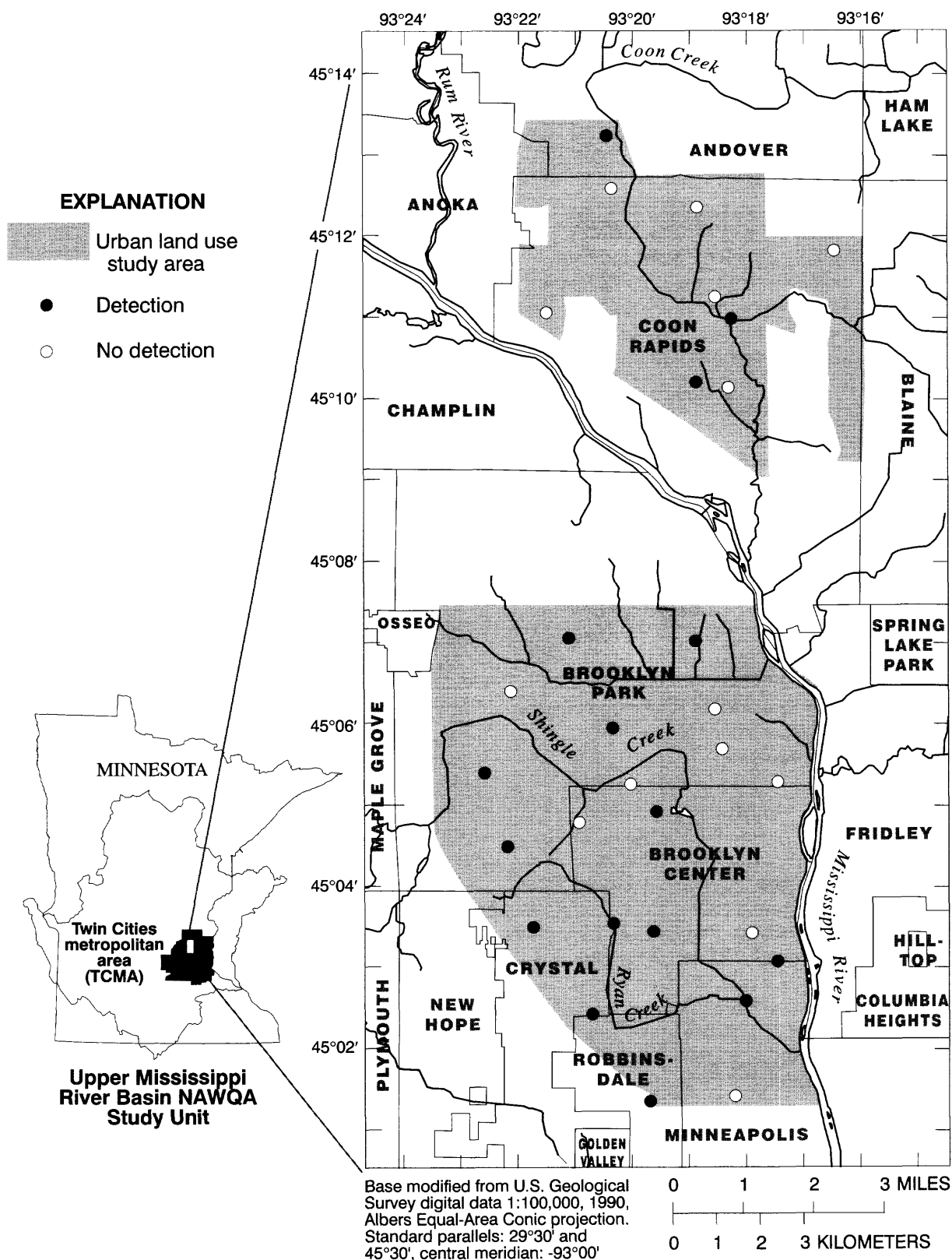


Figure 13.--Locations of urban land use wells with water samples having detectable and nondetectable concentration of pesticides.

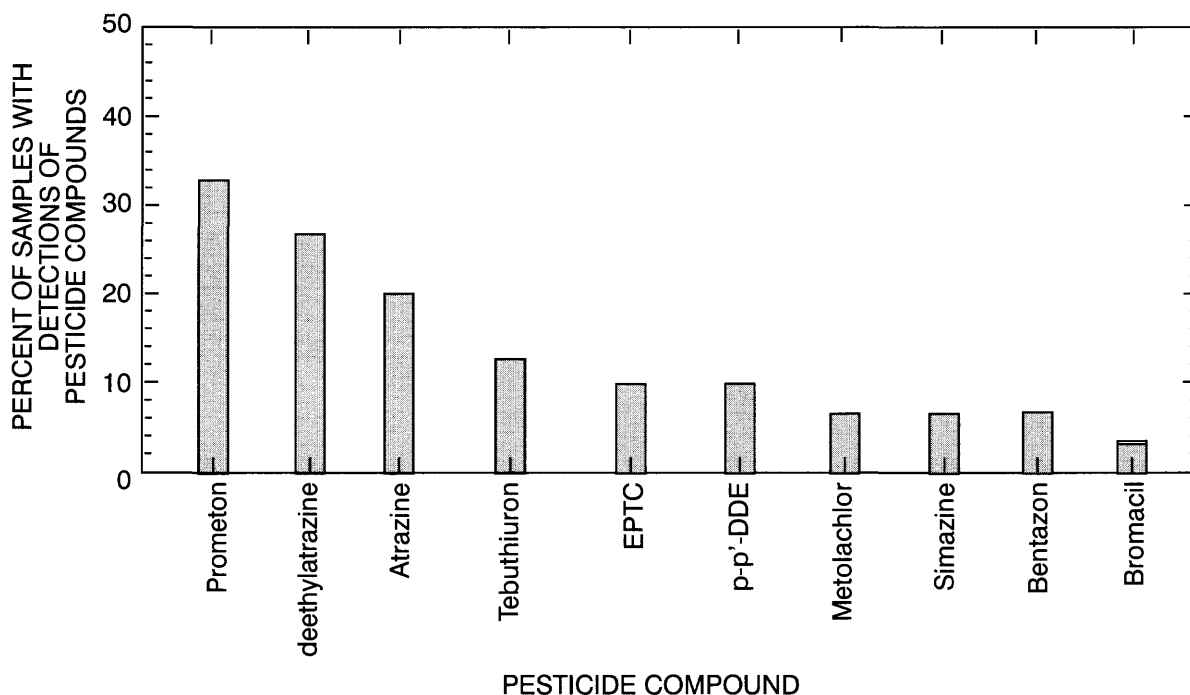


Figure 14.--Frequencies of detection of pesticides in water samples from urban land use study wells.

1987 were 7.6 and 11 lb/mi² in Anoka and Hennepin Counties, respectively (estimated by crop acreage and average application rates from Gianessi and Puffer (1991)). Actual amounts of atrazine applied in the urban study area are probably less, due to its urbanization. Atrazine is a possible carcinogen and has an MCL of 3 µg/L (U.S. Environmental Protection Agency, 1996). No MCL has been established for deethylatrazine (U.S. Environmental Protection Agency, 1996), although it may have similar herbicidal effects and toxic or carcinogenic effects as atrazine (Belluck and others, 1991; Weber, 1994). Concentrations of these compounds in ground-water samples were less than those measured in rainwater at Lake Harriet in southwestern Minneapolis in 1995 (table 10).

Tebuthiuron, an herbicide labelled for use on right-of-ways, was detected in water from four of the wells--HN-Q, HN-R, HN-S, and HN-T, all of which are located in the vicinity of major highways in the southern part of the urban study area (fig. 14). Tebuthiuron is an alkaline pesticide like prometon and atrazine, has a greater solubility, and a lesser sorption coefficient than either of those compounds (Weber, 1994). Tebuthiuron has a relatively long estimated soil half-life of 360 days (Weber, 1994). The USEPA has established a lifetime health-advisory limit of 500 µg/L for tebuthiuron in

drinking water (U.S. Environmental Protection Agency, 1996). Tebuthiuron was not detected in rainwater collected weekly at Lake Harriet during the summer of 1995 (Don Goolsby, U.S. Geological Survey, written commun., 1996). Its long half life, and lack of detection in rainwater and in most ground-water samples, indicate that local applications of tebuthiuron, rather than atmospheric deposition, are the probable sources of this compound. No utilities or transportation agencies operating in the urban study area are known to apply this compound.

EPTC, also known as S-Ethyl dipropylthiocarbamate or EPTAM, was detected in water samples from three wells (HN-M, HN-R, and HN-S) (fig. 14). EPTC is a selective thiocarbamate herbicide applied to beans, forage legumes, potatoes, and corn (Sine, 1993). Average estimated application rates for EPTC in 1987 were 39.9 and 56.9 lb/mi² in Anoka and Hennepin Counties (Gianessi and Puffer, 1991), respectively, making EPTC the most heavily-applied registered pesticide in or adjacent to the urban study area. Due to the lack of cropland in the urban study area, actual applications of this compound are probably less than the averages for the counties. EPTC has a substantial volatility and must be incorporated in soils to reduce volatilization losses (Weber, 1994). EPTC is moderately

Table 10. Reporting and detection limits, number of detections, ranges in concentrations, and maximum contaminant levels of pesticide compounds detected in water samples from the 30 urban land use wells and in 17 rainwater samples collected at Lake Harriet in southwest Minneapolis, April-August 1995 (Don Goolsby, U.S. Geological Survey, written commun., 1996)
[µg/L, micrograms per liter; nd, not detected]

Compound	Reporting limit [detection limit] (µg/L)	Number of samples with detectable concentrations	Range of concentration (µg/L)	Maximum contaminant level	Range of concentrations in rainwater (µg/L) [number of detections]
Prometon	0.018 [0.001]	10	<0.001–0.9	none	0.010 - 0.012 [2]
Deethylatrazine	0.002 [0.001]	8	<0.001–0.035	none	0.004 - 0.90 [13]
Atrazine	0.001 [0.0005]	6	<0.0005–0.046	3.0	0.08 - 2.4 [16]
Tebuthiuron	0.01 [0.005]	4	<0.005–0.053	none	nd
EPTC	0.002 [0.001]	3	<0.001–0.003	none	0.006 - 0.13 [7]
<i>p,p'</i> -DDE	0.006 [0.001]	3	<0.001–0.005	none	nd
Metolachlor	0.002 [0.001]	2	<0.001–0.01	none	0.003 - 0.93 [13]
Simazine	0.005 [0.001]	2	<0.001–0.095	4.0	0.011 [1]
Bentazon	0.014 [0.005]	2	<0.005–0.29	none	nd
Bromacil	0.035 [0.010]	1	<0.010–0.09	none	nd

soluble in water, has a relatively low partition coefficient to organic carbon in soils, has a moderately short half-life of seven days, and is readily degraded by soil micro-organisms (Weber, 1994). EPTC was detected in concentrations ranging from 0.006 to 0.13 µg/L in rainwater samples collected during the spring and summer of 1995 at Lake Harriet in southwestern Minneapolis (Don Goolsby, U.S. Geological Survey, written commun., 1996). The volatility and susceptibility to biodegradation of EPTC reduce the likelihood of this compound leaching to ground water in spite of its high application rates in the area.

