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Water-Quality Assessment of Part of the Upper Mississippi River Basin, Minnesota and Wisconsin—Ground-Water Quality in Three Different Land-Use Areas, 1996-98

By Alison L. Fong

Water-Resources Investigations Report 00-4131

Contribution from the National Water-Quality Assessment Program

U.S. DEPARTMENT OF THE INTERIOR

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URL:http://wwwrvares.er.usgs.gov/nawqa/nawqa_home.html

Information about the Upper Mississippi River Basin Project of the NAWQA Program is available at:

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

Water-Resources Investigations Report 00-4131

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

National synthesis of data analysis, based on aggregation of comparable information obtained from the study units, is a major component of the program. This effort focuses on selected 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.

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Chief Hydrologist

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Conversion Factors, Water Quality Units, and Abbreviations

Multiply	By	To obtain
inch (in.)	2.54	centimeter
inches per year (in./yr)	2.54	centimeters per year
foot (ft)	.3048	meter
square mile (m ²)	2.590	square kilometer
feet per day (ft/d)	.3048	meters per day
gallons per day (gal/d)	3.785	liters per day
million gallons per day (Mgal/d)	.04381	cubic meters per second
degrees Fahrenheit (°F)	(°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.

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by Alison L. Fong

ABSTRACT

The surficial sand and gravel aquifer is susceptible to effects from land-use in the Upper Mississippi River Basin study unit of the National Water-Quality Assessment (NAWQA) Program. The purpose of this report is to describe the ground-water quality and the assessment of how different land-uses affect the shallow ground-water quality in the surficial sand and gravel aquifer. Ground-water quality was compared in three different land-use areas; an urban residential/commercial area on the edge of the Anoka Sand Plain in a portion of the Twin Cities metropolitan area (urban study), an intensive agricultural area in the Anoka Sand Plain (agricultural study), and a forested area in the Bemidji-Bagley Sand Plain (forested study). Ground water was sampled and analyzed for about 200 constituents, including physical parameters, major ions, selected trace elements, nutrients, dissolved organic carbon, selected pesticides, selected volatile organic compounds (VOCs), and tritium. The urban study wells were sampled during June and July 1996. The agricultural study wells were sampled during May and September 1998. The forested study wells were sampled during June 1998.

The depth to water below the land surface generally was less than 20 ft in all three land-use studies. The median pH value in the urban study was 7.2, with medians in the agricultural and forested studies at 7.4 and 7.5, respectively. The median specific conductance was significantly greater in the urban study than in the agricultural and forested studies (914, 553, and 487 $\mu\text{S}/\text{cm}$ respectively). The median dissolved oxygen concentration in the urban study (0.9 mg/L) was significantly less than the median in the agricultural or forested studies (5.3 and 2.3 mg/L respectively). Alkalinities in the agricultural study, with a median of 178 mg/L as CaCO_3 , were significantly less than medians in the urban or forested studies (261 and 246 mg/L as CaCO_3 , respectively).

The water composition in the surficial aquifer in all three land-use studies is dominated by calcium, magnesium, and bicarbonate. Sulfate and chloride concentrations in water samples were significantly greater in the urban study than in the agricultural or forested studies, and concentrations in the forested study were least. Most of the water samples in all three land-use studies were very hard (greater than 180 mg/L as CaCO_3).

Nitrate-nitrogen concentrations were greatest in the agricultural study, in which 38 percent of water samples exceeded the U.S. Environmental Protection Agency's maximum contaminant level (MCL) for nitrate-nitrogen. Nitrate-nitrogen was greater than the MCL in 3 percent of urban study samples. None of the forested study samples exceeded the MCL for nitrate-nitrogen. Concentrations of phosphorus generally were less than 0.05 mg/L, with no significant differences between the land-uses.

A total of 19 pesticides were detected in water samples from one or more land-use study wells, with 11 pesticides detected in the urban study, 14 detected in the agricultural study, and 4 detected in the forested study. Atrazine, deethylatrazine, and simazine were the only pesticides detected in all three land-use studies. A significantly greater percentage of pesticide detections were present in water samples from the agricultural study than from the urban or forested studies (86.2, 56.7, and 46.7 percent, respectively). Prometon was the most frequently detected pesticide in the urban study. Atrazine and deethylatrazine were the most frequently detected pesticides in the agricultural and forested studies.

Twenty-one VOCs were detected in water samples from one or more land-use study wells, with 19 detected in the urban study, 7 detected in the agricultural study, and none detected in the forested study. Chloromethane, trichloromethane, methylbenzene, trichlorofluoromethane, and benzene were all detected in both the urban and agricultural studies. A significantly greater percentage of VOC detections were present in water samples from the urban study than from the agricultural study (90 and 50 percent, respectively). Carbon disulfide was the most frequently detected VOC in the urban study. The compound 1,2,3,4-tetramethyl benzene was the most frequently detected VOC in the agricultural study.

Tritium concentrations indicate that the water in the surficial sand and gravel aquifer has been recharged since 1953. Median tritium concentrations ranged from 11.6 to 12.8 tritium units. No significant difference in tritium concentrations was present between the three land-use studies.

Comparisons of previous land-use studies in Minnesota with the three NAWQA land-use studies generally indicated the same patterns. Ground-water quality in surficial sand and gravel aquifers is affected by land-use practices. Ground water in urban studies has greater specific conductances, alkalinities, chloride, sodium, sulfate, and dissolved solid concentrations than agricultural or forested/undeveloped studies. Nitrate-nitrogen was detected in greater concentrations in agricultural studies than in urban studies, with concentrations in the forested/undeveloped studies less than in the agricultural or the urban studies. Agricultural studies have the greatest detection rates, numbers, and total concentrations of pesticides. Pesticide detection rates and total pesticide concentrations in the urban studies were less than in the agricultural studies, with the most frequently detected pesticides (prometon and dicamba) different than those in the agricultural studies (atrazine and deethylatrazine). A greater number of VOCs were detected in urban studies and at greater concentrations than in agricultural studies. Few pesticides or VOCs were detected in forested/undeveloped studies.

INTRODUCTION

In 1991, the U.S. Geological Survey (USGS) began full implementation of the National Water-Quality Assessment (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 anthropogenic 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 Upper Mississippi River Basin (UMIS) study unit (fig. 1), which encompasses an area of about 47,000 mi², includes the entire drainage area of the Upper Mississippi River, in Minnesota and Wisconsin, from the source at Lake Itasca to the outlet of Lake Pepin. The study unit includes areas of agricultural lands, forests, wetlands, prairies, and a major urban area (Twin Cities metropolitan area (TCMA)). 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 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 domestic water systems in the study unit. Two types of aquifers are present that are important sources of water: bedrock aquifers in rocks of Paleozoic age and sand and gravel aquifers in deposits of Pleistocene age. Ground water in the unconfined

sand and gravel aquifers and in the near-surface bedrock aquifers is susceptible to degradation from materials used at the land surface. These shallow aquifers also are the source of recharge to underlying bedrock aquifers (Schoenberg, 1990; Stark and others, 1996).

NAWQA divides the ground-water component of the program into studies at three different scales. Large-scale studies, called study unit surveys, describe ground-water quality across the basin or aquifer. Medium-scale studies of shallow ground-water quality in a targeted land-use area are called land-use studies. Small-scale studies of ground-water quality along a flowpath within a land-use study are called flowpath studies. This report compares the ground-water quality in the UMIS study unit collected during three land-use studies: urban, agricultural, and forested. The study design for the UMIS study unit is described in Stark and others (1999).

Purpose and Scope

The purpose of this report is to describe the current ground-water quality and the assessment of how three different land-uses affect the shallow ground-water quality in the surficial sand and gravel aquifer in part of the UMIS study unit. Ground-water quality is compared in three different land-use areas; an urban residential/commercial area on the edge of the Anoka Sand Plain in a portion of the TCMA (urban study) (fig. 1a), an intensive agricultural area in the Anoka Sand Plain (agricultural study) (fig. 1b), and a forested area in the Bemidji-Bagley Sand Plain (forested study) (fig. 1c). Ground water was sampled from 30 wells in the urban study, 29 wells in the agricultural study, and 15 wells in the forested study. Water samples were analyzed for about 200 constituents, including physical parameters, major ions, selected trace elements, nutrients, dissolved organic carbon (DOC), selected pesticides, volatile organic

compounds (VOCs), and tritium. The urban study wells were sampled during June and July 1996. The agricultural study wells were sampled during May and September 1998. The forested study wells were sampled during June 1998.

Previous Studies

The environmental setting and study design for the UMIS study unit is described in Stark and others (1996 and 1999), including the ground-water hydrology, ground-water quality, and the ground-water sampling design. Historical water-quality data for the study unit include VOCs (Andrews and others, 1995), nitrogen and phosphorus (Kroening and Andrews, 1997), and pesticides (Fallon and others, 1997). Ruhl (1987) describes the hydrogeology and water-quality of glacial-drift aquifers across Minnesota. Water-quality analyses, including major ions and nitrite plus nitrate-nitrogen, are summarized by Ruhl (1987) to compare the unconfined and confined glacial-drift aquifers. Baseline ground-water quality for each aquifer is summarized by surface-water basin by the Minnesota Pollution Control Agency (1999b).

The urban study is described in detail in Andrews and others (1998). Norvitch and others (1973) describe the water resources of the TCMA. The ground-water quality of aquifers in the TCMA is described in Maderak (1965). Ground-water flow models are used to examine the hydrogeology, ground-water flow, and the effects of present and projected ground-water pumping on aquifers in the TCMA (Guswa and others, 1982; Stark and Hult, 1985; Lorenz and Stark, 1990; Schoenberg, 1990; and Lindgren, 1995).

The agricultural study is described in detail in Ruhl and others (2000). Anderson (1993) describes the effects of agricultural and residential land-use on ground-water quality in the Anoka Sand Plain. Monitoring and domestic wells were sampled in residential, irrigated agricultural, non-

irrigated agricultural, and undeveloped areas. Water-quality data is summarized by land use, depth, and areal differences (eastern, western, and Elk River areas). Lindholm (1980) describes the presence, availability, and quality of ground water in the western part of the Anoka Sand Plain. Sampling activities described in that report included the measurement of ground-water levels, streamflow, lake levels, aquifer tests, and water-quality sampling. Work done at the Management Systems Evaluation Area Program site near the city of Princeton, Minnesota, is described in Landon and Delin (1995) and Landon and others (1998). The study was part of an interagency initiative to evaluate the effects of agricultural systems on water quality in the Midwest corn belt, and focused on the effects of selected farming systems on ground-water quality in a sand-plain area. The Minnesota Department of Natural Resources conducted a regional hydrogeologic assessment of the Anoka Sand Plain, studying the surficial geology, water-table hydrogeology, water well data-base distribution, and the sensitivity of the water-table system to contamination. The results are published as a series of maps (Minnesota Department of Natural Resources, 1993).

The forested study consisted of a well network installed for the Bemidji-Bagley study described in Stark and others (1991). Stark and others (1991) describe the hydrogeology and water quality of glacial-drift aquifers in the Bemidji-Bagley area. The water quality of both the unconfined and confined glacial-drift aquifers is described. In addition, water quality of the unconfined glacial-drift aquifer is summarized by land-use (residential, agricultural, forested, and commercial). Oakes and Bidwell (1968) describe the water resources of the Mississippi Headwaters watershed in north-central Minnesota, including both surface- and ground-water hydrology.

The Minnesota Pollution Control Agency (MPCA) began a study in 1996 to determine the effects of land-use on ground-water quality (Minnesota Pollution Control Agency 1998a, 1998b, 1999a, and 1999b). The study was conducted in the city of St. Cloud and the surrounding area. The sampling network included monitoring wells, domestic wells, surface-water gaging stations, and a weather station. The land-uses studied included sewer residential, unsewered residential, irrigated agricultural, non-irrigated agricultural, undeveloped, and commercial/industrial areas.

Description of the Study Areas

Environmental variables that can influence ground-water quality include climate, hydrogeologic setting, land use and land cover, population, and water use. Stark and others (1996) describe those variables for the entire UMIS study unit.

Climate

Seasonal fluctuations in temperature and precipitation can affect relative amounts of runoff and infiltration, seasonal loadings of pesticides in rainfall, solubilities of VOCs in rainfall, volatilization of VOCs to the atmosphere, and processes such as sorption and denitrification, which can affect the quality of ground water. Average monthly temperatures in January over the UMIS study unit range from 2 degrees Fahrenheit in the north to 12 degrees Fahrenheit in the south, and in July the average monthly temperatures range from 68 to 73 degrees Fahrenheit, respectively (Midwestern Regional Climate Center, electronic commun., 2000). Average annual precipitation ranges from 26.3 in. in the city of Cass Lake, 27.7 in. in the city of St. Cloud, to 28.5 in. in the city of Minneapolis (Midwestern Regional Climate Center, electronic commun., 2000). About three-fourths of the annual precipitation in Minnesota falls from May through September (Baker and others, 1979). Mean

annual evaporation is approximately 30 in. in the Bemidji area and 36 in. in the TCMA (Farnsworth and others, 1982). The urban study wells were sampled in 1996, when annual precipitation was 26.1 in. in the city of Minneapolis, approximately 2.5 in. below normal. The agricultural and forested study wells were sampled in 1998, when annual precipitation was 25.3 in. in the city of St. Cloud and 24.7 in. in the city of Cass Lake, approximately 2.4 and 1.6 in. below normal, respectively. The cumulative departure from normal precipitation, for the year preceding each sampling, indicated approximately normal precipitation at the cities of Minneapolis, St. Cloud, and Cass Lake.

Hydrogeologic Setting

The three land-use studies are located in areas with surficial sand and gravel aquifers—the Anoka Sand Plain and the Bemidji-Bagley Sand Plain aquifers (fig. 2). The thickness of surficial sand and gravel aquifers across the UMIS study unit ranges from less than 20 to greater than 400 ft. Sands and gravels were deposited as glacial outwash, in the form of alluvial, ice-contact, river terrace or overbank deposits, from the Des Moines and Superior glacial lobes (Ruhl, 1987; Stark and others, 1996). The permeability and chemical compositions of unsaturated soils and glacial materials can affect the presence and concentrations of many constituents in ground water. Soils underlying the three study areas generally are well-drained sandy soils having little slope, with scattered occurrences of flat-lying, poorly drained peaty soils (Grimes, 1968; Lueth, 1974; Chamberlain, 1977; Larson, 1997; Richardson, 1997). Recharge rates vary among the three study areas mainly due to differences in precipitation and evapotranspiration. The relatively high permeability and low clay and organic matter contents of soils formed on sandy materials in the study areas make the soils susceptible

