National Water-Quality Assessment Program

Water-Quality Assessment of the Cambrian-Ordovician Aquifer System in the Northern Midwest, United States

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U.S. Department of the Interior
U.S. Geological Survey

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By John T. Wilson

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Foreword

The U.S. Geological Survey (USGS) is committed to providing the Nation with reliable scientific information that helps to enhance and protect the overall quality of life and that facilitates effective management of water, biological, energy, and mineral resources (*http://www.usgs.gov/*). Information on the Nation's water resources is critical to ensuring long-term availability of water that is safe for drinking and recreation and is suitable for industry, irrigation, and fish and wildlife. Population growth and increasing demands for water make the availability of that water, measured in terms of quantity and quality, even more essential to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program in 1991 to support national, regional, State, and local information needs and decisions related to water-quality management and policy (*http://water.usgs.gov/nawqa*). The NAWQA Program is designed to answer: What is the quality of our Nation's streams and groundwater? How are conditions changing over time? How do natural features and human activities affect the quality of streams and groundwater, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities. From 1991 to 2001, the NAWQA Program completed interdisciplinary assessments and established a baseline understanding of water-quality conditions in 51 of the Nation's river basins and aquifers, referred to as Study Units (*http://water.usgs.gov/nawqa/studies/study_units.html*).

In the second decade of the Program (2001–2012), a major focus is on regional assessments of water-quality conditions and trends. These regional assessments are based on major river basins and principal aquifers, which encompass larger regions of the country than the Study Units. Regional assessments extend the findings in the Study Units by filling critical gaps in characterizing the quality of surface water and groundwater, and by determining water-quality status and trends at sites that have been consistently monitored for more than a decade. In addition, the regional assessments continue to build an understanding of how natural features and human activities affect water quality. Many of the regional assessments employ modeling and other scientific tools, developed on the basis of data collected at individual sites, to help extend knowledge of water quality to unmonitored, yet comparable areas within the regions. The models thereby enhance the value of our existing data and our understanding of the hydrologic system. In addition, the models are useful in evaluating various resource-management scenarios and in predicting how our actions, such as reducing or managing nonpoint and point sources of contamination, land conversion, and altering flow and (or) pumping regimes, are likely to affect water conditions within a region.

Other activities planned during the second decade include continuing national syntheses of information on pesticides, volatile organic compounds (VOCs), nutrients, trace elements, and aquatic ecology; and continuing national topical studies on the fate of agricultural chemicals, effects of urbanization on stream ecosystems, bioaccumulation of mercury in stream ecosystems, effects of nutrient enrichment on stream ecosystems, and transport of contaminants to public-supply wells.

The USGS aims to disseminate credible, timely, and relevant science information to address practical and effective water-resource management and strategies that protect and restore water quality. We hope this NAWQA publication will provide you with insights and information to meet your needs, and will foster increased citizen awareness and involvement in the protection and restoration of our Nation's waters.

The USGS recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for cost-effective management, regulation, and conservation of our Nation's water resources. The NAWQA Program, therefore, depends on advice and information from other agencies—Federal, State, regional, interstate, Tribal, and local—as well as nongovernmental organizations, industry, academia, and other stakeholder groups. Your assistance and suggestions are greatly appreciated.

William H. Werkheiser

USGS Associate Director for Water

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Conversion Factors and Datums

Multiply	By	To obtain
	Length	
inch (in)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
meter (m)	3.281	foot (ft)
mile (mi)	1.609	kilometer (km)
kilometer (km)	0.6214	mile (mi)
	Area	
acre	0.4047	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)
	Flow rate	
inch per year (in/yr)	2.54	centimeter per year (cm/yr)
million gallons per day (Mgal/d)	3,785.0	cubic meter per day (m^3/d)
	Radioactivity	
picocurie per liter (pCi/L)	0.037	becquerel per liter (Bq/L)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

°F=(1.8×°C)+32

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

°C=(°F-32)/1.8

Vertical coordinate information is referenced to the national Geodetic Vertical Datum of 1929 (NGVD29)

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83)

Altitude, as used in this report, refers to distance above the vertical datum.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

Other Abbreviations

CSU	combined standard uncertainty
HBSL	Health-Based Screening Level
Illinois EPA	Illinois Environmental Protection Agency
ISWS	Illinois State Water Survey
K_{sp}	solubility product
MCL	Maximum Contaminant Level
MDH	Minnesota Department of Health
MGS	Minnesota Geological Survey
MPCA	Minnesota Pollution Control Agency
Michigan DEQ	Michigan Department of Environmental Quality
Missouri DNR	Missouri Department of Natural Resources
NAWQA	National Water-Quality Assessment Program
NWIS	National Water Information System
RASA	Regional Aquifer-System Analysis
RSD	relative standard deviation
SDWA	Safe Drinking Water Act
SDWR	Secondary Drinking Water Regulation
ssL_C	sample-specific critical level
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VOC	volatile organic compound
Wisconsin DNR	Wisconsin Department of Natural Resources

Water-Quality Assessment of the Cambrian-Ordovician Aquifer System in the Northern Midwest, United States

By John T. Wilson

Abstract

Water quality of the Cambrian-Ordovician aquifer system was assessed primarily with data collected from 1995 through 2007 as part of the National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey (USGS). Physical properties and concentrations of major ions, trace elements, radionuclides, nutrients, pesticides, and volatile organic compounds were measured in raw water samples from as many as 155 wells. The distributions of constituent concentrations were related to various factors such as confining conditions, well type, land use, and groundwater age. Constituent concentrations were compared to water-quality benchmarks for human health, either U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Levels (MCLs) or USGS Health-Based Screening Levels (HBSLs). Concentrations were also compared to USEPA Secondary Drinking Water Regulations (SDWRs) established for aesthetic quality or other non-health reasons. Data for raw water samples from other USGS sources and state agencies were combined with NAWQA data to help fill gaps in data coverage for mapping concentrations of selected water-quality constituents.

The Cambrian-Ordovician aquifer system is an important water resource in the northern Midwest, and it accounts for a large proportion of total groundwater withdrawals in Illinois, Iowa, Minnesota, and Wisconsin. Water withdrawals from the aquifer system are not as high in the Upper Peninsula of Michigan as in other states because of the small geographic area and low population density. In northeastern Missouri, water withdrawals from the aquifer system are limited to an eight-county area just north of the Missouri River where the aquifer system contains freshwater. The primary use of groundwater withdrawal is for public supply; however, the aquifer system is an important source for domestic supply in the northern areas where it is at relatively shallow depth.

The Cambrian-Ordovician aquifer system is a complex, multilayered sequence of marine sedimentary rock with major sandstone aquifers separated by leaky confining units consisting of dolomite, shale, and shaly sandstone. Contrasting areas of regional confinement influence the distribution of concentrations of natural and anthropogenic contaminants. The aquifer system is considered to be regionally confined where it is covered by the Maquoketa Shale and younger bedrock and regionally unconfined where the Maquoketa Shale and younger bedrock are absent. Generally, natural contaminants such as major ions, trace elements, and radium occur at higher concentrations in regionally confined areas than in regionally unconfined areas. Anthropogenic contaminants such as pesticides, volatile organic compounds, and nitrate are detected more often in regionally unconfined areas than in regionally confined areas.

The aquifer system is regionally unconfined over much of its extent in Minnesota, Wisconsin, and the Upper Peninsula. Other areas where the aquifer system is regionally unconfined are north-central Illinois, a small portion of northeastern Iowa, and in a small area along the Missouri River in northeastern Missouri. The aquifer system is regionally confined over much of its extent in Iowa and Illinois, and along Lake Michigan in eastern Wisconsin and the Upper Peninsula. Groundwater in regionally unconfined areas is generally associated with more oxic conditions, lower dissolved solids (compared to regionally confined areas), and modern recharge (post-1953). Groundwater in regionally confined areas is generally associated with anoxic conditions, higher dissolved solids, and recharge that originated before 1953. The redox status of the aquifer system was mostly anoxic; 60 percent of the wells sampled by NAWQA showed anoxic conditions, 26 percent showed oxic conditions, and 14 percent showed mixed source conditions. For the most part, wells with oxic conditions also had modern recharge and were in regionally unconfined areas.

Radon-222 and radium were the constituents most frequently measured at concentrations greater than their human-health benchmark, but their geographic distributions were related to different types of regional confinement. Radon-222 was detected in 96 percent of the wells sampled by NAWQA and had a median concentration of 250 picocuries per liter (pCi/L). Radon-222 concentrations were significantly higher in wells in regionally unconfined areas than in confined areas. Radon-222 concentrations were greater than the proposed MCL (300 pCi/L) in 43 percent of the wells sampled by NAWQA, of which 90 percent were in regionally unconfined areas. Radium-226 and radium-228 were detected in 94 and 83 percent of the wells sampled by NAWQA, and concentrations were significantly higher in wells in regionally confined areas than in unconfined areas. Radium had a strong positive correlation with dissolved solids and sulfate. High radium

concentrations were associated with anoxic, reducing conditions. The MCL for radium-226 + radium-228 (5 pCi/L) was exceeded in 40 percent of the wells sampled by NAWQA, of which 89 percent were in regionally confined areas.

Radium-226 and radium-228 are chemically similar, but their distribution in groundwater can be different because of the different properties of their parent isotopes and the large difference in half-life. Concentrations of radium-226 greater than 5 pCi/L are common throughout the aquifer system, especially in wells in regionally confined areas. Concentrations of radium-228 greater than 5 pCi/L are mostly limited to wells in northeastern Illinois and in Minnesota near the western boundary of the aquifer system. In Minnesota, data from multiple sources showed that concentrations of radium-226 and radium-228 were significantly higher in wells open to the Mount Simon Sandstone than in wells open to other aquifers above the Mount Simon Sandstone.

Water in the aquifer system was typically hard to very hard (>180 milligrams per liter (mg/L) as calcium carbonate ($CaCO_3$)), and samples collected by NAWQA had a median hardness of 299 mg/L as $CaCO_3$. Dissolved solids concentrations were significantly higher in wells in the regionally confined areas than in the unconfined areas, but it was common for dissolved solids to exceed the SDWR (500 mg/L) throughout the aquifer system. Twenty-nine percent of the wells sampled by NAWQA exceeded the SDWR for dissolved solids, and 84 percent of those wells were in regionally confined areas. The aquifer system is not used in some areas of southwestern Iowa, northern Missouri, central Illinois, and northwestern Indiana because of high salinity (dissolved solids).

In addition to radon-222 and radium, natural constituents that exceeded a human-health benchmark in NAWQA samples were the trace elements boron, strontium, manganese, and barium. The HBSL for boron (1,000 micrograms per liter, µg/L) was exceeded in 14 percent of the samples; the HBSL for strontium (4,000 µg/L) was exceeded in 9 percent of the samples; and the HBSL for manganese (300 µg/L) was exceeded in 4 percent of the samples. The MCL for barium (2,000 µg/L) was exceeded in one sample from a well in northeastern Illinois. Concentrations of boron and strontium were significantly higher in regionally confined areas than in unconfined areas, and concentrations of manganese and barium were significantly higher in unconfined areas than in confined areas. The maximum concentration of arsenic measured in a NAWQA sample was 9.99 µg/L (just below the MCL of 10 µg/L) from a well in the Upper Peninsula.

Constituents that exceeded SDWRs in NAWQA samples were iron, manganese, sulfate, fluoride, and chloride. Concentrations of all of these constituents, except manganese, were significantly higher in wells from regionally confined areas than in wells from regionally unconfined areas. Iron concentrations were relatively high throughout the aquifer system, with a median concentration of 186 µg/L. Iron concentrations exceeded the SDWR (300 µg/L) in 41 percent of the wells sampled by NAWQA. Manganese concentrations exceeded the SDWR (50 µg/L) in 24 percent of the wells, sulfate concentrations exceeded the SDWR (250 mg/L) in 17 percent of wells, fluoride concentrations exceeded the SDWR (2 mg/L) in 5 percent of wells, and chloride exceeded the SDWR (250 mg/L) in 4 percent of wells sampled by NAWQA. In 2011, the U.S. Department of Health and Human Services proposed a recommended fluoride concentration of 0.7 mg/L for all public water-supply systems. Fluoride concentrations were greater than 0.7 mg/L in 30 percent of the wells sampled by NAWQA.

Nitrate was detected at a concentration greater than 1 mg/L in 21 percent of the wells sampled by NAWQA. Concentrations of nitrate greater than 1 mg/L were assumed to be influenced by human activity. All but one of the wells were in regionally unconfined areas, indicating that the aquifer system is more susceptible to manmade contaminants where it is unconfined (and hence, shallower). Approximately 4 percent of wells sampled by NAWQA had concentrations greater than the MCL (10 mg/L). An evaluation of near-decadal-scale changes in nitrate concentrations in two well networks in regionally unconfined areas showed no significant change in nitrate concentrations over a 7-year period for one network and an 11-year period for the other network, even though concentrations may have varied at individual wells.

Nine different pesticides were detected in wells sampled by NAWQA from 2002 through 2007, but atrazine and its degradate deethylatrazine accounted for 67 percent of all pesticide detections. Concentrations of pesticides were usually less than 0.1 µg/L, and only atrazine, deethylatrazine, and metolachlor were detected at a concentration greater than 0.1 µg/L. Eighty-six percent of wells with a pesticide detection were in regionally unconfined areas. Wells with a pesticide detection were also more likely to have modern recharge, a dissolved oxygen concentration greater than 0.5 mg/L, and a nitrate concentration greater than 1 mg/L.

Several volatile organic compounds (VOCs) were detected in wells sampled by NAWQA from 2002 through 2007, but usually at concentrations less than 0.2 µg/L. The most commonly detected VOCs were solvents, gasoline hydrocarbons, and trihalomethanes. The most frequently detected compounds were the solvents trichloroethene and *cis*-1,2-dichloroethene, the trihalomethane chloroform, and the gasoline hydrocarbon benzene. The compounds 1,1-dichloroethene, methylene chloride, and trichloroethene were each detected once at concentrations greater than their MCLs.

Mixtures of anthropogenic contaminants and contaminant classes were evaluated through the co-occurrence of nitrate (> 1 mg/L), pesticides, and VOCs in wells sampled by NAWQA. A contaminant mixture was the detection of a unique combination of two or more compounds in the same sample, and a contaminant class mixture was the detection of more than one class of contaminant in the same sample. The most commonly detected mixtures were atrazine/deethylatrazine, deethylatrazine/nitrate, atrazine/nitrate, and atrazine/deethylatrazine/nitrate. Mixtures of contaminant classes were identified in 26 of the 122 wells used in the analysis. Fourteen wells (11.5 percent) had a mixture defined by the detection of at least one pesticide and nitrate. Six wells (4.9 percent) had a mixture defined by the detection of at least one pesticide and at least one VOC, and the other six wells had a mixture defined by the detection of at least one pesticide, at least one VOC, and nitrate.

Introduction

The Cambrian-Ordovician aquifer system is an important water resource that underlies approximately 179,000 mi^2 in parts of seven states in the northern Midwest (fig. 1). The aquifer system accounts for a large percentage of total groundwater withdrawals in Illinois, Iowa, Minnesota, and Wisconsin. The primary uses of groundwater are public supply, self-supplied industrial, and irrigation (Maupin and Barber, 2005). The aquifer system is also an important source for domestic supply in the northern areas of its extent where it is at relatively shallow depth yet may be less vulnerable to anthropogenic contamination than the overlying glacial aquifer system. The glacial aquifer system (U.S. Geological Survey, 2003) overlies the Cambrian-Ordovician aquifer system throughout its extent, except in the Driftless Area of Wisconsin and Illinois, and these two systems can be hydraulically connected where Cambrian-Ordovician rocks are at the bedrock surface.

The National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey (USGS) is designed to provide a comprehensive assessment of the status, trends, and factors controlling water-quality conditions in the Nation’s streams and aquifers (Gilliom and others, 1995, 2001). During the first decade of NAWQA studies (1991–2001), study-area boundaries (“study units”) were delineated primarily on the basis of surface-water drainage. That approach was effective for assessing surface-water resources and small aquifers or limited areas of a major aquifer, but it was not suitable for assessing the water quality in regional aquifers (principal aquifers) that underlie multiple surface-water drainages, such as the Cambrian-Ordovician aquifer system. Understanding water-quality conditions in regional aquifers is complicated by spatial variability in the physical framework of the aquifer, such as lithology, hydraulic properties, thickness, depth, and presence or absence of confining layers. The area overlying regional aquifers also can be highly varied in land use and population densities, which affect water-use demands on the aquifer and its vulnerability to anthropogenic contaminants. In the case of the Cambrian-Ordovician aquifer system, the regional framework is controlled by the regional confinement (fig. 2). In much of the northern area (Minnesota, Wisconsin, the Upper Peninsula of Michigan, and northern Illinois), the aquifer system is exposed at the bedrock surface and is covered by glacial deposits of varying thickness. There is also a small area at the southern boundary along the Missouri and Mississippi Rivers where the aquifer system is exposed at the bedrock surface. In much of the southern area (Illinois, Iowa, and northern Missouri) and near the eastern boundary (Indiana, eastern Wisconsin, Upper Peninsula of Michigan), the aquifer system is regionally confined by the Maquoketa Shale (the uppermost Ordovician formation) and younger bedrock. The presence or absence of these confining layers is a controlling factor on the hydrology of the aquifer system (Young, 1992a; Imes, 1985) and its vulnerability to natural and anthropogenic contaminants.

In the second decade of the NAWQA Program (2001–2012), a major focus has been on regional assessments of groundwater quality conditions and trends (Lapham and others, 2005). Regional assessments complement and extend findings of study units to fill gaps in our understanding of groundwater quality and flow over broad regions, and they provide important information at a scale between local study units and national summaries. The NAWQA Program selected 19 of the 62 principal aquifers that underlie the United States for regional assessment, including the Cambrian-Ordovician aquifer system (Lapham and others, 2005). As part of this regional assessment, data collection included resampling of some of the well networks from local study units, a source water-quality assessment, and sampling of additional wells in Iowa and Illinois at a regional scale. Results have been synthesized with data collected during the first decade to develop an assessment of water quality. Where possible, data from other sources, such as other USGS projects and state agencies, have been used to help fill gaps in the data coverage. This study provides an assessment of the occurrence and distribution of water-quality conditions in the Cambrian-Ordovician aquifer system and evaluates water-quality constituent concentrations in relation to human-health benchmarks for drinking water and secondary drinking-water regulations.

Purpose and Scope

This report provides a regional assessment of groundwater quality of the Cambrian-Ordovician aquifer system, based primarily on raw water samples collected by the NAWQA Program during 1995 through 2007. The NAWQA Program has published findings in local study-unit reports encompassing parts of the Cambrian-Ordovician aquifer system. Data collected from the aquifer system were used in national synthesis reports on selected topics such as specific water-quality constituent classes, well type, or aquifer material; however, a synthesis of groundwater quality at the principal aquifer scale has not been completed and is therefore the major purpose of this report.

Water samples collected by the NAWQA Program were analyzed for various classes of characteristics including physical properties, major ions, trace elements, nutrients and dissolved organic carbon, radionuclides (tritium, radon, and radium), pesticides, and volatile organic compounds (VOCs). Subsequent sections of this report provide discussions on these classes of characteristics. The assessment objectives of this report are to (1) summarize constituent concentrations and compare them to human-health benchmarks and non-health

Base from U.S. Geological Survey digital data, 1972,
1:2,000,000 Albers Equal-Area Conic projection,
Standard parallels 29°30'N and 45°30'N;
central meridian -96°00'W

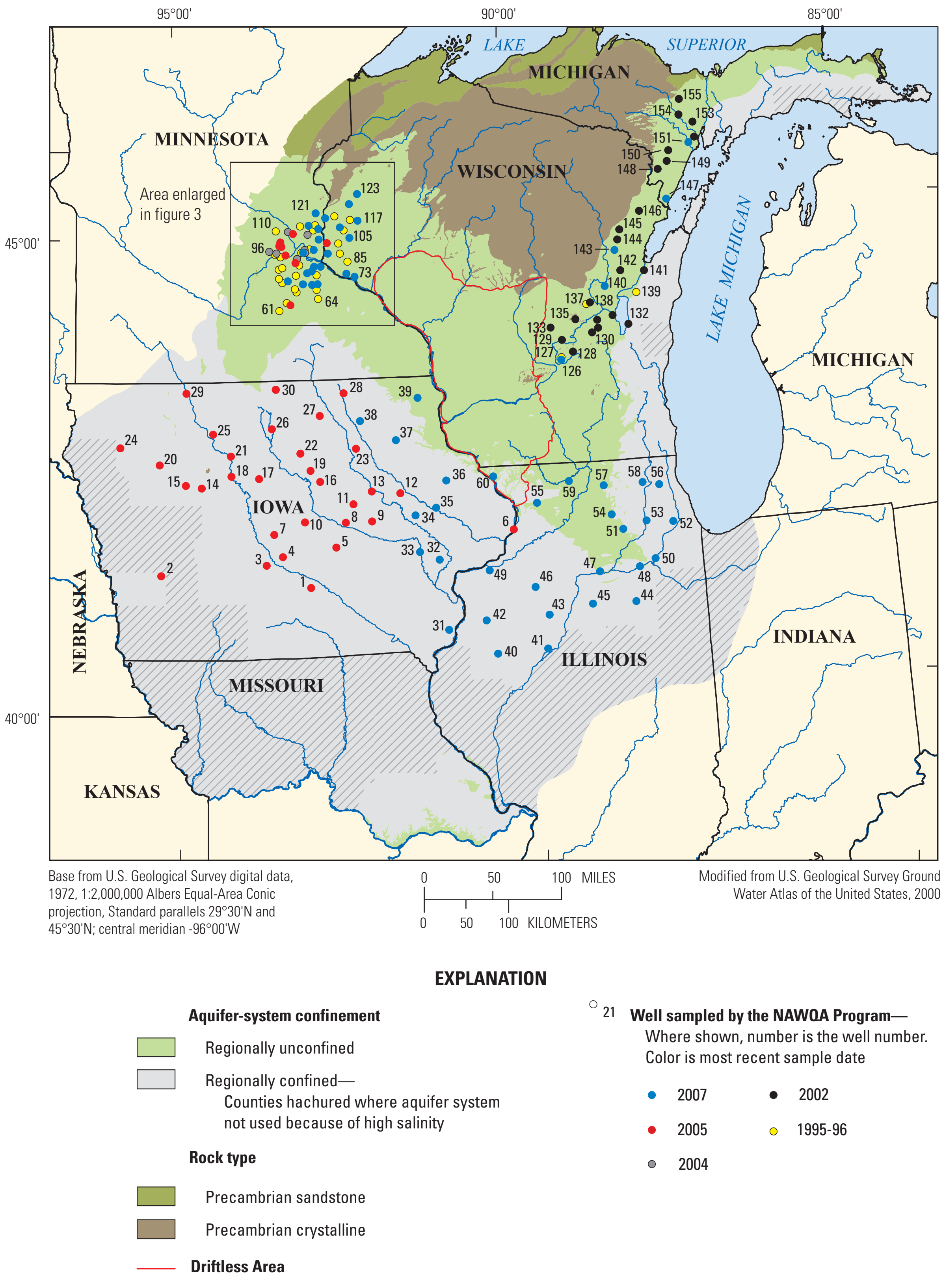
Modified from U.S. Geological Survey Ground
Water Atlas of the United States, 2000

EXPLANATION

🟩 **Cambrian-Ordovician aquifer system—** Counties hachured where aquifer system not used because of high salinity

🟩 **Precambrian sandstones**

Figure 1. Location of the Cambrian-Ordovician aquifer system in the northern Midwest, United States.



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Modified from U.S. Geological Survey Ground Water Atlas of the United States, 2000

Figure 2. Location of wells completed in the Cambrian-Ordovician aquifer system and sampled by the NAWQA Program, 1995–2007. Also shown are the Driftless Area of southwestern Wisconsin and northwestern Illinois and the areas where the aquifer system is regionally unconfined or regionally confined by the Maquoketa Shale or younger bedrock.

guidelines; (2) determine the geographic distribution of constituent concentrations and relate them to various factors such as confining conditions, well type, land use, and groundwater age; and (3) evaluate near-decadal-scale changes in nitrate concentrations and pesticide detections. The most recent sample collected from each well by the NAWQA Program was used for most analyses. Near-decadal-scale changes in nitrate concentrations and pesticide detections were evaluated for selected well networks by using the most recent sample from each well and comparing it to the results from a sample collected 7 or 11 years earlier.

Because some of the NAWQA well networks provide a limited areal coverage of the aquifer system, data for raw water samples from other USGS sources and state agencies were included to expand the data coverage into areas between the NAWQA well networks and into northeastern Missouri. Many of the maps in this report that show concentrations of selected constituents include data from other sources to expand on the geographic area covered by the NAWQA data.

This report covers several aspects of water quality that were not included in the last regional assessment of the aquifer system by the USGS Regional Aquifer-System Analysis (RASA) Program in the 1980s. The RASA study produced a report on the natural geochemistry of groundwater, as well as reports on the hydrology, hydrogeology, and simulated regional groundwater flow in the aquifer system. The data collected by the NAWQA Program (hereafter referred to as "NAWQA data" or "NAWQA samples") allow for an assessment of anthropogenic contaminants such as pesticides, VOCs, and concentrations of nitrate greater than a background level (1 mg/L). The NAWQA data also allow for a broad assessment of concentrations of naturally occurring radionuclides (radon-222, radium-226, and radium-228), whereas the RASA study included only radium-226. This report also includes data from the Upper Peninsula of Michigan (hereafter referred to simply as the "Upper Peninsula"), which was not included in the RASA study. Both the RASA and NAWQA Programs sampled a subset of wells in Iowa, which allows for analysis of the long-term stability of major ions and radium-226.

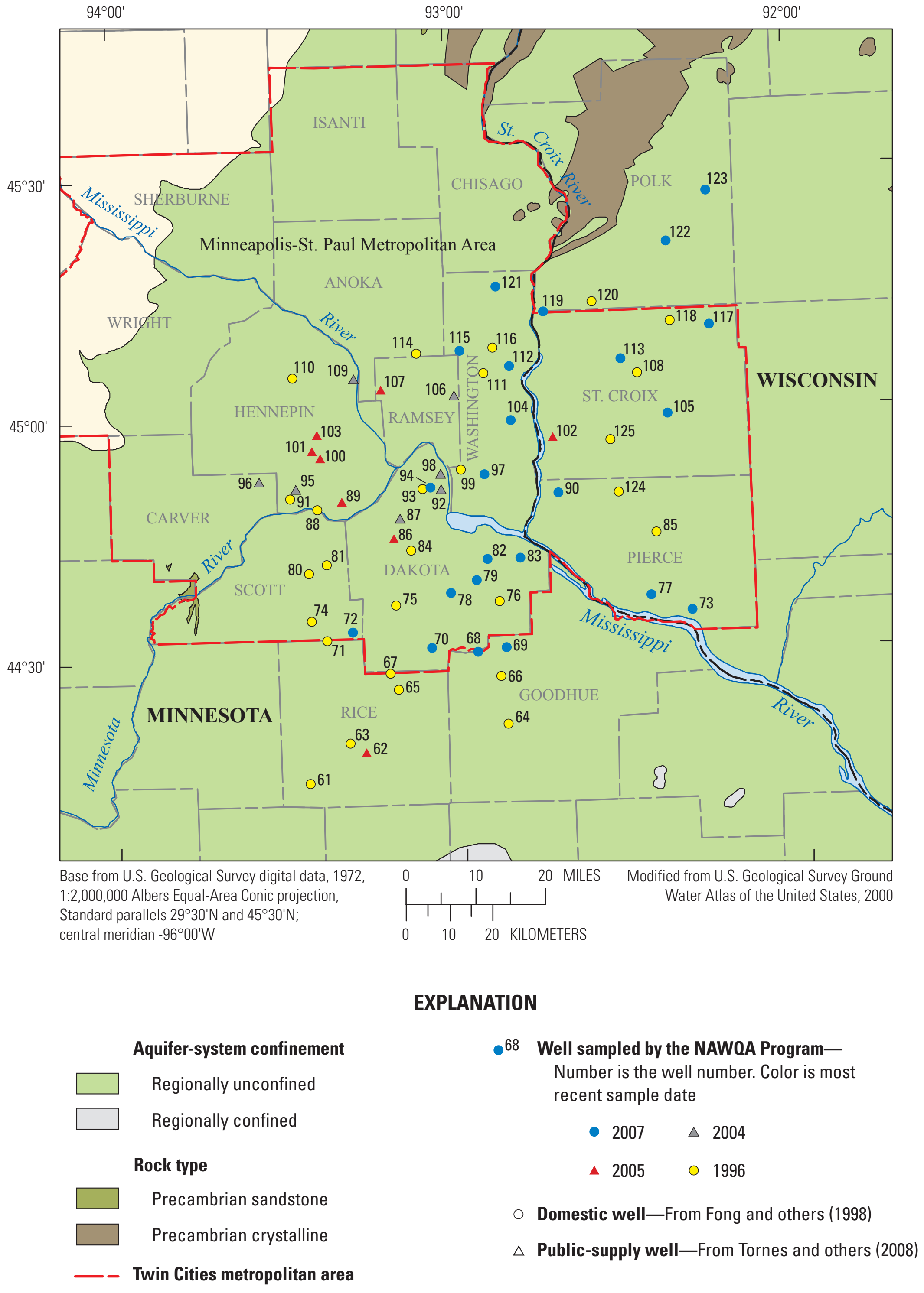
Previous Investigations

The most comprehensive regional investigation of the Cambrian-Ordovician aquifer system is the study done by the RASA Program in the 1980s. Major findings of the RASA study were published in a series of USGS Professional Papers and other USGS reports. Young (1992a, b) summarized the groundwater hydrology of the aquifer system and presented a detailed description of the hydrogeology of the aquifer system. Siegel (1989) presented a detailed analysis of the natural geochemistry of the aquifer system, including isotopic analyses. Mandle and Kontis (1992) simulated the regional groundwater flow in the aquifer system. Imes (1985), who evaluated the groundwater flow in the aquifer system in northern Missouri, constructed detailed potentiometric maps and used a two-dimensional model to show that an eight-county region immediately north of the Missouri River has a local freshwater flow system independent of the regional saline-water flow system in northern Missouri. Burkart and Buchmiller (1990) evaluated the hydrologic factors and effects of pumping from the St. Peter-Jordan aquifer in Iowa.

The USGS Groundwater Atlas of the United States includes an extensive description of all aquifers in the northern Midwest. The atlas includes sections on the hydrogeology, groundwater flow, availability and quality of water, and freshwater withdrawals and water uses for each aquifer. The Cambrian-Ordovician aquifer system in Iowa, Michigan, Minnesota, and Wisconsin is covered in segment 9 of the atlas (Olcott, 1992). Segment 10 of the atlas includes Illinois and Indiana (Lloyd and Lyke, 1995), and segment 3 of the atlas includes Missouri (Miller and Appel, 1997).

To date, the NAWQA Program has published findings in local study-unit reports and in national synthesis reports but not as a synthesis at the principal aquifer scale. Study-unit reports were based on data from their respective well networks in the western Lake Michigan drainages in eastern Wisconsin and the Upper Peninsula (fig. 2) (Saad, 1996) and in the Minneapolis-St. Paul metropolitan area (hereafter referred to in the text as the "Twin Cities metropolitan area") of Minnesota and Wisconsin (fig. 3) (Fong and others, 1998; Tornes and others, 2008). These networks are described in detail in the methods section titled "NAWQA Well Networks."

NAWQA data collected from local well networks have been synthesized on a national scale, and reports have included selected data from these well networks, as appropriate, for specific topics on a water-quality constituent class, a well type (public supply or domestic), or an aquifer lithology type. A national synthesis of pesticides by Gilliom and others (2006) included the pesticide data collected by Saad (1996) and Fong and others (1998), and a national synthesis of VOCs by Zogorski and others (2006) included the VOC data collected by Saad (1996) and Fong and others (1998). A synthesis of water quality from domestic wells in principal aquifers of the United States included data for domestic wells in Minnesota, Wisconsin, and the Upper Peninsula (DeSimone, 2009). Toccalino and Hopple (2010) presented a synthesis of water quality from public-supply wells in the United States using data collected by the NAWQA Program through 2007. A national study of factors affecting water quality in selected carbonate (limestone and dolomite) aquifers evaluated data collected through 2005 and included data from 30 wells completed in the Prairie du Chien aquifer in the Twin Cities metropolitan area of Minnesota and Wisconsin (Lindsey and others, 2009). A national study that summarized the reduction/oxidation (redox) conditions in selected principal aquifers included the Cambrian-Ordovician aquifer system (McMahon and Chapelle, 2008; McMahon and others, 2009). Ayotte and others (2007) summarized the occurrence of uranium and radon-222 in samples collected by NAWQA through 2003 in the glacial aquifer system, the Cambrian-Ordovician aquifer system, and the New York and New England crystalline aquifers; therefore,



Base from U.S. Geological Survey digital data, 1972,
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Standard parallels 29°30'N and 45°30'N;
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Modified from U.S. Geological Survey Ground
Water Atlas of the United States, 2000

Figure 3. Location of wells completed in the Cambrian-Ordovician aquifer system near the Minneapolis-St. Paul (Twin Cities) metropolitan area and sampled by the NAWQA Program, 1996–2007.

the data available to Ayotte and others (2007) were limited to the regionally unconfined areas in Minnesota, Wisconsin, and the Upper Peninsula. A recent study by Szabo and others (2012) compared radium concentrations in water samples from 15 principal aquifers, using NAWQA data collected through 2005; therefore, the data available to Szabo and others (2012) were limited to the network of 30 wells sampled in Iowa during 2005.

In addition to the regional studies and NAWQA publications listed above, many other USGS publications document the findings of local studies related to the Cambrian-Ordovician aquifer system. These publications span several decades and are too numerous to list here. These publications can be found online through the USGS Water Science Center where the study was done by selecting a state at *http://water.usgs.gov/* or by searching on key words at the USGS publications warehouse at *http://pubs.er.usgs.gov/*.

State agencies have published numerous journal articles and reports related to some aspect of the Cambrian-Ordovician aquifer system at various scales. These publications generally cover a relatively small study area within one state, frequently because the study was conducted by a state agency working within its state boundary. Many of these publications are referenced in subsequent sections of this report that cover specific topics related to these publications.

Particular areas of concern have been Chicago and its surrounding counties in northeastern Illinois and the Milwaukee-Waukesha area and surrounding counties in southeastern Wisconsin. Since the late 1800s, groundwater use has caused large amounts of drawdown in the potentiometric surface of the aquifer system. Cones of depression centered in Waukesha County, Wis., and suburban Chicago have intersected so that pumping in one area can affect water levels in the other area (Feinstein and others, 2005a). Feinstein and others (2005a, b) developed a groundwater-flow model to simulate aquifer conditions from predevelopment (1864) through 2000 for the Cambrian-Ordovician aquifer system and shallower aquifers above it. Young and others (1989) and Mandle and Kontis (1992) simulated groundwater flow and the decline in head in the Cambrian-Ordovician aquifer system through 1980 in the Chicago-Milwaukee area. The head in the aquifer system declined more than 900 ft in the deepest cones of depression in the Chicago area from 1864 to 1980 and more than 375 ft in the cone of depression at Milwaukee from about 1880 to 1980 (Young, 1992a, b). Fetter (1981) described how the large cone of depression in the Chicago area contributed to drawdown in southeastern Wisconsin and diverted groundwater flow from southeastern Wisconsin. The Illinois State Water Survey (ISWS) has been monitoring water levels and modeling the aquifer system in the Chicago area for years (Burch, 1991; Visocky, 1982, 1997). The State of Illinois has been diverting water from Lake Michigan for maintenance of the Chicago Sanitary and Ship Canal, stormwater runoff, public drinking water, and other uses. A U.S. Supreme Court Consent Decree (Wisconsin v. Illinois, 388, U.S. 426, 1967) governs the Illinois diversion of Lake Michigan water (U.S. Supreme Court, 1967). In 1980, the consent decree was modified for changes in the accounting procedure involved with the diversion and gave priority of new allocations to domestic use (public supply, commercial, industrial) over other uses. The modified consent decree stated that “to the extent practicable allocations to new users of Lake Michigan water shall be made with the goal of reducing withdrawals from the Cambrian-Ordovician aquifer” (U.S. Supreme Court, 1980). This modification reduced the demand for groundwater withdrawals, which has caused water levels in the Cambrian-Ordovician aquifer system to recover in areas where communities have received allocations of lake water, but not everywhere. Sources and availability of water to meet the future needs of the Chicago metropolitan area were outlined in a recent water supply and demand plan for northeastern Illinois (Chicago Metropolitan Agency for Planning, 2010).

Description of the Study Area

The study area encompasses the Cambrian-Ordovician aquifer system, which underlies about 179,000 mi^2 in parts of seven states in the northern Midwest (Illinois, Indiana, Iowa, Michigan (Upper Peninsula), Minnesota, Missouri, and Wisconsin) (fig. 1). The aquifer is a source of potable water in each state except Indiana; however, there are large areas in south-central Illinois, northern Missouri, and southwestern Iowa where the water is not used for potable purposes because of high salinity. The Cambrian-Ordovician aquifer system is designated as one of 16 sandstone principal aquifers that underlie the United States (U.S. Geological Survey, 2003), but the aquifer system includes several carbonate (limestone and dolomite) rock units with shale layers. Some of the sandstones themselves are interbedded with carbonate units or, in places, contain secondary carbonate mineralization as cementation between grains. The Missouri River forms a natural boundary on the southern edge in Missouri and the southwestern edge in western Iowa. South of the Missouri River, the Cambrian and Ordovician rocks are included in the Ozark Plateau aquifer system, which is designated as one of the carbonate principal aquifers (U.S. Geological Survey, 2003). The northern boundary, from northwestern Iowa to the Upper Peninsula, is defined by the erosional edge of Cambrian rocks overlying Precambrian sedimentary or crystalline rocks. The 10,000-mg/L dissolved solids isoline marks the practical limit of the aquifer system in central Illinois and northwestern Indiana (Young, 1992a). To the east and south of this isoline, the brine-saltwater interface is assumed to be a minimal-flow boundary (Young, 1992a). Although not shown in figure 1, the eastern boundary of the aquifer system extends to the north under Lake Michigan from northwestern Indiana.

The study area is within the Central Lowland physiographic province of the Interior Plains and is bounded on the north by the Superior Upland province of Precambrian crystalline rocks in Wisconsin and Minnesota (Fenneman and Johnson, 1946; Vigil and others, 2000). Surface topography is typically smooth to irregular plains resulting from Pleistocene glaciation, with gently rolling hills and some dissected uplands. The unglaciated Driftless Area (Soller and Packard, 1998) in southwestern Wisconsin and northwestern Illinois (fig. 2) is an area dissected by tributaries of the Mississippi River and consisting of rough terrain compared to most of the study area. Altitude of the land surface ranges from about 400 ft near the confluence of the Missouri and Mississippi Rivers to about 1,600 ft in northwestern Iowa. Surface drainage in most of the study area is to the Mississippi River, either directly or by its major tributaries, including the Missouri River. Surface drainage in eastern Wisconsin is to Lake Michigan, and surface drainage in the Upper Peninsula is to Lake Michigan or Lake Superior.

Climate in the study area ranges from cold winters and relatively cool summers in the north to mild winters and hot summers in the south. Average annual temperature (1971 to 2000) increases to the south from about 39°F (3.9°C) in the Upper Peninsula to about 52°F (11.1°C) at the confluence of the Missouri and Mississippi Rivers (Alan Black, Midwestern Regional Climate Center, written commun., 2009). Average annual precipitation (1971 to 2000) increases northwest to southeast from about 25 in. in northwestern Iowa to about 39 in. near the confluence of the Missouri and Mississippi Rivers (Alan Black, Midwestern Regional Climate Center, written commun., 2009). Most of the study area receives about 30 to 36 in. of average annual precipitation.

Population, Land Use, and Water Use

The population of the study area in 2000 was approximately 21.5 million people (U.S. Census Bureau, 2000a). This estimate is based on the sum of the county populations for those counties where the aquifer system was assumed to be a source of water in some part of the county. In large areas of western Iowa, northern Missouri, and south-central Illinois, the aquifer system is not used as a source of water because of high dissolved solids (figs. 1 and 2), and the population estimates do not include those counties. Population is concentrated in the cities and metropolitan areas and thinly dispersed in the rural agricultural areas. The metropolitan areas of Chicago, Ill. (nine counties), and the Twin Cities of Minneapolis-St. Paul, Minnesota-Wisconsin (13 counties) account for approximately 52 percent of the total population in the study area (11.2 million people). Population density ranges from a low of 7.2 people per square mile in Schoolcraft County, Mich., to a high of 5,572 people per square mile in Cook County, Ill. (U.S. Census Bureau, 2000a). Cook County, Ill., has the largest county population with 5.38 million people, accounting for about 25 percent of the total population.

The large population of the Chicago metropolitan area results in Illinois having the largest state population in the study area (fig. 4). The population of Illinois is almost twice that of Wisconsin, which has the second largest population within the study area. The populations of Michigan and Missouri are relatively small because few counties are within the study area where water is used from the Cambrian-Ordovician aquifer system. These population totals include only eight counties in the Upper Peninsula and eight counties in northern Missouri within the study area. Illinois has had the largest population growth within the study area since 1900, but Wisconsin and Minnesota also had steady population growth. The population growth has been much slower in Iowa, Missouri, and the Upper Peninsula (fig. 4).

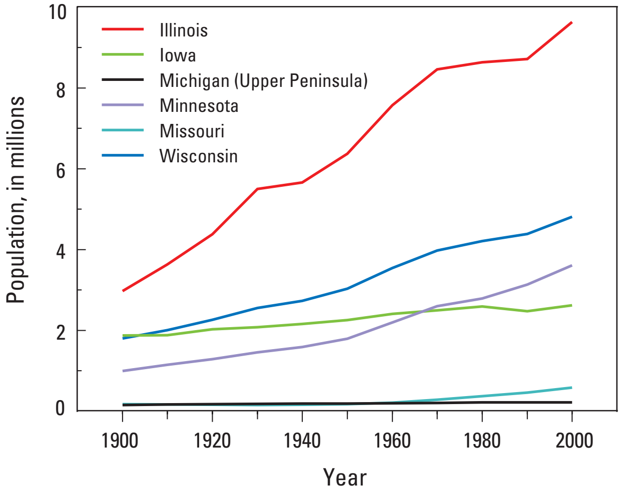
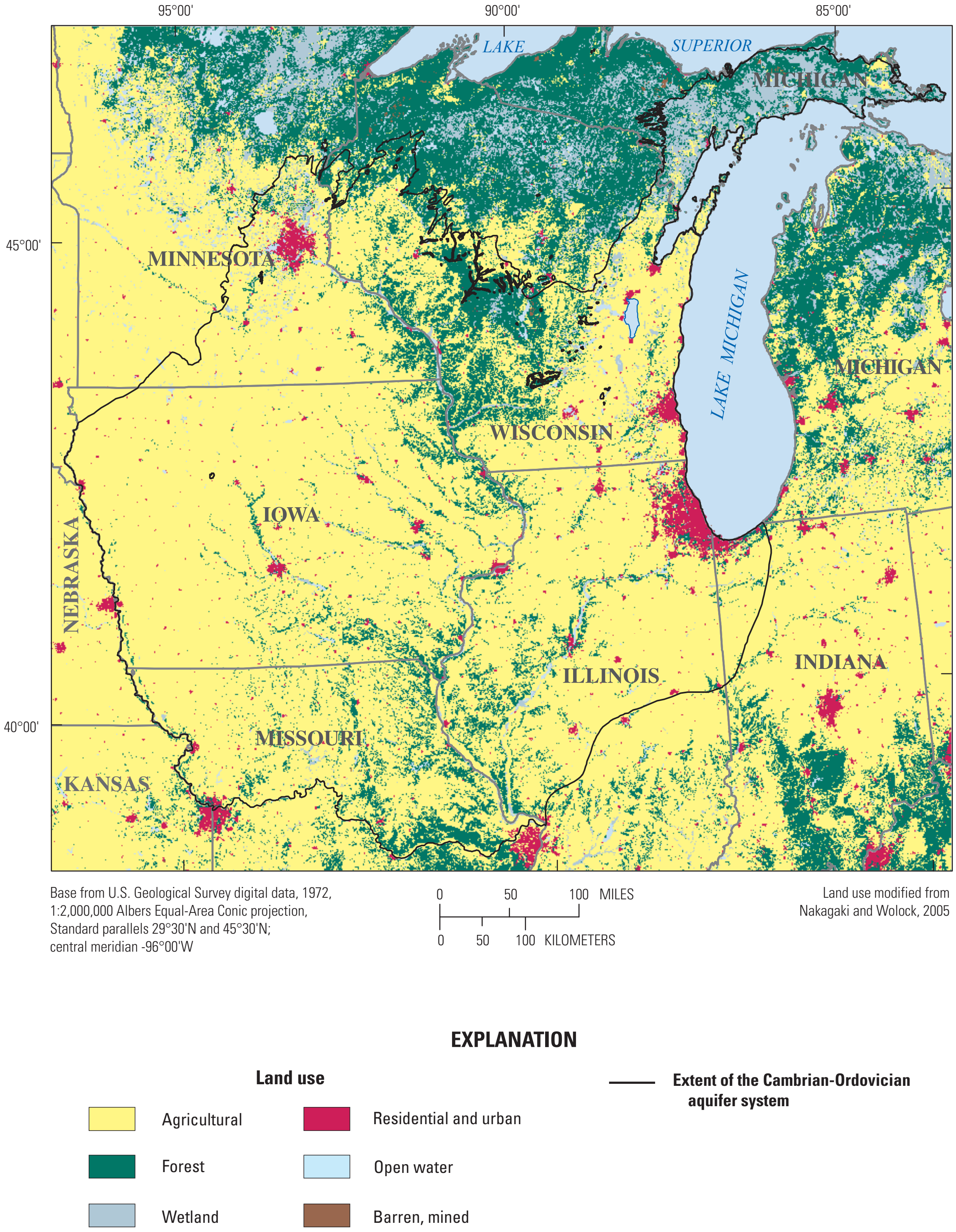


Figure 4. Changes in population in the area of the Cambrian-Ordovician aquifer system, 1900 to 2000 (U.S. Census Bureau, 2000a, b). Excludes counties where the aquifer system is not used because of high salinity.

Not all of the population within the study area uses the Cambrian-Ordovician aquifer system as a source of water. The most noticeable exception is cities along Lake Michigan that use lake water for at least some of their water supply. These include Chicago in Illinois and Milwaukee and Green Bay in Wisconsin. Other sources of water are rivers, reservoirs, and shallow aquifers where they exist; among the shallower aquifers are the glacial aquifer system, the Cretaceous Dakota Sandstone, the Mississippian aquifer, the Silurian-Devonian aquifer, or the Upper Carbonate aquifer (Olcott, 1992). Reservoirs are a common source of water in northern Missouri where the bedrock aquifers have high salinity.

The dominant land uses/land covers in the study area are agricultural lands and forest (fig. 5). Approximately 73 percent of the land is agricultural, and 16.5 percent of the land is forest. The third most abundant land use/land cover is wetland, which accounts for about 4.7 percent of the study area. The residential and urban classification accounts for 3.4 percent of the study area. The major metropolitan areas of Minneapolis-St. Paul, Milwaukee-Waukesha, and Chicago are evident in figure 5 (see fig. 1 for their locations).



Base from U.S. Geological Survey digital data, 1972,
1:2,000,000 Albers Equal-Area Conic projection,
Standard parallels 29°30'N and 45°30'N;
central meridian -96°00'W

Land use modified from
Nakagaki and Wolock, 2005

Figure 5. Land use (1990s) across the Cambrian-Ordovician aquifer system in the northern Midwest.

The land-use dataset used in figure 5 was an enhanced version of the USGS 1992 National Land Cover Data (NLCD), which classified land use for each 30-by-30-m area of land in the conterminous United States. A version with a grid size of 1 km^2 was used to construct figure 5. Vogelmann and others (2001) describe the original version of the NLCD, and Nakagaki and Wolock (2005) describe the enhanced version. To simplify the number of classifications shown in figure 5, agricultural land classifications were combined to include orchards, vineyards, grasslands, pasture/hay, row crops, small grains, and recreational grasses. Row crops and pasture/hay account for 95 percent of the agricultural land use. The forest classification includes deciduous, evergreen, and mixed forest types, as well as shrubland. Deciduous forests account for 87 percent of the forest land. The residential and urban classification comprises low- and high-intensity residential and commercial/industrial/transportation uses.

Land use around each well was also determined by using the four classifications of Gilliom and others (2006): agricultural, urban, undeveloped, and mixed (table 1). These classifications are based on percentages of agricultural and urban land use. Land use was determined for a 500-m radius and a 1-mi radius around each well because, for deep wells, the land use within a 500-m radius may not be representative of the land use where the water that reaches the well was recharged. For wells completed in the confined part of the aquifer system, even the 1-mi radius may not be representative of the land area where the recharge occurred. The most common land use in the 500-m radius around 155 wells sampled by the NAWQA Program was mixed (69 wells or 44 percent), followed by urban (52 wells or 34 percent) and agricultural (32 wells or 21 percent) (table 2). Public-supply wells more frequently had an urban land use in the 500-m radius (60 percent of 80 wells) than did private wells (5 percent of 75 wells). Most private wells are used for domestic supply, but a few institutional wells and one dewatering well were included in the study. The most common land use in the 1-mi radius was mixed (50 percent), followed by agricultural (30 percent) and urban (17 percent) (table 2). Public-supply wells more frequently had a mixed land use (66 percent) or urban land use (29 percent) in the 1-mi radius than did private wells. The most common land use in the 1-mi radius of private wells was agricultural (56 percent), followed by mixed (33 percent).

The dominant agricultural commodities grown in the study area in 2000, in terms of harvested acreage, were corn, soybeans, and hay/alfalfa (fig. 6) (U.S. Department of Agriculture, 2010). In 2000, approximately 27.9 million acres of corn and 25 million acres of soybeans were harvested in the study area. Hay/alfalfa acreage was 6.9 million acres. Corn has been the dominant crop in the area since 1930 (the earliest date there were records for all crops shown), and soybeans have accounted for the second most abundant acreage since 1960 (fig. 6). The total acreage for these crops is based on the data reported by the U.S. Department of Agriculture for counties that overlapped or were within the boundary of the aquifer system shown in figure 1. Therefore, the acreage for some crops in some counties will be overestimated if the county is only partially within the boundary of the aquifer system.

Table 1. Land-use classification used to categorize wells sampled by the NAWQA Program.

[From Gilliom and others (2006). Each well was classified according to the land uses in circular buffer areas of 500-meter radius and 1-mile radius around the well, using land-use data and area-weighted land-use percentages as described in Nakagaki and Wolock (2005)]

Land-use category	Land-use classification criteria
Agricultural	Greater than 50 percent agricultural land and less than or equal to 5 percent urban land.
Urban	Greater than 25 percent urban land and less than or equal to 25 percent agricultural land.
Undeveloped	Less than or equal to 5 percent urban land and less than or equal to 25 percent agricultural land.
Mixed	All other combinations of urban, agricultural, and undeveloped land.

Table 2. Summary of land-use category for wells in the Cambrian-Ordovician aquifer system sampled by the NAWQA Program.

	Number of wells with each land use within a 500-meter radius			Number of wells with each land use within a 1-mile radius		
Land-use category	All	Private	Public supply	All	Private	Public supply
Agricultural	32	30	2	46	42	4
Urban	52	4	48	26	3	23
Undeveloped	2	2	0	5	5	0
Mixed	69	39	30	78	25	53
Total	**155**	**75**	**80**	**155**	**75**	**80**

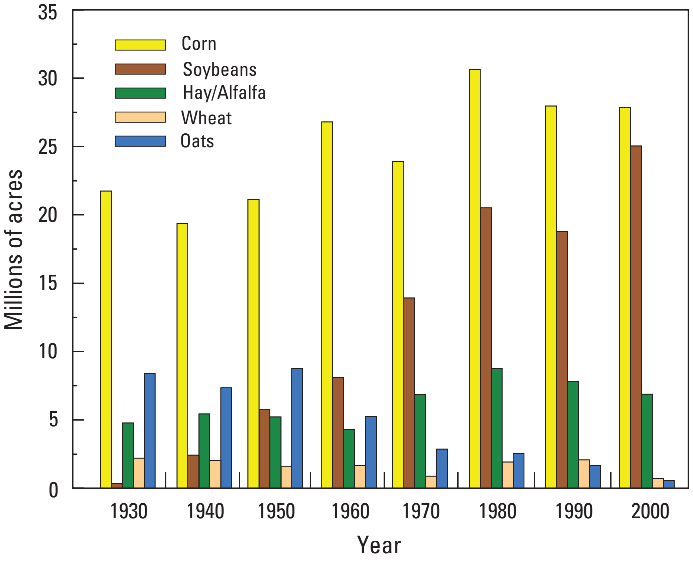


Figure 6. Total harvested acreage for primary crops grown in the northern Midwest where the Cambrian-Ordovician aquifer system occurs (U.S. Department of Agriculture, 2010).

The Cambrian-Ordovician aquifer system is a major source of groundwater in the northern Midwest, ranking second only to the glacial aquifer system. Fresh groundwater withdrawals from the aquifer are used in six of the seven states where the aquifer occurs (the aquifer system is not a source of potable water in northwestern Indiana). Maupin and Barber (2005) estimated withdrawals from principal aquifers in the United States in 2000 for three major categories of use: public supply, self-supplied industrial, and irrigation. Estimated total withdrawal from the Cambrian-Ordovician aquifer system for these three categories was 933 Mgal/d. The dominant water use in the study area in 2000 was public supply (fig. 7), accounting for 63.2 percent (590 Mgal/d) of withdrawals from the aquifer for these three categories. Self-supplied industrial accounted for 26.8 percent (250.6 Mgal/d) and irrigation accounted for 10 percent (92.4 Mgal/d) of withdrawals from the aquifer for these three categories. Other uses of fresh groundwater that were estimated by county but not principal aquifer are domestic, livestock, aquaculture, mining, and thermoelectric power (Hutson and others, 2004). Many private wells are used for domestic supply in the aquifer system in the northern areas where the aquifer is shallow; however, no estimates are presented for total withdrawals from the aquifer system for domestic use because data were not available for all states. Nationally, groundwater withdrawals for domestic use accounted for only 4.2 percent of total withdrawals of fresh groundwater in 2000 (Hutson and others, 2004, p. 9).

Wisconsin withdrew the largest total amount from the aquifer system in 2000 for the three major uses, and Minnesota withdrew the second largest total amount (fig. 8*A*). Wisconsin's total withdrawal was 294 Mgal/d, of which 185 Mgal/d was for public supply. Minnesota's total withdrawal was 271 Mgal/d, of which 209 Mgal/d was for public supply. Withdrawals from Missouri and Michigan were small because of the limited geographic area where the water is suitable for use in Missouri and because of the limited geographic area and low population where the aquifer system occurs in the Upper Peninsula.

In some states, withdrawals from the Cambrian-Ordovician aquifer system account for a large proportion of the total withdrawal from all sources for the three major categories of use (fig. 8*B*). In Iowa, Minnesota, and Wisconsin the aquifer system accounts for more than 50 percent of total withdrawals in the state for public supply and/or self-supplied industrial. In Illinois, the aquifer system accounts for about 33 percent of withdrawals for public supply and about 23 percent of withdrawals for self-supplied industrial. The aquifer system accounts for almost 30 percent of the state withdrawals for irrigation in Wisconsin. In Missouri, the aquifer system accounts for almost 7 percent of the state withdrawals for public supply, even though water is produced from just eight counties along the Missouri and Mississippi Rivers at the southern boundary of the aquifer system.

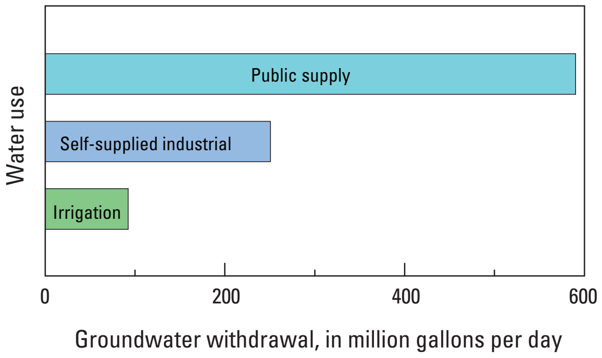


Figure 7. Primary uses of groundwater pumped from the Cambrian-Ordovician aquifer system in 2000 (Maupin and Barber, 2005).

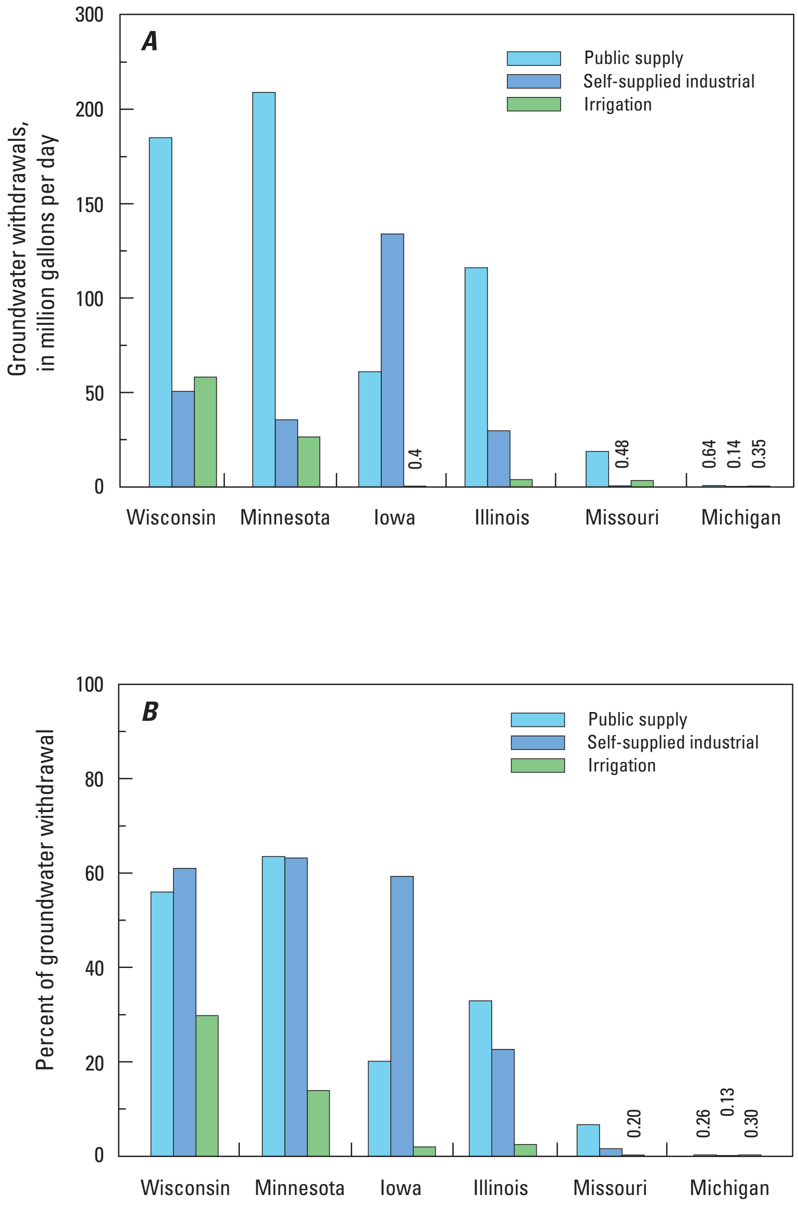


Figure 8. Groundwater withdrawals from the Cambrian-Ordovician aquifer system in 2000: *A*, ranked by state; and *B*, as percentage of groundwater withdrawals for each use category in each state (Maupin and Barber, 2005; Hutson and others, 2004). Values too small to see as a bar are shown as numbers.

Hydrogeology

The regional hydrogeology of the Cambrian-Ordovician aquifer system in the northern Midwest is described in detail in USGS Professional Papers 1305 and 1405–B (Imes, 1985; Young, 1992b). The summary presented here on the structural, lithologic, and hydrologic features of the geologic formations in the study area is, in large part, from those sources. Stratigraphic nomenclature used for geologic formations in each state is similar to what was summarized by Young (1992b, fig. 7), with the addition of the Upper Peninsula.

The bedrock geology of the northern Midwest consists of sandstone, carbonate, and shale sequences that range in age from Precambrian to Cretaceous (fig. 9). These sedimentary rocks overlie the eroded surface of the Precambrian basement complex, which consists of crystalline igneous and metamorphic rocks. Precambrian crystalline rocks form the bedrock surface in much of northern Wisconsin and Minnesota and are associated with structural highs such as the Wisconsin and Transcontinental Arches (fig. 9). Another structural high is the Kankakee Arch, which extends southeast from the Wisconsin Arch through Illinois and into Indiana. Structural lows affecting hydrogeology in the study area include the Illinois basin in southern Illinois, the Michigan basin in central Michigan, and the Forest City basin in southwestern Iowa. The Hollandale Embayment is a structural low in southeastern Minnesota. Subsidence in these structural and topographic lows in the Precambrian crystalline surface during deposition resulted in thick sequences of sedimentary rock. In general, the sedimentary rocks dip away from the structural highs and towards the structural basins, which causes depths to the aquifer system to increase with distance from the structural highs.

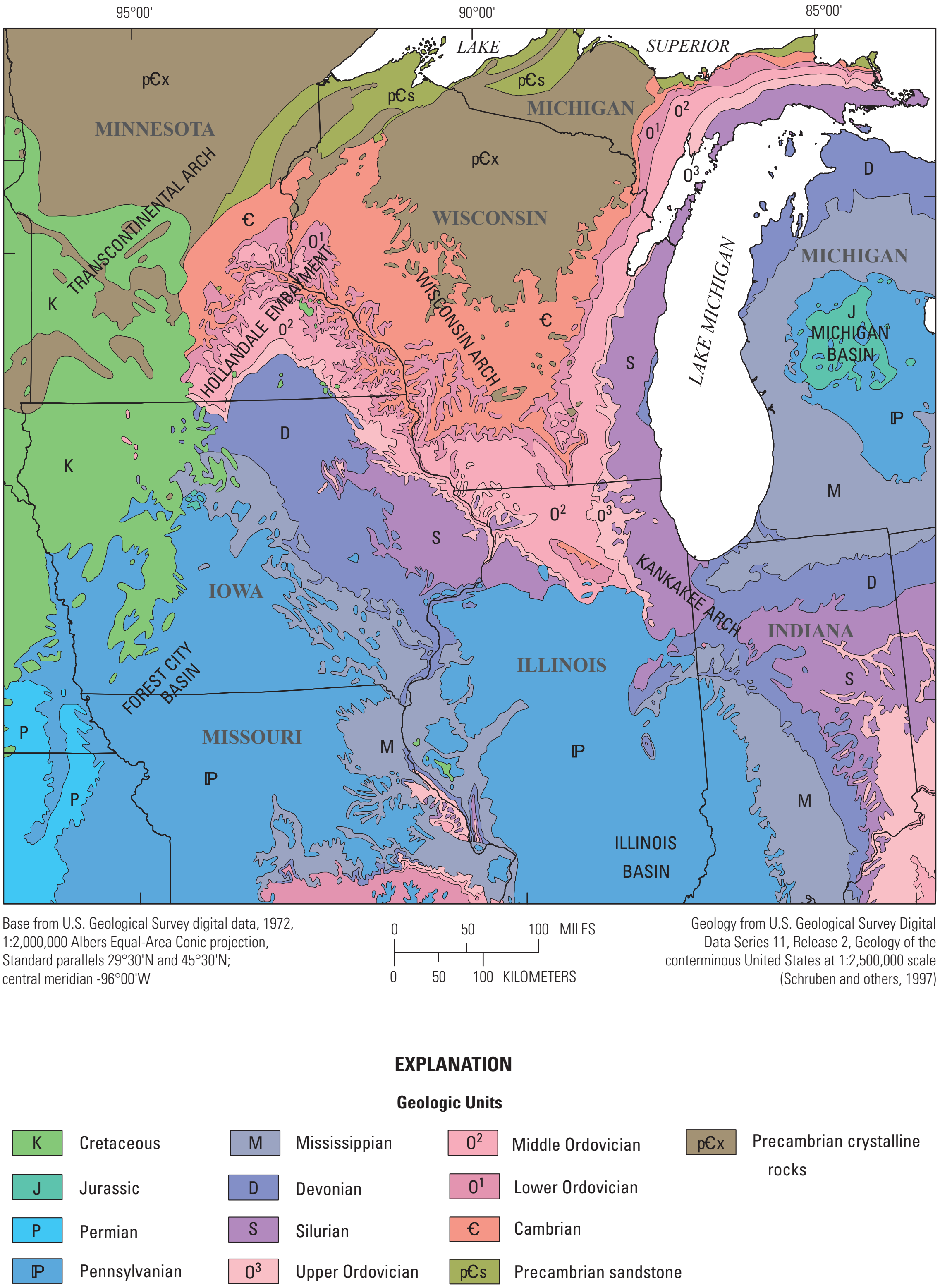
Cambrian and Ordovician rocks crop out or subcrop beneath glacial drift or Holocene deposits in northern Illinois, northeastern Iowa, the Upper Peninsula, southeastern Minnesota, and southern Wisconsin. A band of Silurian and Devonian rocks subcrop beneath glacial drift from the Upper Peninsula, through eastern Wisconsin and northeastern Illinois, and on the western side of the Kankakee Arch in northeastern Iowa and western Illinois. Mississippian and younger rocks border and cover the major sedimentary basins.

The Cambrian-Ordovician aquifer system is a complex, multilayered sequence of marine sedimentary rocks. Leaky confining units consisting of dolomite, shale, and shaly sandstone separate major sandstone aquifers. Young (1992a, b) and (Olcott, 1992) describe the aquifer system as consisting of one sandstone and dolomite aquifer (St. Peter-Prairie du Chien-Jordan) and two sandstone aquifers (Ironton-Galesville and Mount Simon) that are separated by less permeable confining units (fig. 10). However, other Cambrian and Ordovician formations, such as the Galena Dolomite, produce water at a local or subregional scale, at least with sufficient yields for domestic supply. Clastic sedimentary rocks (sandstone and shale) that transition to more carbonate rocks to the south and east in Missouri, Illinois, and Indiana dominate Cambrian strata. Ordovician strata are dominated by carbonates, except for the St. Peter Sandstone.

The stratigraphic position and nomenclature for each state are shown in figure 10, which has been simplified from the correlation chart developed for the RASA study (Young, 1992b, fig. 7, p. 14). Readers interested in more detail than provided in this section are referred to Young (1992b) or the cited references in the text and listed in figure 10. In general, the nomenclature used in this report adopts the group names used by the Wisconsin Geological and Natural History Survey and the formation names used by the Minnesota Geological Survey. One exception to the use of group names is the Maquoketa Group, which is a term used in Illinois and not Wisconsin. Most exceptions to this use of nomenclature are related to formation names in Missouri and Michigan. Indiana is not included in figure 10 because the aquifer system is not a source of potable water in northwestern Indiana. The Cambrian and Ordovician rock units are described briefly in descending stratigraphic order in the following paragraphs. The approximate extents of selected aquifers and confining units are shown in figure 11. The maps are based on boundaries of the structural contour maps of Young (1992b).

The *Upper Ordovician Maquoketa Formation* (O^3 in fig. 9) is the uppermost formation in the aquifer system, and consists primarily of calcareous, silty, dark-colored shale with variable amounts of interbedded dolomite and limestone. For this study, the Maquoketa Formation (hereafter referred to as the “Maquoketa Shale”) represents the boundary between the regionally confined part of the aquifer system and the regionally unconfined part of the aquifer system (fig. 2). The aquifer system is referred to as “regionally confined” in areas where it is buried by the Maquoketa Shale and younger bedrock and “regionally unconfined” in areas where strata from the aquifer system older than the Maquoketa Shale are at the bedrock surface. This conceptual model of confinement is used extensively in this report as the background for mapping chemical constituents and for grouping water-quality data. In some studies, the Maquoketa Shale is combined with the underlying Sinnipee Group and referred to as the “Maquoketa confining unit” (Olcott, 1992; Feinstein and others, 2005a, b). Where the Maquoketa Shale is absent (fig. 11*A*), the carbonate rocks of the Sinnipee Group are more likely to have higher permeability because of weathering. Even though the Maquoketa Shale is a major confining unit, it and the Galena Dolomite make up part of the Upper Carbonate aquifer in southeastern Minnesota, where karst development in a carbonate-rich area has increased the permeability of the rock units (Olcott, 1992).

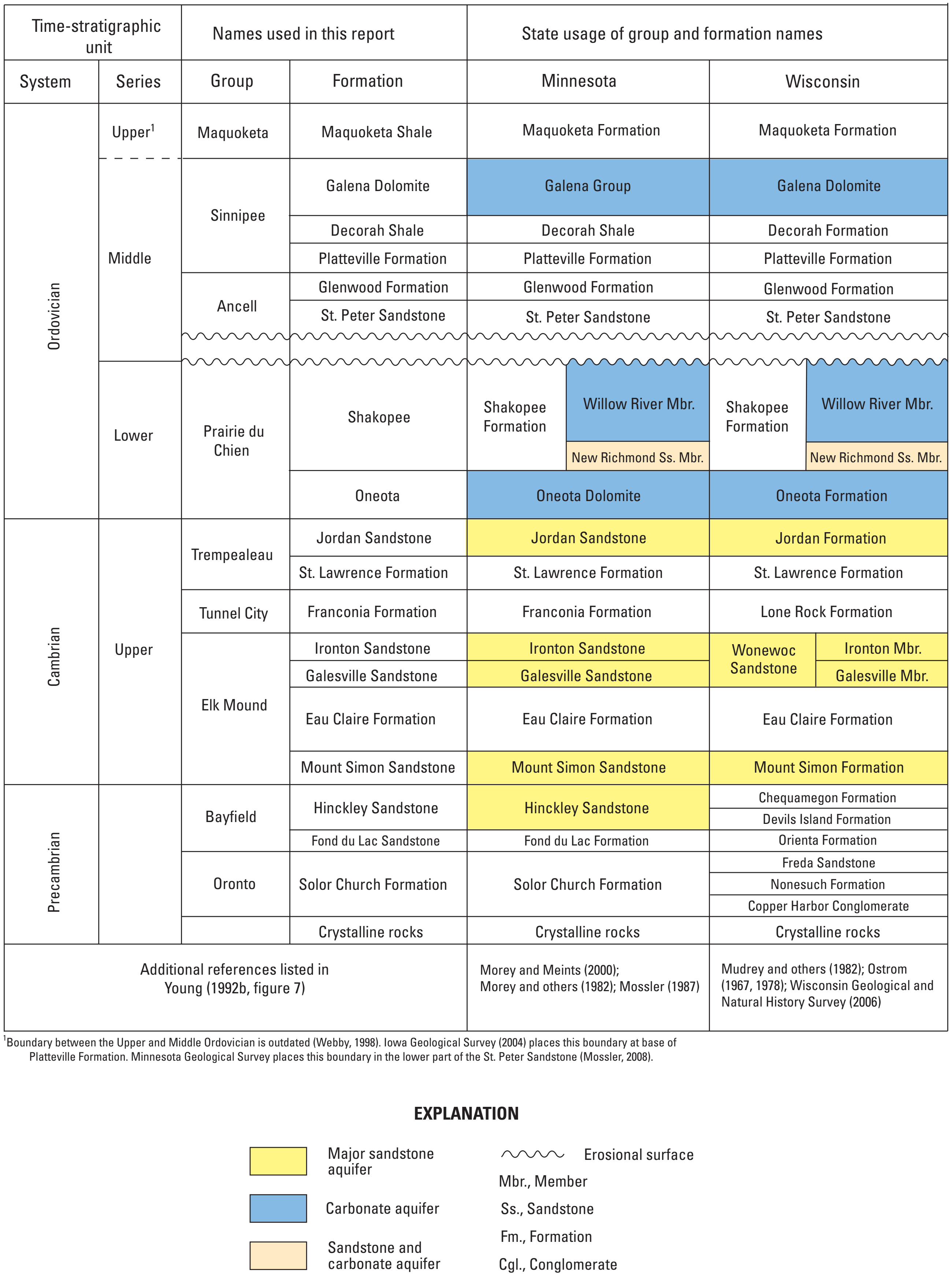
The *Middle Ordovician Sinnipee Group* (O^2 in fig. 9) underlies the Maquoketa Shale and occurs in some areas where the Maquoketa Shale is missing. The Sinnipee Group consists of the Galena Dolomite, Decorah Shale, and Platteville Formation. The Galena Dolomite is primarily a carbonate, either dolomitic limestone or interbedded limestone and dolomite, but thin shale layers also are present in some areas. The Galena Dolomite (fig. 11*B*) and its equivalent in Missouri, the Kimmswick Limestone, are minor aquifers in places with yields typically sufficient for domestic supplies (Imes, 1985). In northern Illinois, wells with long open intervals commonly include the Galena Dolomite. The Decorah Shale is mostly



Base from U.S. Geological Survey digital data, 1972,
1:2,000,000 Albers Equal-Area Conic projection,
Standard parallels 29°30'N and 45°30'N;
central meridian -96°00'W

Geology from U.S. Geological Survey Digital
Data Series 11, Release 2, Geology of the
conterminous United States at 1:2,500,000 scale
(Schruben and others, 1997)

Figure 9. General bedrock geology of the northern Midwest.