The pesticide *p,p'*-DDE was detected in water samples from three wells (CR-C, CR-D, and CR-F), all of which are located in suburban residential settings underlain by organic-rich soils, which may increase sorption and allow slow release of those compounds (figs. 1, 2, 13, 14). In organic-rich soils, DDT (the

parent compound of *p,p'*-DDE) may have also been less likely to be degraded due to the availability of other organic compounds for microbial metabolism. The pesticide *p,p'*-DDE, also known as 1,1,1-trichloro-2,2-bis (p-chlorophenyl) ethane or DDE, is an impurity and breakdown product of the insecticide DDT (Verschuere, 1983). DDE can damage nervous systems of humans and other animals and is a probable human carcinogen (Agency for Toxic Substances and Disease Registry, electronic commun., 1997). Production and application of DDT were banned in the United States in 1972 because of buildup of the compound in the environment, thinning of egg shells of many native bird species, and because of its possible carcinogenicity (Agency for Toxic Substances and Disease Registry, electronic commun., 1997). DDE was detected at a concentration of 82 µg/kg (micrograms/kilogram (parts per billion)) in tissues of white suckers (*catostomus*

commersoni) and at a concentration of 2.3 µg/kg in bed sediments collected in 1996 at Shingle Creek in northwest Minneapolis (Kathy Lee, U.S. Geological Survey, written commun., 1997).

Metolachlor, a chloroacetanilide compound, was detected in water samples from two of the wells (HN-M and HN-S) (figs. 1, 13, 14). Metolachlor is used as a preemergent herbicide for corn, soybeans, grain sorghum, and potatoes (Sine, 1993) and is considered a possible human carcinogen, with a lifetime health advisory limit of 70 µg/L for drinking water (U.S. Environmental Protection Agency, 1996). Estimated metolachlor application rates in Anoka and Hennepin Counties in 1987 were 14.4 and 16.9 lb/mi², respectively (Gianessi and Puffer, 1991), but are probably less in the urban study area. Metolachlor is relatively soluble in water, is moderately volatile, has a relatively low sorption coefficient to organic carbon, and has a half-life of 40 days (Weber, 1994). Degradation of metolachlor is primarily achieved by fungi in soils (Weber, 1994). Susceptibility to degradation may be the reason why metolachlor concentrations in ground water were less than in rainwater samples (table 10).

Simazine, an herbicide commonly applied to corn, was detected in water samples from two wells (HN-Q, and HN-S) (figs. 1, 13, 14). Like atrazine, simazine is an alkaline compound, which is more likely to be sorbed to acidic soils (Weber, 1994). In neutral soils, simazine has a half-life of 90 days (Weber, 1994). The primary use of simazine in the urban study area may be as an herbicide along right-of-ways. The relatively infrequent detection of simazine in rainwater at Lake Harriet in southwestern Minneapolis (table 10) and in ground water indicate that detection of this compound is probably related to local applications, rather than widespread atmospheric deposition.

Bentazon was detected in water samples from two wells--HN-B, and HN-F, both located in the northeastern part of the Hennepin County portion of the urban study area (figs. 1, 13, 14). Bentazon is used for post-emergence control of broadleaf weeds on land planted in alfalfa, cereals, clover, corn, grasses, sorghum, and soybeans (Sine, 1993). Estimated application rates for bentazon in 1987 were 1.1 and 2.5 lb/mi² for Anoka and Hennepin Counties, respectively (Gianessi and Puffer, 1991), but are probably less in the urban study area. Bentazon is moderately soluble in water, has a low volatility, has a low retention coefficient with organic carbon, but has a relatively short soil half-life of 20 days (Weber, 1994). The

USEPA has established an MCL-goal of 20 µg/L for bentazon (U.S. Environmental Protection Agency, 1996), which was not exceeded in any of the water samples (table 10).

Bromacil, detected in the water sample from well HN-F, is an herbicide used for general weed control in noncrop areas, such as lawns (Sine, 1993) (figs. 1, 13, 14). The USEPA classifies bromacil as a possible human carcinogen and has established a lifetime health advisory limit of 90 µg/L for drinking water (U.S. Environmental Protection Agency, 1996). Bromacil has a moderate solubility in water, low volatility, a very low organic-carbon retention coefficient and a relatively long soil half-life of 150 days (Weber, 1994). Those factors indicate that bromacil, if widely used, may occur in trace amounts in shallow ground water. The relatively high analytical detection limit for this compound (0.035 µg/L) may have lessened the frequency of its detection.

Volatile Organic Compounds

VOC's are compounds that evaporate at normal temperature and pressure. VOC's are contained in many commercial products including: gasoline, paints, adhesives, solvents, wood preservatives, dry-cleaning agents, some pesticides, cosmetics, correction fluids, and refrigerants. VOC's may reach ground water through spills and leaks at or near the land surface, from diffusion and dispersion of atmospheric VOC's, and through recharge of rainwater containing VOC's sorbed during passage through the atmosphere.

Concentrations of 82 VOC's were determined in ground-water samples (table 11). VOC's were detected in water samples from 26 of the 30 urban land use wells (fig. 15). None of the concentrations of the 19 detected VOC's exceeded MCL's set by the USEPA for drinking water.

The most frequently detected VOC was carbon disulfide (CS₂), which was detected in water samples from 22 of the 30 urban land use wells (table 12, fig. 16). Carbon disulfide is a colorless liquid with a slightly pungent, sulfurous odor used in the manufacture of rayon, cellophane, carbon tetrachloride, rubber, soil disinfectants, soil conditioners, grain fumigants, herbicides, paper, pharmaceuticals, and electronic vacuum tubes (Verschueren, 1983). Carbon disulfide is also used as a solvent for phosphorus, sulfur, bromine, iodine, selenium, fats, and resins (Verschueren, 1983).

Table 11. Volatile organic compounds analyzed in water samples, by chemical group

<u>Halogenated Alkanes</u>	<u>Halogenated Alkenes</u>	<u>Alkylated Benzenes</u>
1,1,1-trichloroethane (methyl chloroform)	Chloroethene (vinyl chloride)	1,2,4-trimethylbenzene
Bromomethane (methyl bromide)	Bromoethene	Isopropylbenzene
Chloromethane (methyl chloride)	Trichloroethene	Ethylbenzene
Chloroethane	Hexachlorobutadiene	N-propylbenzene
Dichloromethane (methylene chloride)	Tetrachloroethene	N-butylbenzene
1,1,1,2-tetrachloroethane	<i>cis</i> -1,2-dichloroethene	Toluene
1,2-dibromoethane	Trans-1,2-dichloroethene	meta + para-xylene
1,1-dichloroethane	Bromoethene	ortho-xylene
1,2-dichloroethane	<i>cis</i> -1,3-dichloro-1-propene	O-chlorotoluene
Dichloropropane	<i>trans</i> -1,3-dichloro-1-propene	O-ethyltoluene
1,1,2,2-tetrachloroethane	3-chloropropene	P-isopropyl-toluene
1,2-dibromo-3-chloropropane	1,1-dichloropropene	Tert-butyl-benzene
1,2,3-trichloropropane	<u>Alkenes</u>	Sec-butyl-benzene
1,2-dibromoethane	Vinyl acetate	N-butyl-benzene
1,2-dichloroethane	<u>Halogenated Aromatics</u>	1,3,5-trimethylbenzene
<u>Chlorofluorocarbons</u>	1,2,3-trichlorobenzene	1,2,4-trimethylbenzene
Tetrachloromethane/carbon tetrachloride (CFC-10)	1,2-dichlorobenzene	P-chloro-toluene
Trichlorofluoromethane (CFC-11)	1,4-dichlorobenzene	<u>Ethers</u>
Dichlorodifluoromethane (CFC-12)	1,3-dichlorobenzene	Methyl tert-butyl ether (MTBE)
Trichlorotrifluoromethane (CFC-113)	Chlorobenzene	Ethyl ether
<u>Aldehydes</u>	1,2,4-trichlorobenzene	T-pentyl methylether
2-propenenitrile (acrylonitrile)	Methyl iodide	T-butyl ethyl ether
2-propenal (acrolein)	Bromobenzene	Tetrahydrofuran
<u>Ketones</u>	<u>Aromatic Hydrocarbons</u>	<u>Others</u>
Butylmethylketone (2-hexanone)	Benzene	Carbon disulfide
Methyl ethyl ketone (2-butanone)	Naphthalene	Acetone
Methyl isobutyl ketone (hexanone)	Styrene	Methacrylonitrile
	<u>Trihalomethanes</u>	Methyl methacrylate
	Bromodichloromethane	Ethyl methacrylate
	Tribromomethane (bromoform)	Isodurene
	Dibromochloromethane	Prehnitene
	Trichloromethane (chloroform)	Methylacrylate

In addition to a wide variety of industrial uses, carbon disulfide is naturally emitted by bacteria in many soils, particularly soils rich in organic matter (Verschueren, 1983). At airborne concentrations exceeding 100 parts per million, carbon disulfide can cause illness or be toxic to humans, but no MCL for drinking water has been established for the compound. The substantial frequency of detection of low concentrations of this compound in ground water indicates a widespread source of this compound, such as emissions from soils. Lack of knowledge about anthropogenic emissions or measurement of airborne concentrations of this compound precludes assessment as to whether the

origins of this compound in ground water are natural or anthropogenic in the urban study area.

Methyl chloride (CH_3Cl), also known as chloromethane, was the second-most frequently detected VOC (fig. 16), being detected in water samples from 14 wells. Methyl chloride is used in manufacturing silicones, tetraethyllead, synthetic rubber, methyl cellulose, refrigerants, methylene chloride, chloroform, carbon tetrachloride, and fumigants (Verschueren, 1983). Methyl chloride is also used as a low-temperature solvent, in medicines, as a fluid in thermostatic equipment, as an extractant, a propellant, and in herbicides, and is also present in parts-per-

Figure 15.--Locations of urban land use wells with water samples having detectable and nondetectable concentrations of volatile organic compounds.