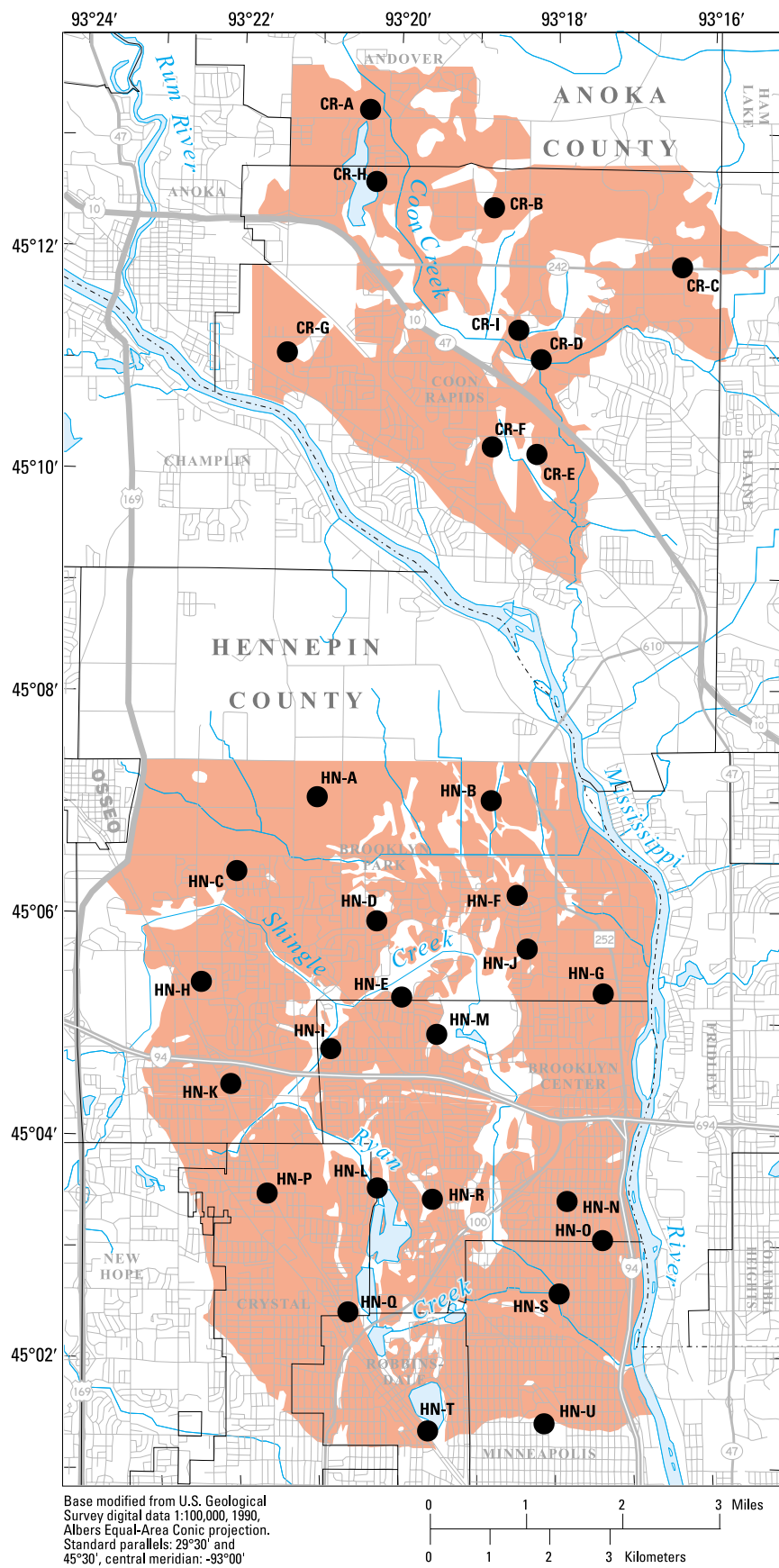
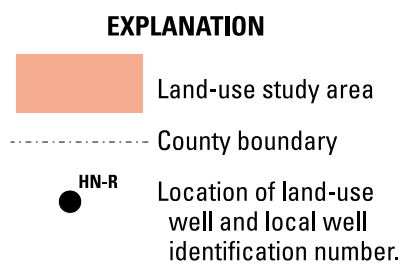
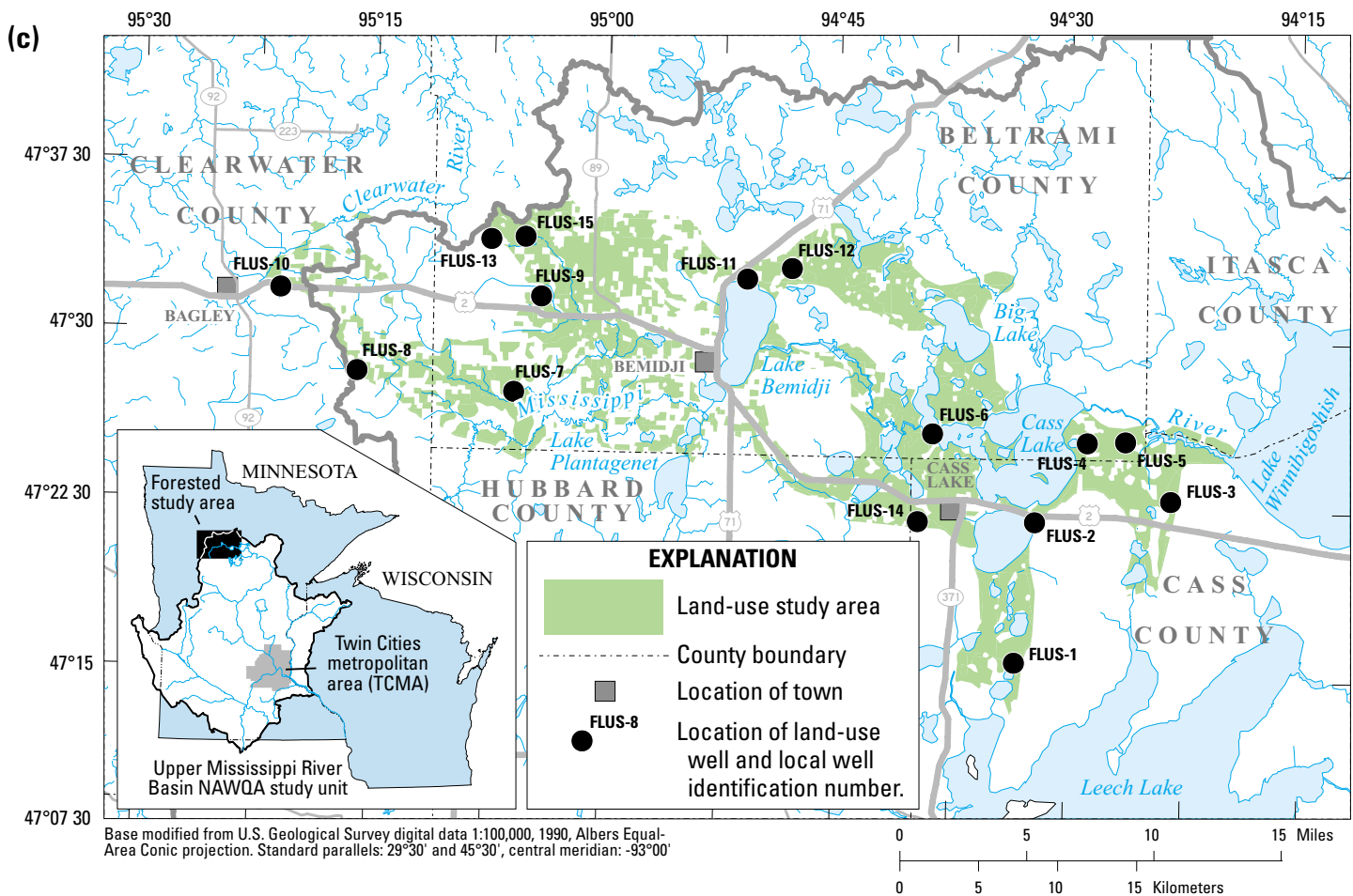
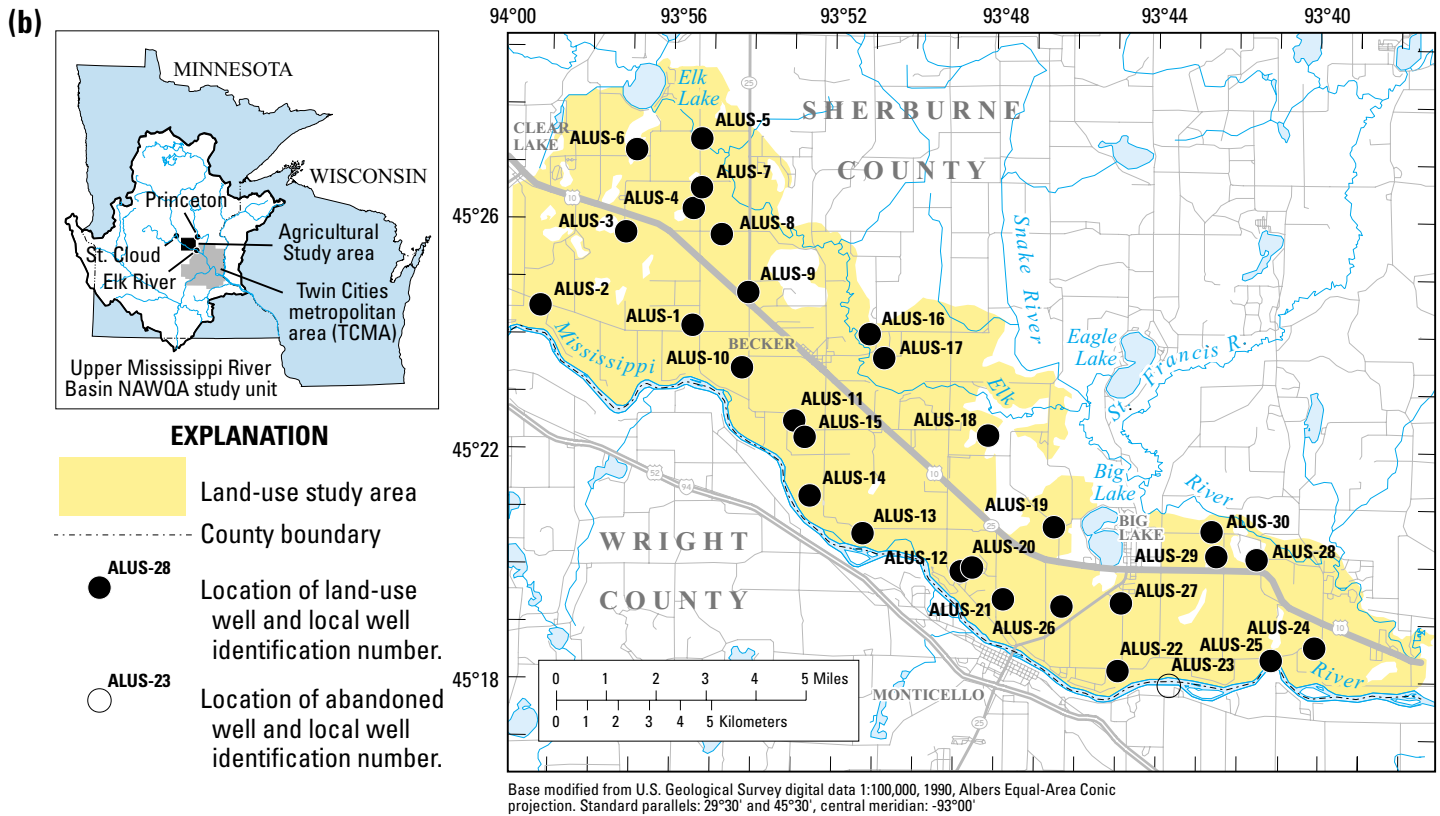


Figure 1.--Location of the Upper Mississippi River Basin National Water-Quality Assessment (NAWQA)



Program study unit and wells sampled for the (a) urban, (b) agricultural, and (c) forested land-use studies.

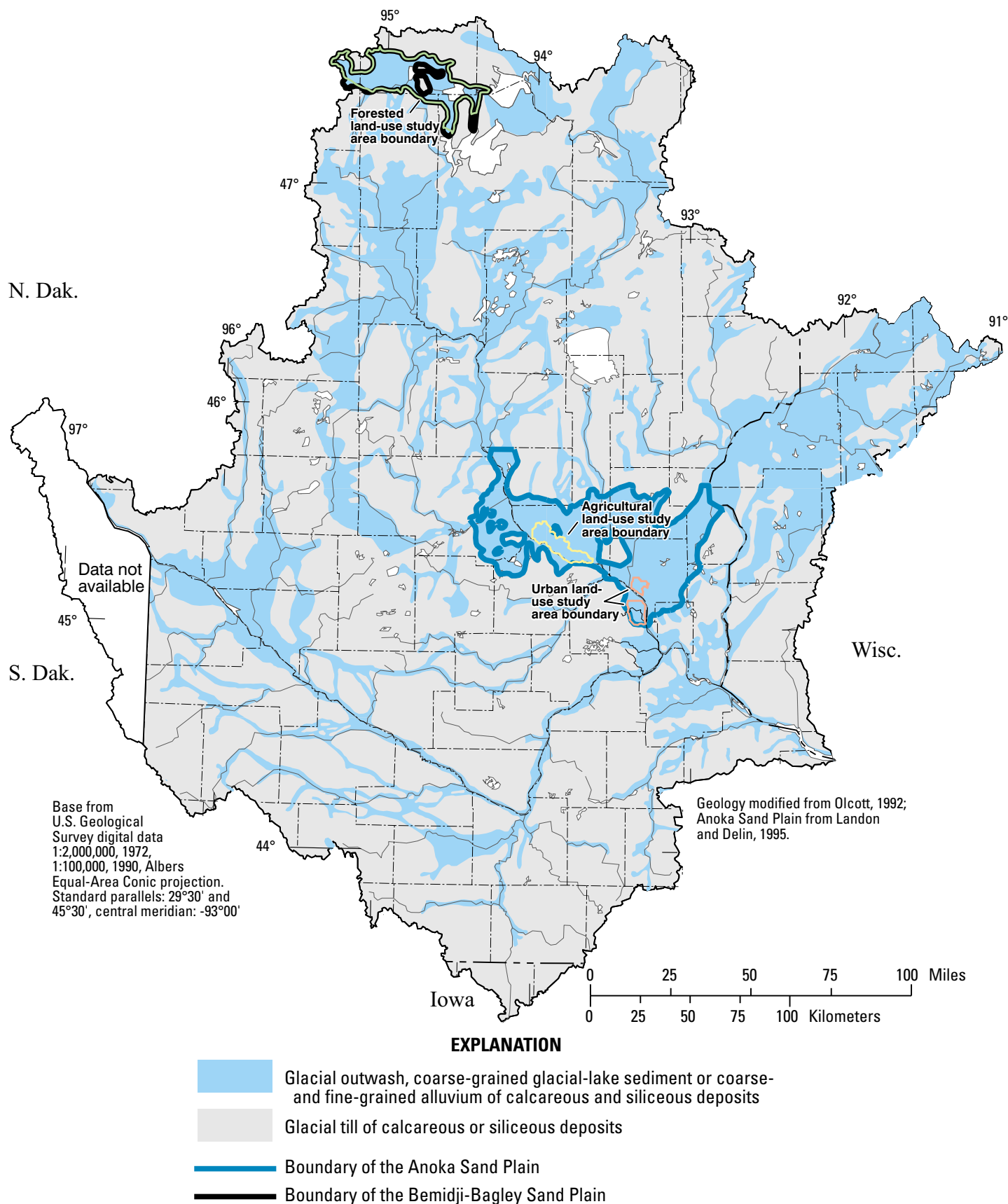


Figure 2.--Surficial geology in the Upper Mississippi River Basin study unit.

to leaching of many constituents from the land surface to ground water.

In the urban study, the surficial sand and gravel aquifer ranges from less than 20 to 115 ft thick and is part of the Anoka Sand Plain aquifer (Helgesen and Lindholm, 1977; Lindholm, 1980; Lindgren, 1990). The hydrogeology of the urban study is described in more detail in Andrews and others (1998). The aquifer consists of sand and gravel mainly in terrace deposits, with flood plain alluvium along the Mississippi River. Recharge to the surficial sand and gravel aquifer in the urban study was estimated to be 11 in./yr (Helgesen and Lindholm, 1977). The hydraulic conductivity varies from 50 to 200 ft/day (Lindgren, 1990). Ground-water flow is toward the Mississippi River, which is the major discharge area for this part of the aquifer.

In the agricultural study, the surficial sand and gravel aquifer ranges from less than 20 to 115 ft thick and is part of the Anoka Sand Plain aquifer (Helgesen and Lindholm, 1977; Lindholm, 1980; Lindgren, 1990). The hydrogeology of the agricultural study is described in more detail in Ruhl and others (2000). The aquifer consists of sand and gravel mainly in terrace deposits, with flood plain alluvium along the Mississippi River. Recharge to the surficial sand and gravel aquifer in the agricultural study was estimated to be 8 in./yr (Lindholm, 1980). The hydraulic conductivity varies from 50 to 1,000 ft/day (Anderson, 1993). Ground-water flow is toward the Mississippi and Elk Rivers, which discharge much of the water from the aquifer.

In the forested study, the surficial sand and gravel aquifer ranges from less than 20 to 130 ft thick and is part of the Bemidji-Bagley Sand Plain aquifer (Stark and others, 1991). The hydrogeology of the forested study is described in more detail in Stark and others (1991). The aquifer consists of sand and gravel deposited by glacial outwash from the St. Louis sublobe of the Des Moines lobe. Recharge to the

aquifer is estimated to be 4 in./yr (Stark and others, 1991). The hydraulic conductivity varies from 250 to 750 ft/d (Stark and others, 1991). Ground-water flow is toward the Mississippi and Clearwater Rivers, which discharge much of the water from the aquifer.

Surficial sand and gravel aquifers are highly susceptible to contamination from land-use activities due to short transport times from the land surface to the water table (Stark and others, 1991; Anderson, 1993; Andrews and others, 1998; Hanson, 1998; Ruhl and others, 2000). Hanson (1998) investigated pesticide and nitrate-nitrogen detections in surficial sand and gravel aquifers in relation to ground-water contamination susceptibility. The greatest rates of contamination are associated with human activities at the land surface in areas with highly-susceptible aquifers (Hanson, 1998). While hydrogeology indicates whether or not an aquifer will be susceptible to contamination, land-use activities also are an important factor in contamination susceptibility.

Land Use and Land Cover

Land use and land cover (fig. 3) are important factors affecting ground-water quality, especially in surficial sand and gravel aquifers. Agricultural and residential areas can be contribution areas of nutrients and pesticides to ground water. Roads and right-of-ways can contribute sodium and chloride (from de-icing salt), herbicides (from applications to road beds and berms), and VOCs (from auto emissions and spills) to ground water. Commercial and industrial activities also may discharge VOCs, metals, and other substances to the atmosphere, surface water, or land surface. Land use in a 500-meter radius around each well was documented using the procedures described in Koterba (1998). The land-use data for the urban, agricultural, and forested studies are summarized in table 1.

Land use in the urban study area is primarily residential, with commercial land-use being concentrated along major roadways. Residential and commercial development in the urban study area generally began in the 1960's and continues today in the northern part of the study area. 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 agricultural with wooded areas in the vicinity of wetlands. Agricultural land still exists between the northern and southern portions of the urban study area, in northern Hennepin County; however, that area is being rapidly developed for residential and commercial purposes.

Land use in the agricultural study area is predominantly agricultural, including several small communities and some undeveloped land (forest and wetlands). The agriculture is mainly irrigated row crops, consisting of potatoes, corn, and soy beans. This part of Sherburne County is one of the most intensely irrigated agricultural areas in Minnesota and is part of the rapidly urbanizing corridor between the TCMA and St. Cloud. The new residential developments are mainly served by private domestic wells and septic systems.

Land use in the forested study area is predominantly second- or third-growth stands of trees used primarily for paper pulp and wood products, and includes some agricultural and residential areas. There are numerous lakes and wetlands in the area, including several larger lakes such as Cass Lake and Lake Bemidji. Agriculture in the area consists of pasture, hay, small-grain crops, corn, and potatoes. Residential land-use is found mainly around the cities of Bemidji, Bagley, and Cass Lake (fig. 1c).

