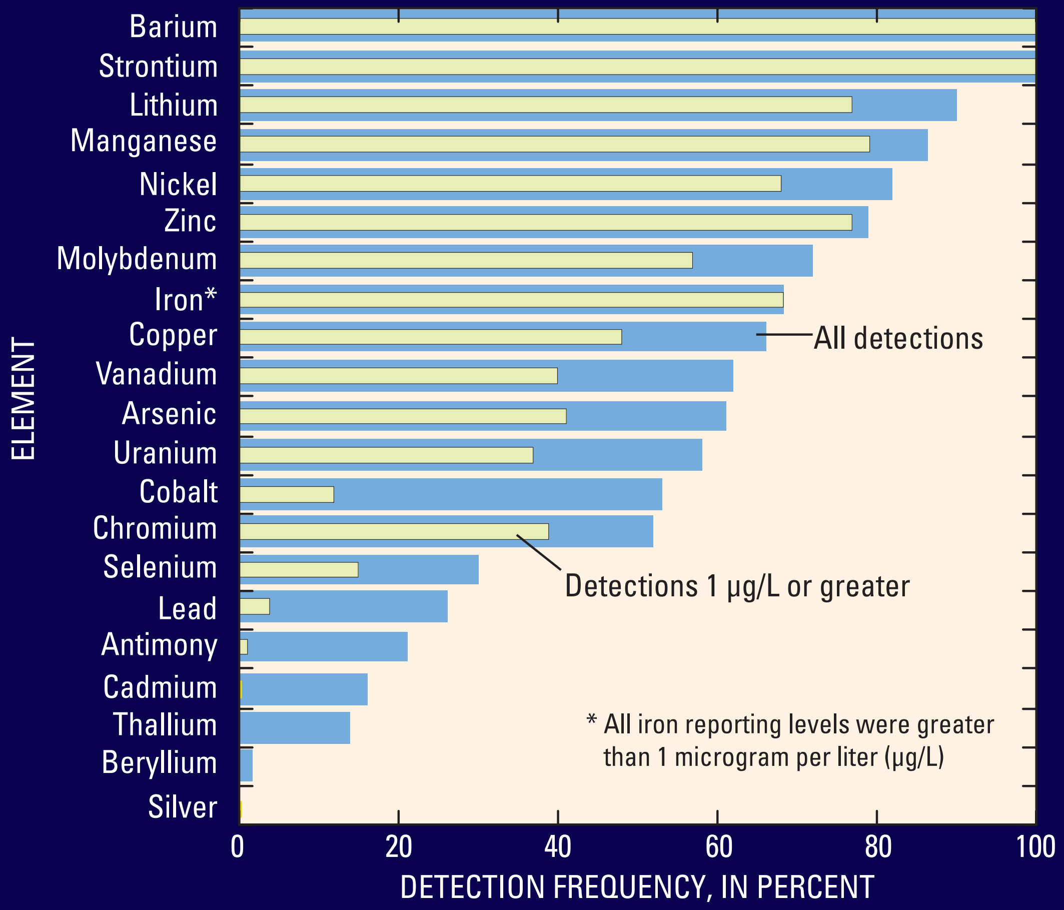
National Water-Quality Assessment Program

Occurrence and Distribution of Iron, Manganese, and Selected Trace Elements in Ground Water in the Glacial Aquifer System of the Northern United States



Scientific Investigations Report 2009–5006

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

Cover. The frequency of detections for selected elements in ground water sampled in the glacial aquifer system.

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By George E. Groschen, Terri L. Arnold, William S. Morrow, and Kelly L. Warner

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Foreward

The U.S. Geological Survey (USGS) is committed to providing the Nation with credible 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, now 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 condition of our Nation's streams and ground water? How are conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, 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 1991–2001, 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/studyu.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 ground water, and by determining 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, selected 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.

Matthew C. Larsen
Associate Director for Water

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Figures

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Conversion Factors and Datums

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square foot (ft^2)	929.0	square centimeter (cm^2)
square foot (ft^2)	0.09290	square meter (m^2)
square inch (in^2)	6.452	square centimeter (cm^2)
section (640 acres or 1 square mile)	259.0	square hectometer (hm^2)
square mile (mi^2)	259.0	hectare (ha)
square mile (mi^2)	2.590	square kilometer (km^2)

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

$$°F=(1.8\times°C)+32$$

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 North American Vertical Datum of 1988 (NAVD 88).

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 conductivity 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).

Abbreviations and Acronyms

BQ	benchmark quotient
DOC	dissolved organic carbon
ecdf	empirical cumulative distribution function(s)
HBSL	Health-Based Screening Level
LHA	Lifetime Health Advisory
LRL	laboratory reporting level
LT-MDL	long-term method detection level
LUS	land-use survey of the National Water-Quality Assessment Program
MAR	Midwestern Agricultural Region
MAS	major-aquifer survey of the National Water-Quality Assessment Program
MCFR	Mountain and Coastal Forested Region
MCL	Maximum Contaminant Level
MRL	minimum reporting level
NAWQA	National Water-Quality Assessment
NGLFR	Northern and Great Lakes Forested Region
NWQL	National Water Quality Laboratory
PVC	polyvinyl chloride
RL	reporting level
ROS	Regression on Order Statistics
SMCL	Secondary Maximum Contaminant Level
STORET	U.S. Environmental Protection Agency database for water quality, biological, and physical data
UIR	Urban-Influenced Region
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
WAGR	Western Agricultural and Grassland Region

Occurrence and Distribution of Iron, Manganese, and Selected Trace Elements in Ground Water in the Glacial Aquifer System of the Northern United States

By George E. Groschen, Terri L. Arnold, William S. Morrow, and Kelly L. Warner

Abstract

Dissolved trace elements, including iron and manganese, are often an important factor in use of ground water for drinking-water supplies in the glacial aquifer system of the United States. The glacial aquifer system underlies most of New England, extends through the Midwest, and underlies portions of the Pacific Northwest and Alaska. Concentrations of dissolved trace elements in ground water can vary over several orders of magnitude across local well networks as well as across regions of the United States. Characterization of this variability is a step toward a regional screening-level assessment of potential human-health implications. Ground-water sampling, from 1991 through 2003, of the National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey determined trace element concentrations in water from 847 wells in the glacial aquifer system. Dissolved iron and manganese concentrations were analyzed in those well samples and in water from an additional 743 NAWQA land-use and major-aquifer survey wells. The samples are from monitoring and water-supply wells. Concentrations of antimony, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, selenium, strontium, thallium, uranium, and zinc vary as much within NAWQA study units (local scale; ranging in size from a few thousand to tens of thousands of square miles) as over the entire glacial aquifer system.

Patterns of trace element concentrations in glacial aquifer system ground water were examined by using techniques suitable for a dataset with zero to 80 percent of analytical results reported as below detection. During the period of sampling, the analytical techniques changed, which generally improved the analytical sensitivity. Multiple reporting limits complicated the comparison of detections and concentrations. Regression on Order Statistics was used to model probability distributions and estimate the medians and other quantiles of the trace element concentrations. Strontium and barium were the most frequently detected and usually were present in the highest concentrations. Iron and manganese were the next most commonly detected and next highest in concentrations. Iron concentrations were the most variable with respect to the range of variations (both within local networks and aquifer-wide) and with respect to the disparity between magnitude of concentrations (detections) and the frequency of samples below reporting limits (nondetections). Antimony, beryllium, cadmium, silver, and thallium were detected too infrequently for substantial interpretation of their occurrence or distributions or potential human-health implications.

For those elements that were more frequently detected, there are some geographic patterns in their occurrence that primarily reflect climate effects. The highest concentrations of several elements were found in the West-Central glacial framework area (High Plains and northern Plains areas). There are few important patterns for any element in relation to land use, well type, or network type. Shallow land-use (monitor) wells had iron concentrations generally lower than the glacial aquifer system wells overall and much lower than major-aquifer survey wells, which comprise mostly private- and public-supply wells. Unlike those for iron, concentration patterns for manganese were similar among shallow land-use wells and major-aquifer survey wells. An apparent relation between low pH and relatively low concentrations of many elements, except lead, may be more indicative of the relatively low dissolved-solids content in wells in the Northeastern United States that comprise the majority of low pH wells, than of a pH dependent pattern.

Iron and manganese have higher concentrations and larger ranges of concentrations especially under more reducing conditions. Dissolved oxygen and well depth were related to iron and manganese concentrations. Redox conditions also affect several trace elements such as arsenic and copper; however, a comparison of redox categories, based in part on iron and manganese concentrations, indicated that the concentrations of many redox-sensitive elements were not significantly different among redox categories. Some of the redox-related patterns were not what would be expected on the basis of solubility constraints. Furthermore, barium is affected by redox conditions in at least one well network even though it is not a redox-sensitive element. Concentrations of barium in portions of the glacial aquifer system are limited by sulfate, which is strongly affected by redox conditions.

Few samples had concentrations of any trace element that exceeded drinking-water standards (Maximum Contaminant Levels), for compounds regulated in drinking water or Health-Based Screening Levels for unregulated trace elements. More unregulated trace elements had concentrations greater than benchmarks than regulated trace elements. More samples had manganese concentrations greater its benchmark than any other element in the glacial aquifer system wells. Of the 1,590 wells sampled for manganese, only 556 are for private or public drinking-water supplies, and of those, 9.9 percent (55) exceeded the manganese Lifetime Health Advisory. Concentrations of arsenic, selenium, and uranium less frequently exceeded Maximum Contaminant Levels. There are 29 wells that had 2 element concentrations that exceeded their respective benchmarks. Most concentrations that exceeded a health-based benchmark were from wells in the West-Central area (Iowa, Minnesota, North and South Dakota, Nebraska, and Kansas); however, there is little geographical pattern to the wells with element concentrations of concern.

Introduction

The glacial aquifer system in the Northern United States is used extensively as a source of drinking water for private and public supply. It is the most heavily used regional aquifer for those uses in the United States. Therefore, water quality is an issue for private well owners, water managers, and health officials. Many natural elements are present in the aquifer material that is derived from various bedrock types, which contain a range of possible elements, such as arsenic, uranium, and radon. Because it is typically at or near land surface, the glacial aquifer system is potentially susceptible to anthropogenic contamination. Trace elements, for example arsenic and cadmium, can pose potentially adverse health effects to people who drink ground water. Better characterization of the distribution and occurrence of dissolved trace elements and iron and manganese in the glacial aquifer system is needed to help assess the implications for drinking water and other water uses.

In 1991, the U.S. Geological Survey (USGS) began the full-scale National Water-Quality Assessment (NAWQA) Program. The long-term goals of the NAWQA Program are to describe the status of and trends in the quality of a large representative part of the Nation’s surface- and ground-water resources and to identify the major natural and human factors that affect the quality. In addressing these goals, the program has already produced a wealth of water-quality information that will be useful to policy makers and water managers at the national, State, and local levels. The NAWQA Program provides a large-scale framework for understanding the regional and national water-quality conditions that cannot be acquired from small-scale programs and studies.

As part of the second cycle (2001–12) of NAWQA studies, the data collected during the first cycle (1991–2001) of the program are analyzed in a regional framework. The basis for this regional assessment of the ground-water data is by regional (principal) aquifers (Lapham and others, 2005). The most extensive regional aquifer is the system of glacial deposits across the Northern United States (Warner and Arnold, 2005). As defined by Warner and Arnold (2005), the aquifer includes all perennially saturated unconsolidated geologic material above bedrock that lies on or north of the line of maximum glacial advance within the United States. The glacial deposits cover portions of 26 States; however, wells were not sampled in all these states as part of the NAWQA Program (fig. 1).

The NAWQA Program sampled ground water for a suite of trace elements. Arsenic and uranium were included in these analyses; however, these constituents are discussed in detail for the glacial aquifer system in separate reports (Ayotte and others, 2007; Thomas, 2007) and are discussed only in general terms in this report. These constituents also are included in the “Elements and Environmental Factors in a Human-Health Context” (page 66) section, of this report.

The 21 elements discussed in this report are listed in table 1. For this report, the term “elements” is used to refer to all the elements listed in table 1 including iron and manganese, both of which are not generally considered “trace.” However, the concentrations of strontium and barium are commonly greater than the concentrations of iron and manganese in the wells sampled in the study area, so the term “trace elements” may be arbitrary when applied to these dissolved constituents in ground water. For the purposes of this report, the term “trace elements” is used to refer primarily to those “typical” trace elements as a group—excluding iron and manganese.

A characteristic of trace elements that sets them apart from many other potential ground-water elements is that they occur naturally in the earth’s crust, surficial deposits, and the soils that develop in these deposits. Under natural conditions, most of these elements are relatively immobile in the minerals and other phases that make up rocks and soils, and therefore natural concentrations in most ground water are negligible to undetectable. Under specific geochemical conditions, or when human-induced changes affect the ground-water geochemical environment, some of these elements dissolve more readily and become potential problems. The tendency of most trace elements to be immobile in rocks and soils has prevented a much greater contamination problem in shallow ground water.

Most of the elements discussed in this report are critical to historical and modern industrial and commercial processes and materials. Such processes and materials, some of which are listed in table 1, would not be possible without the use of these elements. The amount of these elements in the human environment is steadily increasing because they are extracted from the earth and increasingly used in processes and materials. Characterizing the natural occurrence and distribution of these elements in shallow ground water and in regional water-supply aquifers will help identify human-caused contamination.

Base from U.S. Geological Survey 1:2,000,000 Digital Data
Albers Equal-Area Conic projection, standard parallels 29°30′
and 45°30′, central meridian -96°, latitude of origin 23°

Figure 1. Location of the glacial aquifer system of the Northern United States and National Water-Quality Assessment (NAWQA) Program study units.

Table 1. Elements discussed in this report, common uses, forms in freshwater, and oxidation-reduction sensitivity, from Pais and Jones (1997) and U.S. Environmental Protection Agency (2007).

[O, oxygen, H, hydrogen; C, carbon]

Element	Common uses	Common chemical forms in freshwater	Redox sensitive[1]
Antimony (Sb)	Flame retardant. Solder	$Sb(OH)_6^-$	Yes
Arsenic (As)	Legacy pesticides, semiconductors	$HAsO_4^{2-}$, or $H_2AsO_4^-$	Yes
Barium (Ba)	Well drilling, metal alloys, medicinal use, various others	Ba^{2+}	No
Beryllium (Be)	Used in alloys	$Be(OH)_2^+$	No
Cadmium (Cd)	Metal plating, batteries, other uses	Cd^{2+} or $CdOH^+$	No
Chromium (Cr)	Metal alloys, plating, pigments, wood preservative	CrO_4^{2-}, or $Cr(OH)_3$	Yes
Cobalt (Co)	Alloys, magnets, pigments, radiography	Co^{2+} or $CoCO_3$	Yes
Copper (Cu)	Water-supply pipes, alloys	$CuOH^+$ or $CuCO_3$	Yes
Iron (Fe)	Steel, alloys, various uses	$Fe(OH)_2^+$ or Fe^{2+}	Yes
Lead (Pb)	Old plumbing and solder, formerly used in gasoline, used in many manufacturing processes, toy soldiers	$PbCO_3$ or $Pb(CO_3)_2^{2-}$	Yes
Lithum (Li)	Pharmaceuticals	Li^+	No
Manganese (Mn)	Metal alloys	Mn^{2+}	Yes
Molybdenum (Mo)	Metal alloys, pigments	MoO_4^{2-}	Yes
Nickel (Ni)	Metal alloys, coins, batteries	Ni^{2+} or $NiCO_3$	Yes
Selenium (Se)	Photocells, photovoltaic cells, light meters,	SeO_3^{2-}, others	Yes
Silver (Ag)	Coins, tableware, alloys, analogue photography	Ag^+	No
Strontium (Sr)	Cathode ray tubes, magnets, radiopharmaceuticals	Sr^{2+} or $SrOH^+$	No
Thallium (Tl)	Electronic equipment	Tl^+	Yes
Uranium (U)	Ammunition, nuclear power	U^{3+} or UO_2^{2+}	Yes
Vanadium (V)	Metal alloys	$H_2VO_4^-$ or HVO_4^{2-}	Yes
Zinc (Zn)	Galvanized metals, alloys, coins, zinc oxide	$ZnOH^+$, Zn^{2+}, or $ZnCO_3$	No

[1] Redox sensitivity, as used in this report, means that at least one natural oxidation state of the element is much more soluble in freshwater than other natural oxidation states.

Many of these trace elements can exist in the dissolved phase at two or more oxidation states. These oxidation states and oxyanions created under changing conditions may be more or less soluble than other forms. For example, iron in oxidized water is typically in the Fe(III) oxidation state and forms oxy-hydroxy minerals much more readily than the remaining dissolved Fe(II) fraction. Therefore, in oxidizing conditions [defined for this report as a dissolved oxygen concentration higher than 0.5 milligrams per liter (mg/L)], dissolved iron concentrations at equilibrium with solid iron-containing phases will be miniscule to undetectable in neutral to near-neutral pH conditions ($5 < pH < 9$). The reduced form of iron is Fe(II), which can occur in relatively large dissolved concentrations unless sulfide is present. Oxygen-free reduced ground water without a source of reduced sulfur is common under certain conditions, and high concentrations of dissolved iron are found frequently in this type of ground-water environment. However, the major chemical processes that determine the electrochemical environment in ground water are strongly controlled by bacteria and other microorganisms that use various electron-accepting processes for energy. Thermodynamic equilibrium between dissolved and mineral phases, including organic matter and carbon dioxide, may never be present. It is therefore difficult to predict, on the basis of thermodynamic principles alone, concentrations of dissolved trace elements in ground water.

Purpose and Scope

This report presents results of analysis of the occurrence and distribution of iron, manganese, and selected trace elements in ground water of the glacial aquifer system. Results presented include: spatial patterns of these elements in the glacial aquifer system across the Northern United States; patterns identified between concentrations of the elements and environmental or geologic characteristics of the well location and transferability of water-quality conditions to unsampled areas, and; a screening-level assessment of potential human-health implications of individual elements and of the combined trace elements in water samples.

The data used for this report were collected in the first 13 years (1991–2003) of the NAWQA Program from 1,590 wells sampled by the NAWQA Program during Cycle 1 (1991–2001) and the beginning of Cycle 2 (2001–12). All data were obtained from the USGS NAWQA Data Warehouse (Bell and Williamson, 2006). Figure 2 shows the locations of the wells that were sampled, and table 2 lists the well networks and sample periods.

Data from all NAWQA ground-water samples from the glacial aquifer system are used in this report. There are two major study components that include the majority of the data: major-aquifer surveys (MAS; formerly known as study-unit or subunit surveys) and land-use surveys (LUS). Surveys were conducted by using networks of wells to describe water-quality characteristics of various settings. A primary objective of the MAS was to characterize the water quality in major aquifers underlying or adjacent to NAWQA study areas that were being used for drinking-water supply or had the potential to serve as supplies. A primary objective of the LUS was to characterize recently recharged (since about 1970) ground water in areas underlain by specific homogeneous land-uses, such as urban or agricultural land cover (Gilliom and others, 1995). A small number of additional wells were sampled as part of local flow-system studies of limited extent; the data from those samples are included in this report. The different objectives of these ground-water study components have some relevance to the results discussed in this report, as noted in the relevant sections.