Time-stratigraphic unit		Names used in this report		State usage of group and formation names			
System	Series	Group	Formation	Minnesota		Wisconsin	
Ordovician	Upper[1]	Maquoketa	Maquoketa Shale	Maquoketa Formation		Maquoketa Formation	
	Middle	Sinnipee	Galena Dolomite	Galena Group		Galena Dolomite	
			Decorah Shale	Decorah Shale		Decorah Formation	
			Platteville Formation	Platteville Formation		Platteville Formation	
		Ancell	Glenwood Formation	Glenwood Formation		Glenwood Formation	
			St. Peter Sandstone	St. Peter Sandstone		St. Peter Sandstone	
		〰〰〰	〰〰〰	〰〰〰	〰〰〰	〰〰〰	〰〰〰
	Lower	Prairie du Chien	Shakopee	Shakopee Formation	Willow River Mbr.	Shakopee Formation	Willow River Mbr.
					New Richmond Ss. Mbr.		New Richmond Ss. Mbr.
			Oneota	Oneota Dolomite		Oneota Formation	
Cambrian	Upper	Trempealeau	Jordan Sandstone	Jordan Sandstone		Jordan Formation	
			St. Lawrence Formation	St. Lawrence Formation		St. Lawrence Formation	
		Tunnel City	Franconia Formation	Franconia Formation		Lone Rock Formation	
		Elk Mound	Ironton Sandstone	Ironton Sandstone		Wonewoc Sandstone	Ironton Mbr.
			Galesville Sandstone	Galesville Sandstone			Galesville Mbr.
			Eau Claire Formation	Eau Claire Formation		Eau Claire Formation	
			Mount Simon Sandstone	Mount Simon Sandstone		Mount Simon Formation	
Precambrian		Bayfield	Hinckley Sandstone	Hinckley Sandstone		Chequamegon Formation	
						Devils Island Formation	
			Fond du Lac Sandstone	Fond du Lac Formation		Orienta Formation	
		Oronto	Solor Church Formation	Solor Church Formation		Freda Sandstone	
						Nonesuch Formation	
						Copper Harbor Conglomerate	
			Crystalline rocks	Crystalline rocks		Crystalline rocks	
Additional references listed in Young (1992b, figure 7)				Morey and Meints (2000); Morey and others (1982); Mossler (1987)		Mudrey and others (1982); Ostrom (1967, 1978); Wisconsin Geological and Natural History Survey (2006)	

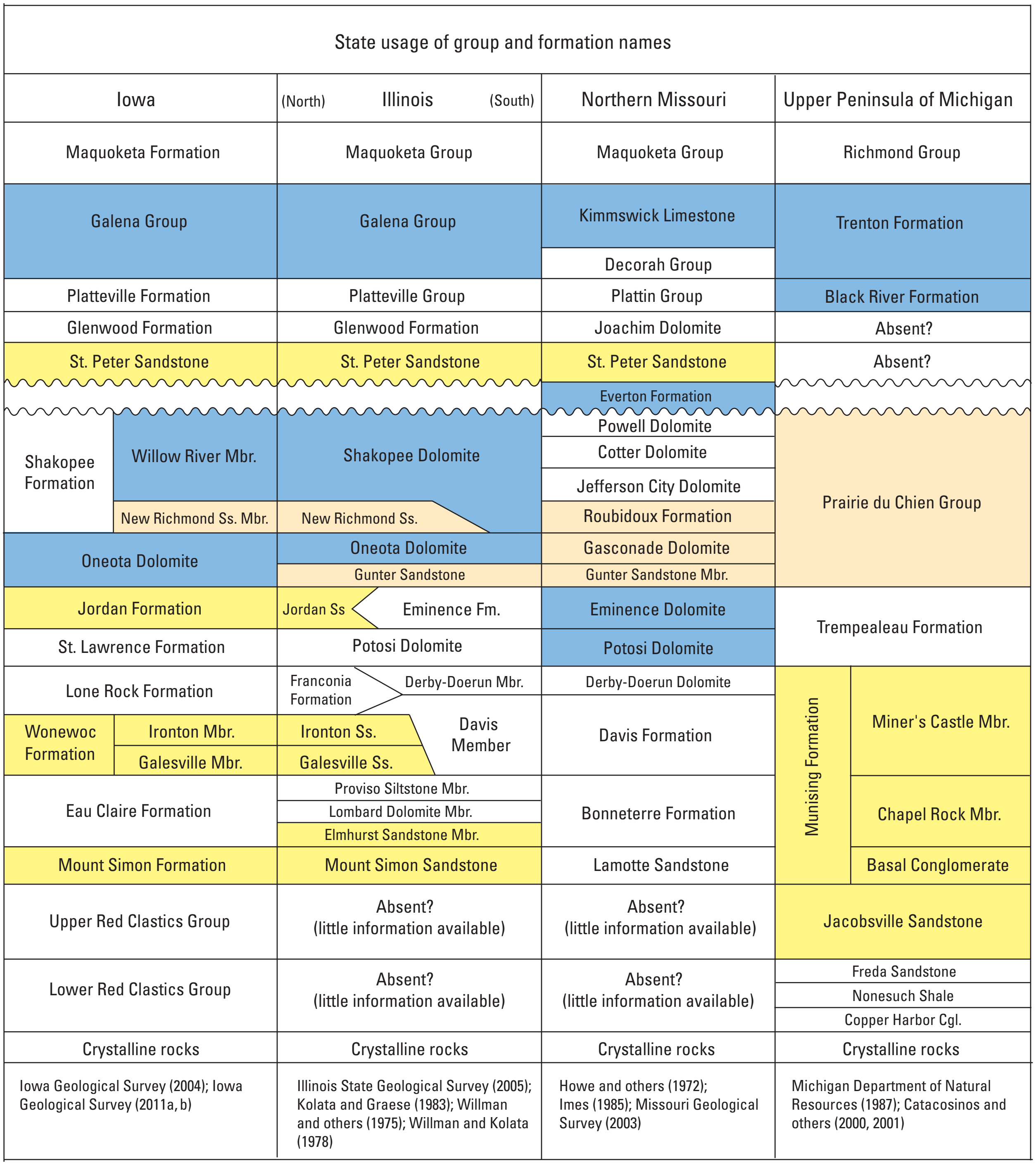
[1]Boundary between the Upper and Middle Ordovician is outdated (Webby, 1998). Iowa Geological Survey (2004) places this boundary at base of Platteville Formation. Minnesota Geological Survey places this boundary in the lower part of the St. Peter Sandstone (Mossler, 2008).

EXPLANATION

🟨	Major sandstone aquifer
🟦	Carbonate aquifer
🟧	Sandstone and carbonate aquifer
〰	Erosional surface

Mbr., Member
Ss., Sandstone
Fm., Formation
Cgl., Conglomerate

Figure 10. Generalized stratigraphic nomenclature of the Cambrian-Ordovician rock units in the northern Midwest (modified from Young, 1992b).



State usage of group and formation names						
Iowa		(North) Illinois	(South)	Northern Missouri	Upper Peninsula of Michigan	
Maquoketa Formation		Maquoketa Group		Maquoketa Group	Richmond Group	
Galena Group		Galena Group		Kimmswick Limestone	Trenton Formation	
				Decorah Group		
Platteville Formation		Platteville Group		Plattin Group	Black River Formation	
Glenwood Formation		Glenwood Formation		Joachim Dolomite	Absent?	
St. Peter Sandstone		St. Peter Sandstone		St. Peter Sandstone	Absent?	
				Everton Formation		
Shakopee Formation	Willow River Mbr.	Shakopee Dolomite		Powell Dolomite	Prairie du Chien Group	
				Cotter Dolomite		
				Jefferson City Dolomite		
	New Richmond Ss. Mbr.	New Richmond Ss.		Roubidoux Formation		
Oneota Dolomite		Oneota Dolomite		Gasconade Dolomite		
		Gunter Sandstone		Gunter Sandstone Mbr.		
Jordan Formation		Jordan Ss	Eminence Fm.	Eminence Dolomite	Trempealeau Formation	
St. Lawrence Formation		Potosi Dolomite		Potosi Dolomite		
Lone Rock Formation		Franconia Formation	Derby-Doerun Mbr.	Derby-Doerun Dolomite	Munising Formation	Miner's Castle Mbr.
Wonewoc Formation	Ironton Mbr.	Ironton Ss.	Davis Member	Davis Formation		
	Galesville Mbr.	Galesville Ss.				
Eau Claire Formation		Proviso Siltstone Mbr.		Bonneterre Formation		Chapel Rock Mbr.
		Lombard Dolomite Mbr.				
		Elmhurst Sandstone Mbr.				
Mount Simon Formation		Mount Simon Sandstone		Lamotte Sandstone		Basal Conglomerate
Upper Red Clastics Group		Absent? (little information available)		Absent? (little information available)	Jacobsville Sandstone	
Lower Red Clastics Group		Absent? (little information available)		Absent? (little information available)	Freda Sandstone	
					Nonesuch Shale	
					Copper Harbor Cgl.	
Crystalline rocks		Crystalline rocks		Crystalline rocks	Crystalline rocks	
Iowa Geological Survey (2004); Iowa Geological Survey (2011a, b)		Illinois State Geological Survey (2005); Kolata and Graese (1983); Willman and others (1975); Willman and Kolata (1978)		Howe and others (1972); Imes (1985); Missouri Geological Survey (2003)	Michigan Department of Natural Resources (1987); Catacosinos and others (2000, 2001)	

Figure 10— Continued.

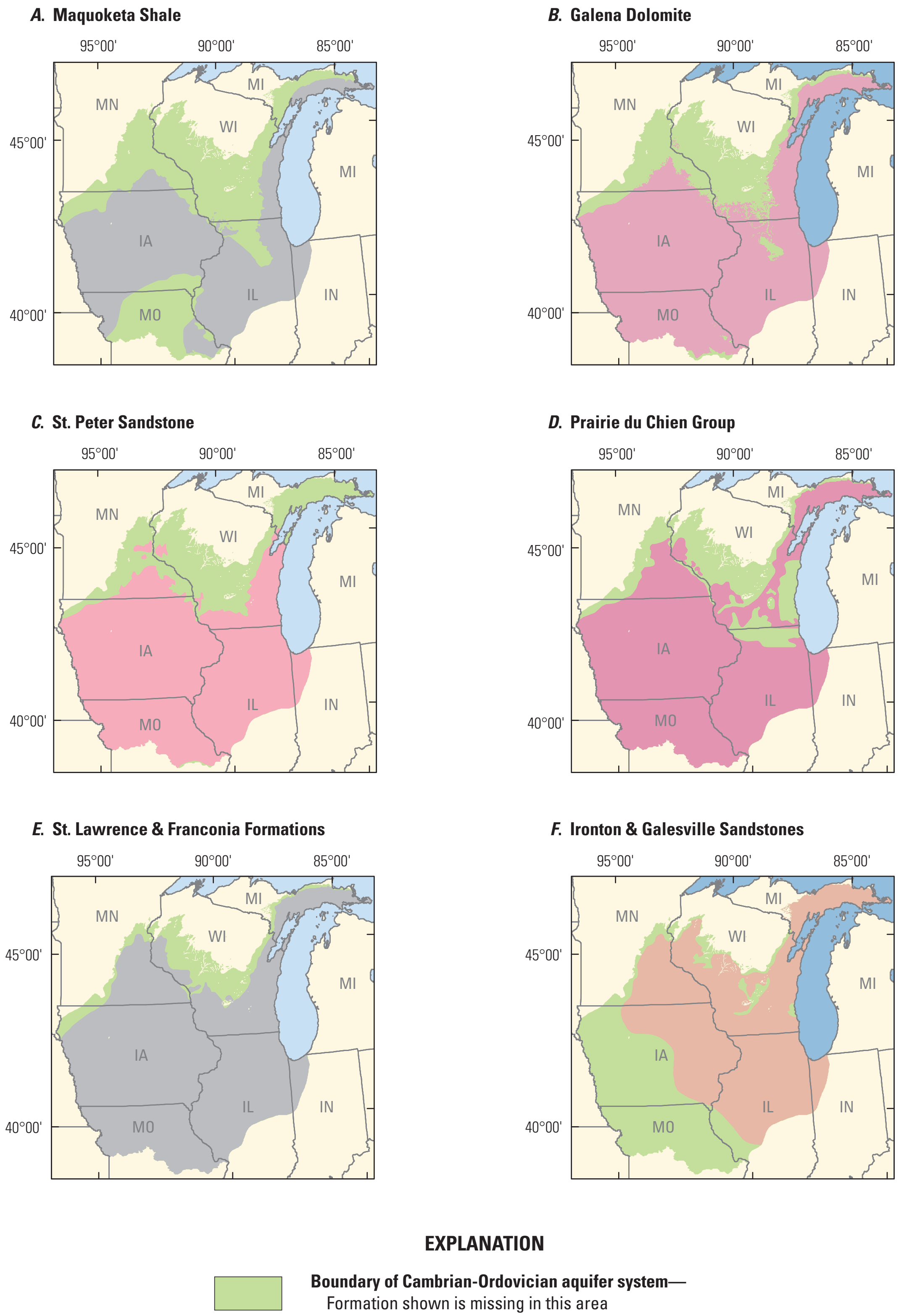
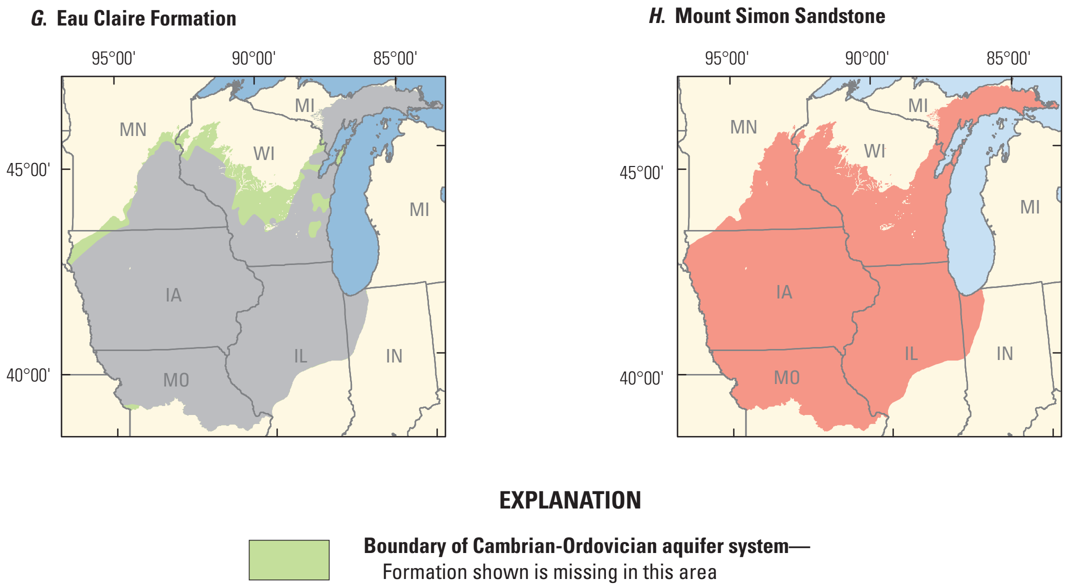


Figure 11. Approximate extent of selected aquifers and confining units within the Cambrian-Ordovician aquifer system in the northern Midwest, in descending order: *A*, Maquoketa Shale; *B*, Galena Dolomite; *C*, St. Peter Sandstone; *D*, Prairie du Chien Group; *E*, combined St. Lawrence and Franconia Formations; *F*, combined Ironton and Galesville Sandstones, *G*, Eau Claire Formation; and *H*, Mount Simon Sandstone (modified from Young, 1992b).


G. Eau Claire Formation

H. Mount Simon Sandstone

Figure 11— Continued.

dolomitic limestone with variable amounts of thin shale beds. The lower part of the Decorah is mainly shale in Missouri and Illinois. The Platteville Formation is mainly a dolomite or limestone. The formations of the Sinnipee Group are considered Upper Ordovician in Iowa (Iowa Geological Survey, 2004) and Minnesota (Mossler, 2008). The term "Middle Ordovician" is now considered mostly Upper Ordovician in internationally proposed series definitions (Webby, 1998).

The *Middle Ordovician Ancell Group* (O^2 on fig. 9) underlies the Sinnipee Group and consists of the Glenwood Formation and the St. Peter Sandstone, the uppermost major sandstone aquifer in the aquifer system (fig. 10). The Glenwood Formation generally consists of shale underlain by dolomitic sandstone. Its thickness averages only 5 ft in Minnesota and increases to 25 to 50 ft in Iowa and Illinois. The St. Peter Sandstone is present throughout most of the northern Midwest south of its outcrop belt and erosional limit (fig. 11*C*). It thins to extinction northeastward in the subsurface in Michigan. The St. Peter Sandstone is a fine- to medium-grained, friable, pure quartzose sandstone. The sand grains are typically well rounded, frosted or pitted, and more than 99 percent quartz. The base of the St. Peter Sandstone includes poorly sorted deposits of cherty conglomerate and clayey sandstone and shale that are the residuum from the pre-St. Peter weathering (Young, 1992b). These deposits act as a confining unit in some areas. In Minnesota, the Glenwood Formation and the upper part of the St. Peter Sandstone are considered Upper Ordovician (Mossler, 2008). In Missouri, the Everton Formation, a dolomite, underlies the St. Peter Sandstone and is older than the St. Peter Sandstone to the north.

The *Lower Ordovician Prairie du Chien Group* (O^1 in fig. 9) underlies the St. Peter Sandstone except in Missouri where the Everton Formation is present. It consists of the Shakopee Formation and the underlying Oneota Dolomite. In extreme northern Illinois and southern Wisconsin, the group was almost totally removed by weathering and erosion (fig. 11*D*). The Shakopee Formation consists of the Willow River Member and the underlying New Richmond Sandstone Member. The major part of the Shakopee Formation is the Willow River Member, a fine-grained, sandy, light gray to tan or buff dolomite. The Oneota Dolomite is fine to coarse grained and tan to light gray, with variable amounts of chert and sand (Young, 1992b).

The *Cambrian Trempealeau Group* (Cambrian strata are undifferentiated on fig. 9) underlies the Prairie du Chien Group and consists of the Jordan Sandstone and the underlying St. Lawrence Formation. The Jordan Sandstone is a major sandstone aquifer, especially in Iowa and Minnesota. The Jordan Sandstone is a fine- to coarse-grained, quartzose sandstone that is loosely cemented in the north, with increasing dolomitic cementation to the south (Horick and Steinhilber, 1978). The Jordan Sandstone occurs in most of the study area south of its outcrop area, but in Illinois it is limited to the extreme western part of the State. As with the Prairie du Chien, the Jordan Sandstone has been eroded away in northern Illinois and eastern Wisconsin. The St. Lawrence Formation is generally considered a confining unit, and it underlies the Jordan Sandstone.

The *Cambrian Tunnel City Group* underlies the St. Lawrence Formation and consists of the Franconia Formation. The Franconia Formation is made up of fine-grained clastics and dolomite. The Franconia Formation and the overlying St. Lawrence (fig. 11*E*) make up a confining unit that separates any combination of the St. Peter-Prairie du Chien-Jordan aquifer above from the Ironton-Galesville aquifer below.

The *Cambrian Elk Mound Group* is the lowermost group of Cambrian strata in the area. The Elk Mound Group, in descending order, consists of the Ironton Sandstone, the Galesville Sandstone, the Eau Claire Formation, and the Mount Simon Sandstone. The Ironton and Galesville Sandstones are medium- to coarse-grained, quartzose sandstones that can be difficult to distinguish from each other in the subsurface. Ostrom (1966) assigned the Ironton and Galesville as members of the Wonewoc Sandstone in Wisconsin. These units are thickest on the northern edge of the Illinois basin and in the Michigan basin and terminate to the south and southwest (fig. 11*F*), where the sandy facies grades into dolomite in central Iowa and central Illinois. The Ironton-Galesville aquifer is the most productive zone of the Cambrian-Ordovician aquifer system in Illinois and Wisconsin, and it yielded much of the water withdrawn from the aquifer system in the Chicago area (Lloyd and Lyke, 1995).

The Eau Claire Formation underlies the Galesville Sandstone and acts as a confining unit between the Ironton-Galesville and Mount Simon aquifers (fig. 11*G*). The Eau Claire Formation consists of silty, quartzose sandstone or shaly siltstone, with various amounts of shale or dolomite. The sandstone facies is dominant in the northern part of the area, but siltstone and shale and then dolomite become dominant southward and toward the structural basins. In northeastern Wisconsin, the Eau Claire, or its silty, shaly facies, is commonly absent, and it is not possible to differentiate the sandstone formations of the Elk Mound Group in the subsurface. In northern Illinois, the basal Elmhurst Sandstone Member (Buschbach, 1964) is included with the Mount Simon Sandstone to form the Elmhurst-Mount Simon aquifer (Visocky and others, 1985).

The basal Cambrian strata consist of the Mount Simon Sandstone and its lateral equivalents in Missouri and the Upper Peninsula. These strata lie on and commonly contain fragments of the Precambrian crystalline basement rock. These sandstones crop out in large areas of northern Wisconsin and eastern Minnesota, where their erosional edge lies on the Precambrian basement. The Mount Simon Sandstone is the most extensive of the Cambrian and Ordovician strata (fig. 11*H*). The Mount Simon Sandstone is a medium- to coarse-grained, sometimes pebbly, quartzose sandstone. The formation tends to be arkosic, coarse grained, and locally conglomeratic, with igneous pebbles near its base. (Arkose is sandstone with at least 25 percent feldspars usually derived from silica-rich igneous rocks.) Thin beds of shale commonly occur in the upper part of the formation throughout the study area and in the lower part of the formation in Illinois. Because of high salinity, the usefulness of the Mount Simon as an aquifer is limited where it is deep. For example, only the upper part contains freshwater in northern Illinois, and the dissolved solids content increases with depth and to the south and east.

Precambrian sandstones that are hydraulically connected and difficult to distinguish from the overlying Cambrian sandstones occur in southeastern Minnesota and the Upper Peninsula. In Minnesota, the Precambrian Hinckley Sandstone is a buff to tan quartz sandstone, and where it underlies the Mount Simon Sandstone the two units form the Mount Simon-Hinckley aquifer. The Fond du Lac Formation is a red to dark-brown shale, feldspathic sandstone, and arkose, and it includes a basal unit of quartz-pebble conglomerate (Morey and Meints, 2000). In the Upper Peninsula, the Precambrian Jacobsville Sandstone is a major aquifer and is in many places indistinguishable from the overlying Munising Formation. In northern Wisconsin, the Bayfield Group and Oronto Group consist of Precambrian sedimentary rock but are not connected with the Cambrian-Ordovician aquifer system.

Recharge and Groundwater Flow

The RASA study of the early 1980s included a detailed investigation of the groundwater hydrology of the Cambrian-Ordovician aquifer system. Recharge, groundwater movement, and discharge were investigated through field data and a groundwater-flow model used to simulate steady-state and transient flow in the aquifer system (Mandle and Kontis, 1992; Young, 1992b). Simulation of steady-state flow was done for predevelopment conditions that were representative of the aquifer conditions before the first known deep wells were drilled around 1864. A transient simulation of groundwater flow was done to show the effects of pumping through 1980. The groundwater-flow model used by Mandle and Kontis (1992) included separate model layers for the major aquifers within the aquifer system: the St. Peter-Prairie du Chien-Jordan aquifer, the Ironton-Galesville aquifer, and the Mount Simon aquifer. Their model also included layers for the overlying Silurian-Devonian aquifer (where it was present) and a composite of the glacial drift aquifer and Cretaceous aquifer (where it was present in Minnesota and northwestern Iowa). The summary of groundwater flow that follows is based on the hydrologic and hydrogeologic data collected by the RASA study (Young, 1992b) and its simulation of groundwater flow (Mandle and Kontis, 1992).

Recharge to the water table occurs by infiltration of precipitation through the soil into the underlying deposits. Glacial drift and alluvial deposits underlie most of the land surface in the northern Midwest and receive most of the initial recharge, which moves through local flow systems and discharges into surface-water bodies or is lost by evapotranspiration. Where the Maquoketa Shale is absent, these surficial deposits are in direct hydraulic connection with the underlying bedrock and provide a source of recharge to the Cambrian-Ordovician aquifers. The Cambrian-Ordovician aquifers are also recharged by direct infiltration of precipitation where they crop out at the land surface, such as in the Driftless Area of southwestern Wisconsin and northwestern Illinois. Direct infiltration of precipitation can also occur in northeastern Iowa and southeastern Minnesota, areas with landscapes similar to the Driftless Area because glacial deposits are thin or absent. Mandle and Kontis (1992) determined through their simulation of predevelopment flow that recharge also leaked downward at a slow rate from the water table through the Maquoketa Shale where the water table was higher than the head in the Cambrian-Ordovician aquifer system. Steady-state simulation of the predevelopment conditions calculated that recharge from the overlying glacial drift or Cretaceous rocks to the St. Peter-Prairie du Chien-Jordan, Ironton-Galesville, and Mount Simon aquifers was 0.24, 0.06, and 0.03 in/yr, respectively (Mandle and Kontis, 1992).

Groundwater flows from topographically high recharge areas to low discharge areas. Most of the groundwater in the glacial aquifers moves within local flow systems of a few miles in length and discharges to small tributaries of major rivers (Young, 1992b). Longer and deeper flow paths that discharge toward the major river valleys characterize groundwater flow in the unconfined areas of the Cambrian-Ordovician aquifer system (fig. 12). The potentiometric-surface map for the St. Peter-Prairie du Chien-Jordan aquifer shows the general patterns of predevelopment regional groundwater flow within the Cambrian-Ordovician aquifer system and is representative of the predevelopment heads in the lower aquifers (Young, 1992b). The potentiometric surface represents the static head in an aquifer and is defined by the levels to which water will rise in tightly cased wells. The flow paths and most of the contour lines in figure 12 are from Young (1992b, fig. 23, p. 64). Some of the contour lines in northeastern Missouri were modified to include detail from Imes (1985, fig. 14, p. 26), and contour lines in the Upper Peninsula were estimated on the basis of predevelopment simulations from a regional groundwater-flow model of the Lake Michigan Basin (Daniel Feinstein, U.S. Geological Survey, written commun., 2010; Feinstein and others, 2010).

In the unconfined areas, the more localized flow systems are controlled by topography, as shown by the irregular pattern of the contour lines that bend where they cross rivers (fig. 12). An example of a groundwater divide is shown by the closed contour line for 1,050 ft in southern Minnesota. This divide separates southerly flow toward Iowa from northerly flow toward the Twin Cities metropolitan area, and it was still present in a potentiometric-surface map of southeastern Minnesota based on water levels for the period 1970–80 (Delin and Woodward, 1984). In the confined areas, groundwater flow is predominantly horizontal. Before development, groundwater moved laterally away from recharge areas toward regional discharge areas (major river valleys and Lake Michigan) or downdip toward the Illinois and Michigan structural basins. Silurian and Devonian rocks underlie Lake Michigan, so the lake did not receive discharge directly from the Cambrian-Ordovician aquifer system (Young, 1992b). Upward leakage from the Cambrian-Ordovician aquifer system through the Maquoketa Shale would have been into Silurian and Devonian rocks. The longest flow paths in the Cambrian-Ordovician aquifer system originated in the recharge areas of northwestern Iowa and extended southeastward to the Illinois basin or the Mississippi and Missouri River Valleys (fig. 12). Other major patterns of confined flow were from eastern Wisconsin toward the Michigan basin and from northeastern Illinois southward to the Illinois basin. Mineralization and salinity increase with distance (and residence time) along these regional flow paths, which eventually reach very saline water and brines near the structural basins. Regional groundwater discharge from the aquifer system was mainly through slow, upward leakage from the confined aquifers along flow paths (Young, 1992b).

Figure 13 shows the potentiometric-surface map for the St. Peter-Prairie du Chien-Jordan aquifer for 1980, which is the most recent potentiometric map that exists of the entire study area. It was beyond the scope of this study to prepare a new potentiometric-surface map for the aquifer system. The potentiometric surface from 1980 shows the change in heads caused by over a century of groundwater development in the Cambrian-Ordovician aquifer system. Most of the contour lines in figure 13 are from Young (1992b, fig. 27, p. 71); however, contour lines in the Upper Peninsula were estimated on the basis of transient simulations of the regional groundwater-flow model of the Lake Michigan Basin (Daniel Feinstein, U.S. Geological Survey, written commun., 2010; Feinstein and others, 2010). In the unconfined areas, there is not much difference between the 1980 heads and the predevelopment heads. In the confined areas, large withdrawals from pumping centers have caused major head declines that create cones of depression on the potentiometric surface and subsequent changes in the direction of flow relative to predevelopment conditions. Water moving downgradient from the recharge areas that would normally discharge to rivers or by leakage to overlying aquifers through confining units is intercepted by pumped wells. Groundwater flow is also induced into the cones from the opposite direction—a reversal of the predevelopment hydraulic gradient (Young, 1992b). Reversals in vertical gradients caused by pumping can induce leakage through overlying and underlying confining units. Development of the confined aquifer also causes an increase in downward leakage from what was simulated for predevelopment conditions. Transient simulation of the 1980 conditions calculated that recharge from the overlying glacial drift or Cretaceous rocks to the St. Peter-Prairie du Chien-Jordan had almost doubled to 0.45 in/yr (Mandle and Kontis, 1992). The effects of groundwater withdrawals on the natural flow system in southeastern Wisconsin were illustrated by Feinstein and others (2010, fig. 17, p. 36). A schematic block diagram was used to show the natural, predevelopment condition of the shallow local flow system and the deep regional flow system (fig. 14*A*). Shallow flow systems of various lengths are topographically controlled and discharge to streams and rivers. Where the Maquoketa Shale is missing, the shallow flow system extends into the Cambrian-Ordovician aquifer system. Under predevelopment conditions, deep regional flow preferentially enters the Cambrian-Ordovician aquifer system west of the subcrop of the Maquoketa Shale and flows laterally downdip toward the Michigan basin or discharges through confining units into the Silurian and Devonian rocks beneath Lake Michigan. Under postdevelopment conditions, pumping wells in the deep sandstone aquifers of the confined area capture and reverse flow that discharged toward Lake Michigan under predevelopment conditions (fig. 14*B*). The postdevelopment conditions also show that the deep groundwater divide has moved to the west (away from the pumping centers) and that vertical leakage through confining units is induced from shallow aquifers.

Base from U.S. Geological Survey digital data, 1972, 1:2,000,000 Albers Equal-Area Conic projection, Standard parallels 29°30'N and 45°30'N; central meridian -96°00'W

Modified from U.S. Geological Survey Ground Water Atlas of the United States, 2000

EXPLANATION

Aquifer-system confinement

🟩 Regionally unconfined

⬜ Regionally confined

Rock type

🟩 Precambrian sandstone

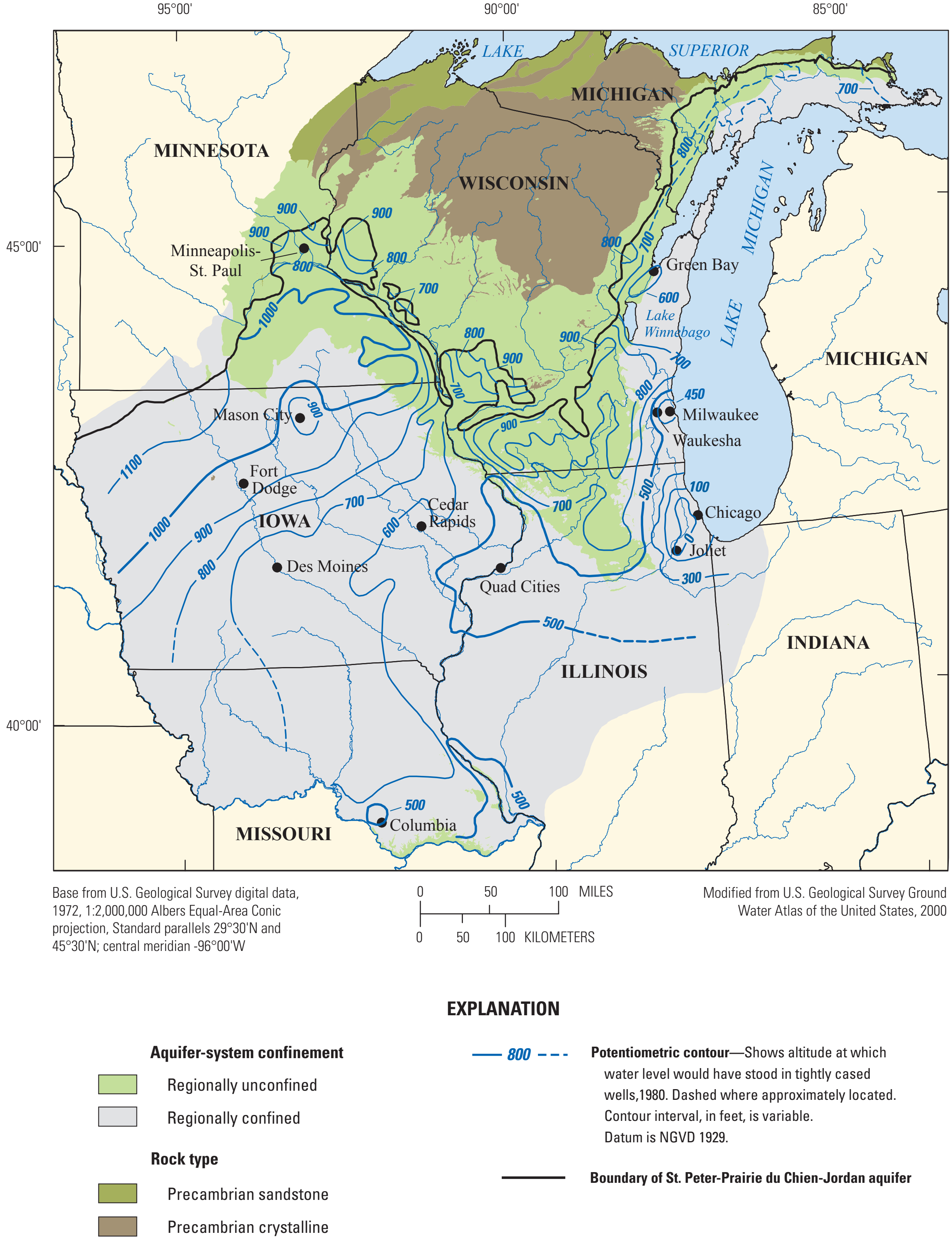
🟫 Precambrian crystalline

— 800 - - - **Potentiometric contour**—Shows altitude at which water level would have stood in tightly cased wells, late 1800s. Dashed where approximately located. Contour interval, in feet, is variable. Datum is NGVD 1929.

→ **Generalized direction of groundwater flow**

— **Boundary of St. Peter-Prairie du Chien-Jordan aquifer**

Figure 12. Approximate predevelopment potentiometric surface for the St. Peter-Prairie du Chien-Jordan aquifer in the northern Midwest (modified from Imes, 1985; and Young, 1992b).



Base from U.S. Geological Survey digital data, 1972, 1:2,000,000 Albers Equal-Area Conic projection, Standard parallels 29°30'N and 45°30'N; central meridian -96°00'W

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Rock type

- 🟩 Precambrian sandstone
- 🟫 Precambrian crystalline

—— 800 - - - **Potentiometric contour**—Shows altitude at which water level would have stood in tightly cased wells,1980. Dashed where approximately located. Contour interval, in feet, is variable. Datum is NGVD 1929.

—— **Boundary of St. Peter-Prairie du Chien-Jordan aquifer**

Figure 13. Generalized potentiometric surface for the St. Peter-Prairie du Chien-Jordan aquifer in the northern Midwest, 1980 (modified from Young, 1992b).

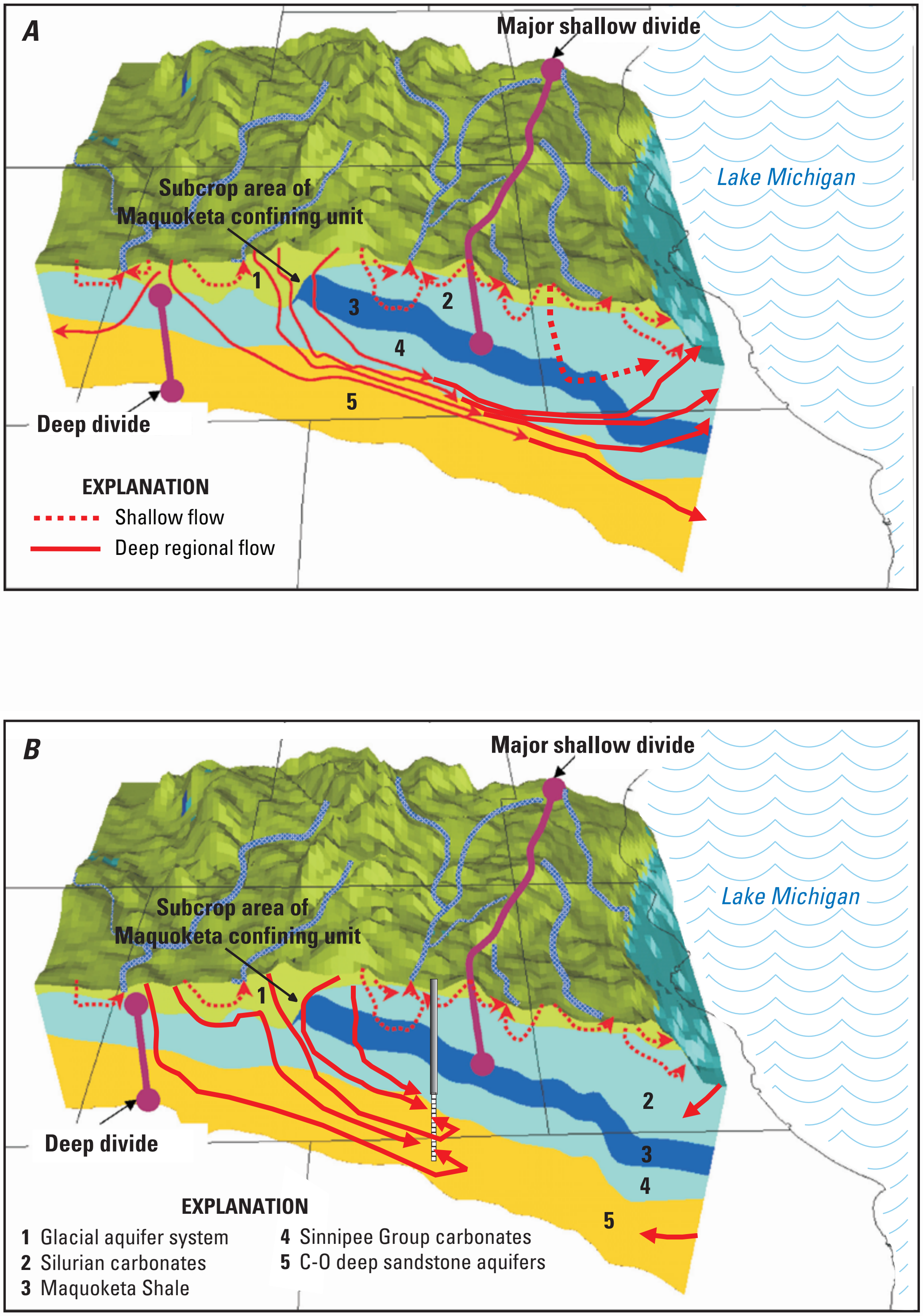


Figure 14. Block schematic of shallow and deep parts of the flow system in southeastern Wisconsin for *A*, natural predevelopment conditions and *B*, postdevelopment conditions after decades of groundwater withdrawal (modified from Feinstein and others, 2010, p. 36; C-O, Cambrian-Ordovician; deep sandstone aquifers include strata from St. Peter Sandstone through Mount Simon Sandstone).

The effects of groundwater withdrawal can be seen in the 1980 potentiometric surface near Mason City, Des Moines, and Cedar Rapids, Iowa; Quad Cities, Ill.; and Columbia, Mo. (fig. 13). In eastern Wisconsin, cones of depression were evident in the 1980 potentiometric surface at Green Bay and Milwaukee. Drawdown at Milwaukee exceeded 375 ft in 1980 (Young, 1992a, b). The largest cone of depression in the 1980 potentiometric surface was in the Chicago area, where drawdown exceeded 900 ft locally (Young, 1992a, b). Total withdrawal from the aquifer system (excluding the Upper Peninsula) in 1980 was about 680 Mgal/d (Young, 1992b). The largest concentrations of groundwater withdrawal in 1980 were in the metropolitan areas of Chicago (177 Mgal/d) and the Twin Cities (178 Mgal/d). The 1980 potentiometric-surface map of the St. Peter-Prairie du Chien-Jordan aquifer does not fully represent the water levels in the deeper Ironton-Galesville and Mount Simon aquifers where overlain by leaky confining units other than the Maquoketa Shale. For example, measured water levels of Delin and Woodward (1984, fig. 3.7–2, p. 49) and simulated water levels of Mandle and Kontis (1992, fig. 34, p. 83) show a cone of depression in the Mount Simon aquifer near the Twin Cities metropolitan area where the aquifer is confined by the Eau Claire Formation.

The 1980 potentiometric surface is obviously outdated in many places, especially near pumping centers. Estimated total withdrawal for the aquifer system increased from 680 Mgal/d in 1980 to 933 Mgal/d in 2000 (Maupin and Barber, 2005). The 1980 potentiometric-surface map is used as an approximation of current conditions because it is the most recent map available for the whole study area. It is assumed that pumping centers from 1980 are still pumping centers today. Cones of depression for 2010 may have different magnitudes and shapes than they had in 1980, but the assumption was made that their general location would be similar to that of 1980. More recent potentiometric-surface maps or drawdown maps are available for parts of the study area, either from direct measurements or from groundwater-flow models (Conlon, 1998; Burch, 2002; Burch, 2008; Feinstein and others, 2005b; Gannon and others, 2009; Feinstein and others, 2010). The ISWS has monitored water levels in northeastern Illinois for years, in part to monitor the effects of replacing water supplies from deep wells with water from Lake Michigan. The general shape of the cone of depression near Chicago in 1980, represented by the 500- and 300-ft contour lines in figure 13, is similar to what is shown in maps for 2000 and 2007 (Burch, 2002, 2008). However, the detailed contours at lower water-level altitudes and areas of maximum drawdown change with time to reflect abandonment of some wells and continued pumping of other wells. In northeastern Wisconsin, a groundwater-flow model was used to simulate the potentiometric surface for 1990 in an area that included Lake Winnebago and Green Bay (Conlon, 1998). In southeastern Wisconsin, a groundwater-flow model was used to simulate drawdown in the aquifer system to the year 2000 (Feinstein and others, 2005b). Feinstein and others (2005b) document the migration of the center of pumping from Milwaukee (in 1950) westward to Waukesha County (in 2000). The Iowa Department of Natural Resources has constructed a groundwater-flow model to monitor drawdown in the St. Peter-Prairie du Chien-Jordan aquifer in Iowa (Gannon and others, 2009). The model will be used as a planning tool for future water-resource development, with the goal of preventing water levels from declining more than 200 ft from the 1975 baseline (prepared by Horick and Steinhilber, 1978) in any high-use areas.

Methods of Investigation

The primary objective of this report is to provide a regional synthesis of the water-quality data collected by the NAWQA Program. Data from other sources were included in several analyses to expand the data coverage to areas where NAWQA did not collect water samples. Current analytical methods used by the USGS and NAWQA typically have reporting levels much lower than older USGS data and non-USGS sources of data. Therefore, the primary analyses and statistical summaries in this report use only data from the NAWQA Program, which are supplemented by maps and additional analyses that incorporate data from other sources.

Sources of Water-Quality Data

Water-quality data for samples collected from wells completed in the Cambrian-Ordovician aquifer system were obtained from (1) the USGS NAWQA Program, (2) the USGS RASA Program, (3) the USGS National Water Information System (NWIS) database, (4) several state agencies that collect data for monitoring and compliance of the Safe Drinking Water Act (SDWA), and (5) state agencies that collected data for a specific project or for background monitoring. The primary source of water-quality data used in this study is the NAWQA Program. The water samples from the NAWQA Program were collected and processed by use of methods designed to yield samples that were representative of environmental conditions, minimally affected by contamination, and comparable among NAWQA studies nationwide. Sampling methods are described in Koterba and others (1995).

The most recent sample of a particular constituent from a well was used for most analyses in this study; however, an older sample was used in some cases because there were results for more constituents for the older sample or there was a known problem with the most recent sample. The stratigraphy of the open interval for each well was verified by checking the well-log information in the USGS Ground Water Site Inventory (GWSI) database and online well records available from state agencies. The stratigraphy of some wells, especially older public-supply wells, was poorly defined, so the primary aquifer and open interval of the well could not be defined better than “Cambrian-Ordovician Systems.” The sources of data used in each of the water-quality constituent maps are summarized in table 3. Sample dates of data used to

Table 3. Sources of data used to map selected water-quality constituents and hydrochemical facies in the Cambrian-Ordovician aquifer system.

[NAWQA, National Water-Quality Assessment Program; RASA, Regional Aquifer-System Analysis Program; NWIS, National Water Information System database; Ill. EPA, Illinois Environmental Protection Agency; ISWS, Illinois State Water Survey; Mich. DEQ, Michigan Department of Environmental Quality; MDH, Minnesota Department of Health; MGS, Minnesota Geological Survey; MPCA, Minnesota Pollution Control Agency; Mo. DNR, Missouri Department of Natural Resources; Wis. DNR, Wisconsin Department of Natural Resources; USEPA, U.S. Environmental Protection Agency; --, not available or not applicable; mg/L, milligrams per liter; µg/L, micrograms per liter; pCi/L, picocuries per liter; VOCs, volatile organic compounds; Mixtures, co-occurrence of some combination of a pesticide, a VOC, and nitrate greater than 1 mg/L]

Water-quality constituent map	Maximum reporting level	Number of samples from each source used to map water quality											
		U.S. Geological Survey			State government agencies								USEPA
		NAWQA	RASA	NWIS	Ill. EPA	ISWS	Mich. DEQ	MDH	MGS	MPCA	Mo. DNR	Wis. DNR	
Dissolved solids	--	154	110	1,490	20	--	--	--	12	68	33	58	8
Hydrochemical facies	--	154	108	96	66	--	--	--	--	65	33	--	--
Sulfate	10 mg/L	154	119	1,753	70	19	31	35	12	69	34	44	7
Chloride	5 mg/L	154	118	1,773	70	19	30	35	12	69	34	58	7
Fluoride	0.2 mg/L	154	119	1,289	66	19	31	--	--	67	34	54	--
Arsenic	2 µg/L	137	112	184	62	19	25	19	--	67	33	90	--
Barium	--	136	127	178	66	19	19	1	20	69	33	50	--
Boron	20 µg/L	107	118	231	64	19	--	2	--	69	--	--	--
Iron	10 µg/L	153	118	778	54	19	10	18	19	69	33	45	--
Manganese	20 µg/L	154	126	784	70	19	--	19	19	69	33	43	--
Strontium	68 µg/L	107	92	173	62	19	--	2	20	69	--	1	--
Radon-222	74 pCi/L	140	--	2	1	--	10	2	16	--	31	74	--
Radium-226	1 pCi/L	88	83	139	9	19	15	162	--	--	36	66	--
Radium-228	1 pCi/L	88	--	77	10	19	14	162	--	--	54	66	--
Radium-226 + radium-228	1 pCi/L	88	24	106	9	19	14	162	--	--	19	65	--
Nitrate	1 mg/L	154	96	609	67	19	31	24	12	69	41	89	--
Ammonia	0.1 mg/L	154	37	310	64	19	--	--	--	--	--	--	--
Pesticides	--	125	--	--	--	--	--	--	--	--	--	--	--
VOCs	--	122	--	--	--	--	--	--	--	--	--	--	--
Mixtures	--	122	--	--	--	--	--	--	--	--	--	--	--

Table 4. Number of samples and ranges in sample dates of data used to map selected water-quality constituents and hydrochemical facies in the Cambrian-Ordovician aquifer system.

[VOCs; volatile organic compounds; Mixtures, co-occurrence of some combination of a pesticide, a VOC, and nitrate greater than 1 mg/L]

Water-quality constituent map	Number of samples	Range in sample dates
Dissolved solids	1,953	1960–2008
Hydrochemical facies	522	1961–2007
Sulfate	2,347	1960–2008
Chloride	2,379	1960–2008
Fluoride	1,833	1960–2008
Arsenic	748	1973–2008
Barium	718	1969–2008
Boron	610	1961–2007
Iron	1,316	1961–2008
Manganese	1,336	1961–2008
Strontium	545	1969–2007
Radon-222	276	1986–2008
Radium-226	617	1969–2008
Radium-228	490	1982–2008
Radium-226 + radium-228	506	1969–2008
Nitrate	1,211	1971–2008
Ammonia	584	1975–2008
Pesticides	125	2002–7
VOCs	122	2002–7
Mixtures	122	2002–7

construct the water-quality constituent maps range from 1960 to 2008 and vary by map (table 4). Most samples collected pre-1980 are from the NWIS database. Although pre-1980 data are much older than the NAWQA data, they represent the most recent sample collected at that well and, in some cases, these older samples are the only data available for an area.

NAWQA Well Networks

The NAWQA Program collected water samples from 155 wells from 6 well networks in the Cambrian-Ordovician aquifer system. Well locations are shown in figures 2 and 3, and appendix 1 lists some basic characteristics for these wells. Wells sampled in the first decade of the NAWQA Program (1991–2001; Cycle I) have a sample date of 1995 or 1996, and wells sampled in the second decade of the NAWQA Program (2001–2012; Cycle II) have sample dates that range from 2002 to 2007. The well locations in figures 2 and 3 are color coded to show the date of the most recent sample. Site information, ancillary data, and water-quality data for wells sampled by NAWQA were obtained from the USGS NAWQA Data Warehouse (Bell and Williamson, 2006; *http://water.usgs.gov/nawqa/data*).

The NAWQA Program first collected water samples from wells in the Cambrian-Ordovician aquifer system in 1995. Water samples were collected from a network of 29 wells in the western Lake Michigan drainages in eastern Wisconsin and the Upper Peninsula (fig. 2). Most of these wells produce water from the St. Peter Sandstone, the Prairie du Chien Group, or Cambrian sandstones (including the Munising Sandstone) (appendix 1). The 29 sampled wells consisted of 22 domestic, 5 public-supply, and 2 institutional wells. Samples were analyzed for major ions, nutrients, pesticides, VOCs, and radionuclides that included tritium and radon-222. An analysis of the water-quality data collected in 1995 is presented in Saad (1996).

This network of wells was resampled in 2002, with one of the original wells replaced with a new well. A subset of five wells was sampled biennially for trends analysis in 2005 and 2007 (fig. 2). Samples collected in 2002 were analyzed for major ions, nutrients, trace elements (new), pesticides, VOCs, and radon-222. Samples collected in 2005 and 2007 from the five trends wells were analyzed for the same constituents except radon-222, and the 2007 samples were analyzed for radium-226 and radium-228. Twenty-six of the wells were used to evaluate the near-decadal-scale (1995 to 2002) changes in nitrate concentrations and pesticide detections in this network of wells.

In 1996, the NAWQA Program collected water samples from two well networks of 25 domestic wells each within the Twin Cities metropolitan area of Minnesota and Wisconsin (fig. 3). The objective of this study was to evaluate differences in water quality in the Prairie du Chien-Jordan aquifer between wells with locally confined conditions and wells with locally unconfined conditions (Fong and others, 1998). Samples were analyzed for major ions, nutrients, trace elements, pesticides, VOCs, tritium, and radon-222. An analysis of the water-quality data collected in 1996 from these wells is presented in Fong and others (1998). The network of wells designed to represent locally unconfined conditions was resampled in 2007, and a subset of five wells was sampled in 2002 and 2005 for trends analysis. The samples collected in 2002 were analyzed for the same constituent classes as the samples collected in 1996 except for tritium, and the samples collected in 2005 were analyzed for the same constituents except for tritium and radon-222. The water samples collected in 2007 were analyzed for major ions, nutrients, trace elements, pesticides, VOCs, radium-226, and radium-228. Twenty-three of the wells sampled in 2007 were used to evaluate the near-decadal-scale (1996 to 2007) changes in nitrate concentrations and pesticide detections in this network of wells.

In 2004 and 2005, a NAWQA source-water quality assessment study in the Twin Cities metropolitan area of Minnesota and Wisconsin sampled 15 public-supply wells for major ions, pesticides, and VOCs (fig. 3). The objective of this study was to evaluate the occurrence of organic compounds in raw water and treated water from wells that produce water from the Cambrian-Ordovician or glacial aquifer systems (Tornes and others, 2008). Raw water samples were collected in 2004, and only wells having samples with several detections were resampled in 2005 for raw water quality and finished water after treatment.

The wells from these three networks near the Twin Cities metropolitan area are in a relatively small geographic area within the regionally unconfined area defined in this report (fig. 3, wells 61–125). Most of the wells produce water from the Prairie du Chien Group, the Jordan Sandstone, or both of these units, which is known collectively as the Prairie du Chien-Jordan aquifer. The Prairie du Chien-Jordan aquifer is the primary source of groundwater for domestic wells and public water supplies in the Twin Cities metropolitan area, supplying approximately 75 percent of groundwater withdrawals (Stark and others, 1996).

In 2005, water samples were collected from a network of 30 public-supply wells covering a large area in the northern two-thirds of Iowa (fig. 2, wells 1–30). Samples were analyzed for major ions, nutrients, trace elements, pesticides, VOCs, and radionuclides that included tritium, radon-222, radium-226, and radium-228. The Prairie du Chien-Jordan aquifer is the primary aquifer for most wells, but the open interval of many of these wells extends into the underlying St. Lawrence Formation. A few wells are completed in the Maquoketa Shale, and a few have long open intervals that span multiple formations within the Cambrian-Ordovician aquifer system. The remarks column in appendix 1 shows that some of these wells are open to Silurian, Devonian, or Mississippian rock units above the Maquoketa Shale; however, it is not known how much these units contribute to the production of the wells. The well log for well number 26 (fig. 2) includes a statement indicating that the Jordan Sandstone accounted for 95 percent of the well's yield.

In 2007, water samples were collected from a network of 30 wells in Illinois and eastern Iowa (fig. 2, wells 31–60) that consisted of 29 public-supply wells and 1 institutional well. Samples were analyzed for the same constituent classes as the network sampled in Iowa in 2005. Nine of the wells from this network were in eastern Iowa, and their primary aquifer was typically the Prairie du Chien-Jordan aquifer, with open intervals that often extended into the St. Lawrence Formation. Primary aquifers for the wells in Illinois were typically the St. Peter Sandstone, the Ironton-Galesville aquifer, or a poorly defined open interval that spanned several formations within the Cambrian-Ordovician aquifer system (appendix 1).

USGS RASA Program and NWIS Database

As part of the RASA study of the Cambrian-Ordovician aquifer system, water samples were collected from 149 sampling sites during 1980–81 (Siegel, 1989). Most of the sampling sites were at wells, but a few springs were sampled in northeastern Iowa. The majority of wells sampled by RASA were in Iowa, Minnesota, and Wisconsin, but several wells were sampled in Illinois and four wells were sampled in Missouri. Samples were collected from public-supply, domestic, industrial, institutional, and test wells. If it was determined that the open interval for the well included strata younger than the Maquoketa Shale, the well was not included in this study.

Water-quality data from 133 wells and 2 springs sampled by RASA were used for this study. These data included physical properties, major ions, trace elements, and radium-226. Six of the wells sampled by RASA in Iowa also were sampled by NAWQA, and the results provide a small dataset for evaluating the stability of water chemistry over the 25-year period between samples.

Water-quality data for wells completed in the Cambrian-Ordovician aquifer system also were retrieved from the NWIS database, with sample dates going back to 1960. The number of constituents available for each well is variable, but some data were available for approximately 1,800 wells. The most commonly available data were for major ions; about half of the wells had some results for trace elements, but they were commonly limited to iron and manganese. In Iowa, data were not available from a state agency but were obtained from the NWIS database, which contains a large amount of data from cooperative water-quality-monitoring projects with the Iowa Department of Natural Resources.

State-Agency Drinking-Water Data and Project Data

Data were obtained from several state agencies that collect water-quality data from public-supply wells as part of the SDWA, or data from specific studies or monitoring networks. To our knowledge, these water-quality data are for raw water samples, meaning water samples not affected by treatment. There are two primary differences between data from the USGS and from state agencies: (1) the USGS filters water samples during sample collection for most constituent classes to obtain dissolved concentrations (major ions, nutrients, trace elements, radium, pesticides), but state agencies typically do not filter samples in the field; and (2) reporting levels used by the state agencies are typically much higher than reporting levels for USGS methods, especially for organics and trace elements. State agencies are concerned primarily with concentrations relative to drinking-water standards (which tend to be much higher than laboratory reporting levels) and not low-level detections. State-agency data related to the SDWA are collected and analyzed by methods approved by the U.S. Environmental Protection Agency (USEPA), and water-quality samples are analyzed at laboratories certified by the state. Their purpose for collecting whole-water samples and not filtered samples is to measure total constituent concentrations in the water being provided to the public by public water supplies. Because public-supply wells are pumped continuously or routinely, they produce water with low turbidity; the assumption was made that the whole-water samples collected by the state agencies would be comparable to the filtered samples collected by the USGS and could be incorporated into the analyses in this report.

Databases managed by state agencies can provide a large number of samples for areas within the aquifer system with little or no USGS data, especially radium-226 and radium-228. Data from state agencies were obtained to augment the USGS data and to expand the geographic coverage of the aquifer system. However, not all data available from the state agencies were used. In some cases, data from multiple wells were available for the same community, so only one of the wells was retained unless the wells produced water from different aquifers. Wells were selected to provide an optimal or complete geographic coverage of the aquifer system by using a target of two wells per county. More than two wells per county were used if multiple aquifers needed to be represented; and, in some cases, fewer than two wells were available per county. The number of water-quality samples from the state agencies varies greatly for the different constituents (table 3).

Water-quality data from Illinois were obtained from the Illinois Environmental Protection Agency (Illinois EPA) and the ISWS. The Illinois EPA provided raw water-quality data for public-supply wells collected and maintained as part of the SDWA. Data for 75 wells were obtained from the Illinois EPA and included results for major ions, nutrients, trace elements, radium-226, radium-228, and radon-222 (one sample). Illinois EPA sample dates ranged from 1979 to 2007. In 2007, the ISWS collected raw water samples from wells in northeastern Illinois as part of a study of high barium and radium concentrations in the Ironton-Galesville aquifer (Kelly, 2008). These data were obtained, and results for 19 wells were used in this study. The data from the ISWS were the only filtered samples from a non-USGS source and included results for physical properties, major ions, nutrients, trace elements, radium-226, and radium-228.

The Michigan Department of Environmental Quality (Michigan DEQ) provided water-quality and stratigraphic information for public-supply and domestic wells in the Upper Peninsula. Data from the Michigan DEQ used in this study included results for 35 wells for major ions, nitrate, trace elements, radium-226, radium-228, tritium, and radon-222. Sample dates ranged from 1990 to 2007.

Water-quality data from Minnesota were obtained from the baseline water-quality survey conducted as part of the groundwater monitoring and assessment program of the Minnesota Pollution Control Agency (1998). Data were also obtained from a study of radium in the Mount Simon aquifer by the Minnesota Geological Survey (MGS) (Lively and others, 1992) and from recent radium investigations and compliance monitoring by the Minnesota Department of Health (MDH). The Minnesota Pollution Control Agency (MPCA) sampled water from Minnesota’s principal aquifers from 1992 through 1996 by using a statewide sampling grid. A subset of 69 wells from the MPCA completed in aquifers within the Cambrian-Ordovician aquifer system was used in this study. The data from the MPCA used in this study included results for physical properties, major ions, nitrate, and trace elements.

A large amount of radium data were obtained from the MDH, which analyzes radium in public-supply wells for compliance purposes and special investigations. A subset of 162 wells from the MDH was used in this study. Data from the MDH included results for physical properties, some major ions, nitrate, some trace elements, radium-226, radium-228, and a few radon-222 samples. Sample dates ranged from 1989 through 2007. Twenty-two wells used from the MDH also were sampled by the MGS in 1989 or 1990 as part of a study of radium in the Mount Simon-Hinckley aquifer (Lively and others, 1992). The data from the MGS included concentrations for some major ions, some trace elements, radium-226, radium-228, and radon-222. Radium values from the MDH are used in this study because they were collected more recently than those from the MGS; however, the MGS data included radon-222 samples for 16 wells.

Water-quality data were obtained from the Missouri Department of Natural Resources (Missouri DNR) for public-supply wells in a limited area north of the Missouri River and west of the Mississippi River. The stratigraphy of the open intervals was determined by using the Missouri DNR online well-log database. Data from 75 wells were used from the Missouri DNR, including results for major ions, nitrate, trace elements, radium-226, radium-228, and radon-222. Sample dates ranged from 1985 to 2007.

Water-quality data and stratigraphic information for wells in Wisconsin were retrieved online from Web sites maintained by the Wisconsin Department of Natural Resources (Wisconsin DNR) (*http://dnr.wi.gov/org/water/dwg/data.htm*). The “High Capacity Wells” database was searched for potential wells in those counties where the Cambrian-Ordovician aquifer system is present. The well name was then used to search the “Public Water Supply Systems” Web site to view wells included in a system and the well construction reports, which have information on the stratigraphy and depths of the open intervals. This Web site also provided links to the water-quality data and the treatment processes so that wells would not be selected if treatment processes might affect the data. A few of the wells that were used listed fluoridation as a treatment process, so the fluoride data were not used. Data from 90 wells were used from the Wisconsin DNR, including results for major ions, nitrate, trace elements, radium-226, radium-228, and radon-222. Sample dates ranged from 1977 to 2008.

Data Treatment

Many wells used in this study were sampled only once, but for wells with multiple samples, the most recent sample was used to characterize water quality through statistical summaries and maps showing the distribution of water-quality properties and constituent concentrations. The date of the most recent sample can differ by constituent if not all constituent classes were analyzed in each water sample. Data from other sources were used for mapping concentrations and comparing to human-health benchmarks and non-health guidelines—summary statistics were calculated only for the NAWQA data.

Censored water-quality data (nondetections) in the NAWQA dataset incorporated the different reporting conventions used by the USGS National Water Quality Laboratory (NWQL) during the study period. The different reporting conventions are minimum reporting levels and laboratory reporting levels (LRLs), which are not strictly comparable because LRLs are set higher than the detection limit to protect against false negatives (Helsel, 2005a). Based on the approach of avoiding a false negative, the LRL is often twice the detection limit (U.S. Environmental Protection Agency, 2003). Therefore, censored values that were reported relative to LRLs were redefined to their long-term method-detection levels (LT-MDLs) for the NAWQA data when calculating summary statistics and detection frequencies for major ions, trace elements, and nutrients. This procedure was used to improve consistency of the reporting conventions in the dataset and to avoid any potential bias in summary statistics that might result from the inclusion of estimated values below LRLs (Helsel, 2005a). Radon values below their sample-specific minimum detectable concentration (ssMDC) were redefined as nondetections less than the ssMDC (McCurdy and others, 2008). Radium values below their sample-specific critical level (ssL_C) were redefined as nondetections less than the ssL_C (McCurdy and others, 2008). The reader is referred to McCurdy and others (2008) for details on how the ssMDC and ssL_C are calculated; in general, for each individual isotope, the ssMDC is about twice the ssL_C.

The numerical values of minimum reporting levels and LT-MDLs for many constituents changed during the study period and often differed considerably among constituents. Constituents with analytical methods that provided lower detection limits may seem to occur more frequently in the environment relative to constituents with higher analytical detection limits. Greater numbers of detections in study areas where analytical methods with low detection limits are used may distort regional patterns of occurrence. In this study, water-quality data were often recensored to assessment levels for calculating detection frequencies. An assessment level is a single concentration threshold used for evaluating the presence or absence of a constituent or a group of constituents within a sample or set of samples on an equal basis (Gilliom and others, 2006). Use of this threshold avoids biases in detection frequencies caused by varying analytical sensitivities to different constituents or over time for a single constituent. This recensoring was done by converting measured values that were less than the assessment level to nondetections relative to the assessment level. Assessment levels were applied to values of trace elements and organic compounds as groups and to values of major ions, nutrients, radium, and radon individually. When multiple constituents within a constituent class are compared, the use of assessment levels prevents the detection frequencies from being biased high for those constituents with the lowest detection level. For trace elements, an assessment level of 1 µg/L was used for all elements except iron (3 µg/L). Two assessment levels were used for pesticides (0.01 and 0.1 µg/L) and VOCs (0.02 and 0.2 µg/L) for calculating detection frequencies, which were compared to detection frequencies calculated when all detections were counted. These assessment levels match those used by Gilliom and others (2006) for their national synthesis of pesticides and Zogorski and others (2006) for their national synthesis of VOCs. Assessment levels can also be set at a concentration determined to have some significance. For example, an assessment level of 1 mg/L is used to calculate the detection frequency of nitrate. The value of 1 mg/L was used as the threshold between possibly natural concentrations of nitrate and those affected by anthropogenic contamination (Dubrovsky and others, 2010).

When assessment levels were used for calculating detection frequencies, values reported as less than a detection limit that was higher than the assessment level were removed from the dataset. These data values usually were isolated cases resulting from problems with the laboratory analysis. During the study period, NAWQA VOC data were reported relative to MDLs that differed by an order of magnitude because of improvements in laboratory analyses. In the 1995 and 1996 data, most VOCs were reported relative to minimum reporting levels of about 0.2 µg/L. In the 2002 and later data, most VOCs were reported relative to minimum reporting levels of about 0.02 µg/L. Because most of the wells sampled in 1995 and 1996 were resampled, this discrepancy in the minimum reporting levels was avoided by using only samples from 2002 to 2007 in the analysis of NAWQA VOC data.

When concentration data from multiple sources (for example, NAWQA, RASA, state agencies) were shown on maps, data reselection methods were used to apply an assessment level that would account for the highest reporting level of interest. For example, the NAWQA radium-226 data have a reporting level of 0.02 picocuries per liter (pCi/L), but reporting levels from other sources range from 0.1 pCi/L to 1.0 pCi/L. On a map of radium-226 data, an assessment level of 1.0 pCi/L was used, and all detections and nondetections of 1.0 pCi/L or less were grouped into the same concentration range of ≤ 1 pCi/L.

Statistical Methods and Data Presentation

Statistical methods were used to summarize the NAWQA data (median and percentile concentrations) and to determine differences in groups of data. All statistical summaries and tests were calculated with the TIBCO Spotfire S+ software package (TIBCO, 2008). Summary statistics for the NAWQA data were calculated for physical properties, major ions, nutrients, dissolved organic carbon, trace elements, and radionuclides. The robust ROS (regression on order statistics of log-transformed data) method was used to calculate summary statistics for constituents with left-censored ("less than") data values.

The ROS method allows for multiple detection limits in the dataset and yields good results even if the data are not log-normally distributed (Helsel and Cohn, 1988; Helsel, 2005b). Summary statistics include frequency of detection, percentiles, and maximum concentrations. Nondetections for trace elements were recensored to the LT-MDL with an upper limit of 1 µg/L except for iron, which had a LT-MDL of 3 µg/L. Nondetections at a concentration above 1 µg/L were removed from the dataset for computing summary statistics and frequency of detection. Because MDLs can vary by sample date and among trace elements, an assessment level of 1 µg/L was used to calculate frequency of detection for comparison between elements. With an assessment level of 1 µg/L, only detections at 1 µg/L or higher are counted as a detection.

The most common statistical tests determine whether two groups of data or paired data have a statistically significant difference. Nonparametric tests were used because they do not require the assumption that the data come from normal distributions. The Wilcoxon rank-sum test was used to test whether two sets of uncensored observations come from the same distribution by testing for differences in values or concentrations between the two groups of data. The Wilcoxon signed-rank test was used to test for differences in uncensored paired data. The generalized Wilcoxon test was used to test for differences in left-censored, two-sample data. The generalized Wilcoxon test computes the Peto-Peto modification to the Gehan test for left-censored data; it is also called the Peto-Prentice test (Peto and Peto, 1972; Prentice, 1978; Helsel, 2005b). Another version of the generalized Wilcoxon test, called the paired-Prentice test, was used to test for differences in paired left-censored data (Helsel, 2005b).

A significance level (alpha value) of 0.05 was used for all statistical tests. The significance level is the probability (p-value) of incorrectly rejecting the null hypothesis. The null hypothesis of a statistical test (for example, there is no difference between two groups of data) is rejected if the p-value is less than or equal to 0.05. A p-value less than or equal to 0.05 means there is only a 5 percent or less chance of getting the observed results (that the two groups of data are different) if the null hypothesis is true. The smaller the p-value, the less likely the observed test statistic may have occurred by random chance when the null hypothesis is true, and the stronger the evidence for rejection of the null hypothesis (Helsel and Hirsch, 1992). The p-value is also considered the significance level attained by the data (Helsel and Hirsch, 1992). Often, the exact p-value cannot be computed for the various Wilcoxon tests because of tied values, and the p-value is based on the normal approximation (TIBCO, 2008). In these cases, a p-value may be reported as "<" a value rather than equal to a value.

The nonparametric Spearman's rank correlation test was used to make a correlation matrix of major inorganics, selected trace elements, radionuclides, physical properties, and selected well characteristics for NAWQA data. The Spearman's rank correlation method uses ranks of data to determine a monotonic relation (a relation in one direction but not necessarily linear) between two variables. The statistics produced are the Spearman's rho coefficient and the p-value. The null hypothesis is that the columns of data are mutually uncorrelated. The null hypothesis is rejected if the p-value is less than the significance level (0.05), indicating that there is a monotonic relation between the two variables. The values of Spearman's rho range from −1 to 1, where larger absolute values indicate a stronger relation. The sign of Spearman's rho is an indicator of whether the relation has a positive or negative slope. In this report, the value of Spearman's rho is shown in the correlation matrix only if the p-value is less than 0.05.

Contingency tables (cross tabulations) and the Pearson's chi-square test for independence were used to determine whether there was a significant association between factors that could be grouped into categories. For example, a contingency table was used to measure the association between tritium-based groundwater (recharge) age and the regional confinement. Recharge age categories were "pre-1953" and "modern," and regional confinement categories were "regionally confined" and "regionally unconfined." A table of counts for all possible combinations of categories is produced, and the chi-square test for independence determines whether the null hypothesis is true; that is, the two categories are independent of each other and have no significant association. The null hypothesis is rejected if the p-value is less than the significance level (0.05), indicating a significant relation or association between the two categories.

In map figures showing the geographic distribution of water-quality properties and constituents, the large number and close proximity of wells resulted in overlapping symbols. Well symbols are layered such that symbols showing higher concentrations are on top of symbols showing lower concentrations, and symbols showing detections are on top of symbols showing nondetections. Well symbols are also layered such that symbols showing NAWQA wells are on top of symbols showing wells from other sources. Contour lines and color-coded point data are used to show regional patterns in the distribution of selected constituent concentrations. The contour lines should be considered as approximate because the data have enough variability that, in many instances, they do not match the value of the contour line. Some of this variability is caused by well depth, where wells in a deeper aquifer will have a different value than wells in a shallower aquifer of the same area. Contour lines are not drawn in areas where the data are too variable to define distinct ranges in concentration.

Boxplots are used to illustrate the distribution of data and to compare the distribution of concentrations of a selected constituent when grouped by grouping variables such as regional confinement or groundwater age. Figure 15 is an explanation of the information shown on boxplots and serves as the explanation for all boxplots used in this report. Portions of a boxplot that fall below a shown reporting level or detection level should be considered as estimated because of nondetections.

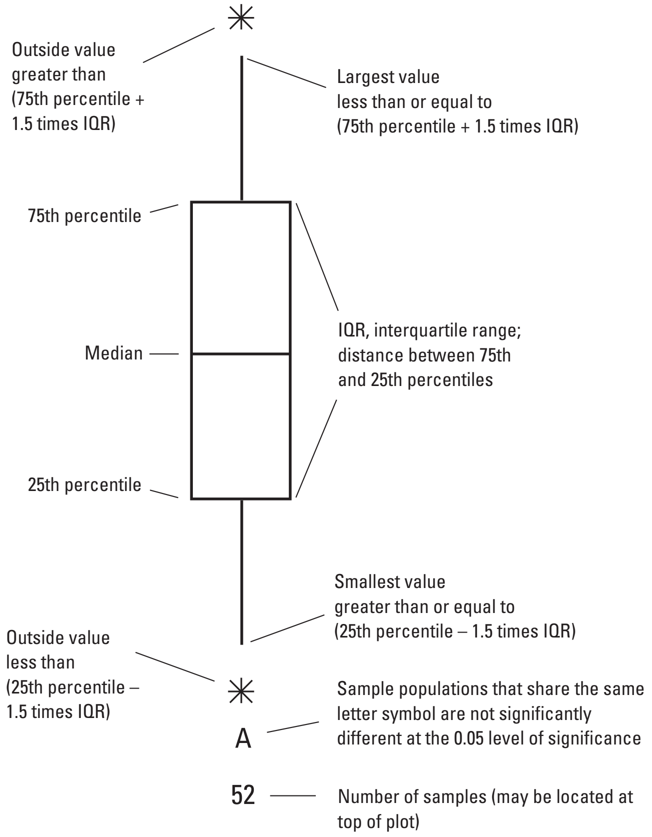


Figure 15. Boxplot explanation.

Analysis of Geochemical Data

The computer program PHREEQCI (Parkhurst and Appelo, 1999; Charlton and Parkhurst, 2002) was used with the NAWQA data to calculate the distribution of aqueous species and saturation indices for mineral phases such as calcite, dolomite, and barite. Concentrations of nitrate, ammonia, major ions, selected trace elements, radium, and alkalinity, along with temperature, dissolved oxygen, and pH, were input to PHREEQCI to define the chemical composition for each sample. The variable pE (negative log of electron activity) was used to assign an approximation of redox intensity for each sample. Redox intensity for each sample was estimated by plotting values of pH and iron concentration on the Eh-pH diagram for iron from Hem (1985, fig. 15). Values of Eh (redox potential, in volts) were converted to values of pE by using the conversion factor of 16.9. Although this may be an imperfect or simplified approach to assigning redox intensity, manually determined values of pE should provide more accurate representations of speciation and saturation indices for elements like iron and uranium than PHREEQC's default pE value of 4.0. Hem (1985) warns that the numerical value of pE is an indicator of redox intensity but is of little value as an indicator of redox capacity.

The PHREEQCI database file was edited to include the thermodynamic data for radium from Langmuir and Riese (1985). All concentrations were entered in units of milligrams per liter, and nondetections were set equal to LT-MDLs for the applicable sample dates. Nondetections with higher than normal reporting levels were removed, but this was necessary for only a few results for trace elements. Nondetections of radium were set equal to the ssL_C for those samples. Inclusion of nondetected constituents in the analysis at the LT-MDL or ssL_C allowed the affected constituents to be included at low concentrations relative to most detections. The value of radium used in PHREEQCI was the sum of the mass concentrations of radium-226 and radium-228. Radium activity in picocuries per liter was converted to units of mass by using the conversion factors of 1 pCi/L = 1.0256×10^{-12} gram per liter for radium-226 and 1 pCi/L = 3.66804×10^{-15} gram per liter for radium-228.

Major cation and anion data were used to classify the hydrochemical facies of the Cambrian-Ordovician aquifer system in accordance with a modified approach that Back (1966) used for part of the Atlantic Coastal Plain. "Hydrochemical facies" is a term used to describe the chemistry of groundwater solutions occurring in the hydrologic system and is analogous to water type, but the facies concept tends to consider water type in the context of spatial distribution and the processes that could lead to the development of the distribution. The facies reflect the response of chemical processes within the lithologic framework and the pattern of groundwater flow (Back, 1966). Separate maps were made for the cation facies and the anion facies because combining them resulted in too much complexity to show on one small map. Cations used in the classification of facies were calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K). Anions used in the classification were bicarbonate (HCO_3), sulfate (SO_4), chloride (Cl), and fluoride (F). Cation facies were classified by using the names and percentages of constituents of Back (1966, p. 13) and were determined by the percentage of Ca + Mg and Na + K (in milliequivalents per liter, meq/L). This results in four possible cation facies: calcium-magnesium, calcium-sodium, sodium-calcium, and sodium-potassium (table 5). The calcium-magnesium facies is composed of 90 percent or more Ca + Mg, the calcium-sodium facies is composed of 50 to <90 percent Ca + Mg, the sodium-calcium facies is composed of 10 to <50 percent Ca + Mg, and the sodium-potassium facies is composed of 0 to <10 percent Ca + Mg.

The classification of anion facies was modified from Back (1966). Anion facies were named in descending order for the two principal anions (in milliequivalents per liter), where the first anion accounted for 50 percent or more of the total anions and the second principal anion accounted for at least 10 percent (table 5). If one anion accounted for more than 90 percent of total anions, the facies was named solely for that anion. If all three anions (HCO_3, SO_4, Cl) accounted for at least 10 percent, then the term "mixed anion" was used. Fluoride never accounted for more than 1.9 percent of total anions. An anion was not included in the facies name if it did not account for at least 10 percent of the total anions.

Table 5. Classification of hydrochemical facies (modified from Back, 1966).