Population and Water Use

Population and water use for the entire study unit is described in more

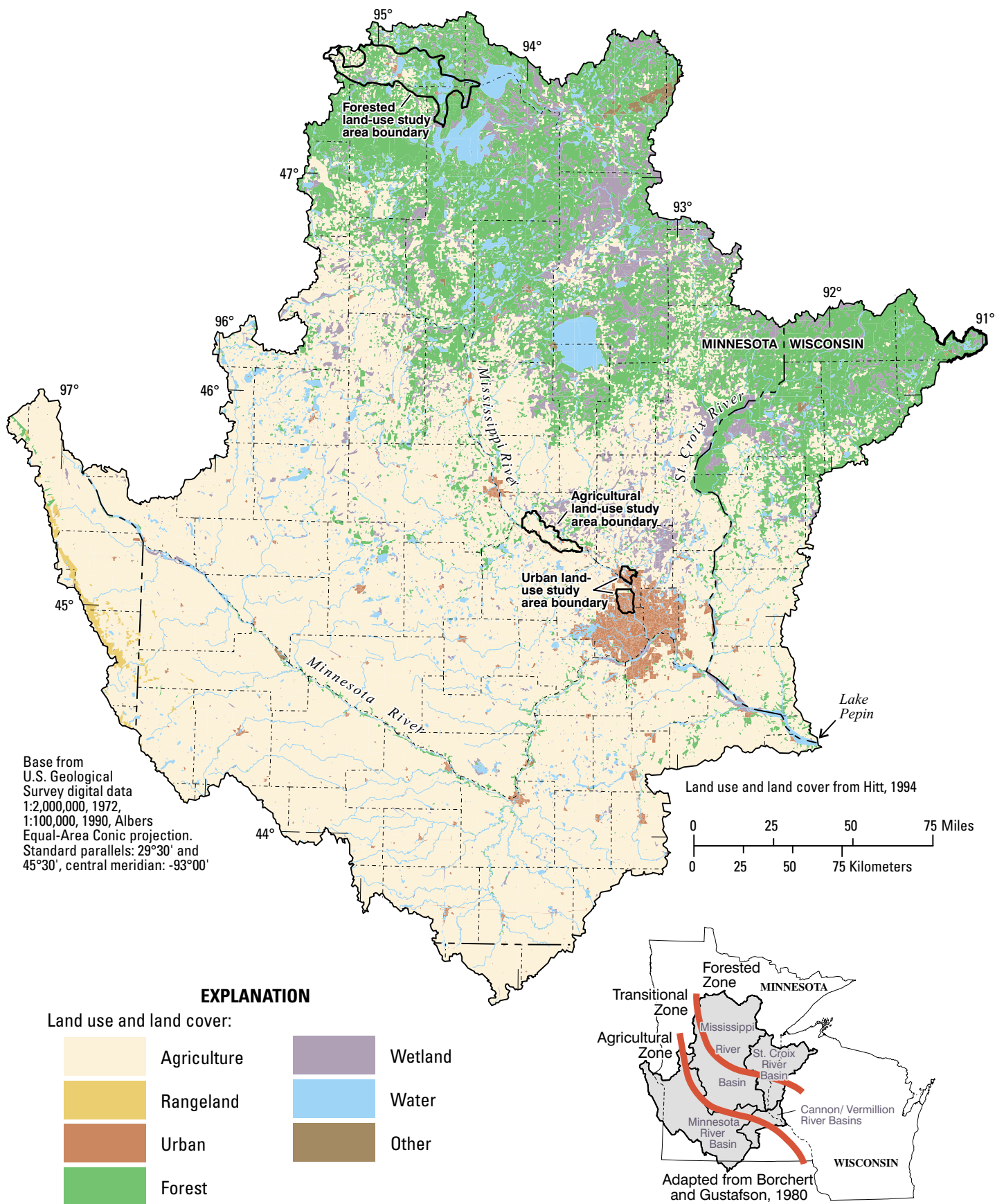


Figure 3.--Land use and land cover in the Upper Mississippi River Basin study unit.

Table 1. Averages and ranges of percent land-use in a 500 meter radius around land-use study wells

Land Use	Urban study area (30 wells)		Agricultural study area (29 wells)		Forested study area (15 wells)	
	Average	Range	Average	Range	Average	Range
Residential	64.8	37.6 – 98.2	13.9	0 – 59.0	1.3	0 – 13.6
Commercial	3.5	0 – 33.3	0.3	0 – 9.0	0	0
Industrial	1.5	0 – 22.1	1.2	0 – 17.5	0	0
Parks	14.9	0 – 49.4	0	0	0	0
Social Services	4.4	0 – 35.0	0	0	0	0
Transportation /Right-of-way	4.1	0 – 32.2	2.4	0 – 25.1	3.0	0 – 14.5
Agricultural	0.1	0 – 2.5	58.6	32.3 – 97.9	4.2	0 – 28.8
Forested/ Undeveloped	0.1	0 – 3.8	14.3	0 – 53.1	68.0	35.2 – 98.8
Rivers, Lakes, Wetlands	6.6	0 – 34.1	9.2	0 – 34.6	21.9	0 – 48.6
Mining	0	0	0.1	0 – 4.4	1.4	0 – 21.3

detail in Stark and others (1996) and is briefly summarized here. The population of the study unit was about 3,640,000 people in 1990 (U.S. Bureau of Census, 1991). Public-water supplies served approximately 2,410,000 people in 1990, using an average of 413 million gallons of water per day (Mgal/d) with 59 percent from ground water and 41 percent of the water coming from surface water. Surface water is used for the public-water supplies of the cities of Minneapolis, St. Paul, and St. Cloud. Ground water is used for public-water supplies for the rest of the communities in the study unit and for private-domestic supplies. Ground water from the surficial aquifers likely will be in increasing demand as a water-supply source due to rapid population growth in many parts of the TCMA and surrounding area. Populations and water-use demands are growing rapidly in the northwestern parts of the urban study area (the cities of Brooklyn Park and Coon Rapids) and parts of the agricultural study area (Becker and Big Lake townships) (fig.1).

In 1990 about 174,200 people were living in the urban study area (approximately 4,297 people/mi²). Water use in the urban study area is described in more detail in Andrews and others (1998). Public-water supplies serve the entire urban study area

with an average water supply of approximately 19.5 Mgal/d; 83 percent of which is from ground water and 17 percent is from the Mississippi River (Gary Oberts, Metropolitan Council, written commun., 1997). The city of Minneapolis in Hennepin County (fig. 1) relies on water from the Mississippi River near Fridley, Minnesota for their public-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 withdraw ground water from wells completed in surficial sand and gravel deposits and in underlying bedrock aquifers for their water supplies. In addition to municipal wells, approximately 1,500 low-capacity domestic or lawn-irrigation wells are present in the urban study area (James Piegat, Hennepin Conservation District, written commun., 1997), which pump an estimated total of 75,000 gal/d from the surficial aquifer during summer months.

In 1990, approximately 10,550 people were living in the agricultural study (approximately 140 people/mi²), not including the cities of Becker, Big Lake, and Clear Lake. The total ground-water use in the agricultural study area was approximately 5,100 Mgal/d during 1997, based on

data from the USGS data base State Water Use Data System (SWUDS). Withdrawals for irrigation accounted for about 88 percent of the total ground-water use. Public-water supply withdrawals were approximately 7 percent of total ground-water use. Withdrawals for rural domestic wells were less than one percent of total ground-water use. Withdrawals for domestic wells were estimated by multiplying the number of people estimated to have been served by this source times a per-capita use coefficient of 100 gal/d. Solley and others (1995) report that water use per capita coefficients for users of domestic wells generally range from 60 to 120 gal/d.

In 1990, approximately 13,700 people were living in the forested study area (approximately 70 people/mi²), not including the cities of Bagley, Bemidji, and Cass Lake. The public- and private-water supplies in the forested study area rely on ground water. The public-water supplies in the cities of Bagley, Bemidji, and Cass Lake withdrew approximately 1.8 Mgal/d in 1995, based on data from the state water use permits (Minnesota Department of Natural Resources, electronic commun., 2000). Also, a number of private-water supplies are present for trailer parks and industrial users. Irrigation,

for wild rice and potatoes, is another major use of ground water and surface water in the forested study area.

Methods

Locations for new monitoring wells and existing wells were selected based on site-selection criteria for NAWQA land-use studies specified by Squillace and Price (1996) and Lapham and others (1995). Information used in selecting existing wells included location, well logs, well construction, and information from site visits. A well network was established using an aerially distributed random pattern over the study area and a site selection program described by Scott (1990). For the urban study, 30 monitoring wells were drilled during May and June 1996 (Andrews and others, 1998). For the agricultural study, 19 monitoring wells were drilled during September 1997, 1 monitoring well was drilled during July 1998, and 6 existing monitoring wells and 3 domestic wells were selected (Ruhl and others, 2000). For the forested study, 14 existing monitoring wells were selected (Stark and others, 1991), and 1 new monitoring well was drilled during June 1998. Site characteristics for each well are described in Stark and others (1999).

New monitoring wells installed for these studies were constructed in accordance with Minnesota Department of Health regulations (Minnesota Department of Health, 1994) and NAWQA specifications for monitoring wells (Lapham and others, 1995). The holes were drilled with 8-in. hollow-stem steel augers. The wells were constructed of threaded 2-in. schedule 40 polyvinyl chloride (PVC) casing and 5-ft PVC screens with 0.010-in. slot size (a 10 ft screen was used in two wells where the screened interval was in a very fine sand). The top of the well screen generally was placed 2 ft below the water table. Sand was allowed to collapse to within 2 ft above the top of the well screen. 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 to within 2 ft of the land surface. The top 2 ft of the borehole were grouted with cement to the land surface. Six-inch diameter steel well protectors with locking aluminum caps were set into the cement and grout to a depth of about 4 ft, with at least 2 ft left standing above land

surface. Wells generally were developed within two weeks of drilling using a centrifugal pump.

Water samples were collected in a sealed system utilizing Teflon tubing and stainless-steel fittings according to NAWQA protocols (Koterba and others, 1995). Physical parameters, including depth to water, water temperature, pH, specific conductance, turbidity, dissolved oxygen, and alkalinity were measured in the field. Three to five standing volumes of water were pumped from the wells prior to sampling. Stability of water chemistry was verified through periodic measurements of water temperature, pH, specific conductance, turbidity, and dissolved oxygen concentrations while purging the wells. Water samples from the urban study wells were collected in June and July 1996, the agricultural study in May and September 1998, and the forested study in June 1998. Water samples from the wells were analyzed for about 200 constituents. Major ions, selected trace elements, nutrients, DOC, pesticides, VOCs, and tritium were analyzed by the USGS National Water Quality Laboratory (NWQL) in Arvada, Colorado (table 2).

Quality-assurance/quality-control (QA/QC) samples were collected

Table 2. Laboratory analytical methods for measured water-quality constituents
[USGS, U.S. Geological Survey; DOC, dissolved organic carbon; UV, ultraviolet; VOCs, volatile organic compounds]

Constituent or constituent group	Analysis Method	Reference
Major ions and trace elements (USGS Schedule 2750)	Atomic absorption spectrometry	Fishman and Friedman (1989)
Nutrients (USGS Schedule 2752)	Various methods	Fishman and Friedman (1989)
DOC (USGS Schedule 2085)	UV-promoted persulfate oxidation and infrared spectrometry	Brenton and Arnett (1993)
Pesticides (USGS Schedule 2001/2010)	Solid-phase extraction technology using a C-18 cartridge and gas chromatography/mass spectrometry	Zaugg and others (1995)
Pesticides (USGS Schedule 2050/2051)	Solid-phase extraction technology using a Carbpak-B cartridge and high performance liquid chromatography with UV detection	Werner and others (1996)
VOCs (USGS Schedule 2020 and USGS custom method 9090)	Purge and trap capillary gas chromatography/mass spectrometry	Conor and others (1998), and Rose and Schroeder (1995)
Tritium (USGS labcode 1565)	Electrolytic enrichment with gas counting	Ostlund and Dorsey (1975)

in accordance with NAWQA protocols (Koterba and others, 1995). These samples included field/equipment blanks (for all constituents), VOC trip blanks, source-solution blanks, spikes (pesticides and VOCs), and replicates (for all constituents). Field/equipment blanks are collected to evaluate the effectiveness of the cleaning procedures for sampling equipment, and to check for contamination introduced during sample collection, processing, handling, and transport. VOC trip blanks are sealed vials of VOC-free water kept in the sampling vehicle during a sampling trip to evaluate if atmospheric contamination of the VOC vials may be occurring during sample transport and analysis. Source-solution blanks are collected to evaluate the purity of water used for the collection of field/equipment blanks. Spikes are collected to determine if pesticide or VOC compounds can escape or degrade during shipping and handling or if there is analytical interference from the sample matrix. Analytic interference can be caused by other compounds in the water sample that look similar to the targeted analytes. Replicate samples are collected to check the stability of water quality during sample collection and to check for variability during sample processing, handling, and analysis. The QA/QC data for the urban and agricultural studies are described in Andrews and others (1998) and Ruhl and others (2000), respectively. The QA/QC data for the forested study are presented in tables 3–6.

A total of 28 QA/QC samples were collected during sampling of the

wells from the three land-use studies. These samples included 6 field/equipment blanks (for all constituents), 3 VOC field/equipment blanks, 3 VOC trip blanks, 2 VOC source solution blanks, 5 pesticide spikes, 5 VOC spikes, and 4 replicates (for all constituents).

One VOC trip blank was placed in the sampling vehicle during each study sample collection trip and was subsequently shipped to the laboratory with other samples. Source-solution blanks are prepared using the same types of water as used in field/equipment blanks, the VOC-free water for source-solution blanks is decanted directly into bottles and vials and shipped to the laboratory.

Several major ions, trace elements, and nutrients, including calcium, iron, magnesium, sodium, silica, DOC, ammonia-nitrogen, and phosphorus, were detected in some of the blank samples (Andrews and others, 1998; Ruhl and others, 2000; and table 3). In general, detected concentrations of analytes in the blank samples were far less than those reported in ground-water samples, indicating a low likelihood of cross-contamination of ground-water samples. When regular ground-water samples were collected, larger volumes of water (30 to 50 gallons) were purged through the sampling system prior to sample collection than when blanks were collected (1 to 3 gallons), which would tend to minimize the concentrations of any constituents contributed by the sampling equipment to those samples (Menheer and Brigham, 1997). No pesticides were detected in any of the

blanks from the three land-use studies.

The VOC-free water supplier and the laboratory method used in determining VOC concentrations were changed by NWQL between the urban study in 1996 and the agricultural and forested studies in 1998. The NWQL used custom method 9090 for determining VOC concentrations in water samples from the urban study, and the approved version of the same method (schedule 2020) was used for the agricultural and forested studies. For the urban study, eight VOCs (bromodichloromethane, dibromochloromethane, trichloromethane, methylbenzene (toluene), benzene, 1,4-dichlorobenzene, carbon disulfide, and 2-butanone) were detected in the field/equipment blanks, no VOCs were detected in the trip blank, and seven VOCs (trichloromethane, methylbenzene (toluene), chlorobenzene, dichloromethane, ethenylbenzene, acetone, and 2-butanone) were detected in the source-solution blank (Andrews and others, 1998). Concentrations of all of the detected VOCs in the field/equipment blanks were reported as estimated values, meaning that the compounds were detected, but the concentration was estimated. Six VOCs (bromodichloromethane, trichloromethane, benzene, dichloromethane (methylene chloride), acetone, and 2-butanone) were detected in certification tests of the “VOC-free” blank water prior to its use. In the agricultural and forested studies, four VOCs (trichloromethane, methylbenzene (toluene), dichloromethane, and 1,3- and 1,4-dimethylbenzene) were detected in

Table 3. Reporting limits and ranges in detected concentrations of analytes in blanks from the forested study area
[mg/L, milligrams per liter; µg/L, micrograms per liter; na, not analyzed; E, detection with estimated concentration]

Compound	Reporting limit and unit	Field blank	Volatile organic compounds trip blank
Calcium	0.02 mg/L	0.023	na
Ammonia-nitrogen	0.02 mg/L	0.05	na
Phosphorus	0.05 mg/L	0.016	na
Dissolved organic carbon	0.1 mg/L	0.2	na
Methylbenzene	0.038 µg/L	E0.009	E0.028

Table 4. Reporting limits, ranges in percent recovery, and mean percent recovery for Schedule 2001 pesticide spike from the forested study area
[µg/L, micrograms per liter; nd, not determined]

Compound	Reporting limit (µg/L)	Range in percent recovery	Mean percent recovery
Acetochlor	0.002	101.7–105.3	103.5
Alachlor	.002	102.5–107.1	104.8
Atrazine	.001	91.9–97.2	94.6
Azinphos-methyl	.001	183.6–194.5	189.0
Benfluralin	.002	72.5–78.9	75.7
Butylate	.002	103.1–111	107.1
Carbaryl	.003	202.4–202.5	202.5
Carbofuran	.003	156.5–158.4	157.4
Chlorpyrifos	.004	83.4–89.3	86.4
Cyanazine	.004	128.2–130.5	129.3
Dacthal (DCPA)	.002	113–123	118.0
<i>p,p'</i> -DDE	.006	55.9–64.1	60.0
Deethylatrazine	.002	44.9–49.2	47.1
Diazinon	.002	91.9–96.3	94.1
Dieldrin	.001	92.3–98	95.2
2,6-Diethylaniline	.003	87.9–92.7	90.3
Disulfoton	.017	89.8–94.6	92.2
EPTC (Eptam)	.002	100.2–107	103.6
Ethalfuralin	.004	90.8–94.9	92.8
Ethoprop	.003	135–143.4	139.2
Fonofos	.003	91.1–96.3	93.7
α-HCH	.002	87–94.5	90.7
γ-HCH (Lindane)	.004	96.3–104	100.1
Linuron	.002	116–123.8	119.9
Malathion	.005	77.8–81	79.4
Methyl parathion	.006	77.5–78.2	77.9
Metolachlor	.002	103.1–109	106.1
Metribuzin	.004	84.6–88.4	86.5
Molinate	.004	100.8–107.1	103.9
Napropamide	.003	104.3–112.5	108.4
Parathion	.004	89.3–94.5	91.9
Pebulate	.004	106.1–113	109.5
Pendimethalin	.004	81.9–85.7	83.8
<i>cis</i> -Permethrin	.005	54.8–57.6	56.2
Phorate	.002	70.5–73	71.8
Prometon	.018	5.6–6.3	5.9
Pronamide	.003	94.6–99.9	97.2
Propachlor	.007	119.7–120.2	120.0
Propanil	.004	114–120.6	117.3
Propargite	.013	132.6–139	135.8
Simazine	.005	104.3–108	106.2
Tebuthiuron	.010	129.1–130.5	129.8
Terbacil	.007	103.4–111.6	107.5
Terbufos	.013	76.1–76.3	76.2
Thiobencarb	.002	107.8–115.2	111.5
Triallate	.001	91.9–97.2	94.6
Trifluralin	.002	75.3–81.4	78.3
Surrogates			
Diazinon- <i>d</i> 10	nd	105–108	107
α-HCH- <i>d</i> 6	nd	99.1–105	102
Terbuthylazine	nd	116–120	118

the field/equipment blanks, one VOC (methylbenzene) was detected in the trip blanks, and no VOCs were detected in the source solution blanks (Ruhl and others, 2000; table 3). Low-level detections of these compounds in the field/equipment blanks indicate that detection of similar levels of these compounds in the ground-water samples may be artifacts of sampling. Caution should be used in interpreting the results for these compounds in the ground-water samples. However, because water samples from several wells in each study had no VOC detections, the sampling methods used probably were not introducing contamination and the source of the detections in the blank samples most likely was the blank water.