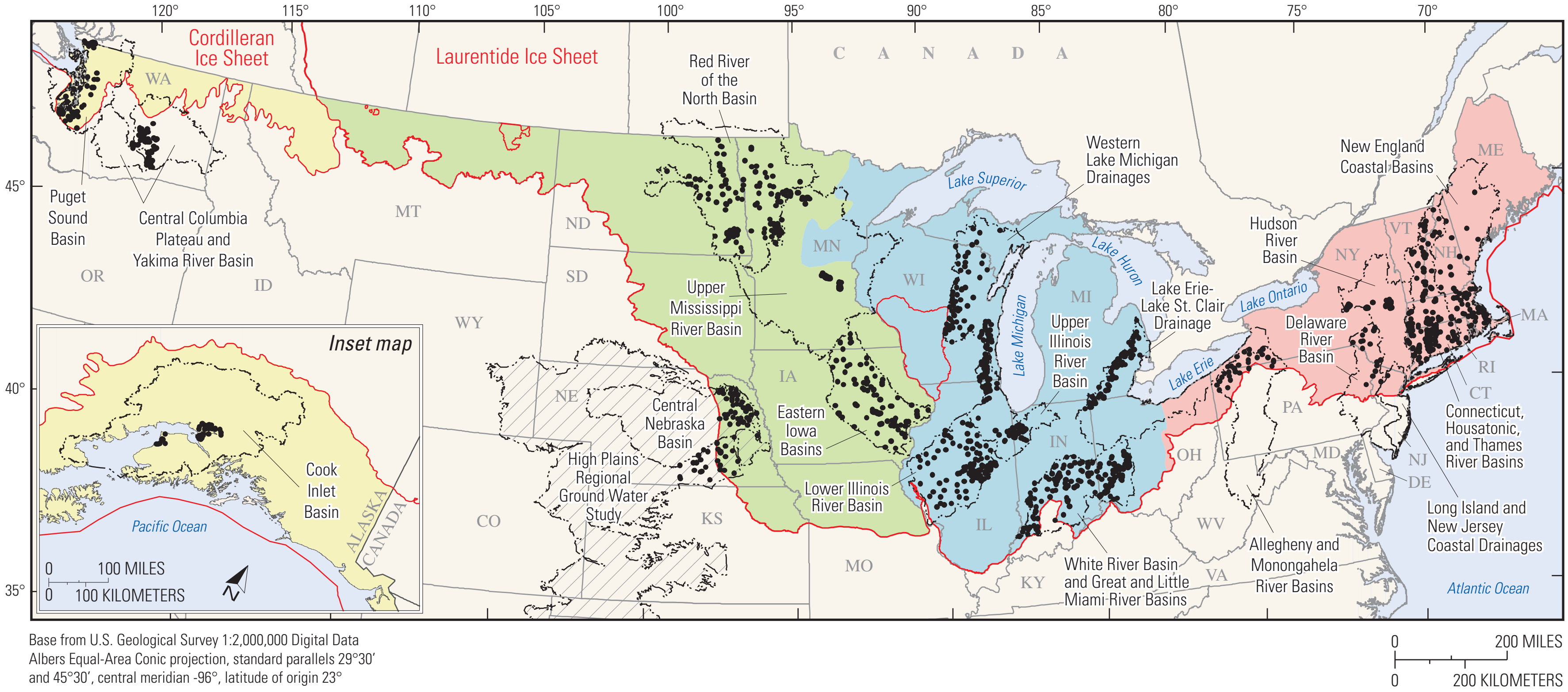
This report also includes data from five ground-water networks that lie, at least partly, outside of the limit of glaciation in Washington State and Nebraska but are in glacially derived or reworked sediments. These five well networks are included in this discussion because they are in unconsolidated geologic materials that are similar in composition and age to materials in the glacial aquifer system and expand the geographic distribution of wells in the northwestern part of the study area. Therefore, the ground-water chemistry at these wells may be more similar to the ground-water chemistry of the glacial aquifer system than to that of adjacent bedrock or other aquifers; thus, these wells are referred to in this report as part of the glacial aquifer well networks. Finally, eight wells in two networks are located just north (less than 2 kilometers) of the Washington State border in British Columbia, Canada. Although these wells are technically outside the Northern United States, they are constructed in glacial aquifer materials and are grouped with the wells discussed in this report.

The sampling and analytical methods were the same for all well samples. More than half (55 percent) of the wells are in LUS areas and the rest (45 percent) are in MAS areas. Koterba and others (1995) described the field sampling procedures for all well samples. All samples were analyzed at the USGS National Water Quality Laboratory (NWQL) in Denver, Colo. Methods varied for several trace elements (Faires, 1993); however, most trace elements were analyzed by inductively coupled plasma–mass spectrometry (Garbarino, 1999) and had very low [commonly less than 1 microgram per liter (μg/L)] reporting levels. Table 3 lists, by element, the methods for each element through time and associated reporting levels and long-term method detection levels (National Water Quality Laboratory, written commun., 2005). All data in this report represent the total dissolved element concentration (operationally defined as the fraction of all species of the element that passes through a filter with 0.45-micron pores) for samples collected between August 1991 and October 2003. The reporting levels in table 3 are those used for regular standard freshwater samples. Occasionally, unusually high dissolved analyte or high dissolved solids concentrations, presence of interfering elements, or other matrix effects, require the sample to be diluted, or other extraordinary procedures carried out, to determine the concentration of a specific analyte. For these extraordinary analyses, the analyst will assign a higher reporting level to the analysis that is appropriate to the procedure. Often, the reporting level assigned to that analysis may be an order of magnitude or greater than those listed in table 3.

Previous Studies

The results of many studies of one to several trace elements have been reported for the glacial aquifer system or related aquifer systems on regional or national scales and include those from several recent studies. Welch and others (2000) examined the occurrence and distribution of arsenic in the ground water of the United States. Focazio and others (2001) examined the distribution of selected radionuclides in the drinking water from ground-water sources in the United States. Thomas reported on arsenic in the glacial aquifer system at a subregional scale (Thomas, 2003) and across the Northern United States (Thomas, 2007). Ayotte and others (2003) presented results of a local eastern New England ground-water arsenic study. Ayotte and others (2007) reported on uranium and radon in the glacial aquifer system of the Northern United States. Thomas (2007) and Ayotte and others (2007), as well as this report, are in the series of reports from the Glacial Aquifer System regional studies of the USGS NAWQA program.

Newcomb and Rimstidt (2002) examined ground-water trace element data compiled from the U.S. Environmental Protection Agency (USEPA) STORET database (U.S. Environmental Protection Agency, 2004b). They applied statistical methods (probabilistic) described by Helsel (1990) to characterize distributions of trace elements in ground water with multiply censored (less than the detection limit) values. Newcomb and Rimstidt (2002) examined data from all aquifers represented in the STORET database that include both ambient and contamination-related dissolved concentration data. The STORET data are from disparate laboratories and agencies and, in general, are not attributed to specific aquifers. They concluded that most of the trace element concentrations examined were log-normally distributed and ranged over many orders of magnitude resulting from the various processes and reactions that affect the concentrations. In addition,



Base from U.S. Geological Survey 1:2,000,000 Digital Data
Albers Equal-Area Conic projection, standard parallels 29°30′
and 45°30′, central meridian -96°, latitude of origin 23°

EXPLANATION

Glacial framework area—Shown only in the United States. Initially defined by physiography and glacial lobes

🟦 Central
🟨 West
🟥 East
🟩 West central

Glacial aquifer system boundary (approximate)

Study-unit boundary

• **Ground-water sampling site**

Figure 2. Location of study wells and framework areas of the glacial aquifer system.

Table 2. Well networks in the glacial aquifer system and history of sampling for iron, manganese, and trace elements during 1991–2003.

Network identifier	Network type	Number of wells	Approximate sampling period for network	States with wells
almnsus2	Major-aquifer survey	30	Sep.–Oct. 1996	New York and Pennsylvania
ccptlusag2a	Land-use survey	13	Jun.–Jul. 1993; May–Sep. 1994	Washington
ccptlusag2b	Land-use survey	27	Jun. 1993; Sep. 1994; Jul.–Aug. 2002	Washington
ccptlusor1a	Land-use survey	9	Apr.–Jun. 1994; Jul. 1995	Washington
ccptlusor1b	Land-use survey	19	Mar. 1994; Oct. 1994; Jun. 1995; Jul. 2002	Washington
cnbrluscr1	Land-use survey	28	Apr.–Jun. 2003	Nebraska
cnbrrefpa1	Reference	2	May–Jun. 2003	Nebraska
conndwgs1	Source-water assessment	10	Oct. 2002; Apr. 2003	Connecticut
connfpsur1	Flow-system study	13	Jul.–Sep. 1994	Connecticut
connlusag1	Land-use survey	33	Jul.–Sep. 1993; Jul.–Sep. 1994; Jul. 1995	Connecticut, Massachusetts, New Hampshire, and Vermont
connlusur1	Land-use survey	39	Aug.–Sep. 1993, Jun.–Aug. 1994; Jul. 1995	Connecticut, Massachusetts, New Hampshire, and Vermont
connlusfo1	Land-use survey	2	Aug.–Sep. 2003	Connecticut, Massachusetts, New Hampshire, and Vermont
connlusrc1	Land-use survey	29	Jul.–Sep. 2003	Connecticut and Massachusetts
connsus2	Major-aquifer survey	30	May–Nov. 2002	Connecticut, Massachusetts, New Hampshire, and Vermont
cooksus1a	Major-aquifer survey	29	Jul.–Oct. 1999	Alaska
cooksus1b	Major-aquifer survey	5	Jul.–Aug. 1999	Alaska
delrsus3	Major-aquifer survey	16	Jul.–Aug. 2001	Pennsylvania, New Jersey, and New York
eiwaluscr1	Land-use survey	31	Jun.–Aug. 1997	Iowa
eiwalusrc1	Land-use survey	30	Jun.–Aug. 1997	Iowa
eiwaspcg1	Special Study	27	Jul.–Aug. 1996; Aug. 1998	Iowa
eiwasus2	Major-aquifer survey	32	Jun.-Jul. 1998	Iowa
hdsnfpsag1	Flow-system study	25	Sep. 1993; May–Sep. 1994; Jun. 1995	New York
hdsnlusag1	Land-use survey	14	Sep. 1993; Jul.–Aug. 1994	New York
hdsnlusur1	Land-use survey	27	Jul.–Sep. 1993; Jul.–Aug. 1994	New York
hdsnsus1	Major-aquifer survey	2	Oct. 1994	New York
hpgwdwgs1	Source-water assessment	15	Oct.–Dec. 2002; Jan. 2003	Nebraska, Kansas, and Texas
hpgwsus4	Major-aquifer survey	27	Mar.–Jul. 2003	Nebraska, Kansas, and Texas
leriluscr1	Land-use survey	29	Jun.–Aug. 1998	Ohio
lerilusrc1	Land-use survey	29	Nov.–Dec. 1996; Jan. 1997	Ohio and Michigan
lerispcg1	Special Study	25	Jun.–Jul. 1997	Ohio
lerisus1	Major-aquifer survey	27	Jun.–Sep. 1998	Ohio
linjsus1	Major-aquifer survey	1	Sep. 1997	New Jersey
lirbluscr1	Land-use survey	28	Jun.–Aug. 1997	Illinois
lirbluscr2	Land-use survey	29	Aug.–Nov. 1997	Illinois
lirbsus1	Major-aquifer survey	30	Jun.–Jul. 1997	Illinois
lirbsus2	Major-aquifer survey	30	Jul.–Nov. 1996	Illinois
miamluscr1	Land-use survey	26	Jul.–Aug. 2000	Ohio and Indiana
miamluscr1a	Land-use survey	8	Jul.–Aug. 2000	Ohio and Indiana
miamlusrc1	Land-use survey	25	Oct.–Dec. 2001	Ohio and Indiana

Table 2. Well networks in the glacial aquifer system and history of sampling for iron, manganese, and trace elements during 1991–2003.—Continued

Network identifier	Network type	Number of wells	Approximate sampling period for network	States with wells
miamrefot1	Reference	2	Oct.–Nov. 2001	Ohio and Indiana
miamspcb1	Special Study	15	May–Jun. 1999	Ohio and Indiana
miamsus1	Major-aquifer survey	30	May–Jul. 1999	Ohio and Indiana
necblusrc1	Land-use survey	29	Jul.–Sep. 1999	Maine and New Hampshire
necbsus3	Major-aquifer survey	30	Jul.–Oct. 2001	Maine and New Hampshire
pugtfpscr1	Flow-system study	3	Feb. 1997; Sep. 1997; Nov. 1997	Washington
pugtluscr1	Land-use survey	5	Feb. 1997; Aug.–Sep. 1997; Nov. 1997; Feb. 1998; Apr. 1998	Washington
pugtlusrs1	Land-use survey	27	Nov.–Dec. 1996; May–Aug. 1997; Jul. 1998	Washington
pugtsus1	Major-aquifer survey	30	Jul.–Sep. 1996	Washington
rednfpsag1	Flow-system study	6	Jun. 1994; Jun. 1995	Minnesota and North Dakota
rednfpsag2	Flow-system study	7	Jul.–Aug. 1993; Jul.–Aug. 1994; Jun. 1995	Minnesota
rednlusag1	Land-use survey	29	Jun.–Jul. 1994	Minnesota and North Dakota
rednlusag2	Land-use survey	28	Jul.–Aug. 1993	Minnesota and North Dakota
rednsus1	Major-aquifer survey	20	Aug. 1991; Jun.–Aug. 1992; Jul.–Aug. 1993; Aug.–Sep. 1994; May–Jun. 1995	Minnesota and North Dakota
rednsus2	Major-aquifer survey	22	Aug.–Oct. 1993; Jun.–Jul. 1994	Minnesota and North Dakota
rednsus3	Major-aquifer survey	14	Aug. 1993; Aug.–Sep. 1994; Apr.–Jun. 1995	Minnesota and North Dakota
rednsus5	Major-aquifer survey	34	Aug. 1991; Jun.–Nov. 1992; Aug. 1994; Nov. 1994; Jun. 1995	Minnesota and North Dakota
uirbluscr1	Land-use survey	29	Jun.–Sep. 1999	Illinois and Indiana
uirblusrc1	Land-use survey	26	Apr.–Jun. 2000	Illinois and Wisconsin
uirbsus1	Major-aquifer survey	27	Mar.–May 2001	Illinois and Indiana
uirbsus2	Major-aquifer survey	23	Aug.–Oct. 2000	Illinois and Wisconsin
umisfpsur1	Flow-system study	17	May–Oct. 1997; Aug. 1998	Minnesota
umisluscr1	Land-use survey	29	May–Oct. 1998	Minnesota
umislusrc1	Land-use survey	30	Jun.–Jul. 1996	Minnesota
umislusfo1	Land-use survey	15	Jun. 1998	Minnesota and Wisconsin
whitfpsag1	Flow-system study	12	Oct. 1993; Apr. 1994; Jul. 1995	Indiana
whitfpsag2	Flow-system study	2	Jun.–Oct. 1994	Indiana
whitluscr1	Land-use survey	43	Jul.–Sep. 1994; Aug.–Sep. 2002	Indiana
whitluscr3a	Land-use survey	24	May–Aug. 1995	Indiana
whitluscr3b	Land-use survey	6	Jul.–Aug. 1995	Indiana
whitlusur1a	Land-use survey	25	May–Aug. 1995	Indiana
whitlusur1b	Land-use survey	3	Jun.–Aug. 1995	Indiana
wmicfpsag1a	Flow-system study	9	Jun. 1994; Jun.–Jul. 1995	Wisconsin
wmicfpsag1b	Flow-system study	8	Jun. 1994; Aug. 1995	Wisconsin
wmiclusag1a	Land-use survey	25	Sep. 1993; Jun.–Aug. 1994	Wisconsin
wmiclusag2	Land-use survey	28	Sep. 1994; Jul.–Sep. 2002	Wisconsin
wmicsus2	Major-aquifer survey	28	May–Aug. 2003	Wisconsin

Table 3. Methods used by the National Water Quality Laboratory, 1991–2003, to analyze ground-water samples for the elements discussed in this report.

[Concentrations in micrograms per liter, HG-AAS, Hydride Generation Atomic Absorption Spectrophotometry; MRL, method reporting level; na, not applicable; ICP-MS, Inductively Coupled Mass Spectrometry; LRL, laboratory reporting level; GF-AAS, Graphite-Furnace Atomic Absorption Spectrophotometry; ICP-AES, Inductively Coupled Atomic Emission Spectroscopy; DCP-AES, Direct-Coupled Plasma, Atomic Emission Spectroscopy]

Element	Method	Start date	End date	Type of reporting	Long-term method detection level	Reporting level
Antimony (Sb)	HG-AAS	1/1/1992	9/30/1998	MRL	na	1
	ICP-MS	10/17/1994	9/30/2000	MRL	na	1
	ICP-MS	10/1/2000	9/30/2002	LRL	0.024	.048
	ICP-MS	10/1/2002	9/30/2003	LRL	.15	.3
	ICP-MS	10/1/2003	na	LRL	.1	.2
Arsenic (As)	HG-AAS	1/1/1992	9/30/1998	MRL	na	1
	GF-AAS	10/1/1998	9/30/1999	MRL	na	1
	ICP-MS	9/1/1999	9/30/2000	MRL	na	.9
	ICP-MS	10/1/2000	9/30/2002	LRL	.09	.18
	ICP-MS	10/1/2002	9/30/2003	LRL	.13	.26
	ICP-MS	10/1/2003	na	LRL	.1	.2
Barium (Ba)	ICP-AES	1/1/1992	12/30/1997	MRL	na	2
	ICP-AES	12/31/1997	9/30/1998	MRL	na	1
	ICP-MS	10/17/1994	9/30/2002	MRL	na	1
	ICP-MS	10/1/2002	9/30/2003	LRL	.03	.05
	ICP-MS	10/1/2003	na	LRL	.1	.2
Beryllium (Be)	ICP-AES	1/1/1992	12/22/1997	MRL	na	.5
	ICP-AES	12/23/1997	9/30/1998	MRL	na	1
	ICP-AES	10/1/1998	10/17/2000	LRL	.8	1.6
	ICP-AES	10/18/2000	9/30/2001	LRL	.5	1
	ICP-AES	10/1/2001	4/30/2003	LRL	.3	.5
	ICP-AES	5/1/2003	9/30/2004	LRL	.2	.4
	ICP-AES	10/1/2004	na	LRL	.1	.2
	ICP-MS	10/17/1994	9/30/2000	MRL	na	1
	ICP-MS	10/1/2000	na	LRL	.03	.06
Cadmium (Cd)	ICP-AES	1/1/1992	12/22/1997	MRL	na	1
	ICP-AES	12/23/1997	9/30/1998	MRL	na	8
	ICP-AES	10/1/1998	4/30/2003	LRL	3	8
	ICP-AES	5/1/2003	9/30/2003	LRL	1.2	2
	ICP-AES	10/1/2003	9/30/2004	LRL	1.6	3.2
	ICP-AES	10/1/2004	na	LRL	1	2
	GF-AAS	1/1/1992	9/30/1999	MRL	na	1
	GF-AAS	10/1/1999	9/30/2001	LRL	.07	.14
	GF-AAS	10/1/2001	9/30/2002	LRL	.06	.12
	GF-AAS	10/1/2002	na	LRL	.11	.22
	ICP-MS	10/17/1994	9/30/2000	MRL	na	1
	ICP-MS	10/1/2000	9/30/2002	LRL	.018	.037
	ICP-MS	10/1/2002	9/30/2003	LRL	.018	.037
Chromium (Cr)	ICP-AES	1/1/1992	12/21/1997	MRL	na	5
	ICP-AES	12/23/1997	9/30/1998	MRL	na	14
	ICP-AES	10/1/1998	10/17/2000	LRL	7	14
	ICP-AES	10/18/2000	4/30/2003	LRL	5	10
	ICP-AES	5/1/2003	9/30/2003	LRL	2.4	5
	ICP-AES	10/1/2003	9/30/2004	LRL	2.1	4.2
	ICP-AES	10/1/2004	na	LRL	1	2
	DCP-AES	1/1/1992	10/11/1994	MRL	na	1
	ICP-MS	10/17/1994	3/8/2001	MRL	na	1
	GF-AAS	1/1/1992	9/30/1999	MRL	na	1
	GF-AAS	10/1/1999	na	LRL	.4	.8

Table 3. Methods used by the National Water Quality Laboratory, 1991–2003, to analyze ground-water samples for the elements discussed in this report.—Continued

[Concentrations in micrograms per liter, HG-AAS, Hydride Generation Atomic Absorption Spectrophotometry; MRL, method reporting level; na, not applicable; ICP-MS, Inductively Coupled Mass Spectrometry; LRL, laboratory reporting level; GF-AAS, Graphite-Furnace Atomic Absorption Spectrophotometry; ICP-AES, Inductively Coupled Atomic Emission Spectroscopy; DCP-AES, Direct-Coupled Plasma, Atomic Emission Spectroscopy]