[<, less than; --, not applicable; >, greater than; sum of cations consists of Ca, Mg, Na, and K; sum of anions consists of HCO_3, SO_4, Cl, and fluoride]

	Percentage of constituents relative to sum of cations or anions, in milliequivalents per liter				
	Ca + Mg	**Na + K**	**HCO_3**	**SO_4**	**Cl**
		Cation facies			
Calcium-magnesium (Ca-Mg)	90 to 100	0 to < 10	--	--	--
Calcium-sodium (Ca-Na)	50 to < 90	10 to < 50	--	--	--
Sodium-calcium (Na-Ca)	10 to < 50	50 to < 90	--	--	--
Sodium-potassium (Na-K)	0 to < 10	90 to 100	--	--	--
		Anion facies			
Bicarbonate (HCO_3)	--	--	90 to 100	< 10	< 10
Bicarbonate-sulfate (HCO_3-SO_4)	--	--	50 to < 90	> 10	< 10
Bicarbonate-chloride (HCO_3-Cl)	--	--	50 to < 90	< 10	> 10
Mixed anion	--	--	> 10	> 10	> 10
Sulfate-bicarbonate (SO_4-HCO_3)	--	--	> 10	50 to < 90	< 10
Sulfate (SO_4)	--	--	< 10	90 to 100	< 10
Sulfate-chloride (SO_4-Cl)	--	--	< 10	50 to < 90	> 10
Chloride-bicarbonate (Cl-HCO_3)	--	--	> 10	< 10	50 to < 90
Chloride-sulfate (Cl-SO_4)	--	--	< 10	> 10	50 to < 90

NAWQA Quality-Control Data

Water-quality data are subject to bias and variability during sample collection, processing, and laboratory analysis. The type and magnitude of bias and variability can be determined by analysis of quality-control samples (Mueller and others, 1997). Field-blank samples can verify that sample collection, processing, and analytical protocols were sufficient to prevent the introduction of contaminants into samples. Replicate environmental sample pairs allow assessment of measurement variability due to sample collection, processing, and laboratory analysis protocols. Recoveries in field matrix spikes are used to evaluate the analytical bias of laboratory measurements of pesticide and VOC concentrations. Recovery is the proportion of a target compound that is quantified by an analytical method, and it is measured by analysis of quality-control water samples to which known “spiked” amounts of the target compound have been added. Matrix spikes are prepared in the field, where the spike is added to a groundwater sample. Laboratory reagent spikes are produced in the laboratory, where the spike is added to distilled water. A recovery of less than 100 percent implies that concentrations in environmental samples are biased low, and a recovery of greater than 100 percent implies that concentrations in environmental samples are biased high.

Quality-control samples, including field blanks, replicates, and field matrix spikes, were collected according to NAWQA quality-assurance protocols (Koterba and others, 1995). Quality-control data collected by NAWQA Program personnel while sampling wells in the Cambrian-Ordovician aquifer system are discussed separately for each constituent class (major ions, trace elements, and so forth) in appendix 4.

Water-Quality Benchmarks for Human Health

Constituents in drinking water are of concern when they approach concentrations that may be harmful to human health. In this report, two types of benchmarks were used to identify concentrations of concern: MCLs and health-based screening levels (HBSLs). USEPA MCLs are legally enforceable standards for drinking water that specify the maximum permissible level of a constituent in water that is delivered by public water systems. MCLs are set as close as feasible to concentrations at which there are no known or anticipated adverse human-health effects, and they include a margin of safety (U.S. Environmental Protection Agency, 2009a). HBSLs are non-enforceable benchmark concentrations that can be used in screening-level assessments to evaluate water-quality data within the context of human health; they are available in a Web-based database (Toccalino and Norman, 2006; Toccalino, 2007; Toccalino and others, 2008). Because HBSLs are calculated by using USEPA toxicity information and standard USEPA Office of Water equations for establishing drinking-water guideline values, HBSLs are equivalent to existing USEPA Lifetime Health Advisory and Cancer Risk Concentration values (where they exist), except for unregulated compounds for which more recent toxicity information has become available (Toccalino, 2007).

Water-quality data from wells in this study were compared to USEPA MCLs and USGS HBSLs in a screening-level assessment, which can provide an initial perspective on the potential significance of contaminant occurrence to human health and can help prioritize future studies (Toccalino, 2007; Toccalino and others, 2008). This kind of assessment also provides a perspective on the areas where adverse effects of contaminants in well water are more likely to occur and which contaminants may be responsible for those effects. A screening-level assessment is not designed to evaluate specific effects of contaminants in well water on human health; neither is it suitable for a comprehensive risk assessment, which includes additional factors such as multiple avenues of exposure (Toccalino, 2007; Toccalino and others, 2008).

Water-Quality Assessment of the Cambrian-Ordovician Aquifer System

Groundwater quality of the Cambrian-Ordovician aquifer system is described in this report by using analyses of physical properties, major ions, trace elements, radionuclides, nutrients, pesticides, and volatile organic compounds. Physical properties and constituents analyzed in NAWQA-collected water samples are listed in appendix 2. For the most part, major ions, trace elements, and radionuclides are considered to be naturally occurring constituents that make up the groundwater geochemistry. Nitrate is a naturally occurring nutrient, but at some concentration greater than a background value, it can be considered an anthropogenic contaminant like pesticides and VOCs. The sections that follow describe the occurrence and distribution of selected water-quality properties and constituents, which are often controlled by the presence or absence of the Maquoketa Shale. Constituent concentrations also are related to land use, well type, and groundwater age. Water-quality constituent concentrations are compared to human-health benchmarks (MCLs and HBSLs) and non-health guidelines (Secondary Drinking Water Regulations, or SDWRs; also called Secondary Maximum Contaminant Levels, or SMCLs). SDWRs are not enforceable standards; they are guidelines to assist public water systems in managing their drinking water for aesthetic considerations, such as taste, color, and odor (U.S. Environmental Protection Agency, 1992).

Some discussions and descriptions are based solely on water-quality data collected by the NAWQA Program, such as summary statistics, detection frequencies, and comparisons to human-health benchmarks and non-health guidelines. Some discussions and descriptions are expanded to include data from other sources to provide a more complete geographic coverage of the aquifer system. Data from other sources are included with NAWQA data to map the concentrations of selected major ions, trace elements, radionuclides, and nutrients. These maps use a combination of color-coded points and contour lines to show the distribution of selected constituent concentrations. The contour lines are only approximate lines of equal concentration because the point data can be highly variable, even over short distances. The color-coded points help to show wells where concentrations deviate from the local pattern of the contour lines. The sections on pesticides and VOCs are based solely on NAWQA data. The assessment of water quality begins with a discussion of tritium-based residence time or groundwater age, because groundwater age may be used as a grouping variable to explain differences in the distribution of sample populations of major ions, trace elements, radionuclides, nutrients, pesticides, and VOCs.

Most descriptions, comparisons and statistical analyses are based on the most recent sample collected at each well, except when the objective is to look for temporal stability or changing concentrations with time. Both the RASA and NAWQA Programs sampled a subset of wells in Iowa, which allows for analysis of the long-term stability (over approximately 25 years) of major ions and radium-226. Temporal variability of radon-222 concentrations was evaluated for a subset of wells sampled twice by the NAWQA Program. Near-decadal-scale changes in nitrate concentrations and pesticide detections were evaluated for selected well networks by using the most recent sample from each well and comparing it to the results from a sample collected 7 or 11 years earlier.

Tritium

Groundwater age-dates are not available for the NAWQA samples; however, for most of the wells sampled by NAWQA (137 of 155), a water sample was analyzed for tritium to estimate the relative residence time of water in the aquifer. Tritium (^3H) is a radioactive isotope of hydrogen with a half-life of 12.32 years (Lucas and Unterweger, 2000) and decays by emitting a beta particle to produce helium-3. Tritium is produced naturally by the interaction of cosmic radiation with gases in the upper atmosphere, where it is incorporated into water and falls to earth as precipitation. Tritium is also produced as a fission product in nuclear weapons tests and in nuclear reactors. Atmospheric testing of nuclear weapons starting in 1953 produced elevated concentrations of tritium in precipitation compared to the natural background value. The elevated tritium concentrations in precipitation peaked in the early 1960s and have declined since. Thatcher (1962) estimated the pre-1953 natural, background value of tritium in precipitation of the north-central area of the United States to be 8 Tritium Units (TU) or 25.76 pCi/L by using a conversion factor of 3.22 pCi/L to 1 TU.

Tritium concentrations can be used to estimate generalized groundwater age by employing a radioactive decay function or curve. The estimate of age is limited to older than 1953 (referred to as “pre-1953” from here on) or younger than 1953 (referred to as “modern” from here on). This relative distinction in groundwater age based on the semiquantitative distinction between modern and pre-1953 is useful for interpreting the presence or absence of anthropogenic contaminants and aquifer susceptibility. Relative groundwater age for water samples collected by the NAWQA Program were estimated by determining the elapsed time (in years) between 1953 and the sample date and solving the decay function for tritium, starting with the natural background value of Thatcher (1962). Groundwater derived from precipitation that fell before 1953 would have contained no more than about 2.4 pCi/L (0.75 TU) in 1995 when the first wells were sampled and no more than about 1.2 pCi/L (0.37 TU) in 2007 when the last NAWQA samples used in this study were collected. Tritium activities higher than these maximum values indicate the presence of modern recharge that fell as precipitation after 1953. The thresholds for determining pre-1953 recharge from modern recharge are based on the reported tritium concentration for each sample and do not consider the combined standard uncertainty (CSU) of the tritium measurement.

The tritium-based age is presumed to represent the time of recharge when the water was separated from the atmospheric source of tritium. The age is an “apparent” age because it is calculated on the basis of tritium concentrations, which in a sample from a well can be affected by mixing of waters with different tritium concentrations. Wells with long screened intervals can produce a mixture of waters of different recharge ages. A well with a long open interval may produce a water sample without detectable tritium even though the opening intercepts a zone of water that contains tritium. In this case, dilution with nontritiated water is so great that the tritium in the mixture of water of different recharge ages is not detected by the measurement techniques. Conversely, a well with a long open interval may produce a water sample with detectable tritium even though the opening intercepts a zone of water that contains no tritium. In this case, after dilution with the nontritiated water, the tritium in the mixture of water is great enough to be readily detected by the measurement techniques. Additional information on determining timescales of groundwater flow can be found in Cook and Böhlke (2000).

A nonparametric test of independence using a contingency table showed a significant association ($p < 0.001$) between tritium-based groundwater age and regional confinement. Of the 137 wells with a tritium sample, 56 (41 percent) were determined to include water with a substantial fraction of modern recharge, and 81 (59 percent) were determined to contain water recharged mostly or only pre-1953. All but one well determined to contain modern recharge (55 of 56) were regionally unconfined. The one well within the confined region determined to contain a substantial fraction of modern recharge was well 21, in north-central Iowa (fig. 2). Well 21 has a relatively shallow casing depth of 220 ft compared to a median of 1,050 ft for all confined wells sampled by NAWQA. The primary aquifer penetrated by this well is the Maquoketa Shale, the uppermost Ordovician rock unit. The open interval of well 21 also includes Devonian and Mississippian carbonates and sandstones, according to the geologist’s well log (Iowa Geological Survey, Geologic Sample Database at *http://www.igsb.uiowa.edu/webapps/geosam/*). Water production from the Devonian and Mississippian rock units would short-circuit the regional confinement of the Maquoketa Shale. The Maquoketa Shale is a dolomite at this well, and it is possible that it and the overlying rock units have some fracturing and dissolution features that increase permeability and shorten traveltime for water since recharge.

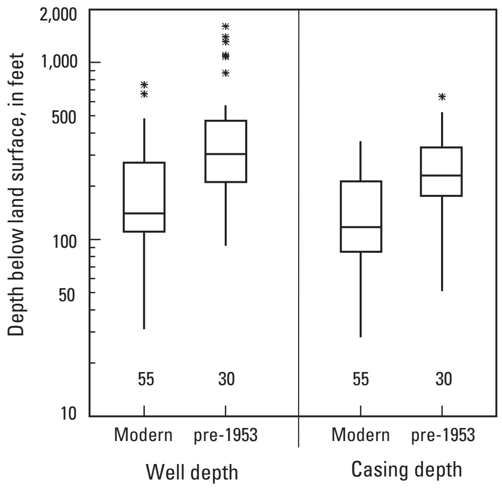


Figure 16. Comparison of tritium-based groundwater age with well depth and casing depth for wells in the regionally unconfined area of the Cambrian-Ordovician aquifer system sampled by the NAWQA Program, 1995–2007.

The majority of wells (51 of 81) determined to contain pre-1953 recharge were regionally confined (63 percent); however, 30 wells (37 percent) classified as regionally unconfined contained pre-1953 recharge. This can be explained by the fact that several formations below the Maquoketa Shale with low hydraulic conductivity act as leaky confining units. Another possible explanation is that the glacial deposits may contain till deposits that are thick enough and extensive enough to reduce the recharge reaching the bedrock underneath. Well depth and casing depth can also explain why wells in the regionally unconfined area might not have detectable modern recharge on the basis of the tritium sample. There was a significant difference ($p < 0.001$) in well depth between wells in the regionally unconfined area that contained pre-1953 recharge (median = 302 ft) and wells that contained modern recharge (median = 140 ft) (fig. 16). There was also a significant difference ($p < 0.001$) in casing depth between wells in the regionally unconfined area that contained pre-1953 recharge (median = 230 ft) and wells that contained modern recharge (median = 117 ft) (fig. 16). There is less chance for local recharge to penetrate the aquifer intervals intercepted by deep wells, and there is a greater likelihood that water flowing to the deep wells is from a more regional flow path with older water (longer residence time) when casing depth and well depth increase.

Physical Properties and Dissolved Solids

Physical properties include those properties of water that are often measured in the field, such as alkalinity, specific conductance, dissolved oxygen, water temperature, and pH. These physical properties are general indicators of water quality and can affect how chemical constituents behave in water. Variability in these properties results mostly from variability associated with natural sources such as precipitation chemistry, amount of recharge, climate, soil properties, and the physical and chemical characteristics of aquifer materials. The dissolved solids content (the amount of mineralization) of water is another indicator of water quality and the suitability of water for drinking and other uses. The dissolved solids content in water is mostly the result of dissolution of soil and aquifer materials, but it can be affected by human activities such as irrigation, induced recharge, and waste disposal. No health guidelines have been established for physical properties or dissolved solids, but extreme values of pH, alkalinity, dissolved oxygen, and dissolved solids may cause aesthetic problems or may affect the concentrations of other constituents. Non-health guidelines (SDWRs) have been set for pH (within the range of 6.5 to 8.5) and dissolved solids (500 mg/L) (U.S. Environmental Protection Agency, 2009a).

Specific conductance is a measure of the capability of the water to conduct an electric current. The presence of charged ionic species in solution makes the solution conductive. As ion concentrations increase, conductance of the solution increases. Specific conductance and dissolved solids were closely related for the wells sampled by NAWQA (Spearman's rho = 0.96, linear $R^2 = 0.95$). Appendix 3 is a matrix of the Spearman rank correlation coefficients for selected physical properties of, and constituents measured in, water samples collected by NAWQA. Specific conductance had a strong positive correlation with many of the major ions, trace elements, ammonia, radium-226, hardness, and well depth. Specific conductance had a negative correlation with silica, nitrate, barium, radon-222, tritium, and pH. Specific conductance of most of the 154 samples (80 percent; 10th through 90th percentiles) ranged from 386 to 1,738 µS/cm at 25°C, with a median value of 618 µS/cm at 25°C (table 6). Specific conductance was significantly higher ($p < 0.001$) for wells in the regionally confined areas of the aquifer than for the regionally unconfined areas (fig. 17*A*; table 7). The median specific conductance for wells in the confined area was 1,106 µS/cm at 25°C, and the median specific conductance for wells in the unconfined area was 548 µS/cm at 25°C. Specific conductance was significantly higher ($p < 0.001$) in water samples determined to be pre-1953 (median = 840 µS/cm at 25°C) than in water samples determined to be modern (median = 537 µS/cm at 25°C) (fig. 18*A*).

Dissolved solids concentration was determined in 154 NAWQA samples by measuring the residue on evaporation at 180°C (Fishman and Friedman, 1989). Dissolved solids had a strong positive correlation with many of the major ions and trace elements (appendix 3). Dissolved solids also had a positive correlation with well depth and casing depth. Dissolved solids had a negative correlation with silica, nitrate, barium, radon-222, tritium, and pH, many of which are general indicators of modern, less mineralized water. Dissolved solids concentration in most samples (80 percent) ranged from 219 to 1,292 mg/L, with a median value of 352 mg/L (table 6). More than 10 percent of the samples would be considered as slightly saline (dissolved solids, 1,000–3,000 mg/L) per the classification of Robinove and others (1958). The USEPA SDWR for dissolved solids, 500 mg/L, was exceeded in 29.2 percent of the NAWQA samples collected from the aquifer system (table 8). Noticeable effects of dissolved solids concentrations greater than the SDWR are hardness, scaly deposits in pipes and fixtures, colored water, staining, and salty taste (U.S. Environmental Protection Agency, 1992). Dissolved solids concentrations were significantly higher ($p < 0.001$) in wells from the regionally confined area of the aquifer than from the regionally unconfined area (fig. 17*B*; table 7). The median dissolved solids concentration from the confined area was 714 mg/L, and the mean was 907 mg/L; the median dissolved solids concentration from the unconfined area was 321 mg/L, and the mean was 367 mg/L. The data are not normally distributed, so the mean is greater than the median. The two outliers with the highest values of dissolved solids in the unconfined area correspond to NAWQA wells 132 and 147, which also had the two highest concentrations of sulfate among the NAWQA samples. The correlation between dissolved solids and sulfate has a Spearman's rho of 0.84, the highest correlation with dissolved solids of any of the major ions or trace elements in the correlation matrix. Well 132 is just east of Lake Winnebago in eastern Wisconsin, and well 147 is just across the Michigan State line in the Upper Peninsula; both wells are just west of the subcrop of the Maquoketa Shale (fig. 2). Dissolved solids concentrations typically increase with groundwater age and distance along flow paths because of longer contact time between the water and the aquifer materials. Dissolved solids was significantly higher ($p < 0.001$) in water determined to be pre-1953 (median = 491 mg/L) than in younger (presumed modern) water (median = 317 mg/L) (fig. 18*B*). NAWQA wells 132 and 147 both contained pre-1953 recharge.

Data from other sources (table 3) were combined with NAWQA data to map concentrations of dissolved solids in the Cambrian-Ordovician aquifer system (fig. 19). Few samples have a dissolved solids concentration of 100 mg/L or less, but those that do tend to be from shallow wells in western Wisconsin where the Ordovician rocks are absent. This area of lowest concentrations of dissolved solids is enclosed within a broader area where values of dissolved solids are mostly less than 250 mg/L. Generally, dissolved solids concentrations were lowest in regionally unconfined areas and increased to the south and east in the regionally confined areas. In the Upper Peninsula, dissolved solids ranged from less than 250 mg/L to more than 1,000 mg/L and increased in the direction of the Michigan basin. Dissolved solids concentrations also increased to the west in Iowa. In Minnesota, dissolved solids

Table 6. Summary statistics for physical properties of, and major ions in, samples collected for the NAWQA Program, 1995–2007.

[Assessment level, most common method detection level for data set is shown; µS/cm, microsiemens per centimeter; °C, degrees Celcius; mg/L, milligrams per liter; CaCO$_3$, calcium carbonate; --, not applicable; <, less than]

Physical property or ion	No assessment level								Assessment level as indicated			
	Number of samples	Number of detections	Concentration or value percentile					Maximum Concentration or value	Level	Number of samples	Number of detections	Frequency of detection, in percent
			10th	25th	Median	75th	90th					
Physical properties												
Temperature (°C)	154	154	9.6	10.1	11.8	14.9	19.5	25.7	--	154	154	--
Specific conductance (µS/cm at 25°C)	154	154	386	491	618	928	1,738	2,950	--	154	154	--
Dissolved oxygen (mg/L)	152	119	<0.18	<0.18	0.28	1.2	6.3	11.5	0.18	152	103	67.8
pH (standard units)	154	154	6.95	7.15	7.32	7.49	7.61	8.05	--	154	154	--
Alkalinity as CaCO$_3$ (mg/L)	154	154	164	216	262	297	338	438	--	154	154	--
Major ions (mg/L)												
[1]Bicarbonate	154	154	200	264	319	361	412	534	--	154	154	100
Bromide	154	143	0.01	0.02	0.04	0.1	0.43	2.36	0.01	150	143	95.3
Calcium	154	154	46.4	55.2	68.7	87.0	104	530	0.02	154	154	100
Chloride	154	152	0.7	1.8	7.1	24.4	110	589	0.1	153	152	99.3
Fluoride	154	148	0.1	0.14	0.24	1.2	1.7	3.32	0.05	151	148	98.0
Magnesium	154	154	19.3	24.9	30.2	37.0	47.6	109	0.01	154	154	100
Potassium	154	154	0.84	1.3	2.4	11.3	17.3	42.9	0.1	154	154	100
Silica	154	154	7.5	8.8	12.9	18.2	22.9	30.0	0.01	154	154	100
Sodium	154	154	2.6	4.0	8.3	58.5	181	504	0.2	154	154	100
Sulfate	154	154	7.5	13.9	26.2	141	540	1,697	0.1	154	154	100
Hardness, as CaCO$_3$	154	154	195	247	299	364	450	1,772	--	154	154	100
Dissolved solids	154	154	219	288	352	590	1,292	2,812	--	154	154	100

[1] When not provided, calculated as alkalinity/0.8202 (Hem, 1985).

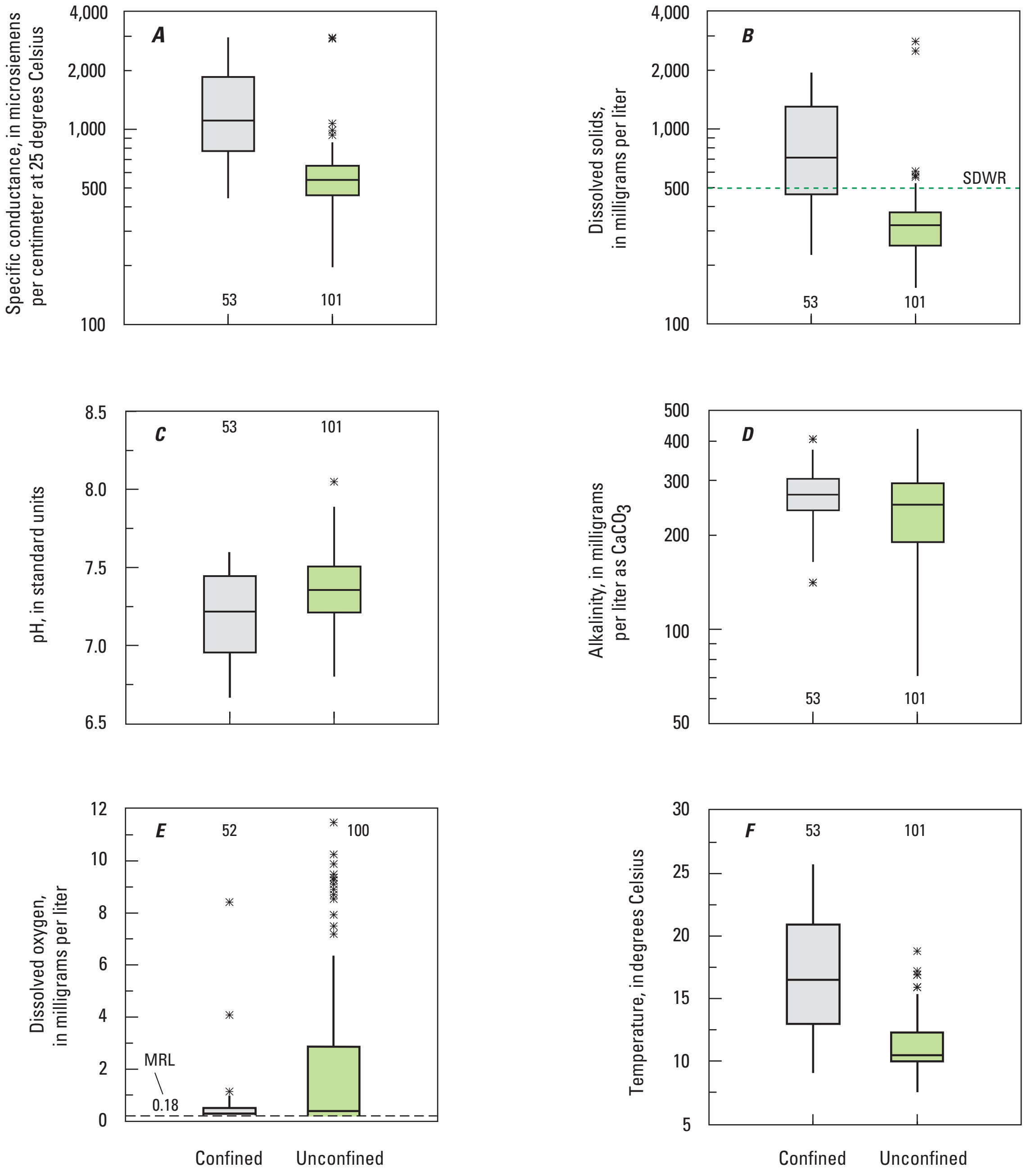


Figure 17. Distribution of physical properties and dissolved solids by regional confinement for water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 1995–2007 (SDWR, Secondary Drinking Water Regulation; MRL, maximum reporting level).

Table 7. Summary of significant differences in physical properties and constituent concentrations, when grouped by regional confinement, for samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 1995–2007.

[--, no significant difference at the 0.05 significance level]

Property or constituent	Statistically significant difference in values or concentrations when grouped by regional confinement? ("Yes" identifies the region with higher values)	
	Confined	Unconfined
Physical properties		
Alkalinity	Yes	
Dissolved oxygen	--	--
pH		Yes
Specific conductance	Yes	
Temperature	Yes	
Major ions, hardness, and dissolved solids		
Bicarbonate	Yes	
Bromide	Yes	
Calcium	Yes	
Chloride	Yes	
Fluoride	Yes	
Hardness	Yes	
Magnesium	Yes	
Potassium	Yes	
Silica		Yes
Sodium	Yes	
Sulfate	Yes	
Dissolved solids	Yes	
Trace elements		
Arsenic		Yes
Barium		Yes
Boron	Yes	
Iron	Yes	
Lithium	Yes	
Manganese		Yes
Strontium	Yes	
Uranium		[1]Yes
Radionuclides		
Radium-226	Yes	
Radium-228	Yes	
Radon-222		Yes
Nutrients		
Ammonia	Yes	
Dissolved organic carbon		Yes
Nitrate (nitrate + nitrite)		Yes

[1] Statistically significant difference in concentrations between confined and unconfined wells only after removing elevated nondetections above a detection level of 0.02 µg/L.

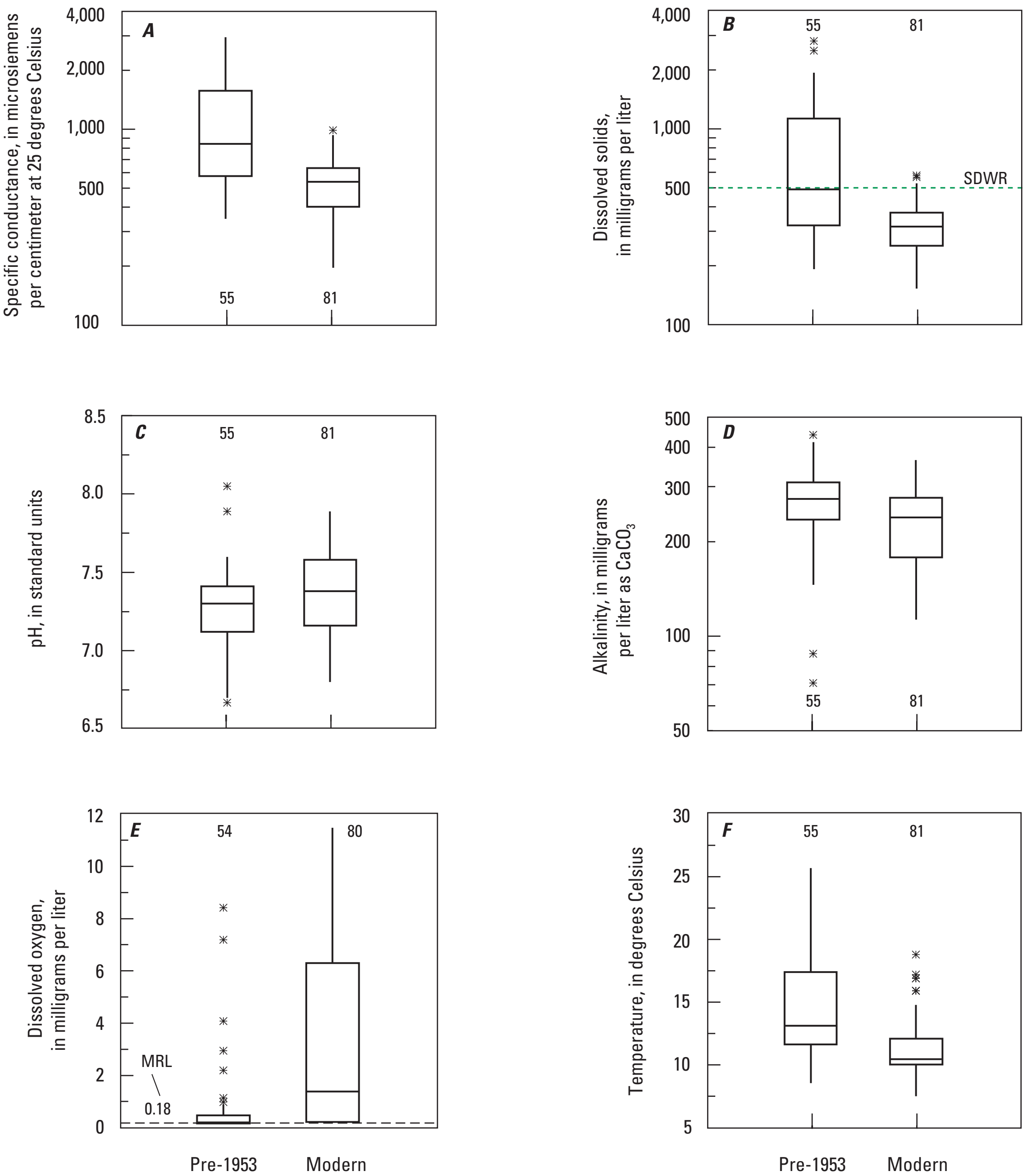


Figure 18. Distribution of physical properties and dissolved solids by tritium-based apparent recharge age for water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 1995–2007 (SDWR, Secondary Drinking Water Regulation; MRL, maximum reporting level).

Table 8. Comparison of physical properties and major ions analyzed in samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 1995–2007, with human-health benchmarks and non-health guidelines for drinking water.

[SDWRs are Secondary Drinking Water Regulations that are non-enforceable Federal guidelines regarding cosmetic or aesthetic effects of drinking water; mg/L, milligrams per liter; MCLs are U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Levels for public water supplies; ROE, residue on evaporation at 180 degrees Celsius; --, not applicable]

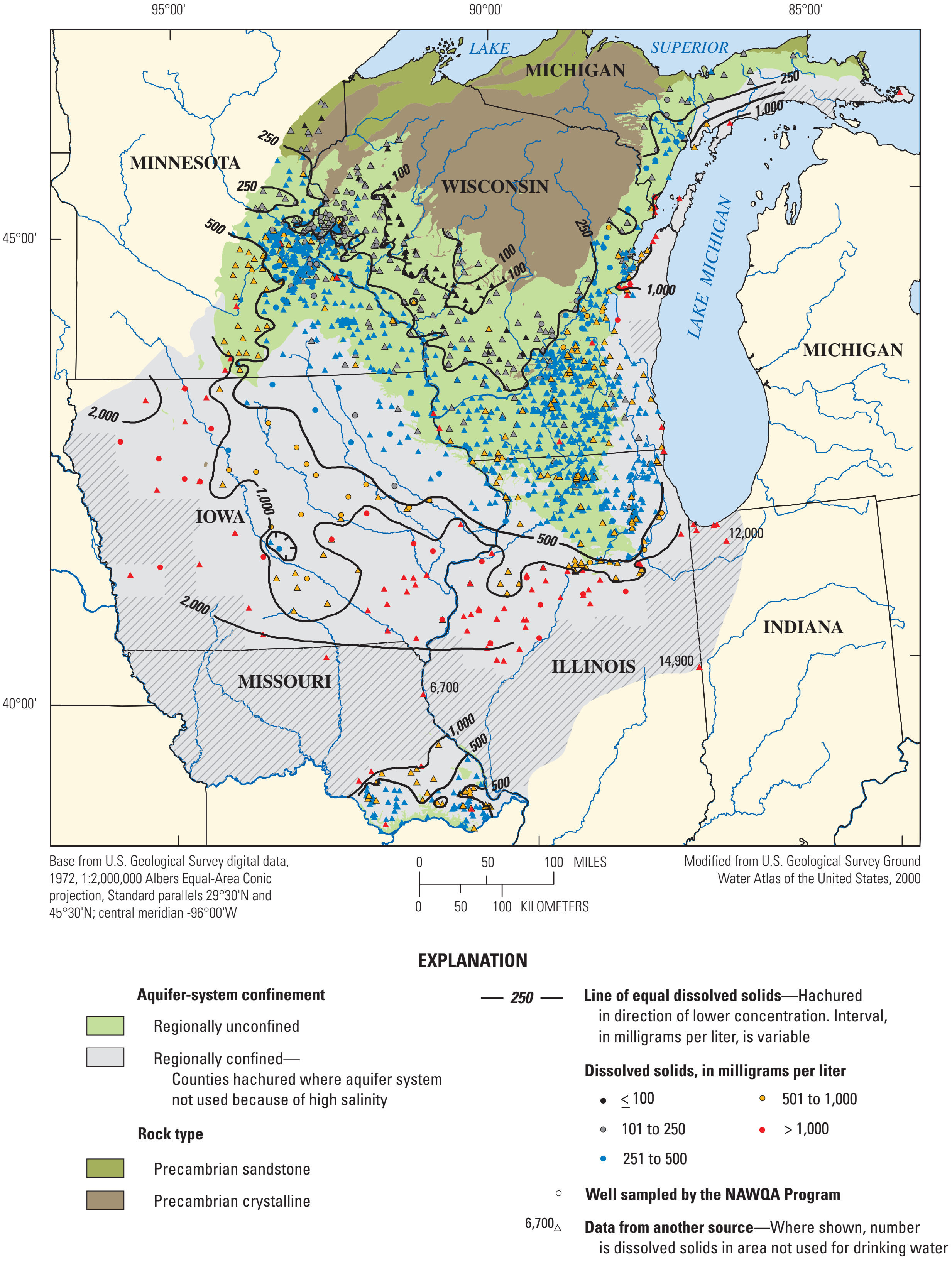
Property or major ion	Benchmark or guideline				Wells exceeding benchmarks or non-health guidelines			
	Human-health benchmark		Non-health guideline		Human-health benchmark		Non-health guideline	
	Value	Type	Value	Type	Count	Percent	Count	Percent
Physical properties								
pH (standard units)	--	--	[1]6.5–8.5	SDWR	--	--	0	0.00
Major ions (mg/L)								
Chloride	--	--	250	SDWR	--	--	7	4.54
Fluoride	4	MCL	2.0	SDWR	0	0.00	8	5.19
Sulfate	--	--	250	SDWR	--	--	26	16.9
Dissolved solids (ROE)	--	--	500	SDWR	--	--	45	29.2

[1] Guidelines recommend that pH values be within this range.

concentrations were greater than 500 mg/L near the western edge of the aquifer system, even though the Maquoketa Shale was absent. In northeastern Missouri, dissolved solids concentrations were greater than 250 mg/L for all the available data. Dissolved solids concentrations tend to increase to the north away from the roughly eight-county area in Missouri where the groundwater is fresh enough to use. In central Iowa, there is a large area that trends north-south (as shown by the 1,000-mg/L isoline) where dissolved solids concentrations are lower than in the surrounding area. This area of apparently fresher water was identified in maps produced by the RASA study (Siegel, 1989).

There are large areas of the aquifer system where the water is not used for most purposes because of high salinity (high dissolved solids content). These areas are roughly defined by the hachured areas with no wells in figure 19. These hachured areas are drawn at the county level and only for those counties where no wells are known to exist. Areas of high salinity include extreme western and southwestern Iowa, northern Missouri except for the freshwater area near the Missouri River, much of central Illinois, northwestern Indiana, one county in eastern Wisconsin, and one county in the Upper Peninsula (fig. 19). Values of dissolved solids are labeled for a few wells in these areas. The well in northern Missouri along the Mississippi River with a dissolved solids concentration of 6,700 mg/L is a test well from the RASA study. The well at the eastern edge of the aquifer system on the Illinois State line is an injection well, and the dissolved solids value of 14,900 is for the St. Peter Sandstone. The well in northwestern Indiana is also an injection well, and the dissolved solids value of 12,000 is also for water from the St. Peter Sandstone. Dissolved solids concentration tends to increase drastically with depth in areas where water from the aquifer system is not used for most purposes because of high salinity. For example, at the injection well on the Illinois-Indiana State line, dissolved solids was 14,900 mg/L in the St. Peter Sandstone at a depth of 2,620 ft. Dissolved solids concentration was 34,600 mg/L in the St. Lawrence Formation (Potosi Dolomite locally) at a depth of 3,933 ft; 112,000 mg/L in the Ironton-Galesville Sandstone at a depth of 4,166 ft; and 207,800 mg/L in the Mount Simon Sandstone at a depth of 5,425 ft (Illinois Environmental Protection Agency, written commun., 2007).

The hydrogen ion activity, or pH, is the effective concentration of hydrogen ions in a solution and is controlled by interrelated chemical reactions that produce or consume hydrogen ions (Hem, 1985). A measure of the acidity of water, pH is an important control on the solubility of many metals. The pH of most of the 154 NAWQA samples (80 percent) ranged from 6.95 to 7.61, and the median value was 7.32 (table 6). None of the NAWQA samples had a pH outside the SDWR guideline of 6.5 to 8.5 (table 8). Most significant Spearman rank correlations between pH and other properties and constituents were negative, with the largest values of rho for calcium, magnesium, and hardness (which is a measure of combined calcium and magnesium) (appendix 3). pH had positive correlations with silica, nitrate, and tritium. Values of pH were significantly higher ($p = 0.001$) in water samples from regionally unconfined wells (median = 7.36) than from confined wells (median = 7.22) (fig. 17*C*; table 7) and were significantly higher ($p = 0.011$) in samples determined to contain modern recharge (median = 7.38) than in samples determined to contain only pre-1953 recharge (median = 7.30) (fig. 18*C*). These results indicate that acid-generating reactions occur in regionally confined areas, perhaps including reactions such as sulfide oxidation, pyrite oxidation, iron precipitation, or increase in partial pressure of carbon dioxide gas (pCO_2) (Zoltan Szabo, U.S. Geological Survey, written commun., 2011).



Base from U.S. Geological Survey digital data, 1972, 1:2,000,000 Albers Equal-Area Conic projection, Standard parallels 29°30'N and 45°30'N; central meridian -96°00'W

Modified from U.S. Geological Survey Ground Water Atlas of the United States, 2000

Figure 19. Concentration of dissolved solids in water samples from wells completed in the Cambrian-Ordovician aquifer system, 1960–2008.

Alkalinity is a measure of the capacity of water—or more specifically, the solutes it contains—to react with and neutralize acid. Most natural waters contain substantial amounts of dissolved carbon dioxide species (bicarbonate, carbonate), which are the principal sources of alkalinity (Hem, 1985). Dissolved carbon dioxide is added to natural water from carbon dioxide in the atmosphere and from atmospheric and biogenic gases in the soil and unsaturated zones. Alkalinity in most of the 154 NAWQA samples (80 percent) ranged from 164 to 338 mg/L as calcium carbonate ($CaCO_3$), with a median of 262 mg/L as $CaCO_3$ (table 6). Alkalinity was significantly higher ($p = 0.029$) in water samples from regionally confined wells (median = 271 mg/L as $CaCO_3$) than water samples from regionally unconfined wells (median = 250 mg/L as $CaCO_3$) (fig. 17*D*; table 7). Alkalinity was also significantly higher ($p = 0.001$) in water samples determined to contain pre-1953 recharge (median = 274 mg/L as $CaCO_3$) than in samples determined to contain modern recharge (median = 239 mg/L as $CaCO_3$) (fig. 18*D*). The two outliers with low concentrations of alkalinity in the pre-1953 group correspond to NAWQA wells 132 and 147, mentioned previously, which have the two highest concentrations of sulfate in the NAWQA samples. Alkalinity can increase because of rock weathering (especially weathering of carbonates), but it can be consumed by reactions that create acidity, such as sulfide or pyrite oxidation.

Concentrations of dissolved oxygen ranged from less than 0.18 to 6.3 mg/L for most of the 152 NAWQA samples (80 percent), with a median concentration of 0.28 mg/L (table 6). This low median value of dissolved oxygen indicates that at least half of the wells have anoxic conditions according to the dissolved oxygen concentration threshold of 0.5 mg/L proposed by McMahon and Chapelle (2008). Dissolved oxygen originates in groundwater from recharge and by interaction with air in unsaturated material above the water table, allowing dissolved oxygen to get trapped in percolating water. This oxygen is depleted along a groundwater flow path with time and distance through reaction with oxidizable materials, primarily organic material and reduced minerals such as pyrite (FeS_2) and siderite ($FeCO_3$) (Hem, 1985), and to a lesser extent iron-bearing silicate minerals. Dissolved oxygen concentrations have a positive correlation with silica, nitrate, lead, zinc, and tritium (appendix 3). The remainder of the constituents, properties, or well characteristics in the matrix correlate negatively with dissolved oxygen concentrations, with the largest values of rho (−0.41 to −0.45) for fluoride, ammonia, iron, radium-226, and radium-228. The absence of any large values of rho is probably the result of there being so many nondetections of dissolved oxygen (32 percent). There was no significant difference ($p = 0.219$) between dissolved oxygen concentrations in water samples from regionally confined and unconfined wells (fig. 17*E*; table 7). The group of data for the unconfined wells had a large range and more high values; however, there was not much difference in the median values because of the large number of nondetections in both groups. Dissolved oxygen concentrations were significantly higher ($p < 0.001$) in water samples determined to contain modern recharge (median = 1.38 mg/L) than in samples determined to contain pre-1953 recharge (median = 0.21) (fig. 18*E*). This result is expected, given the lack of time for dissolved-oxygen-bearing young (modern) groundwater to be part of reactions that consume the dissolved oxygen along a flow path.

Temperature of most of the 154 water samples collected by NAWQA (80 percent) ranged from 9.6 to 19.5°C, with a median value of 11.8°C (53°F) (table 6). Field measurements of water temperature can be affected by the air temperature during sampling; however, if flow rates are sufficiently high, a good approximation of the actual groundwater temperature can be obtained. Water temperature had a positive correlation with several water-quality constituents, properties, or well characteristics in the correlation matrix, including well depth and casing depth (appendix 3). The largest positive values of Spearman's rho were for the trace elements boron (rho = 0.75), lithium (0.76), strontium (0.69), and radium-226 (0.65). Water temperature had a negative correlation with silica, nitrate, dissolved organic carbon, arsenic, barium, lead, radon-222, tritium, and dissolved oxygen. Water temperature was significantly higher ($p < 0.001$) in samples from wells in regionally confined areas (median = 16.5°C) than in samples from wells in unconfined areas (median = 10.4°C) (fig. 17*F*; table 7). This difference can be attributed to deeper wells in the regionally confined areas of the aquifer system than in the regionally unconfined areas and water temperatures being affected by the natural geothermal gradient in the deeper wells. Davis (1990) estimated the geothermal gradient to average 1.03°F (0.56°C) per 100 ft by using data from deep wells near the center of the Illinois basin. The median well depth in the confined area is 1,660 ft, and the median depth in the unconfined area is 235 ft. The contrast in well depths among the wells used to collect the NAWQA data also relates to well type; most wells in the confined area are deep public-supply wells, and most wells in the unconfined area are shallow private wells for domestic use. Water temperature is also significantly higher ($p < 0.001$) in samples determined to only contain pre-1953 recharge (median = 13.1°C) than in samples that contain modern recharge (median = 10.4°C) (fig. 18*F*), with older (pre-1953) water occurring in the generally deep wells in the confined area.

Redox Conditions

Reduction/oxidation (redox) processes affect the quality of groundwater in aquifers and play an important role in controlling chemical processes in groundwater, such as speciation of naturally occurring elements (arsenic, iron, sulfur, and uranium) and the transformation and biodegradation of anthropogenic compounds (nitrate, pesticides, and VOCs). Microbial activity typically drives redox reactions, which involve the transfer of electrons from one material to another. Microorganisms that drive redox processes in natural systems compete for limited resources and tend to favor redox processes that generate the maximum amount of available energy (McMahon and Chapelle, 2008). Dissolved and particulate organic carbon are often the most common electron donors available in groundwater systems (Thurman, 1985), although some reduced forms of nitrogen, iron, and sulfur could be important electron donors. Dissolved oxygen (O_2) is the preferred electron acceptor by subsurface microorganisms because it produces the most energy per mole of organic carbon oxidized than any other commonly available electron acceptor (McMahon and Chapelle, 2008). As dissolved oxygen is consumed along aquifer flow paths, the aquifer will become anoxic. Under anoxic conditions, the next most favorable naturally available electron acceptor is nitrate (NO_3^-), followed by manganese IV (Mn^{4+}), ferric iron (Fe^{3+}), sulfate (SO_4^{2-}), and carbon dioxide (CO_2). Some common anthropogenic contaminants in groundwater systems, such as chlorinated ethenes, may also act as electron acceptors (McMahon and Chapelle, 2008).

Redox status of 155 groundwater samples collected by the NAWQA Program was determined on the basis of threshold concentrations of dissolved oxygen, manganese, and iron (McMahon and Chapelle, 2008) by use of the spreadsheet developed by Jurgens and others (2009). Samples were grouped into three redox categories—oxic, mixed source, and anoxic (table 9). Sixty percent (93 of 155) of the wells had water samples with anoxic conditions, 26 percent of the wells had oxic conditions, and 14 percent of the wells had a mixed source. Anoxic conditions indicate that the predominant redox process is NO_3^- reduction, Mn^{4+} reduction, or Fe^{3+}/SO_4^{2-} reduction. Oxic conditions indicate that O_2 reduction is the predominant redox process, and mixed source conditions indicate that the criteria for more than one redox process were met (McMahon and Chapelle, 2008). Comparison of samples according to redox status and confinement category showed that most of the samples collected from regionally confined areas (40 of 53, or 75 percent) were designated as anoxic, and the remaining samples were designated as mixed source (19 percent) and oxic (6 percent). Fifty-two percent of samples collected from regionally unconfined areas (53 of 102) were designated as anoxic, 36 percent were designated as oxic, and 12 percent were designated as mixed source (fig. 20*A*). Comparison of samples according to redox status and tritium-based groundwater age showed that most of the samples representing recharge prior to 1953 (63 of 81, or 78 percent) were designated as anoxic, and the remaining samples were designated as mixed source (17 percent) and oxic (5 percent) (fig. 20*B*). Fifty-seven percent of samples representing modern recharge (32 of 56) were designated as oxic, and the remaining samples were designated as anoxic (34 percent) and mixed source (9 percent). The high percentage of samples designated as anoxic in the older water samples (pre-1953 recharge) is consistent with the assumption that oxygen is consumed over time.

Table 9. Threshold concentrations for identifying redox category.

[≥, greater than or equal to; <, less than; >, greater than; NA, no threshold applicable]

Redox-status category	Water-quality threshold (milligrams per liter) Dissolved oxygen	Manganese	Iron
Oxic	≥ 0.5	< 0.05	< 0.1
Mixed source	≥ 0.5	> 0.05	> 0.1
Anoxic	< 0.5	NA	NA

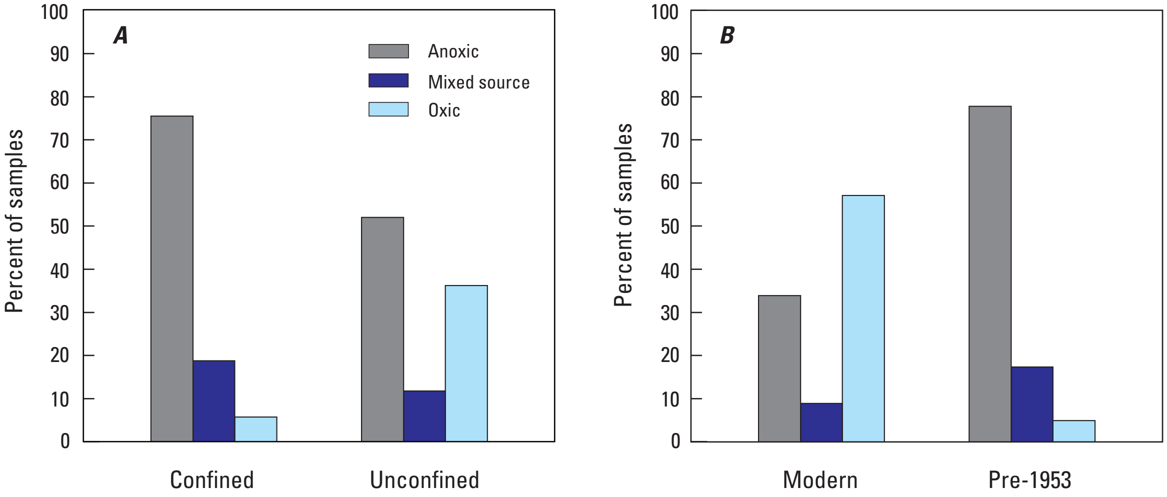


Figure 20. Redox status grouped by *A*, regional confinement category and *B*, tritium-based groundwater age for water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 1995–2007.

Major Ions

Major ions analyzed in water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program included calcium, magnesium, sodium, potassium, sulfate, chloride, fluoride, bromide, and silica. Bicarbonate, the most abundant anion, was determined from alkalinity titration and, if not reported, was calculated as alkalinity/0.8202 (Hem, 1985). Concentrations of major ions and hardness are plotted by regional confinement category in figure 21. Concentrations of all major ions and hardness were significantly higher ($p < 0.05$) in water samples from wells in the regionally confined area than wells from the unconfined area, except silica (SiO_2), which was significantly higher ($p < 0.001$) in the regionally unconfined area (table 7). Major-ion composition was used to classify water types by using a trilinear diagram and to map the hydrochemical facies. Saturation indices for calcite ($CaCO_3$) and dolomite [$CaMg(CO_3)_2$] were calculated to determine whether groundwater was in equilibrium with those minerals.

Major-ion samples collected by the NAWQA Program are filtered; therefore, the following discussions of major-ion concentrations refer to dissolved concentrations. Data from other sources are used to map the distribution of major-ion concentrations throughout the aquifer system. Other sources of USGS data (RASA Program and NWIS database) and data from the ISWS are also for filtered samples and represent dissolved concentrations, but major-ion data from all other state agencies are for unfiltered samples and represent whole-water or total concentrations. A primary source of major ions in groundwater is generally the interaction of water and rock or water and sediments derived from weathered rock. Table 10 lists the average composition of selected major ions and trace elements in sedimentary rocks common in the aquifer system (Horn and Adams, 1966; Lively and others, 1992).

Table 10. Average composition of some sedimentary rocks.

[Average composition is in parts per million; --, not available; <, less than]

Element	From Horn and Adams (1966)			From Lively and others (1992)	
	Shale	Sandstone	Carbonate	Mount Simon Sandstone[1]	Jordan Sandstone[2]
Arsenic	9	1	1.8	4.8	5.6
Barium	250	193	30	388	355
Boron	194	90	16	24	1.7
Bromide	4.3	1.0	6.6	--	--
Calcium	22,500	22,400	272,000	--	--
Chloride	170	15	305	--	--
Fluoride	560	220	112	--	--
Lithium	46	15	5.2	8.4	5.9
Magnesium	16,400	8,100	45,300	--	--
Manganese	575	392	842	--	--
Iron	38,800	18,600	8,190	--	--
Potassium	24,900	13,200	2,390	--	--
Silicon	260,000	359,000	34	--	--
Sodium	4,850	3,870	393	--	--
Strontium	290	28.2	617	105	56
Sulfur	1,850	945	4,550	--	--
Thorium	13	3.9	2	5.4	2.1
Uranium	4.5	1	2.2	1.6	< 2

[1] Average of 35 analyses of core samples from five wells in Minnesota; includes 2 samples from the overlying Eau Claire Formation.

[2] Average of 9 analyses of core samples from 3 wells in Minnesota.

Occurrence and Distribution

Calcium and magnesium are the two major ions that make up hardness, a property of water important to water users because hard water can require treatment with water softeners. Hardness is used to describe the effectiveness of soap in water and the tendency of water to form scale in boilers and pipes. Hardness is calculated by multiplying the sum of calcium and magnesium (in milliequivalents per liter) by 50 and is reported in terms of an equivalent concentration of $CaCO_3$ (Hem, 1985). Durfor and Becker (1964) developed a classification of hardness where 0–60 mg/L is considered “soft,” 61–120 mg/L is considered “moderately hard,” 121–180 mg/L is considered “hard,” and more than 180 mg/L is considered “very hard.” On the basis of this classification, all 154 NAWQA samples were hard or very hard (minimum of 128 mg/L) and more than 90 percent of the NAWQA samples were very hard (table 6). Hardness was positively correlated with most of the water-quality constituents, physical properties, and well characteristics in the correlation matrix, but it was negatively correlated with pH ($\rho = -0.61$), tritium (-0.28), and radon-222 (-0.17) (appendix 3). Hardness was significantly higher ($p = 0.001$) for water samples from the regionally confined area (median = 346 mg/L as $CaCO_3$) than for samples from the unconfined area (median = 289 mg/L as $CaCO_3$) (fig. 21). Data from other sources indicated an area of soft water in western Wisconsin in the same general area as the low-dissolved-solids wells shown in figure 19. Ordovician carbonate rocks are missing in this area, and the relatively low values of hardness probably indicate an absence of carbonates in the Cambrian strata.

Calcium was the most abundant cation, with a median concentration of 68.7 mg/L, followed by magnesium, with a median concentration of 30.2 mg/L (table 6). Calcium and magnesium concentrations showed a strong positive correlation with each other ($\rho = 0.79$) and separately with dissolved solids and bicarbonate (appendix 3). Bicarbonate was the most abundant anion, with a median concentration of 319 mg/L (table 6). Calcium, magnesium, and bicarbonate in groundwater occur primarily through the dissolution of the carbonate minerals calcite and dolomite and secondarily through dissolution of silicate minerals. Carbonate rocks are relatively abundant in the aquifer system, especially the Ordovician strata and in younger bedrock above the Maquoketa Shale where they have not been eroded away. Recharge from the glacial deposits also has relatively high concentrations of calcium, magnesium, and bicarbonate. Arnold and others (2008) reported median values of 86 mg/L, 33 mg/L, and 391 mg/L for calcium, magnesium, and bicarbonate, respectively, for glacial deposits in what they described as the Midwestern agricultural region that includes most of the study area for the Cambrian-Ordovician aquifer system.

Major-ion composition of the NAWQA samples is shown in a trilinear diagram that uses different symbols for the regional confinement and different colors for the sampling area (fig. 22). The most common water type was calcium magnesium bicarbonate, especially in the unconfined well networks in the Twin Cities metropolitan area and the eastern Wisconsin-Upper Peninsula area. The majority of these wells make up the clusters of green and magenta triangles between the calcium and magnesium endpoints and near the bicarbonate endpoint. The cation field at the bottom left shows the transition of cation dominance in Iowa and Illinois from calcium-magnesium in unconfined wells, to calcium-sodium, then to sodium-calcium in the confined wells (fig. 22). The two unconfined wells mentioned previously (wells 132 and 147) with the high concentrations of sulfate stand out in the anion field (bottom right) because they are low in bicarbonate and plot near the sulfate endpoint.

The geochemical model PHREEQCI was used to calculate the saturation state of the groundwater samples with respect to calcite and dolomite (fig. 23). The saturation index (SI) is a measure of whether water will tend to dissolve or precipitate a particular mineral. Its value is negative when the solution is undersaturated and the mineral may be dissolved, positive when the solution is supersaturated and the mineral may be precipitated, and zero when the water and mineral are in thermodynamic equilibrium. The SI is the log of the saturation ratio, which is calculated by comparing the chemical activities of the dissolved ions of the mineral (ion activity product, IAP) with the solubility product of the mineral (K_{sp}). In equation form, $SI = \log(IAP/K_{sp})$. When the two are equal, the sample is exactly at equilibrium with respect to the mineral, the ratio is exactly 1, and the log is zero. The SI can be used as an indicator of chemical stability and potential behavior of groundwater in wells where there may be concern over possible deposition of carbonate precipitates on well screens, gravel packs, and rock surfaces of open boreholes (Hem, 1985).

The saturation indices for calcite and dolomite in the NAWQA samples were positively correlated with pH (Spearman’s $\rho = 0.60$ for both). The saturation indices for calcite and dolomite were also positively correlated ($\rho = 0.94$, linear $R^2 = 0.91$). The calculated SI for calcite ranged from -0.33 to 0.19 for most samples (80 percent), with a median value of -0.03. The calcite SI for 71 percent of the samples was within ±0.2, which is a commonly used error band about the value of 0 for saturation equilibrium, though values as great as ±0.5 can be used. Of the remaining samples, 9 percent were supersaturated (greater than 0.2) and 20 percent were undersaturated (less than -0.2). There was no significant difference ($p = 0.28$) in the saturation index of calcite between samples from confined and unconfined areas, and there was no significant difference ($p = 0.51$) between samples representing modern and pre-1953 recharge.

The calculated SI for dolomite ranged from -0.89 to 0.18 for most samples (80 percent), with a median value of -0.23. The dolomite SI for 40 percent of the samples was within ±0.2. Of the remaining samples, 8 percent were supersaturated (greater than 0.2) and 52 percent were undersaturated (less than -0.2). There was no significant difference ($p = 0.94$) in the saturation index of dolomite between samples from confined and unconfined areas, and there was no significant difference ($p = 0.22$) between samples representing modern and pre-1953 recharge.

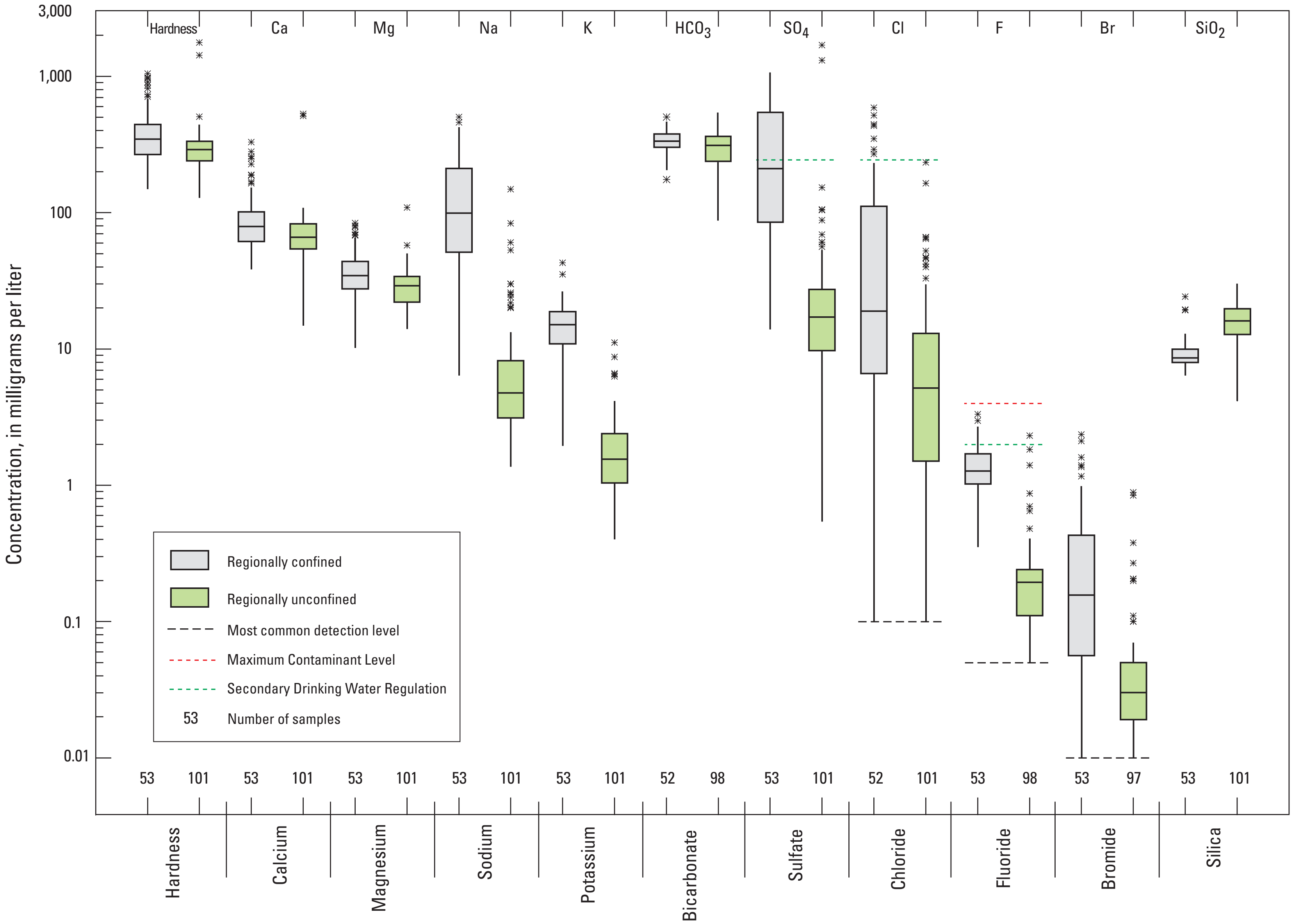


Figure 21. Distribution of major-ion concentrations and hardness by regional confinement for water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 1995–2007.

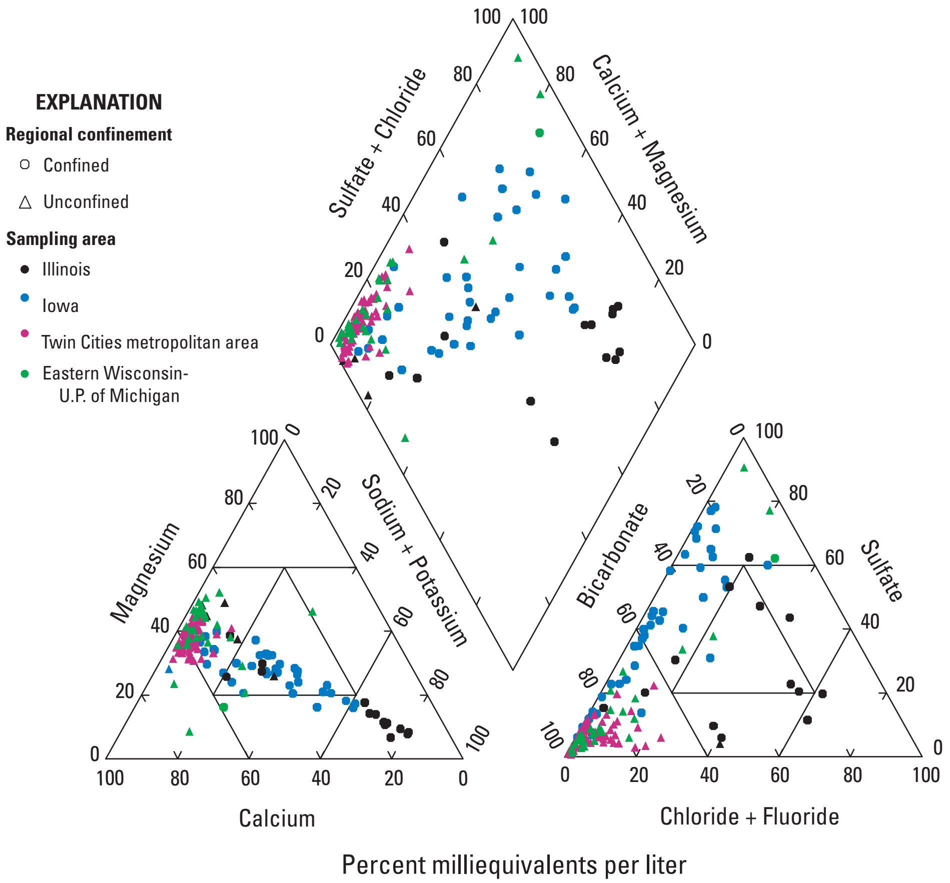


Figure 22. Major-ion composition of water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 1995–2007.

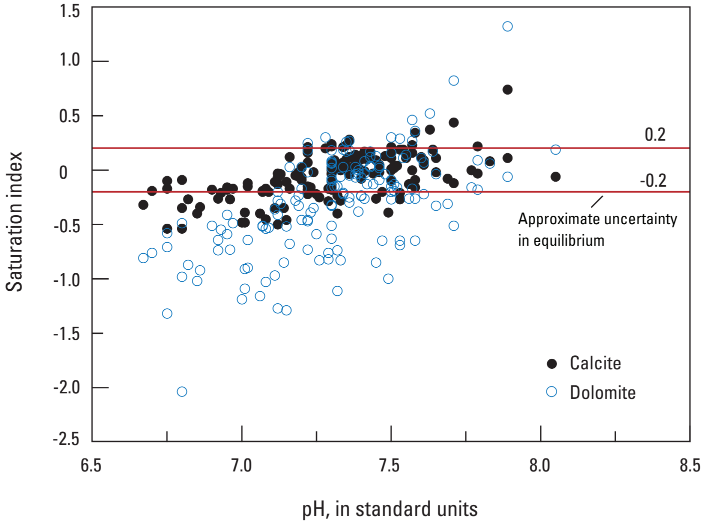


Figure 23. Relation of saturation indices for calcite and dolomite with pH for water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 1995–2007.

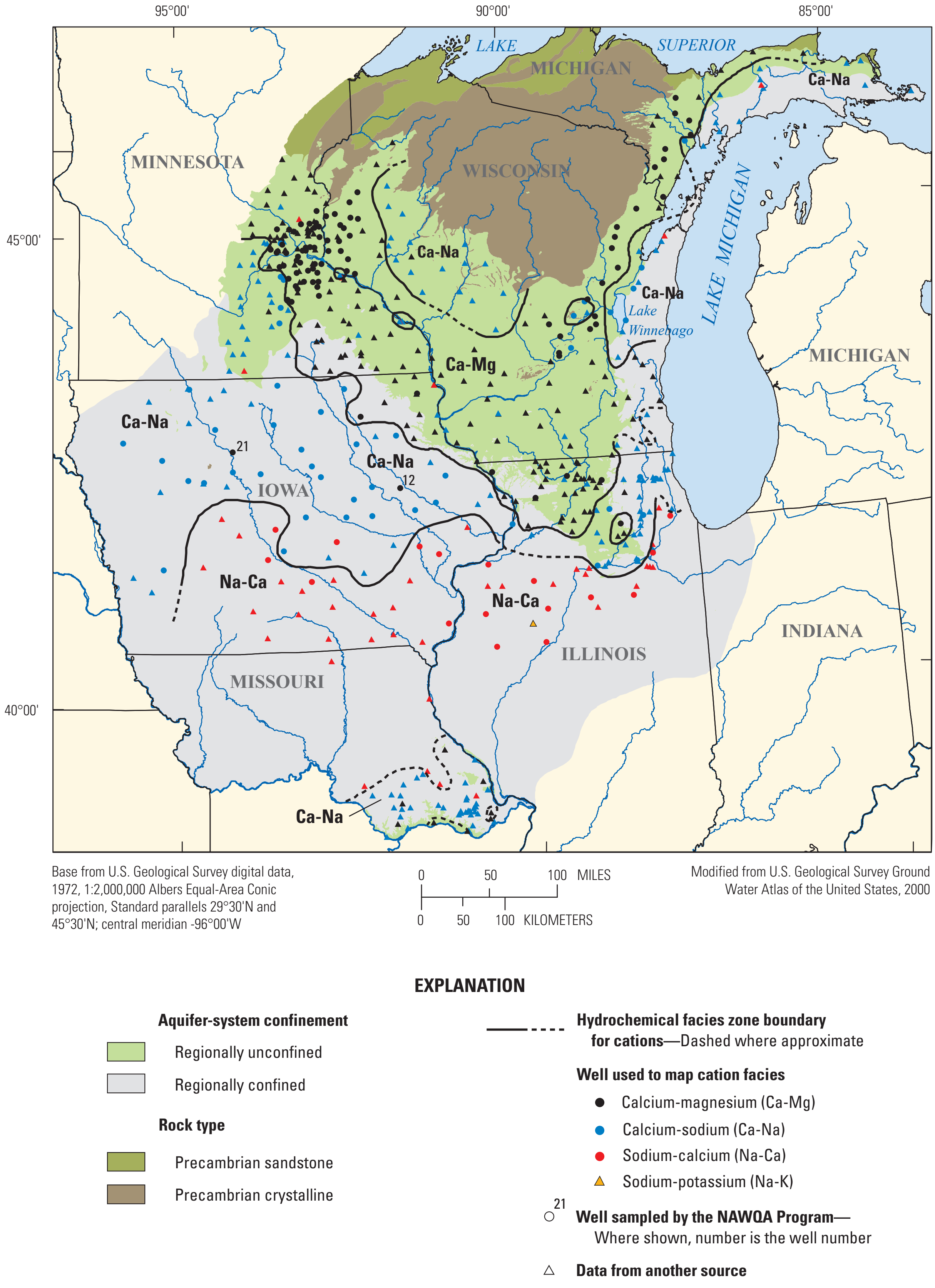
Major-ion chemistry data from 522 wells were used as control points to construct the hydrochemical facies maps that are a composite for all of the aquifers in the system. Hydrochemical facies can change with well depth, and isolated data points that differ from the regional facies may be due to a well producing water from a shallower or deeper aquifer than most of the wells in that area. The control points are color coded to show facies that do not match the regional trend but were too small to map. The cation facies map illustrates increased mineralization of the groundwater from the freshwater recharge in the northern unconfined areas to the deeply buried confined aquifers to the south and east. The calcium-magnesium facies occurs in most of the regionally unconfined area in Minnesota, Wisconsin, and the Upper Peninsula (fig. 24). The calcium-sodium facies occurs in a wide area of western Iowa and narrows towards Illinois, where it parallels the calcium-magnesium facies with the boundary near the southern limits of the unconfined area in Illinois. The calcium-sodium facies also occurs in a large area in eastern Wisconsin from south of Lake Winnebago to north of Green Bay, in the Upper Peninsula, and in western Wisconsin between the Mississippi River and the erosional edge of the Cambrian rocks. There are a few areas of calcium-magnesium facies within the calcium-sodium facies in northern Illinois and at two of the NAWQA wells in Iowa. The open intervals of these two wells in Iowa include Mississippian and Devonian rocks in well 21 and Silurian rocks in well 12 (fig. 24). The major-ion chemistry of samples from these wells is probably affected by water from the younger and shallower rocks. The sodium-calcium facies primarily occurs south of the calcium-sodium facies in a large area of southern Iowa, northern Missouri, and central Illinois. A lack of wells in northern Missouri and central Illinois makes it impossible to identify a southern limit to this facies or to identify whether there is any widespread occurrence of the sodium-potassium facies. Of the wells selected as control points for the hydrochemical facies maps, there was only one well in central Illinois with a cation facies of sodium-potassium (fig. 24). Cation facies in relation to concentrations of radon-222 and radium are discussed in the section on radionuclides.

The classification of anion data used for mapping resulted in nine anion facies, but the majority of the aquifer system was represented by four facies: bicarbonate, bicarbonate-sulfate, sulfate-bicarbonate, and mixed anion. The bicarbonate facies occurs in a large part of the unconfined area (fig. 25) in a pattern similar to the calcium-magnesium facies; this similarity is expected, because the most common water type in the unconfined area is calcium magnesium bicarbonate. The next anion facies on the gradient of increased mineralization is the bicarbonate-sulfate facies, which occurs in a large area of northeastern Iowa where the aquifer system is confined. This facies extends from Iowa into southern Minnesota, where it occurs in a large area near the western limit of the aquifer system. The bicarbonate-sulfate facies occurs in several other areas but at a more limited extent.

The sulfate-bicarbonate facies occurs in a large area of northwestern Iowa and a large area of south-central Iowa, with the two areas separated by an area of mixed anion facies (fig. 25). Siegel (1989) identified these areas of sulfate-bicarbonate facies and attributed this facies in northwestern Iowa to the dissolution of carbonates and the oxidation of pyrite in the overlying Dakota Formation (Cretaceous in fig. 9).

The mixed-anion facies is characterized by having no dominant anion. It occurs in much of southern Iowa, southeastern Iowa, and central Illinois, where it is usually associated with the sodium-calcium cation facies (fig. 25). The mixed-anion facies also occurs in several other areas but at a more limited extent, and it is usually associated with the calcium-sodium cation facies. A chloride-bicarbonate facies occurs downgradient from the mixed-anion facies in east-central Illinois and in the Upper Peninsula (fig. 25). A well along the Mississippi River in northeastern Missouri sampled by the RASA study was the only well (in the dataset used to map facies) found to intercept water with the chloride-sulfate facies (fig. 25). Siegel (1989) classified areas around this well and to the east in central Illinois as a sodium chloride cation-anion facies.

The cation facies map shows the increased proportion of sodium away from the unconfined areas. This enrichment of sodium is controlled by cation exchange, whereby divalent Ca^{2+} and Mg^{2+} ions are exchanged onto clay minerals, yielding two monovalent Na^{+} ions for each divalent ion (Appelo, 1994; Grundl, 2000). Most of the 154 NAWQA samples (80 percent) had a sodium concentration that was between 2.6 and 181 mg/L; median sodium concentration was 8.3 mg/L. However, there was a large contrast in the distribution of sodium between the confined and unconfined regions (fig. 21). Sodium concentrations were significantly higher ($p < 0.001$) in water samples from the confined area (median = 99 mg/L) than from the unconfined area (median = 4.7 mg/L). Sodium had a strong positive Spearman rank correlation with most water-quality constituents, properties, and characteristics that correlate with increased mineralization (appendix 3). The most notable negative Spearman rank correlation was with sodium and tritium (rho = −0.71). Potassium concentrations are much lower than sodium concentrations, but there is a strong correlation between the two (rho = 0.86, linear $R^2 = 0.80$). Potassium concentrations of most NAWQA samples (80 percent) ranged from 0.84 to 17.3 mg/L, with a median of 2.4 mg/L (table 6). Like sodium, there was a large contrast in the distribution of potassium between the confined and unconfined regions (fig. 21). Potassium concentrations were significantly higher ($p < 0.001$) in water samples from the confined area (median = 15.1 mg/L) than from the unconfined area (median = 1.6 mg/L). The ratio of sodium to potassium, using milliequivalents per liter, was also significantly higher ($p < 0.001$) in water samples from wells in the confined area (median = 10.8) than in samples from wells in the unconfined area (median = 5.68).



Base from U.S. Geological Survey digital data, 1972, 1:2,000,000 Albers Equal-Area Conic projection, Standard parallels 29°30'N and 45°30'N; central meridian -96°00'W

Modified from U.S. Geological Survey Ground Water Atlas of the United States, 2000

Figure 24. Hydrochemical facies for major cations in groundwater of the Cambrian-Ordovician aquifer system.