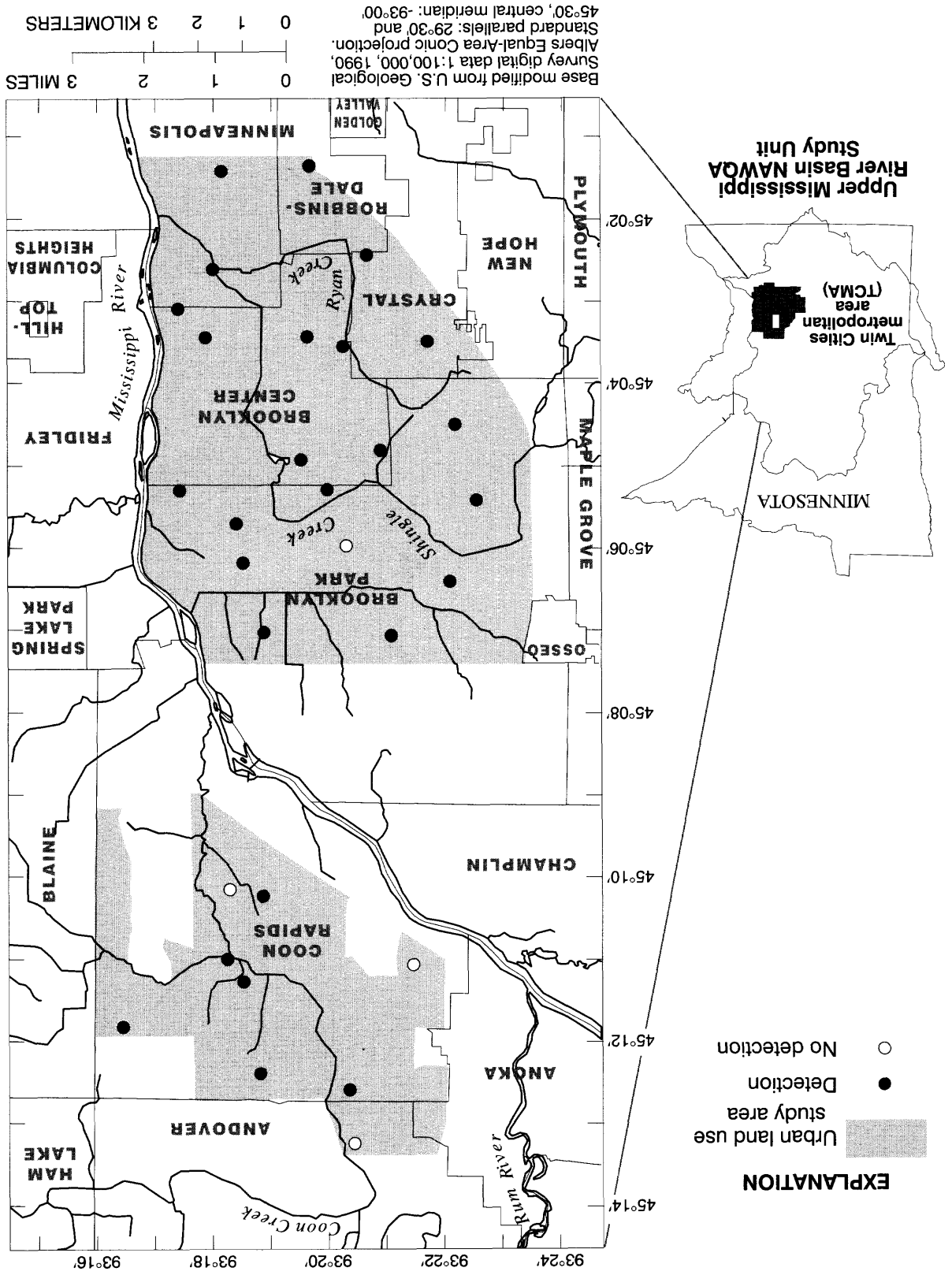


Table 12. Detection limits, number of detections, ranges in concentrations, and maximum contaminant levels of volatile organic compounds detected in water samples from the 30 urban land use wells, ranges of volatile organic compound concentrations in air in downtown Minneapolis (Gary Eckhardt, Minnesota Pollution Control Agency, electronic commun., 1997), and ranges of equilibrium volatile organic compound concentrations in rainwater [µg/L, micrograms per liter; na, not analyzed]

Compound	Detection limit (µg/L)	Number of detections in ground-water samples	Range in concentrations in ground water (µg/L)	Maximum contaminant level (µg/L)	Range in detected concentrations in air (parts per billion, volumetric)	Equilibrium concentrations in rainwater at 10 degrees Celsius (µg/L) [based on air concentrations]
Carbon disulfide	0.01	22	<0.01–0.52	none	na	--
Methyl chloride	0.01	14	<0.1–0.15	none	na	--
Acetone	0.5	5	<0.5–6	none	na	--
Dichlorodifluoromethane (CFC-12)	0.01	4	<0.01–0.23	none	0.18–1.8	0.0004 - 0.004
Tetrahydrofuran	0.5	4	<0.5–1.6	none	na	--
Trichlorofluoromethane (CFC-11)	0.01	3	<0.01–0.05	none	0.092–1.1	0.00022 - 0.0027
Methyl iodide	0.01	3	<0.01–0.04	none	na	--
1,1-dichloroethane	0.01	3	<0.01–0.09	7.0	<0.001–0.017	<0.000038 - 0.00063
Chloroform	0.01	3	<0.01–12.1	80 ¹	0.002–0.19	0.00013 - 0.012
Toluene	0.01	3	<0.01–0.17	1,000	0.30–6.0	0.0086 - 0.18
1,1,1-trichloroethane	0.01	3	<0.01–0.06	200	0.033–0.68	0.00056 - 0.012
Trichloroethene	0.01	2	<0.01–0.12	5.0	0.002–0.52	0.000065 - 0.016
cis-1,2-dichloroethene	0.01	2	<0.01–0.11	70	<0.001–0.025	0.000034 - 0.00085
Methylene chloride	0.01	1	<0.01–0.06	5.0	0.045–12.3	0.0026 - 0.71
Bromodichloromethane	0.01	1	<0.01–0.17	80 ¹	na	--
Benzene	0.01	1	<0.01–0.16	5.0	0.27–1.7	0.0067 - 0.042
Methylisobutylketone	0.5	1	<0.5–0.6	none	na	--
Ethyl ether	0.01	1	<0.01–0.19	none	na	--
Tetrachloroethene	0.01	1	<0.01–0.02	5.0	<0.001–0.90	0.000022 - 0.019

¹ The MCL for trihalomethanes is 80 µg/L for the sum of the concentrations of those compounds.

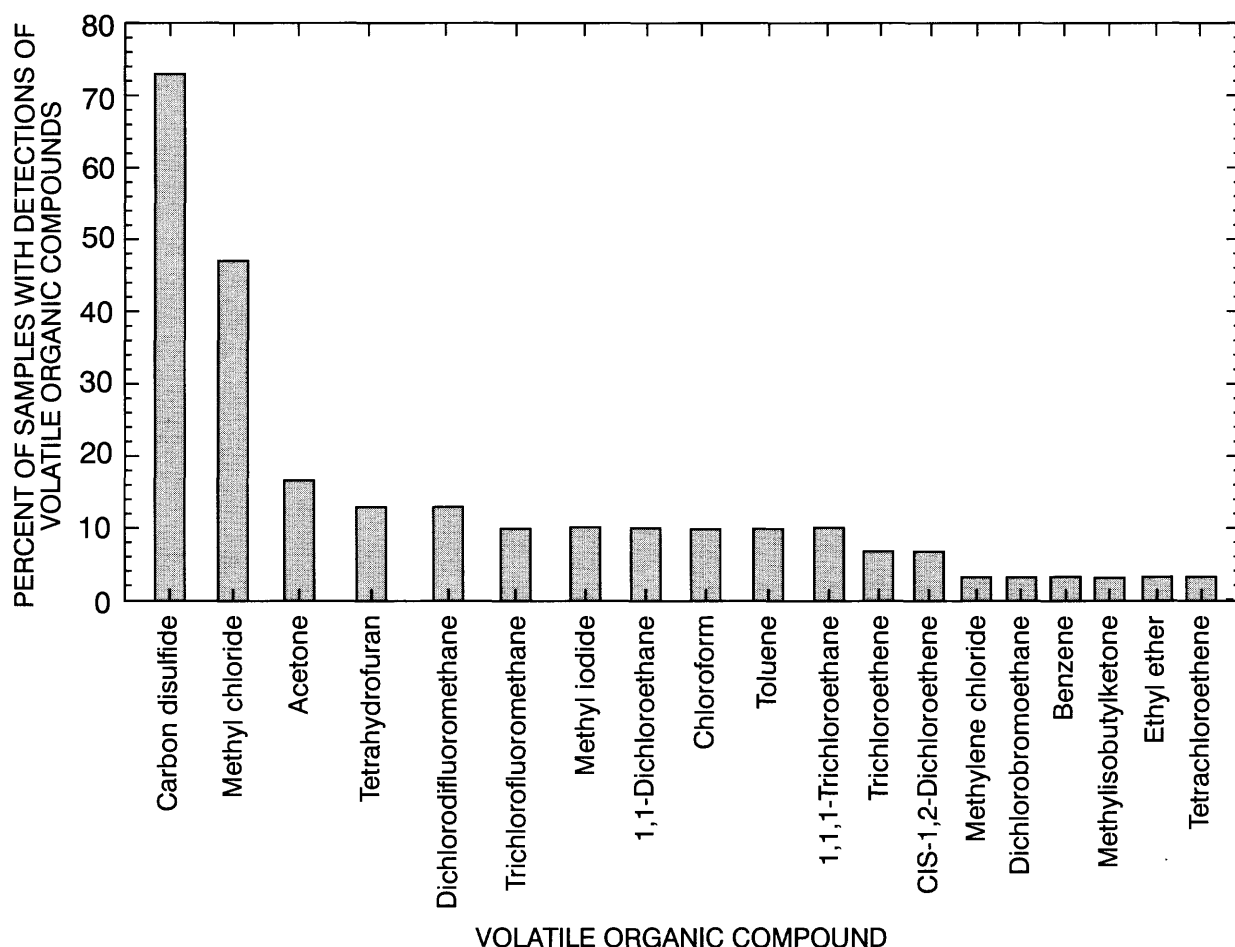


Figure 16.--Frequencies of detection of volatile organic compounds in water samples from urban land use study wells.

thousand concentrations in cigarette smoke (Verschueren, 1983). Low concentrations of methyl chloride may have been created through 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 VOC's. The USEPA has determined that methyl chloride as a possible human carcinogen and has established a lifetime health advisory for this compound of 3 µg/L for drinking water (U.S. Environmental Protection Agency, 1996), which was not exceeded in any of the water samples.

Acetone (CH_3COCH_3) was detected in water samples from five of the wells (HN-B, HN-L, HN-M, HN-O, and HN-T), all of which are located in the Hennepin County part of the urban study area (fig. 1). Acetone is a colorless liquid with a sweet odor, which is used in the manufacture of organic chemicals,

including: smokeless gunpowder, paints, varnishes, lacquers, sealants, and adhesives (Verschueren, 1983). Acetone is also present in cigarette smoke, exhaust from gasoline-burning engines, and may be emitted by the oxidation of humic substances in soils (Verschueren, 1983). According to the Toxic Release Inventory (U.S. Environmental Protection Agency, electronic commun., 1997), releases of acetone to air in Anoka and Hennepin Counties in 1993 were 50,400 lbs and 225,445 lbs, respectively. VOC's generally are detected less frequently and in lesser concentrations in surface water (Andrews and others, 1995), but acetone was detected in concentrations ranging from 7 to 20 µg/L in water samples collected by the USGS during 1996 from Shingle Creek (S. Kroening, U.S. Geological Survey, written commun., 1997). Although airborne concentrations of acetone are not known for the urban study area, the occurrence of acetone in ground water and in surface water and substantial registered

emissions of the compound indicate that it may be a substantial component of VOC's in air in the urban study area. Acetone may also be indigenously created in organic-rich soils covering portions of the urban study area.

Dichlorodifluoromethane (CCl_2F_2), also known as CFC-12 or Freon, was detected in water samples from four of the wells (CR-B, CR-F, HN-A, and HN-H) (fig. 1). CFC-12 has been used as a refrigerant, aerosol propellant, a low-temperature solvent, and a leak-detecting agent, and has been used in the manufacture of plastics and circuit boards, and was the most commonly-used CFC in automobile air conditioners (U.S. Environmental Protection Agency, electronic commun., 1997). In 1993, registered emissions of CFC-12 to air in Anoka and Hennepin Counties in the Toxic Release Inventory compiled by the USEPA were 3,000 and 66,105 lbs, respectively (U.S. Environmental Protection Agency, electronic commun., 1995). The Toxic Release Inventory records emissions of compounds by large manufacturing and disposal facilities and may underestimate total releases of compounds. CFC-12 is relatively non-toxic and has no MCL, but has a lifetime consumption advisory of 1 mg/L for drinking water (U.S. Environmental Protection Agency, 1996). Because of the ability of CFC-12 to destroy atmospheric ozone, which shields the earth from hazardous levels of ultraviolet-B solar radiation (Ciccioli, 1993), production of CFC-12 was banned in the United States as of January 1, 1995 in compliance with an international agreement, the Montreal Protocol (U.S. Environmental Protection Agency, electronic commun., 1997). CFC-12 stockpiled at that time is still being used and when that supply runs out, CFC-12 can be replaced with hydrochlorofluorocarbons, such as HFC-134a.