Element	Method	Start date	End date	Type of reporting	Long-term method detection level	Reporting level
Cobalt (Co)	ICP-AES	1/1/1992	12/21/1997	MRL	na	3
	ICP-AES	12/23/1997	9/30/1998	MRL	na	12
	ICP-AES	10/1/1998	9/30/1999	LRL	4	7
	ICP-AES	10/1/1999	9/30/2001	LRL	6	13
	ICP-AES	10/1/2001	9/30/2002	LRL	7	13
	ICP-AES	10/1/2002	4/30/2003	LRL	4	8
	ICP-AES	5/1/2003	9/30/2003	LRL	1.7	3
	ICP-AES	10/1/2003	9/30/2004	LRL	1.3	2.6
	ICP-AES	10/1/2004	na	LRL	1	2
	ICP-MS	10/17/1994	9/30/2000	MRL	na	1
	ICP-MS	10/1/2000	9/30/2003	LRL	.007	.015
	ICP-MS	10/1/2003	na	LRL	.007	.014
Copper (Cu)	ICP-AES	1/1/1992	9/30/1998	MRL	na	10
	ICP-AES	10/1/1998	10/17/2000	LRL	5	10
	ICP-AES	10/18/2000	9/30/2001	LRL	2.4	4.7
	ICP-AES	10/1/2001	4/30/2003	LRL	2.9	5.8
	ICP-AES	5/1/2003	9/30/2003	LRL	3.4	7
	ICP-AES	10/1/2003	9/30/2004	LRL	2.5	5
	ICP-AES	10/1/2004	na	LRL	1	2
	ICP-MS	10/17/1994	9/30/2000	MRL	na	1
	ICP-MS	10/1/2000	9/30/2002	LRL	.12	.23
	ICP-MS	10/1/2002	9/30/2003	LRL	.12	.23
	ICP-MS	10/1/2003	na	LRL	.2	.4
Iron (Fe)	ICP-AES	1/1/1992	12/22/1997	MRL	na	3
	ICP-AES	12/23/1997	9/30/1998	MRL	na	10
	ICP-AES	10/1/1998	4/30/2003	LRL	5	10
	ICP-AES	5/1/2003	9/30/2003	LRL	3.8	8
	ICP-AES	10/1/2003	9/30/2004	LRL	3.2	6.4
	ICP-AES	10/1/2004	na	LRL	3	6
Lead (Pb)	ICP-AES	1/1/1992	12/21/1997	MRL	na	10
	ICP-AES	12/23/1997	9/30/1998	MRL	na	100
	ICP-AES	10/1/1998	na	LRL	50	100
	GF-AAS	1/1/1992	9/30/1999	MRL	na	1
	GF-AAS	10/1/1999	na	LRL	.5	1
	ICP-MS	10/17/1994	9/30/2000	MRL	na	1
	ICP-MS	10/1/2000	na	LRL	.04	.08
Lithium (Li)	ICP-AES	1/1/1992	9/30/1998	MRL	na	4
	ICP-AES	10/1/1998	9/30/1999	LRL	3	6
	ICP-AES	10/1/1999	4/30/2003	LRL	1.9	3.9
	ICP-AES	5/1/2003	9/30/2003	LRL	1.4	3
	ICP-AES	10/1/2003	9/30/2004	LRL	1.5	3
	ICP-AES	10/1/2004	na	LRL	1	2
	ICP-MS	9/1/1999	9/30/2000	MRL	na	.3
	ICP-MS	10/1/2000	9/30/2002	LRL	.15	.3
	ICP-MS	10/1/2002	9/30/2003	LRL	.25	.5
	ICP-MS	10/1/2003	na	LRL	.3	.6

Table 3. Methods used by the National Water Quality Laboratory, 1991–2003, to analyze ground-water samples for the elements discussed in this report.—Continued

[Concentrations in micrograms per liter, HG-AAS, Hydride Generation Atomic Absorption Spectrophotometry; MRL, method reporting level; na, not applicable; ICP-MS, Inductively Coupled Mass Spectrometry; LRL, laboratory reporting level; GF-AAS, Graphite-Furnace Atomic Absorption Spectrophotometry; ICP-AES, Inductively Coupled Atomic Emission Spectroscopy; DCP-AES, Direct-Coupled Plasma, Atomic Emission Spectroscopy]

Element	Method	Start date	End date	Type of reporting	Long-term method detection level	Reporting level
Manganese (Mn)	ICP-AES	1/1/1992	12/21/1997	MRL	na	1
	ICP-AES	12/23/1997	9/30/1998	MRL	na	4
	ICP-AES	10/1/1998	9/30/1999	LRL	1.5	3
	ICP-AES	10/1/1999	10/17/2000	LRL	1.1	2.2
	ICP-AES	10/18/2000	9/30/2001	LRL	1.6	3.2
	ICP-AES	10/1/2001	4/30/2003	LRL	.8	1.6
	ICP-AES	5/1/2003	9/30/2003	LRL	.2	.4
	ICP-AES	10/1/2003	9/30/2004	LRL	.4	.8
	ICP-AES	10/1/2004	na	LRL	.3	.6
	ICP-MS	8/26/1997	9/30/2000	MRL	na	1
	ICP-MS	10/1/2000	9/30/2002	LRL	.05	.1
	ICP-MS	10/1/2002	9/30/2003	LRL	.09	.18
	ICP-MS	10/1/2003	na	LRL	.1	.2
Molybdenum (Mo)	ICP-AES	1/1/1992	12/21/1997	MRL	na	10
	ICP-AES	12/23/1997	9/30/1998	MRL	na	60
	ICP-AES	10/1/1998	9/30/1999	LRL	25	50
	ICP-AES	10/1/1999	10/17/2000	LRL	17	34
	ICP-AES	10/18/2000	9/30/2002	LRL	23	45
	ICP-AES	10/1/2002	4/30/2003	LRL	15	30
	ICP-AES	5/1/2003	9/30/2004	LRL	2	4
	ICP-AES	10/1/2004	na	LRL	2	4
	ICP-MS	10/17/1994	9/30/2000	MRL	na	1
	ICP-MS	10/1/2000	9/30/2002	LRL	.1	.2
	ICP-MS	10/1/2002	9/30/2003	LRL	.17	.33
	ICP-MS	10/1/2003	na	LRL	.2	.4
Nickel (Ni)	ICP-AES	1/1/1992	12/22/1997	MRL	na	10
	ICP-AES	12/23/1997	9/30/1998	MRL	na	40
	ICP-AES	10/1/1998	10/17/2000	LRL	17	40
	ICP-AES	10/18/2000	9/30/2001	LRL	27	53
	ICP-AES	10/1/2001	4/30/2003	LRL	14	29
	ICP-AES	5/1/2003	9/30/2003	LRL	3.3	7
	ICP-AES	10/1/2003	na	LRL	1	2
	ICP-MS	10/17/1994	9/30/2000	MRL	na	1
	ICP-MS	10/1/2000	na	LRL	.03	.06
Selenium (Se)	HG-AAS	1/1/1992	9/30/1998	MRL	na	1
	GF-AAS	10/1/1998	9/30/1999	MRL	na	1
	GF-AAS	10/1/1999	9/30/2001	LRL	1.2	2.4
	GF-AAS	10/1/2001	9/30/2002	LRL	1	2
	GF-AAS	10/1/2002	na	LRL	1.3	2.6
	ICP-MS	9/1/1999	9/30/2000	MRL	na	.7
	ICP-MS	10/1/2000	9/30/2002	LRL	.17	.33
	ICP-MS	10/1/2002	9/30/2003	LRL	.25	.5
	ICP-MS	10/1/2003	na	LRL	.2	.4

Table 3. Methods used by the National Water Quality Laboratory, 1991–2003, to analyze ground-water samples for the elements discussed in this report.—Continued

[Concentrations in micrograms per liter, HG-AAS, Hydride Generation Atomic Absorption Spectrophotometry; MRL, method reporting level; na, not applicable; ICP-MS, Inductively Coupled Mass Spectrometry; LRL, laboratory reporting level; GF-AAS, Graphite-Furnace Atomic Absorption Spectrophotometry; ICP-AES, Inductively Coupled Atomic Emission Spectroscopy; DCP-AES, Direct-Coupled Plasma, Atomic Emission Spectroscopy]

Element	Method	Start date	End date	Type of reporting	Long-term method detection level	Reporting level
Silver (Ag)	ICP-AES	1/1/1992	12/22/1997	MRL	na	1
	ICP-AES	12/23/1997	9/30/1998	MRL	na	4
	ICP-AES	10/1/1998	9/30/1999	LRL	1.8	4
	ICP-AES	10/1/1999	10/17/2000	LRL	4	7
	ICP-AES	10/18/2000	9/30/2001	LRL	2.3	4.6
	ICP-AES	10/1/2001	4/30/2003	LRL	5	9
	ICP-AES	5/1/2003	9/30/2003	LRL	2.3	5
	ICP-AES	10/1/2003	na	LRL	1.4	2.8
	ICP-MS	10/17/1994	5/11/2001	MRL	na	1
	ICP-MS	5/12/2001	9/30/2002	MRL	na	1
	ICP-MS	10/1/2002	na	LRL	.1	.2
Strontium (Sr)	ICP-AES	1/1/1992	12/22/1997	MRL	na	.5
	ICP-AES	12/23/1997	9/30/1998	MRL	na	1
	ICP-AES	10/1/1998	10/17/2000	LRL	.5	1
	ICP-AES	10/18/2000	9/30/2001	LRL	.4	.8
	ICP-AES	10/1/2001	4/30/2003	LRL	.3	.6
	ICP-AES	5/1/2003	9/30/2003	LRL	.2	.4
	ICP-AES	10/1/2003	9/30/2004	LRL	.7	1.4
	ICP-AES	10/1/2004	na	LRL	.5	1
	ICP-MS	9/1/1999	9/30/2000	MRL	na	.2
	ICP-MS	10/1/2000	9/30/2002	LRL	.04	.08
	ICP-MS	10/1/2002	9/30/2003	LRL	.1	.2
	ICP-MS	10/1/2003	na	LRL	.2	.4
Thallium (Tl)	GF-AAS	7/1/1999	7/31/1999	MRL	na	.5
	ICP-MS	10/17/1994	6/1/2001	MRL	na	1
	ICP-MS	9/1/1999	9/30/2000	MRL	na	.9
	ICP-MS	10/1/2000	na	LRL	.02	.041
Uranium (U)	ICP-MS	10/17/1994	9/30/2000	MRL	na	1
	ICP-MS	10/1/2000	9/30/2003	LRL	.009	.018
	ICP-MS	10/1/2003	na	LRL	.02	.04
Vanadium (V)	ICP-AES	1/1/1992	12/22/1997	MRL	na	6
	ICP-AES	12/23/1997	9/30/1998	MRL	na	10
	ICP-AES	10/1/1998	10/17/2000	LRL	5	10
	ICP-AES	10/18/2000	4/30/2003	LRL	4	8
	ICP-AES	5/1/2003	9/30/2003	LRL	3	6
	ICP-AES	10/1/2003	9/30/2004	LRL	2.3	4.6
	ICP-AES	10/1/2004	na	LRL	1	2
	ICP-MS	10/15/1999	9/30/2000	MRL	na	1
	ICP-MS	10/1/2000	9/30/2002	LRL	.1	.2
	ICP-MS	10/1/2002	9/30/2003	LRL	.07	.13
	ICP-MS	10/1/2003	na	LRL	.07	.14

Table 3. Methods used by the National Water Quality Laboratory, 1991–2003, to analyze ground-water samples for the elements discussed in this report.—Continued

[Concentrations in micrograms per liter, HG-AAS, Hydride Generation Atomic Absorption Spectrophotometry; MRL, method reporting level; na, not applicable; ICP-MS, Inductively Coupled Mass Spectrometry; LRL, laboratory reporting level; GF-AAS, Graphite-Furnace Atomic Absorption Spectrophotometry; ICP-AES, Inductively Coupled Atomic Emission Spectroscopy; DCP-AES, Direct-Coupled Plasma, Atomic Emission Spectroscopy]

Element	Method	Start date	End date	Type of reporting	Long-term method detection level	Reporting level
Zinc (Zn)	ICP-AES	1/1/1992	12/30/1997	MRL	na	3
	ICP-AES	12/31/1997	9/30/1998	MRL	na	20
	ICP-AES	10/1/1998	9/30/1999	LRL	7	20
	ICP-AES	10/1/1999	9/30/2001	LRL	10	20
	ICP-AES	10/1/2001	4/30/2003	LRL	12	24
	ICP-AES	5/1/2003	9/30/2003	LRL	1.6	3
	ICP-AES	10/1/2003	9/30/2004	LRL	1.5	3
	ICP-AES	10/1/2004	na	LRL	3	6
	GF-AAS	1/1/1992	12/31/1993	MRL	na	.2
	ICP-MS	10/17/1994	9/30/2002	MRL	na	1
	ICP-MS	10/1/2002	9/30/2003	LRL	.5	1
	ICP-MS	10/1/2003	na	LRL	.3	.6

they concluded that the statistical method, like that described by Helsel (1990) for estimating the summary statistical values and quantiles by using censored data, is useful for characterizing these elements in ground water.

Lee and Helsel (2005b) examined NAWQA MAS data to define distributions for trace elements in ground water, presented baseline models for trace elements based on the entire NAWQA MAS dataset, and compared model results with similar data from STORET. Lee and Helsel (2005b) also compared the various analytical methods used by the USGS NWQL for selected trace elements and concluded that, for the NAWQA MAS data, there were small differences in distributions in the survey wells attributable to changes in analytical methods for arsenic and chromium.

Description of the Study Area and the Glacial Aquifer System Framework

The study area includes the northern parts of the United States that were at one time covered with continental or alpine glaciers (Warner and Arnold, 2005). The study area includes parts of 26 States including Alaska, Connecticut, Idaho, Illinois, Indiana, Iowa, Kansas, Kentucky, Maine, Massachusetts, Michigan, Minnesota, Missouri, Montana, Nebraska, New Hampshire, New Jersey, New York, North Dakota, Ohio, Pennsylvania, Rhode Island, South Dakota, Vermont, Washington, and Wisconsin (fig. 1). A list of the well networks sampled for trace elements is shown in table 2 along with the type of network.

Warner and Arnold (2005) described the various characteristics of the glacial aquifer system and the framework that was developed as the basis for a series of regional reports on the glacial aquifer system water quality. The characteristics include texture of the deposits (fine-grained or coarse-grained), susceptibility and vulnerability of the aquifers to contamination by land-use practices, physiography, source areas of glacial sediments, and the morphology of the deposits (sheet-like surficial or sinuous buried valley geometry).

The glacial aquifer system framework reflects the natural characteristics of the glacial aquifer system that are most likely to affect water quality in the aquifer on a regional level (Warner and Arnold, 2005). Glacial deposits are highly heterogeneous across the United States but make up productive aquifers throughout the glaciated area of the country. The glacial aquifer system is considered here to include all unconsolidated aquifers above bedrock north of the line of continental glaciation throughout the country (Warner and Arnold, 2005). Many common natural and anthropogenic factors provide a unifying framework for making comparative assessments of water quality within and among NAWQA study units overlying the glacial aquifer.

Warner and Arnold (2005) divided the glaciated area in the United States into four major glacial areas—East, Central, West-Central, and West (fig. 2)—on the basis of differing source material. These framework areas are also based on studies of glacial sediments that show distinct geochemical differences that reflect differences in sediment source area and size (Shacklette and Boerngen, 1984; Shilts, 1993; Shilts, 1995; Randall, 2001). Weathering and leaching can dissolve and mobilize many elements from the sediments but only rarely does the presence of a trace element in the aquifer material alone directly relate to concentrations of concern in ground water. Aquifer conditions, such as reduction-oxidation potential (redox), may directly or indirectly mobilize trace elements within or sorbed to the aquifer materials. In some cases, regional variations in the source of glacial sediments might be used to indicate the potential for relatively higher concentrations of redox-sensitive trace elements in the glacial aquifer system.

Other factors used by Warner and Arnold (2005) to develop glacial framework areas include results from studies done on glacial sediments that determined relative differences in material and texture (Berg and others, 1984; Arnold and Friedel, 2000; Wolock, 2003). The spatial distribution of fine- and coarse-grained deposits east of the Rocky Mountains is derived from Soller (1998). Coarse-grained deposits of the glacial materials are described by Soller (1998) as consisting of layered sand and gravel, with less common silt and clay beds, deposited in fluvial, glaciofluvial, deltaic, and outwash-plain settings. The fine-grained deposits are generally clay, silt, and very fine sand, but include lesser amounts of coarser material, commonly as interbeds. Till consists of poorly sorted sediments that are unstratified and composed of particles ranging in size from clay to large boulders. Figure 3 shows the distribution of wells among the four framework areas of Warner and Arnold (2005). The Central (651 wells, 41 percent) and West-Central (443 wells, 28 percent) wells constitute most of the network.

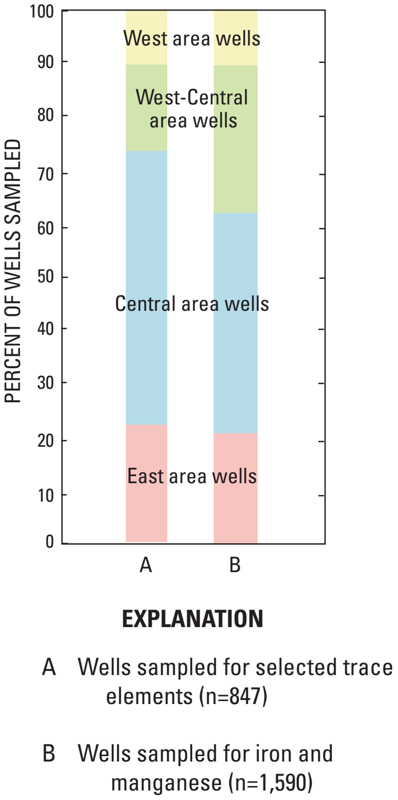


Figure 3. The relative number of wells in each of the framework areas.

Methods and Approach

Water samples for trace element analysis were collected after the field-measured parameters (pH, dissolved oxygen, water temperature, specific conductivity, and turbidity) had stabilized to ensure that the samples were representative of ground water in the aquifer (Koterba and others, 1995). Samples also were analyzed for a comprehensive suite of nutrient and other inorganic constituents. Samples were shipped to the USGS NWQL in Denver, Colo., and iron, manganese, and trace elements typically were analyzed by inductively coupled plasma–mass spectrometry, with a minimum reporting level (MRL) of 1 µg/L (Faires, 1993, Ivahnenko and others, 1996). During the period of data collection, methods were improved and new methods were implemented, often resulting in lower reporting limits (see table 3).

Ground-water samples were collected in 3-year rotational schedules during 1991–2003. Table 2 summarizes the history of well-network sampling by study unit. Two sets of wells were used in the analyses presented in this report. During 1991–2003, samples from 847 wells were collected and analyzed for a suite of trace elements by using a standard analytical suite that included the elements listed in table 1; results from these analyses were used for the trace element discussions in this report. Not all trace elements were analyzed in all 847 wells. Lithium, strontium and vanadium were not included in the suite of elements until about 1997. The number of samples analyzed for each element is listed in table 4. Additionally, a superset of wells, including all the 847 trace element wells and 743 other wells sampled during the period of the study, were analyzed for major ions and dissolved iron and manganese. The data from these 1,590 wells were used for the interpretation of iron and manganese in glacial aquifer samples. Owing to differences in analytical methods, the reporting levels for iron and manganese concentrations in the 743 samples not analyzed for the full trace element suite are typically different from those associated with samples that were analyzed for the suite.

The data used for this report are limited to ground-water data collected from the glacial aquifer system of the United States as defined by Warner and Arnold (2005). The dataset includes a subset of the MAS data from the glacial aquifer system used by Lee and Helsel (2005b); however, data from other well networks were included to provide a more complete representation of the glacial aquifer system. The wells sampled included monitor wells that (mostly) were installed specifically by the NAWQA Program for monitoring recently recharged ground water under selected land uses (Lapham and others, 1995). These wells are also referred to as LUS wells and are typically screened at the water table or just below the water table to enable sampling of the recently recharged ground water. Recently recharged ground water may be affected by land-use management practices. Agricultural land use (mostly row-crop farms) is the largest category of these wells, followed by urban land use. Urban land-use networks for the NAWQA Program were targeted at commercial and

Table 4. Summary of detection frequencies of iron, manganese, and selected trace elements in samples from wells in the glacial aquifer system.