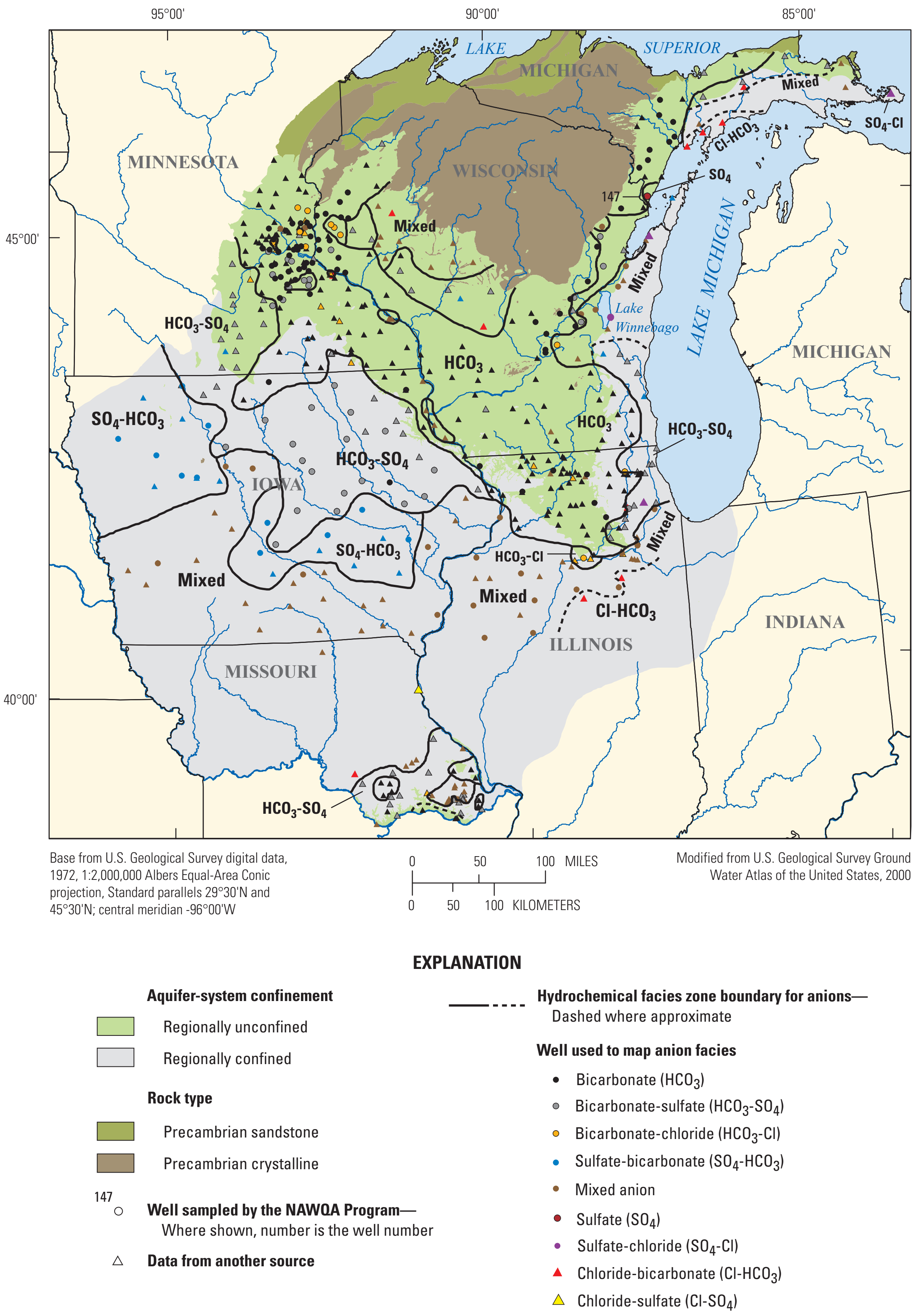


Figure 25 Hydrochemical facies for major anions in groundwater of the Cambrian-Ordovician aquifer system.

The median concentration of sulfate in the NAWQA samples was 26.2 mg/L, but there was a large range—from 7.5 to 540 mg/L—for most of the samples (80 percent), with a maximum concentration of 1,697 mg/L (table 6). There was a large contrast in the distribution of sulfate between the confined and unconfined regions (fig. 21). Sulfate concentrations were significantly higher ($p < 0.001$) in water samples from wells in the confined area (median = 210 mg/L) than from wells in the unconfined area (median = 17.1 mg/L). Sulfate had strong positive correlations with dissolved solids (rho = 0.84), specific conductance (rho = 0.83), radium-226 (0.73), and well depth (0.65) (appendix 3). Sulfate also had strong positive correlations with several major ions (sodium, potassium, fluoride, bromide) and trace elements (boron, lithium, strontium) (appendix 3). Sulfate had negative correlations with tritium (rho = −0.59), silica (−0.44), radon-222 (−0.40), pH (−0.39), lead, barium, dissolved organic carbon (DOC), nitrate, and zinc. Sources of sulfate in groundwater are the dissolution of sulfate minerals (gypsum, anhydrite, and celestite), the oxidation of sulfide-bearing minerals such as pyrite (FeS_2), fertilizer application, atmospheric deposition, degradation of sulfur-rich organic matter, and other sources. Sulfate in groundwater can be reduced to sulfide by anaerobic bacteria, and one product, hydrogen sulfide (H_2S), produces the characteristic "rotten-egg" odor.

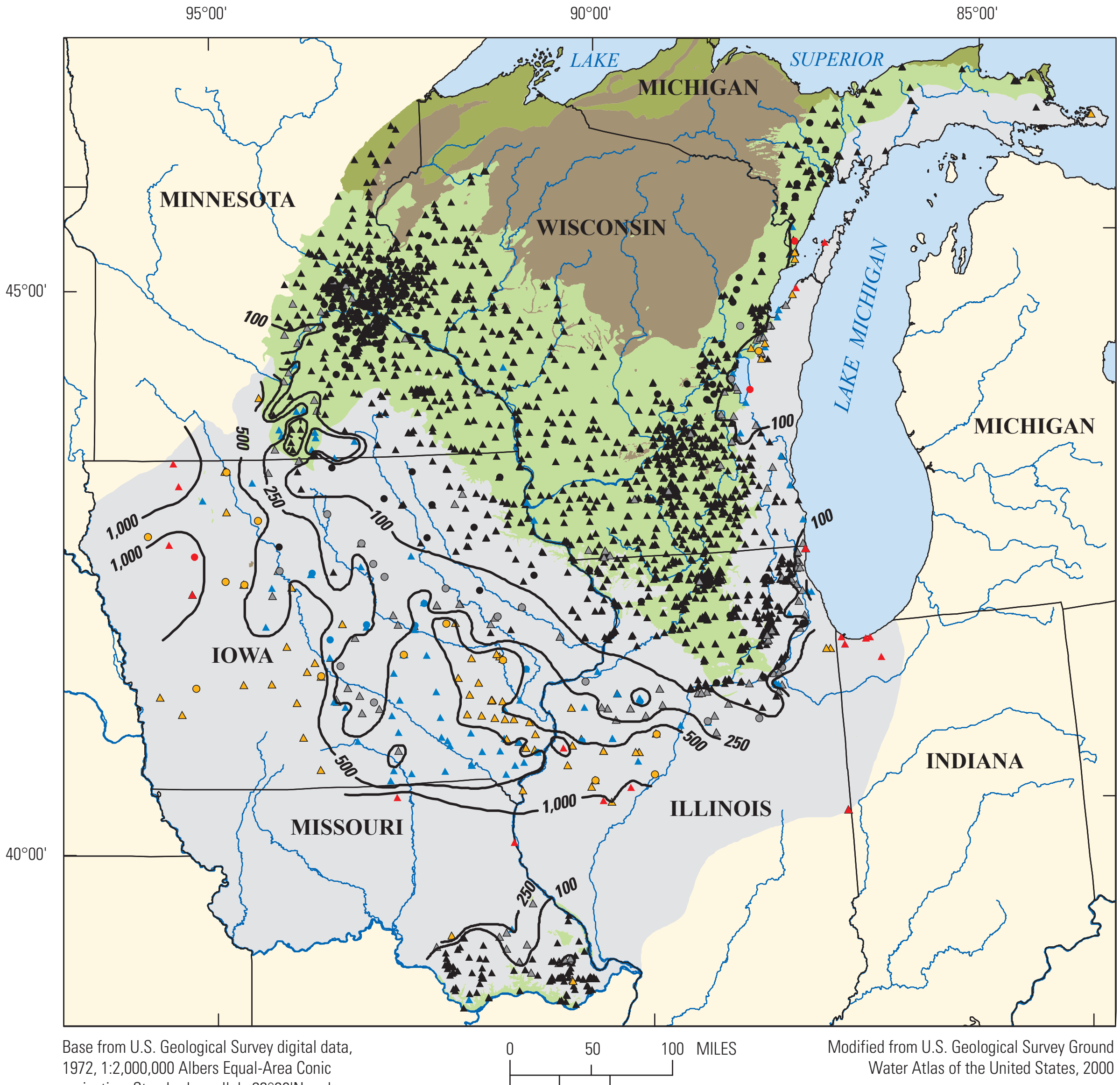
Sulfate concentrations exceeded the USEPA SDWR of 250 mg/L in 16.9 percent of the 154 wells sampled by NAWQA (table 8). Noticeable effects of sulfate concentrations greater than the SDWR are salty taste and a laxative effect in some people (U.S. Environmental Protection Agency, 1992). All but three of the NAWQA wells with sulfate concentrations that exceeded the SDWR of 250 mg/L are in Iowa or western Illinois, at least 30 mi southwest of the boundary between regionally confined and unconfined areas of the aquifer system. The other three wells with such high sulfate concentrations are along the boundary of regional confinement in eastern Wisconsin and the southern end of the Upper Peninsula. Data from other sources (tables 3 and 4) were combined with the NAWQA data to map the concentration of sulfate in the Cambrian-Ordovician aquifer system (fig. 26). The overwhelming majority (88 percent) of wells in the unconfined area have sulfate concentrations below 50 mg/L. Most of the wells that exceeded the SDWR of 250 mg/L are in the confined areas of western Illinois and Iowa. There are also several wells in southern Minnesota that exceed the SDWR, some of which are in the regionally unconfined area but are probably confined by some formation other than the Maquoketa Shale. High sulfate concentrations in northwestern Iowa and southern Minnesota are related to the oxidation of pyrite in the overlying Dakota Formation (Cretaceous in fig. 9) and in the glacial drift derived from the Dakota (Siegel, 1989). Another source of sulfate may be clayey confining units that release sulfate to the aquifer system (leakance), as proposed for the Cretaceous Dakota aquifer itself by Bredehoeft and others (1983).

Saturation indices for sulfate minerals as a function of dissolved (filtered) sulfate concentrations in water samples collected by NAWQA are shown in figure 27. Barite ($BaSO_4$) is the only sulfate mineral that is nearly saturated or is supersaturated in several samples, suggesting barite saturation in the water is a geochemical condition that is common in the aquifer system. Barite is considered one likely control on radium concentrations in the water through the co-precipitation of radium with barite (Gilkeson and others, 1983; Grundl and Cape, 2006). In northeastern Illinois, extremely high concentrations of barium and high values of barite supersaturation are known to occur. Barite is even known to precipitate in wells, causing pump failures and increased maintenance costs (Gilkeson and others, 1983). The sample with a barite saturation index of just above 2.0 (very high, considering saturation point is equal to 0) comes from a confined well in this area with a barium concentration of 11,080 µg/L. Normally, barite precipitation prevents barium concentrations from reaching such extremely high concentrations, but sulfate reduction can remove the sulfate needed for barite to precipitate (Gilkeson and others, 1983).

The NAWQA samples are undersaturated with respect to the other common sulfate minerals shown, gypsum ($CaSO_4 \cdot 2H_2O$), anhydrite ($CaSO_4$), and celestite ($SrSO_4$), which are primarily evaporite-deposit minerals. Saturation indices for all four of the sulfate minerals shown in figure 27 were significantly higher ($p < 0.05$) in samples from regionally confined wells than from unconfined wells.

Gypsum, anhydrite, and celestite are not known to exist as primary deposits in Cambrian or Ordovician rocks of the northern Midwest (Gilkeson and others, 1981) though they do occur in Jurassic, Mississippian, and Devonian strata of Iowa, where gypsum has been quarried for building materials since the 1850s (McKay, 2010). The two water samples with the highest concentrations of sulfate are from wells in the eastern Wisconsin-Upper Peninsula area and are at equilibrium with respect to barite, gypsum, and celestite. These two samples contain relatively little barium but have high concentrations of calcium and strontium. The high values of calcium and sulfate in this area are thought to be from the dissolution of secondary gypsum and anhydrite grains in the aquifer. These secondary minerals are thought to have been emplaced by the dissolution, transport, and re-precipitation of sulfate-rich saline water from Silurian evaporite deposits from the Michigan basin that moved updip into the aquifer when Lake Michigan was covered with glaciers (Gilkeson and others, 1981; Siegel, 1990; Winter and others, 1995). It is also thought that deep basin fluids migrated updip out of the Michigan basin over geologic time, carrying with them evaporite minerals that now occur as secondary minerals in the aquifer (Winter and others, 1995).

Chloride concentrations in most wells sampled by NAWQA ranged from 0.7 to 110 mg/L, with a median value of 7.1 mg/L (table 6). There was a large contrast in the distribution of chloride between the confined and unconfined



Base from U.S. Geological Survey digital data, 1972, 1:2,000,000 Albers Equal-Area Conic projection, Standard parallels 29°30'N and 45°30'N; central meridian -96°00'W

Modified from U.S. Geological Survey Ground Water Atlas of the United States, 2000

EXPLANATION

Aquifer-system confinement

🟩 Regionally unconfined

⬜ Regionally confined

Rock type

🟩 Precambrian sandstone

🟫 Precambrian crystalline

— 250 — Line of equal sulfate concentration— Hachured in direction of lower concentration. Interval, in milligrams per liter, is variable

Sulfate, in milligrams per liter

- ● ≤ 100
- ● 101 to 250
- 🔵 251 to 500
- 🟠 501 to 1,000
- 🔴 > 1,000

○ **Well sampled by the NAWQA Program**

△ **Data from another source**

Figure 26. Sulfate concentrations in water samples from wells completed in the Cambrian-Ordovician aquifer system, 1960–2008.

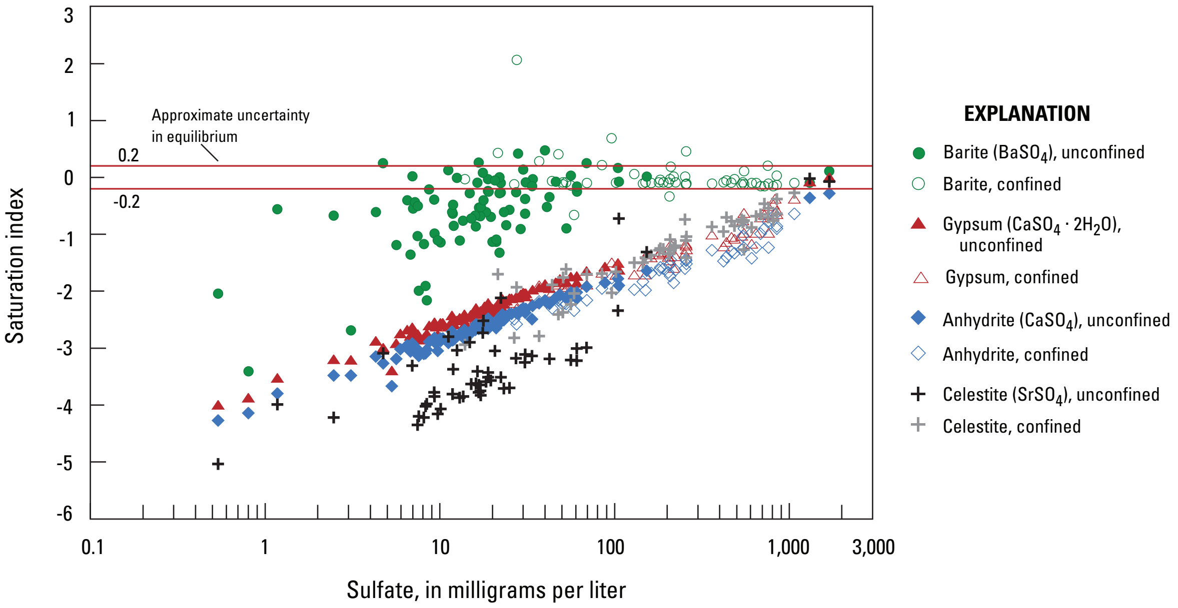
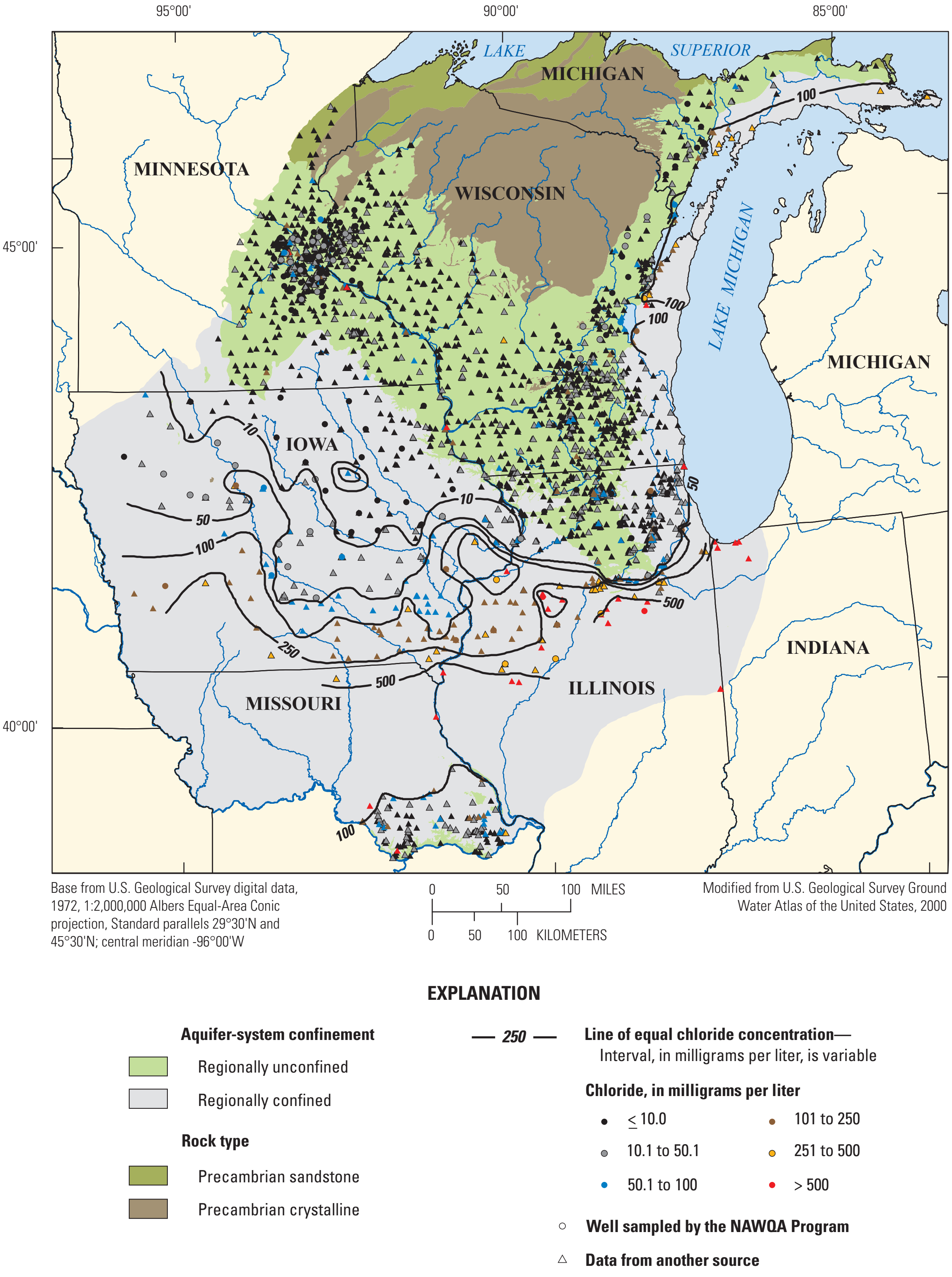


Figure 27. Saturation indices for selected sulfate minerals as a function of sulfate concentration in samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 1995–2007.

regions (fig. 21). Chloride concentrations were significantly higher ($p < 0.001$) in water samples from the confined area (median = 18.9 mg/L) than from the unconfined area (median = 5.2 mg/L). Chloride had strong positive correlations with dissolved solids (rho = 0.63), bromide (0.63), sodium (0.59), and several major ions and trace elements (appendix 3). Chloride had negative correlations with silica, DOC, barium, manganese, radon-222, and tritium, but none of the negative correlations had a large value of Spearman's rho. Sources of chloride in groundwater are (1) the dissolution of chloride-containing minerals in sedimentary rocks or (2) chloride that was retained from the inclusion of connate brine deposited with the marine sediments as sodium chloride crystals or as a solution of sodium and chloride ions (Hem, 1985). Another possible source of chloride is upconing of deep brine as a response to pumping stress in the aquifer system, or from the clayey confining units. Other sources of chloride in modern (post-1953) groundwater can come from anthropogenic sources such as highway deicers, landfill leachate, wastewater effluent, and agricultural sources. Wet deposition is not a major source of chloride in the study area. Mullaney and others (2009) estimated the average concentration of chloride in runoff attributable to wet deposition to be less than 0.5 mg/L for the northern Midwest.

Chloride concentrations exceeded the USEPA SDWR of 250 mg/L in 4.5 percent of the 154 wells sampled by NAWQA (table 8). A noticeable effect of chloride concentration greater than the SDWR is salty taste (U.S. Environmental Protection Agency, 1992). Data from other sources (tables 3 and 4) were combined with the NAWQA data to map the concentration of chloride in the Cambrian-Ordovician aquifer system (fig. 28). The majority of wells in the unconfined area (94 percent) have chloride concentrations below 50 mg/L, and many of those wells (74 percent) have chloride concentrations below 10 mg/L. Most of the wells that exceed the SDWR are in the confined area of central Illinois and extreme southern Iowa. A few wells along the southern boundary of the aquifer system in Missouri also exceed the SDWR. In the eastern part of the study area, a few wells exceed the SDWR in the confined areas of eastern Wisconsin and the Upper Peninsula (fig. 28).

Fluoride concentrations ranged from 0.1 to 1.7 mg/L in most (80 percent) of the wells sampled by NAWQA, with a median value of 0.24 mg/L (table 6). Low concentrations of fluoride in drinking water can prevent tooth decay (as opposed to no fluoride), and public drinking-water systems often add fluoride to their water supplies for this purpose. However, high concentrations in drinking water can cause tooth discoloration or mottled teeth in children, and drinking water for many years with concentrations greater than the MCL may cause bone disease in some people (U.S. Environmental Protection Agency, 2009b). Recommended optimal fluoride concentrations for public water supply systems vary by average maximum daily air temperature, and range from 0.7 mg/L (at 79.3 to 90.5°F) to 1.2 mg/L (at 50.0 to 53.7°F) (U.S. Centers for Disease Control, 1995). Twenty-five percent of the NAWQA samples exceeded this upper limit of 1.2 mg/L (table 6).



Base from U.S. Geological Survey digital data, 1972, 1:2,000,000 Albers Equal-Area Conic projection, Standard parallels 29°30'N and 45°30'N; central meridian -96°00'W

Modified from U.S. Geological Survey Ground Water Atlas of the United States, 2000

EXPLANATION

Aquifer-system confinement

🟩 Regionally unconfined

⬜ Regionally confined

Rock type

🟩 Precambrian sandstone

🟫 Precambrian crystalline

— 250 — **Line of equal chloride concentration**—Interval, in milligrams per liter, is variable

Chloride, in milligrams per liter

● ≤ 10.0	● 101 to 250
● 10.1 to 50.1	● 251 to 500
● 50.1 to 100	● > 500

○ **Well sampled by the NAWQA Program**

△ **Data from another source**

Figure 28. Chloride concentrations in water samples from wells completed in the Cambrian-Ordovician aquifer system, 1960–2008.

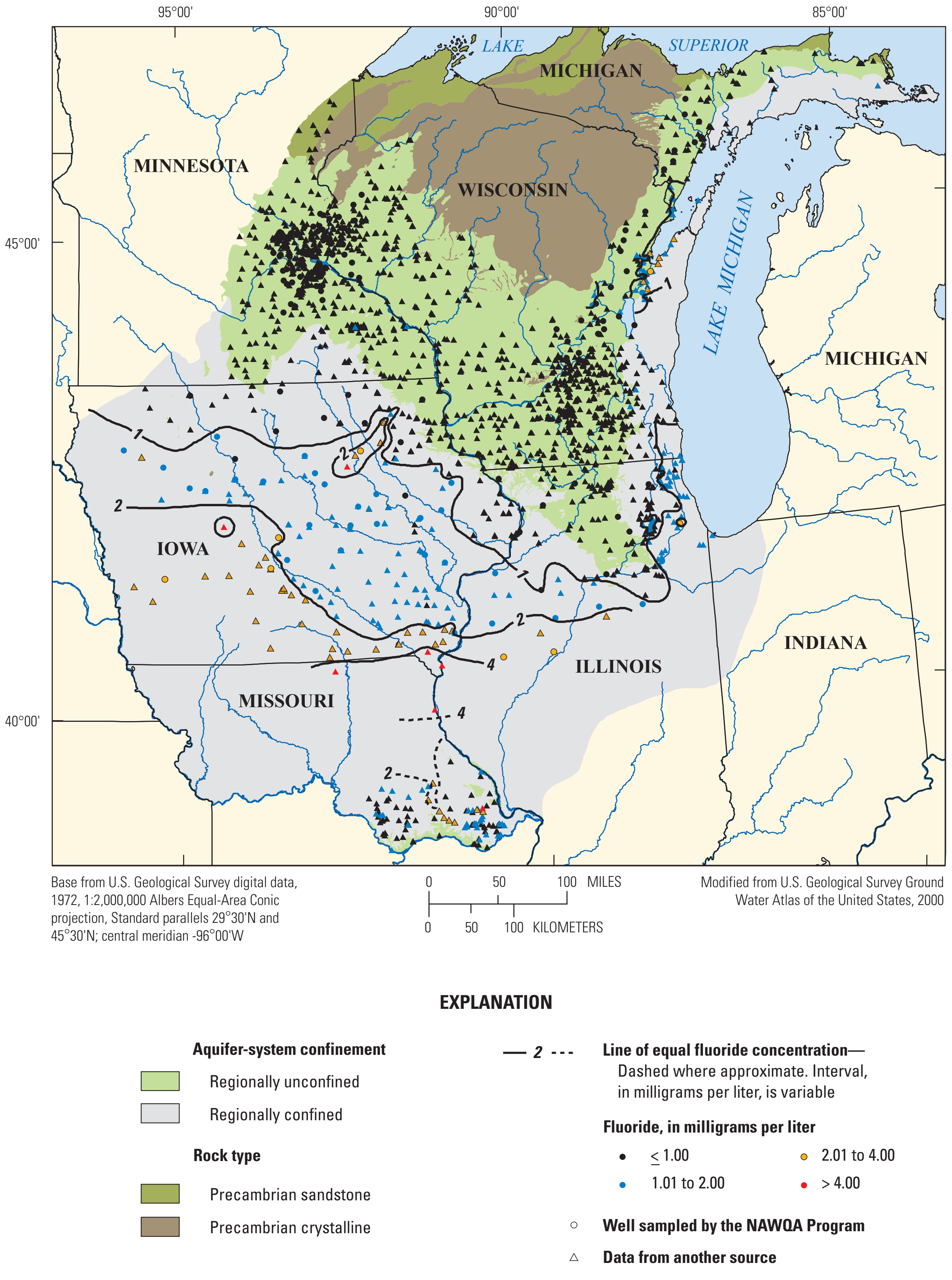
The U.S. Department of Health and Human Services has recently proposed a recommended fluoride concentration of 0.7 mg/L for all public water-supply systems (U.S. Department of Health and Human Services, 2011). Fluoride concentrations were greater than 0.7 mg/L in 30 percent of the wells sampled by NAWQA. Fluoride in groundwater can originate from the dissolution of fluoride-containing minerals in various rock types. Of the sedimentary rocks that occur in the aquifer system, fluoride should be more abundant in shale than in sandstone or carbonates (table 10). Although fluoride has a relatively small range of concentrations in the NAWQA samples, it appears to be a good indicator for older (pre-1953), more mineralized groundwater, as shown by the large contrast in the distribution of fluoride concentrations between the confined and unconfined regions (fig. 21). Fluoride concentrations were significantly higher ($p < 0.001$) in water samples from the confined area (median = 1.27 mg/L) than from the unconfined area (median = 0.19 mg/L). Fluoride has strong positive correlations (large values of Spearman's rho) with most major ions, trace elements, water temperature, and well depth (appendix 3). Fluoride has strong negative correlations with tritium (rho = −0.72), nitrate (−0.55), silica (−0.53), radon-222 (−0.47), and dissolved oxygen (−0.41). The USEPA MCL for fluoride is 4 mg/L, and the SDWR for fluoride is 2 mg/L. None of the NAWQA samples had a fluoride concentration that exceeded the MCL; the maximum concentration was 3.32 mg/L. However, 5.2 percent of the 154 NAWQA samples exceeded the SDWR of 2 mg/L (table 8).

Data from other sources (tables 3 and 4) were combined with NAWQA data to map concentrations of fluoride in water samples from wells completed in the Cambrian-Ordovician aquifer system. The majority of wells in the unconfined area (97 percent) had fluoride concentrations below 1 mg/L, whereas 50 percent of the wells in the confined area had fluoride concentrations greater than 1 mg/L (fig. 29). Most of the wells that exceeded the SDWR of 2 mg/L were in the confined area of southern and western Iowa, at the southern limits of water use from the aquifer in Illinois, and in Missouri. In northeastern Iowa, a cluster of wells had fluoride concentrations greater than 2 mg/L, and one well had a concentration of 8.7 mg/L. However, this well was an exploration well completed in the Mount Simon Sandstone and was not a source of drinking water. There were also a few wells in eastern Wisconsin at the southern end of Green Bay where fluoride concentrations exceeded the SDWR (fig. 29).

Bromide is similar in chemical behavior to chloride but is much less abundant. Bromide concentrations ranged from 0.01 to 0.43 mg/L for most of the NAWQA samples, with a median value of 0.04 mg/L (table 6). As with most of the major ions, bromide concentrations were significantly higher ($p < 0.001$) in the confined areas (median = 0.16 mg/L) than in the unconfined areas (median = 0.03 mg/L). Concentrations of bromide were positively correlated with dissolved solids (rho = 0.72) and several of the major ions and trace elements that indicate the presence of older water and reducing conditions (appendix 3). Concentrations of bromide were negatively correlated with those constituents that indicate the presence of younger, more oxic water, such as tritium, nitrate, and dissolved oxygen.

Chloride:bromide ratios (Cl:Br ratios) have been used to identify the sources of chloride in groundwater (Whittemore, 1988; Davis and others, 1998; Thomas, 2000; Jagucki and Darner, 2001; Panno and others, 2006; Mullaney and others, 2009). The method is based on understanding chloride concentrations and Cl:Br ratios of different chloride sources and the resulting chloride concentrations and Cl:Br ratios when different sources are mixed. Binary mixing curves were calculated by using the mixing equation of Whittemore (1988), which was summarized and applied by Jagucki and Darner (2001). The end-member value for dilute groundwater was based on the two samples with the lowest chloride concentration (0.1 mg/L) and their average bromide concentration (0.014 mg/L). Nitrate was not detected in these samples, and they had a tritium-based age of pre-1953, which indicates that the samples from these wells were probably not affected by anthropogenic activities. The Cl:Br ratio of precipitation in the Midwest is on the order of 47 (Panno and others, 2006). End-member values of chloride concentration and Cl:Br ratio for halite (deicing salt), sewage or animal waste, and potassium chloride fertilizer were those used by Mullaney and others (2009, table 4) in their study of chloride in the glacial aquifer system. The end-member values of chloride concentration (65,000 mg/L) and Cl:Br ratio (330) for basin brines were average values for 19 saline formation water samples from the Illinois basin (Graf and others, 1966).

Samples from unconfined wells tend to plot between the mixing curves for dilute groundwater-sewage or animal waste, dilute groundwater-potassium chloride fertilizer, and dilute groundwater-halite used for deicing (fig. 30). The unconfined wells are shallower than the confined wells and are more susceptible to anthropogenic sources of contamination. Samples from confined wells tend to plot near the mixing curve for dilute groundwater-basin brines. Seven samples from unconfined wells also plot near the mixing curve for dilute groundwater-basin brines. Four of these wells are from the eastern Wisconsin-Upper Peninsula sampling area near the subcrop of the Maquoketa Shale. These wells are in an area where it is thought that sulfate-rich saline water from Silurian evaporite deposits from the Michigan basin moved updip into the aquifer when Lake Michigan was covered with glaciers (Gilkeson and others, 1981; Siegel, 1990; Winter and others, 1995). Of the remaining three unconfined wells that plot near the basin brine curve, two are public-supply wells from the Twin Cities metropolitan area, and one is a public-supply well in north-central Illinois. Samples that do not fall on or near a mixing line may indicate that there are more than two sources of chloride. In addition, actual mixtures of groundwater are probably not mixtures of full-strength end-members and may be diluted with precipitation or dilute groundwater. The shaded area representing the approximate range for dilute groundwater is somewhat subjective; the one shown in figure 30 is from Jagucki and Darner (2001).



Base from U.S. Geological Survey digital data, 1972, 1:2,000,000 Albers Equal-Area Conic projection, Standard parallels 29°30'N and 45°30'N; central meridian -96°00'W

Modified from U.S. Geological Survey Ground Water Atlas of the United States, 2000

Figure 29. Fluoride concentrations in water samples from wells completed in the Cambrian-Ordovician aquifer system, 1960–2008.

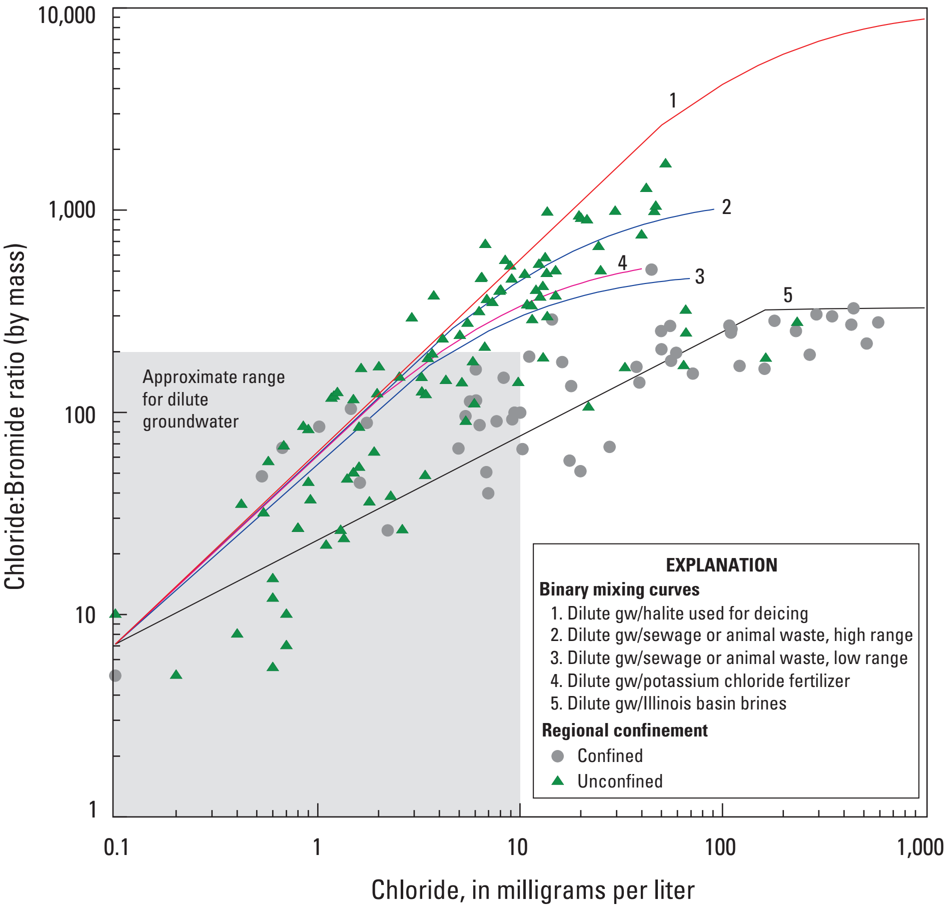


Figure 30. Relation of chloride:bromide ratios (by mass) to chloride concentrations, with binary mixing curves representing sources of chloride, for samples collected from the Cambrian-Ordovician aquifer system by the NAWQA Program, 1995–2007.

Silica is the only major constituent with concentrations significantly higher ($p < 0.001$) in samples from wells in the regionally unconfined area of the aquifer system (median = 16.0 mg/L) than from the confined area (median = 8.6 mg/L) (fig. 21). Silica concentrations in most of the NAWQA samples range from 7.5 to 22.9 mg/L, with a median value of 12.9 mg/L (table 6). Concentrations of silica are positively correlated with tritium (rho = 0.63), nitrate (0.54), radon-222 (0.52), and some other constituents at smaller values of Spearman's rho (appendix 3). Concentrations of silica are negatively correlated with well depth (rho = −0.62), potassium (−0.60), radium-228 (−0.59), and several other constituents that indicate the presence of older, more mineralized water such as sodium, sulfate, fluoride, strontium, and radium-226. Silicon (Si) is second only to oxygen in abundance in the Earth's crust, and the average composition in some sedimentary rocks is listed in table 10. Crystalline silica (SiO_2) as quartz is a major constituent of many igneous rocks, and it makes up the grains in most sandstones. Quartz is resistant to chemical attack by water, and the direct precipitation of quartz is unlikely to control solubility of silica in most natural waters at normal temperatures (Hem, 1985). Most dissolved silica in natural water probably results originally from the chemical breakdown of silicate minerals (feldspars, micas) during weathering processes (Hem, 1985). Dissolved silica in the pH range of the NAWQA samples (6.67 to 8.05) is dominated by the silicic acid H_4SiO_4 (aqueous species).

Temporal Variability of Major Ions

The NAWQA Program and the RASA Program both sampled six public-supply wells in Iowa, with a 25-year time gap between samples. These data allowed for an analysis of the temporal variability of major-ion concentrations with a relatively large time gap between samples (table 11). Although

Table 11. Difference in major-ion concentrations in water samples collected from six Cambrian-Ordovician wells in Iowa by the RASA Program in 1980–81 and the NAWQA Program in 2005 or 2007.

[mg/L, milligrams per liter; P-value, for Wilcoxon signed-rank test of difference between paired samples collected from six individual wells during the first and second sampling event (values in bold indicate statistical significance)]

Constituent	Mean value					P-value
	RASA samples (mg/L)	NAWQA samples (mg/L)	Absolute difference (mg/L)	Percent difference	Relative standard deviation (percent)	
Bicarbonate	317.7	303.4	27.9	9.22	6.52	0.312
Calcium	109.0	109.6	2.48	3.39	2.40	0.562
Chloride	21.5	20.3	1.36	21.8	15.4	0.094
Fluoride	1.20	1.20	0.04	6.25	4.42	0.752
Hardness	416.0	426.6	12.3	3.52	2.49	0.062
Magnesium	35.0	37.2	2.23	6.42	4.54	**0.031**
Potassium	17.8	17.6	0.50	3.93	2.78	0.844
Silica	8.25	8.72	0.49	5.46	3.86	0.094
Sodium	76.6	71.6	5.00	5.57	3.94	**0.031**
Sulfate	305.8	299.0	9.61	5.11	3.61	0.219
Dissolved solids	741.7	749.2	14.2	2.71	1.92	0.312

this is a small sample size, the data suggest that major ion concentrations have not changed much during the 25 years of pumping. Only one constituent, chloride, had a mean percent difference and mean relative standard deviation in concentrations between sample dates that exceeded 10 percent. For most constituents, there was no significant difference ($p > 0.05$) in concentrations between the RASA samples and NAWQA samples when treated as pairs using the Wilcoxon signed-rank test. There were significant differences in magnesium ($p = 0.031$) and sodium ($p = 0.031$) concentrations—magnesium concentrations were greater in NAWQA samples than in RASA samples and sodium concentrations were greater in RASA samples than in NAWQA samples. However, given the small sample size of six, these tests may not be that conclusive. Even though magnesium and sodium were determined to have significant differences between the RASA and NAWQA samples, the mean relative standard deviations were only 4.54 percent for magnesium and 3.94 percent for sodium.

Trace Elements

Trace elements include metals and semi-metallic elements that typically occur in natural waters at concentrations less than 1 mg/L, even though they may be abundant in the Earth's crust. Trace elements analyzed in water samples collected for the NAWQA Program are listed in table 12. These elements occur in groundwater primarily from rock weathering and water-rock interactions in the aquifer. Hem (1985) points out that chemical properties can be more important in controlling concentrations of an element in water than the element's availability in the environment. Under natural conditions, trace elements are relatively immobile in the minerals and other secondary oxide phases that make up rocks and soils (Jenne, 1968), and therefore they occur at low concentrations or are undetectable in groundwater. Under specific geochemical conditions, or when human activities such as mining and waste disposal change the groundwater geochemical environment, some of these elements dissolve more readily, causing increased concentrations in groundwater. Industrial uses of large quantities of some trace elements have increased the availability of these elements to occur in natural water (Hem, 1985). Groschen and others (2009, table 1) tabulated the common uses of many of the trace elements. At high concentrations, many trace elements can have adverse health effects or aesthetic effects; therefore, many of the trace elements have human-health benchmarks and/or SDWRs (table 13).

Trace-element samples collected by the NAWQA Program are filtered; therefore, the following discussions of trace-element concentrations of NAWQA samples refer to dissolved concentrations. Data from other sources are used to map the distribution of trace-element concentrations throughout the aquifer system. Other sources of USGS data (RASA Program and NWIS database) and data from the ISWS are also for filtered samples and represent dissolved concentrations, but trace-element data from all other state agencies are for unfiltered samples and represent whole-water or total concentrations.

Table 12. Summary statistics for trace elements in samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 1996–2007.

[µg/L, micrograms per liter; <, less than]

No assessment level										Assessment level of 1 µg/L		
Trace element	Number of samples	Number of detections	Frequency of detections (percent)	Concentration percentile (µg/L)					Maximum concentration (µg/L)	Number of samples	Number of detections	Frequency of detections, in percent
				10th	25th	Median	75th	90th				
Aluminum	130	38	29.2	0.40	0.64	1.02	1.89	3.00	8.57	130	34	26.2
Antimony	137	12	8.76	<1	<1	<1	<1	<1	.19	137	0	.00
Arsenic	137	85	62.0	.02	.06	.16	.42	1.18	9.99	137	15	11.0
Barium	136	136	100	9.50	13.7	25.4	66.4	144	11,080	136	136	100
Beryllium	137	11	8.03	<1	<1	<1	<1	<1	.06	137	0	.00
Boron	106	106	100	8.40	12.2	160	686	1,208	1,895	106	106	100
Cadmium	137	14	10.2	<1	<1	<1	<1	<1	.60	137	0	.00
Chromium	136	58	42.6	.01	.05	.15	1.26	5.00	7.00	136	37	27.2
Cobalt	137	101	73.7	.02	.03	.09	.22	.54	30.2	137	7	5.11
Copper	130	85	65.4	.10	.25	.92	3.00	12.9	52.8	130	63	48.5
Iron	144	128	88.9	4.68	22.7	186	633	1,077	4,300	144	[1]128	88.9
Lead	137	52	38.0	.01	.02	.04	.15	.43	2.00	137	4	2.92
Lithium	108	107	99.1	1.20	3.08	11.6	90.8	173	650	108	102	94.4
Manganese	154	142	92.2	.34	1.99	9.88	46.5	191	1,040	154	110	71.4
Molybdenum	137	110	80.3	.11	.24	.44	1.00	1.86	8.57	137	40	29.2
Nickel	137	132	96.4	.13	.37	1.41	3.11	6.46	32.9	137	81	59.1
Selenium	137	61	44.5	.02	.04	.12	.37	.75	16.3	137	8	5.84
Silver	137	1	.73	<1	<1	<1	<1	<1	.10	137	0	.00
Strontium	107	107	100	53.0	85.2	645	2,356	3,703	12,340	107	107	100
Thallium	108	43	39.8	<1	<1	<1	<1	<1	.64	108	0	.00
Uranium	137	114	83.2	.04	.15	.35	.72	1.72	6.45	137	23	16.8
Vanadium	108	85	78.7	.02	.05	.21	.69	2.38	7.87	108	23	21.3
Zinc	135	128	94.8	1.53	3.01	8.00	32.8	113	659	135	124	91.8

[1] Assessment level for iron is 3 µg/L.

Table 13. Comparison of trace elements analyzed in samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 1996–2007, with human-health benchmarks and non-health guidelines for drinking water.

[SDWRs are Secondary Drinking Water Regulations that are non-enforceable Federal guidelines regarding cosmetic or aesthetic effects of drinking water; MCLs are U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Levels for public water supplies; HBSLs are Health-Based Screening Levels developed by the U.S. Geological Survey using USEPA toxicity data and methods (Toccalino and Norman, 2006); --, not applicable. Action level is a concentration which, if exceeded, triggers treatment or other requirements in USEPA regulations for public water supplies. All benchmarks and guidelines are in micrograms per liter.]

Trace Element	Benchmark or guideline				Wells exceeding benchmarks or non-health guidelines			
	Human-health benchmark		Non-health guideline		Human-health benchmark		Non-health guideline	
	Value	Type	Value	Type	Count	Percent	Count	Percent
Aluminum	--	--	50 to 200	SDWR	--	--	0	0.00
Antimony	6	MCL	--	--	0	0.00	--	--
Arsenic	10	MCL	--	--	0	0.00	--	--
Barium	2,000	MCL	--	--	1	0.74	--	--
Beryllium	4	MCL	--	--	0	0.00	--	--
Boron	1,000	HBSL	--	--	15	14.2	--	--
Cadmium	5	MCL	--	--	0	0.00	--	--
Chromium	100	MCL	--	--	0	0.00	--	--
Copper	1,300	Action level	1,000	SDWR	0	0.00	0	0.00
Iron	--	--	300	SDWR	--	--	59	41.0
Lead	15	Action level	--	--	0	0.00	--	--
Manganese	300	HBSL	50	SDWR	7	4.5	37	24.0
Molybdenum	40	HBSL	--	--	0	0.00	--	--
Nickel	100	HBSL	--	--	0	0.00	--	--
Selenium	50	MCL	--	--	0	0.00	--	--
Silver	100	HBSL	100	SDWR	0	0.00	0	0.00
Strontium	4,000	HBSL	--	--	10	9.34	--	--
Thallium	2	MCL	--	--	0	0.00	--	--
Uranium	30	MCL	--	--	0	0.00	--	--
Zinc	2,000	HBSL	5,000	SDWR	0	0.00	0	0.00

Occurrence and Distribution

Summary statistics for trace elements analyzed in NAWQA samples are listed in table 12. Sample dates for the most recent sample at each well range from 1996 to 2007. The number of samples varies because some of the trace elements (boron, lithium, strontium, thallium, and vanadium) were not analyzed for well networks sampled in 1996 in the Twin Cities metropolitan area (fig. 3). When all detections were counted (no assessment level), frequency of detections ranged from 0.73 percent (1 detection) for silver to 100 percent for barium, boron, and strontium (table 12). Antimony, beryllium, cadmium, silver, and thallium were not detected at the assessment level of 1 µg/L. Maximum concentrations of the following trace elements did not exceed 10 µg/L: aluminum, arsenic, chromium, lead, molybdenum, uranium, and vanadium. Maximum concentrations of barium, boron, iron, lithium, manganese, strontium, and zinc all exceeded 500 µg/L.

Concentrations of most trace elements were less than available human-health benchmarks for drinking water. Sixteen of the trace elements have an MCL or HBSL, but only barium, boron, manganese, and strontium were measured at concentrations that exceeded their benchmark in at least one of the NAWQA samples (table 13). Concentrations of iron exceeded the SDWR in 41 percent of 144 NAWQA samples, and manganese exceeded the SDWR in 24 percent of 154 NAWQA samples.

Arsenic was detected in 62 percent (85 of 137) of the NAWQA samples, but only in 11 percent of the samples at an assessment level of 1 µg/L (table 12). The maximum concentration detected was 9.99 µg/L, which is just below the USEPA MCL of 10 µg/L (fig. 31). Arsenic concentrations were positively correlated with concentrations of molybdenum (rho = 0.56), silica (0.42), manganese (0.36), uranium (0.35), tritium (0.31), radon-222 (0.27), zinc, and iron (appendix 3). Arsenic concentrations were negatively correlated with casing depth (rho = −0.29), well depth (−0.28), potassium (−0.26), boron, fluoride, and water temperature. The maximum concentration of 9.99 µg/L was detected in a private well in the Upper Peninsula (NAWQA well 148) just across the State line from Wisconsin. Figure 31 shows the distribution of concentrations for selected trace elements by regional confinement. Any portion of a boxplot that is below the assessment level of 1 µg/L should be considered as estimated because these data may include numerous nondetections. The median arsenic concentration appears to be significantly higher in the unconfined wells than the confined wells. However, this may not be accurate because several samples collected from unconfined wells in 1996 had nondetections at a detection level of 1 µg/L. Detection levels used in the more recent sampling of the well networks in the confined area were at least an order of magnitude lower than 1 µg/L. However, most (13 of 15) of the detections greater than 1 µg/L were from wells in the regionally unconfined area (fig. 31).

Nondetections of arsenic at detection levels greater than 0.1 µg/L were removed from the NAWQA dataset to test whether concentrations were significantly different in samples when grouped by regional confinement and tritium-based groundwater age. This resulted in a dataset of 111 samples, 52 from regionally confined wells and 59 from regionally unconfined wells. Of these samples, 108 had a tritium-based age; 40 samples contained modern recharge and 68 samples contained only pre-1953 recharge. Arsenic concentrations were indeed significantly higher ($p < 0.001$) in samples from regionally unconfined wells (median = 0.20 µg/L) than from regionally confined wells (median = 0.12 µg/L) (table 7). Arsenic concentrations were significantly higher ($p < 0.001$) in samples with modern recharge (median = 0.38 µg/L) than in samples with only pre-1953 recharge (median = 0.12 µg/L). Samples from unconfined wells were more likely to have dissolved oxygen concentrations greater than 1 mg/L than samples from confined wells (fig. 32). There was no significant difference in arsenic concentrations for this dataset when grouped by redox condition (oxic, mixed source, anoxic). However, the greatest concentrations of arsenic were in samples from unconfined wells with suboxic (< 1 mg/L) conditions. Most of the samples from confined wells were clustered in the suboxic area, with arsenic concentrations less than 1 µg/L (fig. 32).

Data from other sources (tables 3 and 4) were combined with the NAWQA data to evaluate the distribution of arsenic in the Cambrian-Ordovician aquifer system. Of the available data, 2 percent (16) of the samples exceeded the MCL of 10 µg/L, all but 1 were in the regionally unconfined area, and 75 percent of the wells were in Minnesota. In the Upper Peninsula, the Michigan DEQ measured an arsenic concentration of 21 µg/L for a private well close to NAWQA well 148, where 9.99 µg/L was measured (fig. 33). There were three wells that exceeded the MCL in Wisconsin, but there was no pattern to their location; one well was in northeastern Wisconsin, one was in southeastern Wisconsin, and one was in northwestern Wisconsin. In Minnesota, there was a cluster of six wells that exceeded the MCL in the northwestern half of Hennepin County (refer to fig. 3 for location) west of the confluence of the Minnesota and Mississippi Rivers. High arsenic concentrations in the regionally unconfined area of Minnesota may be associated with the overlying Des Moines glacial lobe (Erickson and Barnes, 2005). The extent of the Des Moines glacial lobe shown in figure 33 is from Schumann (1993). Arsenic samples from wells in Minnesota that exceeded the MCL came from the following aquifers: Galena Dolomite, St. Peter Sandstone, Prairie du Chien Formation, Jordan Sandstone, and Franconia Formation. In sedimentary rock, arsenic is usually more abundant in shale than sandstone or carbonates (table 10). Data from Lively and others (1992) suggest that the Mount Simon and Jordan Sandstones in Minnesota are enriched in arsenic compared to the average composition of sandstone as reported by Horn and Adams (1966) (table 10).

Barium was detected in all 136 NAWQA samples; concentrations ranged from 9.5 to 144 µg/L for most of the samples (80 percent; 10th through 90th percentiles), with a median concentration of 25.4 µg/L (table 12). Barium is an alkaline-earth metal whose average composition is higher in shale and sandstone than in carbonates (table 10). Likely controls on the concentration of barium in natural water are the solubility of barite ($BaSO_4$) (see fig. 27), which is a fairly common mineral, and the adsorption of barium by metal oxides and hydroxides (Hem, 1985). Barium concentrations were significantly higher ($p = 0.015$) in samples from the unconfined area than from the confined area (fig. 31; table 7). However, the maximum concentration of 11,080 µg/L was from the confined area in northeastern Illinois (well 58 in figs. 2 and 34) where sulfate reduction is known to cause extremely high values of barium (Gilkeson and others, 1981, 1983). This was the only NAWQA sample to exceed the USEPA MCL of 2,000 µg/L (table 13). Barium concentrations were positively correlated with concentrations of dissolved organic carbon (rho = 0.37) and bicarbonate (0.32) (appendix 3). All other significant correlations in the matrix were negative, and the strongest correlations for barium concentrations were with concentrations of sulfate and chloride (rho = −0.37 for both), lithium (−0.33), and bromide (−0.29). When barium concentrations were grouped by cation facies (Ca-Mg, Ca-NA, and Na-Ca) there was a significant difference in barium concentrations ($p < 0.05$) between samples with a Ca-Mg facies (median = 37.4 µg/L) and samples with a Na-Ca facies (median = 13.9 µg/L). Barium concentrations were not significantly different between samples with the Ca-Mg and Ca-Na facies and between samples with the Ca-Na and Na-Ca facies (at the 0.05 significance level). Higher concentrations of barium associated with the Ca-Mg facies compared to the Na-Ca facies are consistent with higher concentrations occurring in samples from wells in regionally unconfined areas.

Data from other sources (table 3 and 4) were combined with the NAWQA data to evaluate the distribution of barium in the Cambrian-Ordovician aquifer system. Of the available data, 2 percent (15) of the samples exceeded the MCL of 2,000 µg/L. All of the wells exceeding the MCL were in

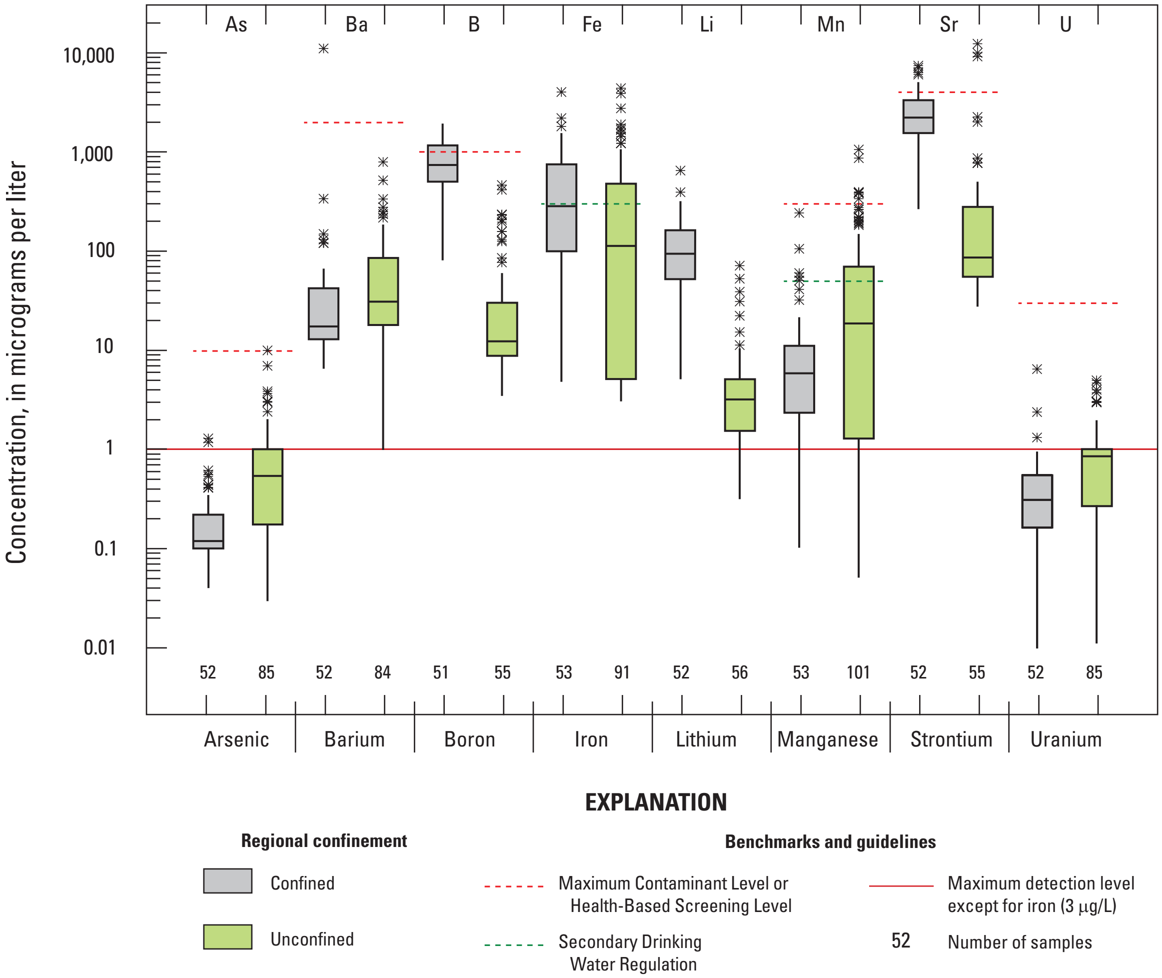


Figure 31. Distribution of selected trace-element concentrations by regional confinement for water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 1995–2007.

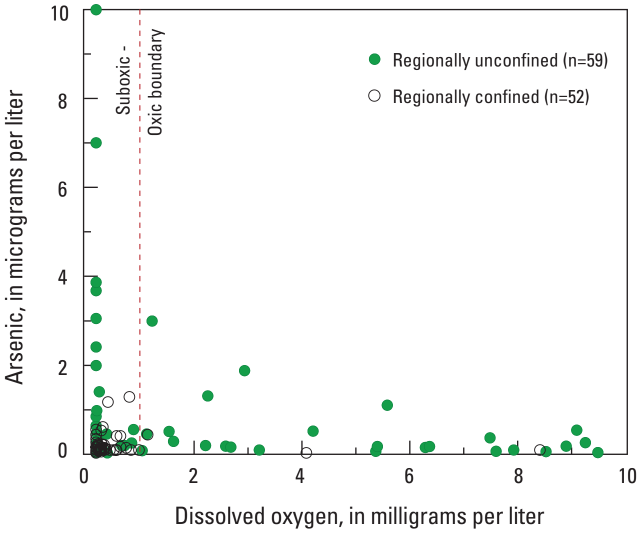
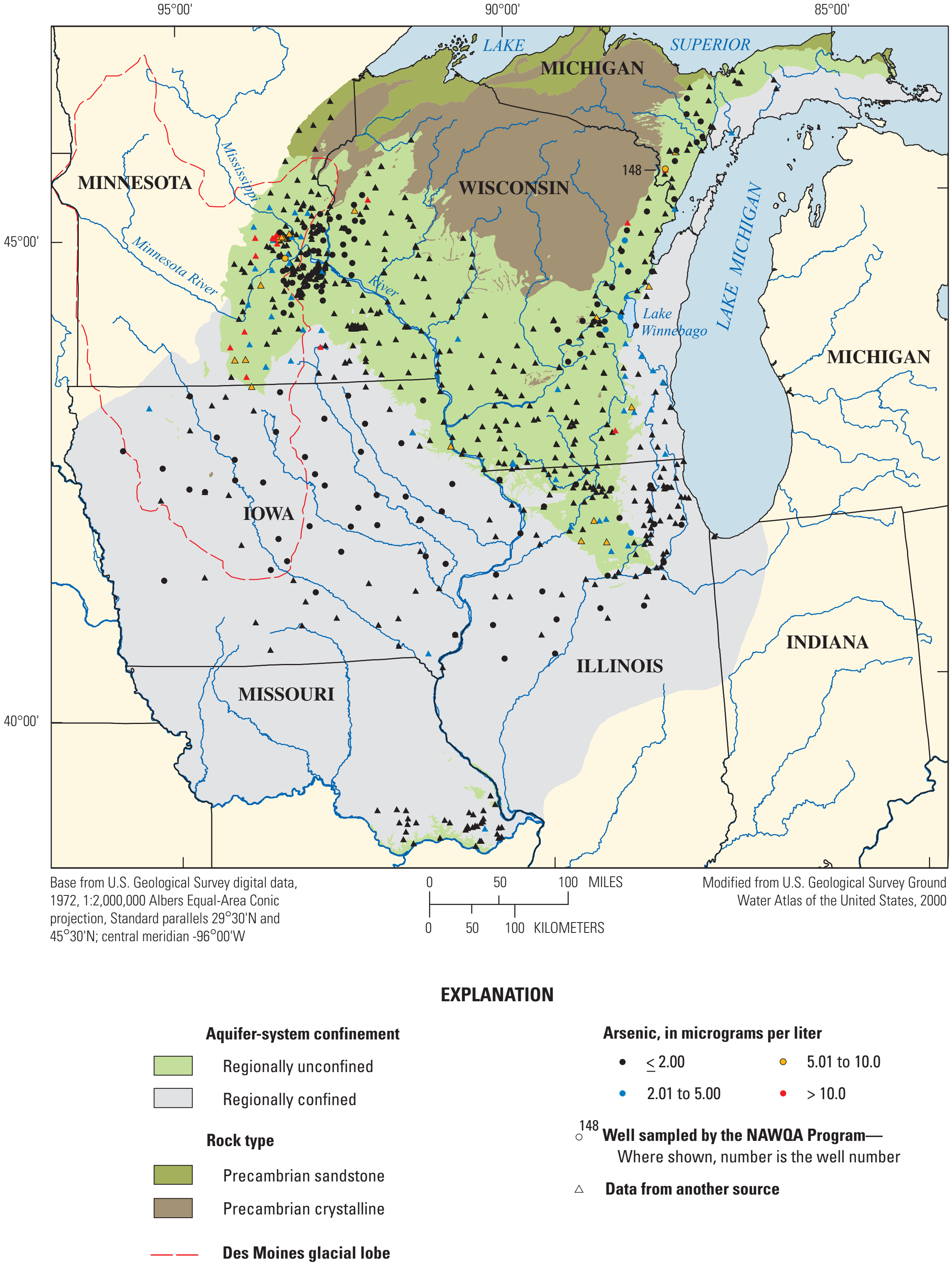


Figure 32. Relation of arsenic concentration to dissolved oxygen concentration for water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 1996–2007. (Nondetections of arsenic at detection levels greater than 0.1 microgram per liter are not included.)



Base from U.S. Geological Survey digital data, 1972, 1:2,000,000 Albers Equal-Area Conic projection, Standard parallels 29°30'N and 45°30'N; central meridian -96°00'W

Modified from U.S. Geological Survey Ground Water Atlas of the United States, 2000

Figure 33. Arsenic concentrations in water samples from wells completed in the Cambrian-Ordovician aquifer system, 1973–2008.

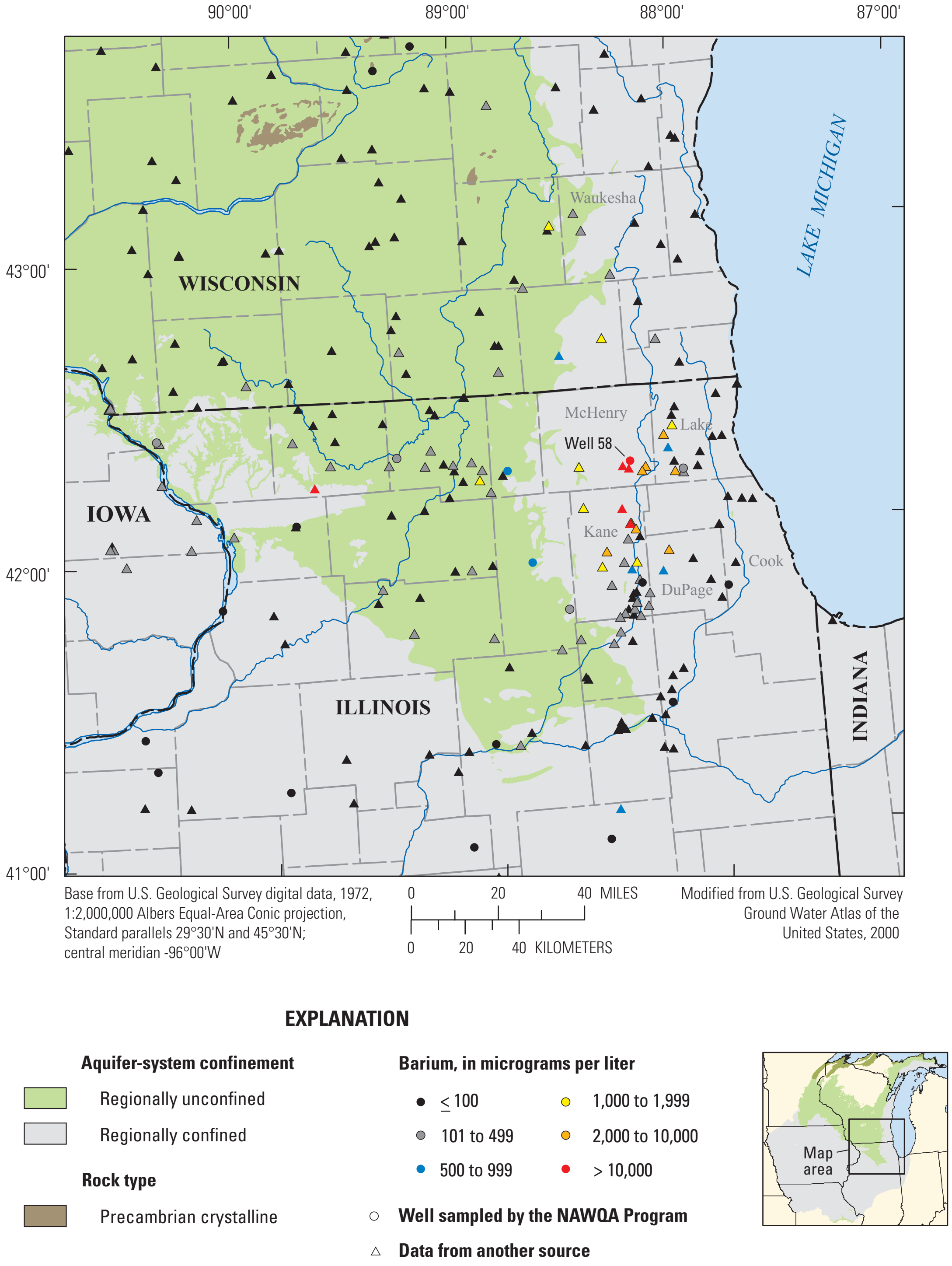
the regionally confined area of northern Illinois, and all but one were east of the unconfined area in northeastern Illinois (fig. 34). There were 23 wells that had a barium concentration of 1,000 µg/L or higher, and they were all in southeastern Wisconsin or northern Illinois (fig. 34). Of the 718 wells with a detected barium concentration, 672 of the wells were also analyzed for sulfate. The median concentration of sulfate was 24 mg/L for all wells and 68.5 mg/L for wells in the confined area. In the 23 wells where the barium concentration was 1,000 µg/L or higher, 21 of the wells had a reported sulfate concentration and the median was 3.6 mg/L. The low concentration of sulfate is consistent with the hypothesis of Gilkeson and others (1981) that elevated concentrations of barium were the result of the removal of sulfate by bacterial sulfate reduction. East (and downgradient) of the area of high barium concentrations, the sulfate concentrations are typically greater than the median value for the regionally confined area. The data from the multiple sources used in this study show that the occurrence of very high concentrations of barium (>1,000 µg/L) was limited to southeastern Wisconsin and northern-northeastern Illinois. There was no significant difference ($p = 0.57$) in barium concentrations between samples from wells in the confined area and wells in the unconfined area when data from all sources were used.

Boron was analyzed in fewer NAWQA samples than most of the trace elements but was detected in all 106 samples. Concentrations of boron ranged from 8.4 to 1,208 µg/L for most of the NAWQA samples (80 percent), with a median concentration of 160 µg/L (table 12). Boron has numerous industrial uses such as cleaning agents, production of glass, fire retardants, and fertilizer; therefore, boron may be present in sewage and industrial waste. Boron also occurs in coal combustion products. In sedimentary rock, boron is most abundant in shale, followed by sandstone (table 10). Boron concentrations were significantly higher ($p < 0.001$) in samples from the confined area than from the unconfined area (table 7). The extreme difference in distribution can be seen in figure 31, where the median boron concentration was 734 µg/L for wells in the confined area and 12.4 µg/L for wells in the unconfined area. Concentrations of boron were positively correlated with concentrations of most water-quality constituents, properties, and characteristics that are indicative of increased mineralization and reducing conditions (appendix 3). The strongest positive correlations were with concentrations of potassium (rho = 0.94), lithium (0.93), sodium (0.90), and fluoride (0.89). The strongest negative correlations of boron concentrations were with concentrations of silica (rho = −0.55), radon-222 (−0.51), lead (−0.46), tritium (−0.40), and nitrate (−0.39). These correlations and the difference in concentrations between the confined area and the unconfined area indicate that natural and not manmade sources of boron are dominant.

Boron concentrations exceeded the HBSL of 1,000 µg/L in 14 percent (15 of 106) of the NAWQA samples (table 13). Each sample that exceeded the HBSL was from a well in the confined area of Illinois or Iowa. Data from other sources (tables 3 and 4) were combined with the NAWQA data to evaluate the distribution of boron in the Cambrian-Ordovician aquifer system. Unfortunately, boron data were not available from Michigan DEQ or Missouri DNR, so data coverage is lacking for the Upper Peninsula and Missouri. Of the available data, the frequency of detection was 91.5 percent, and all nondetections were from wells in the regionally unconfined area. There were 44 wells with a boron concentration that exceeded the HBSL of 1,000 µg/L (fig. 35). All of the wells that exceeded the HBSL except one were in regionally confined areas. One well in southeastern Wisconsin is in a narrow band where the Maquoketa shale is absent; however, the area of missing shale is too small to be seen on the map, and the well could essentially be considered to be within the confined area (fig. 35). Of the wells that exceeded the HBSL, there were four at the same location in northeastern Illinois along Lake Michigan where the RASA study installed a test well (Zion test well) and sampled different aquifers.

Iron was detected in 89 percent (128 of 144) of the NAWQA samples, and concentrations in most samples (80 percent) ranged from 4.7 to 1,077 µg/L (table 12). The median iron concentration was 186 µg/L, and the maximum concentration was 4,300 µg/L. Iron concentrations were significantly higher ($p = 0.003$) in samples from the confined area (median = 276 µg/L) than in samples from the unconfined area (median = 110 µg/L) (fig. 31; table 7). Iron is the third most abundant element in the Earth's crust, and it is quite abundant in shale, sandstone, and carbonates (table 10). Iron is also present in organic wastes and in decaying plant debris and humic compounds in soils (Hem, 1985). The most common form of dissolved iron in groundwater is the ferrous ion, Fe^{2+}, which is typically released to groundwater through the oxidation of ferrous sulfides such as pyrite (FeS_2), weathering of iron-bearing silicate minerals, or reduction of ferric hydroxides (Hem, 1985).

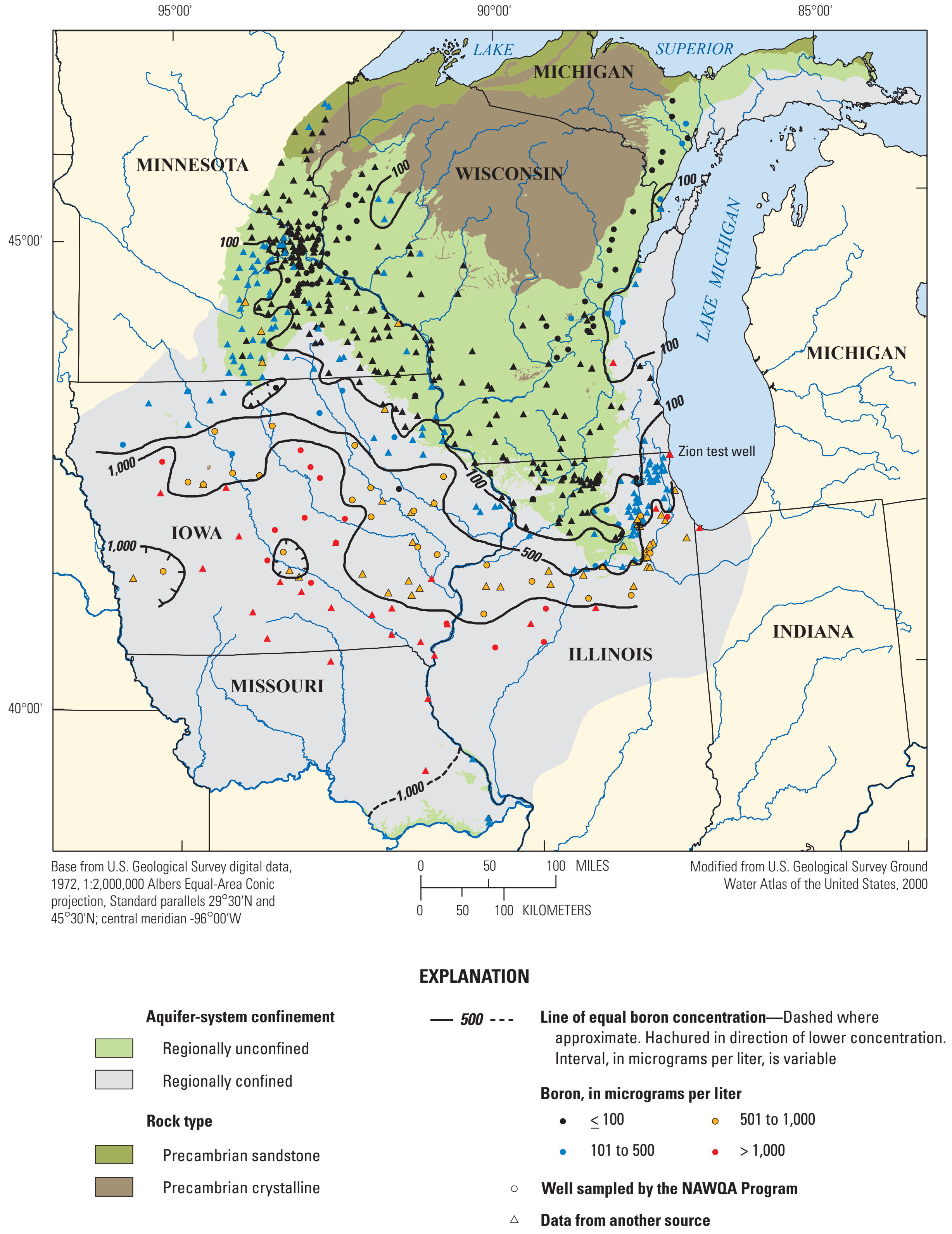
The availability of iron for aqueous solution is affected by changes in degree or intensity of oxidation or reduction. Iron concentrations will be low if the groundwater contains much dissolved oxygen. For example, the median iron concentration of the NAWQA samples was 4.7 µg/L if dissolved oxygen was 1 mg/L or higher, and the median iron concentration was 275 µg/L if dissolved oxygen was less than 1 mg/L. The USEPA SDWR of 300 µg/L was exceeded in 41 percent of the 144 NAWQA wells (table 13) and in both regionally confined and unconfined areas (fig. 31). Seventeen wells (12 percent) produced samples with an iron concentration greater than 1,000 µg/L. Noticeable effects of iron concentrations greater than the SDWR are a rusty color, metallic taste, and reddish or orange staining of laundry and plumbing fixtures (U.S. Environmental Protection Agency, 1992). Iron concentrations have positive correlations with concentrations of most of the major ions and trace elements, but the strongest are with ammonia (rho = 0.56) and manganese (0.53), substances that either formed in reducing waters (ammonia) or are most soluble in reducing waters (manganese) (appendix 3). Iron concentrations are negatively correlated with several properties and constituents in the matrix that are indicative of oxic and young



Base from U.S. Geological Survey digital data, 1972,
1:2,000,000 Albers Equal-Area Conic projection,
Standard parallels 29°30'N and 45°30'N;
central meridian -96°00'W

Modified from U.S. Geological Survey
Ground Water Atlas of the
United States, 2000

Figure 34. Barium concentrations in water samples from wells completed in the Cambrian-Ordovician aquifer system of northern Illinois and southern Wisconsin, 1969–2008.