Tetrahydrofuran ($\text{C}_2\text{H}_4\text{OC}_2\text{H}_4$) was detected in water samples from four wells (CR-F, HN-A, HN-B, and HN-T) (fig. 1). Tetrahydrofuran is a common constituent in glues used to cement PVC piping, but no such glues were used in the construction of the monitoring wells. The wells producing water with detectable concentrations of tetrahydrofuran were in the vicinity of recently-constructed buildings (CR-F, HN-A, and HN-B) or underground sprinkler systems (HN-T). PVC pipes used in plumbing systems in new houses and in lawn irrigation systems are commonly connected with glues containing tetrahydrofuran.

Trichlorofluoromethane (CCl_3F) was detectable in concentrations below 0.1 $\mu\text{g/L}$ in water samples from three wells (CR-I, HN-A, and HN-P) (fig. 1). Trichlorofluoromethane, also known as CFC-11, is a

chlorofluorocarbon that has been used in aerosol sprays, commercial refrigeration equipment, as a blowing agent for polyurethane foams, as a cleaning compound and solvent, and in fire extinguishers (Verschuere, 1983). As with CFC-12, production of CFC-11 was banned in the United States as of January 1, 1995. A total of 5 lbs of this compound were emitted to air in 1993 by registered facilities in Hennepin County, according to the Toxic Release Inventory (U.S. Environmental Protection Agency, electronic commun., 1995).

Methyl iodide (CH_3I), a colorless to brown liquid used in medicine, organic synthesis, and microscopy (Verschuere, 1983), was detected in water samples from three wells (CR-D, HN-G, and HN-H) (fig. 1). Methyl iodide may be weakly mutagenic, but there is no evidence for carcinogenicity of this compound and no MCL or drinking-water advisories have been established.

The chlorinated alkane 1,1-dichloroethane (CHCl_2CH_3), also known as ethylidene chloride, was detected in water samples from three wells (CR-F, HN-E, and HN-S) (fig. 1). 1,1-Dichloroethane is used in the manufacture of vinyl chloride, paints, varnish and finish removers, in organic synthesis, for metal degreasing, and as a constituent of gasoline (Verschuere, 1983). Detected concentrations of 1,1-dichloroethane were all less than the MCL (7 $\mu\text{g/L}$). All three wells with detectable concentrations of this compound are located near creeks and wetlands--well CR-F is near a tributary to Coon Creek, well HN-E is next to lakes draining to Shingle Creek, and well HN-S is within a few yards of Shingle Creek (fig. 1). Detectable concentrations of 1,1-dichloroethane may be related to runoff or discharges to these creeks.

The trihalomethane compound chloroform (CHCl_3) was detected in water samples from three wells (CR-H, HN-P, and HN-Q) (fig. 1). Chloroform affects the central nervous system, liver, and kidneys, and is a probable human carcinogen (Agency for Toxic Substances and Disease Registry, electronic commun., 1997; U.S. Environmental Protection Agency, 1996). Primary sources of chloroform include: pulp and paper mills, pharmaceutical manufacturing plants, chemical manufacturing plants, sewage treatment plants discharging chlorinated wastewater, and water utilities chlorinating drinking water (Agency for Toxic Substances and Disease Registry, electronic commun., 1997). Minor sources of chloroform include automobile exhaust, use as a pesticide, tobacco smoke, decomposition of trichloroethene, and burning of plastics (Agency for Toxic Substances and Disease

Registry, electronic commun., 1997). The greatest concentration of chloroform was detected in water from well HN-Q (12.1 µg/L). Chloroform concentrations in the other two wells were less than 0.06 µg/L. Well HN-Q, which is located in Crystal (fig. 1), uses chlorinated water from the Mississippi River as the source of municipal water supply. Chlorinated surface water generally has greater concentrations of chloroform and other trihalomethanes than ground water (Andrews and others, 1995). Chloroform in water from that well may be due to irrigation of lawns with chlorinated surface water or perhaps due to leaking drinking-water supply lines.

Toluene (C₆H₅CH₃), also known as methyl benzene, was detected in water samples from three wells (HN-B, HN-G, and HN-O) (fig. 1). All of those wells are completed in sand lenses in clayey overbank deposits from the adjacent Mississippi River. Toluene concentrations in water samples collected by the USGS in 1996 from Shingle Creek, a tributary of the Mississippi River in the urban study area, ranged from <0.10 to 7.4 µg/L—generally an order of magnitude greater than concentrations in ground water in the urban study area (S. Kroening, U.S. Geological Survey, written commun., 1997). Lesser concentrations in ground water may be due to biodegradation in the unsaturated zone and in ground water (J. Zogorski, U.S. Geological Survey, written commun., 1997). Toluene can be emitted by petroleum refining and coal tar distillation and is used in the manufacture of benzene derivatives, saccharin, medicines, dyes, perfumes, TNT, and detergent (Verschuieren, 1983). Toluene is a component of gasoline and asphalt; and a solvent for paints, coatings, gums, resins, rubber, lacquer, and adhesives (Verschuieren, 1983). In 1993, in Anoka and Hennepin Counties, 99,202 and 443,311 lbs, respectively, of this compound were released to air, according to Toxic Release Inventory records (U.S. Environmental Protection Agency, electronic commun., 1995). Similar concentrations of toluene in ground water and equilibrium concentrations in air indicate that dispersion from the atmosphere or entrainment in rainfall may be the sources of this compound in ground water in the urban study area.

The chlorinated alkane 1,1,1-trichloroethane (CCl₃CH₃), also known as methyl chloroform, or 1,1,1-TCA; was detected in water samples from three wells (CR-F, 0.02 µg/L; HN-Q, 0.06 µg/L; and HN-S, 0.02 µg/L) (fig. 1). 1,1,1-TCA is used for cleaning metal and plastic molds, vapor degreasing, as a solvent, and as an aerosol (Howard, 1990). In 1993, according to Toxic Release Inventory records, 54,170

lbs of this compound were discharged to air in Anoka County, and none was discharged in Hennepin County (U.S. Environmental Protection Agency, electronic commun., 1995). 1,1,1-TCA has a high vapor pressure and migrates readily through soil into ground water (Howard, 1990). 1,1,1-TCA degrades very slowly in soils and in the unsaturated zone (Howard, 1990).

The chlorinated alkene trichloroethene (CCl₂CHCl), also known as TCE, was detected in water samples from two wells (HN-P, 0.12 µg/L, and HN-S, 0.02 µg/L) (fig. 1). TCE is used for dry-cleaning and metal degreasing; as a solvent for fats, greases, waxes, caffeine, and dyes; and as a refrigerant, fumigant and anesthetic (Verschuieren, 1983). In 1993, in Anoka and Hennepin Counties, 55,417 and 421,458 lbs, respectively, of TCE were released to air, according to records of the Toxic Release Inventory (U.S. Environmental Protection Agency, electronic commun., 1995). In ground water, TCE degrades to less chlorinated alkene compounds such as dichloroethene (DCE) and vinyl chloride.

The chlorinated alkene *cis*-1,2-dichloroethene (CHClCHCl) was detected in water from two wells (HN-N, 0.05 µg/L; and HN-S, 0.11 µg/L), both of which are located in the southeastern part of Hennepin County (fig. 1). This VOC is used as a solvent for fats, phenyls, and camphor; to retard fermentation; as a refrigerant; as an additive to dyes and lacquers; as a solvent for caffeine; as a constituent of perfumes and thermoplastics; in the manufacturing of rubber; and in medicine (Verschuieren, 1983).

Methylene chloride (CH₂Cl₂), also known as dichloromethane, was detected in the water sample from well HN-Q (fig. 1) at a concentration of 0.06 µg/L. Methylene chloride is commonly used for paint stripping and degreasing, as a refrigerant, a fumigant, a spotting agent, a blowing agent in foams, and in the manufacture of aerosols, film, synthetic fibers, pharmaceuticals, and plastics (Verschuieren, 1983). In 1993, in Anoka and Hennepin Counties, 13,300 and 254,559 lbs, respectively, of methylene chloride were released to air by registered facilities (U.S. Environmental Protection Agency, electronic commun., 1995). Water from this well had an unusually large concentration of chloroform, so the methylene chloride may be a breakdown product of chloroform.

Bromodichloromethane (CHBrCl₂), a trihalomethane also known as dichlorobromomethane, was also detected in the water sample from well HN-Q. Bromodichloromethane is used in fire-extinguishers; as a solvent for fats, waxes, and resins (Verschuieren,

1983); and is also created by chlorination of water containing natural organic substances.

Benzene (C_6H_6) was detected at a concentration of 0.16 $\mu\text{g/L}$ in the water sample from well HN-B (fig. 1). Benzene is used in the manufacturing of styrene, phenol, detergents, pesticides, plastics and resins, synthetic rubber, aviation fuel and gasoline, pharmaceuticals, dyes, explosives, PCB's, flavors and perfumes, paints and coatings, nylon intermediates, foods, and photographic chemicals (Verschuere, 1983). Benzene in the environment is most commonly associated with the storage, dispensing, and combustion of gasoline (Verschuere, 1983). Other sources of benzene include tobacco smoke, styrene production, glues, adhesives, cleaning products, and paint strippers (Agency for Toxic Substances and Disease Registry, electronic commun., 1997). Benzene affects the immune system, increases the risk of contracting leukemia, and is teratogenic (Agency for Toxic Substances and Disease Registry, electronic commun., 1997).

Methylisobutylketone ($C_2H_5OC_2H_5$), also known as hexanone, was also detected in the water sample from well HN-B (fig. 1) at an estimated concentration of 0.6 $\mu\text{g/L}$. This VOC is used as a solvent for paints, varnishes, lacquers; is used in extraction processes and organic synthesis; and is a denaturant for alcohol (Verschuere, 1983). In 1993, according to Toxic Release Inventory records, 36,040 lbs of this compound were discharged to air in Hennepin County (U.S. Environmental Protection Agency, electronic commun., 1995).

Ethyl ether ($C_2H_5OC_2H_5$), also known as ether, was also detected in the water sample from well HN-B at a concentration of 0.19 $\mu\text{g/L}$ (fig. 1). Ether is used in the manufacture of ethylene, as an industrial solvent, for analytical chemistry, as an extractant, in perfumes, an anesthetic, and as an alcohol denaturant (Verschuere, 1983). Detection of the three VOC's in water from well HN-B may be associated with the construction of new housing or with the park adjoining this well.

Tetrachloroethene (Cl_2CCCl_2), also known as PCE, was detected at an estimated concentration of 0.02 $\mu\text{g/L}$ in the water sample from well HN-O (fig. 1). PCE is used for dry-cleaning, metal degreasing; as a solvent for fats, greases, waxes, rubber, gums, caffeine, paints, and inks; and in the manufacture of trichloroacetic acid and chlorofluorocarbon compounds (Verschuere, 1983). In 1993, in Hennepin County, 235,928 lbs of PCE were emitted to air, according to records of the Toxic Release Inventory (U.S. Environmental Protection Agency,

electronic commun., 1995). In ground water, PCE can slowly degrade to TCE, DCE, and vinyl chloride.

To determine possible atmospheric deposition of VOC's, ranges of equilibrium concentrations of selected VOC's in rainwater were estimated (table 12), based on ranges in airborne concentrations of those compounds measured in downtown Minneapolis (Gary Eckhardt, Minnesota Pollution Control Agency, electronic commun., 1997). Concentrations were estimated at 10°C (the annual mean air temperature) using the following equation:

$$C_w = [C_a / (H_{10} / RT)] / 1,000 \text{ L/m}^3 \quad (3)$$

where

- C_w is the concentration in rainwater in $\mu\text{g/L}$,
- C_a is the concentration in air in $\mu\text{g/m}^3$,
- H_{10} is the Henry's Law Constant determined experimentally at 10°C in Pascals (m^3)/mol,
- R is the universal gas constant (8.314 Pascals(m^3)/molK), and
- T is temperature in degrees Kelvin.