[µg/L, microgram per liter; --, not applicable]

Element	Number of samples analyzed	Number of samples with concentration at or above any reporting level	Percentage of samples with detection at any reporting level	Number of samples with concentration at 1 µg/L, or higher	Percentage of samples with detection at or above 1 µg/L, in percent	Number of samples below detection at any reporting level	Percentage of samples below detection at any reporting level
Antimony	832	175	21.0	9	1.1	657	79.0
Arsenic	833	506	60.7	341	40.9	327	39.3
Barium	847	846	99.9	846	99.9	1	.1
Beryllium	847	14	1.7	1	.1	833	98.3
Cadmium	847	137	16.2	2	.2	710	83.8
Chromium	839	435	51.8	326	38.9	404	48.2
Cobalt	847	451	53.2	98	11.6	396	46.8
Copper	847	562	66.4	410	48.4	285	33.6
Iron[1]	1,590	1,086	68.3	--	--	504	31.7
Lead	847	223	26.3	34	4.0	624	73.7
Lithium	552	495	89.7	424	76.8	57	10.3
Manganese	1,590	1,375	86.5	1,257	79.1	215	13.5
Molybdenum	847	608	71.8	482	56.9	239	28.2
Nickel	847	692	81.7	574	67.8	155	18.3
Selenium	833	254	30.5	123	14.8	579	69.5
Silver	847	2	.2	2	.2	845	99.8
Strontium	552	551	99.8	551	99.8	1	.2
Thallium	480	67	14.0	0	0	413	86.0
Uranium	832	481	57.8	304	36.5	351	42.2
Vanadium	552	344	62.3	221	40.0	208	37.7
Zinc	847	673	79.5	650	76.7	174	20.5

[1] All reporting levels for iron were greater than 1 microgram per liter.

residential areas that are generally less than 30 years old, primarily to avoid areas that may have industrial legacy soil or ground-water contamination. Another large portion of glacial aquifer wells are MAS wells, which are predominantly private water-supply wells. A small subset of the MAS wells is public-supply wells. The main objective for sampling MAS wells was to characterize the water quality in major drinking-water supply aquifers as part of the occurrence and distribution objective of the first cycle of NAWQA studies. In this report, the LUS and MAS networks are discussed as the two main "network types." Water-use categories, including private supply, public supply, and monitor wells, are discussed in relation to the occurrence and distribution of trace elements.

Quality-Assurance/Quality-Control Plan

A quality-assurance plan for samples analyzed for the suite of trace elements in ground water as part of the NAWQA Program was developed and consisted of quality-control samples, including field blanks, equipment blanks, and replicates. Apodaca and others (2006) examined the quality-control data for the trace element analyses of all ground-water and surface-water samples. They found that in all ground-water samples (including those from the glacial aquifer system), arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), nickel (Ni), selenium (Se), silver (Ag), strontium (Sr), and zinc (Zn) may have systematic positive bias. The 95-percent confidence level for each of the percentiles is well below the respective percentile estimated for these elements (Apodaca and others, 2006; table 1). The bias tends to be well below the applicable USEPA Maximum Contaminant Level (MCL) or other health-related standards; however, Apodaca and others (2006) acknowledging this apparent bias, still suggest these data can be used in studies such as this. During 1993–2001, analytical methods for trace element blank samples differed from those for environmental and replicate samples and had lower detection limits (Garbarino and Taylor, 1996). After 2001, blank and environmental samples were analyzed using identical methods.

No separate examination of trace element quality-control data specific to the glacial aquifer was undertaken for this study. It is assumed that the quality-control data are similar to those from the overall ground-water trace element sampling program as discussed by Apodaca and others (2006).

Statistical Approach

For the selected elements, the sample results range from mostly uncensored detections (quantified concentrations) to mostly, or completely, censored data (semiquantified concentrations or nondetections reported as less than the reporting level). For instance, all samples had detectable and quantifiable concentrations of barium; conversely, all but two samples had no detectable concentrations of silver. The elements, antimony, beryllium, cadmium, silver, and thallium, had less than 20 percent detections in samples. Table 4 lists the number of wells in which samples were collected and analyzed for each element and the number and percent of samples in which each element was below the detection level.

Censored values were reported two ways from the NWQL: (1) estimated concentrations (usually after 1999) or (2) results "less-than-detection" (Childress and others, 1999). The "less-than-detection" results were reported in one of two ways depending on when the samples were analyzed. Prior to about 1999, the "less-than-detection" results were reported as less than the method reporting level (<RL). For the trace element data analyzed between 1991 and 1999, the reporting levels [(RLs) also called method detection limits] typically were about 1.0 µg/L. Since 1999, most "less-than-detection" results were reported as less than the laboratory reporting level (<LRL). To minimize false negative errors for most of these trace elements, the laboratory reporting level (LRL) was set at two times the long-term method detection level (LT-MDL) that is determined by the NWQL over a period of months to years (Childress and others, 1999).

For this investigation, those values reported as estimated concentrations were used unchanged and uncensored, and those values reported as below the LRL, were adjusted to the LT-MDL. Little information was available for the method RL, and thus the values reported as below the RL were not adjusted. Regardless of adjustment, all "less than" values were categorized as "censored" in the Regression on Order Statistics (ROS; Helsel, 2005) procedure and survival statistics used. In the rest of this report, "reporting level" is used as a general term for any type of reporting level (RL, LRL) and to distinguish detected concentrations from censored results.

After this adjustment to the data, robust ROS techniques were used to model probability distributions; to estimate medians, percentiles, and other summary statistics; and to draft box and probability plots. This method does not incorporate assumptions for any particular type of distribution for the concentrations. The software package R (R Development Core Team, 2005) was used for these statistics because an implementation of these methods by Lee and Helsel (2005a) was available. Probability distributions were not modeled for beryllium, cadmium, silver, and thallium, and consequently, summary statistics were not estimated for these elements. ROS was used to estimate the descriptive statistics for all elements because most elements had substantial portions of results reported as below detection (less than the reporting level). Helsel (2005) noted that these "less than" results contain considerable information and to assign arbitrary values, such as zero or one-half the reporting level or other values, to these nondetections may be seriously misleading and a less than thorough data analysis—especially for data with multiple reporting levels. The ROS-modeled summary statistics (means, percentiles, interquartile ranges, and others) presented in figures and tables of this report are often less than the respective reporting levels. They are not meant to be anything other than estimates based on modeled probability distributions.

For comparing factors for significant differences that were not censored, such as well depth, pH, and temperature, Kruskal-Wallis rank sum tests (Helsel and Hirsch, 1995) were used and the p-values tabled. For censored element concentrations and factors, such as dissolved oxygen, tests for significant differences for selected elements between or among groups of samples with respect to environmental or other factors were done by comparing empirical cumulative distribution functions (ecdf), estimated using the Kaplan-Meier method. The tests with censored data are modified "survival statistics" that are used for right-censored data (Helsel, 2005). The modifications implemented in R procedures transform the left-censored element and dissolved oxygen data into right-censored values that can be used in the survival procedures (Lee and Helsel, 2007). The procedure, "cendiff," as implemented in R, tests if there is a difference between two or more ecdf using the G-rho family of tests. As used for this report, cendiff is equivalent to the Peto and Peto modification of the Gehan-Wilcoxon test, the most appropriate for left-censored log-normal data (Lee and Helsel, 2007).

Kendall's tau (τ) was computed to determine correlations between continuous variables, such as well depth, pH, or dissolved solids, and censored element concentrations. The "cenken" procedure in R is a nonparametric test of monotonic association and yields a Kendall's τ and a p-value for a correlation between the two variables (Lee and Helsel, 2007). All these tests indicate a significant difference if the p-value is less than the alpha level of 0.05 or 95-percent confidence that the difference is not random. Finally, the procedure "cenreg" computes a likelihood correlation coefficient that measures the linear association between samples grouped by categories and censored element concentrations and p-value (Lee and Helsel, 2007).

Assessing Potential Human-Health Implications

Most of the elements discussed in this report, when found in drinking-water supplies may be of concern when they approach concentrations that may be harmful to human health. Several types of benchmarks are available to identify element concentrations of potential concern. U.S. Environmental Protection Agency MCLs are legally enforceable standards for drinking water that specify the maximum permissible level of a element in water that is delivered by public-water systems. Currently (2008), MCLs have been established for 11 of the 21 elements considered in this report (U.S. Environmental Protection Agency, 2006a). Copper and lead in delivered water have legally enforceable action levels for concentrations at the tap. A different kind of standard was developed for these elements because they may dissolve in supply pipes and household plumbing (U.S. Environmental Protection Agency, 2006b).

Concentrations for regulated elements—those with USEPA MCLs—were compared to their MCLs as benchmarks, and concentrations of unregulated elements—those without USEPA MCLs—were compared to their Health-Based Screening Levels (HBSLs) as benchmarks (Toccalino, 2007). MCLs are legally enforceable standards for public-supply wells. Other criteria are not legally enforceable, and no drinking-water standards are enforceable for private drinking-water wells or for monitoring wells (911 of the 959 LUS wells discussed in this report are monitoring wells). Health-Based Screening Levels were developed by Toccalino (2007) for those elements without MCLs. The unregulated elements: cobalt, iron, lithium, and vanadium, do not currently have any drinking-water human-health benchmark because of a lack of available toxicity information (Toccalino and others, 2008).

Health-Based Screening Levels are nonenforceable, 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 others, 2008; Toccalino, 2007). For the remainder of this report, MCLs and HBSLs are referred to as benchmark levels and ratios of concentrations to benchmark levels are called benchmark quotients (BQ). Benchmark quotients are used here as screening level tool for assessing the potential human-health context for the elements and their occurrence and distribution. This screening level assessment can provide an initial perspective on the potential significance of element occurrence to human health and can help prioritize future studies (Toccalino and others, 2008; Toccalino, 2007). This kind of assessment also provides a perspective on where adverse effects of elements in well water are more likely to occur, based on the NAWQA data.

A screening-level assessment is not designed to evaluate specific effects of elements in well water on human health; nor is it suitable for a comprehensive risk assessment, which generally includes additional factors such as multiple avenues of exposure (Toccalino and others, 2008). A BQ greater than 1 signifies an element concentration is of potential human-health concern if water with such a concentration were to be ingested without treatment over a lifetime (Toccalino, 2007). Elements with concentrations of the greatest potential human-health concern typically are those that both have BQ values greater than 1 and are frequently detected. Drinking-water standards (MCLs) are not violated, however, if concentrations of regulated elements are greater than MCLs (BQ values are greater than 1) in ground-water samples, because samples collected by the USGS are not collected for compliance with the Safe Drinking Water Act (Toccalino and others, 2008).

Ingestion of water containing a element with a BQ value less than 1 is unlikely to result in adverse human-health effects resulting from that element alone (Toccalino and others, 2008). Concentrations representing BQs greater than or equal to 0.1 ($BQ \geq 0.1$) were identified. These concentration levels, which were within an order of magnitude (or, in other words, within 10 percent) of MCLs or HBSLs, can be used to identify compounds that may warrant additional monitoring to analyze trends in occurrence and to provide an early indication of element concentrations that approach human-health benchmarks (Toccalino and Norman, 2006; Toccalino, 2007).

Occurrence and Distribution of Iron, Manganese, and Selected Trace Elements

Iron, manganese, and selected trace elements are discussed in the following sections of this report in terms of (1) occurrence and distribution, (2) relation to environmental factors, (3) human-health screening level assessment, and (4) transferability of results. Occurrence and distribution of the elements are discussed with respect to the glacial aquifer system framework areas developed by Warner and Arnold (2005); concentrations of elements are discussed with respect to well, water-use, land-use, and chemical factors; and the concentrations are discussed in relation to hydrochemical regions of the glacial aquifer system, as developed by Arnold and others (2008) to aid in determining the transferability of the study results to other areas.

In several of the discussions, iron and manganese are discussed together and first for two reasons: (1) there are many more samples with iron and manganese analyses than with other trace element analyses, and the effects of environmental factors that control the concentrations of iron and manganese in ground water are more apparent in the relatively large variation in the concentrations of these elements; and (2) iron and manganese can be indicators of conditions that would be conducive to high concentrations of trace elements that have similar chemical characteristics. Furthermore, iron and manganese may be surrogates for other, more toxic, trace elements because many trace elements are sorbed to oxyhydroxides of iron and manganese and the sorbed elements are released when the iron and manganese oxyhydroxides are reduced and dissolved (Zachara and others, 2001). High concentrations of dissolved iron or manganese (defined here as greater than or equal to 50 µg/L) indicate that the aquifer geochemical environment is relatively free of dissolved oxygen and dissolved sulfide (HS^- and H_2S) and thus are indicators that chemically similar trace elements may be present in relatively high concentrations.

The detection frequencies of all elements discussed in this report are shown in figure 4 at all reporting levels and at the reporting level of 1 µg/L—the most common reporting level for the analyses. A common reporting level of 1 µg/L was used to compare the frequencies of detections among all the elements, except iron. The most common reporting level for iron was 10 micrograms per liter and no reporting levels for iron were as low as 1 µg/L. Summary statistics for trace elements in all wells are listed in table 5 and shown as box plots in figure 5. In figure 5, the elements are ordered from largest to smallest median concentration. The black horizontal reference line at 1 µg/L indicates that the medians less than 1 µg/L and percentiles of the elements from copper to antimony are estimated. Beryllium, cadmium, and thallium had insufficient detections for estimating percentiles, so only the actual ranges of concentrations are shown. Strontium generally had the highest median and percentiles. Barium and manganese were second and third highest in median concentrations for all glacial aquifer system wells.

Iron and Manganese

There were 1,590 wells sampled and analyzed for iron and manganese. Iron was detected above any reporting level (table 3) in 1,086 wells (68 percent). All reporting levels for iron, regardless of analytical method, were higher than 1 µg/L. A total of 864 well samples (54 percent) had concentrations greater than or equal to 10 µg/L. The median concentration of iron in all glacial wells sampled was 15 µg/L. Manganese was detected above any reporting level in 1,375 well samples (86 percent) and at or above the reporting level of 1 µg/L in 1,257 wells (79 percent). For comparison with iron, 1,009 (63 percent) of samples had manganese concentrations greater than or equal to 10 µg/L—manganese was detected about 9 percent more often than iron in the glacial aquifer system. The median manganese concentration in all glacial well samples was 34 µg/L.

Manganese was the fourth most frequently detected element after barium, strontium, and lithium, in order. Iron was the eighth most frequently detected element. In order of median (50th percentile) concentration, manganese was second and iron was third highest. The geographic distributions

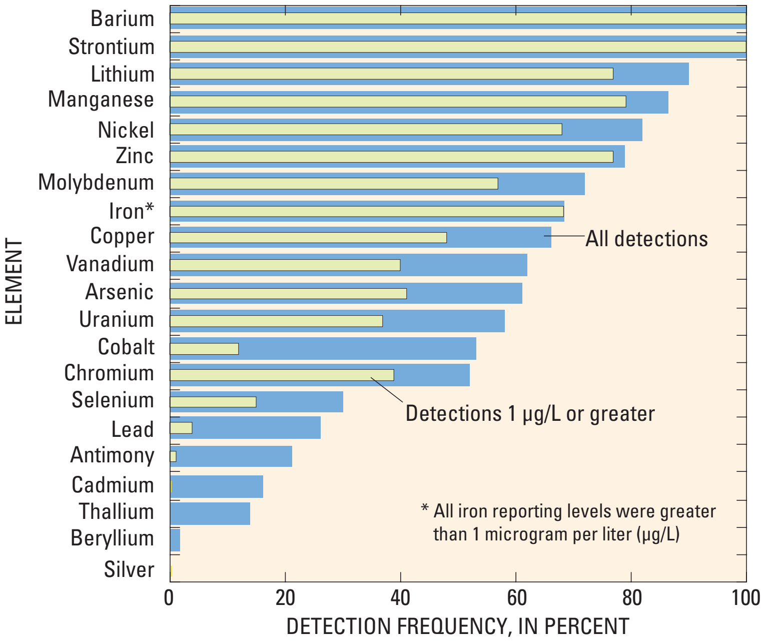


Figure 4. The frequency of detections for selected elements in ground water sampled in the glacial aquifer system.

Table 5. Maximum, minimum, and summary statistics for element concentrations in all samples from wells in the glacial aquifer system.

[All statistics estimated using Regression on Order Statistics method (Lee and Helsel, 2005a); µg/L, microgram per liter; --, not applicable]

Element	Number of samples analyzed	Number of samples below detection at any reporting level	Percentage of samples below detection at any reporting level	Minimum concentration, in µg/L	Maximum concentration, in µg/L	Mean concentration, in µg/L	Standard deviation of the mean	Percentiles, in µg/L							Inter-quartile range, in µg/L	Coefficient of variation, in percent	Regression on Order Statistics r-squared
								Fifth	Tenth	Twenty-fifth	Fiftieth	Seventy-fifth	Nintieth	Ninety-fifth			
Antimony	832	657	79	0.024	3.3	0.090	0.20	0.0032	0.0054	0.013	0.032	0.085	0.22	0.31	0.073	220	0.99
Arsenic	833	327	39	.090	340	4.0	15	.023	.046	.16	.62	3	8.3	16	2.8	370	.99
Barium	847	1	.1	.840	1,630	100	130	6.8	11	29	66	125	240	308	96	130	.98
Beryllium	847	833	98	.032	1.2	--	--	--	--	--	--	--	--	--	--	--	--
Cadmium	847	710	84	.018	1.0	--	--	--	--	--	--	--	--	--	--	--	--
Chromium	839	404	48	.400	22	1.7	2.4	.07	.12	.27	.59	2.2	5	6.5	2.0	140	.92
Cobalt	847	396	47	.007	95	.81	4.4	.03	.046	.1	.21	.45	1	2.4	.35	540	.96
Copper	847	285	34	.126	127	3.7	10	.13	.22	.48	1	2.3	7.5	14	1.8	280	.95
Iron[1]	1,590	504	32	3.00	38,100	820	2,400	.1	.35	2.6	15	680	2,300	3,800	680	300	.92
Lead	847	624	74	.040	9.0	.19	.6	.0022	.0042	.012	.042	.13	.39	.75	.12	310	1.00
Lithium	552	57	10	.040	126	8.2	16	.31	.53	1.4	3.2	7.3	19	31	5.9	190	.99
Manganese	1,590	215	14	.056	28,200	220	970	.15	.38	2	34	191	540	970	190	430	.94
Molybdenum	847	239	28	.105	304	4.1	13	.082	.13	.35	1.4	3.6	7.9	14	3.2	330	.98
Nickel	847	155	18	.035	56	2.6	4.4	.17	.26	.72	1.6	3	5	8	2.3	170	.94
Selenium	833	579	70	.173	223	2.2	12	.0028	.0063	.026	.13	.57	2	6.6	.55	550	.96
Strontium	552	1	.2	1.47	9,120	390	730	28	37	84	185	438	800	1,300	350	190	.99
Thallium	480	413	86	.020	.77	--	--	--	--	--	--	--	--	--	--	--	--
Uranium	832	351	42	.009	162	3.4	11	.0086	.016	.076	.42	1.9	7.5	15	1.8	310	.99
Vanadium	552	208	38	.100	294	4.4	17	.04	.076	.23	.82	2.8	9.2	18	2.6	370	1.00
Zinc	847	174	21	.536	1,000	12	49	.17	.34	1	2.3	6.9	21	51	5.9	400	.98

[1] All reporting levels for iron were greater than 1 microgram per liter.