Base from U.S. Geological Survey digital data, 1972, 1:2,000,000 Albers Equal-Area Conic projection, Standard parallels 29°30'N and 45°30'N; central meridian -96°00'W

Modified from U.S. Geological Survey Ground Water Atlas of the United States, 2000

Figure 35. Boron concentrations in water samples from wells completed in the Cambrian-Ordovician aquifer system, 1961–2007.

groundwater. Strongest negative correlations of iron concentrations are with concentrations of lead (rho = −0.64), nitrate (−0.50), dissolved oxygen (−0.44), tritium (−0.43), and pH (−0.31).

Data from other sources were combined with the NAWQA data to evaluate the distribution of iron in the Cambrian-Ordovician aquifer system (tables 3 and 4). The majority of the wells (70 percent) were in regionally unconfined areas. Of the available data, the frequency of detection was 90 percent. As with the NAWQA dataset, iron concentrations were significantly higher ($p < 0.001$) in samples from the regionally confined area, and 45 percent of all samples exceeded the SDWR of 300 µg/L. However, when just the subset of wells that exceeded 300 µg/L ($n = 596$) were grouped by type of confinement, iron concentrations were significantly higher ($p = 0.002$) in the unconfined area. The distribution of iron concentrations is not shown on a map because high concentrations (> 300 µg/L) occur throughout the aquifer system with no apparent pattern.

Lithium was detected in 99 percent (107 of 108) of NAWQA samples when all detections were counted and in 94 percent of the samples at an assessment level of 1 µg/L. Lithium concentrations in most (80 percent) of the NAWQA samples ranged from 1.2 to 173 µg/L, with a median concentration of 11.6 µg/L (table 12). The maximum concentration detected in a NAWQA sample was 650 µg/L in the Prairie du Chien-Jordan aquifer in central Iowa. Lithium does not have a human-health benchmark or SDWR, but it is included here because of its strong correlation with other water-quality constituents associated with increasing mineralization of the water, including radium-226 and radium-228. Lithium is an alkali metal, and it was positively correlated with the alkali metals sodium (rho = 0.89) and potassium (0.91) (appendix 3). Lithium is a minor constituent in rocks compared to many elements and is more abundant in shale than in sandstone or carbonates (table 10). Even though lithium is a trace constituent, it has a strong positive correlation with dissolved solids and specific conductance (rho = 0.80 for both). Lithium also has strong positive correlations with strontium (rho = 0.89), radium-226 (0.76), radium-228 (0.61), casing depth (0.84), and well depth (0.83). Lithium concentrations, like those of boron, were significantly higher ($p < 0.001$) in samples from wells in the regionally confined area than in samples from the unconfined area (fig. 31; table 7). The median concentration of lithium in samples from regionally confined wells was 94 µg/L, and the median concentration in samples from unconfined wells was 3.2 µg/L.

Manganese is a common constituent in most rock types and is more abundant in carbonates and shale than in sandstone (table 10). Manganese was detected in 92 percent (142 of 154) of the NAWQA samples when all detections were counted and in 71 percent of the samples at an assessment level of 1 µg/L (table 12). Concentrations in most of the NAWQA samples ranged from < 1 to 191 µg/L, with a median value of 9.9 µg/L. The maximum concentration in a NAWQA sample was 1,040 µg/L in the Jordan Sandstone in the Twin Cities metropolitan area. Unlike iron, manganese concentrations were significantly higher ($p = 0.026$) in samples from the unconfined area (median = 18.1 µg/L) than in samples from the confined area (median = 5.7 µg/L) (fig. 31; table 7). Manganese concentrations were low if the groundwater contained high concentrations of dissolved oxygen. The median manganese concentration of the NAWQA samples was 1 µg/L if dissolved oxygen was 1 mg/L or higher, and the median manganese concentration was 13.3 µg/L if dissolved oxygen was less than 1 mg/L. The chemistry of manganese is similar to iron in that both metals participate in redox processes in weathering environments (Hem, 1985). The primary form of dissolved manganese in groundwater is the divalent ion Mn^{2+}, which when released to the aqueous solution during weathering is less likely to be oxidized than ferrous iron (Fe^{2+}). Reduced manganese is less sensitive to the presence of dissolved oxygen than iron, meaning it oxidizes more slowly than does iron. The strongest positive correlations of manganese were with iron (rho = 0.53), molybdenum (0.52), calcium (0.38), DOC (0.36), and arsenic (0.36) (appendix 3). Manganese was negatively correlated with lead (rho = −0.50), dissolved oxygen (−0.35), and chloride (−0.25).

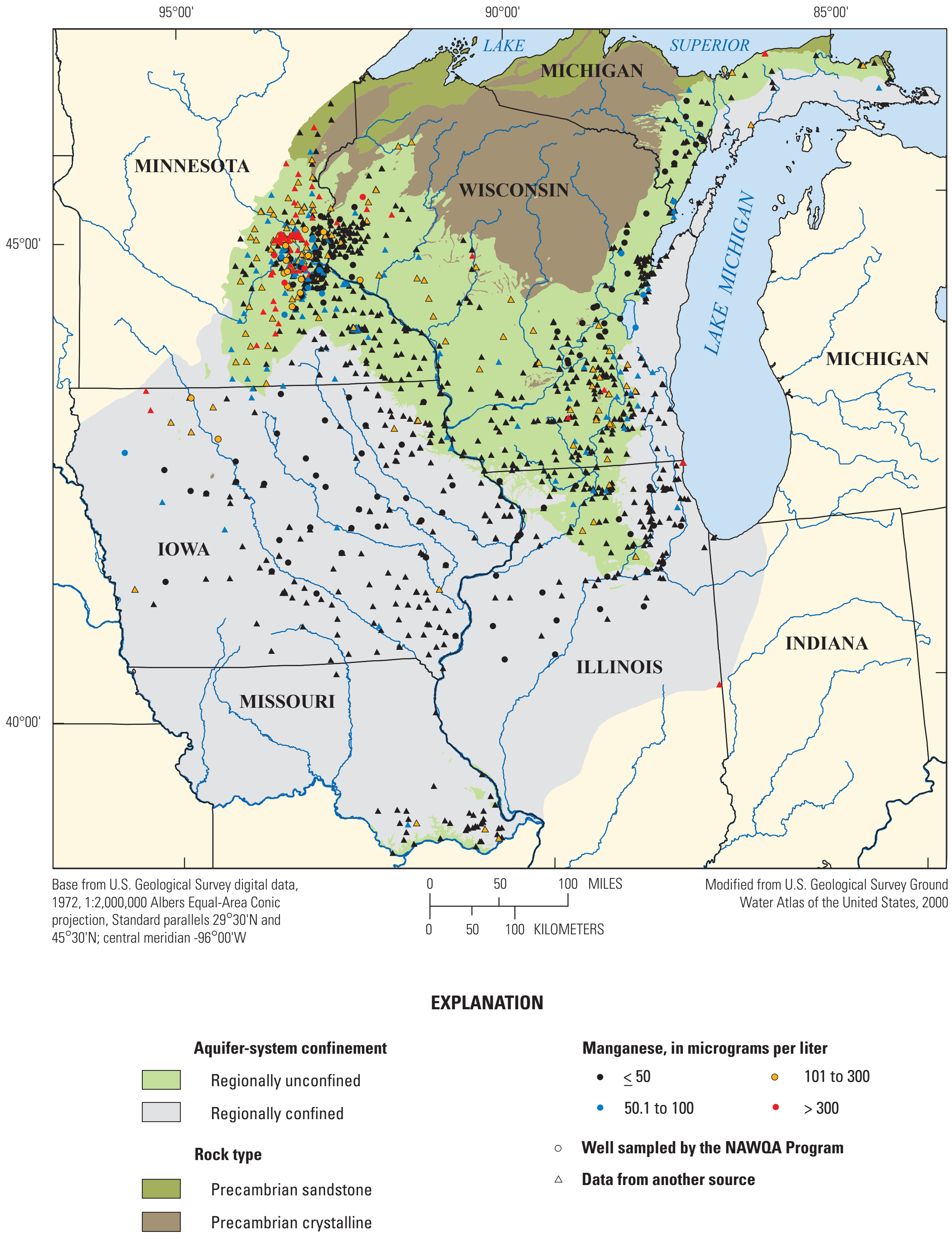
Manganese has an HBSL of 300 µg/L, which was exceeded in 4.5 percent (7 wells) of the NAWQA wells (table 13). Manganese also has a SDWR of 50 µg/L, which was exceeded in 24 percent of the NAWQA wells. The noticeable effects of manganese concentrations greater than the SDWR are a black to brown color, black staining, and a bitter metallic taste (U.S. Environmental Protection Agency, 1992). Most of the NAWQA wells (30 of 37) that exceeded the SDWR of 50 µg/L were in the Twin Cities metropolitan area. The remaining wells that exceeded the SDWR were in the eastern Wisconsin-Upper Peninsula sampling area (4 wells), and in northwestern Iowa (3 wells). All of the NAWQA wells with samples that exceeded the HBSL of 300 µg/L were in the Twin Cities metropolitan area; four of these wells produced water from the Prairie du Chien Formation, and three produced water from the Jordan Sandstone.

Data from other sources (tables 3 and 4) were combined with the NAWQA data to evaluate the distribution of manganese in the Cambrian-Ordovician aquifer system (fig. 36). The majority of the wells (70 percent) were in the unconfined areas, with 36 percent of the wells in Minnesota and 27 percent of the wells in Wisconsin. Of the available data, the frequency of detection was 77 percent. Reporting levels of the nondetections ranged from 0.1 to 20 µg/L, and the most common was 10 µg/L. As with the NAWQA dataset, manganese concentrations were significantly higher ($p < 0.001$) in samples from the unconfined area (median = 22.8 µg/L) than from the confined area (median = 15 µg/L). Of the wells that exceeded the SDWR of 50 µg/L, 64 percent were in Minnesota, and of the wells that exceeded the HBSL of 300 µg/L, 73 percent were in Minnesota (figs. 36 and 37). The percentages of wells in Minnesota exceeding these guidelines are much higher than the 36 percent of all wells in Minnesota. Siegel (1989) indicated that concentrations of arsenic, iron, and manganese increased in northwestern Iowa and southeastern Minnesota where the aquifer system was overlain by the argillaceous Dakota Formation and glacial drift derived from the Dakota. Figure 37 includes the boundary of the Des Moines glacial lobe (Schumann, 1993), which contains silty clays and clay derived from Cretaceous shale to the northwest. Most of the wells with manganese concentrations greater than 100 µg/L are within or near the boundary of the Des Moines lobe. The high concentrations of manganese in Minnesota were not limited to a few aquifers. Concentrations greater than the HBSL were measured in wells that produced from the Platteville, St. Peter Sandstone, Prairie du Chien, Jordan Sandstone, Franconia Formation, Ironton-Galesville, Mount Simon Sandstone, Hinckley Sandstone, and several combinations of these formations. Where glacial cover exists, mildly reducing conditions are known to mobilize arsenic, iron, and manganese (Thomas, 2007).

Strontium was detected in all 107 NAWQA samples and concentrations ranged from 53 to 3,703 µg/L for most of the samples (80 percent), with a median concentration of 645 µg/L (table 12). Strontium is an alkaline-earth metal whose chemistry is similar to that of calcium (Hem, 1985); this similarity probably explains why the average composition in sedimentary rocks is highest in carbonates, as compared to shale and sandstone (table 10). As with boron and lithium, strontium concentrations were significantly higher ($p < 0.001$) in samples from wells in the regionally confined area than in samples from the unconfined area (fig. 31; table 7). The median concentration in the regionally confined wells was 2,219 µg/L, and the median concentration in unconfined wells was 86 µg/L. However, the three highest concentrations were from the unconfined area along the confinement boundary in the eastern Wisconsin-Upper Peninsula sampling area. Nichols and McNall (1957) reported that many wells in eastern Wisconsin yielded water containing more than 1,000 µg/L of strontium, and Grundl and others (2006) found that some samples in southeastern Wisconsin were at saturation with respect to celestite ($SrSO_4$). Negative health effects of strontium at high doses include abnormal bone development. Strontium has an HBSL of 4,000 µg/L, which was exceeded in 9.3 percent (10 wells) of the NAWQA wells with a strontium sample (table 13). Strontium concentrations were positively correlated with concentrations of most major ions, trace elements, or properties that are indicative of mineralization and reducing conditions, including radium-226 (rho = 0.77) and radium-228 (0.67) (appendix 3). Positive correlations with boron, sodium, potassium, lithium, and fluoride all had particularly high values of Spearman's rho, ranging from 0.86 to 0.89. Strontium concentrations were negatively correlated with concentrations of constituents indicative of less mineralized water with shorter residence time such as, silica (rho = −0.54), nitrate (−0.49), radon-222 (−0.48), and dissolved oxygen (−0.39).

Data from other sources (tables 3 and 4) were combined with the NAWQA data to evaluate the distribution of strontium in the Cambrian-Ordovician aquifer system (fig. 38). Of the available data, there were only three nondetections, and the maximum reporting level was 68 µg/L. Data coverage of strontium concentrations in the Upper Peninsula and Missouri was lacking. Of the available data, 11 percent of the wells exceeded the HBSL of 4,000 µg/L, and the majority of those wells were along the eastern edge of the aquifer system from the Upper Peninsula down to northeastern Illinois (fig. 38). Several of the wells in eastern Wisconsin had water with strontium concentrations greater than 10,000 µg/L. The high values of strontium in this area are possibly from the dissolution of secondary celestite ($SrSO_4$) grains in the aquifer matrix. The celestite and other secondary minerals were probably emplaced by the dissolution, transport, and re-precipitation of sulfate-rich saline water from Silurian evaporite deposits from the Michigan basin that moved updip into the aquifer when Lake Michigan was covered with glaciers (Gilkeson and others, 1981; Siegel, 1990; Winter and others, 1995). The Zion test well in northeastern Illinois (fig. 38) had strontium results at seven depths in five different aquifers, and all exceeded the HBSL. The aquifers were the Sinnipee-Ancell groups, St. Peter Sandstone, Ironton-Galesville Sandstone, Elmhurst Sandstone, and the Mount Simon Sandstone. Strontium concentrations increased substantially with depth in the Mount Simon Sandstone, from 13,000 µg/L near the top of the formation at a depth of 1,932 ft to 100,000 µg/L at a depth of 3,120 ft. This trend of increasing concentration with depth suggests a high concentration of strontium in the brines of the deep Mount Simon Sandstone. The value of dissolved solids was 56,000 mg/L at this depth of 3,120 ft.

Uranium was detected in 83 percent (114 of 137) of the NAWQA samples and in 17 percent of the samples at an assessment level of 1 µg/L (table 12). The median uranium concentration was 0.35 µg/L, and 90 percent of the samples had a uranium concentration less than 1.7 µg/L. The maximum concentration measured in a NAWQA sample was 6.45 µg/L, from well 21 in north-central Iowa (see fig. 2). Well 21 produces water from the Maquoketa Shale and overlying carbonates in addition to its primary aquifer, the Jordan Sandstone. Uranium concentrations are low in the NAWQA samples relative to the USEPA MCL of 30 µg/L (fig. 31). There was no significant difference ($p = 0.054$) in uranium concentrations between samples from regionally confined and unconfined wells. Uranium concentrations were positively correlated with concentrations of nitrate (rho = 0.51), silica (0.48), tritium (0.47), and zinc (0.40), which is consistent with the thermodynamic property that the more oxidized forms of uranium are more soluble than the reduced species (Hem, 1985). Uranium is of interest because it has a human-health benchmark and it is the starting point in the radioactive-decay series that includes radium-226 and radon-222. However, uranium does not show strong correlation with either decay product. Uranium concentrations in the NAWQA samples were positively correlated with radon-222 concentrations (rho = 0.22) and negatively correlated with radium-226 concentrations (rho = −0.22). This lack of strong positive correlations between uranium and its decay products is expected, because the chemistry of each of these radionuclides is different (Szabo and Zapecza, 1991).



Base from U.S. Geological Survey digital data, 1972, 1:2,000,000 Albers Equal-Area Conic projection, Standard parallels 29°30'N and 45°30'N; central meridian -96°00'W

Modified from U.S. Geological Survey Ground Water Atlas of the United States, 2000

EXPLANATION

Aquifer-system confinement

- 🟩 Regionally unconfined
- ⬜ Regionally confined

Rock type

- 🟩 Precambrian sandstone
- 🟫 Precambrian crystalline

Manganese, in micrograms per liter

●	$\leq$ 50	●	101 to 300
●	50.1 to 100	●	> 300

○ **Well sampled by the NAWQA Program**

△ **Data from another source**

Figure 36. Manganese concentrations in water samples from wells completed in the Cambrian-Ordovician aquifer system, 1961–2008.

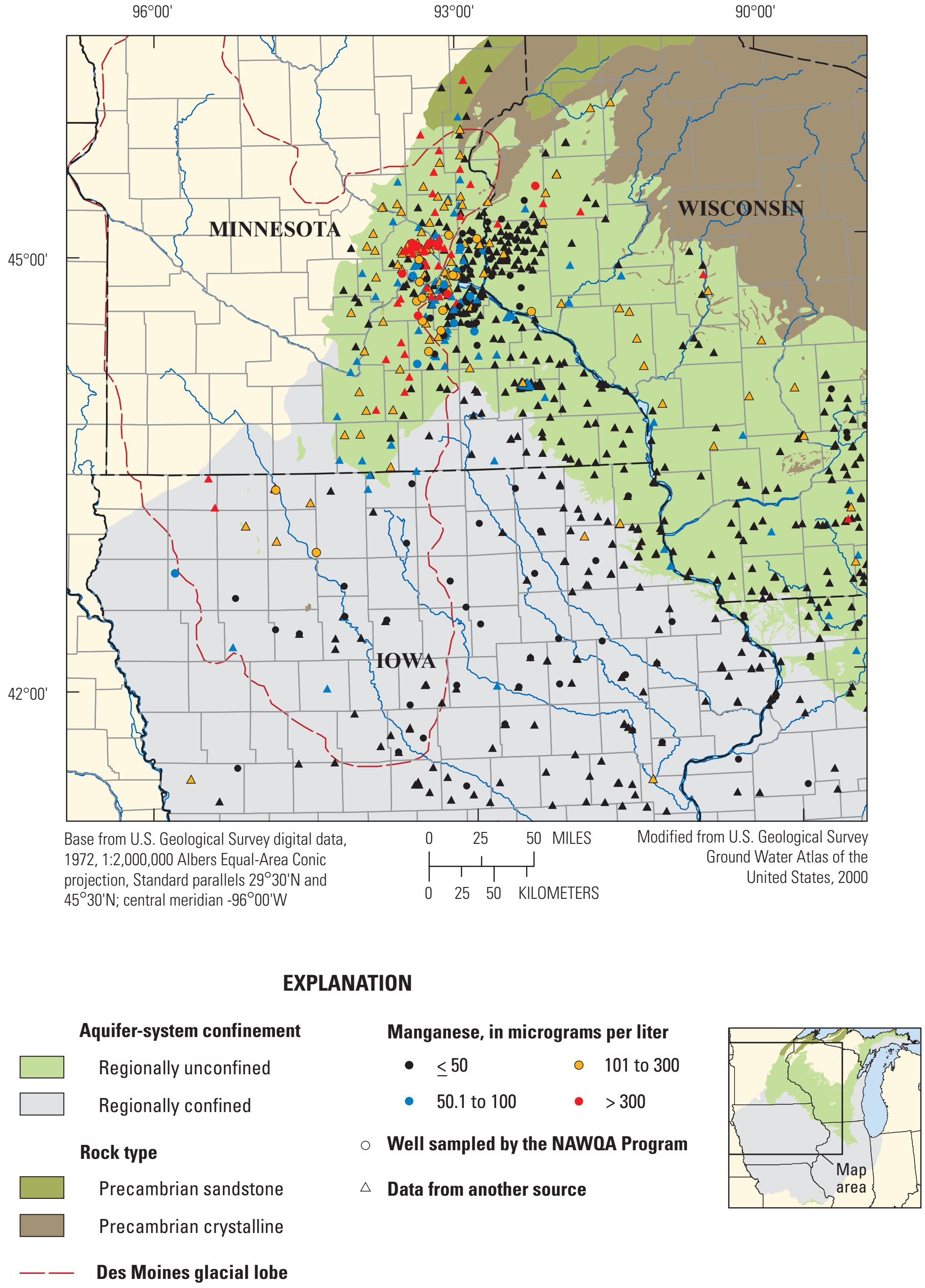


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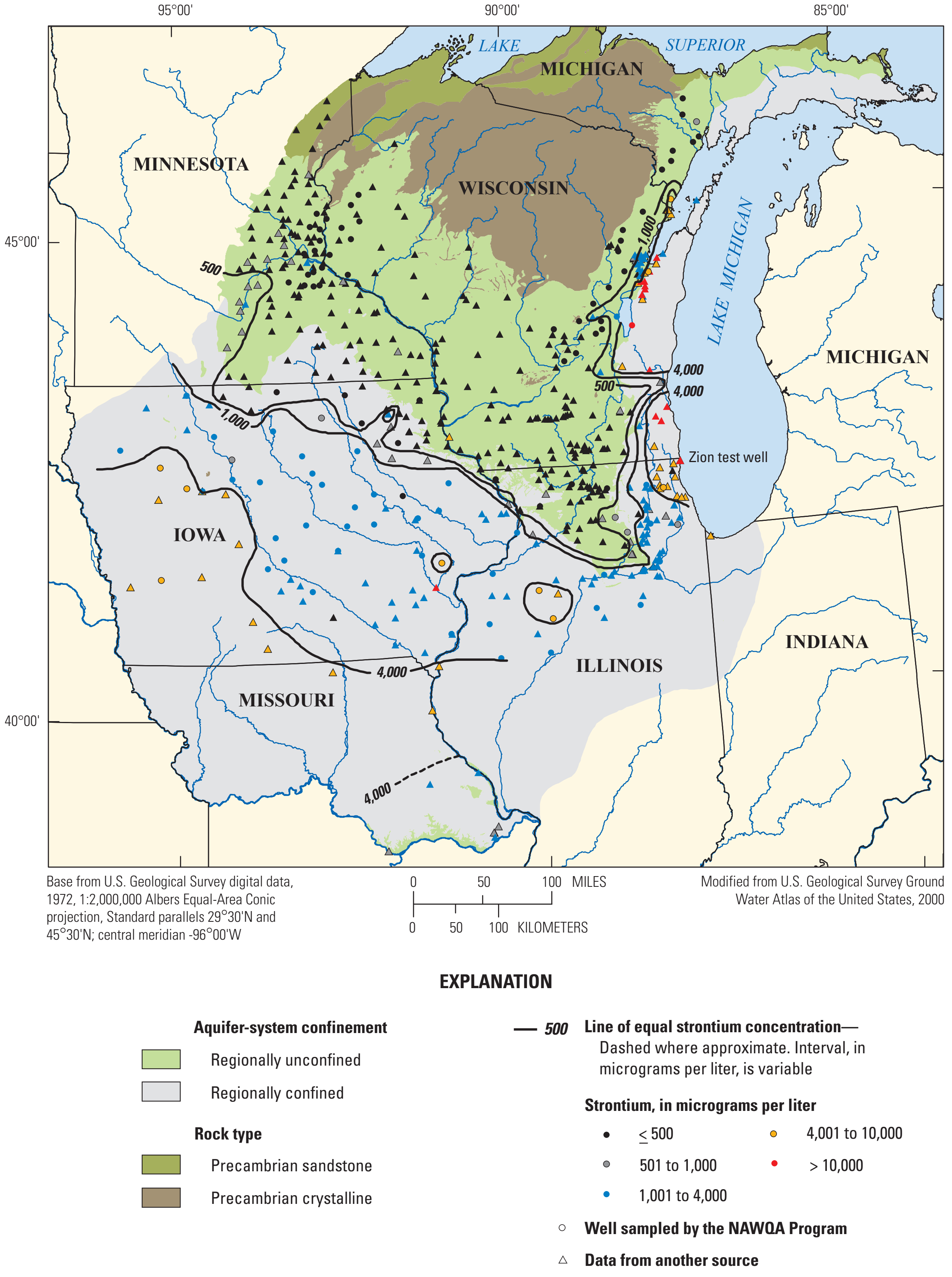
Figure 37. Manganese concentrations in water samples from wells completed in the Cambrian-Ordovician aquifer system in Minnesota and northwestern Iowa, 1961–2008.



Base from U.S. Geological Survey digital data, 1972, 1:2,000,000 Albers Equal-Area Conic projection, Standard parallels 29°30'N and 45°30'N; central meridian -96°00'W

Modified from U.S. Geological Survey Ground Water Atlas of the United States, 2000

Figure 38. Strontium concentrations in water samples from wells completed in the Cambrian-Ordovician aquifer system, 1969–2007.

Nondetections of uranium at detection levels greater than 0.02 µg/L were removed from the NAWQA dataset to test whether concentrations were significantly different in samples when grouped by regional confinement and tritium-based groundwater age. This resulted in a dataset of 119 samples, 52 from regionally confined wells and 67 from regionally unconfined wells. Of these samples, 116 had a tritium-based age; 43 samples contained modern recharge, and 73 samples contained only pre-1953 recharge. Uranium concentrations were significantly higher ($p = 0.02$) in samples from regionally unconfined wells (median = 0.52 µg/L) than from regionally confined wells (median = 0.31 µg/L) (table 7). Uranium concentrations were significantly higher ($p < 0.001$) in samples with modern recharge (median = 0.67 µg/L) than in samples with only pre-1953 recharge (median = 0.30 µg/L). There was no significant difference in uranium concentrations for this dataset when grouped by redox condition (oxic, mixed source, anoxic).

Data from other sources (tables 3 and 4) were combined with the NAWQA data to evaluate the distribution of uranium in the Cambrian-Ordovician aquifer system. Very little data were available for the Upper Peninsula and Missouri. Of the available data, there was only one sample with a uranium concentration greater than 10 µg/L. A uranium concentration of 28.9 µg/L was reported for a RASA sample from the deep Mount Simon Sandstone in the Zion test well (location shown in fig. 38) in northeastern Illinois (Siegel, 1989), which was not a source of drinking water. Grundl and Cape (2006) point to this sample as possible proof that saline brines are capable of transporting uranium (and therefore, radium-226) as the brines migrate updip from structural basins, as suggested by Winter and others (1995). Of the available data, the sample from NAWQA well 21 in north-central Iowa was the only other sample with a uranium concentration greater than 5 µg/L.

Radionuclides

Water samples collected by the NAWQA Program were analyzed for several radionuclides (radioactive species of atoms, commonly considered to be contaminants), including tritium, radon-222, radium-226, and radium-228. Tritium was discussed in an earlier section because of its use for age-dating analysis. The number of radionuclides analyzed in water samples varied by sample date and study objectives. For example, water samples collected from the Cambrian-Ordovician aquifer system during the first decade (1991–2001) of NAWQA were not analyzed for radium, and the source-water quality study near the Twin Cities metropolitan area (2004–5) focused on anthropogenic contaminants and did not include radionuclides in the analysis. Radon-222 was analyzed in samples collected from 1995 through 2007. Radium-226 and radium-228 were analyzed in samples collected during 2005 and 2007.

The radioactivity of water is usually expressed in terms of the rate of radioactive disintegration (curies) per liter of water, where 1 curie is defined as 3.7×10^{10} disintegrations per second. The unit curie is large for expressing natural radioactivity levels, so data are expressed in picocuries per liter (pCi/L), where 1 picocurie is 1×10^{-12} curie. One pCi/L equals 2.2 radioactive disintegrations per minute per liter of water. Equivalent mass concentrations of the radionuclides are extremely small in comparison to mass for most water-quality constituents, and the equivalent mass concentrations are directly proportional to the half-lives. For example, 1 picocurie (pCi) of radon-222 is equivalent to 6.4962×10^{-12} µg, 1 pCi of radium-228 is equivalent to 3.668×10^{-9} µg, and 1 pCi of radium-226 is equivalent to 1.0256×10^{-6} µg. The predominant isotope of natural uranium is uranium-238, which has a long half-life of 4.49×10^{9} years (table 14), and makes up about 99.3 percent of the mass of uranium. One pCi of uranium-238 is equivalent to 2.99 µg, which explains why chemical methods (with units of mass) can be used to measure uranium concentrations in natural waters (Hem, 1985) and why uranium was discussed in the trace element section of this report. McCurdy and others (2008) provide simplified equations for converting activity in picocuries to specific activity per gram for different units of half-life (years, days, hours, and minutes).

Radon-222

Radon-222 is a radioactive gas that is part of the uranium-238 decay series that ultimately terminates with the formation of a stable isotope of lead. Radon-222 is produced directly from the decay of radium-226 and has a half-life of 3.82 days (table 14). Radon-222 decays by alpha-particle emission. An alpha particle is identical to a helium nucleus, having two protons and two neutrons. It is a relatively heavy, high-energy particle, with a positive charge of +2 from its two protons (U.S. Environmental Protection Agency, 2010a). Radon-222 is soluble in water and can be transported in the gas phase. Rogers (1958) calculated that groundwater in a porous aquifer containing 1 part per million of uranium in the solid phase could have a radon activity greater than 800 pCi/L. The average composition of uranium in sedimentary rocks is greater in shale than in carbonates or sandstone (table 10). Radon-222 concentrations in groundwater can be affected by multiple factors, including the distribution of uranium in aquifer materials, aquifer physical characteristics (Wanty and others, 1992), and geochemical conditions that affect the mobility of uranium and radium. Groundwater often contains detectable quantities of radon-222, which may appear large in comparison with the accompanying dissolved radium concentration (Tanner, 1964; Hem, 1985; Szabo and Zapecza, 1991). This large difference is based on units of radioactive disintegrations per volume and not mass. A radon-222 activity of 300 pCi/L is equal to 1.94885×10^{-9} µg/L—an equivalent mass of radium-226 per liter would only have an activity of 0.0019 pCi/L. Because radon-222 has a short half-life of 3.82

Table 14. Partial radioactive decay series and half-lives for uranium-238 and thorium-232.

[α, alpha; β, beta; radionuclides in bold type are discussed in detail in the text]

Uranium-238			Thorium-232		
Isotope	**Mode of decay**	**Half-life**	**Isotope**	**Mode of decay**	**Half-life**
Uranium-238	α particle	4.49×10^9 years	Thorium-232	α particle	1.41×10^{10} years
Thorium-234	β particle	24.1 days	**Radium-228**	β particle	5.75 years
Protactinium-234m	β particle	1.18 minutes	Actinium-228	β particle	6.13 hours
Uranium-234	α particle	2.48×10^5 years			
Thorium-230	α particle	7.54×10^4 years			
Radium-226	α particle	1,622 years			
Radon-222	α particle	3.82 days			
Polonium-218	α particle	3.05 minutes			

Table 15. Summary statistics for radionuclides in samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 1995–2007.

[pCi/L, picocuries per liter; ± is the combined standard uncertainty at the 95-percent confidence level for radon-222 and the 68-percent confidence level for radium-226 and radium-228 (McCurdy and others, 2008)]

Radionuclide	No assessment level								Assessment level as indicated			
	Number of samples	Number of detections	Concentration percentile (pCi/L)					Maximum concentration (pCi/L)	Level (pCi/L)	Number of samples	Number of detections	Frequency of detection, in percent
			10th	25th	Median	75th	90th					
Radon-222	140	134	58.5	130	250	528	768	15,402 ±106	74	140	124	88.6
Radium-226	88	83	0.05	0.36	2.33	4.46	7.45	52.8 ±1.5	1.0	88	62	70.4
Radium-228	88	73	0.22	0.34	1.16	2.38	4.19	9.86 ±0.32	1.0	88	48	54.5
Radium-226 + radium-228	88	83	0.13	0.85	4.03	7.38	10.6	56.0	1.0	88	64	72.7

days, it cannot migrate far from its source. Therefore, the radon-222 concentration in groundwater is likely to be proportional to the radioactivity in the rocks around the well and not necessarily to the concentration of radionuclides in solution (Tanner, 1964; Szabo and Zapecza, 1991). Radon-222 concentrations can be enriched relative to the parent radium-226 through the physical fractionation process of alpha recoil. The energy involved in alpha decay can cause the daughter nuclide to recoil in the opposite direction as the alpha particle is ejected. This recoil can be of sufficient distance to cause a fraction of the daughter nuclide produced during alpha decay to be ejected from the host mineral into the groundwater in pore spaces or into adjacent grains; this ejection, in turn, produces alpha-recoil tracks, which are areas of damage to the crystal structure. An additional fraction of the daughter is left in damaged crystallographic sites within the mineral. The daughter nuclide in damaged crystallographic sites and in alpha-recoil tracks can be mobilized more easily through etching by groundwater (Fleischer, 1980). Alpha recoil gives daughter nuclides of alpha decay a way to leave their host mineral by a process that is independent of their chemistry.

Occurrence and Distribution

Radon-222 was detected in 96 percent of the NAWQA samples (134 of 140) without an assessment level and in 89 percent of the samples at an assessment level of 74 pCi/L (table 15). The assessment level of 74 pCi/L was the highest reporting level for the six samples with nondetections. The concentration (activity) of radon-222 in most of the NAWQA samples (80 percent) ranged from 58.5 to 768 pCi/L, with a median value of 250 pCi/L (table 15). The combined standard uncertainty (CSU) at the 95 percent (2-sigma) confidence level for the radon measurements ranged from 16 to 30 pCi/L for most of the samples (80 percent), with a median of 21 pCi/L and a mean of 23 pCi/L. The high percentage of detections indicates that the parent radionuclide, radium-226, is ubiquitous in the matrix of the Cambrian and Ordovician rocks (Gilkeson and Cowart, 1987). Radon-222 concentrations were positively correlated with concentrations of constituents indicative of the presence of less reduced, more recently recharged groundwater, such as silica (rho = 0.52), tritium (0.45), DOC (0.39), and nitrate (0.37) (appendix 3). Radon-222 concentrations were also positively correlated with concentrations

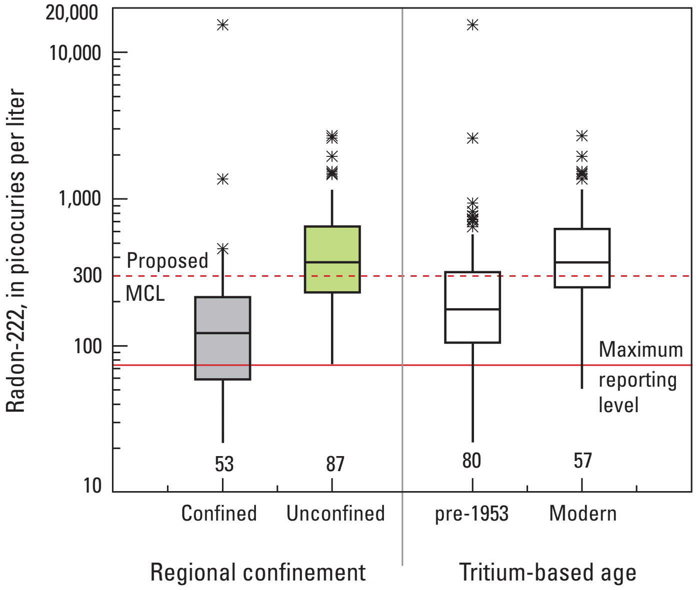


Figure 39. Distribution of radon-222 concentrations by regional confinement and tritium-based groundwater age for water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program (MCL, Maximum Contaminant Level).

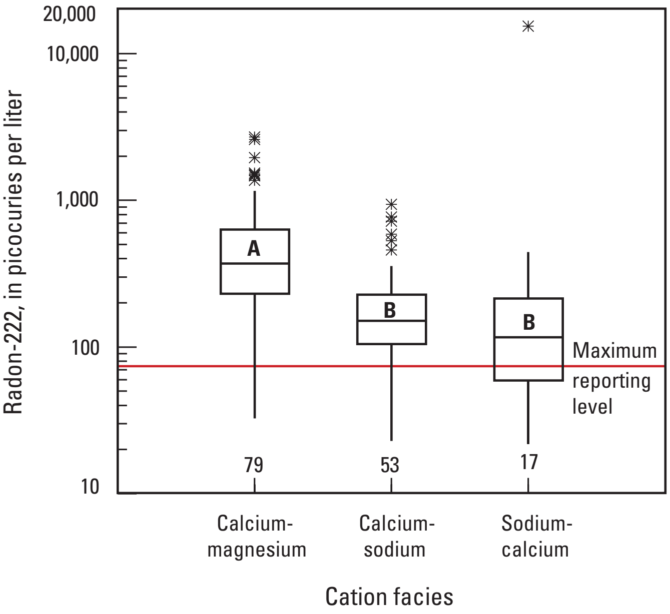


Figure 40. Distribution of radon-222 concentrations by cation facies for samples from a subset of wells used to map hydrochemical facies in the Cambrian-Ordovician aquifer system.

of the trace elements zinc, arsenic, molybdenum, uranium, and manganese. Conversely, radon-222 concentrations were negatively correlated with concentrations of constituents, properties, or characteristics indicative of the presence of older, more reduced, and more mineralized groundwater, such as well depth (rho = −0.61), casing depth (−0.60), boron (−0.51), potassium (−0.49), strontium (−0.48), radium-226 (−0.38), radium-228 (−0.36), and dissolved solids (−0.33). In general, concentrations of radon-222 had opposing correlations with most constituents that concentrations of radium-226 had, even though radon-222 is the direct decay product of radium-226. These opposite correlations illustrate that concentrations of radium-226 and radon-222 are controlled by their different geochemical properties and by the geochemical conditions of the groundwater.

Radon-222 concentrations were significantly higher ($p < 0.001$) in samples from wells that were regionally unconfined than in wells that were regionally confined (fig. 39; table 7). The median concentration was 370 pCi/L in the unconfined wells and 122 pCi/L in the confined wells. Radon-222 concentrations were also significantly higher in wells with a tritium-based recharge age of modern than in wells with a recharge age of pre-1953 (fig. 39). The median concentration was 370 pCi/L in the wells with modern recharge and 177 pCi/L in the wells with pre-1953 recharge. The distribution of radon-222 concentrations can also be grouped by cation facies. A subset of the wells used to make the hydrochemical facies maps had radon-222 samples. Radon-222 concentrations were significantly higher ($p < 0.05$) in wells with a calcium-magnesium cation facies than in wells with a calcium-sodium or sodium-calcium facies (fig. 40). Radon-222 concentrations were generally higher in wells with a calcium-sodium cation facies than in wells with a sodium-calcium facies, but not at the 0.05 significance level. The regionally unconfined area of the aquifer system is characterized by younger, less reduced, less mineralized groundwater that typically has a calcium-magnesium cation facies as opposed to the older, more mineralized groundwater from the confined parts of the aquifer system that has a sodium cation facies. Such geochemical conditions in the unconfined part of the aquifer system are favorable to the mobility of uranium-238, the original parent isotope of the radionuclide decay series, but are not favorable for the mobility of radium-226, the direct parent of radon-222. Most likely, in the unconfined part of the aquifer system, the radium-226 remains immobilized on grain coatings (iron hydroxides) near the rock-water interface (Zoltan Szabo, U.S. Geological Survey, written commun., 2011). The soluble, gaseous radon-222 is readily emitted to the pore water when the radium-226 decays. In the confined parts of the aquifer system, the radium-226 is mobile and accumulates to a much lesser extent on grain coatings. Another factor may be that near-surface weathering in the unconfined part of the aquifer system generates more surface area and degrades the rock matrix to a slightly greater degree than occurs at greater depths under confining units where water circulation is slow. The increased surface area of the rock matrix in unconfined areas would facilitate increased water-rock contact and radon-222 emanation from rock to pore water (Zoltan Szabo, U.S. Geological Survey, written commun., 2011). In these ways, conditions in the unconfined parts of the aquifer system seem to be favorable to the mobility of radon-222, resulting in higher radon-222 concentrations in groundwater.

Radon is known to cause cancer in humans, and the primary health risk is from breathing radon gas in the indoor air of buildings (U.S. Environmental Protection Agency, 2010b). Most of the radon in indoor air comes from the breakdown of uranium in soil and rock beneath buildings. In typical situations, only about 1–2 percent of radon in indoor air comes from water; however, breathing radon released to air from household water use slightly increases the risk of lung cancer over the course of a lifetime. Ingestion of drinking water containing radon also presents a small risk of internal organ cancers, primarily stomach cancer (U.S. Environmental Protection Agency, 2010b). In 1999, the USEPA proposed an MCL of 300 pCi/L and an alternative MCL (AMCL) of 4,000 pCi/L for public water systems. The alternative MCL was proposed for states or community water systems that developed multimedia mitigation programs to reduce the risk of radon from all sources. The proposed MCL of 300 pCi/L, was intended for states and community water systems that do not have such multimedia mitigation programs.

Radon-222 concentrations exceeded the proposed MCL of 300 pCi/L in 43 percent of the wells sampled by the NAWQA Program (table 16). The majority of wells (90 percent) that exceeded the MCL were in the regionally unconfined area (table 17). Of the four NAWQA sampling areas, the eastern Wisconsin-Upper Peninsula wells had the highest median radon-222 concentration (527 pCi/L), followed by the wells in the Twin Cities metropolitan area (median = 366 pCi/L). However, there was no statistical difference in the distribution of radon-222 concentrations between these two sampling areas at the 0.05 significance level. Sixty-eight percent of the radon-222 samples from the eastern Wisconsin-Upper Peninsula area exceeded the proposed MCL of 300 pCi/L, and 64 percent of the samples from the Twin Cities metropolitan area exceeded the proposed MCL. Most of the samples from the Twin Cities metropolitan area that exceeded the proposed MCL came from wells completed in the Prairie du Chien Group. The Prairie du Chien Group produced the highest number of samples that exceeded the MCL, but it also was the most sampled aquifer (table 17). Of the aquifers with at least four NAWQA samples, the four samples from the Munising Formation in the Upper Peninsula and northeastern Wisconsin had the highest median concentration of radon-222 (673 pCi/L). The 40 samples from the Prairie du Chien Group in the Twin Cities metropolitan area and eastern Wisconsin-Upper Peninsula sampling areas had a median radon-222 concentration of 415 pCi/L

The median radon-222 concentration in Iowa wells was 122 pCi/L, and the median radon-222 concentration in Illinois wells was 143 pCi/L. The highest radon-222 concentration (15,402 ±106 pCi/L) was measured in a relatively deep well in the regionally confined area of central Illinois (well 41 in fig. 41). This high value is an unexplained anomaly that does not fit the normal pattern of higher radon-222 concentrations in samples from unconfined areas than in samples from confined areas. Unfortunately, there was not another sample from this well to confirm the high radon-222 concentration. The NAWQA sample from this well had a radium-226 concentration of 16.3 pCi/L, which agrees with the 17.2 pCi/L measured by the Illinois EPA approximately 20 months earlier; however, Illinois EPA did not analyze for radon-222 (Joe Konczyk, Illinois Environmental Protection Agency, written commun., 2010). The presence of uranium- or radium-enriched rock at depth cannot be ruled out as a source of radon in the well.

Samples collected by the NAWQA Program in the Twin Cities metropolitan area allowed for analysis of the variability of radon-222 by aquifer lithology without having the complicating effects of geographic location and changing regional confinement. Wells in this area typically produce water from the Prairie du Chien Formation, the underlying Jordan Sandstone, or both. Data were used from 22 wells that produced water from a sandstone (including one sample from a well completed in the St. Peter Sandstone) and 28 wells that produced water from carbonate rocks (fig. 42). Radon-222 concentrations were significantly higher ($p = 0.006$) in samples from wells that produced water from carbonate rocks (median = 460 pCi/L) than in samples from wells that produced water from sandstone (median = 250 pCi/L). It was mentioned previously that radon-222 concentrations are negatively correlated with well depth and casing depth, which would suggest that radon-222 concentrations should be higher in the carbonate rocks of the Prairie du Chien Formation because it overlies the Jordan Sandstone. However, when only wells within the Twin Cities metropolitan area ($n = 50$) were considered, there was no correlation between concentrations of radon-222 and well depth or casing depth at the 0.05 significance level (probably because of the limited geographic area and small range in depth). There was no significant difference in the distribution of well depth between sandstone wells and carbonate wells at the 0.05 significance level. In addition, there was no relation between tritium-based groundwater age and the two aquifer lithologies, because the majority of samples from both lithologies were modern (post-1953). The carbonate rock wells had nine samples with an age of pre-1953, and the sandstone wells had five samples with an age of pre-1953.

The same analysis was done for concentrations of radon-222 in samples from wells that produced water from sandstone and carbonate rocks in the eastern Wisconsin-Upper Peninsula sampling area. There too, the median radon-222 concentration was higher in wells that produce water from carbonate rocks (587 pCi/L) than in wells that produce water from sandstone (median = 469 pCi/L), but the difference was not significant ($p = 0.341$). The relatively small number of samples from carbonate rock wells in this area ($n = 7$) does not allow the statistical power to determine whether radon-222 concentrations vary by lithology.

Data from other sources (tables 3 and 4) were combined with the NAWQA data to evaluate the distribution of radon-222 in the Cambrian-Ordovician aquifer system (fig. 41). The majority of the wells (66 percent) were in unconfined areas.

Table 16. Comparison of radon and radium samples collected by the NAWQA Program, 1995–2007, with human-health benchmarks for drinking water.

[MCLs are U.S. Environmental Protection Agency Maximum Contaminant Levels for public water supplies. All benchmarks are in picocuries per liter]

Radionuclide	Human-health benchmark		Wells exceeding human-health benchmark	
	Value	Type	Count	Percent
Radon-222	300	Proposed MCL	60	42.9
	4,000	Proposed Alternative MCL	1	0.71
Radium-226 + radium-228	5	MCL	35	39.8

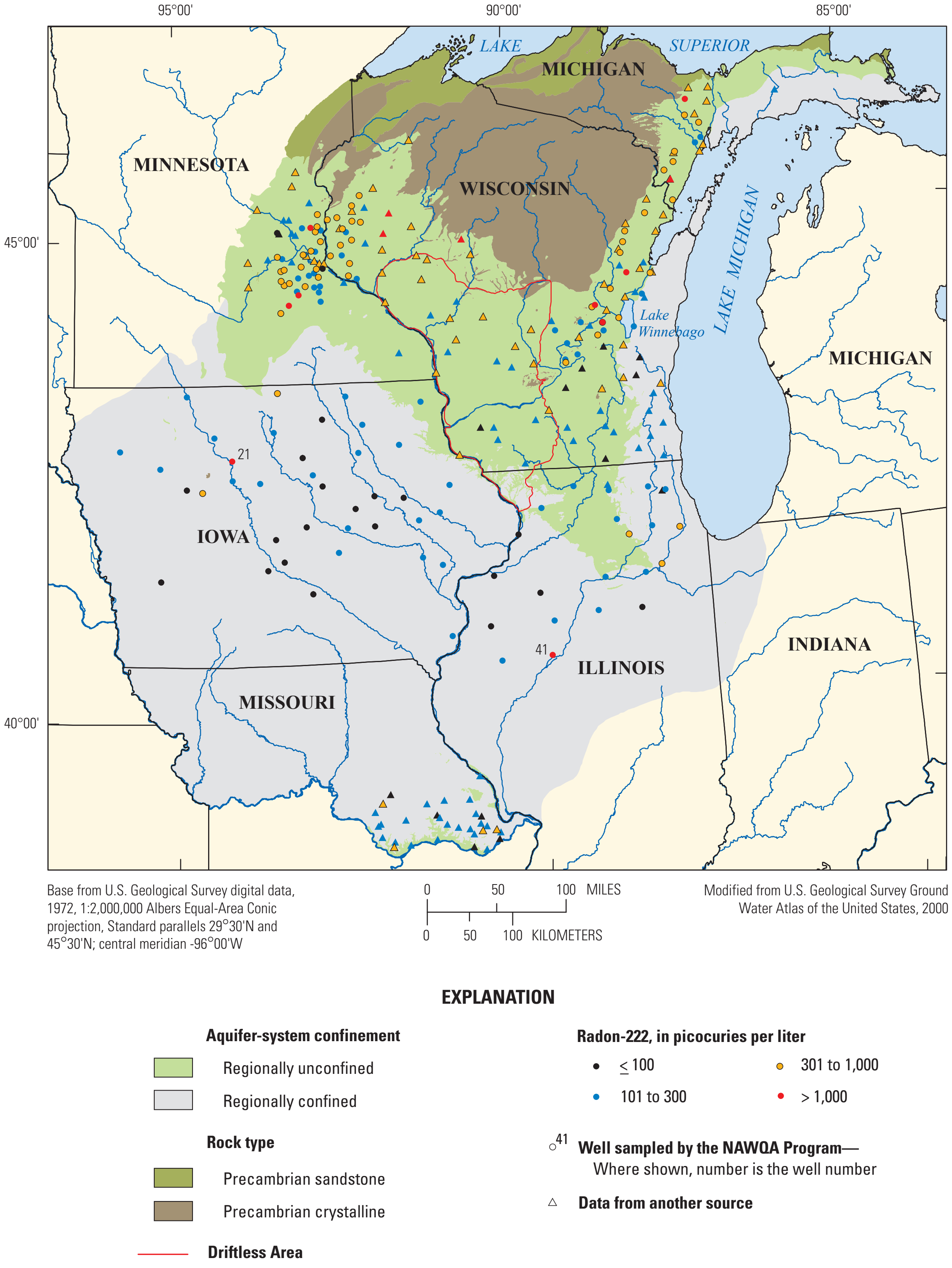
Table 17. Radon-222 and combined radium sample count and exceedances of human-health benchmarks, grouped by aquifer, for samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 1995–2007.

[--, not applicable]

Aquifer	Sample count and (exceedances) of human-health benchmarks grouped by regional confinement					
	Radon-222			Combined radium-226 + radium-228		
	All	Unconfined	Confined	All	Unconfined	Confined
Maquoketa Shale	3 (2)	--	3 (2)	3	--	3
Maquoketa-Galena	1	--	1	1 (1)	--	1 (1)
Galena-Decorah-Platteville	1 (1)	--	1 (1)	--	--	--
St. Peter Sandstone	12 (4)	5 (3)	7 (1)	7 (6)	1 (1)	6 (5)
St. Peter-Prairie du Chien	1 (1)	1 (1)	--	--	--	--
Prairie du Chien Group	40 (30)	40 (30)	--	15 (1)	15 (1)	--
Ordovician System	1	--	1	2 (2)	--	2 (2)
Prairie du Chien-Jordan	22 (1)	1	21 (1)	22 (13)	1	21 (13)
Ordovician-Cambrian Systems	17 (3)	3 (2)	14 (1)	16 (7)	2	14 (7)
Jordan Sandstone (Trempealeau Group)	18 (7)	17 (7)	1	11	10	1
Ironton-Galesville Sandstones	8	4	4	8 (5)	4 (2)	4 (3)
Munising Sandstone	4 (4)	4 (4)	--	--	--	--
Cambrian System	12 (7)	12 (7)	--	3	3	--
Total	140 (60)	87 (54)	53 (6)	88 (35)	36 (4)	52 (31)

As with the NAWQA dataset, radon-222 concentrations were significantly higher ($p < 0.001$) in samples from the unconfined area (median = 363 pCi/L) than from the confined area (median = 135 pCi/L). Approximately 44 percent of the wells had a radon-222 concentration that exceeded the proposed MCL of 300 pCi/L, and 90 percent of those wells were in the unconfined areas (fig. 41). There were 13 wells where the radon-222 concentration exceeded 1,000 pCi/L, of which 2 were in confined areas—the anomalously high value in central Illinois from NAWQA well 41 and NAWQA well 21 in north-central Iowa (fig. 41). Some of the open interval for well 21 is above the Maquoketa Shale, which results in some water-quality constituent concentrations being more indicative of unconfined rather than confined conditions.

The relatively high concentrations of radon-222 in the unconfined areas of the aquifer do not seem to be associated with the glacial aquifer system. Ayotte and others (2007) found that the distributions of radon-222 concentrations were similar between the glacial aquifer system and a subset of the Cambrian-Ordovician wells in Minnesota and Wisconsin. To test whether recharge from the glacial aquifer system was affecting the radon-222 concentrations in the unconfined Cambrian-Ordovician wells, concentrations were compared between 23 wells within the Driftless Area (shown in fig. 41) and 30 unconfined wells outside the Driftless Area but within 50 km of its boundary. There was no significant difference ($p = 0.943$) in radon-222 concentrations between wells in the Driftless Area and those within 50 km of its boundary.



Base from U.S. Geological Survey digital data, 1972, 1:2,000,000 Albers Equal-Area Conic projection, Standard parallels 29°30'N and 45°30'N; central meridian -96°00'W

Modified from U.S. Geological Survey Ground Water Atlas of the United States, 2000

Figure 41. Radon-222 concentrations in water samples from wells completed in the Cambrian-Ordovician aquifer system, 1986–2008.

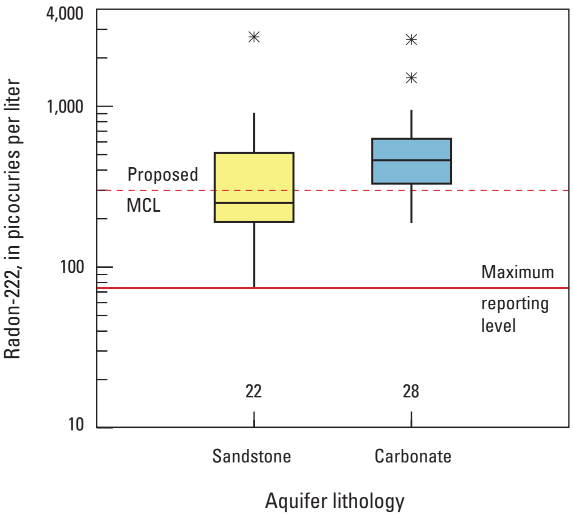


Figure 42. Distribution of radon-222 concentrations by aquifer lithology for samples collected from wells in the Cambrian-Ordovician aquifer system in the Twin Cities metropolitan area of Minnesota and Wisconsin by the NAWQA Program, 1996–2007 (MCL, Maximum Contaminant Level).

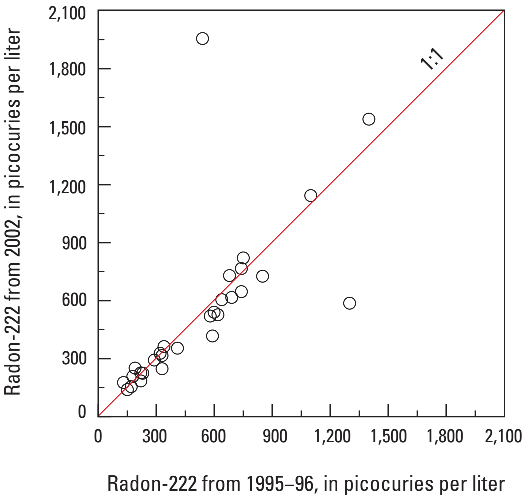


Figure 43. Comparison of radon-222 concentrations from samples collected in 1995–96 with samples collected in 2002 by the NAWQA Program, from 29 wells in the Cambrian-Ordovician aquifer system in Michigan, Minnesota, and Wisconsin.

Temporal Variability of Radon-222

A subset of 29 NAWQA wells was sampled twice, with a 6- to 7-year time gap, allowing for an analysis of the temporal variability of radon-222 concentrations. Four wells in the Twin Cities metropolitan area were sampled in 1996 and again in 2002, and 25 wells in the eastern Wisconsin-Upper Peninsula sampling area were sampled in 1995 and again in 2002. At most of the wells, results were similar for the two samples, but concentrations in samples from two wells differed greatly between 1995 and 2002 (fig. 43). There was no significant difference ($p = 0.304$) between the 1995–96 samples and 2002 samples when paired (by well) using the Wilcoxon signed-rank test. The absolute difference between the samples ranged from 3 to 1,417 pCi/L, which equate to percent differences of 1 and 113 percent. The mean absolute difference between the 1995–96 samples and the 2002 samples was 123 pCi/L, but without the two wells with the largest differences, the mean absolute difference was 54 pCi/L. The mean percent difference between the 1995–96 samples and the 2002 samples was 17.5 percent; without the two wells with the largest difference, it was 11 percent. The mean relative standard deviation of the two samples at each well was 12.4 percent, where the relative standard deviation is the standard deviation of the two samples divided by the mean of the two samples. King and others (1982) concluded that the source of radon-222 was temporally stable in four wells that they sampled in South Carolina at the scale of a few months to 2 years, with a mean relative standard deviation of 5 percent. A longer-term study of temporal variability of radon in 14 wells in North Carolina by Drane and others (1997) showed nearly all results were within ±30 percent of the mean. Extreme variation has been shown for water samples from a small number of wells located in uranium-rich bedrock where the radon concentrations also tended to be high (Dupuy and others, 1992), but such characteristics are not representative of those found in the Cambrian-Ordovician aquifer system.

Radium-226 and Radium-228

The occurrence of natural radium in water from the Cambrian-Ordovician aquifer system has been recognized for decades (Lucas and Ilcewicz, 1958; Scott and Barker, 1961; Emrich and Lucas, 1963). Young (1992a) listed excessive radium concentrations as one of the major concerns regarding water quality in the Cambrian-Ordovician aquifer system. Radium-226 is the fifth decay product in the uranium-238 decay series, and its immediate parent isotope is thorium-230 (table 14). Radium-226 has a half-life of 1,622 years and decays through alpha-particle emission to form radon-222. Radium-228 is the first decay product in the thorium-232 decay series and has a half-life of 5.75 years (table 14). Radium-228 decays through beta-particle emission. Beta particles are subatomic particles ejected from the nucleus of some radioactive atoms; they are equivalent to electrons in terms of mass and typically have an electrical charge of −1.

Radium concentrations in groundwater can be affected by multiple factors, including the distribution of uranium and thorium in aquifer materials, aquifer physical characteristics, and geochemical conditions that affect the mobility of uranium, thorium, and radium. Radium is an alkaline-earth metal and behaves chemically somewhat like calcium, strontium, and barium (Langmuir and Riese, 1985; Hem, 1985). Radium can enter groundwater by (1) decay of dissolved parent isotopes, (2) alpha recoil from mineral grains and surface layers, (3) desorption from aquifer surfaces, (4) dissolution of aquifer solids, and (5) leaching from radiation-damaged crystals (alpha-recoil tracks) (Krishnaswami and others, 1982; Sturchio and others, 1993; Tricca and others, 2001). Input from decay of dissolved parent isotopes is generally considered to be negligible for radium, because the parent thorium isotopes (table 14) are nearly insoluble in groundwater (Langmuir and Herman, 1980; Tricca and others, 2001). Radium can be removed from solution by (1) radioactive decay, (2) adsorption (Ames and others, 1983a, b) or ion exchange, including complexation with adsorbed species, or (3) co-precipitation with minerals that include radium as a trace constituent (Sturchio and others, 1993). Cation exchange, surface complexation, adsorption, and the formation of solid solutions (such as co-precipitation with barite) are considered to be the most significant in the retardation of radium mobility (Ames and others, 1983a,b; Langmuir and Riese, 1985; Shao and others, 2009). Increased radium concentrations in solution can result from increased cation concentration, which leads to competition with radium for adsorption sites (Kraemer and Reid, 1984; Langmuir and Melchior, 1985; Martin and Akber, 1999; Sturchio and others, 2001). This increasing competition explains why high radium concentrations often correlate with high dissolved solids (rho = 0.74, for dissolved solids–radium-226). This process of competition is applicable to the Cambrian-Ordovician aquifer system, where regionally confined areas of the aquifer system have older water with statistically significant higher dissolved solids content and corresponding statistically significant higher radium concentrations than water in regionally unconfined areas.

Radium-226 is the most abundant radium isotope in the environment in terms of mass because of its long half-life, and it accounts for more than 99 percent of the mass of natural radium (Sturchio and others, 1993). Radium-228 and radium-226 are chemically similar, but their distribution in groundwater can be different because of the different properties of their parent isotopes (thorium and uranium, respectively) and the large difference in half-life. The relatively high solubility of uranium, as compared to thorium, is the cause for the widespread distribution of uranium-238 and its daughter products such as radium-226 and radon-222. However, because uranium-238 and radium-226 have different geochemical properties, they do not necessarily occur together. Oxidized species of uranium (where the oxidation state is U^{6+}), such as uranyl (UO_2^{2+}), form soluble complexes in oxygen-rich conditions and are highly mobile; but under low-oxygen conditions, reduced species of uranium (where the oxidation state is U^{4+}) precipitate and become immobile (Langmuir, 1978) and can become enriched in the rock material relative to typical background concentrations. Wherever uranium becomes enriched, there is a possible supply of radium-226 for mobilization if the geochemical conditions permit. Thorium-232, the parent of radium-228 is extremely insoluble and is not mobile in most groundwater environments (Langmuir and Herman, 1980). The enrichment of thorium relative to background concentrations (for example, table 10 values from Horn and Adams, 1966) is a physical process, with thorium being associated with accessory minerals and feldspars that occur in igneous rocks such as granite and feldspar-rich (arkosic) sandstones (Gilkeson and Cowart, 1987; Michel and Cothern, 1986). The physical accumulation of these resistate minerals in stream-channel lag deposits is another process of thorium enrichment (King and others, 1982). The insolubility of thorium limits the distribution of radium-228 in groundwater to (1) areas with enriched thorium in rock material or (2) areas where, despite the absence of thorium-rich rock material, the geochemical environment is so favorable to radium mobility that radium-228 is nevertheless present in the water. The relatively short half-life of radium-228 (5.75 years) and the relatively slow movement of groundwater in most aquifers means that radium-228 cannot migrate far from its source before it decays. Radium-226, with its half-life of 1,622 years, can potentially remain in solution much longer than radium-228 unless it is removed from solution by some geochemical process such as adsorption. Thus, radium-226 can become enriched in water in the confined areas of the Cambrian-Ordovician aquifer system where water movement is slow but high concentrations of cations (and dissolved solids) may prevent radium from readily adsorbing to aquifer solids.

Michel and Cothern (1986) identified three main aquifer types predicted to have a high probability of producing groundwater with high radium-228 concentrations: (1) granitic rock aquifers, (2) arkosic sand and sandstone aquifers, and (3) quartzose sandstone aquifers, possibly with high dissolved solids. Arkosic sandstone, by definition, contains at least 25 percent feldspathic minerals, which can have high thorium content but can also contain the thorium-rich accessory minerals, such as monazite. Quartz sandstones have little sorption or exchange capacity; competition for the available sorption sites on the aquifer solids, especially in quartzose sandstones, is enhanced in high-dissolved-solids waters, thus causing radium to stay in solution (Michel and Cothern, 1986). The Cambrian-Ordovician aquifer system has lithologic and geochemical characteristics of all three of these aquifer types. The Mount Simon Sandstone has been described as arkosic and coarse grained, with igneous-rock pebbles and commonly containing fragments of the underlying Precambrian crystalline rock (Young, 1992b). Thus, the lithologic source of thorium and radium-228 is present in the Mount Simon. The aquifer system contains several quartzose sandstone aquifers (fig. 10), and much of the confined area of the aquifer system contains water with moderately high to high dissolved solids concentration. Data from Lively and others (1992) suggest that the Mount Simon Sandstone in Minnesota is enriched in thorium relative to the Jordan Sandstone and the “average” sandstone of Horn and Adams (1999) (table 10).

Radium samples collected by the NAWQA Program are filtered; therefore, the following discussions of radium concentrations in NAWQA samples refer to dissolved concentrations. Data from other sources are used to map the distribution of radium concentrations throughout the aquifer system. Other sources of USGS data (RASA Program and NWIS database) and data from the ISWS are also for filtered samples and represent dissolved concentrations, but radium data from all other state agencies are for unfiltered samples and represent whole-water or total concentrations. Comparison of filtered and unfiltered samples from municipal water supplies in the Midwest has shown the differences in radium activities to be negligible (Gilkeson and others, 1983; Lucas, 1985; Grundl and others, 2006), and this pattern has also been observed for a confined sand aquifer from the southwestern United States as well (Reynolds and others, 2003).

Occurrence and Distribution

Radium-226 and radium-228 were analyzed in samples from 88 of the NAWQA wells during the period 2005 through 2007. Samples were collected at 39 wells in Iowa, 21 wells in Illinois, 23 wells in the Twin Cities metropolitan area, and 5 wells in the eastern Wisconsin-Upper Peninsula sampling area. This distribution of sampling resulted in 52 wells in the regionally confined area and 36 wells in the regionally unconfined area. Radium-226 was detected in 94 percent (83 of 88) of the NAWQA samples without an assessment level and in 70 percent of the samples at an assessment level of 1 pCi/L (table 15). An assessment level of 1 pCi/L is higher than the ssL_C of any of the NAWQA samples, but it is a common reporting level in older data and data from other sources, indicating that less sensitive analytical techniques were used. The concentration (activity) of radium-226 in most of the NAWQA samples (80 percent) ranged from 0.05 to 7.45 pCi/L, with a median value of 2.33 pCi/L (table 15). The CSU at the 68 percent (1-sigma) confidence level for the radium-226 measurements ranged from 0.013 to 0.216 pCi/L for most of the samples (80 percent), with a median of 0.08 pCi/L and a mean of 0.12 pCi/L. Low values of radium-226 (or radium-228) near the ssL_C have large relative uncertainty associated with them because of the variability of natural background levels of radioactivity and the random nature of radioactive decay. This large variability is reflected in the variability in replicate pairs, which had low concentrations, and in the reported values in field blanks (appendix 4, tables 4–1 and 4–2).

Radium-226 concentrations were positively correlated with radium-228 (rho = 0.76), dissolved solids (0.74), specific conductance (0.74), sulfate (0.73), well depth and casing depth (0.70 for both), and water temperature (0.65) (appendix 3). Radium-226 concentrations were also positively correlated with several major ions and trace elements indicative of older, more mineralized water, such as fluoride, strontium, lithium, sodium, and potassium (appendix 3). Radium-226 concentrations were negatively correlated with several constituents that are indicative of oxic groundwater with modern recharge, including lead (rho = −0.59), nitrate (−0.56), zinc (−0.49), dissolved oxygen (−0.45), tritium (−0.43), silica (−0.41), and radon-222 (−0.38). Correlation between radium concentrations and concentrations of other constituents does not necessarily indicate cause-and-effect relations. However, consistent patterns of co-occurrence among constituents may indicate the presence of specific geochemical environments or geochemical processes.

The relation of radium-228 concentrations to radium-226 concentrations can be shown in units of picocuries per liter (fig. 44*A*) or units of mass (fig. 44*B*). The five samples with radium-226 concentrations below their corresponding ssL_C also had radium-228 concentrations below their corresponding ssL_C. All 15 samples with radium-228 concentrations below their corresponding ssL_C had radium-226 concentrations less than 0.25 pCi/L. In samples where both isotopes were detected, radium-226 concentrations, in units of picocuries per liter, were greater than radium-228 concentrations in most samples (fig. 44*A*). However, in units of mass, radium-226 concentrations are two to three orders of magnitude greater than concentrations of radium-228 (fig. 44*B*). This illustrates the fact that the radium-226 isotope accounts for over 99 percent of radium because of its much longer half-life. Figure 44*A* also illustrates the difference in the ability of the analytical methods for the two isotopes to detect low concentrations of radium. The five nondetections of radium-226 have corresponding values of ssL_C of 0.02 pCi/L, whereas nondetections of radium-228 are an order of magnitude higher and have corresponding values of ssL_C that range from 0.19 to 0.29 pCi/L.

Radium-226 concentrations were significantly higher ($p < 0.001$) in water samples from wells in regionally confined areas than from wells in regionally unconfined areas (fig. 45; table 7). The median concentration was 3.44 pCi/L in samples from confined wells and 0.16 pCi/L in the unconfined wells. Radium-226 concentrations were also significantly higher ($p < 0.001$) in wells with a tritium-based recharge age of pre-1953 than in wells with a recharge age of modern (post-1953). The median concentration was 3.38 pCi/L in samples with pre-1953 recharge and 0.19 pCi/L in samples with modern recharge. The distribution of radium-226 concentrations can also be grouped by cation facies. Samples from a subset ($n = 200$) of the wells from multiple sources used to make the hydrochemical facies maps were analyzed for radium-226. Radium-226 concentrations were significantly different ($p < 0.05$) for all three cation facies, with median concentrations progressively increasing from the calcium-magnesium to the sodium-calcium facies (fig. 46). Median radium-226 concentrations were 0.5 pCi/L for the calcium-magnesium facies, 2.8 pCi/L for the calcium-sodium facies, and 6.0 pCi/L for the sodium-calcium facies. The regionally confined area is characterized by older (pre-1953), more reduced, more mineralized groundwater (high dissolved solids) that typically has a calcium-sodium or sodium-calcium cation facies. These mineralized and reducing conditions are favorable to the mobility of radium-226, resulting in high radium-226 concentrations and associations with high concentrations of many other constituents.

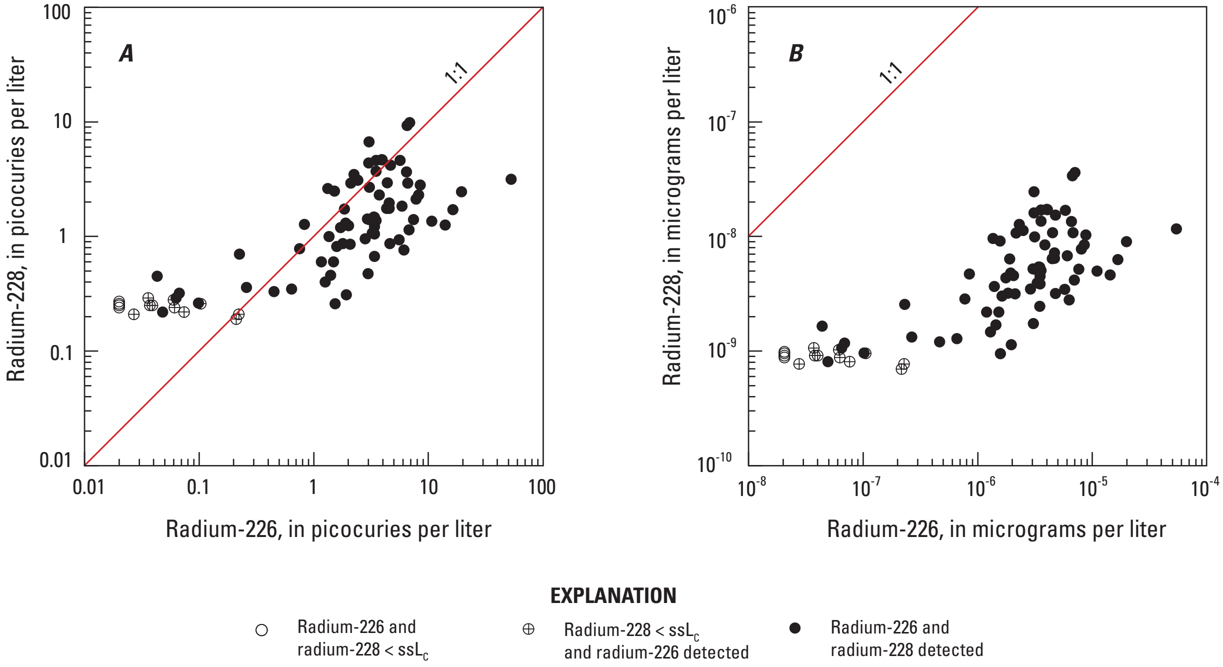


Figure 44. Relation of radium-228 concentrations to radium-226 concentrations in units of *A*, picocuries per liter and *B*, micrograms per liter for water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 2005–7 (ssL_C; sample-specific critical level; see McCurdy and others, 2008).

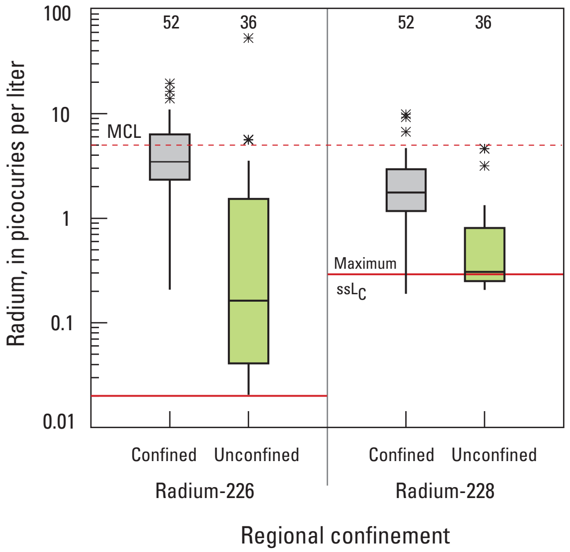


Figure 45. Distribution of radium-226 and radium-228 concentrations by regional confinement for water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 2005–7 (MCL, Maximum Contaminant Level for radium-226 + radium-228; ssL_C; sample-specific critical level).