The conversion from ppb_v (parts per billion volumetric) to $\mu\text{g/m}^3$ was made as follows:

$$C_a (\mu\text{g/m}^3) = 0.0409 (C_a (\text{ppb}_v)) \times MW \quad (4)$$

where

- MW is molar weight of the compound of interest.

Equilibrium concentrations of many of the VOC's in hypothetical rainwater at 10°C were less than detected concentrations in ground-water samples for dichlorodifluoromethane, trichlorofluoromethane, 1,1-dichloroethane, and *cis*-1,2-dichloroethene (table 12). However, equilibrium concentrations of chloroform, toluene, 1,1,1-trichloroethane, trichloroethene, methylene chloride, benzene, and tetrachloroethene were in the ranges of concentrations detected in ground water from some of the urban land use wells (table 12), indicating that a combination of atmospheric recharge of VOC's, as well as point sources such as leaking underground storage tanks, or spills contribute VOC's to shallow ground water in the urban study area.

Tritium

Tritium (^3H or T) is an isotope of hydrogen, usually

occurring in water molecules, that breaks down to deuterium (^2H or D) through emission of a β particle. Tritium decays rapidly, with a half-life of 12.43 years. Tritium is naturally produced in the atmosphere by reactions between atmospheric nitrogen and oxygen. Anthropogenic sources of tritium include nuclear reactors and detonations of thermonuclear weapons. Prior to the advent of atmospheric testing of fusion bombs in 1953, tritium concentrations in rainwater were less than 10 tritium units (1 tritium unit (TU) = one tritium atom/ 10^{18} hydrogen atoms) (Drever, 1988). During the 1960's, at the peak of atmospheric nuclear weapons testing, tritium concentrations in rainwater increased to over 5,000 TU (Plummer and others, 1993). Current tritium concentrations in rainwater are approximately 10 TU (Bob Michael, U.S. Geological Survey, written commun., 1997). Tritium concentrations less than 10 TU indicate that ground water was recharged prior to 1953, making tritium an indicator of ground-water recharge age.

Water samples from 15 of the 30 urban land use wells were analyzed for tritium concentrations to evaluate the hypothesis that ground-water in the relatively permeable, shallow aquifer has been recharged in the past 45 years. Tritium concentrations in those 15 water samples ranged from 10.3 to 27.2 TU's (table 13), indicating that shallow ground water in the urban study area has probably been recharged since the mid-1950's, contemporaneous with urban residential/commercial development.

Quality Assurance/Quality Control

A total of ten quality-assurance/quality-control (QA/QC) samples were collected in accordance with NAWQA protocols (Koterba and others, 1995). These samples included two field/equipment blanks for all constituents), three VOC-only field/equipment blanks, one VOC trip blank, one VOC source-solution blank, two spikes (pesticides and VOC's), and one replicate. Field/equipment blanks are collected to evaluate the cleanliness of sampling equipment and the potential for cross-contamination between wells. Source-solution blanks are collected to evaluate the purity of water used for the collection of field/equipment blanks. Trip blanks are sealed vials of VOC's kept in the sampling vehicle for a specified period of time to evaluate if atmospheric contamination of the VOC vials may be occurring. Spikes are collected to determine if pesticide or VOC compounds can escape or degrade during collection and shipment. Replicate samples are collected to determine if the water was chemically stable during sample collection or if water quality was changing during sample collection, and to determine the precision of sampling and analytical methods.

Blanks taken were one of three types: field/equipment blanks, trip blanks, and source-solution blanks. Field/equipment blanks consist of three types of water prepared to be free of analyzed major ions and nutrients, pesticides, and VOC's, respectively, that have been

Table 13. Tritium concentrations in water samples from selected monitoring wells
[Concentrations in tritium units]

Well	Tritium concentration
CR-B	10.3
CR-D	10.6
CR-F	12.2
CR-H	12.2
HN-A	13.1
HN-C	13.2
HN-D	10.7
HN-G	26.7
HN-I	12.5
HN-K	14.0
HN-M	14.0
HN-O	27.2
HN-Q	11.9
HN-S	14.1
HN-U	24.7

pumped through the sampling system after standard post-sampling cleaning. Field/equipment blanks are used to check the efficacy of cleaning procedures and that field methods, sample shipment, and laboratory procedures are not contaminating samples. Trip blanks consist of vials filled with VOC-free blank water prepared at the USGS National Water-Quality laboratory which are sealed and kept in the sampling vehicle for a defined period of time. Trip blanks verify that VOC vials are not being contaminated during storage, sampling, and shipment to the laboratory, and analysis. One VOC trip blank (composed of three vials) was placed in the sampling vehicle for one week and was subsequently shipped to the laboratory with other samples. Source-solution blanks are comprised of the same types of water used for field/equipment blanks, for source-solution blanks those types of water are decanted directly into bottles and vials and are shipped to the laboratory, as a check for contaminants in the water and

to check contaminants that may be added by the sampling equipment.

Several major ions, trace elements, and nutrients, including calcium, magnesium, sodium, silica, organic carbon, ammonia-nitrogen, phosphorus, chromium, copper, iron, zinc, and aluminum, were detected at low concentrations in some of the blank samples (table 14). Constituents not listed in table 14 were not detected in the blanks. For the most part, detected concentrations of analytes in the blank samples were much less than those reported in ground-water samples, indicating a low likelihood of cross-contamination of ground-water samples. Low concentrations of trace metals in blanks may be due to the stainless steel pump and swagelok fittings in the sampling system and the aluminium foil used to wrap the pump between samples, as reported in Menheer and Brigham (1997). Concentrations of chromium, copper, iron, and zinc were in the lower ranges of those detected in ground-water samples,

Table 14. Reporting and detection limits and ranges in detected concentrations of analytes in blanks
[µg/L, micrograms per liter; na, not analyzed, E, low-level detection with estimated concentration]

Compound	Reporting limit [detection limit] (µg/L)	Field/equipment blanks-- range in concentrations (µg/L)	Trip blank-- concentration (µg/L)	Source-solution blank-- concentration (µg/L)
Calcium	0.02	0.22–0.81	na	<0.02
Magnesium	0.01	0.01–0.04	na	<0.01
Sodium	0.2	<0.2–1.6	na	<0.2
Silica	0.01	0.46–9.1	na	0.01
Organic carbon	0.1	0.2–0.3	na	0.3
Ammonia-nitrogen	0.01	0.02–0.04	na	0.02
Phosphorus	0.01	<0.01–0.07	na	<0.01
Chromium	1.0	2.0–4.0	na	<1.0
Copper	1.0	<1.0–3.0	na	<1.0
Iron	3.0	9.0–28.0	na	<3.0
Zinc	1.0	2.0–7.0	na	1.0
Aluminum	1.0	9.0–91.0	na	4.0
Bromodichloromethane ¹	[0.034]	E0.03–<0.1	<0.1	<0.1
Chlorodibromomethane	[0.087]	E0.02–<0.1	<0.1	<0.1
Chloroform ¹	[0.031]	E0.03–E0.073	<0.05	E0.08
Toluene	[0.035]	<0.05–E0.06	<0.05	0.17
Benzene ¹	[0.033]	<0.05–E0.05	<0.05	<0.05
Chlorobenzene	[0.031]	<0.05	<0.05	E0.08
Methylene chloride ¹	[0.081]	<0.1	<0.1	E0.09
1,4-Dichlorobenzene	[0.037]	<0.05–E0.06	<0.05	<0.05
Carbon disulfide	[0.035]	E0.017–E0.05	<0.05	<0.05
Styrene	[0.03]	<0.05	<0.05	E0.02
Acetone ¹	[0.50]	<5.0	<5.0	13.0
Methyl ethyl ketone ¹	[0.27]	E0.92–<5.0	<5.0	2.8

¹Compound also was detected by the laboratory in certification tests of the blank water used.

indicating that the determined concentrations of those elements in ground water may not reflect their true concentrations. Aluminum concentrations in blanks were in the upper range of concentrations detected in ground-water samples, indicating that aluminum (the primary component of the foil used to wrap the pump after cleaning) detected in ground water was even more likely to be an artifact of sampling equipment. However, when ground-water samples were collected, larger volumes of water (30-50 gallons) are purged through the sampling system prior to sample collection than when blanks were collected (1-3 gallons), which would tend to minimize the concentrations of these metals contributed by the sampling equipment to those samples.

Eight VOC's were detected in the field/equipment blanks, no VOC's were detected in the trip blank, seven VOC's were detected in the source-solution blank, and no pesticides were detected in any blank samples (table 14). Concentrations of all of the detected VOC's in the field/equipment blanks were reported as estimated values, meaning that they were detected at concentrations below the lowest daily calibration standard. Four of the eight VOC's detected in field/equipment blanks were detected in certification tests of the "VOC-free" blank water prior to its use--chloroform, toluene, chlorobenzene, and methyl ethyl ketone. The VOC's determined to be in the water by certification, but not detected in the equipment blanks (chlorobenzene, methylene chloride, styrene, and acetone), may have been lost to the atmosphere while decanting the water into the standpipe in which the pump was placed or while filling the sample vials. VOC's detected in the equipment blanks, but not in the certification tests of the blank water (bromodichloromethane, chlorodibromomethane, benzene; 1,4-dichlorobenzene, and carbon disulfide), may have come from the tap water or the deionized water used to clean the sampling pump and associated Teflon tubing prior to collection of the blank samples or from the atmosphere while collecting the blanks. The two trihalomethanes detected in the equipment/field blanks (bromodichloromethane, and chlorodibromomethane) are commonly associated with chlorinated tap water.

Spike samples were collected to assess the recovery bias and precision/variability in recoveries of pesticides and VOC's due to matrix interference or analyte degradation. Extra water samples collected from wells CR-F and HN-P were spiked with known volumes of solutions containing known concentrations of selected pesticides and VOC's. Two pesticide replicate samples

and three VOC replicate samples were spiked with the identical volumes of their respective spike solutions, except in the case of the sample from HN-P analyzed for schedule 2051, for which only one sample was spiked. In addition to spike samples, surrogates comprised of compounds similar in character to the standard analytes were added to every pesticide and VOC sample before analysis to assess recoveries.

Most pesticides analyzed on Schedule 2010 had mean recoveries ranging between 75 and 120 percent except for deethylatrazine, azinphos-methyl, benfluralin, carbaryl, carbofuran, *p,p'*-DDE, disulfoton, linuron, methyl parathion, metribuzin, pendimethalin, *cis*-permethrin, phorate, and thifluralin (table 15). Relatively low mean percent recoveries for compounds such as deethylatrazine indicate that these compounds degraded in the spiking mixture, volatilized during spiking or may have been subject to interferences during analyses, meaning that frequencies of detection and reported concentrations of those compounds in groundwater may have been underestimated. The mean recoveries for the 2010 surrogates (compounds added to each sample, but not reported as being detected by the lab, including diazinon surrogate, α D6 HCH surrogate, and terbuthylazine) ranged from 99.6 to 120.3 percent (table 15). The recoveries for schedule 2051 pesticides were more variable and less than the recoveries for schedule 2010 pesticides--mean recoveries for schedule 2051 pesticides ranged from 0 to 112 percent (table 16). The mean recovery of the surrogate in schedule 2051, BDMC, was 110 percent. The spike solution for 2051 comes in two parts, acid and base. Two different spike-solution lots were added to the two spiked samples. The base portions of both had the same concentrations of the same compounds, but the two acid portions of both solutions were slightly different in composition, leading to no recoveries of some of those compounds. Mean recoveries in VOC spike samples ranged from 65.4 to 113 percent (table 17). Mean VOC surrogate recoveries ranged from 81.0 to 107 percent for 1,2-dichloroethane; toluene, D8; and for *p*-bromofluorobenzene (table 17).