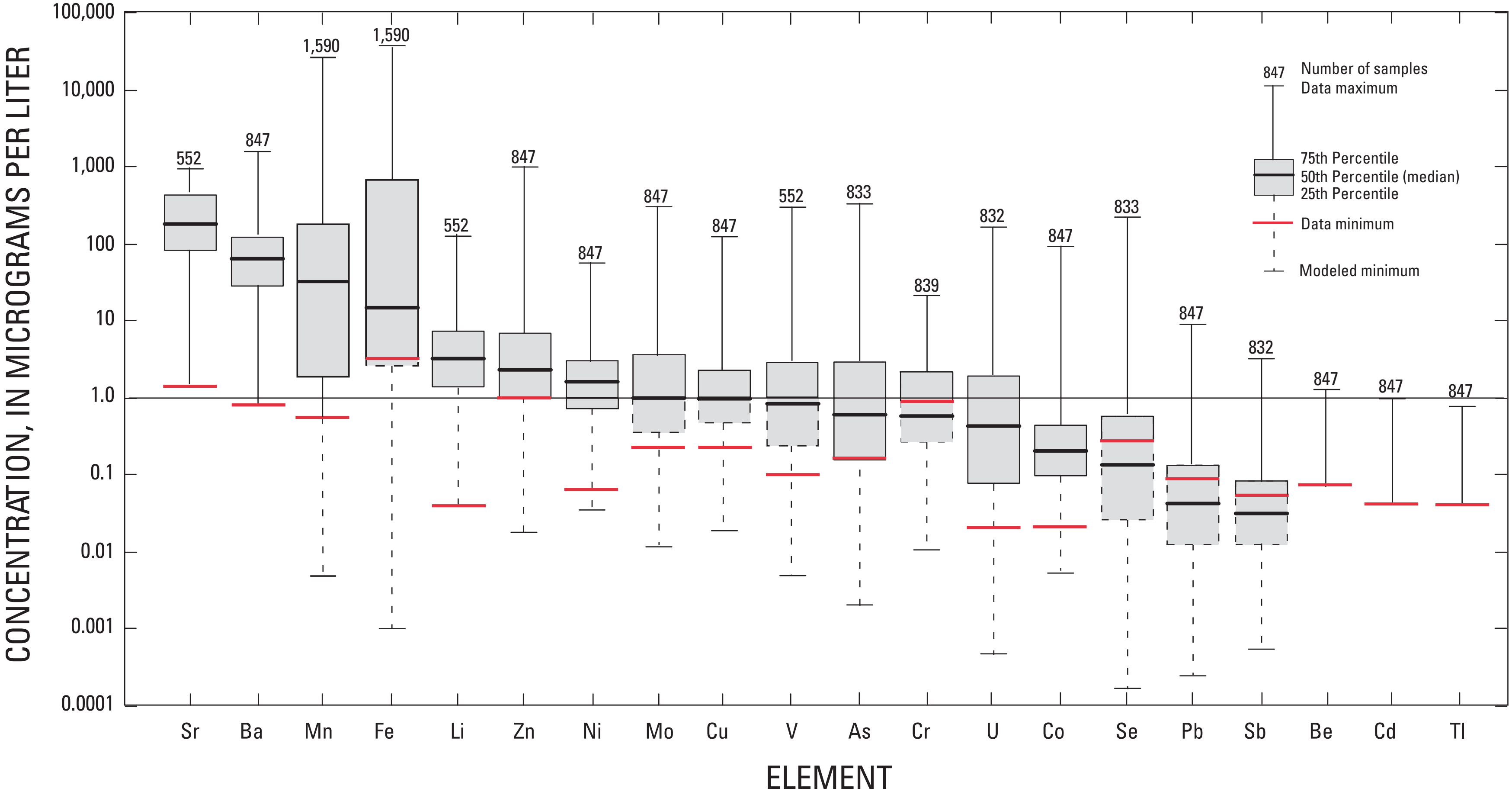


Figure 5. Summary statistics for selected element concentrations in ground water of the glacial aquifer system. Silver (Ag) not shown. Line through concentration of 1 microgram per liter indicates most common reporting level. Percentiles for elements with censored results were modeled using Regression on Order Statistics (ROS) and dashed lines indicate modeled portions of box plots below highest reporting level.

of iron and manganese in the glacial aquifer well samples are shown in figures 6 and 7. The maps in figures 6 and 7 indicate that there is little overall pattern to the high concentrations of these elements. There are local groupings of higher concentrations in western Minnesota and eastern North Dakota and groupings of lower concentrations in Wisconsin and Nebraska. The 95th percentile for iron is 3,800 µg/L. The 80 well samples with an iron concentration 3,800 µg/L or greater are plotted on a map of the glacial aquifer in figure 8. Most of these wells are in the West-Central area. The manganese 95th percentile is 970 µg/L. The 80 wells that had a manganese concentration of 970 µg/L or greater are shown in figure 9.

The average abundance of iron in the earth's crust (lithosphere) is 45 grams per kilogram (g/kg; equivalent to parts per thousand); the average for soils is similar, 50 g/kg or parts per thousand (Pais and Jones, 1997). The corresponding abundances for manganese are 0.95 g/kg for the lithosphere and 0.5 g/kg for soils (Pais and Jones, 1997). The ratios of iron to manganese (Fe/Mn), based on the average abundances, are 47 for the lithosphere and 100 for soils. The mean for iron dissolved in glacial aquifer ground water is 820 µg/L (equivalent to 820 parts per billion), and the mean for dissolved manganese is 220 µg/L. The ratio of the means of dissolved iron to dissolved manganese is 3.7. Assuming that the iron and manganese contents of glacial aquifer materials, on average, are somewhere in the range of those for the lithosphere and soils, manganese appears to be preferentially dissolved into ground water over iron on the basis of simple dissolution from the matrix. Iron and manganese have similar chemistry and they are correlated in the glacial aquifer system: the nonparametric regression of manganese on iron yields a Kendall's τ of 0.40 and a p-value < 0.001 (fig. 10).

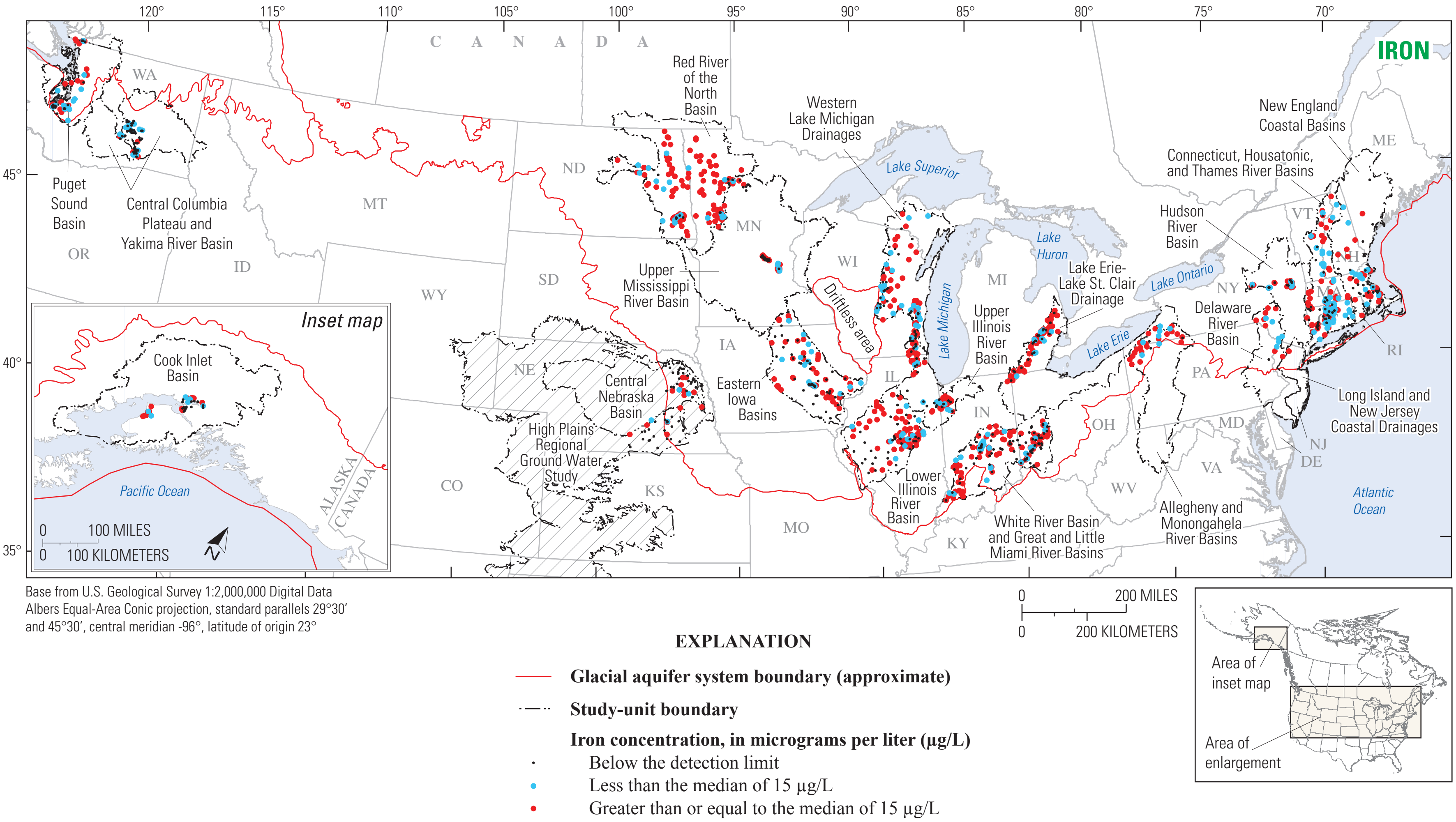
Distributions of Selected Trace Elements

The geographic distributions of selected trace elements are shown in figures 11–22. A comparison of trace element concentrations in ground water to concentrations in soil by overlaying element concentration medians per well network onto maps of the gross distribution of elements in soils and stream sediment (Gustavsson and others, 2001) indicated few weak relationships. For several elements, some local correlation between element concentrations in soils and sediment and those in the underlying glacial aquifer system may exist, but not at a regional scale. For others, such as lead, concentration patterns in ground water were quite different from those in soils and in stream sediment estimated by Gustavsson and others (2001).

Elements in Relation to Glacial Aquifer System Framework Areas

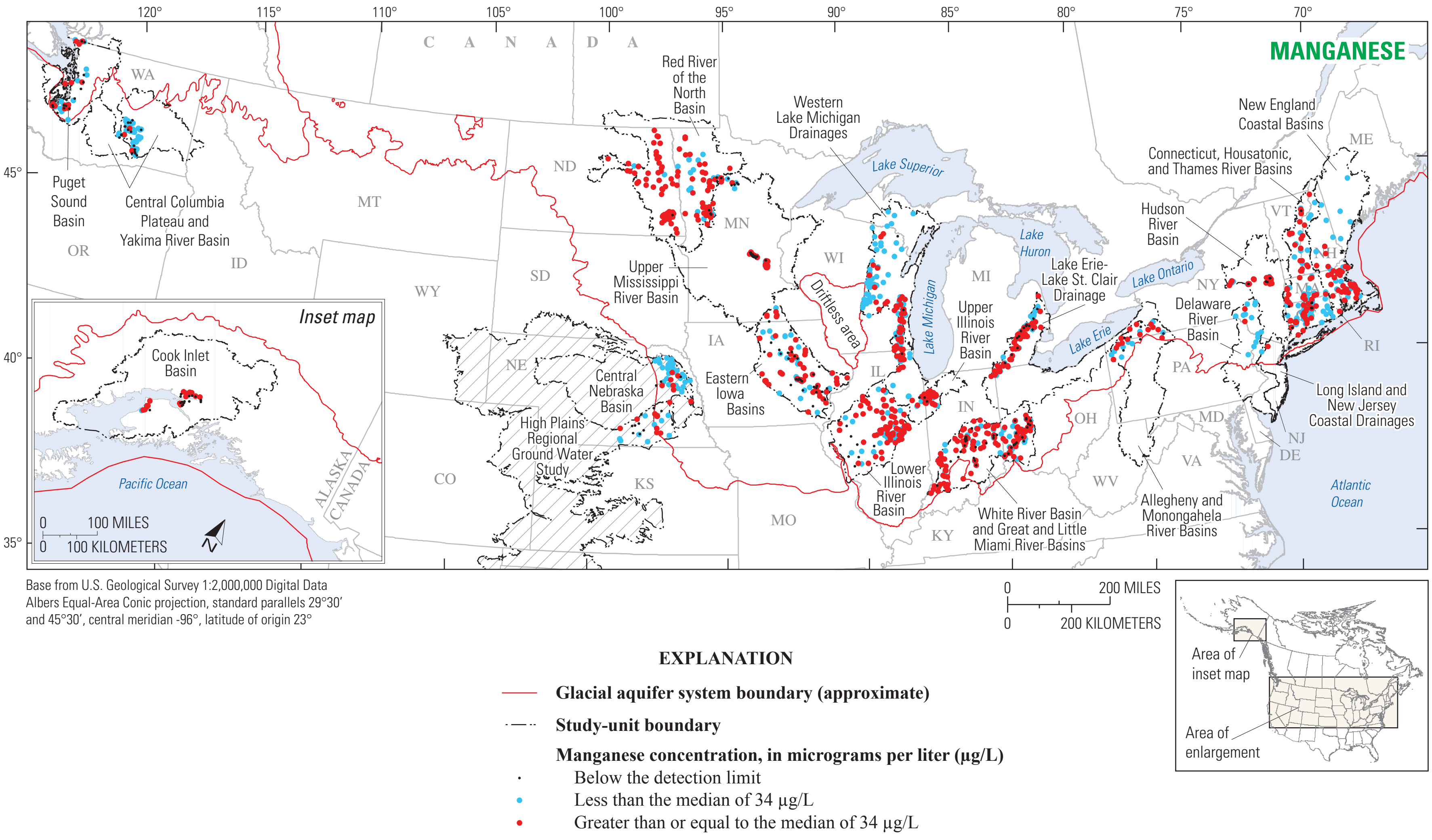
The glacial aquifer system framework devised by Warner and Arnold (2005) organized the interpretation of water-quality data on a regional basis in the glacial aquifer system. In this report, the glacial framework areas are useful for characterizing the geographical distribution of the elements and in a later section, "Elements and Environmental Factors in a Human-Health Context" (page 66). The wells sampled for iron, manganese, and trace elements were grouped into the four areas and summary statistics modeled for the data subsets. The majority of glacial wells are in the Central and West-Central areas, in part, because of the large extent of saturated glacial deposits in those areas and because of the importance of the glacial aquifer to water supply in those areas relative to the East and West glacial framework areas. The distribution of wells among the framework areas is summarized in table 6.

Iron concentrations varied substantially by glacial framework area—the largest were generally in the West-Central area. Compared to the 95th percentile of the overall glacial iron concentration (3,800 µg/L), in the Central area, concentrations in 19 well samples (2.9 percent of Central wells) were at or greater than the 95th percentile; in the East area, 17 wells (5.2 percent of East wells) were at or greater than the 95th percentile; in the West area, 4 wells (2.4 percent of West wells) were at or greater than the 95th percentile; and in the West-Central area, 43 wells (8.8 percent of West-Central wells) were at or greater than the 95th percentile for iron. The box plots in figure 23 show the distributions of iron, manganese, and selected trace element concentrations. These box plots and those in the remaining figures are slightly different from those shown in figure 5 and from usual Tukey type box plots. With the exception of figure 5, the box plots in this report indicate the median and the 25th and 75th quartiles similar to Tukey box plots; however, the "whiskers" extend to the largest data value above the box and to the smallest modeled value from a Kaplan-Meier or ROS estimate below the box. Also indicated in most box plots is an indication of the 95-percent confidence spread of the median. Notches in the boxes indicate ± 1.58 times the interquartile range divided by the square root of the number of samples (n). The notches represent an estimate of the 95-percent confidence level of the median (Chambers and others, 1983). Finally, in most box plots, a horizontal line indicates the highest censoring level (highest laboratory reporting level). All percentiles below the line are modeled estimates. As indicated in figure 23, the West-Central and Central areas have higher concentrations of dissolved iron and manganese, in general, than the other areas. However, the manganese concentration distribution in the framework areas is not simple. In the East area, 22 well samples (3.3 percent of East area wells) had concentrations greater than or equal to the manganese 95th percentile (997 µg/L), in the Central area, 11 wells (1.7 percent of Central wells) had such concentrations, in the West-Central area, 49 well samples (10 percent of West-Central wells) had such concentrations, and in the West area, only one well (less than 0.1 percent of West wells) had such concentrations. In a pattern that is similar to those of iron and other trace elements, manganese concentrations were generally higher in the West-Central area than in the other areas (fig. 23).



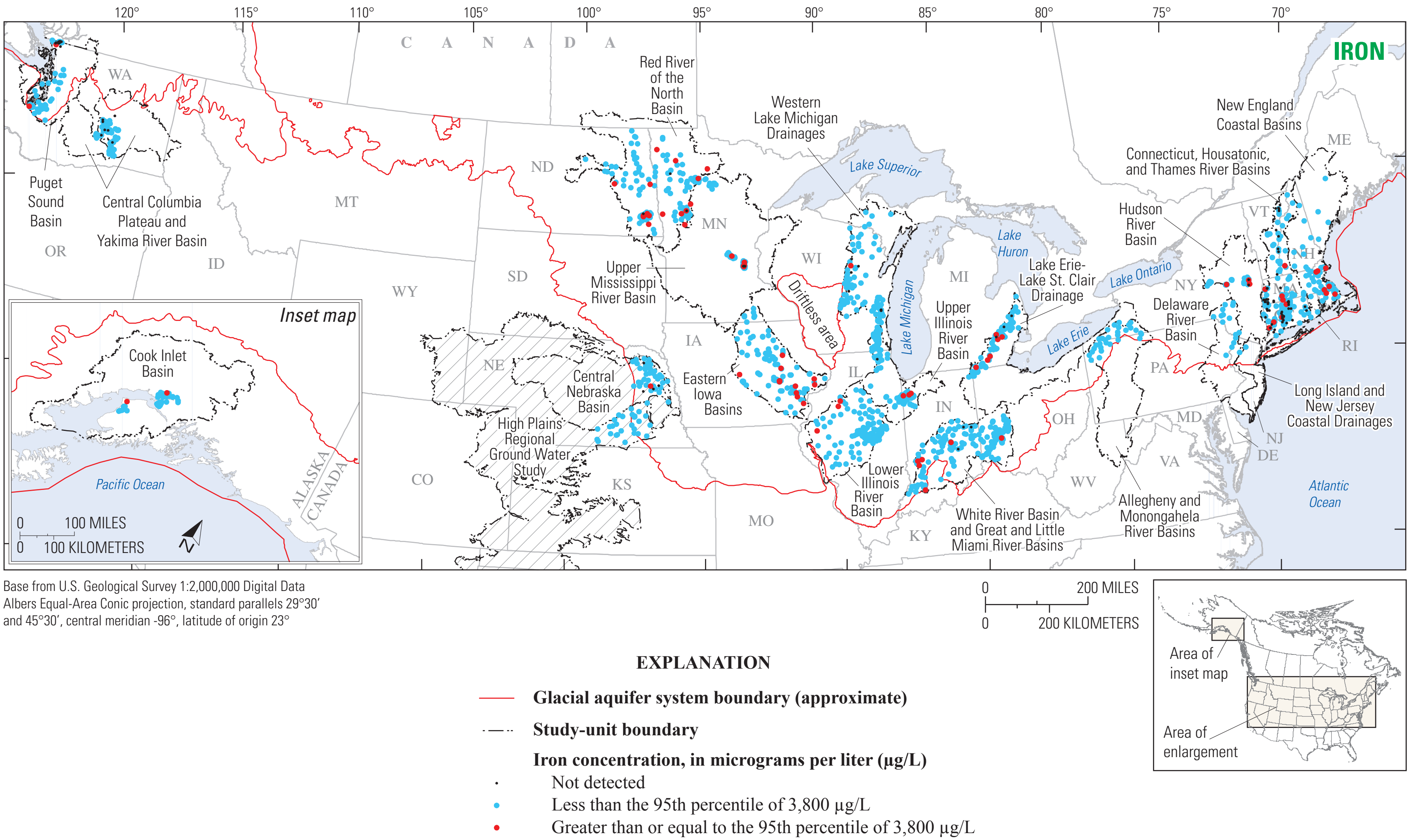
Base from U.S. Geological Survey 1:2,000,000 Digital Data
Albers Equal-Area Conic projection, standard parallels 29°30′
and 45°30′, central meridian -96°, latitude of origin 23°

Figure 6. The distribution of dissolved iron concentrations in ground water of the glacial aquifer system.



Base from U.S. Geological Survey 1:2,000,000 Digital Data
Albers Equal-Area Conic projection, standard parallels 29°30′
and 45°30′, central meridian -96°, latitude of origin 23°

Figure 7. The distribution of dissolved manganese concentrations in ground water of the glacial aquifer system.