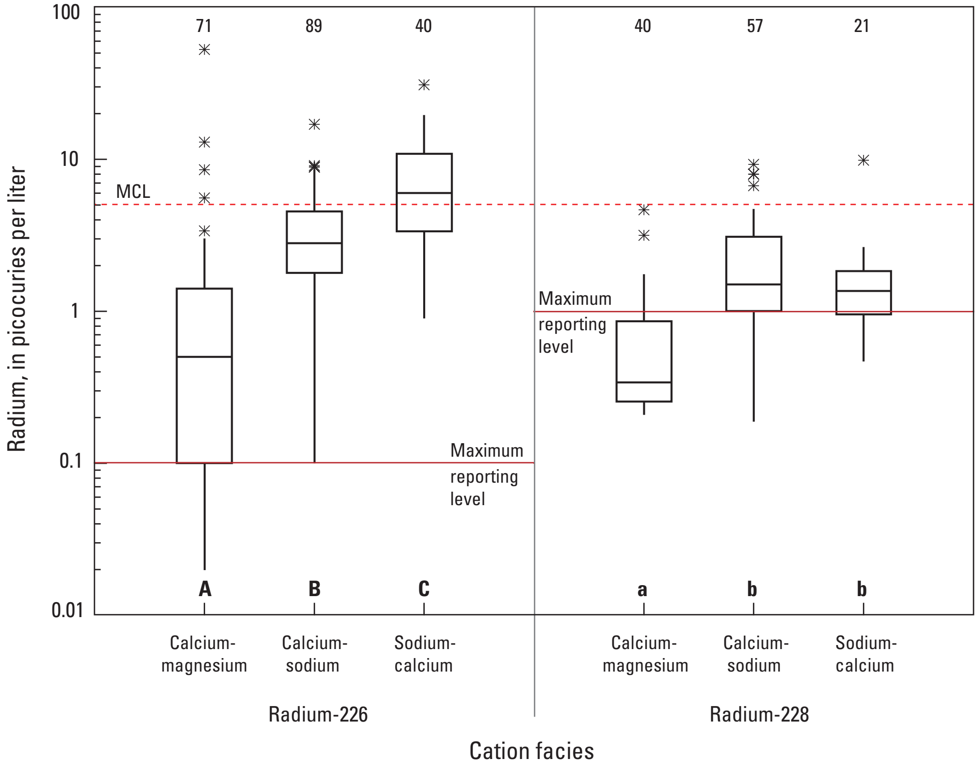


Figure 46. Distribution of radium-226 and radium-228 concentrations by cation facies for a subset of wells used to map hydrochemical facies in the Cambrian-Ordovician aquifer system (MCL, Maximum Contaminant Level).

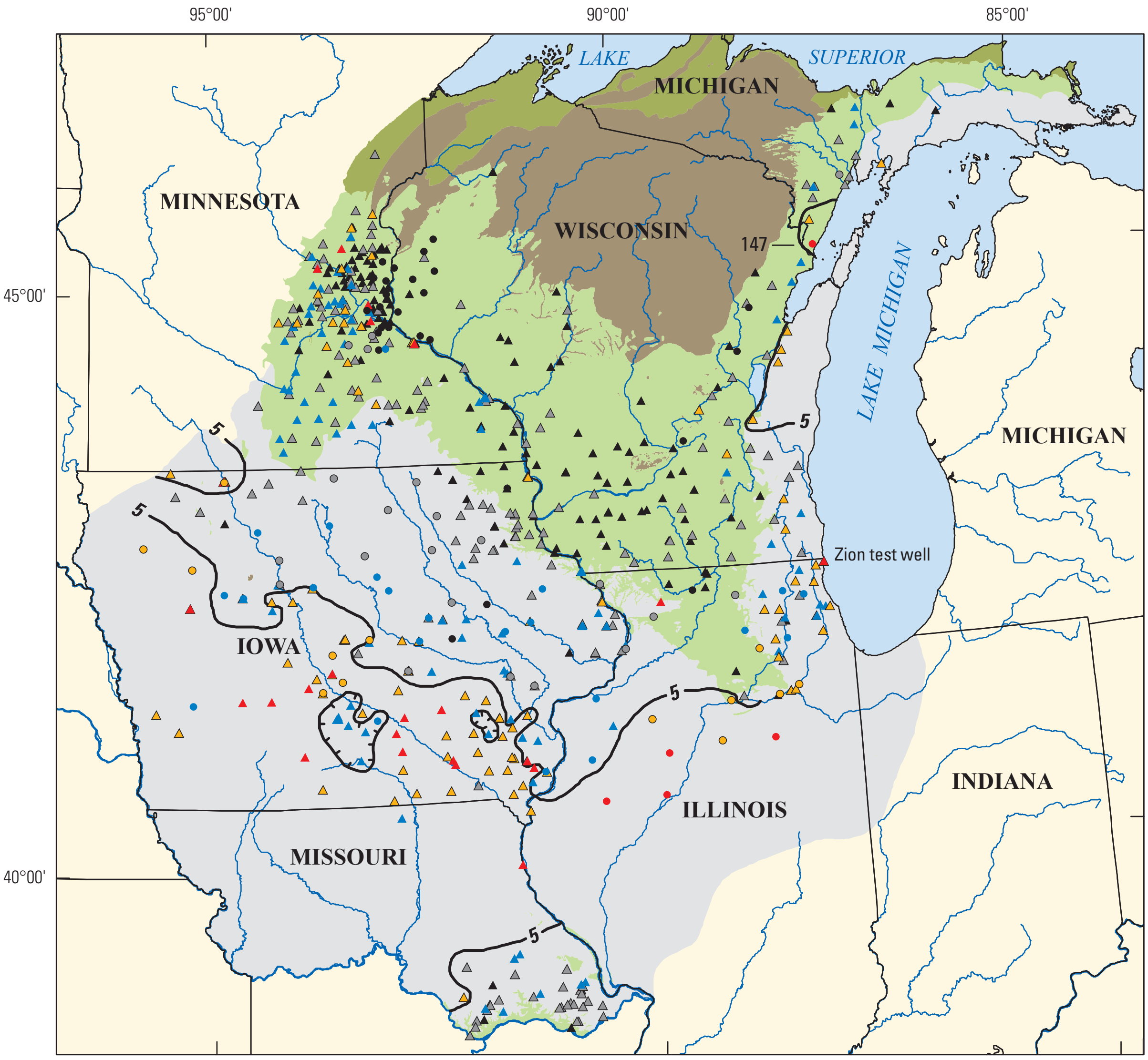
The highest concentration of radium-226 measured by the NAWQA Program (52.8 ±1.5 pCi/L) was in the sample from well number 147 in the Upper Peninsula (shown in figs. 2 and 47). Well 147 is in the regionally unconfined area just west of the boundary of regional confinement at the southern end of the Upper Peninsula. Water from this well has a calcium-magnesium cation facies and contains pre-1953 recharge. It does not fit the general pattern of high radium concentrations in regionally confined wells with a calcium-sodium or sodium-calcium cation facies. However, it does fit other associated patterns, like having high concentrations of dissolved solids, sulfate, fluoride, and strontium. Other wells sampled by NAWQA in this area had high concentrations of sulfate, fluoride, and strontium; however, they were not sampled for radium.

Radium-228 was detected in 83 percent (73 of 88) of the NAWQA samples without an assessment level and in 54 percent of the samples at an assessment level of 1 pCi/L (table 15). An assessment level of 1 pCi/L is higher than the ssL_C of any of the NAWQA samples, but it is a common reporting level in older data and data from other sources. The concentration of radium-228 in most of the NAWQA samples (80 percent) ranged from 0.22 to 4.19 pCi/L, with a median value of 1.16 pCi/L (table 15). The higher 10th-percentile concentration in the population distribution of radium-228 as compared to that of radium-226 is a function of less precision for the radium-228 analytical method. The background for beta particles can be higher than for alpha particles, and beta particles can also be more difficult to detect (Zoltan Szabo, U.S. Geological Survey, written commun., 2011). For values of radium-228 less than the ssL_C, the measured activity could not be distinguished from the background. The CSU at the 68 percent (1-sigma) confidence level for the radium-228 measurements ranged from 0.095 to 0.21 pCi/L for most of the samples (80 percent), with a median of 0.13 pCi/L and a mean of 0.14 pCi/L. In general, radium-228 had the same significant Spearman rank correlations as radium-226, but at slightly lower values of rho (appendix 3).

Radium-228 concentrations were significantly higher ($p < 0.001$) in water samples from wells in regionally confined areas than in samples from wells in regionally unconfined areas (fig. 45; table 7). The median concentration was 1.74 pCi/L in the confined wells and 0.30 pCi/L in the unconfined wells. Radium-228 concentrations were also significantly higher ($p < 0.001$) in wells with a tritium-based recharge age of pre-1953 than in wells with a recharge age of post-1953 (modern). The median concentration was 1.47 pCi/L in the wells with pre-1953 recharge and 0.26 pCi/L in the wells with modern recharge. The distribution of radium-228 concentrations can also be grouped by cation facies. Samples from a subset ($n = 118$) of the wells from multiple sources used to make the hydrochemical facies maps were analyzed for radium-228. Radium-228 concentrations were significantly higher ($p < 0.05$) in samples with calcium-sodium and sodium-calcium cation facies than in those samples with a calcium-magnesium facies (fig. 46). Unlike radium-226, radium-228 concentrations did not increase from the calcium-sodium to the sodium-calcium facies, and the distribution of radium-228 in these facies was not significantly different (fig. 46). Median radium-228 concentrations were 0.32 pCi/L for the calcium-magnesium facies, 1.5 pCi/L for the calcium-sodium facies, and 1.36 pCi/L for the sodium-calcium facies. The difference in the distribution of radium-228 and radium-226 suggests that radium-228 is not as affected by increased mineralization (as is radium-226) and the changes in ion chemistry that occur with it, such as cation exchange of Na^+ for Ca^{+2}. However, the considerable differences in half-lives of the radium isotopes, as well as in the occurrence of the parent radionuclides (thorium and uranium, respectively), may also affect radium isotope distribution. The highest radium-228 concentration measured by the NAWQA Program, 9.86 ±0.32 pCi/L, was from well 45 in central Illinois (shown in fig. 48). This well also had a radium-226 concentration of 6.9 pCi/L, for a combined radium concentration of 16.76 pCi/L.

The USEPA MCL of 5 pCi/L for radium in drinking water is for combined radium-226 and radium-228 (hereafter referred to as combined radium). The MCL was exceeded in 39.8 percent (35 of 88) of the NAWQA samples (table 16). All but four of the samples that exceeded the MCL were from wells in the regionally confined areas (table 17), and all samples that exceeded the MCL had a tritium-based age of pre-1953. This pattern of occurrence agrees with the general understandings that dissolved solids concentrations increase with residence time in response to water-rock interactions and that the increase in dissolved solids is favorable for the mobilization of radium, leading to higher dissolved radium concentrations in the groundwater. There were 18 wells (20.4 percent) that exceeded the MCL only on the basis of the radium-226 concentration, and 3 wells that exceeded the MCL only on the basis of the radium-228 concentration. All samples that exceeded the MCL for combined radium had quantifiable detections of both isotopes. Of the aquifers with at least four NAWQA samples, the seven samples from the St. Peter Sandstone in Illinois and Iowa had the highest median concentration of radium-226 (6.9 pCi/L), and the eight samples from the Ironton-Galesville Sandstone in Illinois had the highest median concentration of radium-228 (4.51 pCi/L). Samples from these two aquifers had a high percentage of exceedance of the MCL for combined radium (table 17). The prevalence of higher concentrations of radium-226 relative to radium-228 is similar to that noted for waters from midcontinent carbonate aquifers by Sturchio and others (2001).

Data from other sources (table 3) were combined with the NAWQA data to evaluate the distribution of radium-226 in the Cambrian-Ordovician aquifer system (fig. 47). Radium-226 samples were available for 617 wells for the period 1969 through 2008 (table 4). Approximately 92 percent of the data were for the period 1980–2008, and 63 percent of the data were for the period 2000–8. The wells were evenly distributed between the confined and unconfined areas, with 53 percent of the wells in confined areas and 47 percent of the wells in unconfined areas. As with the NAWQA dataset, radium-226



Base from U.S. Geological Survey digital data, 1972, 1:2,000,000 Albers Equal-Area Conic projection, Standard parallels 29°30'N and 45°30'N; central meridian -96°00'W

Modified from U.S. Geological Survey Ground Water Atlas of the United States, 2000

EXPLANATION

Aquifer-system confinement

🟩 Regionally unconfined

⬜ Regionally confined

Rock type

🟩 Precambrian sandstone

🟫 Precambrian crystalline

— 5 — **Line of equal radium-226 concentration**—Shows approximate boundary where radium-226 concentrations are usually greater than 5 picocuries per liter. Hachured in direction of lower concentration

Radium-226, in picocuries per liter

● ≤ 1.00
● 1.01 to 3.00
● 3.01 to 5.00
● 5.01 to 10.0
● > 10.0

○147 **Well sampled by the NAWQA Program**—Where shown, number is the well number

△ **Data from another source**

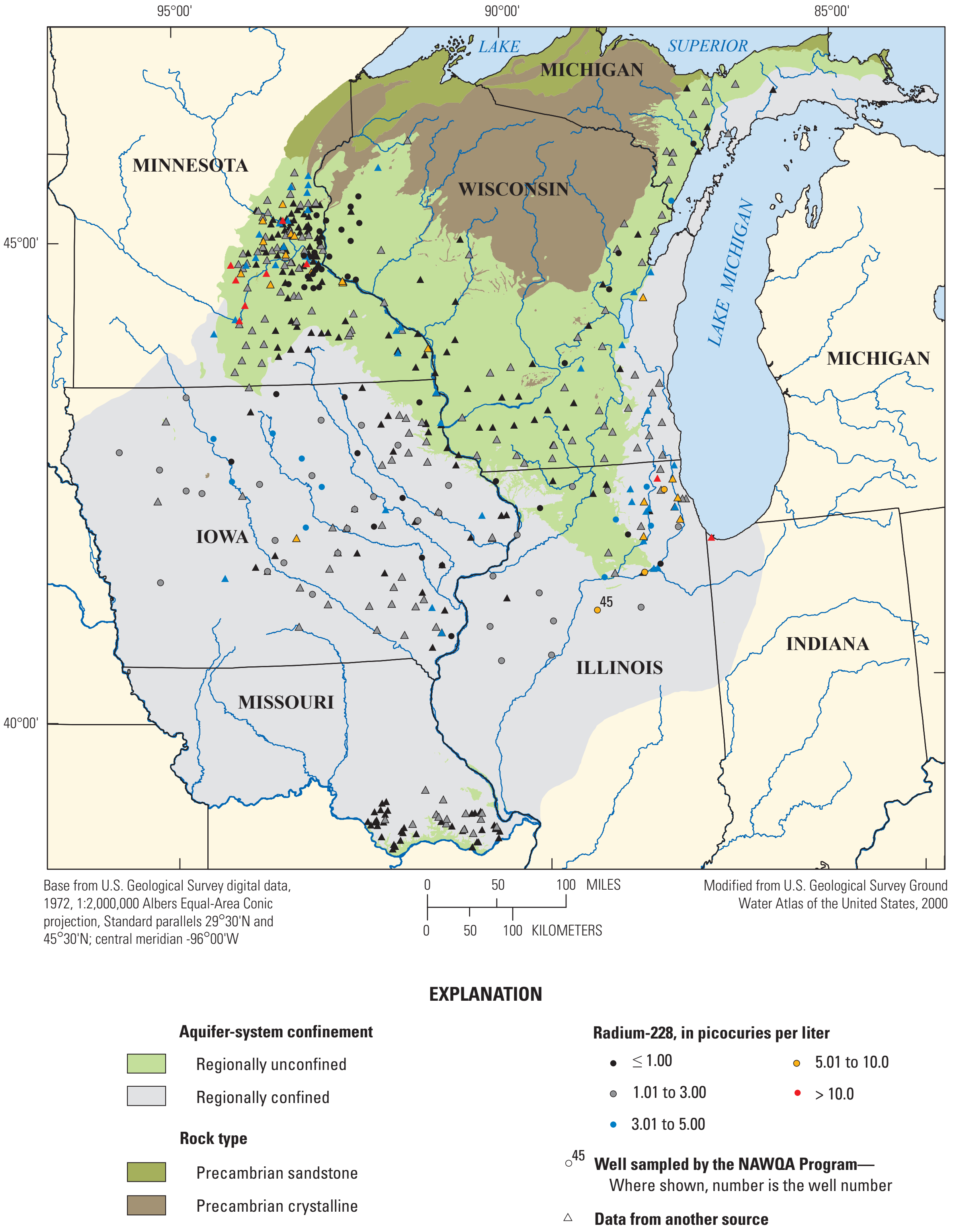
Figure 47. Radium-226 concentrations in water samples from wells completed in the Cambrian-Ordovician aquifer system, 1969–2008.

concentrations were positively correlated with sulfate (rho = 0.65), and radium-226 concentrations were significantly higher ($p < 0.001$) in samples from the regionally confined area (median = 3.8 pCi/L) than in samples from the unconfined area (median = 1.4 pCi/L). Radium-226 concentrations greater than 5 pCi/L occur in samples throughout the study area, but most are from wells in the confined areas of the aquifer system in western and southern Iowa, Illinois, and eastern Wisconsin (fig. 47). In these confined areas, samples from several wells had radium-226 concentrations that exceeded 10 pCi/L. The highest value of radium-226 was 99 pCi/L, which was from the Zion test well in the extreme northeastern corner of Illinois (Siegel, 1989). This value was measured in a sample from the lower part of the Mount Simon Sandstone, at a depth not suitable for drinking water because of high salinity (3,120 ft; 56,000 mg/L). The RASA study also measured radium-226 concentrations of 6.9 pCi/L in a sample from the upper Mount Simon Sandstone and 6.0 pCi/L in a sample from the St. Peter Sandstone at this location (Siegel, 1989).

Data from other sources (table 3) were combined with the NAWQA data to evaluate the distribution of radium-228 in the Cambrian-Ordovician aquifer system (fig. 48). Radium-228 samples were available for 490 wells for the period 1982 through 2008 (table 4). Approximately 79 percent of the data were for the period 2000–2008. Approximately 57 percent of the wells were in the unconfined areas, and 43 percent of the wells were in the confined areas. Of the available data, 105 of the 490 samples (21 percent) were nondetections, with reporting levels that ranged from 0.19 to 1.0 pCi/L. As with the NAWQA dataset, radium-228 concentrations were significantly higher ($p = 0.038$) in samples from the confined area (median = 1.40 pCi/L) than from the unconfined area (median = 1.10 pCi/L). However, the difference in the distributions of radium-228 concentrations in regionally confined and unconfined areas of the aquifer system was not as apparent as it was for concentrations of radium-226. The difficulty in measuring radium-228 concentrations at levels as low as for radium-226 results in a much greater frequency of samples with radium-228 concentrations reported as less than a reporting level of 1.0 pCi/L than is the case for measurements of radium-226. Therefore, differences in concentration distributions are more difficult to resolve for radium-228 than for radium-226. There were fewer samples with a radium-228 concentration greater than 5 pCi/L than there were for radium-226, and the majority of high concentrations were clustered in two areas; northeastern Illinois and in Minnesota (fig. 48). The Mount Simon and Hinckley sandstones of Minnesota are known to have high radium-228 concentrations (Lively and others, 1992). Of the available data, radium-228 exceeded 10 pCi/L in several wells in the Mount Simon Sandstone or Mount Simon-Hinckley aquifer in Minnesota and in one well in the Ironton-Galesville Sandstone in northeastern Illinois. The sample that exceeded 10 pCi/L in northwestern Indiana was from an industrial well in the Cambrian System. The highest value of radium-228 was 23.8 pCi/L in a MDH sample from a well near the Minnesota River in northern Blue Earth County, near the western boundary of the aquifer system (see fig. 50). The high radium-228 concentrations in the Mount Simon-Hinckley aquifer are probably a result of the enriched thorium concentrations (relative to the "average" sandstone of Horn and Adams, 1966) in the aquifer matrix (Lively and others, 1992) (table 10). In Missouri, the maximum concentration of radium-228 was 2.4 pCi/L, and most samples contained less than 1 pCi/L.

Figure 49 shows the distribution of combined radium in the Cambrian-Ordovician aquifer system. There were 506 wells available with sample results for both isotopes, or with a concentration of one isotope that exceeded the MCL of 5 pCi/L by itself. Sample dates ranged from 1969 to 2008, but 95 percent of samples were collected during the period 1980–2008. Of the available data, 22 wells had nondetections for both isotopes of radium, with reporting levels that ranged from 0.24 to 1.0 pCi/L. The wells were evenly distributed between the regionally confined and unconfined areas, with 45 percent of the wells in confined areas and 55 percent of the wells in the unconfined areas. Combined radium concentrations were significantly higher ($p < 0.001$) in samples from wells in the regionally confined areas than in samples from wells in the unconfined areas. The median concentration of combined radium was 6.8 pCi/L in wells in the confined areas and 2.6 pCi/L in wells in the unconfined areas.

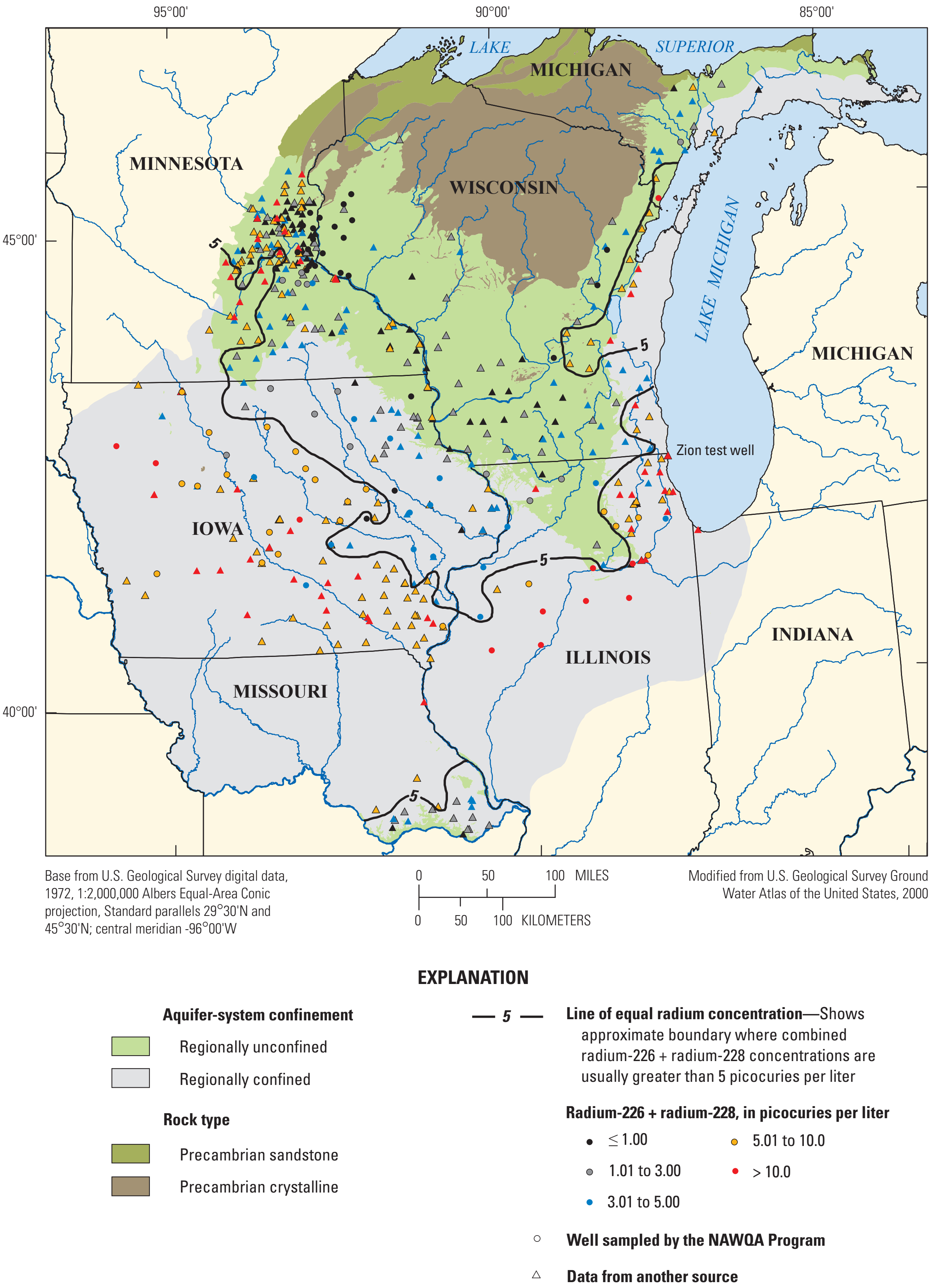
It is apparent from figure 49 that concentrations of combined radium commonly exceed the MCL of 5 pCi/L in Minnesota. Many of the wells in the dataset are completed in the Mount Simon Sandstone or Mount Simon-Hinckley aquifer, which are known to have high radium concentrations in Minnesota (Lively and others, 1992). The aquifer system is regionally unconfined in most of southeastern Minnesota relative to the Maquoketa Shale, which is absent in the area; however, other leaky confining units like the St. Lawrence, Franconia, and Eau Claire Formations probably are effective confining units for aquifers below them. Lively and others (1992) measured carbon-14 concentrations to age-date the time of recharge, and their results suggested confinement at many wells based on extremely long calculated residence times. Age dates for water samples from the Mount Simon-Hinckley aquifer ranged from modern (post 1953) to more than 35,000 years before present. Many of the water samples from the wells had recharge dates exceeding 1,600 years before present. The distribution of combined radium in samples from 182 wells in Minnesota is shown in figure 50. Sources of data were MDH, NAWQA, NWIS, and RASA. Radium concentrations are plotted for two categories of wells; those that are at least partially open to the Mount Simon Sandstone but no shallower aquifer, and those that produce from other aquifers above the Mount Simon Sandstone. Other aquifers and formations represented in this dataset for Minnesota include just about every formation above the Mount Simon Sandstone (fig. 10). Some wells are completed in one formation, and some wells are open to multiple formations. A few of the Mount Simon wells also extend into the underlying Hinckley Sandstone. Concentrations of combined



Base from U.S. Geological Survey digital data, 1972, 1:2,000,000 Albers Equal-Area Conic projection, Standard parallels 29°30'N and 45°30'N; central meridian -96°00'W

Modified from U.S. Geological Survey Ground Water Atlas of the United States, 2000

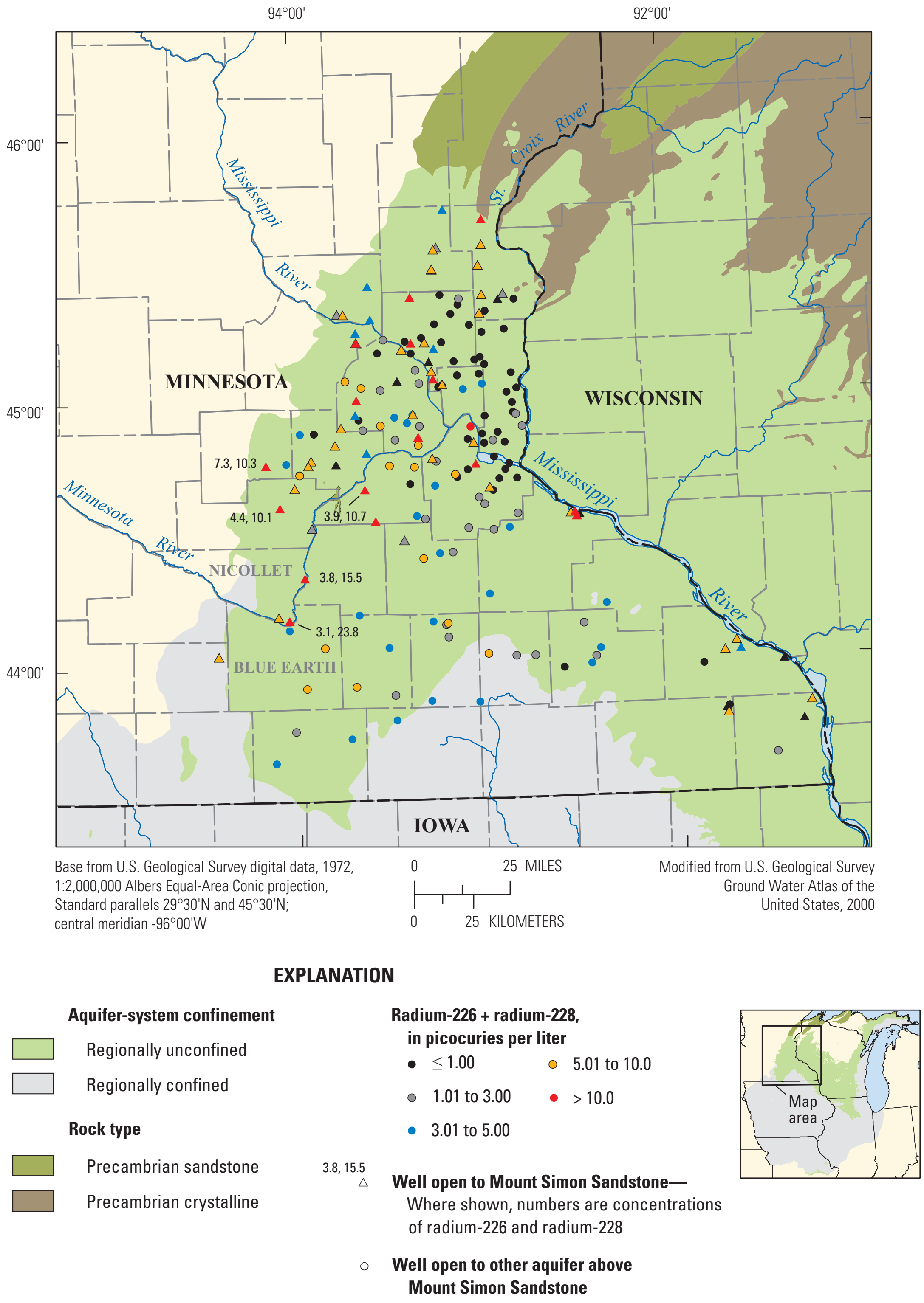
Figure 48. Radium-228 concentrations in water samples from wells completed in the Cambrian-Ordovician aquifer system, 1982–2008.



Base from U.S. Geological Survey digital data, 1972, 1:2,000,000 Albers Equal-Area Conic projection, Standard parallels 29°30'N and 45°30'N; central meridian -96°00'W

Modified from U.S. Geological Survey Ground Water Atlas of the United States, 2000

Figure 49. Combined radium-226 + radium-228 concentrations in water samples from wells completed in the Cambrian-Ordovician aquifer system, 1969–2008.



Base from U.S. Geological Survey digital data, 1972, 1:2,000,000 Albers Equal-Area Conic projection, Standard parallels 29°30'N and 45°30'N; central meridian -96°00'W

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Figure 50. Combined radium-226 + radium-228 concentrations in water samples from wells completed in the Cambrian-Ordovician aquifer system in Minnesota, 1980–2007.

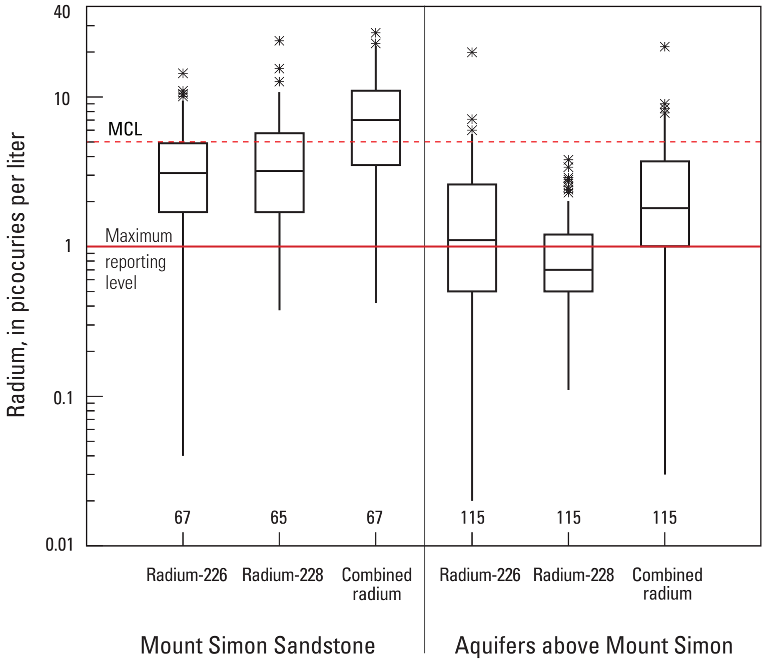


Figure 51. Comparison of radium-226, radium-228, and combined radium concentrations in Minnesota wells open to the Mount Simon Sandstone with wells open to other aquifers above the Mount Simon Sandstone (MCL, Maximum Contaminant Level).

radium greater than the MCL occur throughout the State but are much more common in samples from wells that are open to the Mount Simon Sandstone. Radium concentrations were significantly higher ($p < 0.001$) for wells open to the Mount Simon Sandstone than for wells open to aquifers above the Mount Simon Sandstone (fig. 51). This preferential distribution was the case for radium-226, radium-228, and combined radium. For wells open to the Mount Simon Sandstone, median concentrations of radium-226, radium-228, and combined radium were 3.1, 3.2, and 7.0 pCi/L. For wells open to aquifers above the Mount Simon Sandstone, median concentrations of radium-226, radium-228, and combined radium were 1.1, 0.7, and 1.8 pCi/L. Portions of the boxplots below 1 pCi/L should be considered as estimated because of nondetections (fig. 51). In this particular dataset, 37 percent (67 of 182) of the wells are open to the Mount Simon Sandstone, but they account for 75 percent of the samples with combined radium concentrations greater than 5 pCi/L. Approximately 66 percent of the wells open to the Mount Simon Sandstone have combined radium concentrations greater than 5 pCi/L, and 13 percent of the wells open to other aquifers have combined radium concentrations greater than 5 pCi/L.

Geochemical Controls on Radium Concentrations

The following discussion on geochemical controls on radium concentrations is based on water-quality data from the 88 wells that were sampled by the NAWQA Program. The previous section on the occurrence and distribution of radium showed that both isotopes of radium occur at greater concentrations in the suboxic, more mineralized, reducing waters of the regionally confined areas of the aquifer system. Concentrations of radium-226 and radium-228 were negatively correlated with concentrations of dissolved oxygen (appendix 3). The relation between concentrations of combined radium and concentrations of dissolved oxygen appears to be nearly hyperbolic (fig. 52). Concentrations of combined radium were very low or not detectable when concentrations of dissolved oxygen were measurable, and concentrations of radium were high when concentrations of dissolved oxygen were very low or not detectable. Nondetections of dissolved oxygen were plotted at the maximum reporting level of 0.18 mg/L (fig. 52). The pattern of occurrence among radium and dissolved oxygen is indicative of the strong preference of radium for the reducing geochemical environment. This pattern was also apparent in a larger dataset from a national synthesis of radium

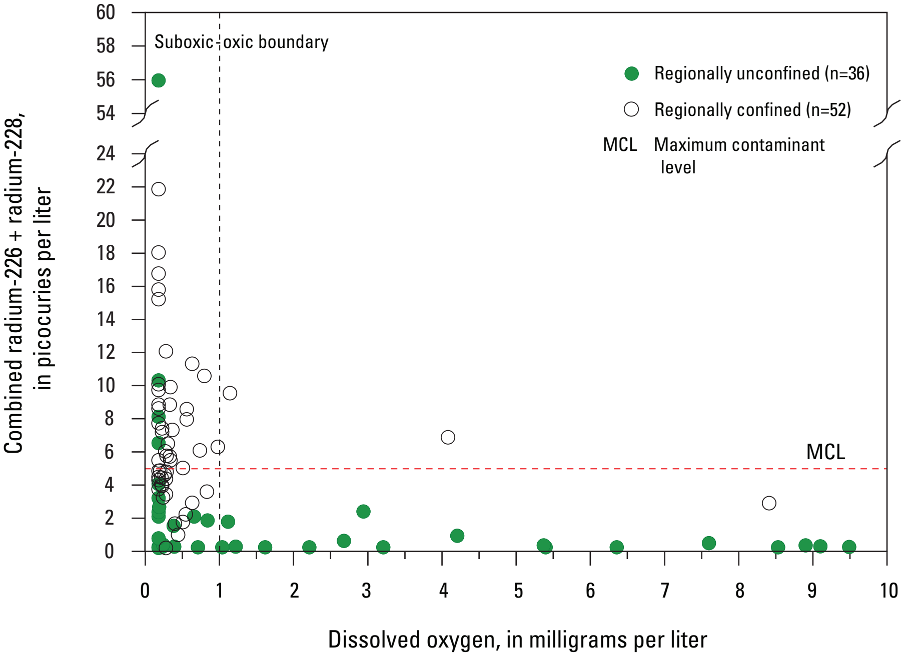


Figure 52. Relation of combined radium (radium-226 + radium-228) concentrations to dissolved oxygen concentrations for water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 2005–7.

by Szabo and others (2012). When combined radium concentrations are grouped by the three redox conditions shown in figure 20 (oxic, mixed source, anoxic), there is a significant difference (at the 0.05 significance level) between oxic samples and samples that are mixed source or anoxic. Combined radium concentrations are significantly lower in oxic samples (median = 0.27 pCi/L) than in anoxic samples (median = 4.88 pCi/L) or mixed redox samples (median = 3.98 pCi/L). However, there is no significant difference in combined radium concentrations between anoxic samples and samples with a mixed redox condition.

A certain set of geochemical processes likely explains why mineralized and reducing conditions are favorable to the mobility of radium. Ames and others (1983a, b) conducted studies of radium adsorption on secondary minerals and found that iron hydroxide adsorbed far more radium than any other secondary minerals. Szabo and Zapecza (1991) concluded that iron hydroxides along fractures in rocks strongly adsorbed radium from solution, exerting control on radium-226 concentration in the groundwater of the clastic sedimentary-rock aquifer system of the Newark basin in central New Jersey. Radium-226 concentrations were highest in reducing waters, where iron hydroxide was unstable and was less abundant or absent on mineral grains, providing few adsorption sites for radium (Szabo and Zapecza, 1991). The same factor is probably important for adsorption sites in the confined parts of the Cambrian-Ordovician aquifer system. The high dissolved solids content of the water allows for extensive competition for the remaining sorption sites, and the radium concentrations are high in the mineralized waters of confined areas (fig. 45). The mineralized and reducing conditions are compatible with the proposed presence of geochemical processes that are favorable to the mobility of radium.

The relation between the radon-222:radium-226 ratio (Rn:Ra226 ratio) and sulfate concentrations illustrates the contrast in mobility of these two radionuclides relative to reducing conditions in groundwater (fig. 53). The Rn:Ra226 ratios are much higher in samples from regionally unconfined wells, where the groundwater is less reducing as indicated by the lower sulfate concentrations. In areas where the aquifer system is oxic and not reducing, fracture surfaces and mineral grains can become coated with secondary minerals, including iron and manganese hydroxides. These hydroxides adsorb radium-226 and thorium-230 from solution, and grain coatings

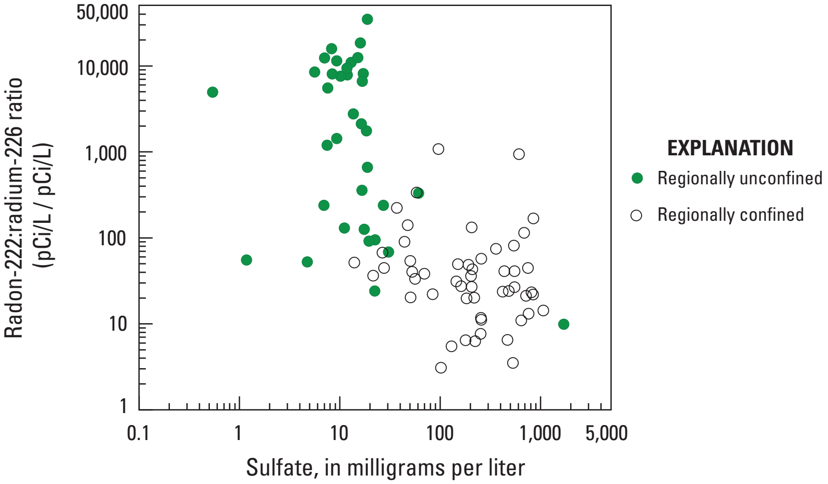


Figure 53. Relation of the radon-222:radium-226 ratio to sulfate concentration for water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 1995–2007.

can become enriched in these isotopes. As radium-226 decays from the surface coatings, radon-222, which does not adsorb to the coatings, enters the pore water by alpha-particle decay and alpha recoil. Because of the alpha recoil of radon-222 from radium-226 in the surface coatings, concentrations of radon-222 in the water will be much higher than if derived solely from dissolved radium-226 (Tanner, 1964; Szabo and Zapecza, 1991). This process may explain why radon-222 concentrations were higher in samples from the Prairie du Chien Group than from the Jordan Sandstone in the Twin Cities metropolitan area (fig. 42). The carbonates of the Prairie du Chien Group may have karst-related fractures and dissolution channels that are coated with radium-enriched hydroxides. Rn:Ra226 ratios are lower in samples from regionally confined wells, or wells that otherwise have reducing conditions, as indicated by the higher sulfate concentrations (fig. 53). The reducing conditions allow for increased radium-226 mobility and, therefore, higher radium-226 concentrations in water.

When concentrations of combined radium were grouped by dominant anion (bicarbonate, n = 64; sulfate, n = 20; chloride, n = 4) there was a significant difference ($p < 0.05$) in radium concentrations between the bicarbonate waters and the sulfate or chloride waters. Samples with bicarbonate as the dominant anion had significantly lower concentrations of combined radium (median = 2.38 pCi/L) than samples with sulfate (median = 7.22 pCi/L) or chloride (median = 9.90 pCi/L) as the dominant anion. There was no significant difference in radium concentrations between the sulfate- and chloride-dominated samples. The chloride-dominated samples had a higher median concentration of radium than did the sulfate-dominated samples, but there were only four samples with chloride as the dominant anion. This distribution of radium concentrations (with lower concentrations in bicarbonate-dominated samples and higher concentrations in sulfate- or chloride-dominated samples) is consistent with the understanding that radium concentrations are higher in anoxic, reducing waters with high dissolved solids concentrations.

Even though fluoride concentrations have a relatively small range, they have a strong positive correlation with concentrations of radium-226 (rho = 0.77) and radium-228 (0.62). Emrich and Lucas (1963) previously demonstrated the positive correlation of radium-226 concentrations with fluoride and dissolved solids concentrations in wells that produce water from the Glenwood-St. Peter Sandstone in Illinois. Ranges in concentrations of combined radium have been incorporated into scatterplots that show the relations between concentrations of dissolved solids and sulfate (fig. 54*A*), sodium and fluoride (fig. 54*B*), and iron and sulfate (fig. 54*C*). Concentrations of these constituents all correlate positively with each other and with concentrations of both radium isotopes. The correlations show that the constituents occur in common in water with similar geochemical conditions. Most samples (28 of 35) with combined radium concentrations greater than 5 pCi/L have sulfate concentrations greater than 100 mg/L and dissolved solids concentrations greater than 500 mg/L (fig. 54*A*). Most samples (8 of 11) with combined radium concentrations greater than 10 pCi/L have dissolved solids concentrations greater than 1,000 mg/L. Of the 35 samples with a combined radium concentration greater than 5 pCi/L, 27 have fluoride concentrations greater than 1 mg/L and sodium concentrations greater than 50 mg/L (fig. 54*B*). Threshold concentrations of iron (100 µg/L) and sulfate (0.5 mg/L) are two variables used for identifying redox processes in groundwater (McMahon and Chapelle, 2008). Most samples (28 of 35) with combined radium concentrations greater than 5 pCi/L occur in wells where the redox process is iron reduction and sulfate reduction, as indicated by concentrations above these thresholds (fig. 54*C*).

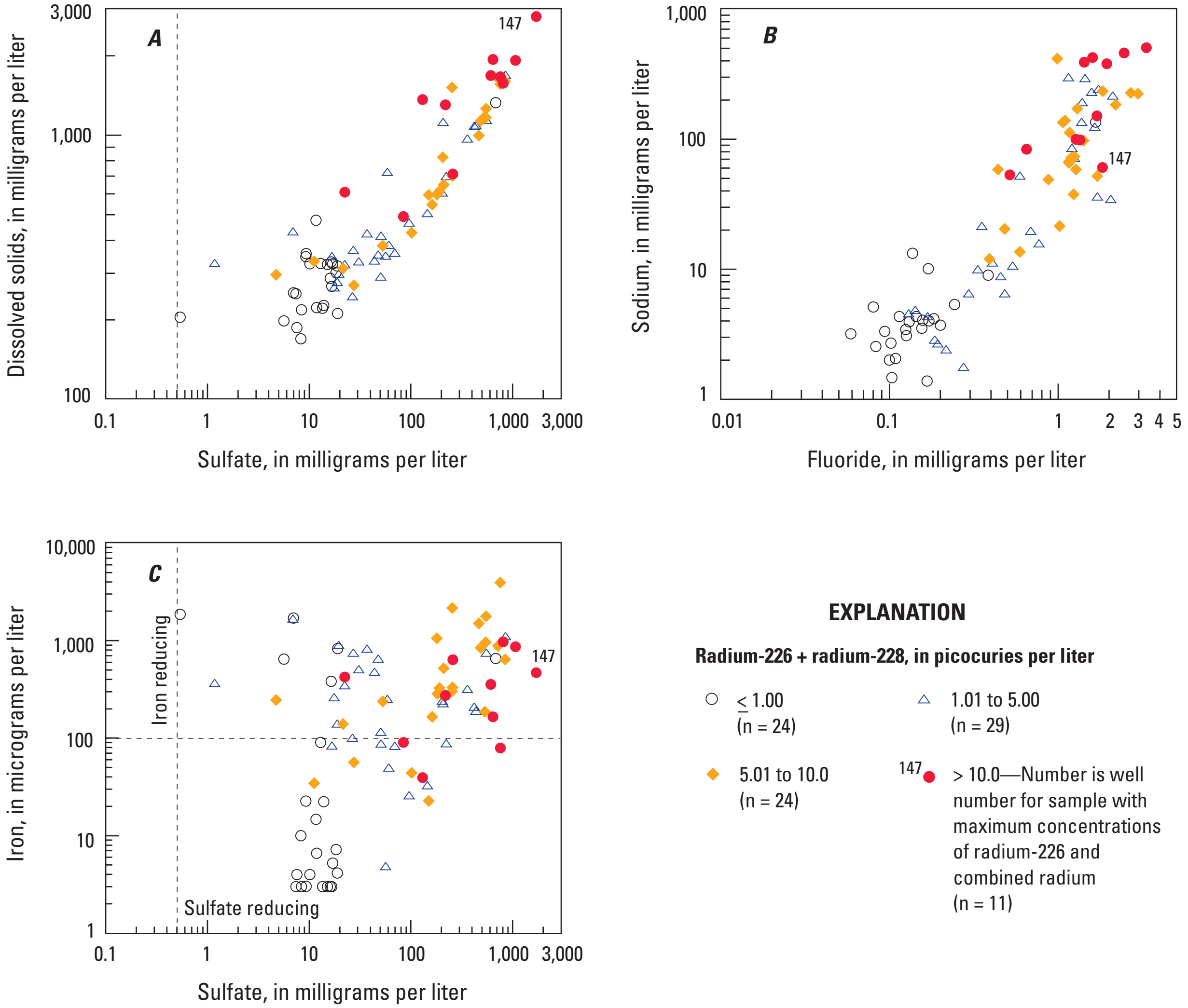
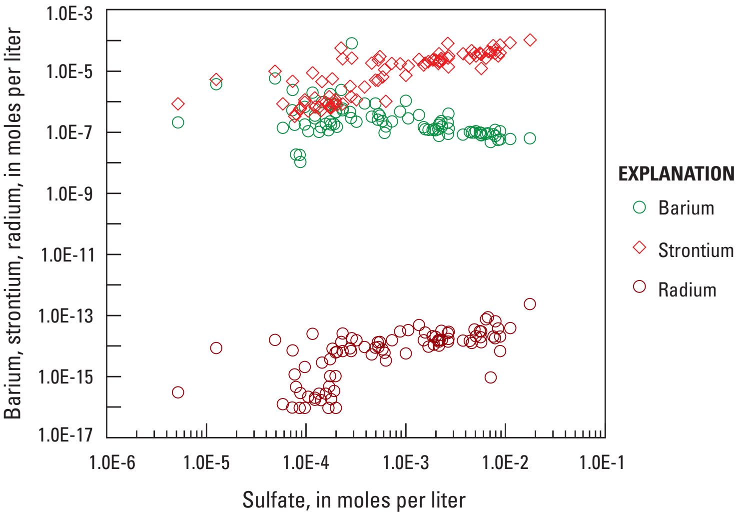


Figure 54. Relations between concentrations of *A*, dissolved solids and sulfate; *B*, sodium and fluoride, and *C*, iron and sulfate, with ranges of combined radium concentrations indicated for water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 2005–7. (Dashed lines are threshold concentrations of iron and sulfate used by McMahon and Chapelle (2008) for identifying redox processes in groundwater.)

Concentrations of radium in natural waters are never high enough to reach saturation with a pure radium solid such as radium sulfate, even though radium sulfate is highly insoluble (Langmuir and Riese, 1985; Langmuir and Melchior, 1985). Maximum radium concentrations are limited by adsorption or solid solution formation (Langmuir and Riese, 1985). The tendency for radium to co-precipitate and form a solid solution with barite ($BaSO_4$) is well known (Doerner and Hoskins, 1925; Langmuir and Riese, 1985; Martin and Akber, 1999). Barium and radium occur in oilfield brines, and barite scales on equipment can become enriched in radium to the extent that it becomes an environmental hazard (Swann and others, 2004). Langmuir and Melchior (1985) suggested that barite, celestite ($SrSO_4$), and to a lesser extent anhydrite ($CaSO_4$) were possible sinks for radium in deep basin brines. Langmuir and Riese (1985) ranked the potential of sulfate minerals to form solid solutions with radium in decreasing order: anhydrite, celestite, anglesite, barite, and gypsum (based on decreasing values of an empirically determined distribution coefficient). These potential host minerals all contain a divalent cation, which is the only state in which radium occurs in the natural environment. The importance of a particular solid solution as a radium sink is directly proportional to the abundance of the host mineral and the distribution coefficient and inversely proportional to the concentration of the host cation (Ca^{2+}, Sr^{2+}, Pb^{2+}, Ba^{2+}) in solution (Langmuir and Riese, 1985). For a trace radium solid solution to be important in radium transport in groundwater, the host mineral must be close to saturation with respect to the groundwater (Langmuir and Riese, 1985; Grundl and Cape, 2006).

Grundl and Cape (2006) studied the Cambrian-Ordovician aquifer system in Waukesha County, southeastern Wisconsin (county shown in fig. 34). They found that, in their study area, the aquifer was at saturation with respect to barite,

Figure 55. Relations of barium, strontium, and combined radium concentrations to sulfate concentrations for water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 2005–7.



and co-precipitation of radium into barite served as a geochemical control on radium concentrations in the unconfined part of the aquifer. In the confined part of the aquifer, radium and sulfate concentrations increased relative to the unconfined part, and barite co-precipitation ceased to control radium activities. The relatively insoluble barite could not control radium in the presence of high levels of sulfate. Grundl and Cape (2006) suggested that an additional source of radium or an additional geochemical process controlled radium concentrations in the confined part of the aquifer. Grundl and others (2006) expanded on the work of Grundl and Cape (2006) to include concentrations of strontium, which averaged 26,000 µg/L in the confined part of their study area. They found that water samples from the confined part of the aquifer were at saturation with respect to celestite but that samples from the unconfined part were undersaturated. Grundl and others (2006) suggested that the effective control on radium concentrations shifted from co-precipitation into barite in the unconfined part of the aquifer to co-precipitation into celestite in the confined part of the aquifer. If the aquifer is at saturation with respect to celestite, radium ions (Ra^{2+}) are able to co-precipitate in the celestite lattice as strontium (Sr^{2+}) continually dissolves and precipitates across the saturated mineral-water interface. Barite, which is also at saturation, also is in continual dissolution and precipitation across the saturated mineral-water interface but cannot supply enough Ba^{2+} to co-precipitate much radium (Grundl and others, 2006).

The relations between concentrations of barium, strontium, sulfate, and combined radium, and the minerals barite and celestite were evaluated for the 88 NAWQA samples. Concentrations of barium, strontium, and radium were plotted against concentrations of sulfate in units of moles per liter so that the wide range in concentrations could be shown on one graph (fig. 55). PHREEQCI was used to convert units to moles per liter, to calculate saturation indices, and to determine the aqueous speciation of barium, strontium, radium, and sulfate. Figure 55 shows how low the trace concentrations of radium are compared to barium and strontium. Barium concentrations have a negative correlation with concentrations of sulfate (rho = −0.54) and strontium (−0.32), but have no significant correlation with concentrations of radium. Strontium concentrations have strong positive correlations with concentrations of sulfate (rho = 0.84) and radium (0.76). Concentrations of radium have a strong positive correlation with concentrations of sulfate (rho = 0.67). Sturchio and others (2001) observed a linear relation between concentrations of strontium and radium in their samples that ranged from drinking water to oilfield brines.

As concentrations of strontium increase, concentrations of barium tend to decrease, and the highest radium concentrations are associated with the higher strontium concentrations (fig. 56*A*). Most samples (33 of 35) with combined radium concentrations greater than 5 pCi/L and all 11 samples with combined radium concentrations greater than 10 pCi/L had strontium concentrations greater than 1 mg/L (1,000 µg/L). Samples with the highest concentrations of strontium typically had barium concentrations less than 0.1 mg/L (fig. 56*A*). Concentrations of Ba^{2+} tend to decrease as SO_4^{2-} concentrations increase because barite solubility forces the Ba^{2+} concentrations to low levels (fig. 56*B*). Barite is relatively insoluble and has a solubility product (K_{sp}) of $10^{-9.97}$. Many of the NAWQA samples are at or above the approximate barite solubility line, including all of the samples with radium concentrations greater than 5 pCi/L. As a reference point, the NAWQA sample from well 147 with the highest concentration of radium is shown (fig. 56*B*). Concentrations of Sr^{2+} show a strong positive correlation with SO_4^{2-} concentrations; but because celestite is much more soluble ($K_{sp} = 10^{-6.63}$) than barite, few of the NAWQA samples are at or above the approximate solubility line (fig. 56*C*). However, the highest concentrations of radium occur in samples with high concentrations of Sr^{2+} and SO_4^{2-}. The maximum concentration of strontium in a NAWQA sample was 9,208 µg/L, which is much less than the average strontium concentration of 26,000 µg/L that Grundl and others (2006) saw in the confined area of Waukesha County, Wisconsin.

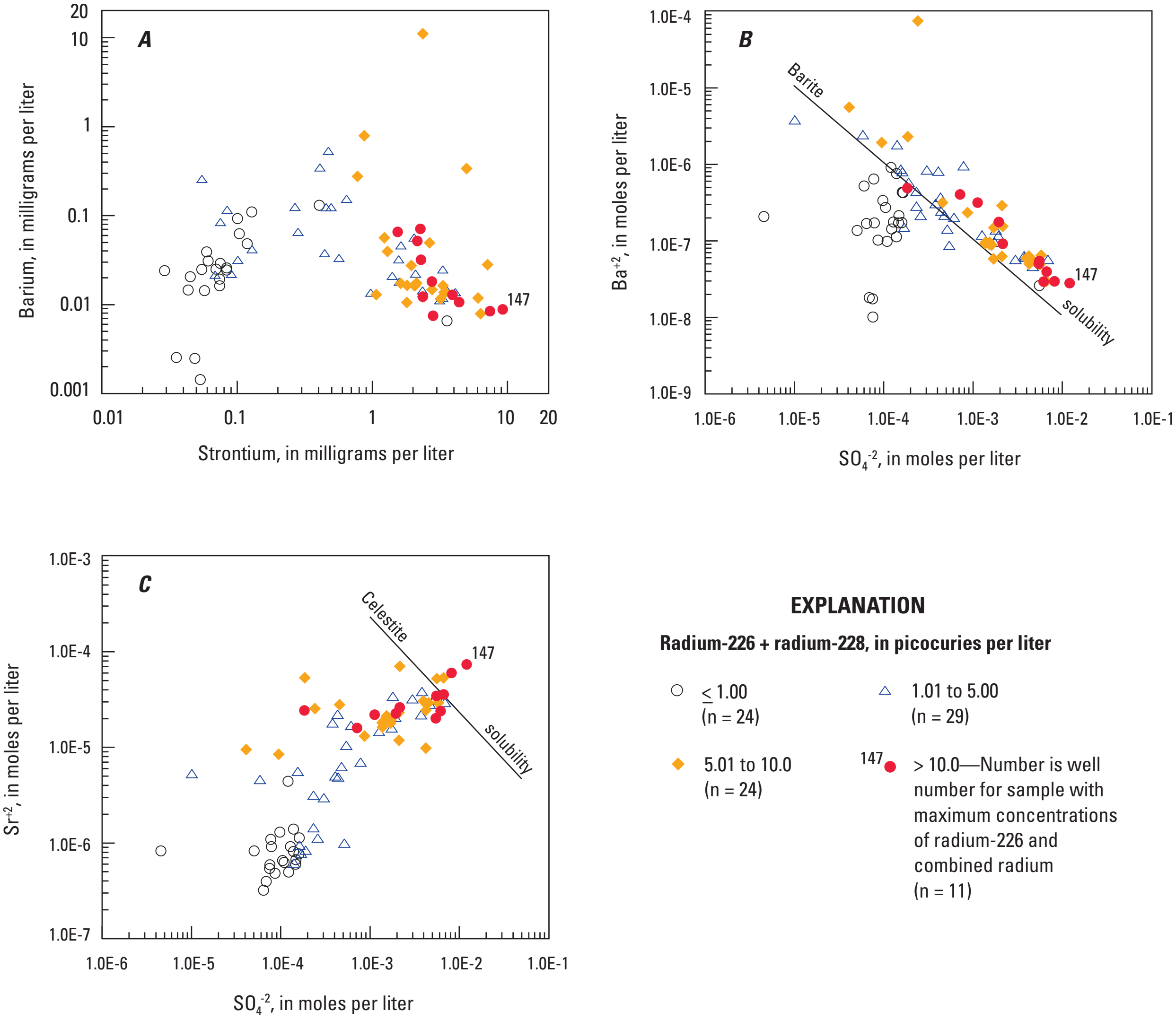


Figure 56. Relations between concentrations of *A*, barium and strontium; *B*, barium and sulfate; and *C*, strontium and sulfate, with ranges of combined radium concentrations indicated for water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 2005–7.

As previously mentioned, a host mineral must be close to saturation with respect to the groundwater for radium co-precipitation to be important in affecting radium concentrations in groundwater (Langmuir and Riese, 1985; Grundl and Cape, 2006). Many of the NAWQA samples are at saturation or supersaturated with respect to barite, especially in regionally confined wells (fig. 57*A*). The median barite saturation index is −0.10 for the NAWQA samples analyzed for radium. Concentrations of combined radium have a positive correlation with the barite saturation index when all samples are included (rho = 0.57) or when samples just from regionally unconfined wells are included (rho = 0.59) (table 18). However, there is no correlation between concentrations of radium and the barite saturation index when only samples from regionally confined wells are included, presumably because most of the samples are at saturation and there is not much range in saturation index. It is interesting to note that concentrations of radium have a positive correlation with the barite saturation index, yet they have no significant correlation with concentrations of barium. This is because radium concentrations continue to increase with sulfate concentrations beyond the barite solubility line, but there is not enough barium available to allow the solution to become supersaturated with respect to barite. Celestite is much more soluble than barite, which is one reason why strontium concentrations are typically much higher than barium concentrations in the NAWQA samples. The median celestite saturation index is −1.83 for the NAWQA samples analyzed for radium, and samples from confined wells, though

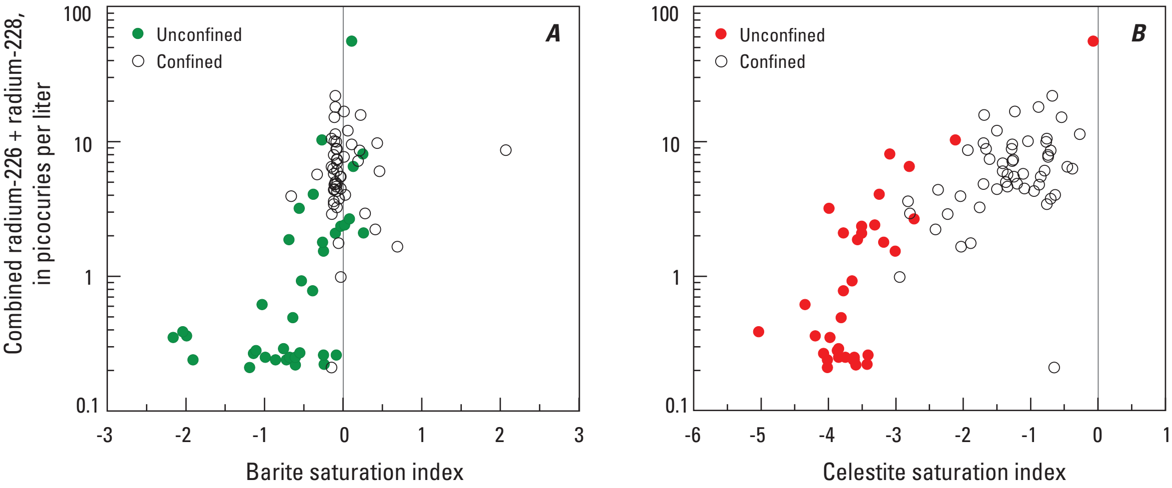


Figure 57. Relations between concentrations of combined radium and the saturation index of *A*, barite, and *B*, celestite, for samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 2005–7.

Table 18. Spearman rank correlation coefficients for concentrations of combined radium measured in, and the calculated saturation index of, selected sulfate minerals for water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 2005–7.

[All coefficients shown are significant at the 95-percent confidence limit ($p < 0.05$); Pb, lead; SO_4, sulfate; Ca, calcium; Ba, barium; Sr, strontium; H_2O, water; --, not significant]

Mineral	Chemical formula	Concentration of combined radium-226 + radium-228 in samples from—			Sample count
		All wells	Unconfined wells	Confined wells	
Anglesite	$PbSO_4$	0.38	--	--	78
Anhydrite	$CaSO_4$	0.65	--	0.32	88
Barite	$BaSO_4$	0.57	0.59	--	88
Celestite	$SrSO_4$	0.73	0.53	0.38	86
Gypsum	$CaSO_4 \cdot 2H_2O$	0.65	--	0.31	88

undersaturated, are typically more saturated with respect to celestite than samples from unconfined wells (fig. 57*B*). There is only one NAWQA sample with a celestite saturation index greater than −0.2, and that is the sample with the highest radium concentration. Concentrations of combined radium have a strong positive correlation with the celestite saturation index when all samples are included (rho = 0.73) (table 18). Concentrations of radium also have positive correlations with the celestite saturation index of samples from unconfined wells (rho = 0.53) and confined wells (0.38). In contrast to the correlation of radium concentrations and the saturation index of sulfate minerals, radium concentrations had no significant correlation with the saturation index of the carbonate minerals calcite and dolomite. Radium does not as readily co-precipitate into carbonate minerals as it does in sulfate minerals (Langmuir and Riese, 1985). This would include strontianite, which is strontium carbonate ($SrCO_3$).

The sulfate minerals anglesite, anhydrite, and gypsum are included in table 18 because, theoretically, they could be significant sinks for radium (Langmuir and Riese, 1985). Concentrations of lead in the NAWQA samples are low, with a median concentration of 0.04 µg/L (table 12). Therefore, the NAWQA samples are undersaturated with respect to anglesite, with a median saturation index of −6.83. The relations between concentrations of combined radium and the saturation indices of anhydrite and gypsum are similar to that of celestite, but anhydrite ($K_{sp} = -4.36$) and gypsum ($K_{sp} = -4.58$) are more soluble than celestite. The NAWQA samples analyzed for radium have a median saturation index of −1.92 with respect to gypsum and a median saturation index of −2.17 with respect to anhydrite. Grundl and others (2006) attributed the increased concentrations of calcium and sulfate in the confined part of their study area to the dissolution of gypsum. The dissolution of celestite is also a source of some of the sulfate and strontium in the confined part of the aquifer system.

Temporal Variability of Radium

The NAWQA and RASA Programs both sampled six public-supply wells in Iowa, with a 25-year time gap between samples. These data allowed for a limited analysis of the temporal variability of radium-226 concentrations with a relatively large time gap between samples (table 19). Although this is a small sample size, the data suggest that the source of radium-226 is relatively stable. Four of the NAWQA samples had a slightly higher value than the corresponding RASA value, which may be an indication of improved analytical methods. RASA samples were analyzed with the planchet counting method, whereas NAWQA samples were analyzed with the radon emanation method. Results for the two samples were similar for most of the wells, but the largest difference for the two samples was at well 17. The more recent NAWQA sample at this well was 3.17 pCi/L less than the RASA sample collected 25 years earlier. It is unknown whether this decrease reflects natural conditions or whether maintenance at this well has changed the open interval, which could affect the supply of radium to the well. There was no significant difference ($p = 0.562$) in radium-226 concentrations between the older RASA samples and the more recent NAWQA samples when treated as pairs using the Wilcoxon signed-rank test; however, this statistical test may not have much power with such a small sample size. The absolute difference between the samples ranged from 0.29 to 3.17 pCi/L, with a mean absolute difference of 1.12 pCi/L and a mean standard deviation of 0.79 pCi/L (table 19). The mean percent difference between the samples was 29 percent, and the mean relative standard deviation of the two samples at each well was 21 percent. These relative measures of difference are high because of the relatively small mean concentrations of radium-226 at each well and because the precision of counting low levels of radioactivity is low, even alpha particle activity (Zoltan Szabo, U.S. Geological Survey, written commun., 2011).

In a detailed evaluation of the temporal variability of radium-226, Kriege and Hahne (1982) looked at 141 public-supply wells in Iowa with multiple samples over an 18-year period from 1963 to 1981. Most of the wells had three or four samples with varying time gaps between samples. Kriege and Hahne (1982) calculated the average percent difference from the mean concentration at each well to be 21 percent. Using the methods shown in table 19, the mean standard deviation at each well was 1.53 pCi/L, and the mean relative standard deviation was 30 percent. The mean standard deviation is affected by wells that had one water sample with an anomalously high or low value. The mean relative standard deviation of the small NAWQA dataset is similar to that determined in the larger study of Kriege and Hahne (1982).

Table 19. Difference in radium-226 concentrations in water samples from six Iowa wells, collected by the RASA Program in 1980–81 and the NAWQA Program in 2005 or 2007.

[pCi/L, picocuries per liter; Percent difference is the absolute difference divided by the mean × 100; Relative standard deviation is the standard deviation divided by the mean × 100]

Well number	Radium-226 activity (pCi/L)				Percent difference	Relative standard deviation, in percent
	RASA sample, collected in 1980 or 1981	NAWQA sample, collected in 2005 or 2007	Absolute difference	Standard deviation		
4	6.5	7.45	0.95	0.67	13.6	9.6
16	3.6	4.65	1.05	0.74	25.5	18.0
17	6.5	3.33	3.17	2.24	64.5	45.6
20	8.0	8.51	0.51	0.36	6.2	4.4
27	2.0	1.71	0.29	0.20	15.6	11.0
38	1.1	1.85	0.75	0.53	50.8	36.0
Mean	4.62	4.58	1.12	0.79	29.4	20.8
Median	5.05	3.99	0.85	0.60	20.5	14.5

Nutrients and Dissolved Organic Carbon

Nutrients are chemical elements that are essential to plant and animal nutrition. Nitrogen and phosphorus are nutrients that are important to aquatic life, but in high concentrations they can be contaminants in water. Nitrate and phosphorus occur in many forms. They are affected by chemical and biological processes that can change their form and can transfer them to or from water, soil, biological organisms, and the atmosphere (Mueller and Helsel, 1996). Nutrients analyzed in water samples collected by the NAWQA Program included nitrate, nitrite, ammonia, and orthophosphate. Nitrate is typically reported as the sum of nitrite plus nitrate as nitrogen ($NO_2^- + NO_{3,}^-$ as N). Because nitrite is usually detected in low concentrations, nitrite plus nitrate will be referred to as “nitrate” in this report. Concentrations of nitrite and orthophosphate were commonly at or near detection levels. Ninety percent of nitrite concentrations were below the assessment level of 0.01 mg/L, and the maximum concentration was 0.13 mg/L as N (table 20). Fifty percent of orthophosphate concentrations were below the assessment level of 0.01 mg/L, 90 percent of the concentrations were at or below 0.03 mg/L, and the maximum concentration was 0.13 mg/L as P (table 20). The discussion of nutrients in this report will focus on nitrate and ammonia.

Nutrient samples collected by the NAWQA Program are filtered; therefore, the following discussions of nutrient concentrations refer to dissolved concentrations. Data from other sources are used to map the distribution of nitrate and ammonia concentrations throughout the aquifer system. Other sources of USGS data (RASA Program and NWIS database) and data from the ISWS are for filtered samples and represent dissolved concentrations, but nitrate and ammonia samples from all other state agencies are unfiltered and represent whole-water or total concentrations.

Nitrate (NO_3^-) is the most common form of nitrogen in groundwater and is readily transported and stable in groundwater over a range of conditions (Hem, 1985). Nitrate is the only nutrient for which there is a human-health benchmark. Excessive concentrations of nitrate in drinking water may cause methemoglobinemia in small children. Nitrate can come from natural processes (such as mineral weathering, decay of organic material, and atmospheric deposition) or from anthropogenic sources (such as septic-tank effluent and agricultural sources (animal wastes and fertilizers). Although nitrate occurs naturally in groundwater, high concentrations are usually attributed to human activity. Nitrogen in reduced or organic forms is converted through oxidation by soil bacteria into nitrite and nitrate (nitrification). Nitrogen used by plants is primarily in the oxidized form. Nitrate in anaerobic conditions can be reduced by other strains of bacteria to nitrous oxide or nitrogen gas (denitrification) (Hem, 1985). Nitrate concentrations in rainfall in the upper Midwest averaged 1.3 mg/L for the 20-year period of 1988 through 2007 based on annual means at 18 National Atmospheric Deposition Program (NADP) stations within or near the aquifer system in Illinois, Iowa, Michigan, Minnesota, Missouri, and Wisconsin (National Atmospheric Deposition Program, 2009).

Table 20. Summary statistics for nutrients and dissolved organic carbon in samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 1995–2007.

[mg/L, milligrams per liter; N, nitrogen; <, less than; --, not applicable; P, phosphorus]

	No assessment level								Assessment level as indicated			
Nutrient	Number of samples	Number of detections	Concentration percentile (mg/L)					Maximum concentration (mg/L)	Level (mg/L)	Number of samples	Number of detections	Frequency of detection, in percent
			10th	25th	Median	75th	90th					
Ammonia, as N	154	118	<0.02	0.02	0.17	0.80	1.37	4.27	0.02	154	114	74.0
Ammonia, as N	--	--	--	--	--	--	--	--	1.0	154	32	20.8
Dissolved organic carbon	140	129	0.24	0.40	0.58	0.92	1.38	5.52	0.2	140	129	92.1
[1]Nitrate, as N	154	54	<0.05	<0.05	<0.05	0.35	4.51	19.4	0.05	154	54	35.1
Nitrate, as N	--	--	--	--	--	--	--	--	1.0	154	33	21.4
Nitrite, as N	154	23	<0.01	<0.01	<0.01	<0.01	<0.01	0.13	0.01	154	8	5.19
Orthophosphate, as P	154	85	<0.01	<0.01	<0.01	0.02	0.03	0.13	0.01	154	52	33.8

[1] Nitrate is nitrate + nitrite (U.S. Geological Survey parameter code 00631).

Occurrence and Distribution

Nitrate concentrations in most of the NAWQA samples (80 percent; 10th percentile to 90th percentile) ranged from < 0.05 to 4.51 mg/L as N, with a median concentration of < 0.05 mg/L as N (table 20). The maximum concentration measured in a NAWQA sample was 19.4 mg/L as N. Nitrate was detected in 35 percent (54 of 154) of the NAWQA samples and in 21 percent of the NAWQA samples at an assessment level of 1 mg/L. An assessment level of 1 mg/L as N was selected as the value above which nitrate concentrations could be considered influenced by human activities (Dubrovsky and others, 2010). A concentration of 1 mg/L is approximately the 79th percentile of nitrate concentration for the NAWQA samples in this study. Concentrations of nitrate were positively correlated with several constituents that are general indicators of oxic, modern recharge, such as tritium (rho = 0.65), dissolved oxygen (0.58), and silica (0.54) (appendix 3). Concentrations of nitrate were negatively correlated with several constituents, properties, and characteristics that are general indicators of less oxic, older, more mineralized groundwater, such as radium-226 (rho = −0.56), fluoride (−0.55), well depth (−0.52), potassium (−0.52), and iron (−0.50). Concentrations of nitrate were significantly higher ($p < 0.001$) in wells from the regionally unconfined area than in wells from the regionally confined area (fig. 58; table 7). The higher nitrate concentrations in the unconfined areas are the result of the relatively shallow well depths compared to the confined areas. Nitrate was detected in 50 percent of the wells in unconfined areas but only in 5.7 percent of wells in confined areas. Concentrations of nitrate usually decrease with well depth because (1) recharge of deep, old groundwater most likely occurred when anthropogenic nitrogen inputs were relatively low and (2) the amount of time for denitrification to take place increases as water moves downward through the aquifer (Dubrovsky and others, 2010). The maximum concentration detected in a NAWQA sample from a confined well (3.13 mg/L as N) was in well 21 of north-central Iowa, which was discussed in previous sections as having water-quality characteristics similar to wells in the unconfined area because the well is open to formations above the Maquoketa Shale. Portions of the boxplots in figure 58 below the maximum detection levels should be considered as estimated because they include nondetections.

The USEPA MCL of 10 mg/L as N was exceeded in samples from 3.9 percent (6 of 154) of the wells sampled by NAWQA. All of these wells were private wells used for domestic supply (drinking water) in the unconfined area of Wisconsin and Minnesota. The wells had depths that ranged from 77 to 270 ft, and they had tritium-based recharge ages of modern. Three of the wells had an agricultural land use for the 500-m radius and three of the wells had a mixed land use. Five of the wells had an agricultural land use for the 1-mi radius and one well had a mixed land use.

Data from other sources (tables 3 and 4) were combined with the NAWQA data to evaluate the distribution of nitrate in the Cambrian-Ordovician aquifer system (fig. 59). The majority of the wells (74 percent) were in regionally unconfined areas, mostly in Minnesota and Wisconsin. As with the NAWQA dataset, nitrate concentrations were significantly

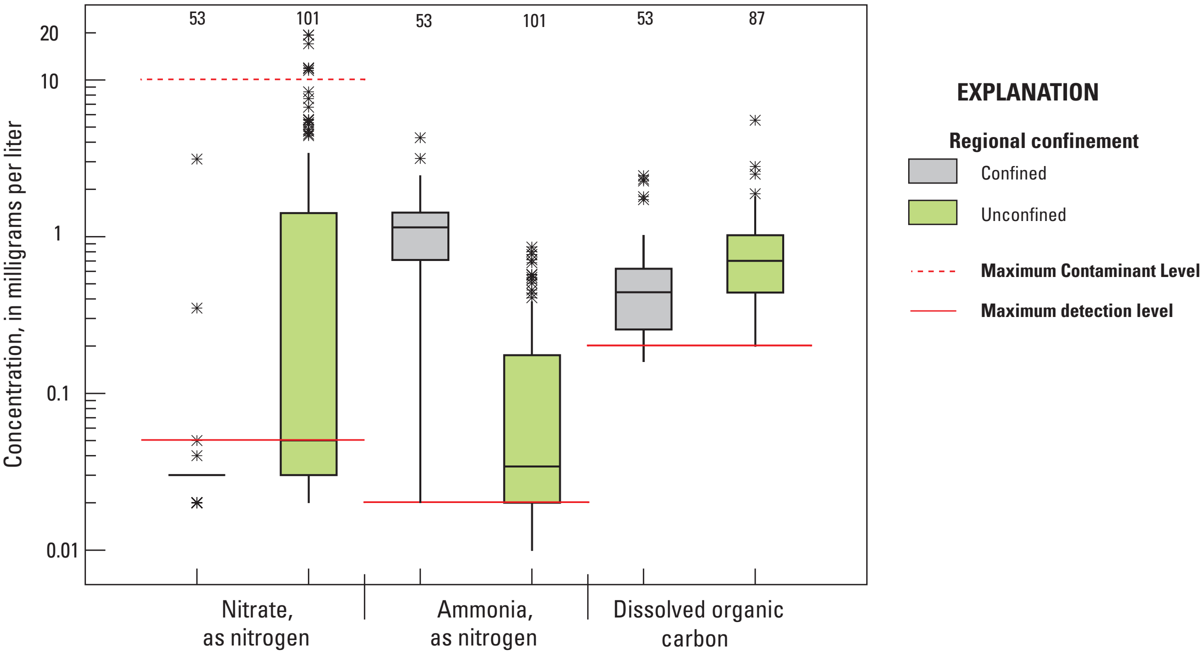


Figure 58. Distribution of nitrate, ammonia, and dissolved organic carbon concentrations by regional confinement for water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 1995–2007.