Five pesticide and five VOC spike samples were collected. Water samples collected from the wells were spiked with known volumes of solutions containing known concentrations of selected pesticides or VOCs. Two pesticide replicate samples and two VOC replicate samples were spiked with the identical volumes of their respective spike solutions. In addition to spiking 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 2001/2010 had mean recoveries ranging between 75 and 120 percent, except for deethylatrazine, azinphos-methyl, benfluralin, carbaryl, carbofuran, cyanazine, DCPA, *p,p'*-DDE, disulfoton, ethalfluralin, ethoprop, linuron, methyl parathion, metribuzin, pendimethalin, *cis*-permethrin, phorate, prometon, propargite, tebuthiuron, terbacil, and trifluralin (Andrews and others, 1998; Ruhl and others, 2000; and table 4). Low mean percent recoveries for these pesticides indicate that these pesticides may have degraded in the spiking mixture, volatilized during spiking, or may have been subject to interferences during analysis, mean-

ing that frequencies of detection and reported concentrations of these pesticides in ground water may have been underestimated from actual concentrations. The mean recoveries for the 2001/2010 surrogates (diazinon-*d*10, *alpha*-HCH-*d*6, and terbuthylazine) ranged from 102 to 118 percent (Andrews and others, 1998; Ruhl and others, 2000; and table 4).

The recoveries for schedule 2050/2051 pesticide spikes were more variable and generally less than the recoveries for schedule 2001/2010 pesticide spikes. Mean recoveries for schedule 2050/2051 pesticide spikes ranged from 0 to 125.3 percent (Andrews and others, 1998; Ruhl and others, 2000). The mean recovery of the surrogate in schedule 2050/2051, BDMC, ranged from 87 to 110 percent (Andrews and others, 1998; Ruhl and others, 2000). Relatively low recoveries for the pesticides in schedule 2050/2051 indicate that these pesticides may have degraded in the spiking mixture, volatilized during spiking, or been subjected to interferences during analysis. Therefore, the frequencies of detection and reported concentrations of the pesticides on schedule 2050/2051 may have been underestimated. Schedule 2050/2051 was not analyzed for in the forested study due to the low likelihood of detection.

The VOC schedule and spike solutions were changed between the urban study in 1996 (custom method 9090) and the agricultural and forested studies in 1998 (schedule 2020). Mean recoveries in VOC spike samples ranged from 67.9 to 106 percent in the urban study, from 29.8 to 93.3 percent in the agricultural study, and from 62.5 to 119.8 percent in the forested study (Andrews and others, 1998; Ruhl and others, 2000; and table 5). Most VOCs analyzed using custom method 9090 had mean recoveries ranging between 75 and 120 percent, except for tribromomethane and tetrachloroethene (Andrews and others, 1998). Most VOCs analyzed using schedule 2020 from the forested study had mean recoveries ranging

between 75 and 120 percent except for 2,2-dichloropropane, chlorobenzene, *cis*-1,3-dichloropropene, diisopropyl ether, ethyl tert-butyl ether (ETBE), ethylbenzene, methyl tert-butyl ether (MTBE), and tert-amyl methyl ether (TAME) (table 5). About 85 percent of the VOCs analyzed on schedule 2020 from the agricultural study had recoveries of less than 75 percent, indicating that frequencies of detection and reported concentrations from the agricultural study may have been less than the actual frequencies of detection and concentrations (Ruhl and others, 2000). Possible reasons for low percent recoveries include the degradation of pesticides in the spiking mixture, volatilization during spiking, or interferences during analysis. Mean VOC surrogate recoveries (1,2-dichloroethane-*d*4; toluene-*d*8; and *p*-bromofluorobenzene) ranged from 82.3 to 107 percent for the urban study and from 100 to 112 percent for the agricultural and forested studies.

One set of replicate samples was collected from a well in each of the three land-use studies. Constituents with concentrations varying by more than five percent between the sample and replicate included ammonia-nitrogen, nitrite-nitrogen, ammonia+organic-nitrogen, phosphorus, orthophosphorus, DOC, calcium, potassium, silica, bromide, sulfate, fluoride, methylbenzene, 1,2,3,4-tetramethylbenzene, 1,2,3,5-tetramethylbenzene, 1,2,4-trimethylbenzene (Andrews and others, 1998; Ruhl and others, 2000; and table 6). The differences in concentrations for these constituents were greater than 5 percent, but the actual differences in concentrations generally were low when compared to reported concentrations in regular samples (0.2 milligrams per liter (mg/L) or less for nutrients, 4.0 mg/L or less for major ions, and 0.05 micrograms per liter (μ g/L) or less for VOCs).

Summaries of water-quality data from the three land-use studies include tables of median values, standard deviations, ranges of values,

Table 5. Reporting limits, ranges in percent recovery, and mean percent recovery for Schedule 2020
volatile organic compound spike from the forested study area

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

Compound	Reporting limit (µg/L)	Range in percent recovery	Mean percent recovery
(1,1-Dimethylethyl)benzene	0.096	86.9–105.4	96.2
(1-Methylethyl)benzene	.032	79.4–85.4	82.4
(1-Methylpropyl)benzene	.048	79–106.5	92.8
1,1,1,2,2,2-Hexachloroethane	.362	89.9–95.3	92.6
1,1,1,2-Tetrachloroethane	.044	75.6–86.7	81.2
1,1,1-Trichloroethane	.032	80.7–96.5	88.6
1,1,2,2-Tetrachloroethane	.132	95–107.3	101.2
1,1,2-Trichloro-1,2,2-trifluoroethane	.032	69–87.8	78.4
1,1,2-Trichloroethane	.064	81.7–98.3	90.0
1,1-Dichloroethane	.066	78.7–99.7	89.2
1,1-Dichloroethene	.044	72.4–102.2	87.3
1,1-Dichloropropene	.026	67.1–92	79.6
1,2,3,4-Tetramethylbenzene	.230	103.6–116.2	109.9
1,2,3,5-Tetramethylbenzene	.240	96.3–97.6	97.0
1,2,3-Trichlorobenzene	.266	87.2–97.4	92.3
1,2,3-Trichloropropane	.070	85.7–96.4	91.1
1,2,3-Trimethylbenzene	.124	94.1–121.6	107.8
1,2,4-Trichlorobenzene	.188	90.8–103.7	97.3
1,2,4-Trimethylbenzene	.056	84.8–117.2	101.0
1,2-Dibromo-3-chloropropane	.214	83.2–107	95.1
1,2-Dibromoethane	.036	76–88	82.0
1,2-Dichlorobenzene	.048	91.6–108.2	99.9
1,2-Dichloroethane	.134	85.2–101.6	93.4
1,2-Dichloropropane	.068	72.6–87.3	80.0
1,2-Dimethylbenzene	.064	81.7–84.1	82.9
1,3 and 1,4-Dimethylbenzene	.064	82.9–83.4	83.2
1,3,5-Trimethylbenzene	.044	78.6–112.9	95.7
1,3-Dichlorobenzene	.054	85–112.7	98.8
1,3-Dichloropropane	.116	76.3–87.2	81.7
1,4-Dichlorobenzene	.050	82.2–105.6	93.9
1-Chloro-2-methylbenzene	.042	80.1	80.1
1-Chloro-4-methylbenzene	.056	78.8–99.6	89.2
1-Isopropyl-4-methylbenzene	.110	77.8–102.6	90.2
2,2-Dichloropropane	.078	61.4–63.6	62.5
2-Butanone	1.650	85.2–99.4	92.3
2-Ethyltoluene	.100	80.7–95.9	88.3
2-Hexanone	.746	85.5–99.7	92.6
2-Propenenitrile	1.230	89.6–93.2	91.4
3-Chloro-1-propene	.196	66–85.4	75.7
4-Methyl-2-pentanone	.374	76.9–78	77.4
Acetone	4.900	91.4–111.1	101.3
Benzene	.032	70.3–85.4	77.9
Bromobenzene	.036	80.3–83.3	81.8
Bromochloromethane	.044	82.6–95	88.8
Bromodichloromethane	.048	82.9–96.1	89.5

Table 5. Reporting limits, ranges in percent recovery, and mean percent recovery for Schedule 2020
volatile organic compound spike from the forested study area (Continued)

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

Compound	Reporting limit (µg/L)	Range in percent recovery	Mean percent recovery
Bromoethene	0.100	72.8–97.9	85.4
Bromomethane	.148	64.8–94.6	79.7
Carbon disulfide	.080	72.8–100.5	86.7
Chlorobenzene	.028	69.4–80.3	74.9
Chloroethane	.120	74.3–83.5	78.9
Chloroethene	.112	69.1–100.7	84.9
Chloromethane	.254	73.8–88.8	81.3
<i>cis</i> -1,2-Dichloroethene	.038	69.2–88.8	79.0
<i>cis</i> -1,3-Dichloropropene	.092	58.8–75.1	67.0
Dibromochloromethane	.182	79.3–92.3	85.8
Dibromomethane	.050	80.7–95	87.9
Dichlorodifluoromethane	.096	86.3–128.9	107.6
Dichloromethane	.382	86.6–101.5	94.0
Diethyl ether	.170	73.9–99	86.5
Diisopropyl ether	.098	63.6–83.6	73.6
Ethenylbenzene	.042	83.7–100.7	92.2
Ethyl methacrylate	.278	75.3–92	83.7
Ethyl <i>tert</i> -butyl ether (ETBE)	.054	48.1–79.7	63.9
Ethylbenzene	.030	67.7–78.6	73.2
Hexachlorobutadiene	.142	93.6–104.2	98.9
Iodomethane	.076	89.2–150.4	119.8
Methyl acrylate	.612	90.2–96.6	93.4
Methyl acrylonitrile	.570	82.6–93.7	88.2
Methyl methacrylate	.350	71.5–93.7	82.6
Methyl <i>tert</i> -butyl ether (MTBE)	.112	61.2–85.7	73.5
Methylbenzene	.038	78.2–83.5	80.8
Naphthalene	.250	97.1–101	99.0
<i>n</i> -Butylbenzene	.186	74.6–93	83.8
<i>n</i> -Propylbenzene	.042	74.3–91.6	83.0
<i>tert</i> -Amyl methyl ether (TAME)	.112	54.2–79.6	66.9
Tetrachloroethene	.038	84.8–98.8	91.8
Tetrachloromethane	.088	77.7–97.2	87.4
Tetrahydrofuran	1.150	77.7–91.1	84.4
<i>trans</i> -1,2-Dichloroethene	.032	75–98.4	86.7
<i>trans</i> -1,3-Dichloropropene	.134	71.4–81.6	76.5
<i>trans</i> -1,4-Dichloro-2-butene	.692	108.9–114	111.4
Tribromomethane	.104	76.7–94	85.4
Trichloroethene	.038	67.1–89	78.1
Trichlorofluoromethane	.092	71.7–100.6	86.1
Trichloromethane	.052	84.8–97.8	91.3
Surrogates			
<i>p</i> -Bromofluorobenzene	nd	94–112	103
1,2-Dichloroethane- <i>d</i> 4	nd	110–114	112
Toluene- <i>d</i> 8	nd	97–109	103

Table 6. Reporting limits and ranges in concentrations of compounds with greater than five percent difference in replicate concentrations from the forested study area

[all values in milligrams per liter; <, less than]

Compound	Reporting limits	Sample concentration	Replicate concentration
Bromide	0.01	0.022	0.018
Calcium	.02	65	61
Dissolved organic carbon	.1	0.8	0.6
Fluoride	.1	<0.1	0.1
Potassium	.1	0.66	0.61
Silica	.1	13	12

boxplots of selected constituents, triangular diagrams of major ions, and bar charts of detection frequencies. An ANOVA (analysis of variance) with a Bonferroni adjustment was used to test for statistically significant differences between data collected for the three land-use studies (Alt, 1982; Pearce, 1982; Miller, 1985; Moore and McCabe, 1993). A confidence level of 95 percent was used to indicate statistically significant differences. The letters A, B, and C are used in the tables to indicate significant differences (matching letters indicate no significant difference). Log transformations were used when needed and censored values were set equal to zero.

Acknowledgments

The author thanks the land owners and private wells owners, whose cooperation made this study possible. Paul Hanson of the U.S. Geological Survey collected the land-use data for each well site and also prepared the maps and illustrations. The author also thanks E. Calvin Alexander of the University of Minnesota, and William Andrews, Geoffrey Delin, and Perry Jones of the U.S. Geological Survey, for reviewing this report.

GROUND-WATER QUALITY

Chemical analyses described in this report include physical parameters, major ions, selected trace elements, nutrients, DOC, pesticides, VOCs, and tritium. Results from the urban and agricultural studies are described in detail in Andrews and others (1998) and Ruhl and others

(2000), respectively. Data are available from the USGS office in Mounds View, Minnesota.

Physical Parameters

Physical parameters measured include depth to water, temperature, pH, specific conductance, dissolved oxygen concentration, turbidity, and alkalinity (fig. 4; table 7). The depth to water below the land surface generally was less than 20 ft. The depth to water was significantly deeper for the agricultural study, with a median of 18.56 ft, than for the urban and forested studies (medians of 10.84 and 7.55 respectively). No significant difference was present between the depth to water for the urban and forested studies. Water temperature medians ranged from 8.1 to 12.2°C for the three land-use studies. Water for the forested study had temperatures ranging from 6.7 to 9.1°C, which generally were less than for the urban or agricultural studies which ranged from 7.0 to 18.7°C. Values of pH measurements ranged from 6.5 to 8.2 for the three land-use studies. The only significant difference in pH was between the urban and agricultural studies, with medians of 7.2 and 7.4, respectively. Specific conductance was significantly greater for the urban study than for the agricultural or forested studies, with a median of 914 microsiemens per centimeter ($\mu\text{S}/\text{cm}$) compared to 553 and 487 $\mu\text{S}/\text{cm}$, respectively. Dissolved oxygen concentrations for the urban study were significantly less than for the agricultural or forested studies. The range of

dissolved oxygen concentrations was from less than 0.1 to 11.2 mg/L for the three land-use studies, with a median concentration for the urban study of 0.9 mg/L. No significant difference was present in median dissolved oxygen concentrations between the agricultural and forested studies, 5.3 and 2.3 mg/L, respectively. Median turbidities ranged from 1.5 to 26 nephelometric turbidity units (NTU) for the three land-use studies, with significantly greater turbidities for the urban study than for the agricultural or forested studies. Alkalinities ranged from 18 to 539 mg/L as calcium carbonate (CaCO_3) for the three land-use studies, with the median for the agricultural study (178 mg/L as CaCO_3) less than for the urban or forested studies, 261 and 246 mg/L as CaCO_3 , respectively. The only significant difference in median alkalinities was between the urban and agricultural studies, with greater alkalinities for the urban study.

Major Ions and Selected Trace Elements

Major ions analyzed in water samples included calcium, magnesium, sodium, potassium, sulfate, chloride, fluoride, bromide, and silica (table 8). Hardness, dissolved solids, iron, and manganese also were included in the water analyses (table 8). Hardness, an important water-quality characteristic to many water users, was calculated by multiplying the sum of calcium and magnesium concentrations in milliequivalents per

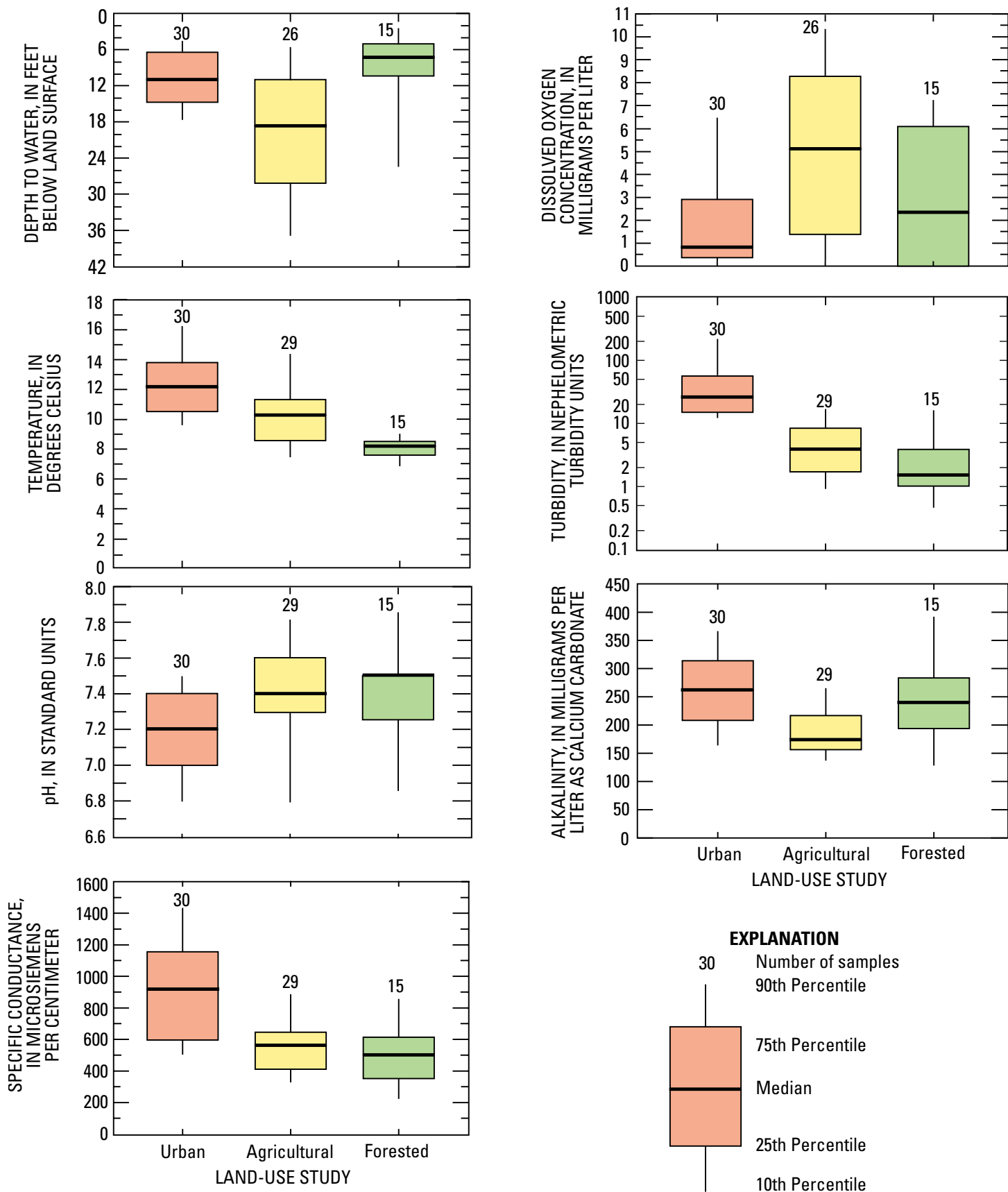


Figure 4.--Field measurements of physical parameters in water samples from land-use study wells.