Base from U.S. Geological Survey 1:2,000,000 Digital Data
Albers Equal-Area Conic projection, standard parallels 29°30′
and 45°30′, central meridian -96°, latitude of origin 23°

EXPLANATION

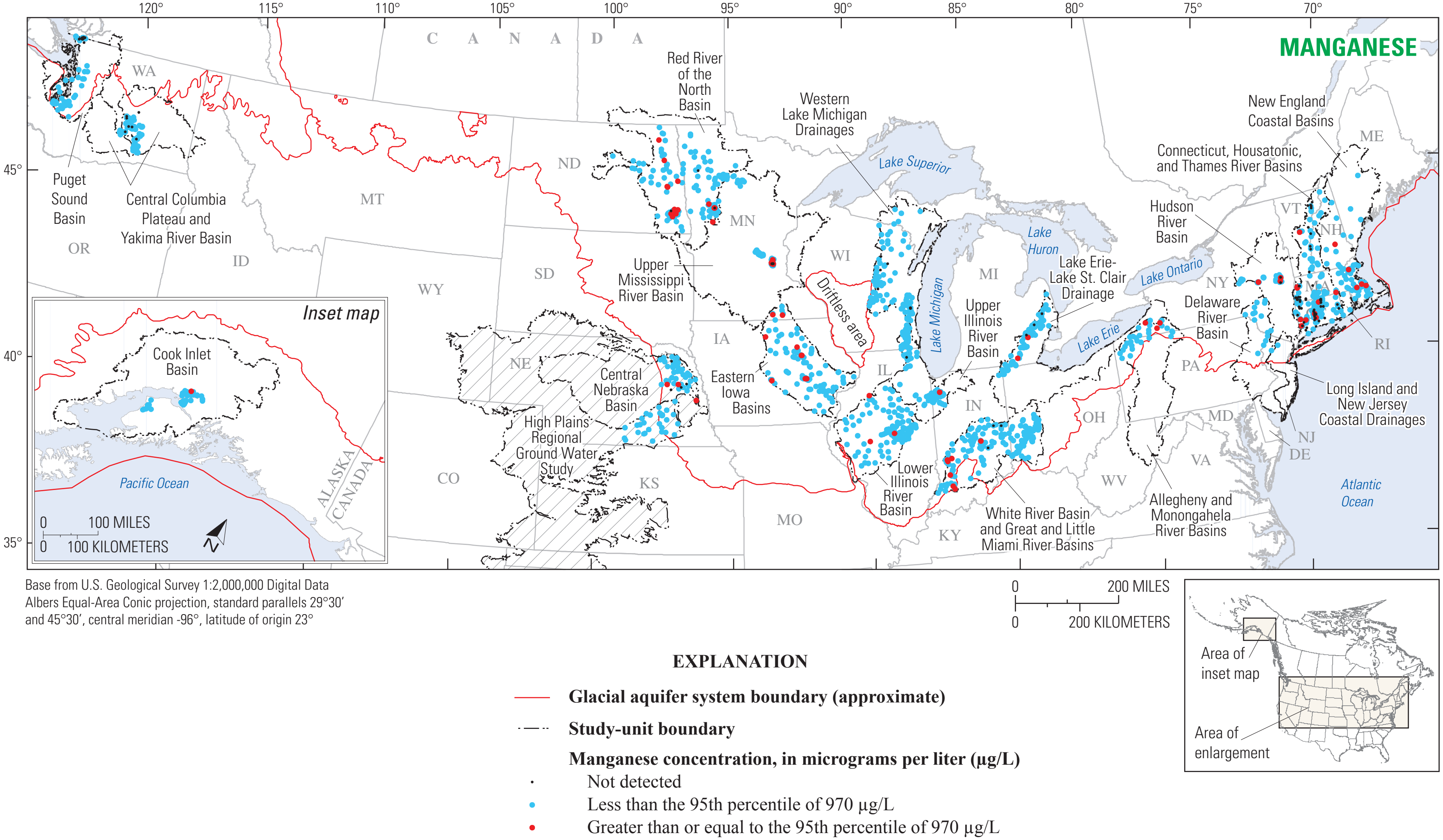
Glacial aquifer system boundary (approximate)

Study-unit boundary

Iron concentration, in micrograms per liter (µg/L)

- · Not detected
- ● Less than the 95th percentile of 3,800 µg/L
- ● Greater than or equal to the 95th percentile of 3,800 µg/L

Figure 8. The distribution of wells that exceed the 95th percentile for dissolved iron concentrations in ground water of the glacial aquifer system.



Base from U.S. Geological Survey 1:2,000,000 Digital Data
Albers Equal-Area Conic projection, standard parallels 29°30′ and 45°30′, central meridian -96°, latitude of origin 23°

Figure 9. The distribution of wells that exceed the 95th percentile for dissolved manganese concentrations in ground water of the glacial aquifer system.

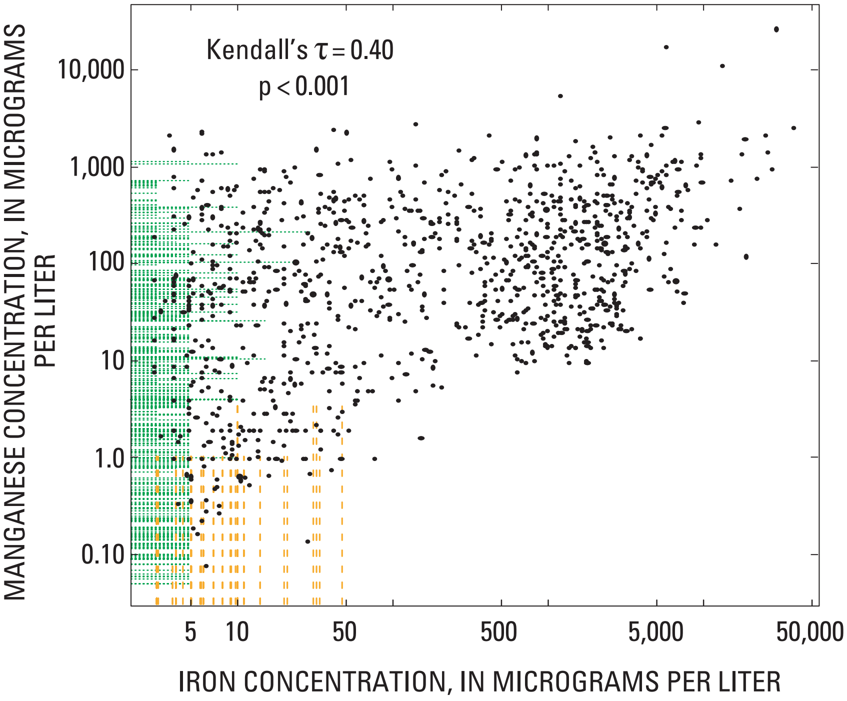


Figure 10. The relation between concentrations of manganese and concentrations of iron in ground water of the glacial aquifer system. For censored results (those results below detection) the "true concentration" lies somewhere in the interval between zero and the reporting level, therefore, vertical orange dashed lines indicate censored manganese results and horizontal green dotted lines indicate censored iron results.

Table 7 lists the p-values for Peto and Peto tests of significant differences between element concentration ecdf with respect to framework areas. The ecdf of chromium, cobalt, lithium, nickel, selenium, and vanadium concentrations are all significantly different with respect to all areas. The ecdf of arsenic, barium, iron, lead, manganese, molybdenum, strontium, and uranium concentrations each have one comparison that is not significantly different. West-Central framework area wells, in general, had substantially higher medians and smaller standard deviations than wells in the other areas. West framework area wells were similar to West-Central wells for strontium but varied from West-Central wells for lithium and molybdenum.

Most element concentrations were lowest in the East area except those for iron, manganese, nickel, and zinc, which were lower in the West, and lead, which was lower in the Central area. Arsenic concentrations increased from East to West, and the pairwise comparisons (table 7) indicate significant differences except between West-Central and West areas—as shown in figure 23. Barium concentrations were greatest in the Central and West-Central areas, and the ecdf for these areas are significantly different from each other and from those for the other two areas. Letter designations above the box plots indicate significant differences—those ecdf (box plots) that share a letter are not significantly different. However, the East and West area barium concentrations were not statistically different. Chromium concentration among areas has a pattern similar to that of barium; however, all ecdf were significantly different in all comparisons. Concentrations of chromium were greatest in the West-Central area, and the chromium ecdf for the other three areas are substantially lower. Cobalt concentrations, similar to the geographic pattern of barium concentrations, were greatest in the West-Central and Central areas and smallest in the West and East areas; however, pairwise comparisons of cobalt concentration ecdf indicate significant differences among areas even though the concentrations in the West-Central and Central areas appear similar in figure 23.

Copper and zinc each have the fewest pairwise comparisons that are significantly different and the geographic patterns of concentrations in the box plots appear to be similar; however, the p-values indicate that different pairwise comparisons are not significantly different. For copper, the East/Central, East/West, and West-Central/West comparisons are not significantly different. For zinc, the East/West-Central, East/West, and Central/West comparisons are not significantly different.

Iron concentration ecdf is greatest for the West-Central and Central areas, and the ecdf for these areas are not significantly different. The ecdf for the West and East areas are significantly different from each other and from those for the other two areas. Manganese is similar in that the West-Central area had the greatest concentrations and the concentrations there were significantly different from all other areas. The manganese concentrations in the East and Central areas were not significantly different, and the concentration in the East was significantly higher than that in the West area.

Lithium concentrations show one of the largest disparities among areas and the ecdf are significantly different. The concentration ecdf for the West-Central area is much higher than those for the other areas, and the ecdf for the West is higher than that for either the Central or East. Molybdenum concentration distributions among the West, West-Central, and Central areas appear to similar (fig. 23) and higher than the East distribution. Only the Central and West area ecdf are not significantly different. Nickel concentration distributions show a geographic pattern similar to those of barium and chromium; however, the East ecdf is higher than the West ecdf, unlike the pattern for barium and chromium. All pairwise comparisons of nickel ecdf are significantly different (table 7).

Lead is the only element for which the East concentration distribution was highest. All pairwise comparisons among ecdf, except that between West-Central and West, are

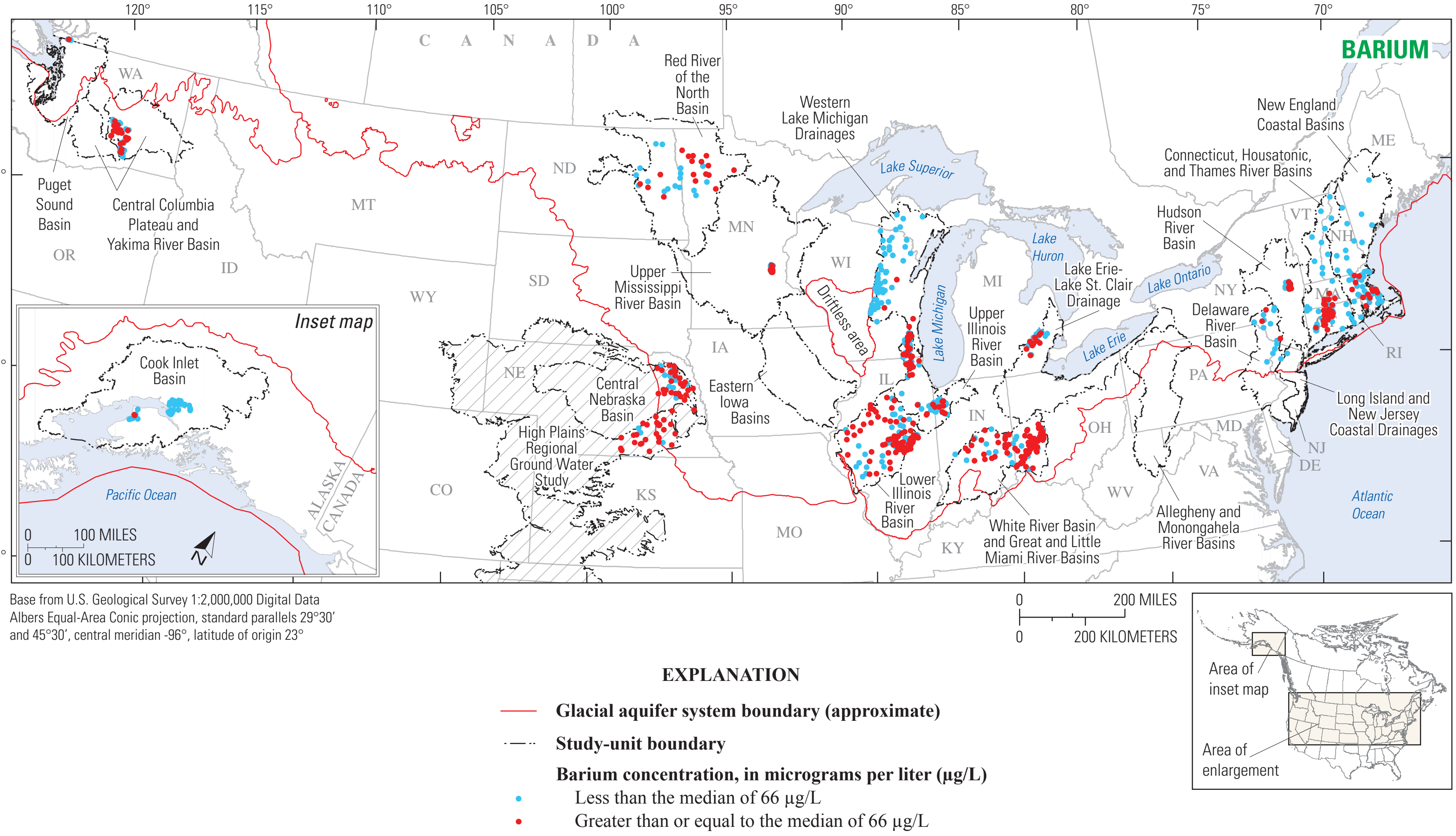
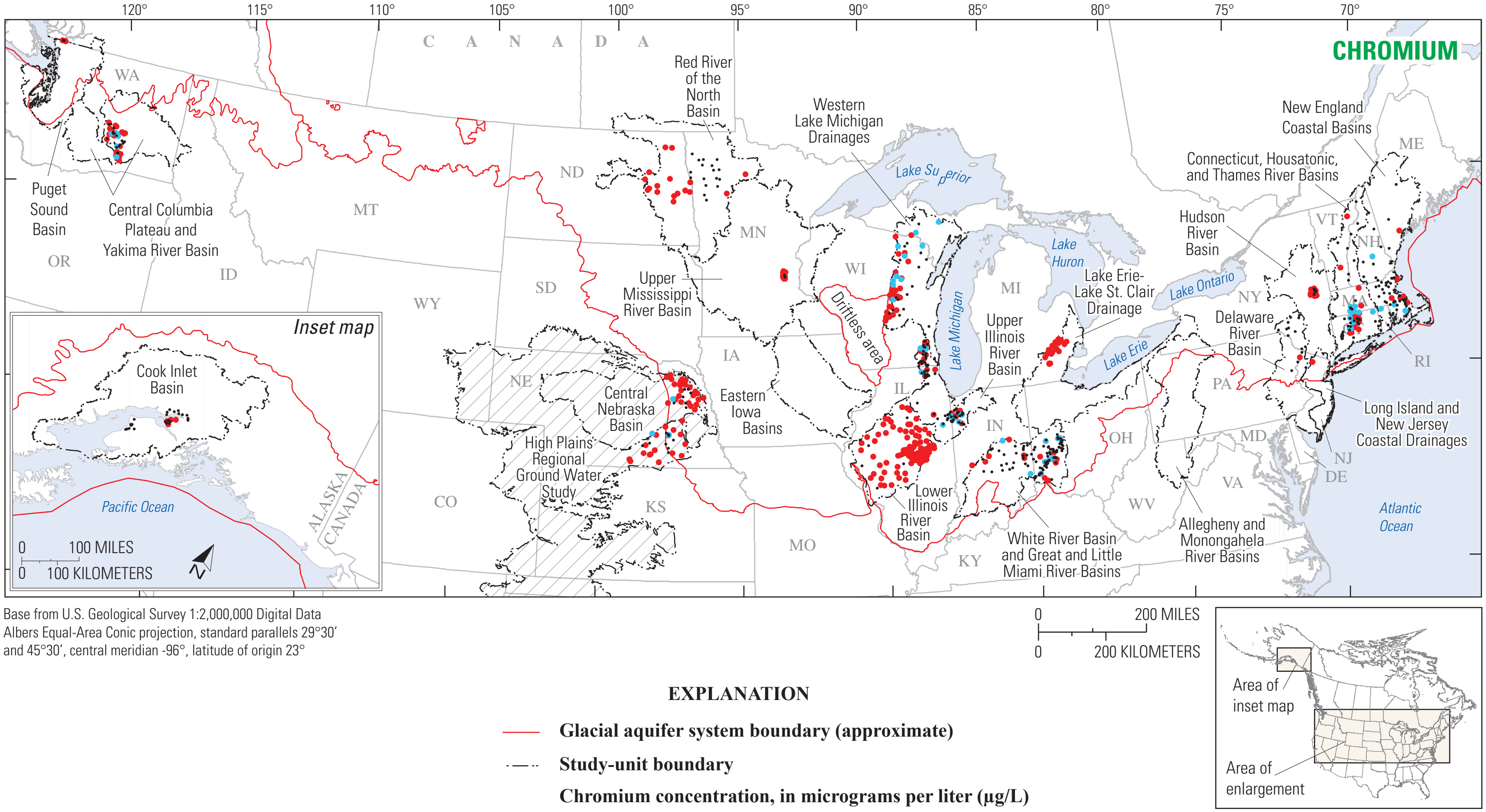


Figure 11. The distribution of dissolved barium concentrations in the ground water of the glacial aquifer system.



Base from U.S. Geological Survey 1:2,000,000 Digital Data
Albers Equal-Area Conic projection, standard parallels 29°30′ and 45°30′, central meridian -96°, latitude of origin 23°

EXPLANATION

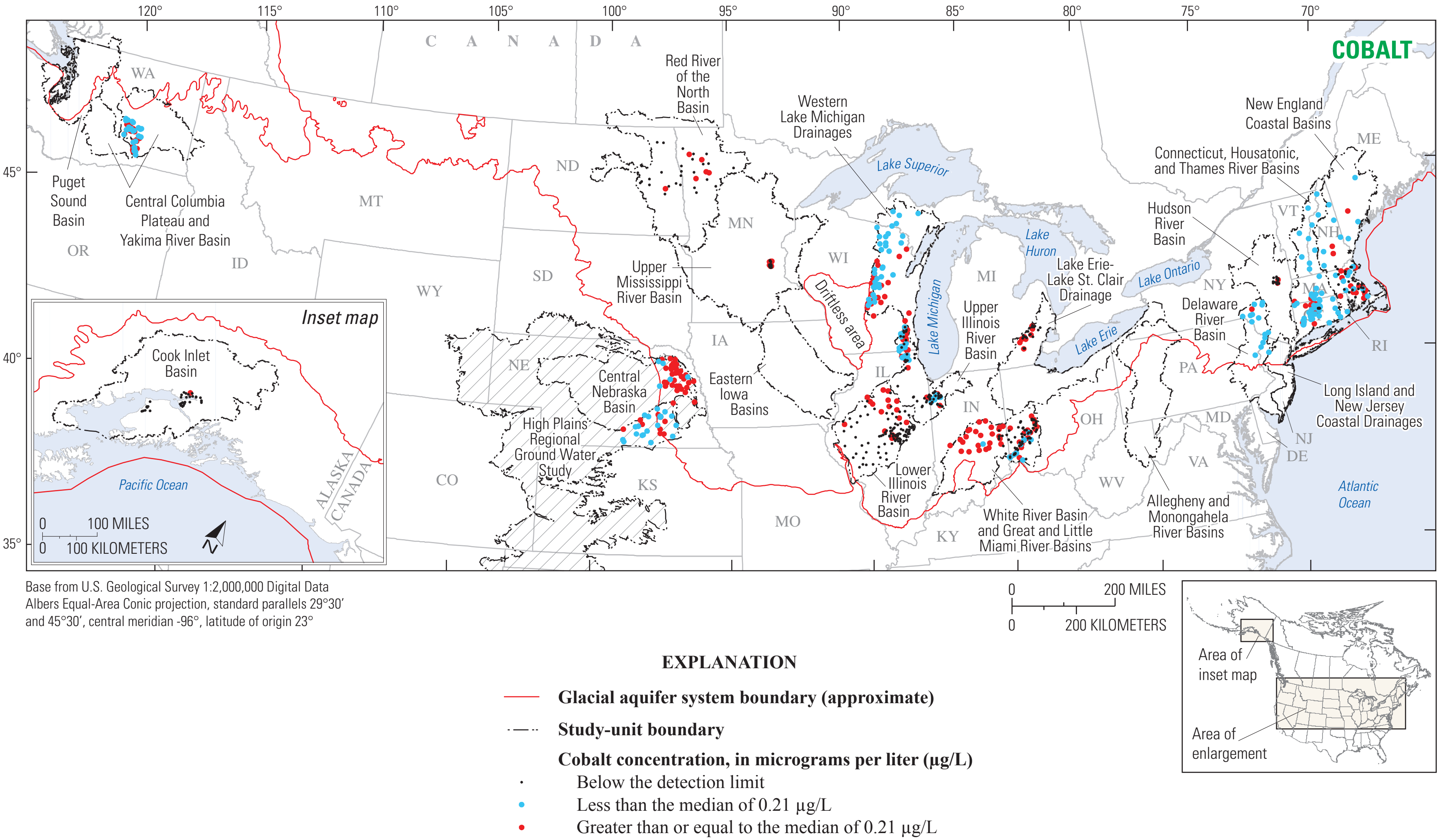
Glacial aquifer system boundary (approximate)

Study-unit boundary

Chromium concentration, in micrograms per liter (µg/L)

- Below the detection limit
- Less than the median of 0.59 µg/L
- Greater than or equal to the median of 0.59 µg/L

Figure 12. The distribution of dissolved chromium concentrations in the ground water of the glacial aquifer system.