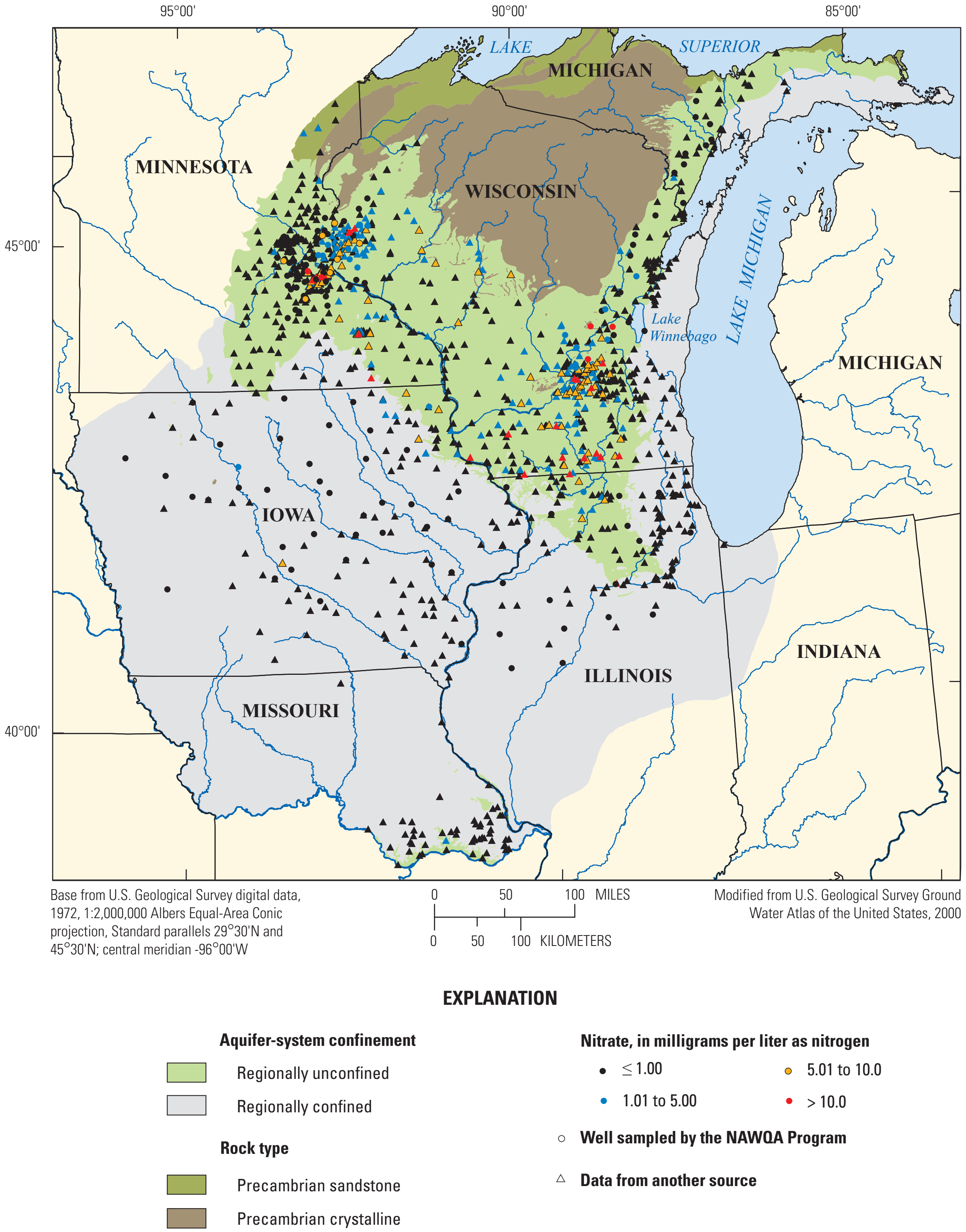
higher ($p < 0.001$) in samples from the unconfined area than from the confined area, even though nondetections were common in the unconfined area. Of the wells with a nitrate concentration that exceeded 1 mg/L, 96 percent were in the regionally unconfined areas. Of the available data, samples from 30 wells had nitrate concentrations that exceeded the USEPA MCL of 10 mg/L as N. These wells were in areas of agricultural land use in Minnesota, Wisconsin, and Illinois and were relatively shallow, with an average casing depth of 74 ft and an average well depth of 136 ft. Only one of the wells that exceeded the MCL was a public-supply well. Of the wells in Missouri, the maximum concentration of nitrate was 1.2 mg/L as N. Most of the wells in Missouri are just north of the Missouri River, where the land use is more forested compared to much of the study area (refer to fig. 5). In addition, the wells in this area tend to be relatively deep (most >500 ft), which would inhibit high concentrations of nitrate from reaching the well. Of the wells in the Upper Peninsula of Michigan, the maximum concentration of nitrate was 1.9 mg/L as N. The Upper Peninsula is an area where the land use is dominated by wetlands and forest and where agriculture is less common than in most of the study area (fig. 5).

Ammonia is one of the primary forms of dissolved nitrogen in natural water. It is a compound of nitrogen and hydrogen. Ammonia in water may be ionic (having an electrical charge; NH_4^+) or un-ionized (having no charge; NH_3). The un-ionized form is more toxic to fish. Ammonia is soluble in water but is not stable in most environments. It is easily transformed to nitrate in aerobic environments and can be transformed to nitrogen gas in anaerobic environments (Mueller and Helsel, 1996). The sources of reduced forms of nitrogen (ammonia) in natural water are probably similar to the sources of nitrate (Hem, 1985). Ammonium (NH_4^+) concentrations in rainfall in the upper Midwest averaged 0.4 mg/L for the 20-year period 1988 through 2007 based on annual means at 18 NADP stations within or near the aquifer system in Illinois, Iowa, Michigan, Minnesota, Missouri, and Wisconsin (National Atmospheric Deposition Program, 2009).

Ammonia was detected in 77 percent (118 of 154) of all NAWQA samples and in 21 percent of the samples at an assessment level of 1 mg/L as N. Concentrations of ammonia in most NAWQA samples (80 percent) ranged from < 0.02 to 1.37 mg/L as N, with a median concentration of 0.17 mg/L as N (table 20). The maximum concentration measured in a NAWQA sample was 4.27 mg/L as N. Concentrations of ammonia were positively correlated with water-quality constituents, properties, and characteristics that are general indicators of older, anoxic, more mineralized groundwater. Many of these correlations had values of Spearman's rho of 0.70 or higher, such as sodium, potassium, fluoride, boron, lithium, strontium, radium-226, well depth, and casing depth (appendix 3). Concentrations of ammonia were negatively correlated with water-quality constituents that are general indicators of oxic, modern recharge such as tritium (rho = −0.70), nitrate (−0.59), radon-222 (−0.47), and dissolved oxygen (−0.41). Concentrations of ammonia in NAWQA samples were significantly higher ($p < 0.001$) in regionally confined wells than in unconfined wells (fig. 58; table 7). The median concentration of ammonia in confined wells was 1.14 mg/L as N, and the median concentration of ammonia in unconfined wells was 0.03 mg/L as N. Ammonia was detected in all but one sample from the confined area (98 percent) and in 65 percent of the samples from the unconfined area. All samples with concentrations of ammonia of 1 mg/L as N or higher were from wells in the confined area of Iowa and Illinois. Schilling (2002) documented the occurrence and distribution of ammonium in Iowa groundwater in a study that looked at 841 municipal water-supply wells. Naturally occurring ammonium was found in all major aquifers in Iowa, including a mean concentration of 0.82 mg/L in Cambrian-Ordovician wells.

Data from other sources (tables 3 and 4) were combined with the NAWQA data to evaluate the distribution of ammonia in the Cambrian-Ordovician aquifer system (fig. 60). The majority of the wells (70 percent) were in regionally unconfined areas, mostly in Minnesota and Wisconsin. As with the NAWQA dataset, ammonia concentrations were significantly higher ($p < 0.001$) in samples from the confined area than from the unconfined area. Of the wells with an ammonia concentration that exceeded 1 mg/L, 88 percent were in the regionally confined areas of Iowa and Illinois. It appears that, once generated, ammonia is preserved in the reducing environment of the confined areas of the aquifer system and remains stable for a long time (Schilling, 2002).

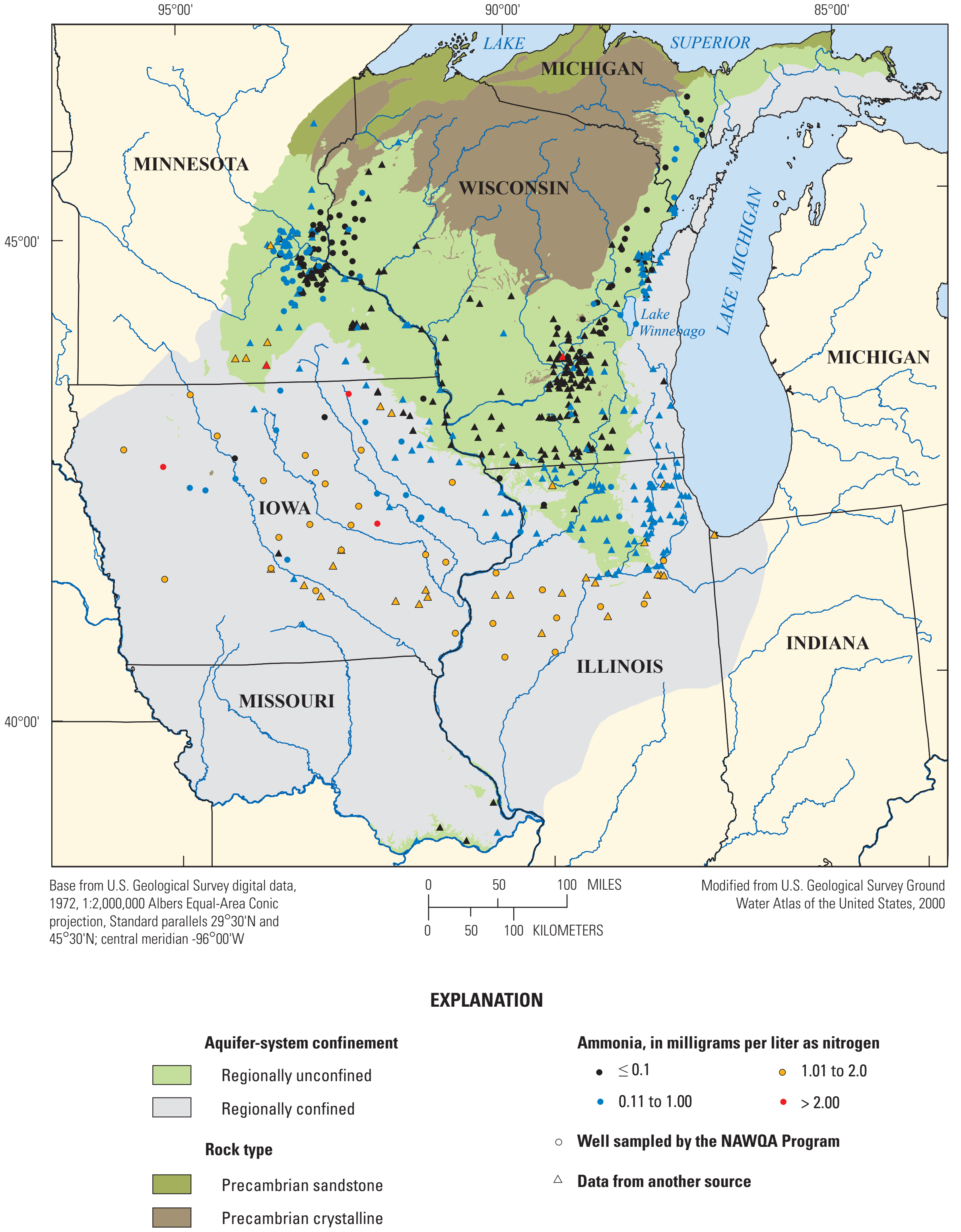
Dissolved organic carbon (DOC) originates naturally from rainfall and the dissolution of organic material in soils and rock by recharge and groundwater. DOC may also enter groundwater as a result of waste disposal and animal production. It can affect redox conditions and the transformation of other chemical species and nutrients in groundwater. Dissolved and particulate organic carbon are the most common electron donors available in groundwater systems for microorganisms that catalyze redox processes (Thurman, 1985). DOC can also react with chlorine during water disinfection to form byproducts called trihalomethanes, which are volatile organic compounds hazardous to human health. DOC was detected in 92 percent of the NAWQA samples, and concentrations in most samples (80 percent) ranged from 0.24 to 1.38 mg/L (table 20). The median DOC concentration was 0.58 mg/L, and the maximum concentration was 5.52 mg/L. DOC concentrations were significantly higher ($p < 0.001$) in samples from the unconfined area (median = 0.70 mg/L) than in samples from the confined area (median = 0.44 mg/L) (fig. 58; table 7). Concentrations of DOC were positively correlated with silica, bicarbonate, barium, manganese, and radon-222, but the highest value of Spearman's rho was only 0.39 for the correlation with radon-222 (appendix 3). Concentrations of DOC were negatively correlated with many of the water-quality constituents, properties, and characteristics that are general indicators of older, more mineralized groundwater, such as casing depth (rho = –0.50), water temperature (−0.45), well depth (−0.43), lithium (−0.37), and fluoride (−0.32).



Base from U.S. Geological Survey digital data, 1972, 1:2,000,000 Albers Equal-Area Conic projection, Standard parallels 29°30'N and 45°30'N; central meridian -96°00'W

Modified from U.S. Geological Survey Ground Water Atlas of the United States, 2000

Figure 59. Nitrate concentrations in water samples from wells completed in the Cambrian-Ordovician aquifer system, 1971–2008.



Base from U.S. Geological Survey digital data, 1972, 1:2,000,000 Albers Equal-Area Conic projection, Standard parallels 29°30'N and 45°30'N; central meridian -96°00'W

Modified from U.S. Geological Survey Ground Water Atlas of the United States, 2000

Figure 60. Ammonia concentrations in water samples from wells completed in the Cambrian-Ordovician aquifer system, 1975–2008.

Evaluation of Decadal-Scale Changes in Nitrate

Two well networks sampled in the first decade of NAWQA (1991–2001) were also sampled in the second decade of NAWQA (2001–12), which allowed for limited analysis of near-decadal-scale changes in nitrate concentrations similar to that of Rupert (2008). Nonparametric statistics were used for the analysis, and all nondetections were treated as detections at 0.05 mg/L, which was a minor adjustment because reporting levels only varied from 0.04 mg/L to 0.06 mg/L. The two samples at each well were treated as paired samples, and the Wilcoxon signed-rank test was used to determine whether there was a significant difference in nitrate concentrations.

A network of 26 wells in the eastern Wisconsin-Upper Peninsula sampling area was sampled in 1995 and in 2002. The wells in this network consisted of 21 private wells (used mostly for domestic supply) and 5 public-supply wells. The wells had a median depth of 140 ft, a median casing depth of 117 ft, and a median depth to bedrock of 48.5 ft (table 21). In 1995, the median nitrate concentration was 0.05 mg/L as N (actually < 0.05 mg/L). Three wells had a nitrate concentration that exceeded the MCL, there were 16 nondetections, and the maximum concentration was 23.0 mg/L as N. In 2002, the median concentration was 0.05 mg/L (< 0.05 mg/L) as N. The same three wells had nitrate concentrations that exceeded the MCL, there were 15 nondetections, and the maximum concentration was 19.4 mg/L as N. The median difference in nitrate concentration from 1995 to 2002 was 0.00 mg/L as N (table 21). The largest increase in nitrate concentration for a single well was 4.78 mg/L, where < 0.05 mg/L as N was measured in 1995 and 4.83 mg/L as N was measured in 2002. The largest decrease in nitrate concentration for a single well was −4.08 mg/L, where 16.0 mg/L as N was measured in 1995 and 11.92 mg/L as N was measured in 2002.

A network of 23 wells in the Twin Cities metropolitan area was sampled in 1996 and in 2007. The wells in this network were all private wells used for domestic supply and had a median depth of 143 ft, a median casing depth of 121 ft, and a median depth to bedrock of 83 ft (table 21). In 1996, the median nitrate concentration was 0.48 mg/L as N. One well had a nitrate concentration that exceeded the MCL, there were four nondetections, and the maximum concentration was 11.0 mg/L as N. In 2007, the median concentration was 0.38 mg/L as N. Two wells had nitrate concentrations that exceeded the MCL, there were nine nondetections, and the maximum concentration was 11.8 mg/L as N. Several of the wells with nondetections in 2007 had detections at or slightly greater than the reporting level in 1996. The median difference

Table 21. Difference in nitrate concentrations measured in groundwater samples from well networks in the Cambrian-Ordovician aquifer system sampled during the first and second decade of the NAWQA Program, 1995–2007.

[U.P., Upper Peninsula of Michigan; mg/L, milligrams per liter; <, less than; P-value, for Wilcoxon signed-rank test of difference between paired samples collected from individual wells during the first and second sampling event (all nondetections equal to 0.05 µg/L)]

Data item	NAWQA sampling area	
	Eastern Wisconsin-U.P.	Twin Cities metropolitan area
Data for first sampling		
Number of wells sampled	26	23
Median depth of well (feet)	140	143
Median depth of well casing (feet)	117	121
Median depth to bedrock (feet)	48.5	83
Year of first sampling event	1995	1996
Wells with nitrate detection	10	19
Mean nitrate concentration (mg/L)	2.52	2.35
Median nitrate concentration (mg/L)	< 0.05	0.48
Data for second sampling		
Number of wells sampled	26	23
Year of second sampling event	2002	2007
Wells with nitrate detection	11	14
Mean nitrate concentration (mg/L)	2.67	2.36
Median nitrate concentration (mg/L)	< 0.05	0.38
Difference from first sampling to second sampling		
Years between sampling events	7	11
Mean difference in nitrate concentration (mg/L)	0.149	0.016
Median difference in nitrate concentration (mg/L)	0.00	−0.02
P-value, for test of difference in nitrate concentration	0.755	0.408

in nitrate concentration from 1996 to 2007 was −0.02 mg/L as N (table 21). The largest increase in nitrate concentration for a single well was 3.6 mg/L, where 7.9 mg/L as N was measured in 1996 and 11.5 mg/L as N was measured in 2007. The largest decrease in nitrate concentration for a single well was −2.94 mg/L, where 3.9 mg/L as N was measured in 1996 and 0.96 mg/L as N was measured in 2007.

There was no significant difference ($p = 0.755$, $p = 0.408$) between the first and second sampling for either network (table 21). The median difference in nitrate concentration for the two networks indicates that there was little or no decadal-scale change for the networks, even though concentrations at individual wells may have changed by 3 or 4 mg/L. However, it is not surprising that these well networks in the Cambrian-Ordovician aquifer system do not show decadal-scale changes in nitrate concentrations because, in places, it is not the shallowest aquifer system. The most change would be expected in the glacial aquifer system, which overlies the Cambrian-Ordovician aquifer system. Rupert (2008) identified a significant increase in nitrate concentration for a network of wells in the glacial aquifer system of eastern Wisconsin.

Pesticides

Pesticides are used to control weeds, insects, and other pests in agricultural areas, urban areas, and rights-of-way. Once released into the environment, pesticides and their degradates can move through the hydrologic system to streams and groundwater, where they may affect humans, aquatic life, or wildlife if concentrations occur at toxic levels (Gilliom and others, 2006). Many factors affect the transport and concentrations of pesticides in groundwater, including the intensity and distribution of their use, natural factors such as climate and soil characteristics, and the physical and chemical properties of the pesticide compounds themselves (Gilliom and others, 2006). The geographic distribution of the use of each pesticide will follow the distributions of crops and pests for which it is applied. The Cambrian-Ordovician aquifer system is in an area where the land use is predominantly agriculture (fig. 5). Much of the study area is in the Corn Belt, an agricultural region that accounts for a major proportion of the national pesticide use (Sullivan and others, 2009). Corn has dominated total harvested acreage in the study area since the 1930s, but there is a trend toward increased soybean acreage (fig. 6).

Occurrence and Distribution

Pesticides were analyzed in water samples collected by NAWQA from 1995 through 2007; however, during that period the number of pesticides and the list of pesticides being analyzed changed. In order to assemble the most comprehensive list of pesticides that were analyzed at the most wells, the analysis of pesticides in this report used samples collected by NAWQA only from 2002 through 2007. Eighty-three pesticide compounds (parent and degradates) were analyzed in water samples (appendix 2). Thirty-five of those compounds were analyzed in samples collected from 1995 and 1996, as well as in samples collected from 2002 through 2007, and for descriptive purposes were designated as Group 1 pesticides (appendix 2). The remaining 48 compounds were analyzed only in samples collected from 2004 through 2007 and were designated as Group 2 pesticides (appendix 2). The predominant uses of the pesticides are as herbicides, insecticides, and fungicides. The number of pesticides analyzed in each sample ranged from 35 to 83, and the number of wells for which each pesticide was analyzed ranged from 78 to 125. The 35 pesticide compounds from Group 1 were included in the comprehensive study of pesticides in the Nation's streams and groundwater by Gilliom and others (2006).

One or more pesticides were detected in samples from 35 of the 125 wells (28 percent) collected from 2002 through 2007. Nine different pesticides were detected in at least one sample (table 22). Deethylatrazine (a degradation product of the herbicide atrazine) and atrazine were the most commonly detected pesticides and together accounted for 67 percent of all detections. Deethylatrazine was detected in 29 wells (23.2 percent) and atrazine was detected in 28 wells (22.4 percent) (fig. 61). The herbicides prometon, metolachlor, and simazine were detected in nine, eight, and seven wells, respectively. The insecticide chlorpyrifos was detected in one well. Atrazine, metolachlor, and alachlor were the first, second, and fourth most intensively used (pounds per square mile) agricultural herbicides for corn and soybeans in 1997 (Gianessi and Marcelli, 2000). Cyanazine, the third most intensively used herbicide for corn and soybeans, was not detected. Prometon and simazine are characterized as urban herbicides but are used for weed control around fences, buildings, and roads within agricultural as well as urban areas (Gilliom and others, 2006).

Six different pesticides were detected at an assessment level of 0.01 µg/L. Assessment levels are used for direct comparison of detection frequencies among pesticides to account for the variations in analytical sensitivity that result in different minimum detectable concentrations (Gilliom and others, 2006). The use of multiple assessment levels (0.01 and 0.1 µg/L) also shows how detection frequencies change with increased concentration thresholds. Atrazine and deethylatrazine were each detected at concentrations equal to or greater than 0.01 µg/L in 19 wells (15.2 percent) and accounted for 84 percent of all detections at an assessment level of 0.01 µg/L (table 22; fig. 61). Prometon was detected in three wells, metolachlor was detected in two wells, and hexazinone and simazine were each detected in one well at an assessment level of 0.01 µg/L. Three pesticides were detected at concentrations of 0.1 µg/L or greater; deethylatrazine was detected in six wells (4.8 percent), atrazine was detected in four wells (3.2 percent), and metolachlor was detected in one well (table 22; fig. 61). Of these six wells, three wells had agricultural land and three had a mixed land use within the 500-m radius around the well. All six of the wells had agricultural land within the 1-mi radius around the well. Atrazine

Table 22. Summary of pesticides detected in samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 2002–7.

[Assessment levels match those used by Gilliom and others (2006); µg/L, micrograms per liter; MCLs are U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Levels for public water supplies; HBSLs are Health-Based Screening Levels developed by the U.S. Geological Survey using USEPA toxicity data and methods (Toccalino and Norman, 2006); DP, degradation product of (parent compound); --, not applicable]

Pesticide	Type of Pesticide	No assessment level				Assessment level of 0.01 µg/L	Assessment level of 0.1 µg/L	Human-health benchmark	
		Number of samples	Number of detections	Frequency of detection	Maximum concentration (µg/L)	Number of detections	Number of detections	Value (µg/L)	Type
Alachlor	Herbicide	125	1	0.80	[1]0.008	0	0	2	MCL
Atrazine	Herbicide	125	28	22.4	[1]1.93	19	4	3	MCL
Chlorpyrifos	Insecticide	125	1	0.80	0.003	0	0	2	HBSL
Deethylatrazine	DP (Atrazine)	125	29	23.2	[1]0.978	19	6	--	--
2,6-Diethylaniline	DP (Alachlor)	125	1	0.80	0.004	0	0	--	--
Hexazinone	Herbicide	103	1	0.80	0.017	1	0	400	HBSL
Metolachlor	Herbicide	125	8	6.40	[1]9.54	2	1	700	HBSL
Prometon	Herbicide	125	9	7.20	0.06	3	0	400	HBSL
Simazine	Herbicide	125	7	5.60	[1]0.011	1	0	4	MCL
Total number of detections			**85**			**45**	**11**		

[1] Maximum concentrations for these five contaminants are from the same sample collected from a private well in Waushara County, Wisconsin.

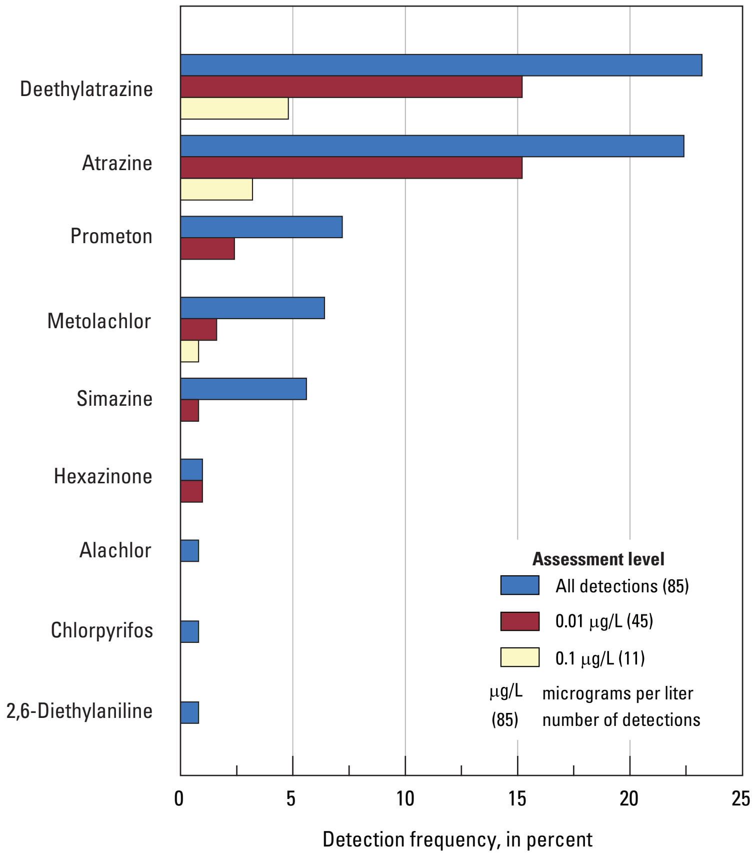


Figure 61. Detection frequency for pesticides in water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 2002–7.

and metolachlor were detected at concentrations of 1 µg/L or greater in one well in eastern Wisconsin. No pesticides were detected at concentrations that exceeded a human-health benchmark.

The distribution of pesticide detections in samples collected from 2002 through 2007 is shown in figure 62. Results from the most recent sample were used if more than one sample was collected at a well. The majority of wells with detections are in unconfined areas near the Twin Cities metropolitan area and in eastern Wisconsin southwest of Lake Winnebago. Two wells had total concentration of pesticides greater than 1 µg/L, one in western Wisconsin in the Twin Cities metropolitan area and one in eastern Wisconsin west of Lake Winnebago. Three pesticides (atrazine, deethylatrazine, and prometon) were detected in one well in the unconfined area of northern Illinois, and four pesticides (atrazine, deethylatrazine, prometon, and simazine) were detected in one well in the unconfined area of northeastern Iowa (fig. 62).

The presence of pesticides in the Cambrian-Ordovician aquifer system was related to regional confinement category, tritium-based groundwater age, and well type. Wells in the unconfined area were significantly more likely to have a pesticide detection than wells in the confined area ($p < 0.001$; chi-square test for independence). Of the 35 wells where at least one pesticide was detected, 30 wells (86 percent) were in areas where the aquifer system was regionally unconfined. Although wells in the regionally unconfined areas accounted for 58 percent of the wells sampled, they account for 91 percent of all pesticide detections (table 23). Wells with samples that contained modern recharge were more likely to have pesticide detections. Approximately 36 percent of the sampled wells had modern recharge, but approximately 86 percent of the wells with pesticide detections had modern recharge, and 94 percent of all pesticide detections were in wells with modern recharge (table 23). Pesticides were detected more frequently in private wells than in public-supply wells. Private wells are predominantly used for domestic supplies in the unconfined areas. Private wells accounted for 22 of the wells (63 percent) with at least one pesticide detection; they also accounted for 66 percent of all pesticide detections (table 23). Pesticides also were detected significantly more often in wells with dissolved oxygen concentrations greater than 0.5 mg/L ($p < 0.001$) and nitrate concentrations greater than 1 mg/L ($p < 0.001$).

Four pesticides (atrazine, deethylatrazine, metolachlor, and prometon) were detected in the sample from well 21 in the confined area of north-central Iowa (fig. 62). However, as mentioned previously, this well is relatively shallow and partially open to younger bedrock above the Maquoketa Shale. Consequently, the water quality of the sample from this well was more consistent with wells in the unconfined area than wells in the confined area. Four other wells in the confined area of Iowa, with pre-1953 recharge, had low-level detections of a different pesticide (atrazine, chlorpyrifos, metolachlor, and prometon). These four wells are relatively deep wells with a minimum casing depth of 930 ft, so their samples would not be expected to contain pesticides. However, pesticides have been reported previously in two regionally confined Cambrian-Ordovician wells in Iowa (Schaap and Linhart, 1998).

There were no pesticide detections in samples from the Upper Peninsula or the six most northerly wells in eastern Wisconsin (fig. 62). The absence of pesticide detections in this area is consistent with the low number of nitrate detections greater than 1 mg/L and may be attributed to less agricultural land use compared to most of the study area, especially in the Upper Peninsula.

Evaluation of Decadal-Scale Changes in Pesticides

Two well networks used in a previous section to evaluate near-decadal-scale changes in nitrate concentrations (table 21) were also used for a limited analysis of near-decadal-scale changes in pesticides. However, because water samples were analyzed for multiple pesticides, different metrics were used to evaluate change. The number of pesticides and the total concentration of pesticides measured in each sample were the parameters used to evaluate decadal-scale changes for the two well networks. Thirty-five pesticides (Group 1, appendix 2) were analyzed in water samples from the two well networks during the first and second decade of NAWQA. Eight different pesticides were detected in at least one sample.

In 1995, at least one pesticide was detected in samples from five wells in the eastern Wisconsin-Upper Peninsula area, and the total number of detections was 14 (table 24). Six different pesticides were detected and, in order of decreasing detection frequency, were atrazine, deethylatrazine, alachlor, metolachlor, prometon, and simazine. The mean and median number of pesticides detected in each well were 0.538 and 0.00, respectively. The mean and median sum of pesticide concentrations measured in each sample were 0.252 µg/L and 0.000 µg/L, respectively. In 2002, at least one pesticide was detected in samples from seven wells, and the total number of detections was 20. Seven different pesticides were detected and, in order of decreasing detection frequency, were deethylatrazine, atrazine, metolachlor, prometon, alachlor, simazine, and 2,6-diethylaniline. The mean and median number of pesticides detected in each well was 0.769 and 0.00, respectively. The mean and median sum of pesticide concentrations measured in each well were 0.509 µg/L and 0.000 µg/L, respectively. The mean and median differences in the number of detections in each well from 1995 to 2002 were 0.231 and 0.00, respectively (table 24). The mean and median difference in the sum of pesticide concentrations measured in each well from 1995 to 2002 were 0.257 µg/L and 0.000 µg/L, respectively. There were five wells with more detections in 2002 than in 1995 and no wells with fewer detections in 2002 than in 1995. The number of pesticides detected in each well in 2002 was significantly higher ($p = 0.027$) than in 1995; however, there was no significant difference ($p = 0.067$) in the sum of pesticide concentrations measured in each well from 1995 to 2002.

Table 23. Pesticide detections in relation to regional confinement, tritium-based groundwater age, and well type for wells in the Cambrian-Ordovician aquifer system sampled by the NAWQA Program, 2002–7.

[Total of 85 detections in 35 of 125 wells sampled by NAWQA Program, 2002–7; 107 of 125 wells were analyzed for tritium, of which 28 had at least one pesticide detection]

Category	Count and (percentage), by category					
	Regional confinement		Tritium-based age		Well type	
	Confined	Unconfined	Modern	Pre-1953	Public supply	Private
All 125 wells	52 (41.6)	73 (58.4)	38 (35.5)	69 (64.5)	79 (63.2)	46 (36.8)
Wells with a pesticide detection	5 (14.3)	30 (85.7)	24 (85.7)	4 (14.3)	13 (37.1)	22 (62.9)
Pesticide detections	8 (9.4)	77 (90.6)	64 (94.1)	4 (5.9)	29 (34.1)	56 (65.9)

Table 24. Differences in number of pesticides detected and sum of pesticide concentrations measured in groundwater samples from well networks in the Cambrian-Ordovician aquifer system sampled during the first and second decade of the NAWQA Program, 1995–2007.

[U.P., Upper Peninsula of Michigan; µg/L, micrograms per liter; P-value, for Wilcoxon signed-rank test of difference between paired samples collected from individual wells during the first and second sampling event]

Data item	NAWQA sampling area	
	Eastern Wisconsin-U.P.	Twin Cities metropolitan area
Data for first sampling		
Number of wells sampled	26	23
Year of first sampling event	1995	1996
Wells with at least one detection	5	14
Total number of detections	14	30
Mean number of detections in each well	0.538	1.304
Median number of detections in each well	0.000	2.000
Mean sum of pesticide concentrations in each well (µg/L)	0.252	0.293
Median sum of pesticide concentrations in each well (µg/L)	0.000	0.013
Data for second sampling		
Number of wells sampled	26	23
Year of second sampling event	2002	2007
Wells with at least one detection	7	14
Total number of detections	20	33
Mean number of detections in each well	0.769	1.435
Median number of detections in each well	0.000	2.000
Mean sum of pesticide concentrations in each well (µg/L)	0.509	0.114
Median sum of pesticide concentrations in each well (µg/L)	0.000	0.014
Difference from first sampling to second sampling		
Years between sampling events	7	11
Mean difference in number of detections in each well	0.231	0.130
Median difference in number of detections in each well	0.00	0.000
P-value, for test of difference in number of detections in each well	**0.027**[1]	0.638
Mean difference in sum of pesticide concentrations in each well (µg/L)	0.257	-0.179
Median difference in sum of pesticide concentrations in each well (µg/L)	0.00	0.000
P-value, for test of difference in sum of pesticide concentrations	0.067	0.342

[1] Number of pesticide detections in 2002 samples is significantly higher than in 1995 samples at the 0.05 significance level

Base from U.S. Geological Survey digital data, 1972, 1:2,000,000 Albers Equal-Area Conic projection, Standard parallels 29°30'N and 45°30'N; central meridian -96°00'W

Modified from U.S. Geological Survey Ground Water Atlas of the United States, 2000

EXPLANATION

Aquifer-system confinement

🟩 Regionally unconfined

⬜ Regionally confined

Rock type

🟩 Precambrian sandstone

🟫 Precambrian crystalline

Total concentration of pesticides detected in most recent sample, in micrograms per liter

- ● No pesticides detected
- ● 0.003 to 0.01
- ● 0.011 to 0.1
- ● 0.11 to 1.0
- ● > 1

○^{2} **Well sampled by the NAWQA Program—** Number is the number of pesticides detected in most recent sample from a potential list of 83 compounds

Figure 62. Total concentration and number of pesticides detected in water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 2002–7.

In 1996, at least 1 pesticide was detected in samples from 14 wells in the Twin Cities metropolitan area, and the total number of detections was 30. Five different pesticides were detected and, in order of decreasing detection frequency, were deethylatrazine, atrazine, diazinon, simazine, and metolachlor. The mean and median number of pesticides detected in each well were 1.304 and 2.00, respectively. The mean and median sum of pesticide concentrations measured in each well were 0.293 µg/L and 0.013 µg/L, respectively. In 2007, at least 1 pesticide was detected in samples from 14 wells, and the total number of detections was 33. Four different pesticides were detected and, in order of decreasing detection frequency, were deethylatrazine, atrazine, simazine, and metolachlor. The mean and median number of pesticides detected in each sample were 1.435 and 2.00, respectively. The mean and median sum of pesticide concentrations measured in each sample were 0.114 µg/L and 0.014 µg/L, respectively. The mean and median difference in the number of detections in each sample from 1996 to 2007 were 0.13 and 0.00, respectively (table 24). The mean and median difference in the sum of pesticide concentrations measured in each sample from 1996 to 2007 were −0.179 µg/L and 0.000 µg/L, respectively. There were four samples with more detections in 2007 than in 1996 and three samples with fewer detections in 2007 than in 1996. There were no significant differences in the number of pesticide detections ($p = 0.638$) in each sample or in the sum of pesticide concentrations measured ($p = 0.342$) in each sample from 1996 to 2007.

Volatile Organic Compounds

Volatile organic compounds (VOCs) are organic compounds with inherent physical and chemical properties that allow them to move between water and air. Some VOCs may occur naturally in the environment, others occur only because of human activities, and some compounds have both origins (Zogorski and others, 2006). VOCs have been used extensively in the United States since the 1940s as common components or additives in many commercial and household products including gasoline, diesel fuel, other petroleum-based products, carpets, paints, varnishes, glues, stain removers, and cleaners (Zogorski and others, 2006). Example industrial applications include the manufacturing of automobiles, electronics, computers, adhesives, dyes, rubber products, and plastics, as well as the synthesis of other organic compounds. VOCs are used in the dry cleaning of clothing, in refrigeration units, and in the degreasing of equipment and home septic systems. VOCs are present in some personal care products such as perfumes and deodorants, and some VOCs have been used as fumigants in agriculture and in households to control insects, worms, and other pests (Zogorski and others, 2006). Chlorinated solvents have been used in industry for almost 100 years (Pankow and Cherry, 1996). Chloroform and other trihalomethanes (THMs) have been present in chlorinated drinking water since the first continuous municipal application of chlorination in 1908 (American Water Works Association, 1971). The large-scale use of solutions of VOCs and products containing VOCs has resulted in considerable quantities of VOCs being released to the environment. Once released to the environment, VOCs can persist in groundwater and migrate to drinking-water supply wells. The presence of high concentrations of VOCs in drinking water is a concern to human health because some VOCs may be carcinogenic. In addition to cancer risk, VOCs may adversely affect several internal organs, as well as the nervous, circulatory, reproductive, and respiratory systems (U.S. Environmental Protection Agency, 2009b). In addition to human-health concerns, the detection of VOCs in groundwater implies aquifer vulnerability (as does the detection of pesticides and nitrate greater than a background level) and the existence of a pathway by which other persistent and potentially toxic compounds may reach drinking-water supply wells (Zogorski and others, 2006).

Occurrence and Distribution

Zogorski and others (2006) presented a comprehensive national assessment of 55 VOCs with an emphasis on the occurrence of VOCs in aquifers that are important sources of drinking water. The occurrence of these 55 VOCs in aquifers of the United States was also summarized by Carter and others (2008). The analysis of VOCs in this report used samples collected by the NAWQA Program from 2002 through 2007, which include 54 VOCs analyzed in water samples from 122 wells in the Cambrian-Ordovician aquifer system (appendix 2). Acrolein, an organic synthesis compound, was not included because of a lack of data, and the combination of *m*- and *p*-xylene was counted as two compounds (Zogorski and others, 2006). The number of VOCs analyzed in most samples was 54; however, some wells in the eastern Wisconsin-Upper Peninsula sampling area had results for only 53 compounds because of a contamination problem in blank water with the fumigant 1,2-dichloropropane.

VOCs were detected in the most recent sample from 28 of the 122 wells (23 percent) analyzed for VOCs from 2002 to 2007. Twenty-three of the 54 VOCs were detected at least once when all detections were counted, without considering that the minimum detectable concentration varies among the different compounds (table 25). There were 67 detections of these 23 compounds, but concentrations generally were low. The median concentration of detected VOCs was 0.087 µg/L. Eighty-seven percent of detections were at concentrations of less than 1 µg/L, 70 percent of detections were at concentrations less than 0.2 µg/L, and approximately 13 percent of detections were at concentrations less than 0.02 µg/L. The solvents trichloroethene (TCE) and *cis*-1,2-dichloroethene (*cis*-1,2-DCE) were the most commonly detected compounds and together accounted for 24 percent (16 of 67) of all detections. Chloroform, a THM, was detected in 5.7 percent (7) of the wells, and benzene, a gasoline hydrocarbon, was detected in 4 percent (5) of the wells (table 25; fig. 63). The remaining VOCs were detected in four wells or fewer.

Table 25. Summary of volatile organic compounds detected in samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 2002–7.

[Assessment levels match those used by Zogorski and others (2006); µg/L, micrograms per liter; Predominant use group is from Zogorski and others (2006)]

Contaminant	Predominant use group	No assessment level				Assessment level of 0.02 µg/L	Assessment level of 0.2 µg/L
		Number of samples	Number of detections	Frequency of detection	Maximum concentration (µg/L)	Number of detections	Number of detections
Benzene	Gasoline hydrocarbon	122	5	4.10	0.101	1	0
Chloroform	Trihalomethane	122	7	5.74	1.94	6	1
Dichlorodifluoromethane (CFC-12)	Refrigerant	122	3	2.46	0.258	3	1
1,1-Dichloroethane (1,1-DCA)	Solvent	122	3	2.46	5.11	3	1
1,2-Dichloroethane (1,2-DCA)	Solvent	122	1	0.82	0.158	1	0
1,1-Dichloroethene (1,1-DCE)	Organic synthesis	122	3	2.46	7.02	2	1
cis-1,2-Dichloroethene (*cis*-1,2-DCE)	Solvent	122	8	6.56	1.50	7	3
trans-1,2-Dichloroethene	Solvent	122	3	2.46	0.111	3	0
Methylene chloride	Solvent	122	3	2.46	5.52	3	2
Ethylbenzene	Gasoline hydrocarbon	122	3	2.46	0.209	2	1
Isopropylbenzene	Gasoline hydrocarbon	122	1	0.82	0.037	1	0
n-Propylbenzene	Solvent	122	1	0.82	0.024	1	0
Styrene	Gasoline hydrocarbon	122	2	1.64	4.34	2	1
Perchloroethene (PCE)	Solvent	122	4	3.28	0.731	3	1
Toluene	Gasoline hydrocarbon	122	3	2.46	0.261	3	2
1,1,1-Trichloroethane (TCA)	Solvent	122	2	1.64	5.07	2	1
Trichloroethene (TCE)	Solvent	122	8	6.56	64.0	8	3
Trichlorofluoromethane (CFC-11)	Refrigerant	122	1	0.82	0.056	1	0
Trichlorotrifluoroethane (CFC-113)	Refrigerant	122	1	0.82	0.184	1	0
Vinyl chloride	Organic synthesis	122	1	0.82	0.224	1	1
m- and *p*-Xylene	Gasoline hydrocarbon	122	2	1.64	0.919	2	1
o-Xylene	Gasoline hydrocarbon	122	2	1.64	0.228	2	1
Total number of detections			**67**			**58**	**21**

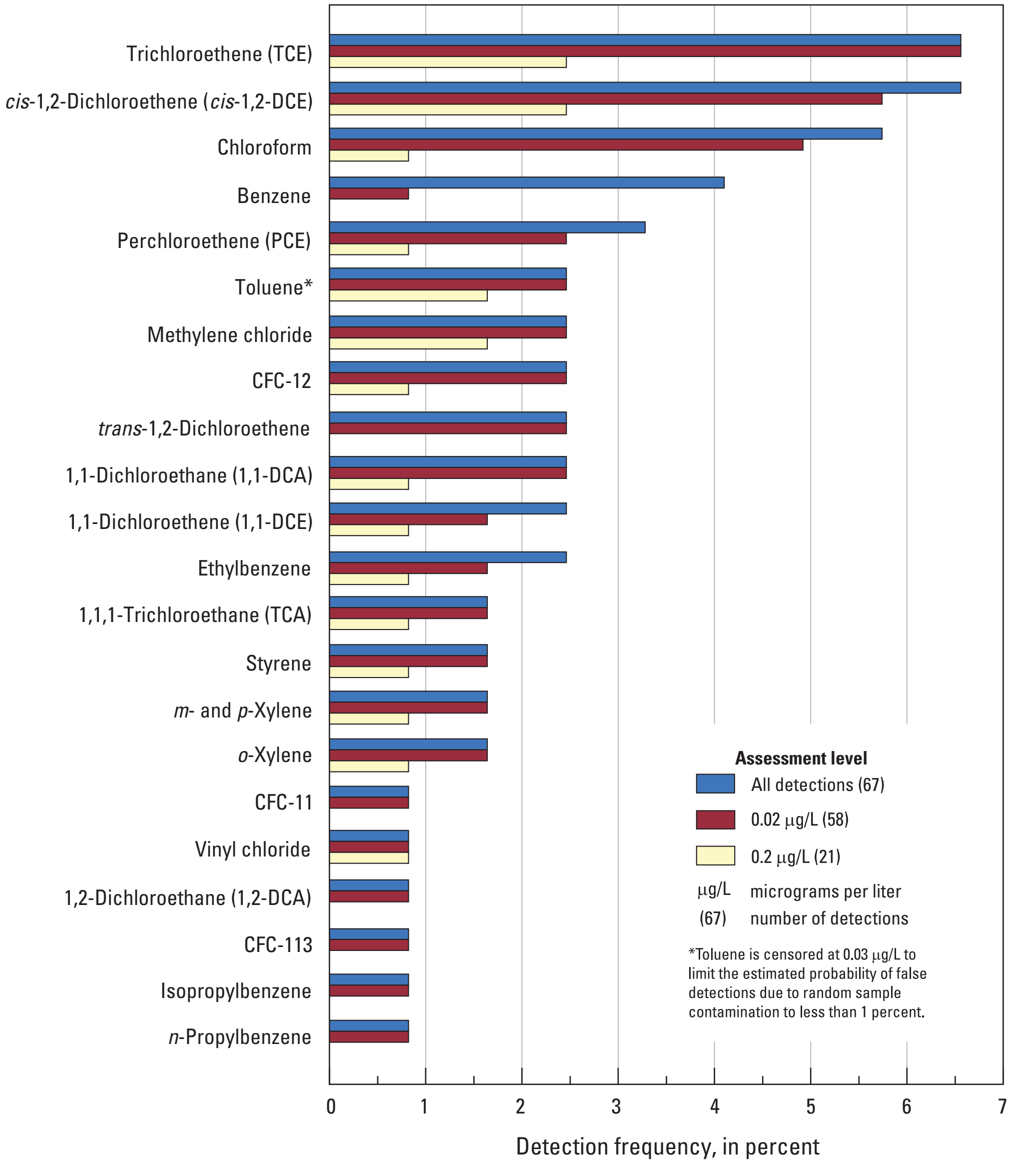


Figure 63. Detection frequency for volatile organic compounds in water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 2002–7.

The number of total detections and the detection frequency of individual compounds at an assessment level of 0.02 µg/L were similar to those when all detections were counted (table 25; fig. 63). The most noticeable drop in detections was with benzene. At an assessment level of 0.2 µg/L, 16 of the 54 VOCs were detected in at least 1 sample, but only *cis*-1,2-dichloroethene (*cis*-1,2-DCE), methylene chloride, toluene, and trichloroethene (TCE) were detected in more than 1 sample (table 25). The solvents TCE and *cis*-1,2-DCE were the most commonly detected compounds at an assessment level of 0.2 µg/L, and each was detected in 2.5 percent (3) of the wells.

VOCs detected in water samples from wells in the Cambrian-Ordovician aquifer system belonged to five predominant use groups. The most frequently detected VOC groups were solvents (33 detections) and gasoline hydrocarbons (18 detections) and together accounted for about 75 percent of all detections regardless of the assessment level (fig. 64). THMs and refrigerants accounted for about 10 and 8.5 percent of the detections, respectively, at an assessment level of 0.02 µg/L. Organic synthesis compounds accounted for 5 percent of the detections at an assessment level of 0.02 µg/L but 9.5 percent of the detections at an assessment level of 0.2 µg/L. Detections of organic synthesis compounds had the highest median concentration (0.13 µg/L); however, there were only four detections at the method detection level (no assessment level applied). Detections of gasoline hydrocarbons had the lowest median concentration (0.059 µg/L), even though they were the second most frequently detected use group. THMs, solvents, and gasoline hydrocarbons were the three most commonly detected use groups in the national assessment of VOCs (Zogorski and others, 2006).

Because of known or suspected human-health concerns, the USEPA has established MCLs that apply to 29 VOCs in drinking water supplied by public water systems. HBSLs have been established for an additional 13 VOCs analyzed in water samples for this study (appendix 2). Three VOCs exceeded an MCL in one sample each. The organic synthesis compound 1,1-dichloroethene exceeded the MCL of 7 µg/L at a concentration of 7.02 µg/L. The solvent methylene chloride exceeded the MCL of 5 µg/L at a concentration of 5.52 µg/L. The solvent TCE exceeded the MCL of 5 µg/L at a concentration of 64 µg/L. TCE and 1,1-dichloroethene exceeded their respective MCLs in the same sample from well 107, a public-supply well in the Twin Cities metropolitan area of Minnesota (fig. 65). Of the 54 VOCs, 10 were detected in the most recent sample collected at well 107, and 5 of the compounds had concentrations greater than 1 µg/L. Methylene chloride exceeded the MCL in well 132, a private well on the eastern side of Lake Winnebago in eastern Wisconsin (fig. 65). Four VOCs were detected in the most recent sample from well 132.

The distribution of VOC detections and their total concentration in samples collected from 2002 through 2007 are shown in figure 65. A slight majority (57 percent) of the wells were in regionally unconfined areas, but 71 percent of the wells with a detection were in unconfined areas (table 26). When all detections were used (no assessment level), there was no significant association between regional confinement and a well having a VOC detection (p = 0.087; chi-square test for independence). However, at an assessment level of 0.02 µg/L, wells in the unconfined area were significantly (p = 0.023) more likely to have a VOC detection. Although pesticides were detected in more wells than were VOCs, the occurrence of VOC compounds is geographically more widespread than the occurrence of pesticides (compare figs. 65 and 62). There were six wells (4.9 percent) where the total concentration of detected VOCs exceeded 1 µg/L (fig. 65).

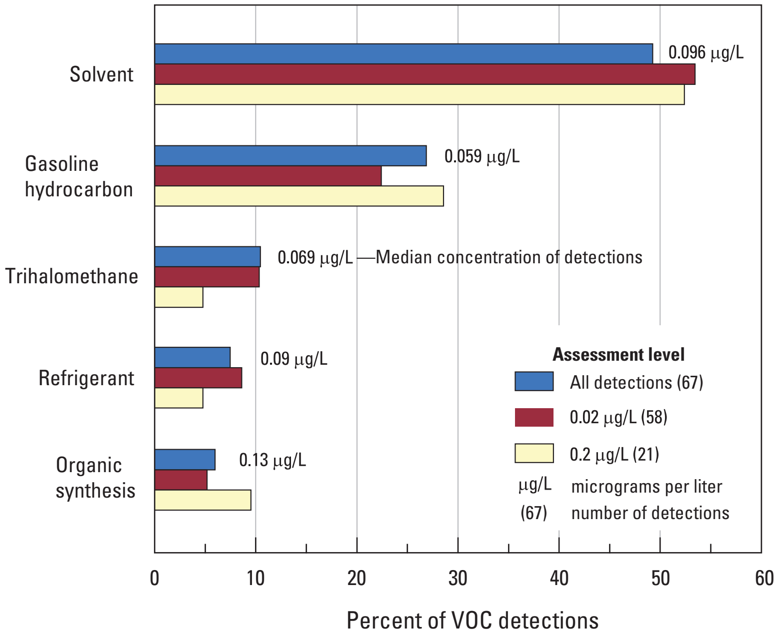
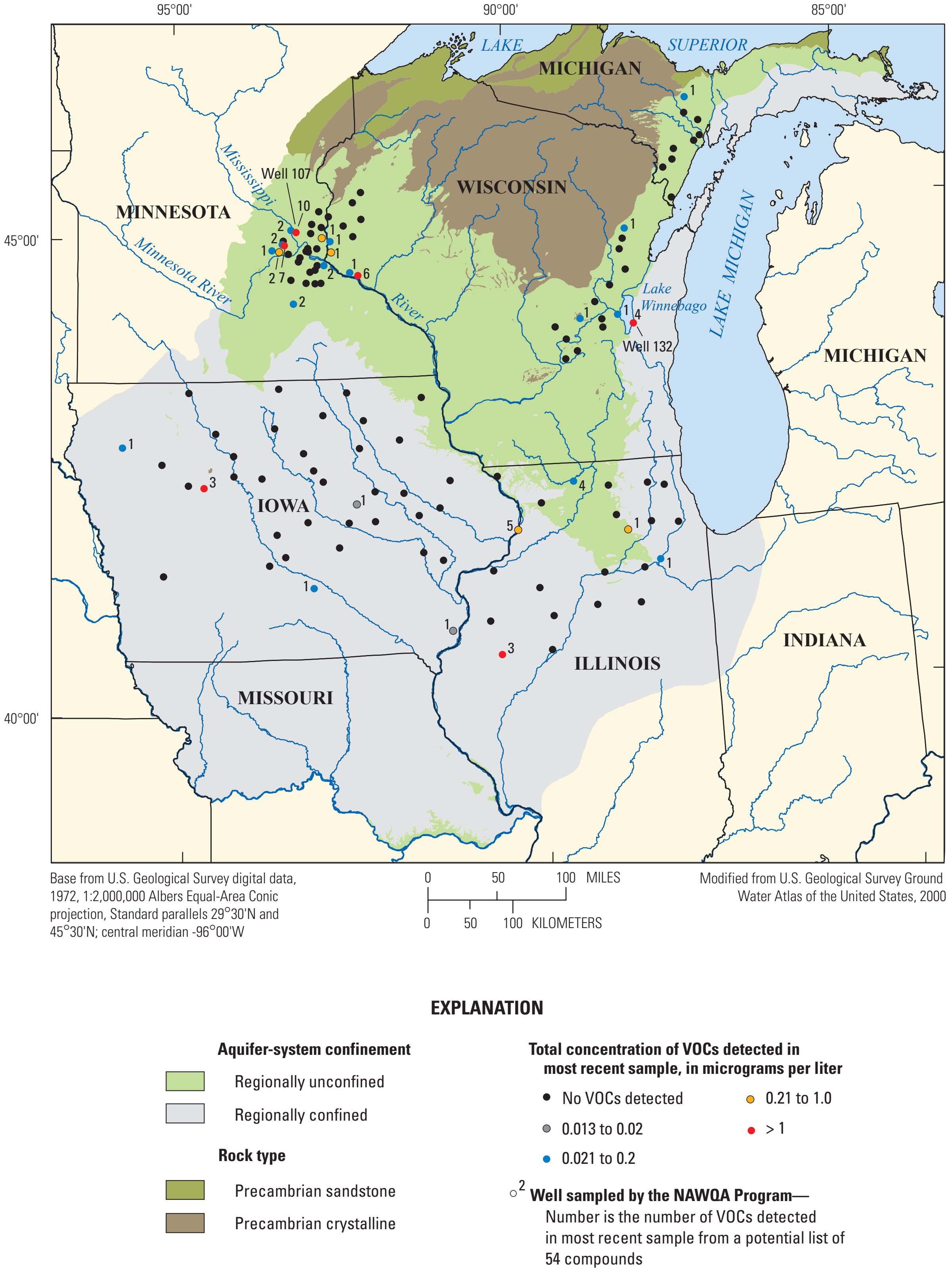


Figure 64. Volatile organic compound detections by predominant use group for water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 2002–7.



Base from U.S. Geological Survey digital data, 1972, 1:2,000,000 Albers Equal-Area Conic projection, Standard parallels 29°30'N and 45°30'N; central meridian -96°00'W

Modified from U.S. Geological Survey Ground Water Atlas of the United States, 2000

Figure 65. Total concentration and number of volatile organic compounds detected in water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 2002–7.

On the basis of available data, there was no significant association (p = 0.108) between tritium-based groundwater age and a well having a VOC detection (table 26). However, at an assessment level of 0.02 µg/L, wells with modern recharge were significantly more likely to have a VOC detection (p = 0.040).

In their national assessment of VOCs, Zogorski and others (2006) found that public-supply wells were more vulnerable to low-level VOC contamination than were domestic (private) wells. They attributed higher detection frequencies in public-supply wells to the higher pumping rates and the proximity to developed areas. In this study, the percentage of public supply and private wells with a VOC detection seems to align with the overall percentage of each well type in the dataset (table 26). The majority of wells in the dataset (61.5 percent) are public-supply wells, and the majority of wells with a VOC detection (67.9 percent) are public-supply wells. There was no significant association between well type and a well having a VOC detection, either when all detections were counted (p = 0.489) or when an assessment level of 0.02 µg/L was used (p = 0.714). The apparent absence of significant association between public-supply wells and VOC detections is probably the result of most public-supply wells being in the regionally confined areas where there were fewer VOC detections. Approximately 16 percent of the public-supply wells in regionally confined areas had a VOC detection, but 44 percent of public-supply wells in the regionally unconfined areas had a VOC detection.

Land use can affect the vulnerability of wells to low-level VOC contamination because the proximity of a well (and its recharge area) to developed areas may increase the likelihood of VOC sources (Zogorski and others, 2006). Developed areas have land uses of urban, agricultural, or some mixture of the two (table 1). Of the 122 wells sampled for VOCs, 49 wells (40 percent) had urban and 49 wells had mixed land use within the 500-m radius (table 27). All but one well with a VOC detection had an urban or mixed land use within the 500-m radius. Seventy percent of all VOC detections were in wells with an urban land use, and 28 percent of all VOC detections were in wells with a mixed land use within the 500-m radius. Mixed land use was the most common within the 1-mi radius, accounting for 52 percent of the wells and 50 percent of the wells with a VOC detection (table 27). Approximately 29 percent of the wells with a VOC detection had an urban land use within the 1-mi radius, and 18 percent of wells with a VOC detection had an agricultural land use within the 1-mi radius. Wells with urban or mixed land uses had an equal number of VOC detections and accounted for 89.6 percent of all VOC detections. As would be expected, these percentages show the association of VOC detections with the urban landscape. Urban areas have the highest population densities and are where most industry is located, and these factors probably correspond to the highest use of VOCs and potentially the greatest releases to the environment.

Table 26. Volatile organic compound detections in relation to regional confinement, tritium-based groundwater age, and well type for wells in the Cambrian-Ordovician aquifer system sampled by the NAWQA Program, 2002–7.

[Total of 67 detections in 28 of 122 wells sampled by NAWQA Program, 2002–7; 104 of 122 wells were analyzed for tritium, of which 20 had at least one VOC detection]

Category	Count and (percentage), by category					
	Regional confinement		Tritium-based age		Well type	
	Confined	Unconfined	Modern	Pre-1953	Public supply	Private
All 122 wells	52 (42.6)	70 (57.4)	36 (34.6)	68 (65.4)	75 (61.5)	47 (38.5)
Wells with a VOC detection	8 (28.6)	20 (71.4)	10 (50)	10 (50)	19 (67.9)	9 (32.1)
VOC detections	16 (23.9)	51 (76.1)	19 (47.5)	21 (52.5)	49 (73.1)	18 (26.9)

Table 27. Volatile organic compound detections in relation to land use for wells in the Cambrian-Ordovician aquifer system sampled by the NAWQA Program, 2002–7.

[Total of 67 detections in 28 of 122 wells sampled by NAWQA Program, 2002–7]

Land-use	Count and (percentage) by land use within a 500-meter radius			Count and (percentage) by land use within a 1-mile radius		
	All wells	Wells with a detection	VOC detections	All wells	Wells with a detection	VOC detections
Agricultural	22 (18.0)	1 (3.6)	1 (1.5)	30 (24.6)	5 (17.8)	6 (8.9)
Urban	49 (40.2)	13 (46.4)	47 (70.1)	23 (18.9)	8 (28.6)	30 (44.8)
Undeveloped	2 (1.6)	0 (0.0)	0 (0.0)	5 (4.1)	1 (3.6)	1 (1.5)
Mixed	49 (40.2)	14 (50.0)	19 (28.4)	64 (52.4)	14 (50.0)	30 (44.8)

There were eight wells in the regionally confined areas of Iowa and Illinois where at least one VOC was detected (fig. 65). The VOC detections in these relatively deep wells (casing depths ranged from 350 to 1,900 ft) probably do not represent the presence of VOCs in the aquifer. The VOC detections may be related to operator practices at these wells. The RASA study determined through carbon-14 data that groundwater age in the Prairie du Chien-Jordan aquifer in most of Iowa was at least 15,000 years before present (Siegel, 1989). Groundwater of that age would not contain manmade VOCs: five different gasoline hydrocarbons, four different solvents, one THM, and one refrigerant. Examples of possible operator practices that could result in low-level VOC detections would be lubrication of turbine shafts with petroleum-based lubricants or chlorinated (treated) drinking water and backflushing of filters with chlorinated drinking water that enters the well. Treated water entering the well could account for low-level detections of THMs. Operator practices that could possibly cause low-level VOC detections would be a potential issue with all public-supply wells, not just the deep, confined wells.

Co-occurrence of Nitrate, Pesticides, and Volatile Organic Compounds

The toxicology of contaminant mixtures is not well understood because most toxicology studies have dealt with single, pure compounds. Human-health benchmarks, such as USEPA MCLs, are based on exposure to large concentrations of a single compound. In reality, there probably are few single chemical exposures (Yang, 1997). Most people are exposed to mixtures of anthropogenic and naturally occurring contaminants at concentrations less than concentrations known to cause adverse effects (Carpenter and others, 2002). There is evidence that exposure to much lower concentrations than human-health benchmarks also can be harmful (Ashford and Miller, 1998; Yang, 1994; Hasegawa and others, 1994). Endocrine disruption, particularly at low concentrations, is an area of intensive research. The health effects of contaminant mixtures in drinking water are uncertain, but the potential exists that some mixtures of contaminants may pose more health risks than occurrence of contaminants individually. For example, health effects may be additive for contaminants that have similar modes of action, and some combinations of contaminants may have synergistic interactions resulting in greater than additive effects. The possibility also exists that some combinations of contaminants may have antagonistic interactions or no interaction at all (Squillace and others, 2002).

In this study, the occurrence of nitrate, pesticides, and VOCs as mixtures was assessed by determining the frequency of contaminant mixtures and the geographic distribution of mixtures of contaminant classes. Therefore, this analysis deals with the co-occurrence of compounds that have anthropogenic sources. Some VOCs have natural sources (Zogorski and others, 2006), but VOCs can usually be considered to have anthropogenic sources, and nitrate detections are only counted at concentrations greater than 1 mg/L to avoid counting low-level detections that may have a natural source. The analysis of mixtures is based on water samples collected from 122 wells by the NAWQA Program during the period 2002 to 2007. A mixture is defined as a unique combination of two or more particular compounds, regardless of the presence of other compounds that may occur in the same sample (Squillace and others, 2002). A mixture of contaminant classes is the detection of more than one class of contaminant (nitrate, pesticides, VOCs) in the same sample. For each sample, as many as 83 pesticides, 54 VOCs, and nitrate were analyzed. All detections of pesticides and VOCs were counted, and nitrate concentrations greater than 1 mg/L were considered to have an anthropogenic origin. Unique mixtures were determined by using the methods of Squillace and others (2002) (Jon Scott, U.S. Geological Survey, written commun., 2010). A single sample can contain many unique mixtures, each of which may have different health effects. For example, a sample containing compounds A, B, and C contains four unique mixtures—AB, AC, BC, and ABC. The number of unique mixtures in one sample can be large if many compounds are detected. A sample with 2 compounds contains only 1 mixture, but a sample with 5 compounds contains 26 unique mixtures. For this study, 2,384 unique mixtures of nitrate, pesticides, and VOCs were identified in 39 of the 122 wells. Most (2,210) of the unique mixtures had only one occurrence.

The 18 most frequently detected mixtures occurred in at least six wells (4.9 percent) each (fig. 66). The contaminant mixtures were dominated by pesticides and nitrate; more specifically, atrazine, deethylatrazine, simazine, and nitrate. The mixture of atrazine/deethylatrazine was the most frequently detected mixture, occurring in 21 percent of wells. The mixture of deethylatrazine/nitrate was detected in 16.4 percent of wells, and the mixtures of atrazine/nitrate and atrazine/deethylatrazine/nitrate were each detected in 15.6 percent of wells. The mixture of *cis*-1,2-dichloroethene/trichloroethene (*cis*-1,2-DCE/TCE) was detected in 6 wells (4.9 percent) and was the only unique mixture with a VOC that was detected in more than four wells. Samples with at least one contaminant mixture were significantly more likely ($p < 0.05$) to come from wells in regionally unconfined areas than confined areas, from wells with modern recharge than pre-1953 recharge, and from private wells than public-supply wells. Eighty-seven percent of wells with a contaminant mixture were in the regionally unconfined areas, 85 percent of the wells with a contaminant mixture contained modern recharge, and 61.5 percent of wells with a mixture were private wells (table 28).

Mixtures of contaminant classes were identified in 26 of the 122 wells, of which all but three were in regionally unconfined areas (fig. 67). Most of the wells (14 of 26) had a mixture that consisted of at least one pesticide and nitrate. Six wells had a mixture that consisted of at least one pesticide and at least one VOC, and the other six wells had a mixture of

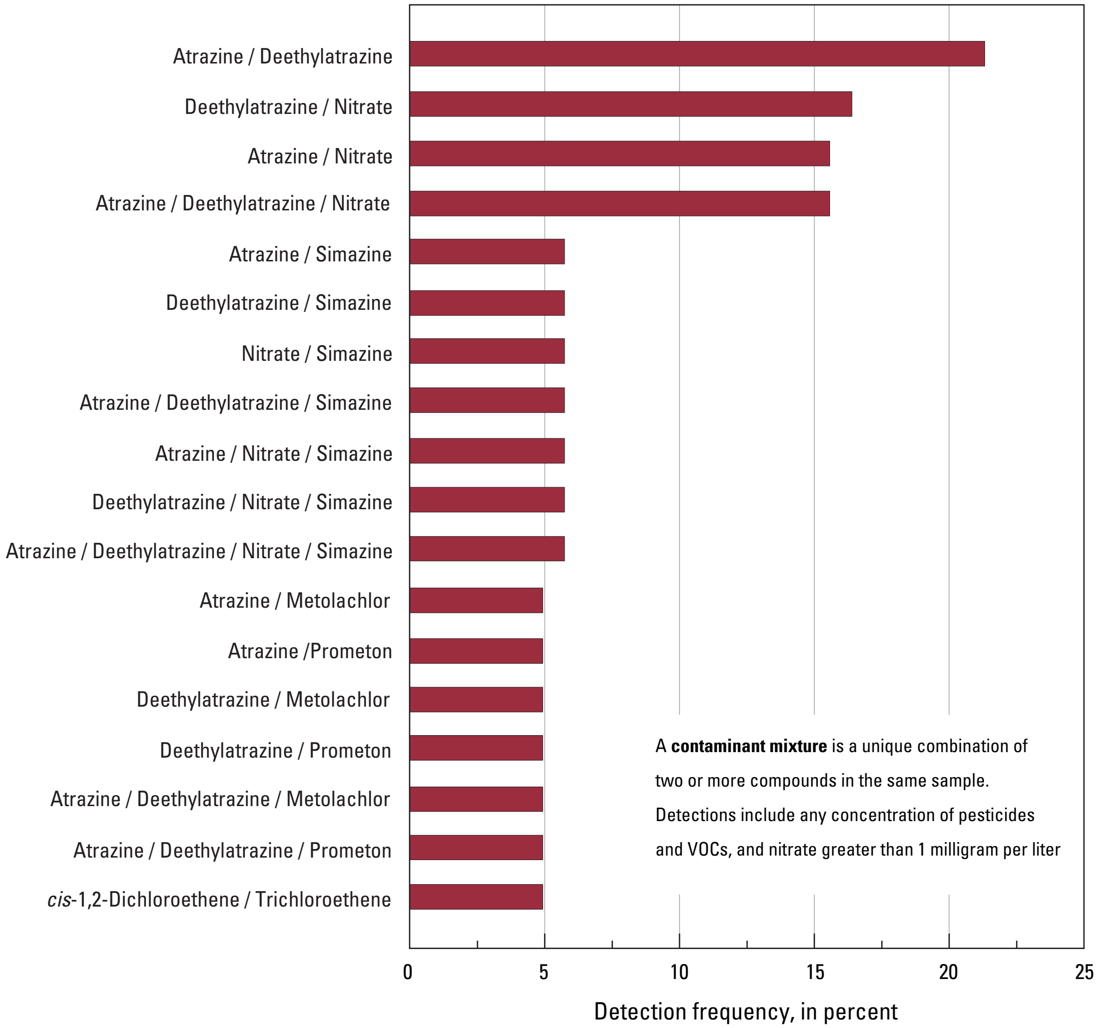


Figure 66. Detection frequency for the most commonly detected mixtures of nitrate, pesticides, and volatile organic compounds in water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 2002–7.

Table 28. Occurrence of contaminant mixtures and mixtures of contaminant classes in relation to regional confinement, tritium-based groundwater age, and well type for samples from wells in the Cambrian-Ordovician aquifer system collected by the NAWQA Program, 2002–7.

[Contaminant mixture is defined as a unique combination of two or more compounds; Mixture of contaminant classes is defined as the detection of more than one class of contaminant in the same sample, including the detection of a pesticide or volatile organic compound at any concentration and nitrate greater than 1 milligram per liter]

Category	Count and (percentage), by category					
	Regional confinement		Tritium-based age		Well type	
	Confined	Unconfined	Modern	Pre-1953	Public supply	Private
All 122 wells	52 (42.6)	70 (57.4)	35 (42.7)	47 (57.3)	76 (62.3)	46 (37.7)
Wells with at least one mixture detected	5 (12.8)	34 (87.2)	23 (85.2)	4 (14.8)	15 (38.5)	24 (61.5)
Wells with a mixture of contaminant classes	3 (11.5)	23 (88.5)	17 (89.5)	2 (10.5)	9 (34.6)	17 (65.4)

Base from U.S. Geological Survey digital data, 1972, 1:2,000,000 Albers Equal-Area Conic projection, Standard parallels 29°30'N and 45°30'N; central meridian -96°00'W

Modified from U.S. Geological Survey Ground Water Atlas of the United States, 2000

EXPLANATION

Aquifer-system confinement

🟩 Regionally unconfined

⬜ Regionally confined

Rock type

🟩 Precambrian sandstone

🟫 Precambrian crystalline

Contaminant class mixture—Detection of more than one class of contaminant in the same sample; detection of a pesticide or VOC at any concentration and nitrate greater than 1 mg/L. Samples were analyzed for up to 83 pesticides and 54 VOCs

● Pesticide-VOC-nitrate detected

● Pesticide and VOC detected

● Pesticide and nitrate detected

● No mixture of contaminants, but one class of contaminant detected

▲ No detections, or nitrate < 1 mg/L

○ 3 **Well sampled by the NAWQA Program**—Number is the number of contaminants detected in the most recent sample

Figure 67. Mixtures of contaminant classes and number of contaminants detected in water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 2002–7.

at least one pesticide, at least one VOC, and nitrate. Samples with a mixture of contaminant classes were significantly more likely ($p < 0.05$) to come from wells in regionally unconfined areas than regionally confined areas, from wells with modern recharge than with pre-1953 recharge, and from private wells than public-supply wells. Eighty-eight percent of wells with a mixture of contaminant classes were in regionally unconfined areas, 89.5 percent of wells with a mixture of contaminant classes had modern recharge, and 65.4 percent of wells with a mixture of contaminant classes were private wells. Nitrate was detected at a concentration greater than 1 mg/L in 21 of the 122 wells used in the analysis of mixtures. Of those 21 wells, 20 had at least 1 contaminant mixture and by default, a mixture of contaminant classes. This finding suggests that detections of nitrate at concentrations greater than 1 mg/L may be a good indicator of a well's susceptibility to low-level detections of pesticides and VOCs.

Limitations of Water-Quality Data and Analyses

The majority of analyses presented in this report are based on water-quality data collected for the NAWQA Program from 1995 through 2007. A major benefit of the NAWQA Program is that data were collected in a uniform, systematic way, with water samples being analyzed at the same laboratory regardless of where the sample was collected. However, some analyses of water quality may be influenced by the number and location of samples because of the regional framework of the aquifer system. As was shown in this report, high concentrations of contaminants can preferentially occur where the aquifer system is regionally confined or regionally unconfined, depending on the contaminant. In the first decade of NAWQA, well networks in Minnesota and Wisconsin were established within surface drainage basins, with scopes of study that were more localized than at the principal aquifer scale. This resulted in a large number of wells in a relatively small geographic area, especially in the Twin Cities metropolitan area, and a lack of wells in the regionally confined areas of Minnesota, Wisconsin, and the Upper Peninsula of Michigan. NAWQA well networks in the Twin Cities metropolitan area sampled only the Prairie du Chien-Jordan aquifer over a limited geographic area. Therefore, the NAWQA data in Minnesota may not represent the water-quality conditions in the Prairie du Chien-Jordan aquifer away from the Twin Cities metropolitan area or in deeper aquifers throughout the State. However, it should be pointed out that a large percentage of the groundwater withdrawals in the Twin Cities metropolitan area come from the Prairie du Chien-Jordan aquifer.

The definition of regional confinement used in this report is that the aquifer system is covered by the Upper Ordovician Maquoketa Shale or younger bedrock. However, it is acknowledged that the Maquoketa Shale is not the only confining unit within the Cambrian-Ordovician aquifer system. Several leaky confining units within the aquifer system can effectively confine the aquifers in areas where the aquifer system is otherwise regionally unconfined. For example, the dolomites and shales of the Sinnipee Group and the Glenwood Formation can confine the St. Peter Sandstone, the St. Lawrence and Franconia Formations can confine the Ironton-Galesville Sandstones, and the Eau Claire Formation can confine the Mount Simon Sandstone. Because the boundary of the Upper Ordovician (the Maquoketa Shale) is on geologic maps, it provided a logical and convenient boundary for separating regionally confined areas from regionally unconfined areas.