Table 7. Median values, standard deviations, and ranges of physical parameters in water samples from land-use study wells
[ft, feet; °C, degrees Celsius; µS/cm, microseimens per centimeter; mg/L, milligrams per liter; NTU, nephelometric turbidity unit; <, less than; CaCO₃, calcium carbonate]

Physical Parameter	Units	Study	Statistical group ¹	Median	Standard deviation	Range
Depth to water	ft below land surface	Urban	B	10.84	5.22	2.39 – 23.14
		Agricultural	A	18.56	10.70	3.31 – 37.68
		Forested	B	7.55	7.61	0.69 – 29.27
Water temperature	°C	Urban	A	12.2	2.5	8.9 – 18.7
		Agricultural	B	10.3	2.4	7.0 – 18.1
		Forested	C	8.1	0.7	6.7 – 9.1
pH	standard units	Urban	B	7.2	0.3	6.6 – 7.9
		Agricultural	A	7.4	0.3	6.6 – 8.2
		Forested	AB	7.5	0.4	6.5 – 8.2
Specific conductance	µS/cm at 25 °C	Urban	B	914	418	150 – 2,450
		Agricultural	A	553	193	234 – 984
		Forested	A	487	215	194 – 969
Dissolved oxygen	mg/L	Urban	B	0.9	2.3	0.1 – 7.5
		Agricultural	A	5.3	3.6	<0.1 – 11.2
		Forested	A	2.3	3.0	<0.1 – 7.4
Turbidity	NTU	Urban	B	26	169	4.7 – 730
		Agricultural	A	3.9	8.8	0.6 – 46
		Forested	A	1.5	6.5	0.3 – 24
Alkalinity	mg/L as CaCO ₃	Urban	B	261	101	18 – 539
		Agricultural	A	178	54	61 – 283
		Forested	AB	246	85	91 – 418

¹The letters A, B, and C are used to indicate statistically significant differences between studies (matching letters indicate no statistically significant difference).

liter by 50 and is expressed as mg/L of CaCO₃ (Hem, 1985).

Median sulfate and chloride concentrations were significantly different among all three land-use studies, with the greatest concentrations for the urban study and the least for the forested study (fig. 5; table 8). Secondary standards are unenforceable guidelines regulating cosmetic and aesthetic effects in drinking water set by the U.S. Environmental Protection Agency (USEPA) (U.S. Environmental Protection Agency, 1996). Sulfate and chloride concentrations exceeded the USEPA secondary standard of 250 mg/L for both compounds, in 13 and 3 percent of the water samples from the urban study, respectively. None of the water samples from the agricultural or forested studies exceeded the secondary standards.

Median concentrations of calcium, sodium, potassium, and silica were all significantly greater for the urban study than for the agricultural or forested studies (fig. 5; table 8). No significant difference was present between the agricultural and forested studies. For magnesium, fluoride, bromide, iron, and manganese concentrations, there were no significant differences between the three land-use studies (table 8).

Most of the water samples were very hard (greater than 180 mg/L as CaCO₃) using the hardness scale developed by Durfor and Becker (1964). Dissolved solids were significantly greater for the urban study than for the agricultural or forested studies, which were not significantly different from each other. For the urban study, 57 percent of the water samples

exceeded the USEPA secondary standard of 500 mg/L for dissolved solids (U.S. Environmental Protection Agency, 1996). For the agricultural and forested studies, 14 and 13 percent of the water samples exceeded the USEPA secondary standard for dissolved solids, respectively. USEPA secondary standards for iron and manganese concentrations of 0.3 and 0.05 mg/L, respectively (U.S. Environmental Protection Agency, 1996) were exceeded in 37 and 77 percent of water samples from the urban study, respectively, 14 and 31 percent for the agricultural study, and 27 and 33 percent for the forested study.

Trilinear plots graphically show relative proportions of major ions dissolved in water. Water composition in the surficial aquifer is dominated by calcium, magnesium, and bicarbon-

Table 8. Median values, standard deviations, and ranges in concentrations of major ions and selected trace elements dissolved in water samples from land-use study wells

[all concentrations in milligrams per liter; <, less than]

Constituent	Study	Statistical group ¹	Median	Standard deviation	Range
Hardness, as CaCO ₃	Urban	B	380	191	52 – 880
	Agricultural	A	250	97	73 – 470
	Forested	A	260	97	100 – 430
Calcium	Urban	B	110	55	15 – 240
	Agricultural	A	67	27	22 – 130
	Forested	A	70	26	31 – 130
Magnesium	Urban	A	26	15	3.6 – 69
	Agricultural	A	20	8	4.2 – 37
	Forested	A	15	9	6.0 – 36
Sodium	Urban	B	18	49	3.6 – 230
	Agricultural	A	4.4	13	2.3 – 66
	Forested	A	3.1	7.0	1.6 – 28
Potassium	Urban	B	2.7	4.5	0.4 – 26
	Agricultural	A	1.3	1.3	0.28 – 7.3
	Forested	A	0.92	0.7	0.28 – 3.3
Sulfate	Urban	A	72	122	8.6 – 520
	Agricultural	B	20	16	2.3 – 61
	Forested	C	5.1	4.0	<0.1 – 16
Chloride	Urban	A	46	74	4.3 – 370
	Agricultural	B	17	18	1.1 – 88
	Forested	C	1.2	24	0.17 – 93
Fluoride	Urban	A	0.15	0.12	<0.1 – 0.4
	Agricultural	A	<0.1	0.06	<0.1 – 0.19
	Forested	A	<0.1	0.05	<0.1 – 0.14
Bromide	Urban	A	0.04	0.05	<0.01 – 0.18
	Agricultural	A	0.043	0.04	<0.01 – 0.14
	Forested	A	0.022	0.04	<0.01 – 0.14
Silica	Urban	B	24	6.4	14 – 38
	Agricultural	A	15	3.8	7.8 – 25
	Forested	A	20	3.5	10 – 23
Dissolved solids	Urban	B	544	245	95 – 1210
	Agricultural	A	322	120	132 – 596
	Forested	A	268	99	118 – 505
Iron	Urban	A	0.063	5.4	0.003 – 26
	Agricultural	A	<0.01	1.1	<0.01 – 4.8
	Forested	A	<0.01	1.6	<0.01 – 5.8
Manganese	Urban	A	0.45	0.75	<0.001 – 2.7
	Agricultural	A	<0.004	0.12	<0.004 – 0.39
	Forested	A	<0.004	0.14	<0.004 – 0.41

¹The letters A, B, and C are used to indicate statistically significant differences between studies (matching letters indicate no statistically significant difference).

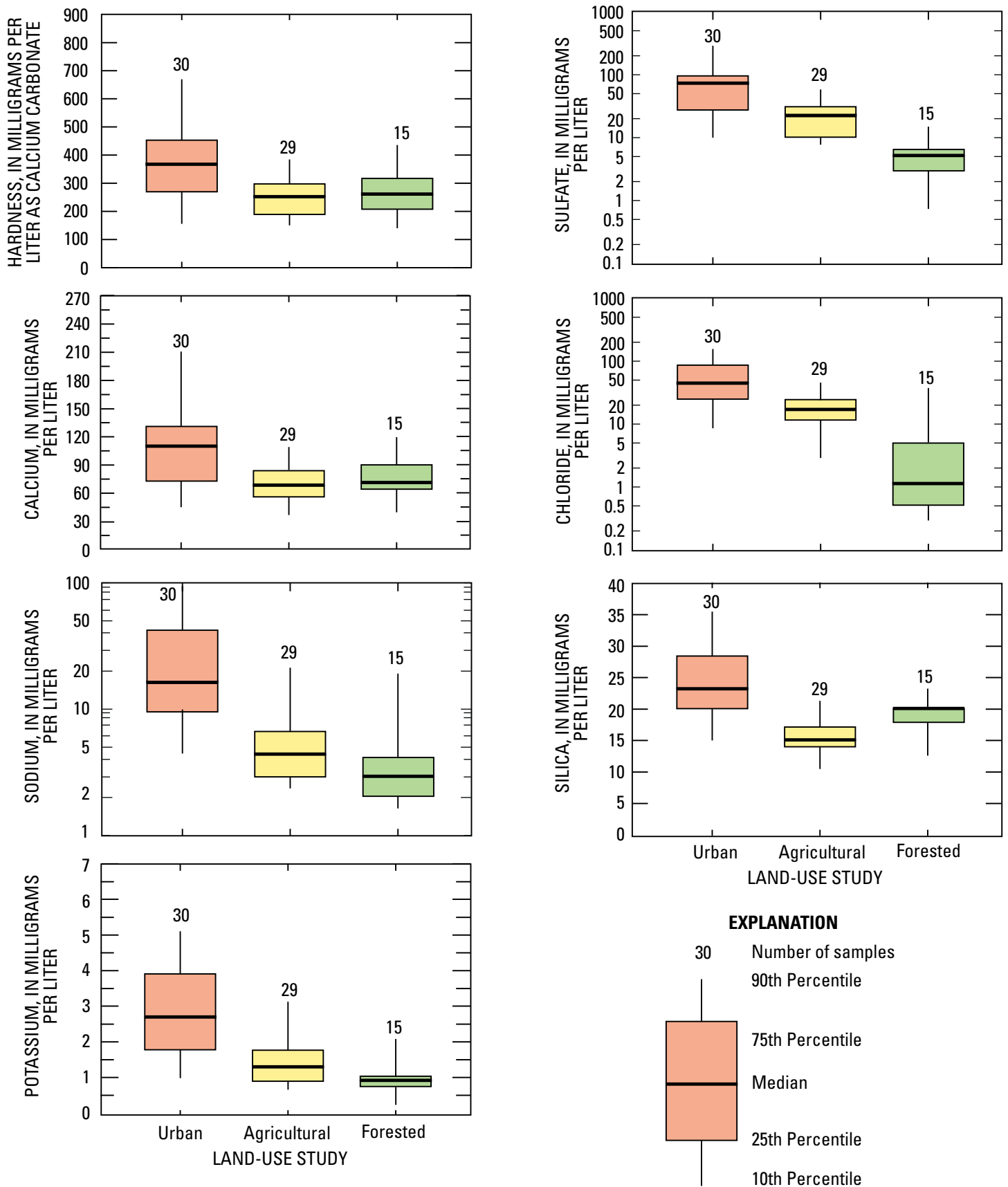


Figure 5.--Dissolved major ions and hardness in water samples from land-use study wells.

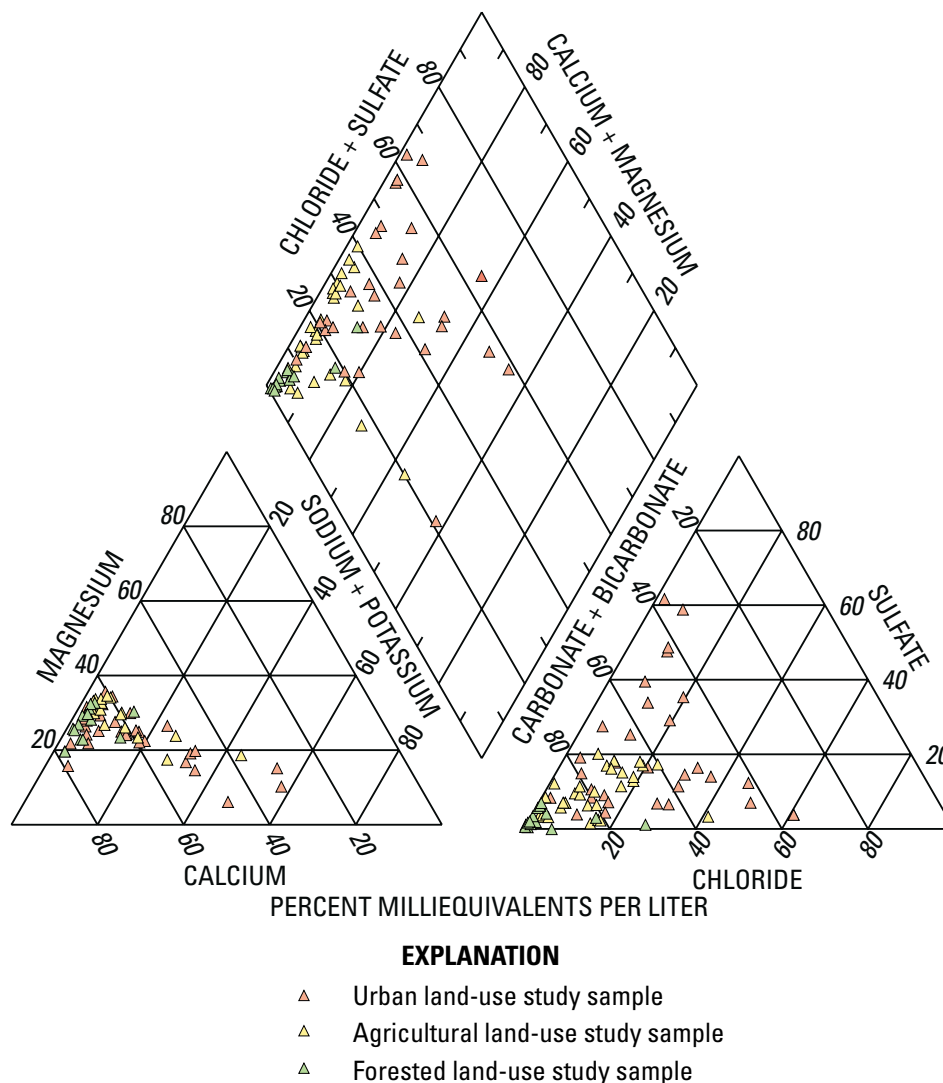


Figure 6.--Major ion concentrations in water samples from land-use study wells.

ate for all three land-use study areas, as indicated on the trilinear plot of major ion concentrations (fig. 6). However for the urban study, the water composition is more variable due to greater sodium and chloride concentrations.

Nutrients and Dissolved Organic Carbon

Nutrients analyzed in water samples include nitrite plus nitrate-nitrogen, nitrite-nitrogen, ammonia-nitrogen, ammonia plus organic-nitrogen, phosphorus, orthophosphorus, and DOC (fig. 7; table 9). The primary nutrients in ground water are nitrate and phosphorus. Nitrate is typically reported as the sum of nitrite

(NO_2^-) plus nitrate (NO_3^-) as nitrogen. Because nitrite is usually detected in concentrations much less than those for nitrate, nitrite plus nitrate nitrogen will be referred to as nitrate nitrogen in this report. Elevated concentrations of nitrate-nitrogen in drinking water exceeding the USEPA Maximum Contaminant Level (MCL) of 10 mg/L (U.S. Environmental Protection Agency, 1996) have been associated with “blue-baby” syndrome (methemoglobinemia) and other health risks. Nitrate-nitrogen and phosphorus in ground water discharged to surface water can also lead to eutrophication of lakes and wetlands. As a result, fish and other aquatic species can be killed.

Nitrate-nitrogen concentrations were significantly greater in the agricultural study area than in the urban or forested study areas. No significant difference was present between the urban and forested study areas. The USEPA MCL for nitrate-nitrogen was exceeded in 38 percent of samples from the agricultural study area, 3 percent of samples from the urban study area, and no samples from the forested study area. Nitrate-nitrogen concentrations above 3 mg/L indicate possible human inputs (Madison and Burnett, 1984). Seventy-two percent of agricultural study area samples and 30 percent of urban study area samples were above 3 mg/L, indicating that the effects of anthropogenic

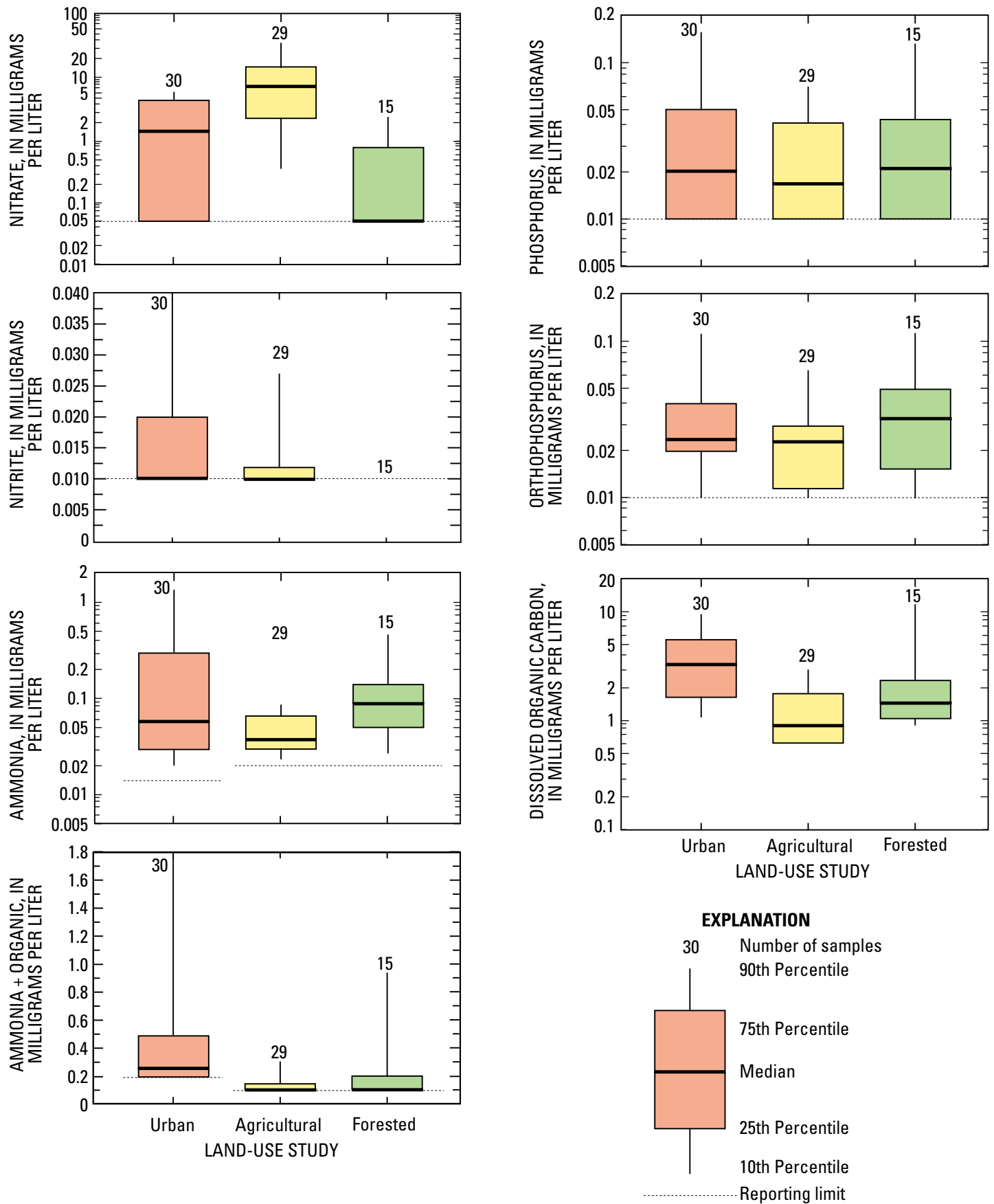


Figure 7.--Nutrients and dissolved organic carbon in water samples from land-use study wells.