Base from U.S. Geological Survey 1:2,000,000 Digital Data
Albers Equal-Area Conic projection, standard parallels 29°30′ and 45°30′, central meridian -96°, latitude of origin 23°

EXPLANATION

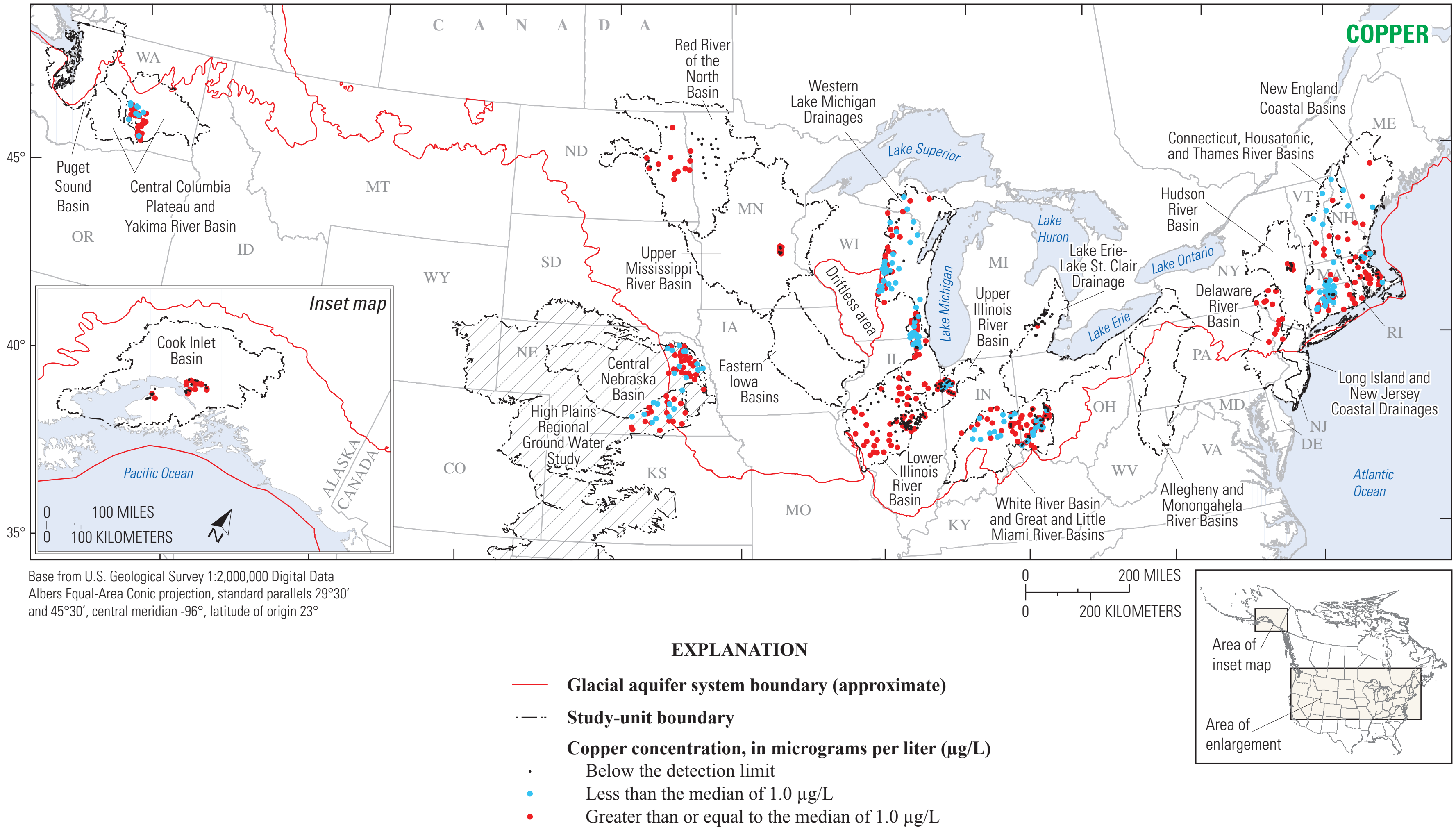
Glacial aquifer system boundary (approximate)

Study-unit boundary

Cobalt concentration, in micrograms per liter (µg/L)

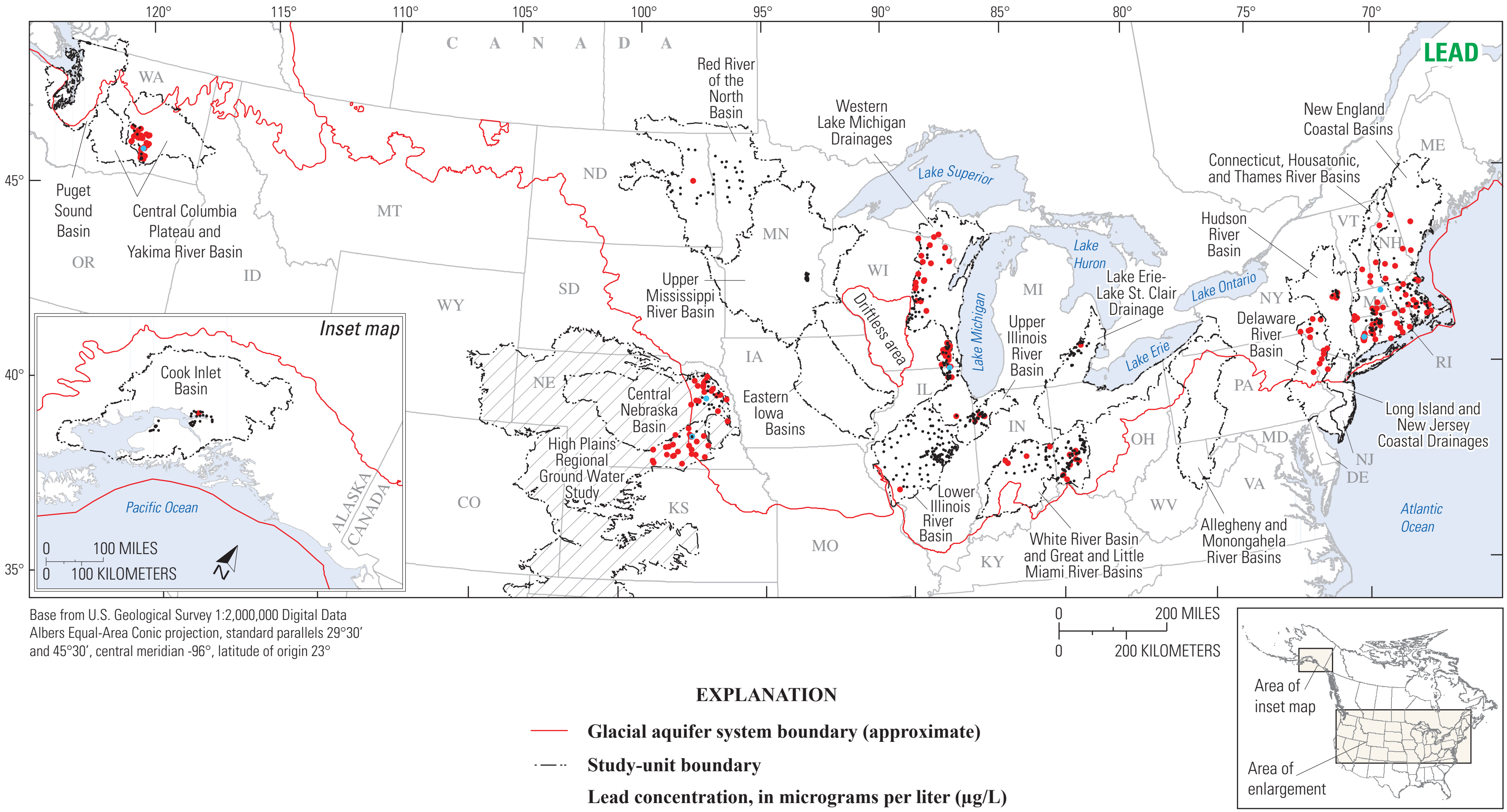
- Below the detection limit
- Less than the median of 0.21 µg/L
- Greater than or equal to the median of 0.21 µg/L

Figure 13. The distribution of dissolved cobalt concentrations in the ground water of the glacial aquifer system.



Base from U.S. Geological Survey 1:2,000,000 Digital Data
Albers Equal-Area Conic projection, standard parallels 29°30′ and 45°30′, central meridian -96°, latitude of origin 23°

Figure 14. The distribution of dissolved copper concentrations in the ground water of the glacial aquifer system.



Base from U.S. Geological Survey 1:2,000,000 Digital Data
Albers Equal-Area Conic projection, standard parallels 29°30′
and 45°30′, central meridian -96°, latitude of origin 23°

EXPLANATION

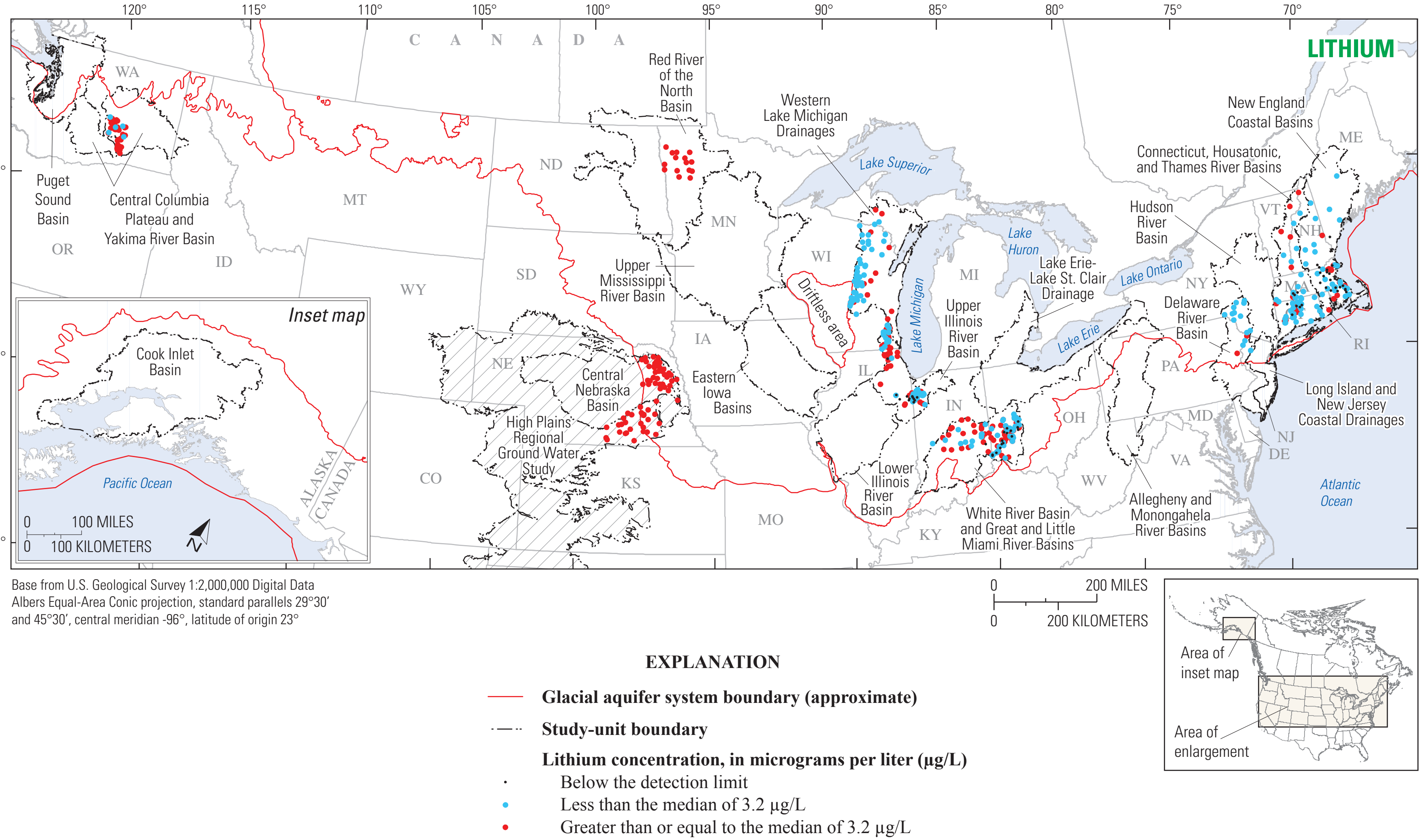
Glacial aquifer system boundary (approximate)

Study-unit boundary

Lead concentration, in micrograms per liter (µg/L)

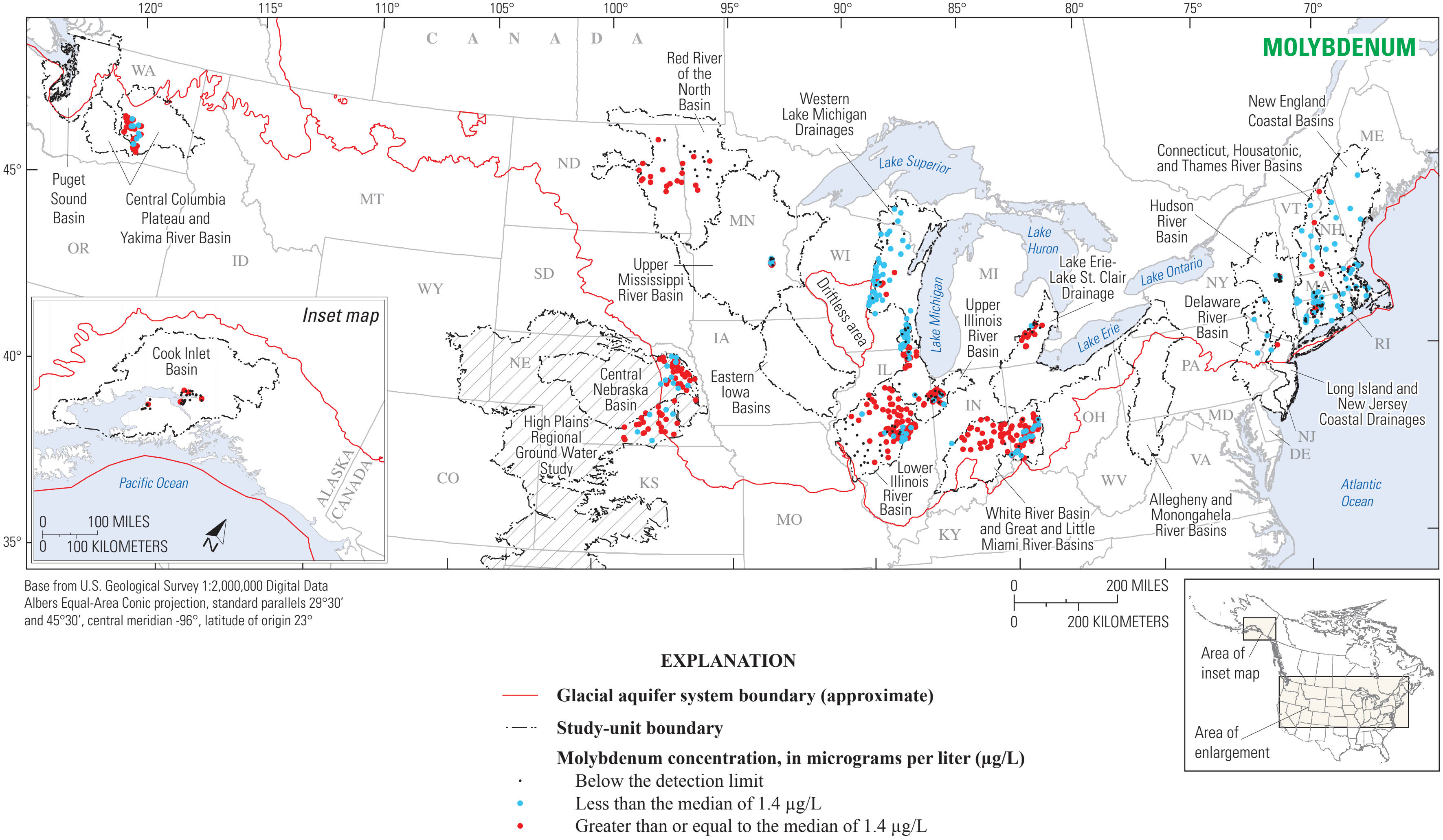
- • Below the detection limit
- • Less than the median of 0.042 µg/L
- • Greater than or equal to the median of 0.042 µg/L

Figure 15. The distribution of dissolved lead concentrations in the ground water of the glacial aquifer system.



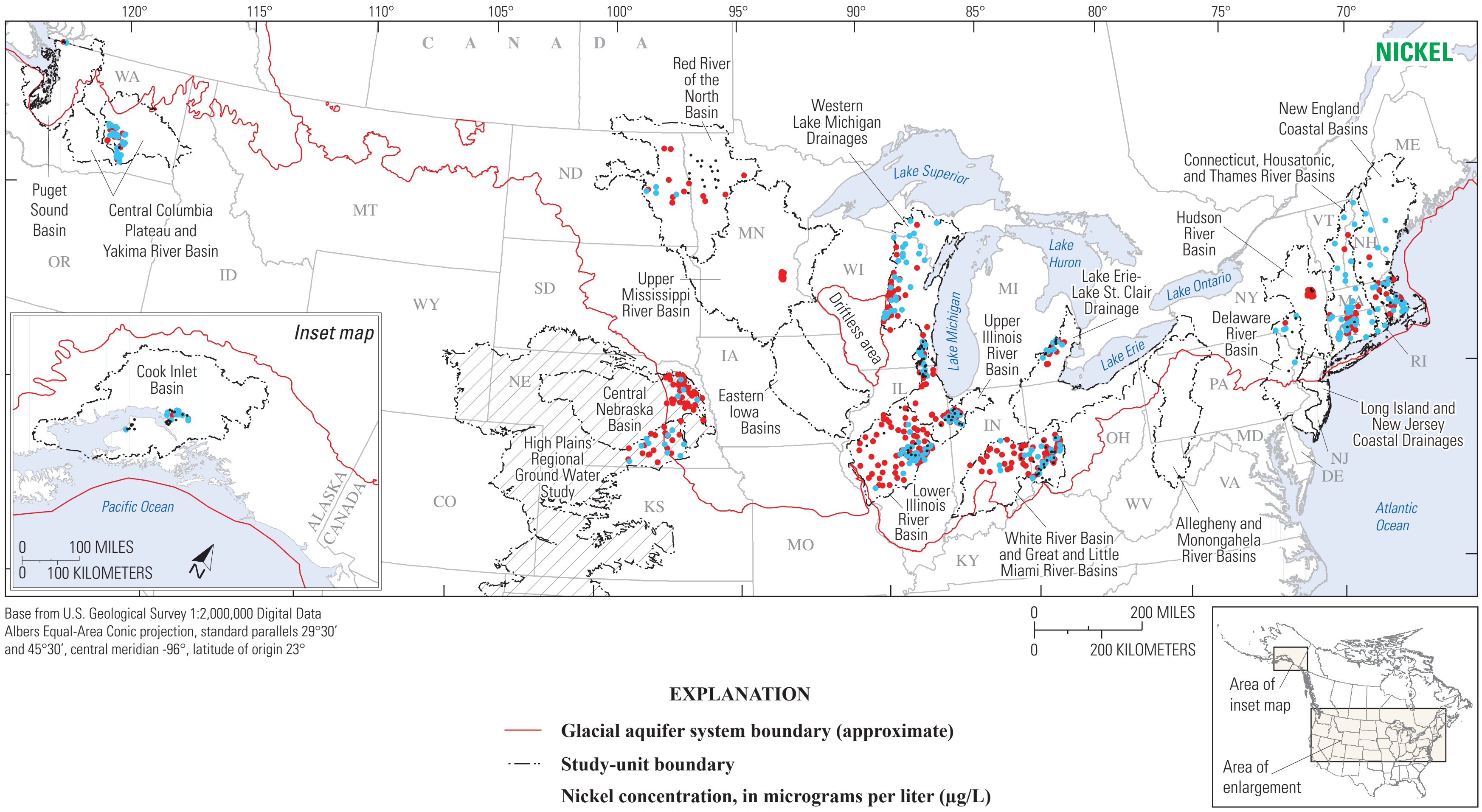
Base from U.S. Geological Survey 1:2,000,000 Digital Data
Albers Equal-Area Conic projection, standard parallels 29°30′ and 45°30′, central meridian -96°, latitude of origin 23°

Figure 16. The distribution of dissolved lithium concentrations in the ground water of the glacial aquifer system.