The purpose of collecting replicate samples was to look at the variability due to sample collection and laboratory analysis. One set of replicate samples was collected from well CR-E (table 18, fig. 1). Constituents with concentrations varying by more than 5 percent between the sample and replicate included ammonia, nitrite nitrogen, ammonia+organic-nitrogen, phosphorus, orthophosphorus, chromium, molybdenum,

Table 15. Reporting limits, ranges in recovery percents, and mean recovery percents from Schedule 2010 pesticide spikes

[µg/L, micrograms per liter; nd, not determined]

Compound	Reporting limit (µg/L)	Range in percent recovery	Mean percent recovery	
			Well CR-F	Well HN-P
Acetochlor	0.002	84.2–95.2	89.5	89.7
Alachlor	0.002	87.9–105	98.7	96.3
Atrazine	0.001	87.1–99.7	92.1	98.3
Deethylatrazine	0.002	29.3–50.8	31.1	45.2
Azinphos-methyl	0.001	102–310	310	151
Benfluralin	0.002	55.3–81.9	60.1	69.6
Butylate	0.002	73.5–90.7	79.1	89.6
Carbaryl	0.003	110–238	113	235
Carbofuran	0.003	116–219	118	207
Chlorpyrifos	0.004	92.5–109	104	98.6
Cyanazine	0.004	89.7–124	89.8	117
DCPA (dacthal)	0.002	102–125	118	103
<i>p,p'</i> -DDE	0.006	56.7–76.2	60.0	73.7
Diazinon	0.002	85.4–105	91.3	96.3
Dieldrin	0.001	72.1–91.4	75.7	86.4
Diethylaniline	0.003	72.7–86.6	74.8	85.4
Disulfoton	0.017	50.9–85.7	74.2	68.3
EPTC (eptam)	0.002	83.7–89.7	86.1	87.7
Ethalfuralin	0.004	58.3–105	61.9	93.1
Ethoprop	0.003	91.4–114	95.6	108
Fonofos	0.003	71.7–95.2	76.6	88.8
α-HCH	0.002	86.3–105	90.8	98.6
γ-HCH (lindane)	0.004	90.5–105	95.2	98.6
Linuron	0.002	99.9–133	106	122
Malathion	0.005	92.2–124	97.9	108
Methyl parathion	0.006	47.6–114	48.7	113
Metolachlor	0.002	91.6–114	101	103
Metribuzin	0.004	61.0–95.2	61.6	86.0
Molinate	0.004	80.2–95.2	84.9	93.9
Napropamide	0.003	76.5–95.2	79.3	93.9
Parathion	0.004	101.7–122	118	103
Pebulate	0.004	80.1–92.3	85.9	91.5
Pendimethalin	0.004	53.0–92.3	55.4	78.5
<i>cis</i> -permethrin	0.005	16.9–95.2	19.1	89.2
Phorate	0.002	49.9–83.8	70.9	66.9
Prometon	0.018	94.5–111	98.9	105
Pronamide	0.003	86.3–105	90.8	98.6
Propachlor	0.007	84.1–114	87.9	108
Propanil	0.004	93.9–114	101	108
Propargite	0.013	84.2–98.1	91.1	91.1
Simazine	0.005	86.3–105	89.5	103
Tebuthiuron	0.01	95.6–124	96.4	117
Terbacil	0.007	80.1–133	81.8	127
Terbufos	0.013	62.9–95.2	87.0	79.1
Thiobencarb	0.002	85.4–105	90.4	103
Triallate	0.001	84.2–95.4	89.8	90.1
Trifluralin	0.002	56.6–87.6	60.7	75.7
Surrogates				
Diazinon	nd	92.5–112	110	99.6
α D6 HCH	nd	99.5–121	118	104
Terbuthylazine	nd	106–124	120.3	108

Table 16. Reporting limits, ranges in recovery percents, and mean recovery percents from Schedule 2051 pesticide spikes
[µg/L, micrograms per liter; nd, not determined]

Compound	Reporting limit (µg/L)	Range in percent recovery	Mean percent recovery	
			Well CR-F	Well HN-P
Acifluorfen	0.035	33.4–58.7	42.7	58.7
Aldicarb	0.016	0–54.5	27.3	-- ²
Aldicarb sulfone	0.021	0–34.6	17.3	13.3
Aldicarb sulfoxide	0.016	47.3–84.2	80.5	47.3
Bentazon	0.014	43.4–65.2	48.8	65.2
Bromacil	0.035	68.6–93.1	76.2	93.1
Bromoxynil	0.035	42.5–69.1	54.0	69.1
Carbaryl	0.008	38.2–76.8	49.2	76.8
Carbofuran	0.028	56.0–73.4	64.7	73.0
3-hydroxycarbofuran	0.014	47.2–65.9	50.9	65.9
Chlorothalonil	0.035	12.6–46.8	44.6	12.6
Clopyralid	0.05	0–46.3	0	46.3
2,4-D	0.035	28.8–70.9	49.8	67.2
2,4-DB	0.035	33.9–64.9	45.3	64.9
Dacthal (DCPA)	0.017	40.8–67.8	47.0	67.8
Dicamba	0.035	0–60.3	3.5	60.3
Dichlobenil	0.02	51.5–57.6	51.5 ¹	57.6
Dichlorprop	0.032	33.8–64.9	44.8	64.9
Dinoseb	0.035	43.0–63.0	51.5	63.0
Diuron	0.02	64.1–86.3	67.7	86.3
DNOC	0.035	44.3–63.3	47.2	63.3
Esfenvalerate	0.019	10.8–56.6	18.1	56.6
Fenuron	0.013	66.1–72.0	67.3	72.0
Fluometuron	0.035	58.9–93.9	84.3	58.9
Linuron	0.018	71.1–81.3	76.2	72.6
MCPA	0.05	46.0–67.1	56.2	67.1
MCPB	0.035	29.6–60.0	40.0	60.0
Methiocarb	0.026	57.8–77.5	61.9	77.5
Methomyl	0.017	51.1–84.4	67.7	71.9
1-naphthol	0.007	0	0	0
Neburon	0.015	54.0–72.8	62.7	72.8
Norflurazon	0.024	69.9–112.0	90.9	74.5
Oryzalin	0.019	44.4–63.1	44.4 ¹	63.1
Oxamyl	0.018	33.8–56.1	45.0	55.9
Picloram	0.05	20.4–61.8	23.2	61.8
Propham	0.035	94.0	-- ¹	94.0
Propoxur	0.035	55.0–63.8	55.9	63.8
Silvex	0.021	41.7–68.4	47.7	68.4
2,4,5-T	0.035	39.4–67.0	45.3	67.0
Triclopyr	0.05	25.7–70.0	28.3	70.0
Surrogates				
BDMC	nd	81–118	98.7	110

¹Only one sample was analyzed for this compound

²Not analyzed due to interference

Table 17. Detection limits, ranges in recovery percents, and mean recovery percents from VOC field spikes
[µg/L, micrograms per liter; nd, not determined]

Compound	Detection limit (µg/L)	Range in percent recovery	Mean percent recovery	
			Well CR-F	Well HN-P
Bromodichloromethane	0.01	86.9–113	104	91.3
Bromoform	0.02	65.4–84.6	84.6	67.9
Carbon tetrachloride	0.05	76.2–100	90.5	93.7
Chlorodibromomethane	0.01	79.2–100	94.4	80.5
1,4-dichlorobenzene	0.05	77.3–100	95.5	80.3
1,2-dichloroethane	0.05	95.2–110	106	98.4
1,1-dichloroethene	0.01	82.6–100.0	94.2	84.0
Ethylbenzene	0.05	86.4–104	98.5	90.9
MTBE	0.01	79.2–95.8	94.4	80.5
Tetrachloroethylene	0.01	66.7–85.7	74.6	85.7
1,1,1-trichloroethane	0.05	94.1–114	106	96.7
Trichloroethylene	0.05	81.8–100.0	92.4	93.4
Vinyl chloride	0.01	62.5–100.0	87.5	70.8
Surrogates				
1,2-dichloroethane	nd	99.0–107	105	103
Toluene, D8	nd	97.0–102	102	97.7
P-bromofluorobenzene	nd	81.0–107	107	82.3

Table 18. Reporting limits and ranges in concentrations of compounds with greater than 5 percent differences in replicate concentrations

Compound	Reporting limit	Well CR-E concentration	Well CR-E replicate concentration
Ammonium-nitrogen (mg/L)	0.01	0.02	0.03
Nitrite-nitrogen (mg/L)	0.01	0.05	0.02
Ammonia + organic-nitrogen (mg/L)	0.2	0.4	0.2
Phosphorus (mg/L)	0.01	0.05	<0.01
Orthophosphorus (mg/L)	0.01	0.03	0.02
Chromium (µg/L)	1.0	4.0	3.0
Molybdenum (µg/L)	1.0	2.0	1.0
Zinc (µg/L)	1.0	2.0	4.0
Aluminum (µg/L)	1.0	5.0	6.0

zinc, and aluminum (table 18). The differences in concentrations for these constituents between the sample and replicate were less than 0.2 mg/L for nutrients and less than 2.0 µg/L for the trace metals. Constituents not listed in table 18 had differences of less than 5 percent between the original sample and the replicate.

Effects of Land Use On Ground-Water Quality

Land use is one of the most important factors affecting water quality. Volatile organic compounds are more

likely to be detected in ground and surface water near industrial and commercial facilities and landfills, where those compounds are used or disposed of in large quantities (Andrews and others, 1995). Pesticides and nutrients are more likely to be detected in agricultural areas, where they are most heavily applied. Sodium, chloride and certain herbicides are more likely to be detected in ground water adjacent to highways or other right-of-ways where those compounds are applied. As mentioned previously, differences are apparent in median concentrations or in ranges in concentrations for some constituents between wells in the urban study area and wells sampled in part of the UMIS study unit (Stark and others, 1996). This part of the UMIS study unit

encompasses areas of urban, agricultural, and forested/undeveloped land covers, whereas the urban study area includes only urban residential/commercial land covers.

The median nitrate concentrations were greater in water samples from the 30 urban land use wells (1.4 mg/L) than in water samples from 642 wells completed in surficial sand and gravel aquifers throughout the UMIS focused study area (0.9 mg/L) (table 7, Stark and others, 1996). Anderson (1993), however, reported greater median nitrate concentrations in ground-water samples from unconfined sand and gravel aquifers overlain by agricultural (2.0 to 5.3 mg/L) and residential (4.2 mg/L) areas of the Anoka Sand Plain. Landon and Delin (1995) reported a range of nitrate concentrations from 0.1 to 21 mg/L, with a median of 10 mg/L, in water samples from 19 shallow monitoring wells in agricultural areas of the Anoka Sand Plain.