Table 9. Median values, standard deviations, and ranges in concentrations of nutrients and organic carbon dissolved in water samples from land-use study wells
[all units in milligrams per liter; nd, not determined; <, less than]

Constituent	Study	Reporting limit	Statistical group ¹	Median	Standard deviation	Range
Nitrite plus nitrate-nitrogen	Urban	0.05	B	1.45	3.46	<0.05 – 16
	Agricultural	0.05	A	7.11	12.42	<0.05 – 46.6
	Forested	0.05	B	<0.05	0.83	<0.05 – 2.46
Nitrite-nitrogen	Urban	0.01	A	<0.01	0.02	<0.01 – 0.07
	Agricultural	0.01	A	<0.01	0.03	<0.01 – 0.15
	Forested	0.01	A	<0.01	nd	<0.01
Ammonia-nitrogen	Urban	0.01	B	0.060	0.482	0.02 – 1.6
	Agricultural	0.02	A	0.039	0.062	<0.02 – 0.313
	Forested	0.02	AB	0.084	0.174	<0.02 – 0.684
Ammonia plus organic-nitrogen	Urban	0.2	B	0.25	0.62	<0.2 – 2.0
	Agricultural	0.1	A	<0.1	0.19	<0.1 – 0.91
	Forested	0.1	AB	<0.1	0.44	<0.1 – 1.7
Phosphorus	Urban	0.01	A	0.020	0.281	<0.01 – 1.5
	Agricultural	0.05	A	0.016	0.030	<0.05 – 0.119
	Forested	0.05	A	0.021	0.047	<0.05 – 0.166
Orthophosphorus	Urban	0.01	A	0.025	0.025	<0.01 – 0.5
	Agricultural	0.01	A	0.020	0.027	<0.01 – 0.122
	Forested	0.01	A	0.032	0.045	<0.01 – 0.189
Dissolved organic carbon	Urban	0.1	A	3.5	2.9	1.0 – 11
	Agricultural	0.1	A	0.8	1.9	0.4 – 9.1
	Forested	0.1	A	1.5	10.4	0.8 – 42

¹The letters A and B are used to indicate statistically significant differences between studies (matching letters indicate no statistically significant difference).

activities on the land surface were being reflected in the nitrate-nitrogen concentrations in the ground water. None of the forested study area nitrate-nitrogen samples were above 3 mg/L.

The only significant differences in ammonia-nitrogen and ammonia plus organic-nitrogen were between the urban and agricultural study areas, with greater median concentrations in the urban study area than in the agricultural study area. Ranges in median concentrations for all three land-use study areas were very small, 0.039–0.084 mg/L for ammonia-nitrogen and from less than 0.1 to 0.25 mg/L for ammonia plus organic-nitrogen.

Nitrite-nitrogen, phosphorus, and orthophosphorus concentrations were not significantly different among

land-use study areas. Concentrations of nitrite-nitrogen, phosphorus, and orthophosphorus generally were less than 0.05 mg/L. Median values for these constituents ranged from less than 0.01 to 0.032 mg/L.

Median concentrations of DOC ranged from 0.8 to 3.5 mg/L with no significant differences among the land-use study areas. The range of concentrations was 0.4–42 mg/L with most concentrations generally less than 5 mg/L.

Pesticides

In the agricultural and urban study areas, analyses were done for 83 pesticides and pesticide metabolites (referred to as pesticides in this report) in water samples (table 10). In the forested study area, only 47 of the

83 pesticides were analyzed, due to the low likelihood of detection. A total of 19 individual pesticides were detected in water samples from one or more land-use study wells (fig. 8; table 11). None of the concentrations of the detected pesticides exceeded MCLs set by the USEPA for drinking water (U.S. Environmental Protection Agency, 1996). A total of 11 different pesticides were detected in water samples from the urban study area, 14 in the agricultural study area, and 4 in the forested study area. Atrazine, deethylatrazine, and simazine were the only pesticides detected in water samples from all three land-use study areas. In water samples from the urban study area, 56.7 percent had one or more pesticide detections, compared to 86.2 percent in the agricul-

Table 10. Pesticides in water samples, by chemical group

Triazines	Organophosphates	Organochlorines	Carbamates	Dinitroaniline	Miscellaneous. acids
Atrazine	Azinphos-methyl	Chlorothalonil	3-Hydroxycarbofuran	Benfluralin	Acifluorfen
Deethylatrazine	Chloropyrifos	Dacthal	Aldicarb	Ethalfuralin	Bromoxynil
Cyanazine	Diazinon	Dacthal, mono acid	Aldicarb-sulfone	Oryzalin	Chloramben
Metribuzin	Disulfoton	<i>p,p'</i> -DDE	Aldicarb-sulfoxide	Pendimethalin	Chlopyralid
Prometon	Ethoprop	Dichlobenil	Butylate	Trifluralin	Dicamba
Simazine	Fonofos	Dieldrin	Carbaryl	Uracils	Dinoseb
Pyrethroid	Malathion	α -HCH	Carbofuran	Bromacil	DNOC
cis-Permethrin	Methyl parathion	γ -HCH (lindane)	EPTC	Terbacil	Picloram
Ureas	Parathion	Amides	Methiocarb	Chlorphenoxy acids	Propargite
Diuron	Phorate	Acetochlor	Methomyl	2,4,5-T	Trichlopyr
Fenuron	Terbufos	Alachlor	Molinate	2,4,5-TP (Silvex)	Miscellaneous
Fluometuron		2,6-Diethylaniline	Oxamyl	2,4-D	Bentazon
Linuron		Metolachlor	Pebulate	2,4-DB	Norflurazon
Neburon		Napropamide	Propham	Dichlorprop	
Tebuthiuron		Pronamide	Propoxur	MCPA	
		Propachlor	Thiobencarb	MCPB	
		Propanil	Triallate		

tural study area, and 46.7 percent in the forested study area (table 12). There was a significantly greater percentage of pesticide detections in the

agricultural study area than in the urban or forested study areas. The urban and forested study areas were not significantly different from each

other. In the urban study area, the median number of pesticides detected in water samples was one, in the agricultural study area the median was

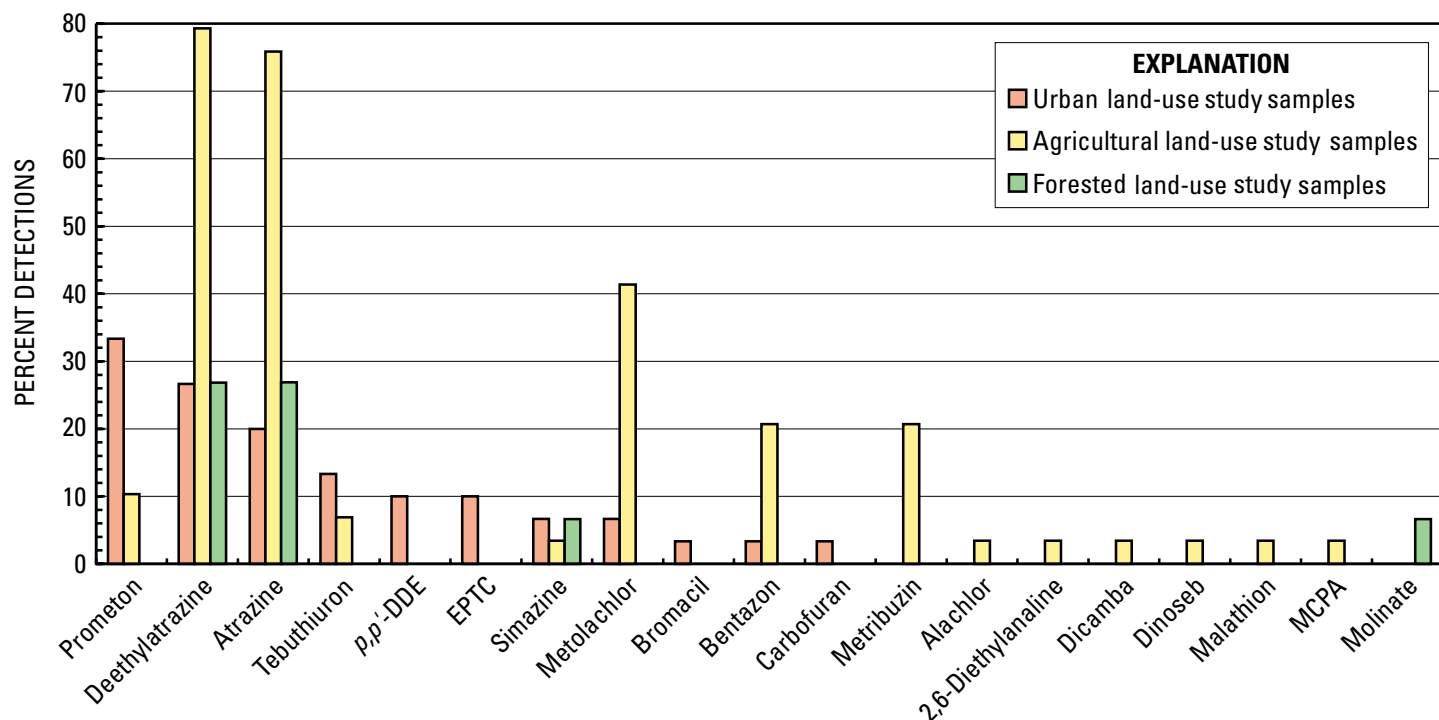


Figure 8.--Frequencies of detection of pesticides in water samples from land-use study wells.

Table 11. Reporting limits, numbers of detections, ranges in concentrations, and maximum contaminant levels of pesticides detected in water samples from land-use study wells

[µg/L, micrograms per liter; E, detection with estimated concentration; na, not analyzed; <, less than]

Compound	Reporting limit, in µg/L	Study	Number of samples with detectable concentrations	Range of concentration, in µg/L	Maximum Contaminant level ¹ , in µg/L
Prometon	0.018	Urban	10	<0.018 – 0.9	none
		Agricultural	3	<0.018 – 0.0231	
		Forested	0	<0.018	
Deethylatrazine	.002	Urban	8	<0.002 – E0.035	none
		Agricultural	23	<0.002 – E0.149	
		Forested	4	<0.002 – E0.0254	
Atrazine	.001	Urban	6	<0.001 – 0.046	3.0
		Agricultural	22	<0.001 – 0.275	
		Forested	4	<0.001 – 0.009	
Tebuthiuron	.01	Urban	4	<0.01 – 0.053	none
		Agricultural	2	<0.01 – 0.0767	
		Forested	0	<0.01	
<i>p,p'</i> -DDE	.006	Urban	3	<0.006 – E0.005	none
		Agricultural	0	<0.006	
		Forested	0	<0.006	
EPTC	.002	Urban	3	<0.002 – E0.003	none
		Agricultural	0	<0.002	
		Forested	0	<0.002	
Simazine	.005	Urban	2	<0.005 – 0.095	4.0
		Agricultural	1	<0.005 – 0.0107	
		Forested	1	<0.005 – 0.0121	
Metolachlor	.002	Urban	2	<0.002 – 0.009	none
		Agricultural	12	<0.002 – 0.199	
		Forested	0	<0.002	
Bromacil	.035	Urban	1	<0.035 – 0.09	none
		Agricultural	0	<0.035	
		Forested	na	na	
Bentazon	.014	Urban	1	<0.014 – E0.29	none
		Agricultural	6	<0.014 – 0.810	
		Forested	na	na	
Carbofuran	.003	Urban	1	<0.003 – 0.037	40.0
		Agricultural	0	<0.003	
		Forested	0	<0.003	
Metribuzin	.004	Urban	0	<0.004	none
		Agricultural	6	<0.004 – 0.142	
		Forested	0	<0.004	
Alachlor	.002	Urban	0	<0.002	2.0
		Agricultural	1	<0.002 – 0.029	
		Forested	0	<0.002	
2,6-Diethylaniline	.003	Urban	0	<0.003	none
		Agricultural	1	<0.003 – E0.0011	
		Forested	0	<0.003	
Dicamba	.035	Urban	0	<0.035	none
		Agricultural	1	<0.035 – E0.008	
		Forested	na	na	
Dinoseb	.035	Urban	0	<0.035	7.0
		Agricultural	1	<0.035 – E0.01	
		Forested	na	na	
Malathion	.005	Urban	0	<0.005	none
		Agricultural	1	<0.005 – 0.006	
		Forested	0	<0.005	
MCPA	.17	Urban	0	<0.17	none
		Agricultural	1	<0.17 – ² (0.02 – 1.28)	
		Forested	na	na	
Molinate	.004	Urban	0	<0.004	none
		Agricultural	0	<0.004	
		Forested	1	<0.004 – E0.0031	

¹ U.S. Environmental Protection Agency (1996)

² MCPA was detected in the water sample, but the lab was unable to quantify the concentration (between 0.02 – 1.28 µg/L).

Table 12. Total pesticide concentrations and percent of wells with pesticide detections
[µg/L, micrograms per liter]

Study area	Statistical group ¹	Median total pesticide concentration, in µg/L	Standard deviation, in µg/L	Range, in µg/L	Percent of wells with pesticide detections	Statistical group ¹
Urban (30 wells)	A	0.003	0.20	0 – 1.067	56.7	B
Agricultural (29 wells)	A	.074	.29	0 – 1.2404	86.2	A
Forested (15 wells)	B	.0	.01	0 – 0.0334	46.7	B

¹The letters A and B are used to indicate statistically significant differences between studies (matching letters indicate no statistically significant difference).

three, and in the forested study area the median was zero. The total pesticide concentrations were significantly greater in the agricultural and urban study areas than in the forested study area, with median concentrations of 0.074, 0.003, and 0 µg/L, respectively (fig. 9; table 12). The greatest total pesticide concentration was 1.240 µg/L in a water sample from the agricultural study area.

Atrazine and its metabolite deethylatrazine were the most frequently detected pesticides, detected in 43 and 47 percent of all water samples, respectively (fig. 8). Atrazine and deethylatrazine were the most frequently detected pesticides in the agricultural study area, at 76 and 79 percent, respectively, and in the for-

ested study area at 27 percent each (fig. 8). Metolachlor was the third most frequently detected pesticide at 19 percent (fig. 8). Prometon was the fourth most frequently detected pesticide at 18 percent, and was the most frequently detected pesticide in the urban study area (33 percent of water samples) (fig. 8). The one detection of molinate in a water sample from the forested study area is most likely a false positive because molinate is not used in Minnesota and is not observed in precipitation (Paul Capel, U.S. Geological Survey, written commun., 2000). All of the pesticides detected in the land-use study areas were herbicides, except for the insecticides *p,p'*-DDE (a metabolite of DDT), carbofuran, and malathion. The most fre-

quently detected group of pesticides were the triazines, which includes some of the most frequently detected pesticides (prometon, atrazine, simazine, and metribuzin).