Another consequence of the design of well networks established in the first decade of NAWQA is large areas with no wells exist between the well networks. The well networks established in the second decade of NAWQA in Iowa and Illinois essentially covered the full extent of usable aquifer in those states. To fill gaps in data coverage between the well networks, and to add data for northeastern Missouri and the Upper Peninsula, data from other sources were included for mapping selected water-quality constituents and for testing for significant differences in concentration between the regionally confined and unconfined areas. Inclusion of data from other sources resulted in the use of some data that were older than the NAWQA data, as well as data for unfiltered samples for selected constituents for which the USGS typically filters samples.

This report does not go into detail about the potential issues related to wells with long open intervals that span multiple aquifers or formations. Public-supply wells with long open intervals are most common in the regionally confined areas of eastern Wisconsin and Illinois and to a lesser extent in Iowa. Wells with long open intervals can allow for mixing of waters in the well bore from the different productive intervals, and these waters can have different characteristics—especially if the open interval straddles a local confining unit. Obviously, water samples collected from these wells will be a composite of the gross water quality at the well and may not reflect the normal chemistry of a discrete aquifer at that location. Wells with long open intervals have also been a source of uncertainty for investigators trying to map or simulate heads in the Cambrian-Ordovician aquifer system. Water levels measured in those wells will reflect a composite head of the different aquifers to which the well is open. Wells open to multiple aquifers, or old wells with failed casing, can also serve as conduits for leakage between aquifers if a hydraulic gradient exists.

Summary and Conclusions

The water-quality assessment of the Cambrian-Ordovician aquifer system was based primarily on data collected from 1995 through 2007 as part of the USGS NAWQA Program. Physical properties and concentrations of major ions, trace elements, radionuclides, nutrients, pesticides, and volatile organic compounds were measured in raw water samples from as many as 155 wells. The distribution of constituent concentrations were related to various factors such as confining conditions, well type, land use, and groundwater age. Constituent concentrations were compared to water-quality benchmarks for human health, either USEPA MCLs or USGS HBSLs. Concentrations were also compared to USEPA SDWRs established for aesthetic or other non-health reasons. Data from other USGS sources and state agencies were added to NAWQA data to help fill gaps in data coverage for mapping concentrations of selected water-quality constituents.

The Cambrian-Ordovician aquifer system is an important water resource in the northern Midwest, and it accounts for a large proportion of total groundwater withdrawals in Illinois, Iowa, Minnesota, and Wisconsin. Water withdrawals from the aquifer system are not as high in the Upper Peninsula of Michigan as in other states because of the small geographic area and low population density. In northeastern Missouri, water withdrawals from the aquifer system are limited to an eight-county area just north of the Missouri River where the salinity is low enough for the water to be usable. The primary uses of groundwater withdrawal are for public supply, self-supplied industrial, and irrigation; however, the aquifer system is an important source for domestic supply in the northern areas where it is relatively shallow.

The Cambrian-Ordovician aquifer system is a complex, multilayered sequence of marine sedimentary rock with major sandstone aquifers separated by leaky confining units consisting of dolomite, shale, shaly sandstone, or a combination of these rock types. Rock units that act as major aquifers, in descending order, include the St. Peter Sandstone, Prairie du Chien Group (mostly dolomite), Jordan Sandstone, Ironton-Galesville Sandstones, and the Mount Simon Sandstone. Other Cambrian and Ordovician formations are sources of water but at a more local scale. Contrasting areas of regional confinement influence the distribution of concentrations of natural and anthropogenic contaminants. Generally, natural contaminants such as major ions, trace elements, and radium occur at higher concentrations in wells in regionally confined areas than in unconfined areas. Anthropogenic contaminants such as pesticides, volatile organic compounds, and nitrate are detected more often in wells in regionally unconfined areas than in confined areas. The aquifer system is regionally confined where it is covered by the Maquoketa Shale and younger bedrock, and it is regionally unconfined where the Maquoketa Shale and younger bedrock are absent. The subcrop of the Maquoketa Shale was used in this study for defining the boundary of regional confinement; however, other leaky confining units in the aquifer system can effectively confine aquifers at a more local scale.

The aquifer system is regionally unconfined over much of its extent in Minnesota, Wisconsin, and the Upper Peninsula. Other areas where the aquifer system is regionally unconfined are north-central Illinois, a small part of northeastern Iowa, and in a small area along the Missouri River in northeastern Missouri. The aquifer system is regionally confined over much of its extent in Iowa and Illinois, as well as along Lake Michigan in eastern Wisconsin and the Upper Peninsula. Groundwater in regionally unconfined areas is associated with oxic conditions, lower dissolved solids (compared to regionally confined areas), and modern recharge (post-1953). Groundwater in regionally confined areas is associated with anoxic conditions, higher dissolved solids, and recharge that originated before 1953. The redox status of the aquifer system was mostly anoxic; 60 percent of the wells sampled by NAWQA showed anoxic conditions, 26 percent showed oxic conditions, and 14 percent showed mixed source conditions. For the most part, wells with oxic conditions also had modern recharge and were in regionally unconfined areas.

Water in the aquifer system was typically hard to very hard (>180 mg/L), and samples collected by NAWQA had a median hardness of 299 mg/L as $CaCO_3$. Dissolved solids concentrations were significantly higher in wells in the regionally confined area than the unconfined area, but it was common for dissolved solids to exceed the SDWR (500 mg/L) throughout the aquifer system. Twenty-nine percent of the wells sampled by NAWQA exceeded the SDWR for dissolved solids, and 84 percent of those wells were in regionally confined areas. The aquifer system is not used in some areas of southwestern Iowa, northern Missouri, central Illinois, and northwestern Indiana because of high salinity (dissolved solids). All major ions analyzed by NAWQA, except silica, had significantly higher concentrations in wells from regionally confined areas than unconfined areas. Among wells sampled by NAWQA, concentrations of chloride, fluoride, and sulfate exceeded their SDWRs in roughly 5, 5, and 17 percent, and exceedances occurred almost exclusively in wells in regionally confined areas. None of the wells sampled by NAWQA had a fluoride concentration greater than the MCL; however, a previous study showed that fluoride concentrations did exceed the MCL in a few wells in southeastern Iowa and northeastern Missouri.

The trace elements barium, boron, manganese, and strontium exceeded their human-health benchmark in at least one well sampled by NAWQA. Only one well sampled by NAWQA exceeded the barium MCL (2,000 micrograms per liter, µg/L), and it was in northeastern Illinois where previous studies have identified an area where barium concentrations are much greater than the MCL. Elevated concentrations of barium (>2,000 µg/L) in northeastern Illinois are associated with sulfate reduction, which prevents the normal precipitation of barium as barite ($BaSO_4$) by removing the sulfate. Among wells sampled by NAWQA, the HBSLs for boron (1,000 µg/L), manganese (300 µg/L), and strontium (4,000 µg/L) were exceeded in approximately 14, 4, and 9 percent. Concentrations of boron and strontium were significantly higher in regionally confined areas than unconfined areas, and concentrations of manganese were significantly higher in unconfined areas than confined areas. Data from other sources showed that elevated concentrations of strontium (>10,000 µg/L) occurred near the eastern boundary of the aquifer system in eastern Wisconsin. The majority of wells with samples that exceeded the manganese HBSL were in Minnesota and northwestern Iowa, in an area overlain by the Des Moines glacial lobe. This finding suggests that recharge from glacial deposits in this lobe may transport manganese and other trace elements to the underlying Cambrian-Ordovician aquifers. Iron concentrations were relatively high throughout the aquifer system, with a median concentration of 186 µg/L in wells sampled by NAWQA. Iron concentrations exceeded the SDWR (300 µg/L) in 41 percent of the wells sampled by NAWQA and were significantly higher in wells in regionally confined areas than in wells in regionally unconfined areas.

Radon and radium were the constituents most frequently measured at concentrations greater than their human-health benchmark. Radon was detected in 96 percent of the 140 wells sampled by NAWQA, at a median concentration of 250 picocuries per liter (pCi/L). Radon concentrations were significantly higher in wells in regionally unconfined areas than in confined areas. Radon concentrations were greater than the proposed MCL (300 pCi/L) in 43 percent of the wells sampled by NAWQA, of which 90 percent were in regionally unconfined areas. Radium-226 and radium-228 were detected in 94 and 83 percent of the 88 wells sampled by NAWQA, and concentrations were significantly higher in wells in regionally confined areas than in unconfined areas. Radium had a strong positive correlation with dissolved solids. It is thought that competition with cations for adsorption sites prevents the adsorption of radium, which can result in high radium concentrations in groundwater. The MCL for radium-226 + radium-228 (5 pCi/L) was exceeded in 40 percent of the wells sampled by NAWQA, of which 89 percent were in regionally confined areas.

Radium-226 and radium-228 are chemically similar, but their distribution in groundwater can be different because of the different properties of their parent isotopes and the large difference in half-life. The relatively high solubility of uranium, and a half-life of 1,622 years, contributes to the widespread distribution of radium-226 in the aquifer system. Radium-228 has a half-life of 5.75 years, and its parent isotope, thorium-232, is insoluble in most groundwater environments. The insolubility of thorium, the short half-life, and the slow movement of groundwater limit the distribution of radium-228 in groundwater to areas with enriched thorium in the aquifer matrix. Concentrations of radium-226 greater than 5 pCi/L are common throughout the aquifer system, especially in wells in regionally confined areas. Concentrations of radium-228 greater than 5 pCi/L are limited mostly to wells in northeastern Illinois and in Minnesota near the western boundary of the aquifer system. Data from multiple sources showed that radium-226 and radium-228 concentrations were significantly higher in Minnesota wells open to the Mount Simon Sandstone than in wells open to other aquifers above the Mount Simon Sandstone.

Nitrate was detected at a concentration greater than 1 mg/L in 21 percent of the wells sampled by NAWQA. Concentrations of nitrate greater than 1 mg/L are assumed to be influenced by human activity. All but one of the wells were in regionally unconfined areas, indicating that the aquifer system is more susceptible to manmade contaminants where it is unconfined (and hence, shallower). Approximately 4 percent of wells sampled by NAWQA had concentrations greater than the MCL (10 mg/L). An evaluation of near-decadal scale changes in nitrate concentrations in two well networks showed no significant change in nitrate concentrations between samples collected during the first decade (1995–96) and second decade (2002–7) of the NAWQA Program, even though concentrations may have varied at individual wells.

Nine different pesticides (from a potential list of 83) were detected in samples from 35 of 125 wells sampled by NAWQA from 2002 through 2007, but atrazine and its degradate deethylatrazine accounted for 67 percent of all detections. Concentrations of pesticides were usually less than 0.1 µg/L, and only atrazine, deethylatrazine, and metolachlor were detected at a concentration greater than 0.1 µg/L. The detection of these herbicides is consistent with the land use being 77 percent agricultural and corn being the leading crop in terms of harvested acreage since the 1930s. Eighty-six percent of wells with a pesticide detection were in regionally unconfined areas. Wells with a pesticide detection were also more likely to have modern recharge, a dissolved oxygen concentration greater than 0.5 mg/L, and a nitrate concentration greater than 1 mg/L.

Twenty-three different VOCs (from a potential list of 54) were detected in 28 of 122 wells sampled by NAWQA from 2002 to 2007, but usually at concentrations less than 0.2 µg/L. The most commonly detected VOC use groups were solvents, gasoline hydrocarbons, and trihalomethanes. The most frequently detected compounds were the solvents trichloroethene and *cis*-1,2-dichloroethene, the trihalomethane chloroform, and the gasoline hydrocarbon benzene. The compounds 1,1-dichloroethene, methylene chloride, and trichloroethene each exceeded their respective MCLs in one well.

Mixtures of anthropogenic contaminants and contaminant classes were evaluated through the co-occurrence of nitrate (>1 mg/L), pesticides, and VOCs in 122 wells sampled by NAWQA. The health effects of contaminant mixtures in drinking water are uncertain, but the potential exists that some contaminants may pose more health risks as mixtures than when the contaminants occur individually. The most commonly detected mixtures were atrazine/deethylatrazine, deethylatrazine/nitrate, atrazine/nitrate, and atrazine/deethylatrazine/nitrate. Mixtures of contaminant classes were identified in 26 of the 122 wells used in the analysis. Fourteen wells had a mixture defined by the detection of at least one pesticide and nitrate, six wells had a mixture defined by the detection of at least one pesticide and at least one VOC, and the other six wells had a mixture defined by the detection of at least one pesticide, at least one VOC, and nitrate. Of the wells with a mixture of contaminant classes detected, 88 percent were in regionally unconfined areas and 89 percent of those with a tritium sample contained modern (post-1953) recharge.

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Appendix 1

Table of characteristics of wells completed in the Cambrian-Ordovician aquifer system sampled by the NAWQA Program, 1995–2007 (Table 1–1 available online)

http://pubs.usgs.gov/sir/2011/5229/

Appendix 2

Table of physical properties and constituents analyzed in samples collected for the NAWQA Program, and associated human-health benchmarks for drinking water

Table 2–1. Physical properties and constituents analyzed in samples collected for the NAWQA Program and associated human-health benchmarks for drinking water.

[USGS, U.S. Geological Survey; CASRN, Chemical Abstracts Service Registry Number®; Common long-term method detection levels (LT-MDLs) apply to the sampling periods 1995–96 and 2002–7. Predominant use group is from Gilliom and others (2006) and Zogorski and others (2006). Pesticide degradation products are designated by "DP" with parent compound indicated in parentheses. MCL, U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Level for public water supplies; AMCL, USEPA proposed Alternative Maximum Contaminant Level for public water supplies; HBSL, Health-Based Screening Level developed by USGS using USEPA toxicity information and methods (Toccalino and Norman, 2006); °C, degrees Celsius; µS/cm, microsiemens per centimeter; $CaCO_3$, calcium carbonate; mg/L, milligrams per liter; ROE, residue on evaporation; µg/L, micrograms per liter; pCi/L, picocuries per liter; --, not available or not applicable]

Property or constituent	Units	USGS parameter code	[1]CASRN	Predominant use group	Common LT-MDLs	Human-health benchmark		Number of analyses
						Value	Type	
Physical properties								
Temperature	°C	00010	--	--	--	--	--	154
Specific conductance	µS/cm at 25°C	00095	--	--	--	--	--	154
Dissolved oxygen	mg/L	00300	--	--	0.1, 0.18	--	--	152
pH	Standard units	00400	--	--	--	--	--	154
Alkalinity, as $CaCO_3$	mg/L	--	--	--	--	--	--	150
Major ions								
[2]Bicarbonate	mg/L	--	71-52-3	--	--	--	--	150
Bromide	mg/L	71870	24959-67-9	--	0.01	--	--	154
Calcium	mg/L	00915	7440-70-2	--	0.02	--	--	154
Chloride	mg/L	00940	16887-00-6	--	0.1	--	--	154
Fluoride	mg/L	00950	16984-48-8	--	0.05	4	MCL	154
Magnesium	mg/L	00925	7439-95-4	--	0.01	--	--	154
Potassium	mg/L	00935	7440-09-7	--	0.1	--	--	154
Silica	mg/L	00955	7631-86-9	--	0.01	--	--	154
Sodium	mg/L	00930	7440-23-5	--	0.2	--	--	154
Sulfate	mg/L	00945	14808-79-8	--	0.1	--	--	154
[3]Hardness, as $CaCO_3$	mg/L	00900	--	--	--	--	--	154
Dissolved solids (ROE)	mg/L	70300	--	--	10	--	--	154
Trace elements								
Aluminum	µg/L	01106	7429-90-5	--	1.6	--	--	137
Antimony	µg/L	01095	7440-36-0	--	1	6	MCL	137
Arsenic	µg/L	01000	7440-38-2	--	1	10	MCL	137
Barium	µg/L	01005	7440-39-3	--	1	2,000	MCL	136
Beryllium	µg/L	01010	7440-41-7	--	1	4	MCL	137
Boron	µg/L	01020	7440-42-8	--	7	1,000	HBSL	107
Cadmium	µg/L	01025	7440-43-9	--		5	MCL	137
Chromium	µg/L	01030	7440-47-3	--		100	MCL	137

Table 2–1. Physical properties and constituents analyzed in samples collected for the NAWQA Program and associated human-health benchmarks for drinking water.—Continued

[USGS, U.S. Geological Survey; CASRN, Chemical Abstracts Service Registry Number®; Common long-term method detection levels (LT-MDLs) apply to the sampling periods 1995–96 and 2002–7. Predominant use group is from Gilliom and others (2006) and Zogorski and others (2006). Pesticide degradation products are designated by "DP" with parent compound indicated in parentheses. MCL, U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Level for public water supplies; AMCL, USEPA proposed Alternative Maximum Contaminant Level for public water supplies; HBSL, Health-Based Screening Level developed by USGS using USEPA toxicity information and methods (Toccalino and Norman, 2006); °C, degrees Celsius; µS/cm, microsiemens per centimeter; $CaCO_3$, calcium carbonate; mg/L, milligrams per liter; ROE, residue on evaporation; µg/L, micrograms per liter; pCi/L, picocuries per liter; --, not available or not applicable]

Property or constituent	Units	USGS parameter code	[1]CASRN	Predominant use group	Common LT-MDLs	Human-health benchmark		Number of analyses
						Value	Type	
Trace elements—Continued								
Cobalt	µg/L	01035	7440-48-4	--		--	--	137
Copper	µg/L	01040	7440-50-8	--		1,300	Action level	137
Iron	µg/L	01046	7439-89-6	--	3–10	--	--	144
Lead	µg/L	01049	7439-92-1	--		15	Action level	137
Lithium	µg/L	01130	7439-93-2	--		--	--	108
Manganese	µg/L	01056	7439-96-5	--		300	HBSL	154
Molybdenum	µg/L	01060	7439-98-7	--		40	HBSL	137
Nickel	µg/L	01065	7440-02-0	--		100	HBSL	137
Selenium	µg/L	01145	7782-49-2	--		50	MCL	137
Silver	µg/L	01075	7440-22-4	--		100	HBSL	137
Strontium	µg/L	01080	7440-24-6	--		4,000	HBSL	107
Thallium	µg/L	01057	7440-28-0	--		2	MCL	108
Uranium	µg/L	22703	7440-61-1	--		30	MCL	137
Vanadium	µg/L	01085	7440-62-2	--		--	--	108
Zinc	µg/L	01090	7440-66-6	--		2,000	HBSL	136
Radionuclides (radon and radium)								
Radon-222	pCi/L	82303	14859-67-7	--	20–74	300 4,000	Proposed MCL and AMCL	140
Radium-226	pCi/L	09511	13982-63-3	--	0.02	--	--	88
Radium-228	pCi/L	81366	15262-20-1	--	0.19–0.29	--	--	88
Radium-226 + radium-228	pCi/L	--	--	--	--	5	MCL	88
Nutrients and dissolved organic carbon								
Ammonia as N	mg/l	00608	7664-41-7	--	0.01–0.02	--	--	154
Dissolved organic carbon	mg/l	00681	--	--	0.1–0.2	--	--	140
[4]Nitrate, as N	mg/l	00631	14797-55-8	--	0.02–0.05	10	MCL	154
Nitrite, as N	mg/l	00613	14797-65-0	--	0.001–0.01	--	--	154
Orthophosphate, as P	mg/l	00671	14265-44-2	--	0.003–0.01	--	--	154

Table 2–1. Physical properties and constituents analyzed in samples collected for the NAWQA Program and associated human-health benchmarks for drinking water.—Continued

[USGS, U.S. Geological Survey; CASRN, Chemical Abstracts Service Registry Number®; Common long-term method detection levels (LT-MDLs) apply to the sampling periods 1995–96 and 2002–7. Predominant use group is from Gilliom and others (2006) and Zogorski and others (2006). Pesticide degradation products are designated by "DP" with parent compound indicated in parentheses. MCL, U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Level for public water supplies; AMCL, USEPA proposed Alternative Maximum Contaminant Level for public water supplies; HBSL, Health-Based Screening Level developed by USGS using USEPA toxicity information and methods (Toccalino and Norman, 2006); °C, degrees Celsius; µS/cm, microsiemens per centimeter; $CaCO_3$, calcium carbonate; mg/L, milligrams per liter; ROE, residue on evaporation; µg/L, micrograms per liter; pCi/L, picocuries per liter; --, not available or not applicable]

Property or constituent	Units	USGS parameter code	[1]CASRN	Predominant use group	Common LT-MDLs	Human-health benchmark		Number of analyses
						Value	Type	
				Pesticides, Group 1 (1995–2007)				
Acetochlor	µg/L	49260	34256-82-1	Herbicide	0.003	[5]1	HBSL	125
Alachlor	µg/L	46342	15972-60-8	Herbicide	0.002, 0.003	2	MCL	125
Atrazine	µg/L	39632	1912-24-9	Herbicide	0.004	3	MCL	125
Azinphos-methyl	µg/L	82686	86-50-0	Insecticide	0.02-0.06	10	HBSL	125
Benfluralin	µg/L	82673	1861-40-1	Herbicide	0.002–0.005	4	HBSL	125
Carbaryl	µg/L	82680	63-25-2	Insecticide	0.02, 0.03	[5]40	HBSL	125
Carbofuran	µg/L	82674	1563-66-2	Insecticide	0.01	40	MCL	111
Chlorpyrifos	µg/L	38933	2921-88-2	Insecticide	0.003	2	HBSL	125
Cyanazine	µg/L	04041	21725-46-2	Herbicide	0.009, 0.01	1	HBSL	111
Dacthal	µg/L	82682	1861-32-1	Herbicide	0.002	70	HBSL	125
Deethylatrazine	µg/L	04040	6190-65-4	DP (Atrazine)	0.003, 0.007	--	--	125
Diazinon	µg/L	39572	333-41-5	Insecticide	0.003	1	HBSL	125
Dieldrin	µg/L	39381	60-57-1	DP (Aldrin)	0.002, 0.004	[5]0.002	HBSL	125
2,6-Diethylaniline	µg/L	82660	579-66-8	DP (Alachlor)	0.006	--	--	125
Disulfoton	µg/L	82677	298-04-4	Insecticide	0.011, 0.02	0.9	HBSL	111
EPTC	µg/L	82668	759-94-4	Herbicide	0.001, 0.002	200	HBSL	111
Ethoprophos (Ethoprop)	µg/L	82672	13194-48-4	Insecticide	0.002, 0.006	[5]1	HBSL	111
Fonofos	µg/L	04095	944-22-9	Insecticide	0.001–0.005	10	HBSL	125
Malathion	µg/L	39532	121-75-5	Insecticide	0.008, 0.014	50	HBSL	125
Metolachlor	µg/L	39415	51218-45-2	Herbicide	0.003–0.006	700	HBSL	125
Metribuzin	µg/L	82630	21087-64-9	Herbicide	0.003, 0.006	90	HBSL	125
Molinate	µg/L	82671	2212-67-1	Herbicide	0.001–0.012	0.7	HBSL	111
Parathion-methyl	µg/L	82667	298-00-0	Insecticide	0.003–0.008	1	HBSL	125
Pendimethalin	µg/L	82683	40487-42-1	Herbicide	0.006, 0.011	70	HBSL	125
cis-Permethrin	µg/L	82687	54774-45-7	Insecticide	0.003, 0.005	[5]4	HBSL	125
Phorate	µg/L	82664	298-02-2	Insecticide	0.006, 0.02	4	HBSL	125
Prometon	µg/L	04037	1610-18-0	Herbicide	0.005, 0.007	400	HBSL	125

Table 2–1. Physical properties and constituents analyzed in samples collected for the NAWQA Program and associated human-health benchmarks for drinking water.—Continued

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Property or constituent	Units	USGS parameter code	[1]CASRN	Predominant use group	Common LT-MDLs	Human-health benchmark		Number of analyses
						Value	Type	
				Pesticides, Group 1 (1995–2007)—Continued				
Propanil	µg/L	82679	709-98-8	Herbicide	0.003, 0.005	6	HBSL	111
Propargite	µg/L	82685	2312-35-8	Acaricide	0.01–0.02	[5]1	HBSL	111
Propyzamide (Pronamide)	µg/L	82676	23950-58-5	Herbicide	0.002	[5]1	HBSL	125
Simazine	µg/L	04035	122-34-9	Herbicide	0.002, 0.003	4	MCL	125
Tebuthiuron	µg/L	82670	34014-18-1	Herbicide	0.008	1,000	HBSL	125
Terbufos	µg/L	82675	13071-79-9	Insecticide	0.006-0.008	0.4	HBSL	125
Thiobencarb	µg/L	82681	28249-77-6	Herbicide	0.002, 0.005	70	HBSL	111
Trifluralin	µg/L	82661	1582-09-8	Herbicide	0.003, 0.005	20	HBSL	125
				Pesticides, Group 2 (2004–7)				
Azinphos-methyl-oxon	µg/L	61635	961-22-8	DP (Azinphos-methyl)	0.012, 0.021	--	--	103
2-Chloro-2,6-diethylacetanilide	µg/L	61618	6967-29-9	DP (Alachlor)	0.002–0.005	--	--	103
4-Chloro-2-methylphenol	µg/L	61633	1570-64-5	DP (MCPA)	0.001, 0.002	--	--	103
Chlorpyrifos, oxygen analog	µg/L	61636	5598-15-2	DP (Chlorpyrifos)	0.01	--	--	103
cis-Propiconazole	µg/L	79846	60207-90-1	Fungicide	0.001–0.003	--	--	89
Cyfluthrin	µg/L	61585	68359-37-5	Insecticide	0.008–0.026	200	HBSL	103
Cypermethrin	µg/L	61586	52315-07-8	Insecticide	0.001–0.023	40	HBSL	103
Desulfinylfipronil	µg/L	62170		DP (Fipronil)	0.006	--	--	103
Desulfinylfipronil amide	µg/L	62169		DP (Fipronil)	0.015	--	--	103
Diazinon, oxygen analog	µg/L	61638	962-58-3	DP (Diazinon)	0.002	--	--	103
3,4-Dichloroaniline	µg/L	61625	95-76-1	DP (Diuron)	0.002, 0.003	--	--	103
3,5-Dichloroaniline	µg/L	61627	626-43-7	DP (Iprodione)	0.002–0.006	--	--	89
Dichlorvos	µg/L	38775	62-73-7	Insecticide	0.003, 0.006	0.4	HBSL	103
Dicrotophos	µg/L	38454	141-66-2	Insecticide	0.016	0.05	HBSL	100
Dimethoate	µg/L	82662	60-51-5	Insecticide	0.001, 0.003	2	HBSL	103
Disulfoton sulfone	µg/L	61640	2497-06-05	DP (Disulfoton)	0.001, 0.007	--	--	89
Alpha-endosulfan	µg/L	34362	95-99-88	Insecticide	0.001–0.005	[6]40	HBSL	89
Endosulfan sulfate	µg/L	61590	1031-07-8	DP (alpha-Endosulfan)	0.004, 0.011	--	--	89
Ethion	µg/L	82346	563-12-2	Insecticide	0.001	4	HBSL	103

Table 2–1. Physical properties and constituents analyzed in samples collected for the NAWQA Program and associated human-health benchmarks for drinking water.—Continued

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Property or constituent	Units	USGS parameter code	[1]CASRN	Predominant use group	Common LT-MDLs	Human-health benchmark		Number of analyses
						Value	Type	
				Pesticides, Group 2 (2004–7)—Continued				
Ethion monoxon	µg/L	61644	17356-42-2	DP (Ethion)	0.001, 0.011	--	--	103
2-Ethyl-6-methylaniline	µg/L	61620	24549-06-2	DP (Metolachlor)	0.002, 0.005	--	--	103
Fenamiphos	µg/L	61591	22224-92-6	Nematocide	0.015	0.7	HBSL	103
Fenamiphos sulfone	µg/L	61645	31972-44-8	DP (Fenamiphos)	0.009, 0.027	--	--	103
Fenamiphos sulfoxide	µg/L	61646	31972-43-7	DP (Fenamiphos)	0.009, 0.02	--	--	98
Fipronil	µg/L	62166	120068-37-3	Insecticide	0.008, 0.01	--	--	103
Fipronil sulfide	µg/L	62167	120067-83-6	DP (Fipronil)	0.006	--	--	103
Fipronil sulfone	µg/L	62168	120068-36-2	DP (Fipronil)	0.012	--	--	103
Hexazinone	µg/L	04025	51235-04-2	Herbicide	0.004–0.013	400	HBSL	103
Iprodione	µg/L	61593	36734-19-7	Fungicide	0.005–0.269	[5]0.8	HBSL	103
Isofenphos	µg/L	61594	25311-71-1	Insecticide	0.001–0.006	6	HBSL	103
lambda-Cyhalothrin	µg/L	61595	91465-08-6	Insecticide	0.001–0.007	--	--	89
Malaoxon	µg/L	61652	1634-78-2	DP (Malathion)	0.008–0.019	--	--	103
Metalaxyl	µg/L	61596	57837-19-1	Fungicide	0.002, 0.003	600	HBSL	103
Methidathion	µg/L	61598	950-37-8	Insecticide	0.001–0.004	1	HBSL	103
Myclobutanil	µg/L	61599	88671-89-0	Fungicide	0.001–0.017	200	HBSL	103
1-Naphthol	µg/L	49295	90-15-3	DP (carbaryl/napropamide)	0.02, 0.036	--	--	103
Oxyfluorfen	µg/L	61600	42874-03-3	Herbicide	0.002–0.008	20	HBSL	89
Paraoxon-methyl	µg/L	61664	950-35-6	DP (Methyl parathion)	0.005–0.01	--	--	103
Phorate oxygen analog	µg/L	61666	2600-69-3	DP (Phorate)	0.008, 0.013	--	--	103
Phosmet	µg/L	61601	732-11-6	Insecticide	0.001	8	HBSL	84
Phosmet oxon	µg/L	61668	3735-33-9	DP (Phosmet)	0.008	--	--	78
Prometryn	µg/L	04036	7287-19-6	Herbicide	0.002, 0.003	300	HBSL	103
Tebuconazole	µg/L	62852	107534-96-3	Fungicide	0.002, 0.009	--	--	89
Tefluthrin	µg/L	61606	79538-32-2	Insecticide	0.001, 0.002	40	HBSL	89
Terbufos oxygen analog sulfone	µg/L	61674	56070-15-6	DP (Terbufos)	0.018, 0.022	--	--	103
Terbuthylazine	µg/L	04022	5915-41-3	Herbicide	0.004	2	HBSL	103
trans-Propiconazole	µg/L	79847	60207-90-1	Fungicide	0.001–0.017	--	--	89
Tribufos	µg/L	61610	78-48-8	Defoliant	0.001, 0.018	7	HBSL	89

Table 2–1. Physical properties and constituents analyzed in samples collected for the NAWQA Program and associated human-health benchmarks for drinking water.—Continued

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Property or constituent	Units	USGS parameter code	[1]CASRN	Predominant use group	Common LT-MDLs	Human-health benchmark		Number of analyses
						Value	Type	
				Volatile organic compounds				
Acrylonitrile	µg/L	34215	107-13-1	Organic synthesis	0.2–0.6	[5]0.06	HBSL	122
tert-Amyl methyl ether (TAME)	µg/L	50005	994-05-8	Gasoline oxygenate	0.02–0.04	--	--	122
Benzene	µg/L	34030	71-43-2	Gasoline hydrocarbon	0.008–0.017	5	MCL	122
Bromodichloromethane	µg/L	32101	75-27-4	Trihalomethane	0.014–0.024	[7]80	MCL	122
Bromoethene	µg/L	50002	593-60-2	Organic synthesis	0.05, 0.06	--	--	122
Bromoform (Tribromomethane)	µg/L	32104	75-25-2	Trihalomethane	0.03–0.05	[7]80	MCL	122
Bromomethane	µg/L	34413	74-83-9	Fumigant	0.13–0.2	100	HBSL	122
n-Butylbenzene	µg/L	77342	104-51-8	Gasoline hydrocarbon	0.06–0.09	--	--	122
Carbon tetrachloride (Tetrachloromethane)	µg/L	32102	56-23-5	Solvent	0.03, 0.04	5	MCL	122
Chlorobenzene	µg/L	34301	108-90-7	Solvent	0.01, 0.014	100	MCL	122
Chloroethane	µg/L	34311	75-00-3	Solvent	0.05, 0.06	--	--	122
Chloroform (Trichloromethane)	µg/L	32106	67-66-3	Trihalomethane	0.01–0.02	[7]80	MCL	122
Chloromethane	µg/L	34418	74-87-3	Solvent	0.05, 0.09	30	HBSL	122
Dibromochloromethane	µg/L	32105	124-48-1	Trihalomethane	0.05–0.09	[7]80	MCL	122
Dibromochloropropane (DBCP)	µg/L	82625	96-12-8	Fumigant	0.17, 0.5	0.2	MCL	122
Ethylene dibromide (EDB)	µg/L	77651	106-93-4	Fumigant	0.018, 0.02	0.5	MCL	122
1,2-Dichlorobenzene	µg/L	34536	95-50-1	Solvent	0.01–0.024	600	MCL	122
1,3-Dichlorobenzene	µg/L	34566	541-73-1	Solvent	0.015–0.02	600	MCL	122
1,4-Dichlorobenzene	µg/L	34571	106-46-7	Fumigant	0.01–0.025	75	MCL	122
Dichlorodifluoromethane (CFC-12)	µg/L	34668	75-71-8	Refrigerant	0.07, 0.09	1,000	HBSL	122
1,1-Dichloroethane (1,1-DCA)	µg/L	34496	75-34-3	Solvent	0.018–0.03	--	--	122
1,2-Dichloroethane (1,2-DCA)	µg/L	32103	107-06-2	Solvent	0.03–0.07	5	MCL	122

Table 2–1. Physical properties and constituents analyzed in samples collected for the NAWQA Program and associated human-health benchmarks for drinking water.—Continued

[USGS, U.S. Geological Survey; CASRN, Chemical Abstracts Service Registry Number®; Common long-term method detection levels (LT-MDLs) apply to the sampling periods 1995–96 and 2002–7. Predominant use group is from Gilliom and others (2006) and Zogorski and others (2006). Pesticide degradation products are designated by "DP" with parent compound indicated in parentheses. MCL, U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Level for public water supplies; AMCL, USEPA proposed Alternative Maximum Contaminant Level for public water supplies; HBSL, Health-Based Screening Level developed by USGS using USEPA toxicity information and methods (Toccalino and Norman, 2006); °C, degrees Celsius; µS/cm, microsiemens per centimeter; $CaCO_3$, calcium carbonate; mg/L, milligrams per liter; ROE, residue on evaporation; µg/L, micrograms per liter; pCi/L, picocuries per liter; --, not available or not applicable]

Property or constituent	Units	USGS parameter code	[1]CASRN	Predominant use group	Common LT-MDLs	Human-health benchmark		Number of analyses
						Value	Type	
				Volatile organic compounds—Continued				
1,1-Dichloroethene (1,1-DCE)	µg/L	34501	75-35-4	Organic synthesis	0.01–0.02	7	MCL	122
cis-1,2-Dichloroethene (*cis*-1,2-DCE)	µg/L	77093	156-59-2	Solvent	0.01–0.019	70	MCL	122
trans-1,2-Dichloroethene (*trans*-1,2-DCE)	µg/L	34546	156-60-5	Solvent	0.009, 0.016	100	MCL	122
Methylene Chloride	µg/L	34423	75-09-2	Solvent	0.02–0.08	5	MCL	122
1,2-Dichloropropane	µg/L	34541	78-87-5	Fumigant	0.01, 0.015	5	MCL	106
cis-1,3-Dichloropropene	µg/L	34704	10061-01-5	Fumigant	0.02–0.05	[5,8]0.3	HBSL	122
trans-1,3-Dichloropropene	µg/L	34699	10061-02-6	Fumigant	0.04, 0.05	[5,8]0.3	HBSL	122
Diisopropyl ether (DIPE)	µg/L	81577	108-20-3	Gasoline oxygenate	0.03, 0.05	--	--	122
Ethyl *tert*-butyl ether (ETBE)	µg/L	50004	637-92-3	Gasoline oxygenate	0.015–0.03	--	--	122
Ethylbenzene	µg/L	34371	100-41-4	Gasoline hydrocarbon	0.01–0.02	700	MCL	122
Hexachlorobutadiene	µg/L	39702	87-68-3	Organic synthesis	0.03–0.07	[5]0.9	HBSL	122
Hexachloroethane	µg/L	34396	67-72-1	Solvent	0.07, 0.1	0.7	HBSL	122
Isopropylbenzene	µg/L	77223	98-82-8	Gasoline hydrocarbon	0.019–0.03	700	HBSL	122
Methyl *tert*-butyl ether (MTBE)	µg/L	78032	1634-04-4	Gasoline oxygenate	0.05, 0.08	--	--	122
Naphthalene	µg/L	34696	91-20-3	Gasoline hydrocarbon	0.1–0.5	100	HBSL	122
Perchloroethene (PCE)	µg/L	34475	127-18-4	Solvent	0.013–0.02	5	MCL	122
n-Propylbenzene	µg/L	77224	103-65-1	Solvent	0.02, 0.021	--	--	122
Styrene	µg/L	77128	100-42-5	Gasoline hydrocarbon	0.02, 0.021	100	MCL	122
Toluene	µg/L	34010	108-88-3	Gasoline hydrocarbon	[9]0.03	1,000	MCL	122
1,2,3-Trichlorobenzene	µg/L	77613	87-61-6	Organic synthesis	0.04–0.14	--	--	122
1,2,4-Trichlorobenzene	µg/L	34551	120-82-1	Fumigant	0.04–0.06	70	MCL	122
1,1,1-Trichloroethane (TCA)	µg/L	34506	71-55-6	Solvent	0.01–0.02	200	MCL	122
1,1,2-Trichloroethane	µg/L	34511	79-00-5	Solvent	0.02, 0.03	5	MCL	122
Trichloroethene (TCE)	µg/L	39180	79-01-6	Solvent	0.01, 0.019	5	MCL	122

Table 2–1. Physical properties and constituents analyzed in samples collected for the NAWQA Program and associated human-health benchmarks for drinking water.—Continued

[USGS, U.S. Geological Survey; CASRN, Chemical Abstracts Service Registry Number®; Common long-term method detection levels (LT-MDLs) apply to the sampling periods 1995–96 and 2002–7. Predominant use group is from Gilliom and others (2006) and Zogorski and others (2006). Pesticide degradation products are designated by "DP" with parent compound indicated in parentheses. MCL, U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Level for public water supplies; AMCL, USEPA proposed Alternative Maximum Contaminant Level for public water supplies; HBSL, Health-Based Screening Level developed by USGS using USEPA toxicity information and methods (Toccalino and Norman, 2006); °C, degrees Celsius; µS/cm, microsiemens per centimeter; $CaCO_3$, calcium carbonate; mg/L, milligrams per liter; ROE, residue on evaporation; µg/L, micrograms per liter; pCi/L, picocuries per liter; --, not available or not applicable]

Property or constituent	Units	USGS parameter code	[1]CASRN	Predominant use group	Common LT-MDLs	Human-health benchmark		Number of analyses
						Value	Type	
Volatile organic compounds—Continued								
Trichlorofluoromethane (CFC-11)	µg/L	34488	75-69-4	Refrigerant	0.04, 0.05	2,000	HBSL	122
1,2,3-Trichloropropane	µg/L	77443	96-18-4	Fumigant	0.06-0.08	40	HBSL	122
Trichlorotrifluoroethane (CFC-113)	µg/L	77652	76-13-1	Refrigerant	0.019–0.03	200,000	HBSL	122
1,2,4-Trimethylbenzene	µg/L	77222	95-63-6	Gasoline hydrocarbon	[9]0.05	--	--	122
Vinyl chloride	µg/L	39175	75-01-4	Organic synthesis	0.04, 0.06	2	MCL	122
m- and *p*-Xylene	µg/L	85795	108-38-3, 106-42-3	Gasoline hydrocarbon	0.03, 0.04	[10]10,000	MCL	122
o-Xylene	µg/L	77135	95-47-6	Gasoline hydrocarbon	0.019–0.04	[10]10,000	MCL	122

[1] This report contains CAS Registry Numbers®, which is a Registered Trademark of the American Chemical Society. CAS recommends the verification of the CASRNs through CAS Client Services^{SM}.

[2] When not provided, bicarbonate is calculated as alkalinity/0.8202 (Hem, 1985).

[3] Hardness is calculated as the sum of calcium and magnesium, in milliequivalents per liter × 50 (Hem, 1985).

[4] Nitrate (USGS parameter code 00631) is nitrate plus nitrite.

[5] HBSL value is low end of range, associated with 10^{-6} cancer risk (Toccalino and others, 2008).

[6] HBSL is for endosulfan.

[7] MCL is for sum of four trihalomethanes.

[8] HBSL is for sum of *cis*-1,3-dichloropropene and *trans*-1,3-dichloropropene.

[9] Censoring level; concentrations below this value were treated as nondetections.

[10] MCL is for sum of xylenes.

Appendix 3

Table of Spearman rank correlation coefficients for selected physical properties of, and constituents measured, in water samples collected for the NAWQA Program, 1995–2007

Also available as Plate 1

Table 3–1. Spearman rank correlation coefficients for selected physical properties of, and constituents measured, in water samples collected for the NAWQA Program, 1995–2007.

[All coefficients shown are significant at the 95-percent confidence limit ($p < 0.05$). Coefficients of 0.60 and higher are bold. DOC, dissolved organic carbon; SC, specific conductance]

	Ca	Mg	Na	K	Si	HCO_3	SO_4	Cl	F	Br	DS	NH_3	NO_3	DOC
Calcium (Ca)	1													
Magnesium (Mg)	**0.79**	1												
Sodium (Na)	0.47	0.45	1											
Potassium (K)	0.45	0.44	**0.86**	1										
Silica (Si)			-0.45	**-0.60**	1									
Bicarbonate (HCO_3)	0.54	0.55	0.27	0.33		1								
Sulfate (SO_4)	0.58	0.58	**0.75**	**0.72**	-0.44	0.19	1							
Chloride (Cl)	0.28	0.25	0.59	0.40	-0.19		0.57	1						
Fluoride (F)	0.33	0.34	**0.81**	**0.87**	-0.53	0.22	**0.67**	0.33	1					
Bromide (Br)	0.49	0.40	**0.72**	**0.66**	-0.30	0.17	**0.70**	**0.63**	**0.62**	1				
Dissolved solids (DS)	**0.73**	**0.70**	**0.81**	**0.73**	-0.32	0.42	**0.84**	**0.63**	**0.66**	**0.72**	1			
Ammonia (NH_3)	0.38	0.39	**0.80**	**0.82**	-0.41	0.37	0.59	0.24	**0.81**	0.61	**0.63**	1		
Nitrate (NO_3)			-0.43	-0.52	0.54		-0.28		-0.55	-0.30	-0.30	-0.59	1	
DOC			-0.18	-0.20	0.27	0.34	-0.29	-0.32	-0.32	-0.25				1
Arsenic (As)				-0.26	0.42				-0.19					
Barium (Ba)			-0.22			0.32	-0.37	-0.37	-0.18	-0.29	-0.28			0.37
Boron (B)	0.45	0.39	**0.90**	**0.94**	-0.55	0.32	**0.79**	0.48	**0.89**	**0.75**	**0.77**	**0.87**	-0.39	-0.29
Iron (Fe)	0.40	0.32	0.34	0.46	-0.29	0.30	0.35		0.43	0.35	0.34	0.56	-0.50	
Lead (Pb)		-0.26	-0.34	-0.49	0.35		-0.39		-0.42	-0.29	-0.32	-0.55	0.57	-0.23
Lithium (Li)	0.48	0.42	**0.89**	**0.91**	-0.46	0.27	**0.83**	0.50	**0.90**	0.76	**0.80**	**0.84**	-0.38	-0.37
Manganese (Mn)	0.38	0.19			0.32	0.28		-0.25				0.17	-0.17	0.36
Molybdenum (Mo)	0.27			-0.18	0.38			-0.21						0.21
Nickel (Ni)	0.55	0.50	0.33	0.38		0.40	0.47		0.28	0.41	0.40	0.42		
Strontium (Sr)	0.50	0.42	**0.87**	**0.88**	-0.54		**0.80**	0.52	**0.89**	**0.76**	**0.77**	**0.81**	-0.49	-0.28
Uranium (U)	0.32	0.29		-0.19	0.48	0.20			-0.19			-0.24	0.51	
Zinc (Zn)			-0.26	-0.40	0.49		-0.23		-0.42			-0.39	0.47	
Radium-226	0.39	0.45	**0.76**	**0.76**	-0.41	0.32	**0.73**	0.47	**0.77**	**0.66**	**0.74**	**0.70**	-0.56	
Radium-228	0.32	0.36	0.61	0.72	-0.59	0.38	0.57	0.35	0.62	0.54	0.55	0.58	-0.56	
Radon-222	-0.17	-0.18	-0.46	-0.49	0.52		-0.40	-0.23	-0.47	-0.32	-0.33	-0.47	0.37	0.39
Tritium	-0.26	-0.29	**-0.71**	**-0.73**	**0.63**	-0.27	-0.59	-0.21	**-0.72**	-0.40	-0.56	**-0.70**	**0.65**	
Dissolved oxygen (DO)			-0.27	-0.38	0.26				-0.41	-0.26		-0.41	0.58	
SC	**0.75**	**0.72**	**0.84**	**0.76**	-0.29	0.47	**0.83**	0.59	**0.68**	**0.77**	**0.96**	**0.69**	-0.29	
Water temperature (Temp)		0.17	0.58	**0.60**	-0.39		0.51	0.37	**0.64**	0.56	0.46	0.53	-0.22	-0.45
pH	-0.58	-0.58	-0.25	-0.33	0.27	-0.43	-0.39		-0.18	-0.20	-0.48	-0.23	0.21	-0.30
Hardness	**0.96**	**0.92**	0.47	0.45		0.57	0.59	0.27	0.34	0.46	**0.75**	0.40		
Well depth	0.31	0.32	**0.72**	**0.81**	**-0.62**	0.24	**0.65**	0.39	**0.80**	0.56	**0.60**	**0.73**	-0.52	-0.43
Casing depth	0.28	0.25	**0.66**	**0.77**	-0.55	0.19	**0.63**	0.34	**0.80**	0.56	0.55	**0.71**	-0.46	-0.50
Depth to bedrock	0.22	0.19	0.18	0.22	0.22	0.29			0.22			0.31		

Table 3–1. Spearman rank correlation coefficients for selected physical properties of, and constituents measured, in water samples collected for the NAWQA Program, 1995–2007.—Continued

[All coefficients shown are significant at the 95-percent confidence limit ($p < 0.05$). Coefficients of 0.60 and higher are bold. DOC, dissolved organic carbon; SC, specific conductance]

	As	Ba	B	Fe	Pb	Li	Mn	Mo	Ni	Sr	U	Zn	Radium-226
Calcium (Ca)													
Magnesium (Mg)													
Sodium (Na)													
Potassium (K)													
Silica (Si)													
Bicarbonate (HCO_3)													
Sulfate (SO_4)													
Chloride (Cl)													
Fluoride (F)													
Bromide (Br)													
Dissolved solids (DS)													
Ammonia (NH_3)													
Nitrate (NO_3)													
DOC													
Arsenic (As)	1												
Barium (Ba)		1											
Boron (B)	-0.23	-0.28	1										
Iron (Fe)	0.21		0.44	1									
Lead (Pb)			-0.46	-0.64	1								
Lithium (Li)		-0.33	**0.93**	0.46	-0.46	1							
Manganese (Mn)	0.36			0.53	-0.50		1						
Molybdenum (Mo)	0.56			0.34			0.52	1					
Nickel (Ni)			0.50	0.37	-0.34	0.43	0.33	0.22	1				
Strontium (Sr)		-0.26	**0.86**	0.49	-0.47	**0.89**	0.28		0.36	1			
Uranium (U)	0.35						0.22	0.39	0.20		1		
Zinc (Zn)	0.24		-0.31		0.41	-0.26		0.31		-0.26	0.40	1	
Radium-226			**0.73**	0.36	-0.59	**0.76**			0.44	**0.77**	-0.22	-0.49	1
Radium-228			**0.65**	0.38	**-0.60**	**0.61**	0.22		0.46	**0.67**	-0.26	-0.45	**0.76**
Radon-222	0.27		-0.51	-0.19		-0.46	0.19	0.26		-0.48	0.22	0.28	-0.38
Tritium	0.31		-0.40	-0.43	0.39	-0.43		0.39		-0.36	0.47	0.49	-0.43
Dissolved oxygen (DO)		-0.27	-0.31	-0.44	0.50	-0.33	-0.35			-0.39		0.31	-0.45
SC		-0.23	**0.78**	0.39	-0.31	**0.80**			0.45	**0.78**			**0.74**
Water temperature (Temp)	-0.24	-0.25	**0.75**	0.24	-0.20	**0.76**	-0.19		0.26	**0.69**			**0.65**
pH			-0.22	-0.31	0.28				-0.48	-0.20			-0.26
Hardness			0.43	0.38	-0.22	0.47	0.33	0.22	0.54	0.47	0.32		0.42
Well depth	-0.28		**0.83**	0.29	-0.32	**0.83**	-0.18		0.25	**0.78**	-0.21	-0.39	**0.70**
Casing depth	-0.29		**0.83**	0.31	-0.35	**0.84**			0.24	**0.78**		-0.36	**0.70**
Depth to bedrock			0.22	0.16	-0.20	0.25	0.31		0.19	0.28			

Table 3–1. Spearman rank correlation coefficients for selected physical properties of, and constituents measured, in water samples collected for the NAWQA Program, 1995–2007.—Continued

[All coefficients shown are significant at the 95-percent confidence limit ($p < 0.05$). Coefficients of 0.60 and higher are bold. DOC, dissolved organic carbon; SC, specific conductance]

	Radium-228	Radon-222	Tritium	DO	SC	Temp	pH	Hardness	Well depth	Casing depth	Depth to bedrock
Calcium (Ca)											
Magnesium (Mg)											
Sodium (Na)											
Potassium (K)											
Silica (Si)											
Bicarbonate (HCO_3)											
Sulfate (SO_4)											
Chloride (Cl)											
Fluoride (F)											
Bromide (Br)											
Dissolved solids (DS)											
Ammonia (NH_3)											
Nitrate (NO_3)											
DOC											
Arsenic (As)											
Barium (Ba)											
Boron (B)											
Iron (Fe)											
Lead (Pb)											
Lithium (Li)											
Manganese (Mn)											
Molybdenum (Mo)											
Nickel (Ni)											
Strontium (Sr)											
Uranium (U)											
Zinc (Zn)											
Radium-226											
Radium-228	1										
Radon-222	-0.36	1									
Tritium	-0.34	0.45	1								
Dissolved oxygen (DO)	-0.43		0.40	1							
SC	0.55	-0.36	-0.59	-0.20	1						
Water temperature (Temp)	0.58	-0.40	-0.38	-0.22	0.51	1					
pH	-0.36		0.32		-0.43		1				
Hardness	0.34	-0.17	-0.28		**0.77**	0.16	**-0.61**	1			
Well depth	**0.68**	**-0.61**	**-0.67**	-0.29	**0.62**	**0.60**	-0.23	0.31	1		
Casing depth	**0.62**	**-0.60**	**-0.67**	-0.29	0.57	**0.62**		0.27	**0.93**	1	
Depth to bedrock					0.16			0.22			1

Appendix 4. NAWQA Quality-Control Data

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The following discussions cover quality-control data that were collected by the NAWQA Program while sampling wells in the Cambrian-Ordovician aquifer system. Data used in this analysis were obtained from the NAWQA Data Warehouse (Bell and Williamson, 2006; *http://water.usgs.gov/nawqa/data*).

NAWQA Quality-Control Data for Major Ions

There were 12 field blanks collected for major ions by the NAWQA Program (table 4–1). Bromide, fluoride, and sulfate were each detected once at estimated concentrations below their respective reporting levels. Calcium was the most commonly detected major ion in blanks, but the maximum concentration was 0.23 mg/L, 200 times less than the 10th-percentile concentration of environmental samples (46.4 mg/L). Magnesium was detected in 6 of 12 blanks, but the maximum concentration was 0.017 mg/L, more than 1,000 times less than the 10th-percentile concentration of the environmental samples (19.3 mg/L). Silica was detected in 6 of 12 blanks, with a maximum concentration of 2.53 mg/L, compared to a minimum concentration of 4.15 mg/L and a 10th-percentile concentration of 7.5 mg/L for environmental samples. Sodium was detected in 7 of the 12 blanks, with a maximum concentration of 0.49 mg/L, compared to a minimum concentration of 1.38 mg/L and a 10th-percentile concentration of 2.6 mg/L for environmental samples.

Replicate samples for major ions were collected at 18 wells sampled by the NAWQA Program. The relative standard deviation (RSD) was used to assess the variability in concentration of replicate pairs, which consist of an environmental sample and a replicate sample. RSD was calculated as the standard deviation of the concentrations of the replicate pair divided by the mean concentration of the replicate pair, multiplied by 100. The variability in concentrations of replicate pairs was analyzed by combining the results for all of the major ions into one group with 186 replicate pairs that had quantifiable detections in both the environmental and replicate sample (table 4–2). The mean RSD was 2.93 percent, the median RSD was 0.81 percent, and the 90th-percentile RSD was 6.5 percent. Eighty-six percent of the replicate pairs had an RSD of 5 percent or less, and 95 percent of the replicate pairs had an RSD of 10 percent or less. Sulfate had the lowest mean RSD (0.39 percent) and bromide had the highest mean RSD (14 percent). Bromide was the only constituent that had a mean RSD greater than 4 percent. The RSD for bromide was higher than for the other constituents because of the relatively low mean concentration of the replicate pairs (0.12 mg/L). The blank and replicate data indicate that sample processing and analysis did not introduce enough variation in the environmental data collected by the NAWQA Program to affect the interpretation of results.

NAWQA Quality-Control Data for Trace Elements

The NAWQA Program collected 15 field blanks for analysis of trace elements. Table 4–1 lists the constituents that were detected in field blanks. Aluminum was detected in 4 of 15 field blanks, with a maximum concentration of 26.4 µg/L. This concentration of aluminum exceeded the maximum concentration measured in all of the environmental samples (8.57 µg/L) (table 12), which indicates that flushing groundwater through the sampling equipment during well purging cleans the sampling equipment before environmental samples are collected. The high maximum concentrations of chromium, copper, lead, and zinc in field blanks relative to concentrations in environmental samples also indicate that sampling equipment can be cleaned during the well purging process. The maximum concentrations of these elements detected in field blanks all exceeded at least the median concentration of their respective environmental samples. Recent investigations by the USGS has determined that detections of VOCs in field blanks at concentrations greater than environmental samples, or when not detected in environmental samples, may be caused by insufficient rinsing of equipment with blank water prior to collecting the blank (Thiros and others, 2011). Insufficient rinsing of equipment with blank water is also a likely cause of some detections of trace elements in field blanks, which, like VOCs, are measured in parts per billion (micrograms per liter).

Of the eight trace elements discussed in detail in this report (shown in fig. 31), five were detected in at least one field blank—barium, boron, iron, manganese, and strontium (table 4–1). Strontium was the most commonly detected trace element in field blanks, but the maximum concentration was 0.887 µg/L, approximately 32 times less than the minimum concentration of environmental samples (28.1 µg/L). Barium was detected in 6 of 15 blanks, with a median concentration of 0.223 µg/L and a maximum concentration of 0.884 µg/L, which was less than the minimum concentration of environmental samples (1.00 µg/L) and about 10 times less than the 10th-percentile concentration of the environmental samples (9.5 µg/L). Boron was detected in 3 of 15 blanks, with a maximum concentration of 24.5 µg/L. All three detections of boron were in field blanks collected in Iowa, where the highest boron concentrations in the aquifer system occur. The 10th-percentile concentration of boron in Iowa was 159 µg/L, and the median concentration was 711 µg/L. It is possible that some of the boron survived the cleaning of the equipment between samples in Iowa but at relatively low concentrations compared to the environmental samples. Iron was detected in 2 of 12 blanks, with a maximum concentration of 3.96 µg/L, which was less than the 10th-percentile concentration (4.68 µg/L) for environmental samples. Manganese was detected in 4 of 16 blanks, with a median concentration of 0.09 µg/L and a maximum concentration of 0.11 µg/L, which was about 3 times less than the 10th-percentile concentration of 0.34 µg/L for environmental samples (table 12).

Table 4–1. Concentration of water-quality constituents detected in field blanks collected by the NAWQA Program while sampling wells in the Cambrian-Ordovician aquifer system, 2002–7.

[mg/L, milligrams per liter; --, not applicable or not determined; µg/L, micrograms per liter; pCi/L, picocuries per liter; reporting levels are given as a range when more than two were used]

Constituent	Number of blanks / number of detections	Reporting levels	Median concentration	Maximum concentration
		Major ions, in mg/L		
Bromide	12 / 1	0.02, 0.03	--	0.016
Calcium	12 / 10	0.012–0.02	0.03	0.232
Fluoride	12 / 1	0.1	--	0.051
Magnesium	12 / 6	0.008, 0.014	0.007	0.017
Silica	12 / 6	0.018–0.13	0.202	2.53
Sodium	12 / 7	0.09–0.2	0.131	0.488
Sulfate	12 / 1	0.1, 0.18	--	0.05
		Trace elements, in µg/L		
Aluminum	15 / 4	1.0, 1.6	1.66	[1]26.4
Antimony	15 / 1	0.05–0.2	--	0.024
Barium[2]	15 / 6	0.08–1.0	0.223	0.884
Boron[2]	15 / 3	7.0, 8.0	--	[3]24.5
Chromium	15 / 3	0.08, 0.12	--	0.41
Copper	15 / 5	0.2, 0.4	2.20	[4]12.7
Iron[2]	12 / 2	6.0, 10.0	--	3.96
Lead	15 / 7	0.08, 0.12	0.18	0.849
Manganese[2]	16 / 4	0.1, 0.2	0.09	0.11
Molybdenum	15 / 2	0.12–0.4	--	0.209
Nickel	15 / 9	0.06	0.045	0.17
Strontium[2]	15 / 11	0.08–0.8	0.244	0.887
Vanadium	15 / 3	0.04–0.2	--	0.106
Zinc	15 / 6	0.6, 1.0	1.44	[5]15.7
		Radionuclides, in pCi/L		
Radium-226	2 / 2	0.015, 0.017	--	0.093
		Nutrients, in mg/L		
Nitrate	11 / 1	0.05, 0.06	--	0.023
Dissolved organic carbon	8 / 3	0.33, 0.4	--	2.76
		Pesticides, in µg/L		
Metolachlor	15/1	0.006–0.013	--	0.006
		Volatile organic compounds, in µg/L		
[6]1,2-Dichloropropane	16 / 3	0.02, 0.029	--	0.028
Ethylbenzene	16 / 1	0.02–0.04	--	0.029
Toluene	16 / 3	0.009–0.05	--	0.03
1,2,4-Trimethylbenzene	16 / 2	0.04, 0.056	--	0.084
m- + *p*-Xylene	16 / 2	0.06, 0.08	--	0.077
o-Xylene	16 / 1	0.038–0.07	--	0.029

[1] Aluminum not detected in environmental samples related to this field blank.

[2] Detailed discussion of this trace element in this report.

[3] Median concentration of boron in environmental samples from this sampling area (Iowa) was 711 µg/L.

[4] Maximum concentration of copper in field blank exceeds concentration in environmental samples collected prior to and after blank.

[5] Maximum concentration of zinc in field blank exceeds concentration in environmental sample collected prior to blank.

[6] All detections are from same network where contamination was identified with this compound. Affected environmental samples were deleted.

Table 4–2. Variability of concentrations in replicate pairs collected for the NAWQA Program, 1995–2007.

[Relative standard deviation, calculated as the standard deviation of the replicate pair divided by the mean concentration of the replicate pair × 100]

Analyte class	Number of replicate pairs	Relative standard deviation, in percent				Percent of replicate pairs with a relative standard deviation less than or equal to	
		Mean	Median	75th percentile	90th percentile	5 percent	10 percent
Major ions (calcium, magnesium, potassium, sodium, silica, bicarbonate, sulfate, chloride, fluoride, bromide, dissolved solids)	186	2.93	0.81	2.62	6.47	86	95
Trace elements (aluminum, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, iron, lead, lithium, manganese, molybdenum, nickel, selenium, strontium, thallium, uranium, vanadium, zinc)	209	8.14	2.43	8.26	24.8	66	79
Nutrients (ammonia, nitrate)	20	3.01	0.83	1.75	3.47	92	94
Dissolved organic carbon	19	10.1	4.41	18.5	26.2	53	63
Pesticides (2,6-diethylaniline, alachlor, atrazine, deethylatrazine, metolachlor, prometon, simazine)	26	4.21	2.72	7.02	10.2	61	88
Volatile organic compounds (1,1-dichloroethane, 1,1-dichloroethene, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,2-dichloroethane, benzene, CFC-113, CFC-12, methylene chloride, tetrachloroethene, toluene, trichloroethene, chloroform, vinyl chloride, *cis*-1,2-dichloroethene, *trans*-1,2-dichloroethene)	17	3.48	1.60	4.39	7.91	82	88
Radon-222	15	5.33	5.28	7.70	8.49	47	93
Radium-226, radium-228	4	29.1	28.0	--	--	0	0

Replicate samples for trace elements were collected at 16 wells sampled by the NAWQA Program. The variability in concentrations of replicate pairs was analyzed by combining the results for all of the trace elements into one group with 209 replicate pairs that had quantifiable detections in both the environmental and replicate sample (table 4–2). The mean RSD was 8.14 percent, the median RSD was 2.43 percent, and the 90th-percentile RSD was 24.8 percent. Sixty-six percent of the replicate pairs had an RSD of 5 percent or less, and 79 percent of the replicate pairs had an RSD of 10 percent or less. Uranium and strontium had the lowest mean RSDs (2.43 and 2.47 percent, respectively), and copper had the highest mean RSD (16.6 percent). For the eight trace elements discussed in detail in this report, the mean RSD was 5.44 percent and the 90th-percentile RSD was 13.8 percent.

The blank data indicate that for some of the trace elements there is a possibility of carryover of low concentrations from one well to the next. However, there is also evidence that the process of purging the well and flushing ambient groundwater through the sampling equipment helps to clean the equipment prior to collection of the environmental sample. Any carryover of residual trace elements from well to well would only affect low concentrations, not the higher concentrations that would be important for comparison to human-health benchmarks and SDWRs. The replicate data indicate that, on average, the RSD is about 8 percent and that 79 percent of the replicate pairs have an RSD less than 10 percent.

NAWQA Quality-Control Data for Radon-222

Replicate samples for radon-222 were collected at 15 wells sampled by the NAWQA Program during 1995 (4 replicates), 1996 (4), 2002 (3), 2005 (2), and 2007 (2). The median RSD was 5.3 percent, and the 90th-percentile RSD was 8.5 percent (table 4–1). Almost half of the replicate pairs (47 percent) had an RSD of 5 percent or less, and 93 percent of the replicate pairs had an RSD of 10 percent or less. These replicate-sample concentration data indicate that sample processing and analysis did not introduce variability in the same scale as the variability noted among the temporal samples in the environmental data collected by the NAWQA Program and so did not affect the data interpretation.

NAWQA Quality-Control Data for Radium

The NAWQA Program collected two field blanks each, for analysis of radium-226 and radium-228 in groundwater from the Cambrian-Ordovician aquifer system. Radium-228 concentrations of <0.29 ± 0.12 and <0.20 ± 0.085 pCi/L were below the respective ssL_C and therefore were considered nondetections. Radium-226 was in both blanks at very low concentrations of 0.04 ± 0.012 and 0.093 ± 0.017 pCi/L, which were above their respective ssL_C, and therefore were considered detections (table 4–1). The difference illustrates the much lower detection capability for the radium-226 isotope than for the radium-228 isotope. There were several NAWQA samples from wells in Minnesota and Wisconsin with reported radium-226 concentrations less than 0.1 pCi/L. The results of the two field blanks for radium-226 suggest that these low-level detections at less than 0.1 pCi/L are suspect. However, no specific interpretations of radium-226 occurrence rely on the quantified values of these low-level detections because they were simply classified in the group with the data range of less than 1 pCi/L.

Replicate samples for radium-226 and radium-228 were collected at two wells in the Cambrian-Ordovician aquifer system sampled by the NAWQA Program. The two replicate pairs for radium-226 had absolute differences of 0.56 and 0.96 pCi/L, mean CSUs of 0.07 and 0.06 pCi/L, and RSDs of 19.9 and 42.6 percent. The RSDs appear high because of the relatively small values of the mean concentration of the replicate pairs (1.99 and 1.59 pCi/L). The precision of counting low levels of radioactivity, even alpha particle activity, is low (Zoltan Szabo, U.S. Geological Survey, written commun., 2011). The two replicate pairs for radium-228 had absolute differences of 0.35 and 0.34 pCi/L, mean CSUs of 0.14 and 0.20 pCi/L, and RSDs of 36.1 and 17.7 percent. As with radium-226, the RSDs appear high because of the relatively small values of the mean concentration of the replicate pairs (0.68 and 1.36 pCi/L). With only two replicate samples for each isotope, any analysis of variability is limited. However, the available data suggest that there is, on average, about 29 percent variability in the measurement of radium-226 and radium-228 concentrations (table 4–2). The mean CSU of the replicate pairs is relatively small for radium-226 compared to the absolute differences between the environmental sample and replicate sample. This suggests that the variability is natural because the principal contributor to the CSU is the uncertainty of the count rate, or counting error (McCurdy and others, 2008). The mean CSU of the replicate pairs is relatively large for radium-228 compared to the absolute differences between the environmental sample and replicate sample. This suggests that, for radium-228, some of the variability may be a function of random "noise" introduced during sample processing and analysis and that the variability is probably affected by the less precise method of counting beta particle activity compared to counting alpha particle activity.

NAWQA Quality-Control Data for Nutrients and Dissolved Organic Carbon

The NAWQA Program collected 11 field blanks for analysis of nutrients and 8 field blanks for analysis of DOC. Ammonia, nitrite, and orthophosphate were not detected in any of the blanks. Nitrate was detected in one field blank at a concentration of 0.023 mg/L as N, which was below the reporting level of 0.05 mg/L (table 4–1). DOC was detected in three of eight field blanks at concentrations of 0.24, 1.02, and 2.76 mg/L. Two of these detections were high relative to the environmental samples, which had a 90th-percentile concentration of 1.38 mg/L (table 20). Sampling equipment can easily be contaminated with respect to DOC during equipment cleaning from detergent and methanol, which contain carbon. Apparently, residual DOC can be detected even after large volumes of rinse water have been run through the equipment.

Replicate samples for nutrients were collected at 18 wells sampled by the NAWQA Program. The variability in concentrations of replicate pairs was analyzed by combining the results for ammonia and nitrate into one group with 20 replicate pairs that had quantifiable detections in both the environmental and replicate sample (table 4–2). The mean RSD was 3.0 percent, the median RSD was 0.83 percent, and the 90th-percentile RSD was 3.5 percent. Ninety-two percent of the replicate pairs had an RSD of 5 percent or less, and 94 percent of the replicate pairs had an RSD of 10 percent or less. Replicate pairs for nitrate had a mean RSD of 0.98 percent, and replicate pairs for ammonia had a mean RSD of 5.5 percent. There were 19 replicate pairs for DOC that had quantifiable detections. The mean RSD was 10.1 percent, the median RSD was 4.4 percent, and the 90th-percentile RSD was 26.2 percent. Fifty-three percent of the DOC replicate pairs had an RSD of 5 percent or less, and 63 percent of the replicate pairs had an RSD of 10 percent or less. The variability in DOC replicate pairs is noticeably higher than in nitrate and ammonia replicate pairs.

On the basis of quality-control data, it was determined that sample processing and analysis did not introduce enough variation in the environmental data collected by the NAWQA Program to affect the interpretation of nitrate and ammonia results. Field blanks for DOC indicate the possibility that some DOC environmental data may be affected by carryover from equipment cleaning; however, this does not seem to be a systematic occurrence because DOC was detected in only three of the eight blanks.

NAWQA Quality-Control Data for Pesticides

There were 15 field blanks collected for analysis of pesticides by the NAWQA Program during the second decade of sampling from 2002 through 2007 (table 4–1). Metolachlor was detected in one field blank at a concentration of 0.006 µg/L.

Replicate samples for pesticides were collected at 16 wells for Group 1 compounds and 10 wells for Group 2 compounds. The variability in concentrations of replicate pairs was analyzed by combining the results for all pesticides into one group with 26 replicate pairs that had quantifiable detections in both the environmental and replicate sample (table 4–2). Seven pesticides from Group 1 had quantifiable detections for at least one replicate pair. The mean RSD was 4.2 percent, the median RSD was 2.7 percent, and the 90th-percentile RSD was 10.2 percent. Sixty-one percent of the replicate pairs had an RSD of 5 percent or less, and 88 percent of the replicate pairs had an RSD of 10 percent or less. The RSD is skewed somewhat high because of low-level detections of pesticides. The most commonly detected pesticides in environmental samples, deethylatrazine and atrazine, had mean RSDs of 7.3 percent and 3.6 percent.

Recovery in field matrix spikes was used to evaluate the analytical bias of laboratory measurement of pesticide concentrations. Recoveries for six matrix spikes were available for the Group 1 pesticides detected in NAWQA samples (table 4–3). Median recoveries for most of the pesticides were about 88 to 100 percent; however, deethylatrazine had a median recovery of 40 percent. Martin and others (2009) found that recovery of deethylatrazine was low in matrix spikes and reagent spikes, indicating that the low recovery of deethylatrazine was a function of the analytical method. Because of the known poor performance of deethylatrazine, all concentrations are flagged as estimated. Pesticide concentrations were not adjusted for analytical recovery in this study.

NAWQA Quality-Control Data for Volatile Organic Compounds

There were 16 field blanks collected for analysis of VOCs by the NAWQA Program during the second decade of sampling from 2002 through 2007 (table 4–1). The fumigant 1,2-dichloropropane was detected in three field blanks from the eastern Wisconsin-Upper Peninsula sampling area, where contamination in blank water was identified. Several apparent detections of 1,2-dichloropropane in this sampling area were deleted from the dataset because of the remark code indicating that they were affected by contamination. There were no environmental detections of 1,2-dichloropropane throughout the study area. The other five VOCs detected in field blanks were all gasoline hydrocarbons. Ethylbenzene was detected in one field blank, but none of the three detections in environmental samples were from the same network as the blank detection. Toluene was detected in three field blanks at a maximum concentration of 0.03 µg/L. Toluene is commonly detected at low concentrations in field blanks, resulting in environmental detections in NAWQA samples being censored at concentrations of 0.03 µg/L to limit the probability of false detections due to random sample contamination (John Zogorski, U.S. Geological Survey, written commun., 2008). The minimum concentration of a toluene detection in an environmental sample was 0.087 µg/L. The gasoline hydrocarbon 1,2,4-trimethylbenzene was detected in two field blanks at a maximum concentration of 0.084 µg/L. This compound (1,2,4-trimethylbenzene) is commonly detected at low concentrations in field blanks, resulting in environmental detections in NAWQA samples being censored at concentrations of 0.05 µg/L to limit the probability of false detections due to random sample contamination (John Zogorski, U.S. Geological Survey, written commun., 2008). There were no detections of 1,2,4-trimethylbenzene in environmental samples. The gasoline hydrocarbons *m*- and *p*-xylene were detected in two field blanks at a maximum concentration of 0.077 µg/L. The *m*- and *p*-xylene combination was also detected in two environmental samples,

Table 4–3. Percent recoveries of field matrix spikes for pesticides and volatile organic compounds detected in water samples collected from wells in the Cambrian-Ordovician aquifer system by the NAWQA Program, 1995–2007.

Compound	Number of spikes	Percent recovery			
		Minimum	Mean	Median	Maximum
		Pesticides			
Alachlor	6	89.3	101.6	104.3	108.1
Atrazine	6	86.1	97.4	95.4	120.5
Chlorpyrifos	6	81.0	90.3	90.0	101.8
Deethylatrazine	6	23.7	41.3	40.0	60.7
Diazinon	6	88.1	94.0	93.7	102.2
2,6-Diethylaniline	6	88.5	95.7	92.7	113.8
Metolachlor	6	84.8	97.5	100.6	104.3
Prometon	6	77.3	96.8	96.2	117.6
Simazine	6	58.4	86.0	88.2	105.2
		Volatile organic compounds			
Benzene	4	95.9	105.4	106.9	112.1
Chloroform	4	96.5	104.9	104.8	113.6
Dichlorodifluoromethane (CFC-12)	4	70.5	78.3	78.0	86.6
1,1-Dichloroethane (1,1-DCA)	4	95.1	103.6	101.9	115.4
1,2-Dichloroethane (1,2-DCA)	10	96.2	107.4	106.2	123.2
1,1-Dichloroethene (1,1-DCE)	10	85.0	99.8	93.5	123.2
cis-1,2-Dichloroethene (cis-1,2-DCE)	4	98.8	103.1	101.7	110.1
trans-1,2-Dichloroethene	4	89.0	98.2	96.2	111.4
Methylene chloride	4	85.6	96.2	94.8	109.8
Ethylbenzene	10	80.8	97.2	97.1	106.5
Isopropylbenzene	4	97.6	102.8	102.5	108.5
n-Propylbenzene	4	91.4	95.0	95.4	97.9
Styrene	4	87.3	94.1	95.3	98.5
Perchloroethene (PCE)	10	84.6	97.0	95.6	109.4
Toluene	4	93.4	99.5	98.4	107.7
1,1,1-Trichloroethane (TCA)	10	80.8	96.0	97.1	116.9
Trichloroethene (TCE)	10	89.7	98.2	99.2	108.6
Trichlorofluoromethane (CFC-11)	4	86.4	102.5	102.9	117.7
Trichlorotrifluoroethane (CFC-113)	4	71.4	86.7	82.0	111.4
Vinyl chloride	10	69.5	93.2	91.8	125.4
m- and *p*-Xylene	4	98.6	100.7	100.4	103.6
o-Xylene	4	101.4	104.6	103.4	110.0

but those detections were not associated with the field blanks. The gasoline hydrocarbon *o*-xylene was detected in one field blank and in two environmental samples from different networks than the blank detection.

Replicate samples for VOCs were collected at 12 wells sampled by the NAWQA Program. The variability in concentrations of replicate pairs was analyzed by combining the results for all VOCs into one group with 17 replicate pairs that had quantifiable detections in both the environmental and replicate sample (table 4–2). Sixteen compounds had quantifiable detections for at least one replicate pair. The mean RSD was 3.5 percent, the median RSD was 1.6 percent, and the 90th-percentile RSD was 7.9 percent. Eighty-two percent of the replicate pairs had an RSD of 5 percent or less, and 88 percent of the replicate pairs had an RSD of 10 percent or less.

It was determined that sample processing and analysis did not introduce enough variation in the environmental data collected by the NAWQA Program to affect the interpretation of VOCs. Field blanks and source-solution blanks were used to identify contamination with one compound in the eastern Wisconsin-Upper Peninsula sampling area, for which the affected environmental samples were removed from the dataset.

Recovery in field matrix spikes was used to evaluate the analytical bias of laboratory measurement of VOC concentrations. Recoveries for 4 to 10 matrix spikes were available for VOCs detected in NAWQA samples (table 4–3). Median recoveries ranged from 78 percent (CFC-12) to 107 percent (benzene), and all but two compounds had recoveries within ±10 percent of 100 percent (CFC-12 and CFC-113). Concentrations of VOCs were not adjusted for analytical recovery in this study.

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