The median chloride concentration was approximately one order of magnitude greater in water samples from the 30 urban land use wells (46 mg/L) than in water samples from 992 wells completed in unconfined sand and gravel aquifers (5.8 mg/L) sampled throughout the UMIS focused study area (Stark and others, 1996). Anderson (1993) similarly reported the greatest median chloride concentration in ground-water beneath residential (26 mg/L), as opposed to agricultural (6.0 to 19 mg/L), areas of the Anoka Sand Plain. Landon and Delin (1995) reported a median chloride concentration of about 15 mg/L in water from 17 wells completed in agricultural portions of the Anoka Sand Plain. The primary source of greater chloride in water samples from the urban study area wells is sodium chloride salt applied with sand to deice roads during the winter. The density of multi-lane highways, where most of the salt is applied, is much greater in the urban study area than in the surrounding less-developed areas. Additionally, concentrations of other major ions, such as calcium and magnesium, and of the trace metals iron and manganese, were greater in water samples from the 30 urban land use wells than in water from 28 wells sampled in residential parts of the Anoka Sand Plain, as reported by Anderson (1993). Whereas trichloroethene was the most frequently detected VOC in water from wells completed in sand and gravel aquifers in part of the UMIS study unit (3.6 percent of 333 wells sampled by the USGS and other agencies) (Andrews and others, 1995), trichloroethene occurrence was exceeded by the much greater frequencies of detection and concentrations of the VOC's carbon disulfide (22 of 30 wells), acetone (5 of 30 wells), and several chlorofluorocarbons in water samples from the wells in

the urban study area (table 12).

In the water samples collected in the urban study area, prometon, an herbicide generally applied to right-of-ways, was the most frequently detected pesticide (detected in samples from 10 of 30 wells, whereas atrazine was detected in water from 6 of 30 wells). For sand and gravel aquifers in part of the UMIS study unit, however, atrazine was the most frequently detected pesticide (32 percent of 85 wells) in water samples from unconfined sand and gravel aquifers (J.D. Fallon, U.S. Geological Survey, written commun., 1997). Throughout the Anoka Sand Plain, where agriculture is the dominant land use, Anderson (1993) reported detection of atrazine in water from 8 of 18 wells, and Landon and Delin (1995) reported detection of atrazine in water from 11 of 34 wells.

To further evaluate the effects of land use on ground-water quality in the urban study area, local land uses, population densities, and distances to features that could affect ground-water quality were quantified or estimated in the vicinity of each of the 30 urban land use wells. Land uses within a 500-meter (m) radius of each well were determined through digitization of aerial photographs and field verification of local features. The predominant land use surrounding the wells was residential--predominantly detached single-family houses (table 19). Parks, schools, wetlands, open water, right-of-ways, health care facilities, commercial establishments, and industrial facilities were secondary land uses in the vicinity of many of the wells. Population densities within a 500-m radius of each well were estimated by counting numbers of residences and multiplying single-family homes by an assumed average of 2.3 persons/home. Populations for multifamily residential units were similarly estimated by sizes of complexes.

Land uses surrounding the wells significantly affected the frequencies of detection and detected concentrations of some of the analyzed constituents, based on results of the nonparametric Kendall tau test (Kendall, 1975) (table 20). Magnesium and sulfate concentrations tended to be greater in water from wells in areas with greater than 70 percent residential land use. Because residential areas are generally better-drained with deeper water tables (wetlands are usually the last areas to be developed), there is greater opportunity for dissolution of minerals containing those constituents. Areas with greater percentages of residential land uses also tended to have lesser frequencies of detection and lesser detected concentrations (negative tau values) of prometon and

Table 19. Primary and secondary land uses and estimated population densities within a 500-meter radius of each well

Well	Predominant land use [percentage of land area]	Secondary land uses [percentage of land area]	Estimated population densities (persons per square kilometer)
CR-A	Residential [59]	School [17], Park [14]	350
CR-B	Residential [86]	Park [8.8], Wetlands [4.0]	740
CR-C	Residential [62]	Park [27], Open Water [2.0]	795
CR-D	Residential [45]	Park [28], Industrial [3.3], School [1.5]	900
CR-E	Residential [59]	Park [18], Wetland [14], Health care [5.4]	960
CR-F	Residential [38]	Wetland [27], School [14], Park [9.6], Industrial [4.4]	420
CR-G	Residential [65]	Commercial [15], Park [12], Wetland [4.0], Right-of-Way [4.0]	880
CR-H	Residential [56]	Open Water [34], Park [9.5]	490
CR-I	Residential [69]	Park [13], Commercial [1.2]	1,260
HN-A	Residential [86]	School [7.0], Park [5.4]	738
HN-B	Residential [68]	Park [26], Open Water [2.9], Industrial [1.2]	1,200
HN-C	Residential [79]	School [8.6], Park [5.4], Open Water [2.7], Wetland [1.6]	1,070
HN-D	Residential [81]	Park [10], School [8.4]	960
HN-E	Residential [63]	Park [19], Wetland [13], Open Water [2.7], School [2.6]	960
HN-F	Residential [82]	Park [14], Open Water [2.1], Wetland [1.6]	950
HN-G	Residential [74]	Park [13], Right-of-Way [8.9], School [1.4]	1,440
HN-H	Residential [57]	Commercial [33], Right-of-Way [5.5], School [1.9], Health care [1.3]	1,540
HN-I	Residential [80]	School [6.6], Park [6.5], Open Water [2.5], Right-of-Way [2.0]	1,140
HN-J	Residential [83]	Park [11], Commercial [2.7], School [2.7]	770
HN-K	Residential [62]	Right-of-Way [15], Industrial [14], Park [6.0], Commercial [1.2]	1,720
HN-L	Residential [61]	Open Water [19], Wetland [7.3], Park [5.2], Right-of-Way [3.7]	910
HN-M	Residential [45]	Park [34], Wetland [17], Open Water [3.1]	860
HN-N	Residential [98]	Right-of-Way [1.8]	390
HN-O	Residential [80]	Right-of-Way [11], Park [7.1], Commercial [1.6]	1,530
HN-P	Residential [52]	Right-of-Way [32], Commercial [13]	1,480
HN-Q	Residential [49]	Open Water [20], Right-of-Way [11], Park [10], Commercial [2.4]	1,170
HN-R	Residential [48]	Commercial [20], Park [14], Right-of-Way [9.5], School [4.3], Wetland [2.6]	1,900
HN-S	Residential [53]	Industrial [22], Park [11], Right-of-Way [6.4], School [5.7], Commercial [1.0]	2,150
HN-T	Residential [50]	Park [16], Commercial [15], Open Water [13], Right-of-Way [6.6]	1,820
HN-U	Residential [48]	Park [16], Commercial [0.7]	1,970

Table 20. Ground-water constituent concentrations with significant correlations (α less than or equal to 0.05, using the Kendall Tau nonparametric test) to urban land use characteristics within 500 meters of the wells
[(X), tau value; (α), alpha value]

Land use characteristics										Well area characteristics		
Residential	Commercial	School	Health care	Industrial	Right-of-way	Park	Wetland	Water	Distance to road	Distance to water	Population density	
Magnesium (0.27, 0.04)	Organic plus ammonium nitrogen (0.42, 0.005)	Chloride (0.33, 0.02)	Phosphorus (0.36, 0.03)	Bromacil (0.060, 0.0007)	Deethylatrazine (0.32, 0.04)	Turbidity (0.26, 0.04)	Bromide (-0.34, 0.02)	Chloroform (0.41, 0.01)	Barium (-0.29, 0.03)	Bromacil (-0.32, 0.05)	Barium (0.38, 0.004)	
Sulfate (0.33, 0.01)	Orthophosphorus (0.38, 0.01)	Manganese (0.33, 0.02)	Orthophosphorus (0.32, 0.05)	1,1-Dichloroethane (0.46, 0.009)	Trichloroethane (0.33, 0.05)	Dichlorofluoromethane (-0.30, 0.05)				p,p'-DDE (-0.32, 0.04)	Orthophosphorus (0.39, 0.004)	
Phosphorus (-0.49, 0.0005)	Nitrite (-0.35, 0.03)	Dissolved oxygen (-0.31, 0.02)	Organic plus ammonium nitrogen (0.33, 0.05)	1,1,1-Trichloroethane (0.44, 0.01)	Orthophosphorus (0.43, 0.004)	Methyl Chloride (0.34, 0.02)					Silica (0.28, 0.03)	
Organophosphorus (-0.29, 0.03)	pH (-0.33, 0.02)	1,1-Dichloroethane (0.34, 0.04)	Selenium (0.64, 0.0004)		Tebuthiuron (0.40, 0.01)						Tritium (0.43, 0.03)	
Tebuthiuron (-0.34, 0.03)	Tebuthiuron (0.44, 0.008)	Bromacil (0.33, 0.05)									Sodium (0.29, 0.02)	
Prometon (-0.46, 0.001)	Prometon (0.30, 0.05)										Bromide (0.42, 0.002)	
Deethylatrazine (-0.35, 0.02)											Chloride (0.29, 0.03)	
Atrazine (-0.37, 0.01)											Tebuthiuron (0.40, 0.009)	
EPTC (-0.32, 0.04)											Carbon disulfide (0.36, 0.009)	
1,1,1-Trichloroethane (-0.32, 0.04)												

tebuthiuron, herbicides primarily used on right-of-ways, perhaps due to fewer major roadways near those wells. Concentrations of phosphorus, orthophosphorus, atrazine, deethylatrazine, and EPTC were generally greater in areas with lesser percentages of residential land use. Areas with lesser densities of residential development in the urban study area are typically more recently developed and are in closer proximity to land currently or recently used for agricultural purposes, for which most of those herbicides are applied. The three wells producing water with detectable concentrations of 1,1,1-TCA were also located in areas with lesser percentages of residential development. Two of those wells were within 200 m of industrial facilities. Concentrations of 1,1-dichloroethane, another chlorinated solvent used by industry, were also positively correlated to percent of industrial land use (table 20).

Causes of some of the correlations listed in table 20 are difficult to ascertain and may be due to factors other than land use. For example, greater manganese and lesser dissolved oxygen concentrations in ground water in areas with greater percentages of schools may be due to factors other than that land use. Similarly, the significant positive correlations between percentages of schools and prometon in ground water may not be due to use of prometon on school grounds, but rather to the proximity of schools to roadways along which that chemical may have been applied. Because of uncertainties in delineating local ground-water flow directions, land uses were not delineated for upgradient areas from the wells, but are summarized for the radial area within 500 m of each well. Correlations between some land uses and water-quality constituent concentrations may have been weakened by not limiting land-use analysis to areas upgradient of the wells.

Summary and Conclusions

As part of a national analysis of the effects of urban land use on ground-water quality for the National Water Quality Assessment Program, the U.S. Geological Survey installed, developed, and sampled 30 shallow monitoring wells completed in a surficial aquifer near the Mississippi River in the northwestern part of the Twin Cities metropolitan area in Minnesota during the spring of 1996. Sediment samples collected during drilling were analyzed for pH, grain-size distribution and organic-carbon content. Water levels were measured and a water-table potentiometric map of the urban study area was made. Water samples from each well were analyzed for approximately 240 compounds, including

physical parameters, major ions, trace metals, nutrients, pesticides, VOC's, and tritium (from selected wells).

Split-spoon samples of sediments were collected below soils and below the water table during drilling for most wells. Most sediment samples had relatively high hydraulic conductivities (ranging from 0.01 to 238 feet per day), low organic-carbon concentrations (0.10–41 grams per kilogram), and mostly alkaline pH values (5.1–9.6) indicating a high susceptibility to leaching of fertilizers and organic substances applied or spilled to the land surface, particularly alkaline pesticides.