Volatile Organic Compounds

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

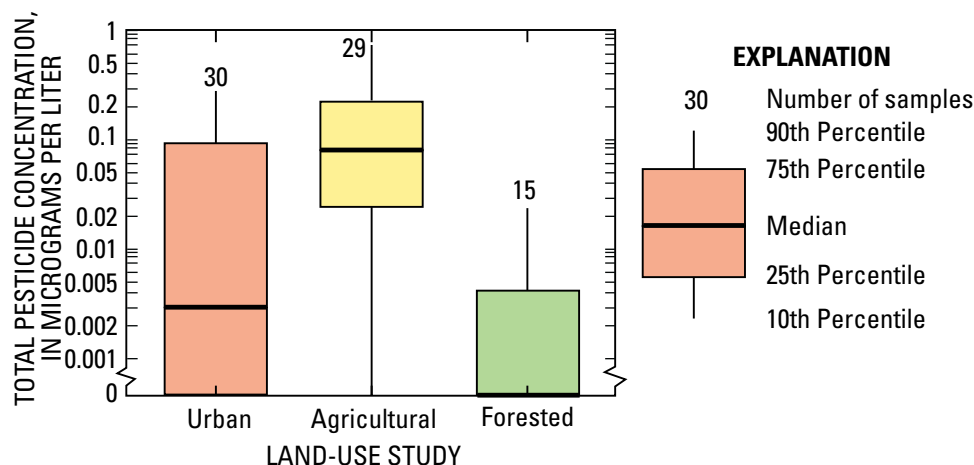


Figure 9.--Total concentrations of pesticides in water samples from land-use study wells

Table 13. Volatile organic compounds in water samples, by chemical group

Alkanes	Alkenes	Alkyl Benzenes
1,1,1-Trichloroethane / Methyl chloroform	Chloroethene / Vinyl chloride	(1-Methylethyl) benzene / Isopropylbenzene
Bromomethane / Methyl bromide	Bromoethene	Ethylbenzene
Chloromethane / Methyl chloride	Trichloroethene	<i>n</i> -Propylbenzene
Chloroethane	Hexachlorobutadiene	<i>n</i> -Butylbenzene
Dichloromethane / Methylene chloride	Tetrachloroethene	Methylbenzene / Toluene
1,1,1,2-Tetrachloroethane	<i>cis</i> -1,2-Dichloroethene	1,3-Dimethylbenzene and 1,4-Dimethylbenzene / <i>m</i> - and <i>p</i> -Xylene
Dibromomethane	<i>trans</i> -1,2-Dichloroethene	1,2-Dimethylbenzene / <i>o</i> -Xylene
1,1-Dichloroethane	<i>cis</i> -1,3-Dichloropropene	2-Ethyltoluene / <i>o</i> -Ethyltoluene
1,2-Dichloroethane	<i>trans</i> -1,3-Dichloropropene	1-Isopropyl-4-methylbenzene / <i>p</i> -Isopropyl-toluene
1,2-Dichloropropane	3-Chloro-1-propene	(1,1-Dimethylethyl) benzene / <i>tert</i> -Butyl-benzene
1,1,2,2-Tetrachloroethane	1,1-Dichloropropene	(1-Methylpropyl) benzene / <i>sec</i> -Butyl-benzene
1,2-Dibromo-3-chloropropane	<i>trans</i> -1,4-Dichloro-2-butene	1,2,3-Trimethylbenzene
1,2,3-Trichloropropane	1,1-Dichloroethene	1,2,4-Trimethylbenzene
1,2-Dibromoethane	Halogenated Aromatics	1,3,5-Trimethylbenzene
1,1,2-Trichloroethane	1,2,3-Trichlorobenzene	1,2,3,4-Tetramethylbenzene / Prehnitene
1,1,1,2,2,2-Hexachloroethane	1,2-Dichlorobenzene	1,2,3,5-Tetramethylbenzene / Isodurene
Bromochloromethane	1,3-Dichlorobenzene	Ethers and other oxygenated compounds
2,2-Dichloropropane	1,4-Dichlorobenzene	Methyl <i>tert</i> -butyl ether / MTBE
1,3-Dichloropropane	Chlorobenzene	Diethyl ether / Ethyl ether
Iodomethane / Methyl iodide	1,2,4-Trichlorobenzene	Diisopropyl ether
Tetrachloromethane / Carbon tetrachloride / CFC-10	Bromobenzene	<i>tert</i> -Amyl methyl ether / <i>t</i> -Pentyl methylether
Trichlorofluoromethane / CFC-11	1-Chloro-2-methylbenzene / <i>o</i> -Chlorotoluene	Ethyl <i>tert</i> -butyl ether / <i>t</i> -Butyl ethyl ether
Dichlorodifluoromethane / CFC-12	1-Chloro-4-methylbenzene / <i>p</i> -Chlorotoluene	Tetrahydrofuran
1,1,2-Trichloro-1,2,2-trifluoroethane / Freon 113	Aromatic Hydrocarbons	Acetone
Bromodichloromethane	Benzene	2-Hexanone
Tribromomethane / Bromoform	Naphthalene	2-Butanone / Methyl ethyl ketone
Dibromochloromethane	Ethenylbenzene / Styrene	4-Methyl-2-pentanone / Methyl isobutyl ketone
Trichloromethane / Chloroform		Others
		Carbon disulfide
		2-Propenenitrile / Acrylonitrile
		2-Propenal / Acrolein
		Methyl acrylonitrile
		Methyl methacrylate
		Ethyl methacrylate
		Methyl acrylate

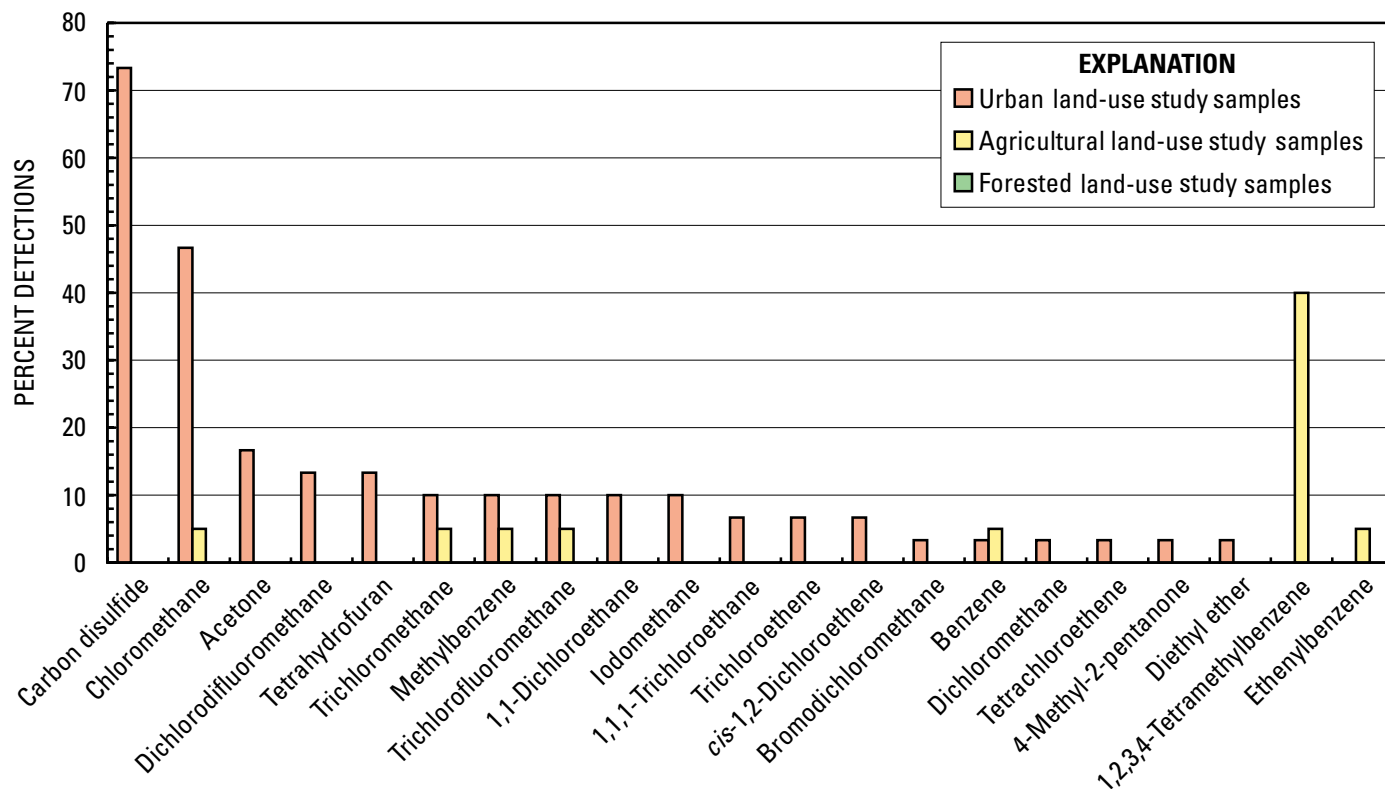


Figure 10.--Frequencies of detection of volatile organic compounds in water samples from land-use study wells.

VOCs scavenged during passage through the atmosphere.

Concentrations of 86 VOCs were determined in ground-water samples from the land-use study areas (table 13). Of the 86 VOCs sampled, only 21 were detected in one or more land-use study wells (fig. 10; table 14). None of the concentrations of the detected VOCs exceeded MCLs set by the USEPA for drinking water (U.S. Environmental Protection Agency, 1996). A total of 19 different VOCs were detected in the urban study area and 7 in the agricultural study area. No VOCs were detected in the forested study area. One or more VOCs were detected in 90 percent of water samples from the urban study area and in 50 percent of water samples from the agricultural study area (table 15). Detection rates for one or more VOCs were significantly differ-

ent from each other in all three land-use study areas. The median number of VOCs detected per water sample in the urban study area was two, and in the agricultural study areas it was less than one. The median total VOC concentrations also were significantly different among the three land-use study areas, with the highest median total VOC concentration in the urban study area at 0.18 µg/L (fig. 11; table 15). Total VOC concentrations generally were less than 1 µg/L.

Five of the 21 VOCs detected (chloromethane, trichloromethane, methylbenzene, trichlorofluoromethane, and benzene) were detected in both the urban and agricultural study areas (fig. 10; table 14). The most frequently detected VOC in the urban study was carbon disulfide (73 percent of water samples) (fig. 10). The most frequently detected

VOC in the agricultural study area was 1,2,3,4-tetramethyl benzene (prehnitene) (40 percent of water samples) (fig. 10). Chloromethane is probably an artifact of VOC sample preservation using hydrochloric acid. The most frequently detected group of VOCs were the halogenated alkanes, which includes the chlorofluorocarbons and trihalomethanes.

Tritium

Tritium (^3H) is a radioactive isotope of hydrogen, usually present in water molecules. Tritium decays rapidly, with a half-life of 12.43 years, and is naturally produced in the atmosphere by the interaction of cosmic rays with nitrogen and oxygen (Drever, 1988). Anthropogenic sources of tritium include nuclear reactors and detonations of fusion or thermonuclear devices. Prior to the advent of atmospheric testing of

Table 14. Reporting limits, numbers of detections, ranges in concentrations, and maximum contaminant levels of volatile organic compounds detected in water samples from land-use study wells

[µg/L, micrograms per liter; <, less than; E, detection with estimated concentration; CFC, chlorofluorocarbon; VOC, volatile organic compound]

Compound	Reporting limit, in µg/L	Maximum Contaminant Level ² , in µg/L	Study ¹	Number of samples with detectable concentrations	Range of concentration, in µg/L
Carbon disulfide	0.05	none	Urban	22	<0.05 – 0.52
	0.370	none	Agricultural	0	<0.370
Chloromethane (methyl chloride)	0.20	none	Urban	14	<0.20 – E0.15
	0.250	none	Agricultural	1	<0.250 – E0.099
Acetone	5.0	none	Urban	5	<5.0 – 6.0
	5.0	none	Agricultural	0	<5.0
Dichlorodifluoromethane (CFC–12)	0.20	none	Urban	4	<0.20 – E0.23
	0.140	none	Agricultural	0	<0.140
Tetrahydrofuran	5.0	none	Urban	4	<5.0 – 1.6
	9.0	none	Agricultural	0	<9.0
Trichloromethane (chloroform)	0.05	² 100	Urban	3	<0.05 – 12.1
	0.052	² 100	Agricultural	1	<0.052 – E0.020
Methylbenzene (toluene)	0.05	1,000	Urban	3	<0.05 – 0.17
	0.050	1,000	Agricultural	1	<0.050 – E0.083
Trichlorofluoromethane (CFC–11)	0.10	none	Urban	3	<0.01 – E0.05
	0.090	none	Agricultural	1	<0.090 – E0.032
1,1-Dichloroethane	0.05	none	Urban	3	<0.05 – E0.09
	0.066	none	Agricultural	0	<0.066
Iodomethane (methyl iodide)	0.05	none	Urban	3	<0.05 – E0.04
	0.210	none	Agricultural	0	<0.210
1,1,1-Trichloroethane	0.05	200	Urban	2	<0.05 – E0.06
	0.032	200	Agricultural	0	<0.032
Trichloroethene	0.05	5.0	Urban	2	<0.05 – 0.12
	0.038	5.0	Agricultural	0	<0.038
<i>cis</i> -1,2-Dichloroethene	0.05	70	Urban	2	<0.05 – 0.11
	0.038	70	Agricultural	0	<0.038
Bromodichloromethane	0.10	² 100	Urban	1	<0.10 – 0.17
	0.048	² 100	Agricultural	0	<0.048
Benzene	0.05	5.0	Urban	1	<0.05 – 0.16
	0.100	5.0	Agricultural	1	<0.100 – E0.120
Dichloromethane (methylene chloride)	0.10	5.0	Urban	1	<0.10 – E0.06
	0.380	5.0	Agricultural	0	<0.380
Tetrachloroethene	0.05	5.0	Urban	1	<0.05 – E0.02
	0.100	5.0	Agricultural	0	<0.100
4-Methyl-2-pentanone (methylisobutylketone)	5.0	none	Urban	1	<5.0 – E0.6
	0.370	none	Agricultural	0	<0.370
Diethyl ether (ethyl ether)	0.10	none	Urban	1	<0.10 – 0.19
	0.170	none	Agricultural	0	<0.170
1,2,3,4-Tetramethyl benzene (prehnitene)	0.05	none	Urban	0	<0.05
	0.230	none	Agricultural	8	<0.230 – E0.062
Ethenylbenzene (styrene)	0.05	100	Urban	0	<0.05
	0.042	100	Agricultural	1	<0.042 – E0.029

¹No VOCs were detected in the water samples from the forested study.

²U.S. Environmental Protection Agency (1996)

³The MCL for trihalomethanes is 100 µg/L for the sum of the concentrations of those pesticides (bromodichloromethane, tribromomethane / bromoform, dibromochloromethane, and trichloromethane / chloroform).

Table 15. Total volatile organic compound concentrations and percent of wells with volatile organic compound detections
[VOC, volatile organic compound; µg/L, micrograms per liter]

Study area	Statistical group ¹	Median total VOC concentration, in µg/L	Standard deviation, in µg/L	Range, in µg/L	Percent of wells with VOC detections	Statistical group ¹
Urban (30 wells)	A	0.18	2.76	0 – 12.42	90	A
Agricultural (20 wells)	B	0.0145	0.073	0 – 0.331	50	B
Forested (15 wells)	C	0	0	0	0	C

¹The letters A, B, and C are used to indicate statistically significant differences between studies (matching letters indicate no statistically significant difference).

fusion devices in 1953, tritium concentrations in rainwater were 2 to 8 tritium units (1 tritium unit (TU)= one tritium atom/10¹⁸ hydrogen atoms) (Plummer and others, 1993). During the 1960's, at the peak of atmospheric nuclear devices testing, tritium concentrations in rainwater increased to over 5,000 TU (Plummer and others, 1993). Because of its short half-life and lack of atmospheric testing since the 1960's, tritium concentrations in rainfall are gradually decreasing toward the pre-1953 levels. Current (1999) tritium concentrations in Minnesota precipitation have an annual average of 10 TU with a seasonal variation ranging from 5 to 20 TU

(Jim Walsh, Minnesota Department of Health, written commun., 1999).

Water samples from the study areas were analyzed for tritium concentrations to test whether or not the ground-water had been recharged since 1953. Tritium concentrations in the water samples ranged from 6.3 to 27.2 TU, with median concentrations ranging from 11.6 to 12.8 TU (table 16). Tritium concentrations in most of the water samples were within the range of tritium concentrations in rainfall (decay corrected to a common date), indicating that shallow ground water in the study areas generally has been recently recharged. The only water samples with tritium concentrations greater than 20 TU were from

three wells along the Mississippi River in the urban study area. These samples indicate that there probably is a deeper flow path converging on the river bringing up slightly older water. No significant differences in the tritium concentrations were present among the three land-use study areas.

EFFECTS OF LAND USE ON GROUND-WATER QUALITY

The effects of land-use on ground-water quality in surficial sand and gravel aquifers in Minnesota has been discussed in previous reports by Stark and others (1991), Anderson (1993), and Minnesota Pollution Control Agency (1999a). Each of these reports discussed the ground-water

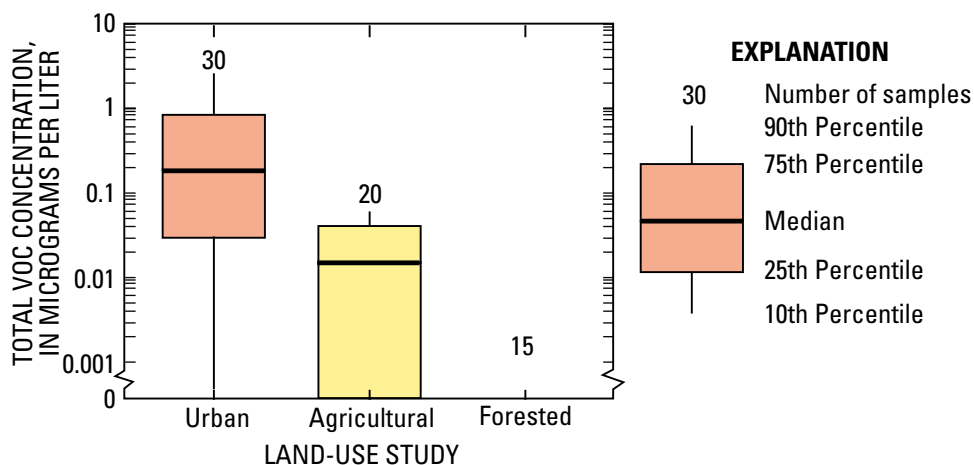


Figure 11.--Total concentrations of volatile organic compounds in water samples from land-use study wells

Table 16. Tritium concentrations in water samples from land-use study wells

[TU, tritium units]

Study area	Statistical group	Median concentration in TU	Standard deviation in TU	Range in concentration in TU
Urban (30 wells)	A	12.8	4.7	8.1 – 27.2
Agricultural (29 wells)	A	12.5	2.4	7.5 – 18.8
Forested (15 wells)	A	11.6	3.4	6.3 – 19.7

¹The letters A, B, and C are used to indicate statistically significant differences between studies (matching letters indicate no statistically significant difference).

quality in several different land-uses. Comparisons of these three land-use studies with the three UMIS NAWQA land-use studies (the UMIS urban study area, the UMIS agricultural study area, and the UMIS forested study area) are presented in this section. The Stark and others (1991) study had three components; these are referred to herein as the Bemidji urban study, the Bemidji agricultural study, and the Bemidji forested study. The Anderson (1993) study had three components; these are referred to as the Anoka Sand Plain urban study, the Anoka Sand Plain agricultural study (irrigated and nonirrigated), and the Anoka Sand Plain undeveloped study. The Minnesota Pollution Control Agency (1999a) study had three components; these are referred to as the St. Cloud urban study, the St. Cloud agricultural study (irrigated and nonirrigated), and the St. Cloud undeveloped study. In this section, urban study refers to all the urban studies cited above, agricultural study refers to all the agricultural studies cited above, and forested/undeveloped study refers to all the forested and undeveloped studies cited above.

Although all the studies were designed to look at the effects of land-use on ground-water quality in surficial sand and gravel aquifers, differences are present among the studies, including the sample collection methods, reporting limits, and laboratories used. There also may be differences in the composition of materials in the unsaturated zone and in the aquifer.

Similar patterns in specific conductance were reported in all of the land-use studies. Specific conductances generally were the greatest in urban studies, with medians ranging from 560 to 914 $\mu\text{S}/\text{cm}$. The greatest median specific conductances were measured in the UMIS urban study area (914 $\mu\text{S}/\text{cm}$) and the St. Cloud urban study (sewered and unsewered) (808, and 802 $\mu\text{S}/\text{cm}$, respectively). The greater specific conductances in the urban studies were probably due to greater concentrations of chloride, sodium, and sulfate. Agricultural studies had the second greatest specific conductances with medians ranging from 300 to 742 $\mu\text{S}/\text{cm}$. Greater specific conductances were reported in agricultural studies that were in irrigated areas than in nonirrigated areas. Greater specific conductances in the agricultural studies than in the forested/undeveloped studies probably were due to fertilizer applications and increased dissolution from irrigation. Forested/undeveloped studies had specific conductances with medians ranging from 330 to 487 $\mu\text{S}/\text{cm}$, which were generally less than in agricultural or urban studies.

Alkalinity generally was slightly greater in the urban studies than in the agricultural or forested/undeveloped studies with the medians ranging from 221 to 263 mg/L as CaCO_3 for urban studies, 98 to 242 mg/L as CaCO_3 for agricultural studies, and 131 to 246 mg/L as CaCO_3 for forested/undeveloped studies. In general, the median alkalinities were less in the agricultural studies than in either the urban

or forested/undeveloped studies. Septic systems can contribute to increased alkalinities (Harman and others, 1996; Wilhelm and others, 1994). In the UMIS urban study, approximately one-half the water samples had dissolved oxygen concentrations less than 1 mg/L and often smelled of sulfur; therefore, sulfate reduction also could be contributing to the greater alkalinities in that study by releasing carbon dioxide (Hem, 1985).

Dissolved oxygen concentrations were only reported in the UMIS and St. Cloud land-use studies. The median dissolved oxygen concentration in the UMIS urban study area was less than the medians in the UMIS agricultural or forested study areas. In the St. Cloud studies, the median dissolved oxygen concentration was least in sewer (4.9 mg/L) and much greater in the unsewered (9.7 mg/L). The medians in the agricultural (irrigated and nonirrigated) or undeveloped studies were 6.4, 5.2, and 5.1 mg/L, respectively. The amount of organic material also can affect the dissolved oxygen concentrations. For example, water samples from the UMIS urban study area had greater DOC concentrations and less dissolved oxygen than in the UMIS agricultural and forested study areas.

In general, most of the water samples were very hard (greater than 180 mg/L as CaCO_3) on the hardness scale developed by Durfor and Becker (1964). The calcium/magnesium ratios were relatively more constant than the concentrations. Calcium and magnesium concentrations generally

were greater in the urban studies, which also resulted in harder water.

Sodium concentrations were greater in water samples from the urban studies (medians ranging from 13 to 68.8 mg/L) than in agricultural and forested/undeveloped studies (medians ranging from 2.7 to 7.7 mg/L). Chloride concentrations were greatest in water samples from urban studies, with medians ranging from 26 to 85.5 mg/L, less in agricultural studies from 2.8 to 44.6 mg/L, and least in forested/undeveloped studies from 1.2 to 3.5 mg/L. Chloride concentrations generally also were greater in water samples from irrigated agricultural studies than from nonirrigated agricultural studies. The ratio of chloride to bromide was generally less than

500 in the UMIS agricultural and forested studies, but the ratio generally ranged from 500 to 3,500 in the UMIS urban study (fig. 12). This indicates different sources for the chloride. The greater sodium and chloride concentrations in the urban studies probably were from the de-icing salts used on roadways in winter (McConnell and Lewis, 1972; Scott, 1980; Howard and others, 1993;). Sources of sodium and chloride in the agricultural studies include manure and fertilizers applied to the fields, and septic systems (Robertson and others, 1991).

The greatest sulfate concentrations were detected in the urban studies, with medians ranging from 7.3 to 72 mg/L. Sulfate concentration medians ranged from 2.9 to 22 mg/L for

the agricultural and forested/undeveloped study areas. The UMIS urban study area had the greatest median sulfate concentration at 72 mg/L. The sources of greater sulfate concentrations in the urban studies probably include contamination from the burning of fossil fuels, applications of lawn fertilizers, and septic systems (Hem, 1985; Canadian Council of Resource and Environment Ministers, 1987).

Dissolved solids concentrations were greatest in water samples from the urban studies with medians ranging from 320 to 544 mg/L. Concentrations were less in the agricultural studies with medians ranging from 150 to 496 mg/L and in the forested/undeveloped studies with medians

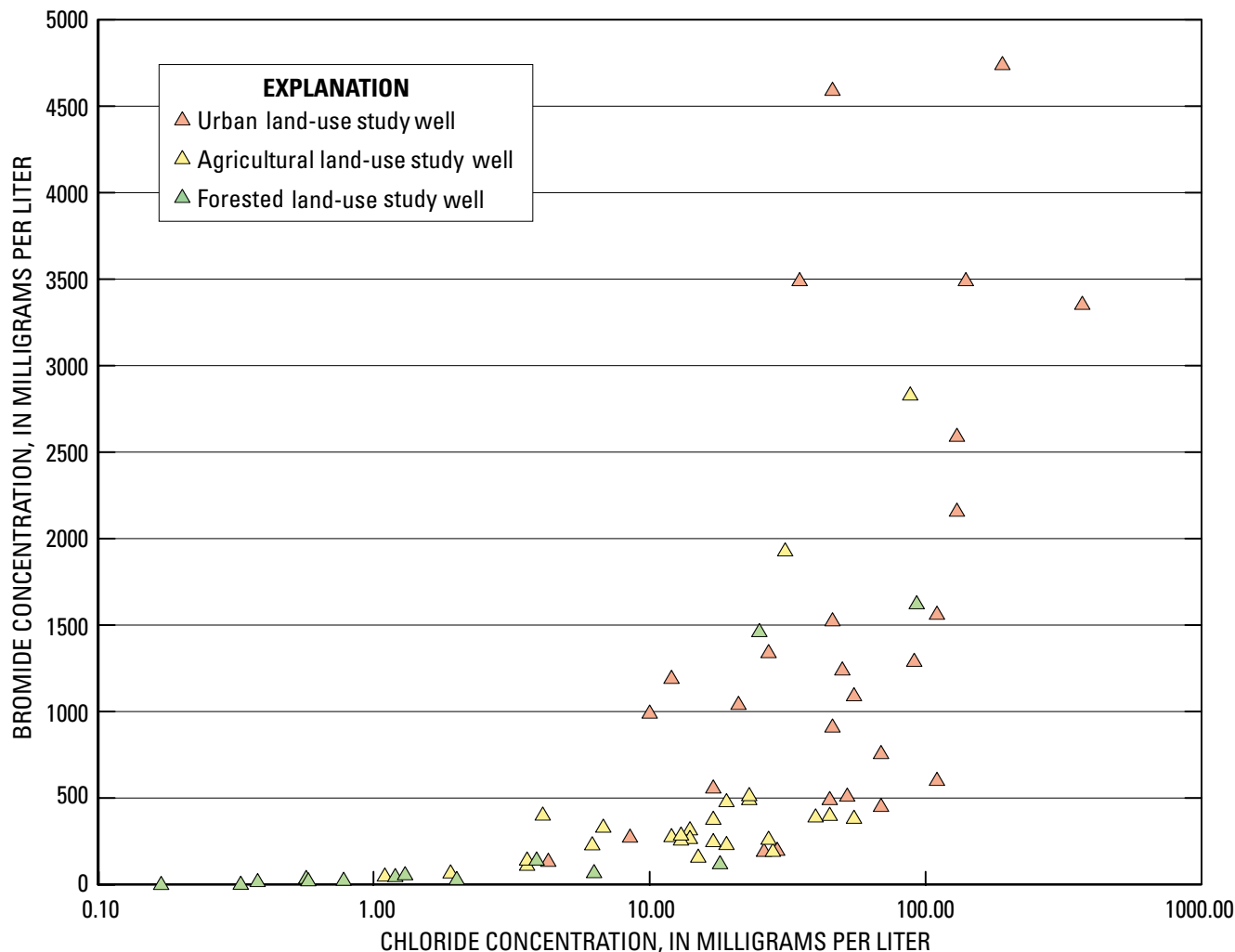


Figure 12.--Chloride/bromide ratio in water samples from land-use study wells.

ranging from 190 to 272 mg/L. Dissolved solids concentrations generally were greater in water samples from irrigated agricultural studies than from nonirrigated agricultural studies. Greater dissolved solids concentrations in the urban studies were due to the greater concentrations of calcium, magnesium, sulfate, and chloride.

Nitrate-nitrogen concentrations were the greatest in the agricultural studies, with medians ranging from 1.0 to 16.94 mg/L. Irrigated agricultural studies had greater median concentrations (5.3 to 16.94 mg/L) than nonirrigated agricultural studies (1.0 to 3.81 mg/L). Urban studies had the second greatest nitrate-nitrogen concentrations with medians ranging from 1.45 to 7.83 mg/L. Nitrate-nitrogen concentrations in the forested/undeveloped studies were less than in urban studies, with medians in the forested/undeveloped studies ranging from less than 0.05 to 0.69 mg/L. The greater nitrate-nitrogen concentrations in the agricultural studies are due to the application of manure and fertilizers (Hem, 1985; Canadian Council of Resource and Environment Ministers, 1987). In urban studies, the source of nitrate-nitrogen probably is lawn fertilizers and septic systems (Robertson and others, 1991; Tinker, 1991).

Ammonia-nitrogen concentrations were all low, with medians ranging from 0.02 to 0.09 mg/L. The greatest concentrations were in the forested/undeveloped studies, with medians ranging from 0.05 to 0.09 mg/L. Urban studies had the second greatest ammonia-nitrogen concentrations, with medians ranging from 0.02 to 0.075 mg/L. Ammonia-nitrogen concentrations in the agricultural studies generally were less than in the urban studies, with agricultural medians ranging from 0.02 to 0.06 mg/L. Dissolved oxygen concentrations generally were less in urban and forested studies than in agricultural studies, which may explain the greater ammonia concentrations. Microbial reduction of nitrate to ammonia also may

account for some of the greater ammonia concentrations (Chapelle, 1993). Ammonia-nitrogen in this concentration range can also be from atmospheric deposition (National Atmospheric Deposition Program, National Trends Network, electronic commun., 2000).

Prometon and 10 other pesticides were detected one or more times in the UMIS urban study area. The only other urban study to analyze for pesticides was conducted by the MPCA. Prometon and dicamba were the only two pesticides detected in the St. Cloud urban study (sewered). Analyses were done for pesticides in all of the agricultural studies. Atrazine was the most frequently detected pesticide in all of the agricultural studies. Each study analyzed for different suites of pesticides and metabolites and had different reporting limits, which makes it difficult to compare the studies. Other pesticides (and metabolites) detected in one or more of the agricultural studies include 2,6-diethylaniline, acetochlor ESA (ethane sulfonic acid), acetochlor oxanilic acid, alachlor, alachlor ESA, alachlor oxanilic acid, bentazon, cyanazine, cyanazine-amide, cyprazine, deethylatrazine, deisopropylatrazine, dicamba, dinoseb, malathion, metolachlor, metolachlor ESA, metolachlor oxanilic acid, metribuzin, prometon, simazine, and tebuthiuron. Agricultural studies have the greatest detection rates, numbers detected, and total concentrations of pesticides. Urban studies have pesticide detection rates and total pesticide concentrations that were less than in agricultural studies. The most frequently detected pesticides in the urban studies (prometon and dicamba) were different than in agricultural studies (atrazine and deethylatrazine).

Analyses for VOCs were done in the UMIS studies and St. Cloud studies. Comparisons between the studies is difficult because the two studies analyzed for different suites of VOCs and had different reporting limits. VOCs detected by both studies

include benzene, bromodichloromethane, chloroform, chloromethane, dichlorodifluoromethane, tetrachloroethene, and trichloroethene. A greater number of VOCs were detected in urban studies and at greater concentrations than in agricultural studies.

No patterns by land-use were present for pH or many of the major ions, trace elements, and nutrients, including potassium, fluoride, bromide, silica, iron, manganese, nitrite-nitrogen, ammonia plus organic-nitrogen, phosphorus, orthophosphorus, and DOC.

SUMMARY AND CONCLUSIONS

Surficial sand and gravel aquifers are susceptible to effects from land-use. Ground-water quality was compared in three different land-use areas; an urban area on the edge of the Anoka Sand Plain in a portion of the Twin Cities metropolitan area (urban study), an intensive agricultural area in the Anoka Sand Plain (agricultural study), and a forested area in the Bemidji-Bagley Sand Plain (forested study). Ground water was sampled and analyzed for about 200 constituents, including physical properties, major ions, selected trace elements, nutrients, dissolved organic carbon, selected pesticides, selected volatile organic compounds (VOCs), and tritium. Urban study area water samples were collected during June and July 1996. Agricultural study area water samples were collected during May and September 1998. Forested study area water samples were collected during June 1998.

The depth to water below the land surface in all three land-use study areas generally was less than 20 ft. The agricultural study area had the greatest depth to water with a median of 18.56 ft. The median pH value in the urban study area was 7.2, with medians of 7.4 and 7.5 in the agricultural and forested study areas, respectively. Specific conductance was significantly greater in the urban study area with a median value of 914 microsiemens per centimeter ($\mu\text{S}/\text{cm}$), which was almost twice as high as the medians for the agricultural and forested study areas (553 and 487 $\mu\text{S}/\text{cm}$, respectively). The dissolved oxygen concentration median in the urban study area (0.9 milligrams per liter (mg/L)) was significantly less than medians in the agricultural or forested study areas (5.3 and 2.3 mg/L , respectively). Alkalinities in the agricultural study area (median of 178 mg/L as CaCO_3) were significantly less than in the urban or forested study areas (261 and 246 mg/L as CaCO_3 , respectively).

Water in the surficial aquifers in all three land-use study areas is dominated by calcium, magnesium, and bicarbonate. Sulfate and chloride concentrations were significantly greater in the urban study area than in the agricultural or forested study areas, with values in the forested study area being the least. In general, concentrations of the other major ions (including iron and manganese) were greater in the urban study area than in the agricultural or forested study areas. Most of the water samples in all three land-use study areas were very hard (greater than 180 mg/L as CaCO_3).

Nitrate-nitrogen concentrations were greatest in the agricultural study area in which 38 percent of water samples exceeded the U.S. Environmental Protection Agency's maximum contaminant level (MCL) of 10 mg/L . Nitrate-nitrogen concentrations were greater than the MCL in 3 percent of urban study area samples. None of the forested study area samples exceeded the MCL for nitrate-nitrogen. Concentrations of phosphorus generally were less than 0.05 mg/L , with no significant differences among the land-uses.

In the urban and agricultural study areas, analyses were done for 83 pesticides and metabolites in water samples, while in the forested study, only 47 of the 83 pesticides were analyzed. A total of 19 individual pesticides were detected in water samples from one or more land-use study areas, with 11 in the urban study area, 14 in the agricultural study area, and 4 in the forested study area. Atrazine, deethylatrazine, and simazine were the only pesticides detected in water samples

from all three land-use study areas. A significantly greater percentage of pesticide detections were present in water samples from the agricultural study area (86.2 percent) than from the urban or forested study areas (56.7, and 46.7 percent, respectively). The median number of pesticides detected in a water sample and the total pesticide concentration in a water sample was greater in the agricultural study area than in the urban or forested study areas. Prometon was the most frequently detected pesticide in the urban study, and atrazine and deethylatrazine were the most frequently detected pesticides in the agricultural and forested study areas. Triazines were the most frequently detected group of pesticides.

Of the 86 volatile organic compounds (VOCs) sampled, only 21 were detected in one or more land-use study areas, with 19 in the urban study area, 7 in the agricultural study area, and none in the forested study area. Chloromethane, trichloromethane, methylbenzene, trichlorofluoromethane, and benzene were detected in water samples from the urban and agricultural study areas. There was a significantly greater percentage of VOC detections in water samples from the urban study area than from the agricultural study area (90 and 50 percent, respectively). The median number of VOCs detected and the total VOC concentration in a water sample were greater in the urban study area than in the agricultural study area. Carbon disulfide was the most frequently detected VOC in the urban study area. The compound 1,2,3,4-tetramethyl benzene was the most frequently detected VOC in the agricultural study area. Alkanes, which include chlorofluorocarbons and trihalomethanes, were the most frequently detected group of VOCs.

Tritium concentrations indicate that the water in the surficial sand and gravel aquifers has been recharged since 1953. Median tritium concentrations ranged from 11.6 to 12.8 tritium units. No significant difference in tritium concentrations was present among the three land-use studies.

Comparisons of previous land-use studies in Minnesota with the three NAWQA land-use studies generally indicated the same patterns. Ground-water quality in surficial sand and gravel aquifers is affected by land-use practices. Ground water in urban studies has greater specific conductances, alkalinities, sodium, sulfate, chloride, and dissolved solids concentrations than agricultural or forested/undeveloped studies. Nitrate-nitrogen was detected in greater concentrations in agricultural studies than in the urban studies, with concentrations in the forested/undeveloped studies the least. Agricultural studies have the greatest detection rates, numbers, and total concentrations of pesticides. Pesticide detection rates and total pesticide concentrations in the urban studies were less than in the agricultural studies, with the most frequently detected pesticides (prometon and dicamba) different than those in the agricultural studies (atrazine and deethylatrazine). A greater number of VOCs were detected in urban studies and at greater concentrations than in agricultural studies. Few pesticides and no VOCs were detected in forested/undeveloped studies.

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