Water levels measured in the monitoring wells, which ranged from about 2 to 23 feet below land surface, indicated that shallow ground water flows primarily toward the Mississippi River in the urban study area. Most of the water samples had low dissolved oxygen concentrations (less than 3 milligrams per liter). Specific conductances generally were greater than 600 microsiemens per centimeter. Calcium, magnesium, sodium, bicarbonate, chloride, and sulfate were the primary dissolved constituents in water samples. Sodium and chloride concentrations generally were greater than commonly reported in the region, probably due to leaching of sodium chloride applied to roads during the winter. Iron and manganese concentrations exceeded secondary maximum contaminant levels of 300 and 50 micrograms per liter, respectively, in many of the water samples. Most other trace-metal concentrations were less than 10 micrograms per liter and many were below reporting limits. Mineral saturation indices indicated that calcite, dolomite, and gypsum were slightly undersaturated in most water samples, and that quartz, and many oxides and hydroxides of iron and manganese were near equilibrium or oversaturated in all of the water samples.

Elevated concentrations of nutrients in ground water can affect human health (nitrate) and can contribute to eutrophication of lakes and streams (nitrate and phosphorus). The median concentration of nitrate-nitrogen, the primary nutrient of concern in ground water, ranged from less than 0.05–16 mg/L with a median concentration of 1.4 mg/L. Dissolved phosphorus concentrations ranged from less than 0.01 to 1.5 milligrams per liter in the water samples. Water from one well was oversaturated with hydroxyapatite, a phosphatic mineral that has been used as a fertilizer.

Pesticides were detected in water from 16 of the wells, but detected concentrations of those compounds were generally less than 1.0 microgram per liter. Prometon, an herbicide commonly used on right-of-

ways, was the most commonly detected pesticide, being detected in water from 10 of the wells. Atrazine, and its metabolite deethylatrazine, were detectable in water samples from six and eight wells, respectively. Atrazine is commonly applied to land planted with corn and was detected in rainfall at concentrations which were generally less than 1 microgram per liter in a study conducted near the urban study area in 1995. Other pesticide compounds used in agriculture, right-of-way weed control, or lawn care that were detected in ground-water samples included: tebuthiuron, EPTC, *p,p'*-DDE, metolachlor, simazine, bentazon, and bromacil.

Volatile organic compounds were detected in water samples from 26 of the 30 urban land use wells, but the detected concentrations of most those compounds were less than 1 microgram per liter and none of the detected concentrations exceeded MCL's. Carbon disulfide, which may be produced by bacteria in soils, was the most commonly detected volatile organic compound in water samples from the wells. Other detected volatile organic compounds included: methyl chloride, acetone, dichlorofluoromethane, tetrahydrofuran, trichlorofluoromethane, methyl iodide, 1,1-dichloroethane, chloroform, toluene, 1,1,1-trichloroethane, trichloroethene, *cis*-1,2-dichloroethene, methylene chloride, bromodichloromethane, benzene, methylisobutylketone, ethyl ether, and tetrachloroethene.

Tritium concentrations, analyzed in water samples from 15 of the wells, indicated that shallow ground water in the urban study area probably has been recharged since the mid-1950's, meaning that water samples from most of the wells could be affected by residential and commercial land uses developed over the past 40 years.

Urban land uses affected concentrations of several water-quality constituents. Concentrations of nitrate, chloride, and frequencies of detection of pesticides used on right-of-ways were generally greater in ground-water samples collected from the unconfined sand and gravel aquifer underlying the urban study area, compared to concentrations and frequencies of detection in similar aquifers in part of the UMIS study unit. Land uses within 500-meter radii of each well were quantified by digitizing overlays of aerial photographs, that were verified and updated in the field. Land uses had significant correlations with detected concentrations of several of the water-quality constituents. Magnesium, and sulfate concentrations were greater in ground water beneath areas with greater percentages of residential development or population densities, perhaps due to more opportunity for recharge and mineral dissolution

in the more permeable unsaturated zones underlying those areas. Concentrations of sodium and chloride were generally greater in ground water in areas with denser populations, probably due to greater applications of salt to roadways during winters in those areas.

Concentrations of some VOC's used in industry and herbicides used on right-of-ways were greater in ground water in areas with greater proportions of industrial and transportation land uses. Ground water in areas with less dense residential development, mostly the more recently-developed areas, tended to have lesser concentrations of right-of-way herbicides and industrial VOC's and greater concentrations of nutrients and of agricultural herbicides, which may be relicts of previous agricultural land use.

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., Fallon, J.D., and Kroening, S.E., 1995, Water-quality assessment of part of the Upper Mississippi River Basin, Minnesota and Wisconsin--Volatile organic compounds in surface and ground water, 1978-94: U.S. Geological Survey, Water-Resources Investigations Report 95-4216, 39 p.
- Baker, D.G., Nelson, W.W., and Kuehnast, E.L., 1979, Climate of Minnesota Part XII--The hydrologic cycle and soil water: Agricultural Experiment Station Technical Bulletin 322, University of Minnesota, 24 p.
- Belluck, D.A., Benjamin, S.L., and Dawson, T., 1991, Ground-water contamination by atrazine and its metabolites--Risk assessment, policy, and legal implications, *in* Somasundaram, 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. 254-273.
- Bloomgren, B.A., Cleland, J.M., and Olsen, B.M., 1989, Depth to bedrock and bedrock topography, *in* Balaban, N.H., ed., 1989, Geologic Atlas--Hennepin County, Minnesota: Minnesota Geological Survey, County Atlas Series, C-4, 8 pl.

- Bonestroo, Rosene, Anderlik, and Associates, 1995, City of Maple Grove Water Supply and Distribution Plan, 60 p.
- 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 UV-promoted persulfate oxidation and infrared spectrometry: U.S. Geological Survey Open-File Report 92-480, 12 p.
- Chamberlain, L.M., 1977, Soil survey of Anoka County, Minnesota: U.S. Soil Conservation Service, 92 p., 71 pl.
- Ciccioli, P., 1993, VOCs and air pollution, *in* Chemistry and analysis of volatile organic compounds in the environment, H.J.T. Bloemen and J. Burn, eds.: Blackie Academic and Professional Press, London, p. 92-174.
- Dorsch, M.M., and others, 1984, Congenital malformations and maternal drinking water supply in rural South Australia--A case-control study: *American Journal of Epidemiology*, v. 119, p. 473-480.
- Drever, J.I., 1988, The geochemistry of natural waters, 2nd ed.: Prentice-Hall, Englewood Cliffs, NJ, 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.
- Fallon, J.D., Fong, A.I., and Andrews, W.A., 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.
- 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.
- 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, New Jersey, 604 p.
- Fuge, R., 1973, Bromine--I, *in* Wedepohl, K.H., ed.: Handbook of geochemistry, v. II-3, Springer-Verlag, Berlin, p. 351-1-351-4.
- Gianessi, L.P., and Puffer, C.A., 1991, Herbicide use in the United States: Resources for the Future, Washington D.C., variously paged.
- Guy, H.P., 1969, Laboratory theory and methods for sediment analysis: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chapter C1, 58 p.
- 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.
- Helsel, D.R., and Cohn, T.A., 1988, Estimation of descriptive statistics for multiply censored water quality data: *Water Resources Research*, v. 24, p. 1997-2004.
- 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., 1991, Digital map file of major land uses in the United States: U.S. Geological Survey, Reston, VA scale 1:7,500,000.
- Howard, P.H., ed., 1990, Handbook of environmental fate and exposure data for organic chemicals, v. II, solvents: Lewis Publishers, Chelsea, Mich., p. 450-460.
- Hurlbut, C.S., Jr., and Klein, C., 1977, Manual of mineralogy (19th ed.): John Wiley and Sons, Inc., 532 p.

- Kanivetsky, R., 1989, Water-table system, *in* Balaban, N.H., ed., 1989, *Geologic Atlas--Hennepin County, Minnesota*: Minnesota Geological Survey, County Atlas Series, C-4, 8 pl
- Kendall, M.G., 1975 *Rank correlation methods*, 4th edition: Charles Griffin, London, 202 p.
- 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.
- 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.
- 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.
- Lueth, R.A., 1974, Soil survey of Hennepin County, Minnesota: U.S. Soil Conservation Service, 159 p., 81 pl.
- 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.
- Majewski, M.S., and Capel, P.D., 1995, Pesticides in the hydrologic system, v. 1--Pesticides in the atmosphere: Ann Arbor Press, Inc., Chelsea, Mich., 250 p.
- 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., 1993, Geologic sensitivity of the uppermost aquifer to pollution, *in* Meyer, G.N., Falteisek, J., Meints, J., and Dahlman, B., Regional hydrogeologic assessment, Anoka Sand Plain, Anoka, Chisago, Isanti, and Sherburne Counties, Minnesota: Minnesota Department of Natural Resources Regional Hydrogeologic Assessment, RHA-1, 3 pl.
- Meyer, G.N., and Hobbs, H.C., 1989, *Surficial Geology, in* Balaban, N.H., ed., 1989, *Geologic Atlas--Hennepin County, Minnesota*: Minnesota Geological Survey, County Atlas Series, C-4, 8 pl.
- 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.
- National Research Council, 1985, *The health effects of nitrate, nitrite, and N-nitroso compounds*: National Academy of Press, Washington, D.C., 723 p.
- Nelson, D.W., and Sommers, L.E., 1982, Total carbon, organic carbon, and organic matter, *in* Page, A.L., Miller, R.H., and Keeney, C.R., eds., *Methods of soil analysis, Part 2, Chemical and microbiological properties*: American Society of Agronomy, Madison, Wisconsin, p. 539-594.
- Norvitch, R.F., Ross, T.G., and Brietkrietz, A., 1973, Water resources outlook for the Minneapolis-Saint Paul Metropolitan Area, Minnesota: Twin Cities Metropolitan Council, 219 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., 1989, Water-table hydrogeology, *in* Balaban, N.H., ed., 1989, *Geologic Atlas--Hennepin County, Minnesota*: Minnesota Geological Survey, County Atlas Series, C-4, 8 pl.
- Parkhurst, D.L., 1995, User's guide to PHREEQC--C computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 95-4227, 143 p.
- Peigat, J., 1989, Sensitivity of ground-water systems to pollution, *in* Balaban, N.H., ed., 1989, *Geologic*

- Atlas—Hennepin County, Minnesota: Minnesota Geological Survey, County Atlas Series, C-4, 8 pl.
- 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., Regional ground-water quality: Van Nostrand Reinhold, New York, p. 255-294.
- Rao, P.S.C., and Alley, W.M., 1993, Pesticides, *in* Alley, W.M., ed., Regional ground-water quality: Van Nostrand Reinhold, New York, p. 345-382.
- Rose, D.L., and Schroeder, M.P., 1995, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory--Determination of volatile organic compounds in water by purge and trap capillary gas chromatography/mass spectrometry: U.S. Geological Survey Open-File Report 94-708, 26 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: Meister Publishing Company, Willoughby, Ohio, variously paged.
- Spencer, W.F., and Cliath, M.M., 1990, Movement of pesticides from soil to the atmosphere, *in* Long range transport of pesticides: Lewis Publishers, Inc., Chelsea, Michigan, 462 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.
- U.S. Bureau of the Census, 1991, Census of Population and Housing, 1990: Public Law (P.L.) 94-171, data from compact disk ROM (Iowa, Minnesota, North Dakota, South Dakota, and Wisconsin), 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: Van Nostrand Reinhold, New York, 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: Lewis Publishers, Boca Raton, Fla., p. 15-41.
- Werner, S.L., Burkhardt, M.R., and DeRousseau, 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, chapter A3, 80 p.
- Winkelmann, D.A., and Klaine, S.J., 1991, Atrazine metabolite behavior in soil-core microcosms--Formation, disappearance, and bound residues, *in* Somasundaram, 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.
- 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.