Base from U.S. Geological Survey 1:2,000,000 Digital Data
Albers Equal-Area Conic projection, standard parallels 29°30′ and 45°30′, central meridian -96°, latitude of origin 23°

Figure 17. The distribution of dissolved molybdenum concentrations in the ground water of the glacial aquifer system.



Base from U.S. Geological Survey 1:2,000,000 Digital Data
Albers Equal-Area Conic projection, standard parallels 29°30′
and 45°30′, central meridian -96°, latitude of origin 23°

EXPLANATION

Glacial aquifer system boundary (approximate)

Study-unit boundary

Nickel concentration, in micrograms per liter (µg/L)

- Below the detection limit
- Less than the median of 1.6 µg/L
- Greater than or equal to the median of 1.6 µg/L

Figure 18. The distribution of dissolved nickel concentrations in the ground water of the glacial aquifer system.

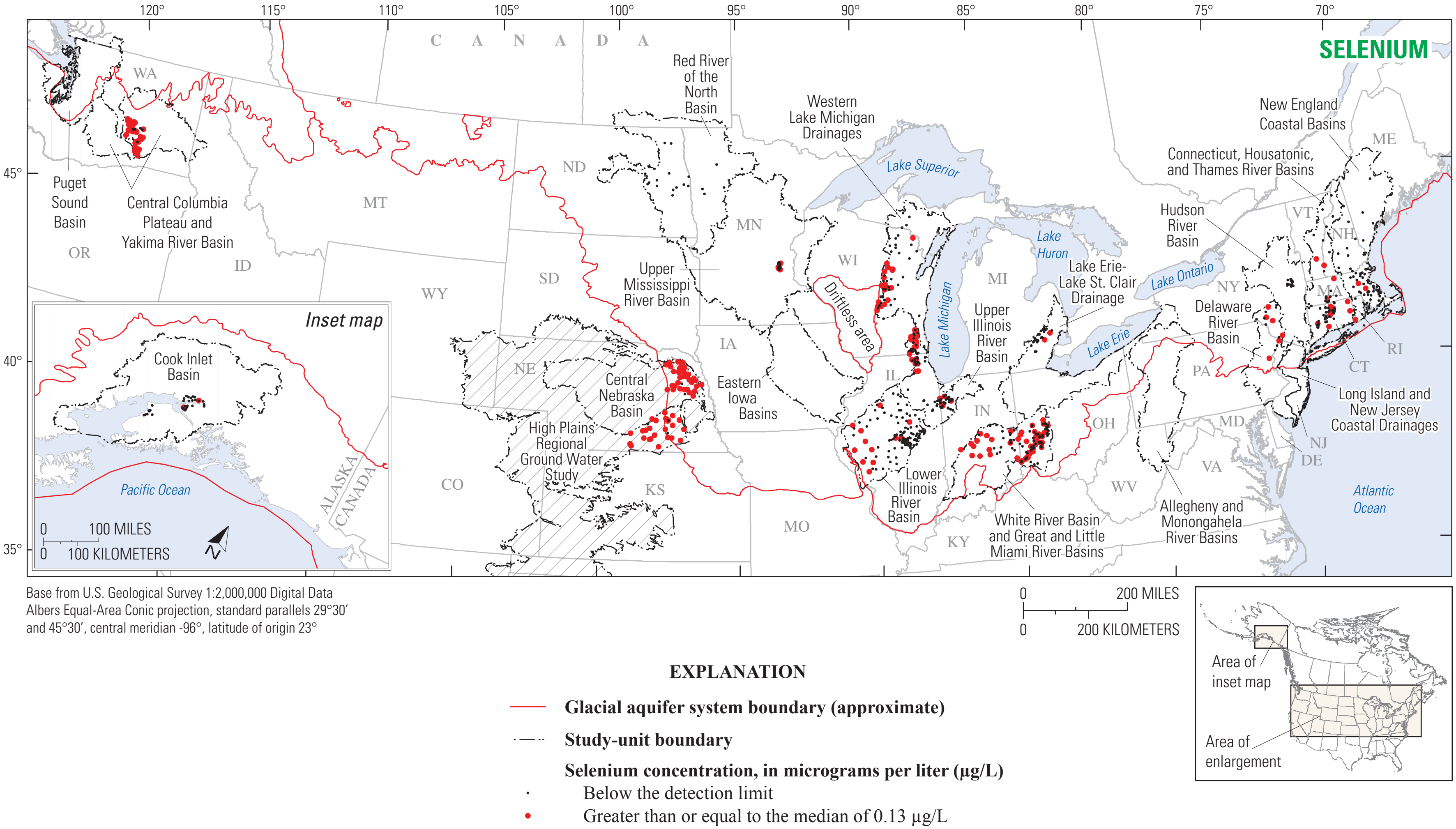


Figure 19. The distribution of dissolved selenium concentrations in the ground water of the glacial aquifer system. No concentrations were less than the estimated median of 0.13 micrograms per liter.

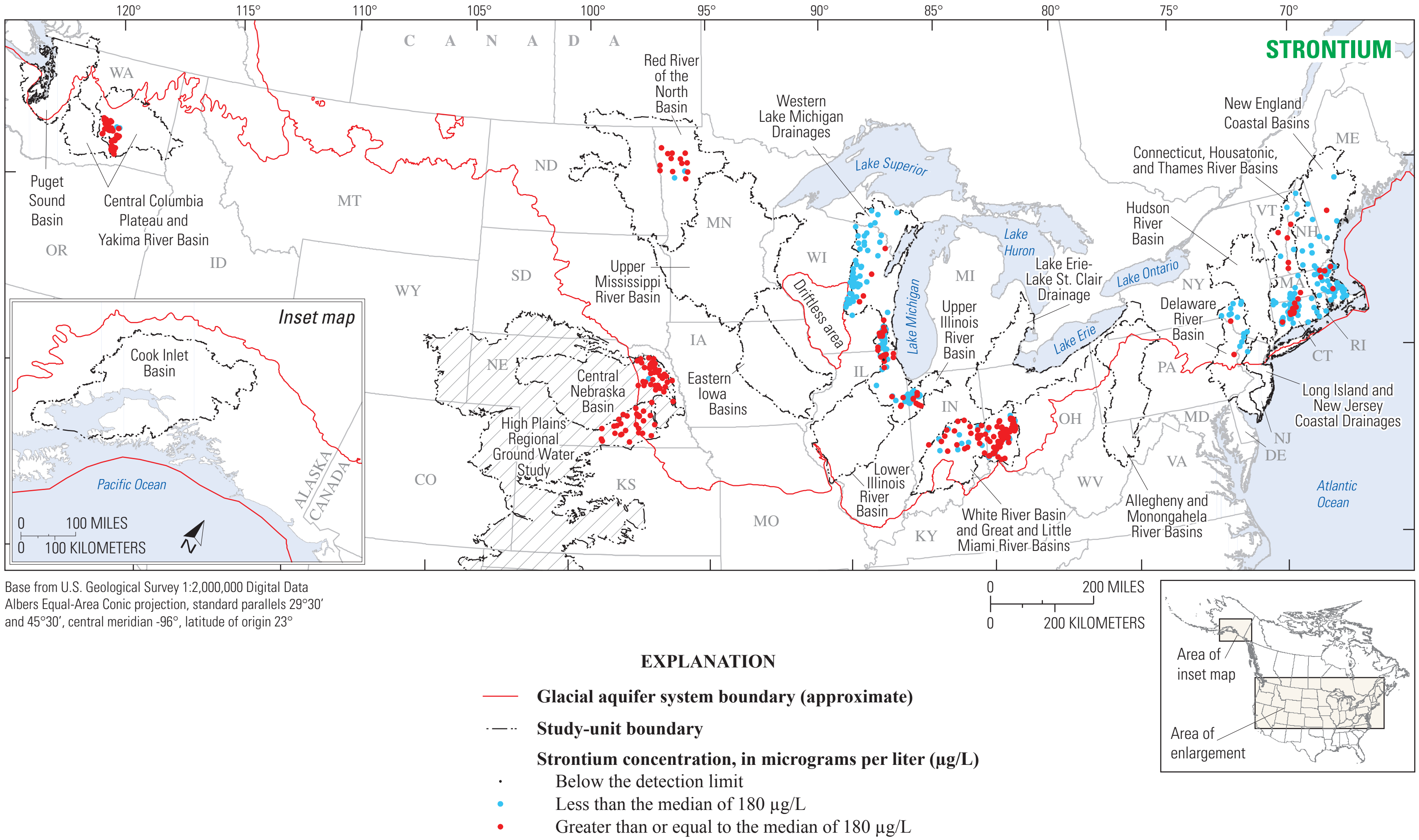


Figure 20. The distribution of dissolved strontium concentrations in the ground water of the glacial aquifer system.

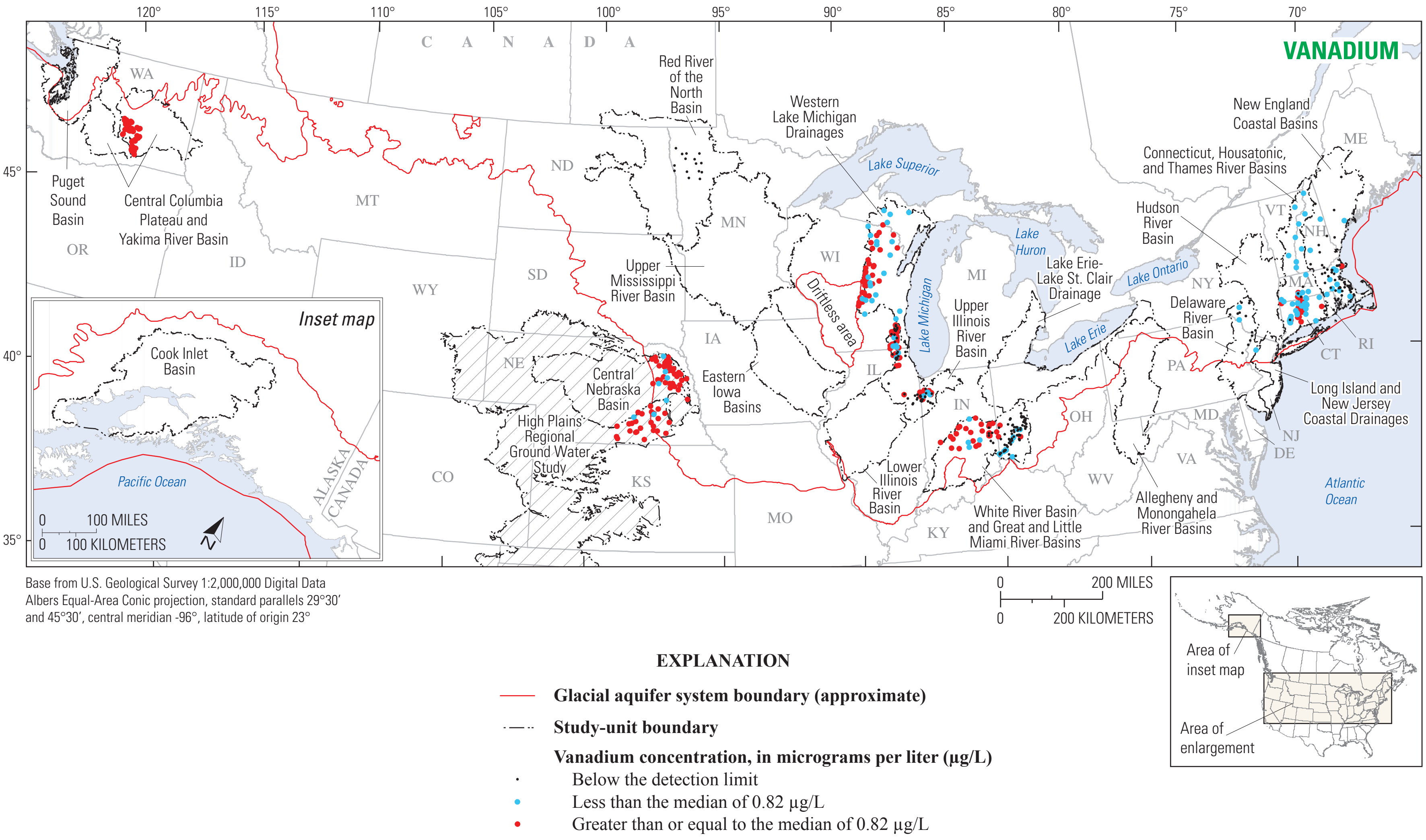
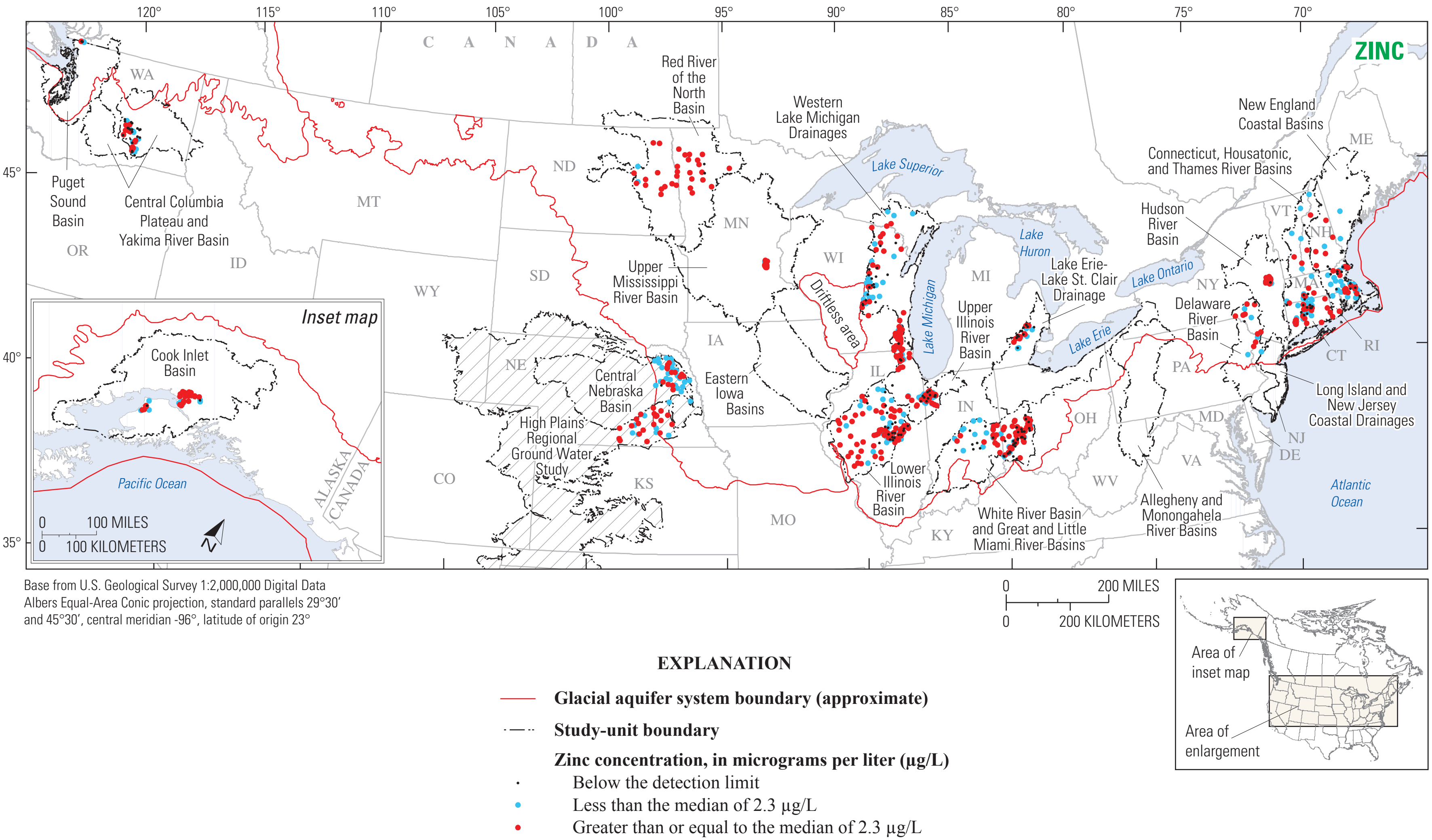


Figure 21. The distribution of dissolved vanadium concentrations in the ground water of the glacial aquifer system.



Base from U.S. Geological Survey 1:2,000,000 Digital Data
Albers Equal-Area Conic projection, standard parallels 29°30′
and 45°30′, central meridian -96°, latitude of origin 23°

Figure 22. The distribution of dissolved zinc concentrations in the ground water of the glacial aquifer system.

Table 6. Summary of glacial aquifer system wells sampled for iron, manganese, and selected trace elements by glacial framework area.

[See table 1 for list of elements]

Framework area	Number of wells sampled for iron and manganese	Percentage of all wells sampled for iron and manganese	Number of wells sampled for selected trace elements	Percentage of all wells sampled for selected trace elements
East	329	21	187	22
Central	651	41	436	52
West-Central	443	28	136	16
West	167	10	88	10

significantly different for lead concentration. Selenium was greatest in the West-Central area, followed by the West, Central, and East areas in decreasing order (fig. 23). All selenium concentration pairwise comparisons of ecdf indicate significant differences. In general, strontium, uranium, and vanadium geographic patterns are similar—concentrations decreased from highest in the West to lowest in the East. Uranium was slightly higher in the West-Central area than in the West area. The p-value for the West/West-Central comparison of uranium ecdf indicates that the two values are not significantly different. The same is true for strontium. Vanadium has the same general geographic pattern but had the largest relative monotonic decrease in concentrations from West to East of all elements.

Figure 24 shows box plots of well depth, dissolved oxygen concentration, pH, residue on evaporation (dissolved solids), temperature, dissolved organic carbon (DOC) and bicarbonate concentration by glacial framework area. Well depth varies significantly by framework area—the West area has the deepest wells; the West-Central area has the shallowest, but the depths are not significantly different from those in the East; and the Central and East areas have wells of similar depth. Dissolved oxygen concentration also varied significantly by framework area—the West area had the highest dissolved oxygen followed by the East area, and the West-Central and Central areas had the lowest concentrations, which are not statistically different from one another. Framework area pH was highest in the West, intermediate and similar in the West-Central and Central areas, and lowest in the East. Differences in pH are related to bicarbonate and (or) dissolved solids concentrations. Residue on evaporation and bicarbonate concentration had very similar patterns among the areas except that the bicarbonate concentration was lowest in the East and concentrations there were statistically different from those in the other three areas. In table 8, p-values for pairwise Kruskal-Wallis or Peto and Peto tests indicate significant differences in residue on evaporation between all framework areas except between East and West. These differences in environmental factors among the wells in each framework area are important for interpreting the geographic distribution of element concentrations and reflect hydrogeologic (well depth) or chemical environment along with possibly climatological effects of geography across the Northern United States.

Elements in Relation to Environmental Factors

The factors examined in the following discussion in relation to trace elements are water use, well depth, network type, and land use near the well. These factors are often substantially interrelated making it difficult to attribute observed

Table 7. P-values for pairwise Peto and Peto tests of significant differences in empirical cumulative distribution functions of element concentrations by glacial framework area.

[Blue cells indicate $p < 0.05$]

Element	Paired glacial framework areas					
	East/Central	East/West-Central	East/West	Central/West-Central	Central/West	West-Central/West
Arsenic	0.00	0.00	0.00	0.00	0.00	**0.22**
Barium	.00	.00	**.52**	.00	.00	.00
Chromium	.00	.00	.05	.00	.02	.00
Cobalt	.00	.00	.00	.02	.02	.00
Copper	**.22**	.01	**.29**	.00	.00	**.27**
Iron	.00	.00	.00	**.33**	.00	.00
Lead	.00	.00	.02	.00	.00	**.17**
Lithium	.00	.00	.00	.00	.00	.00
Manganese	**.86**	.00	.00	.00	.00	.00
Molybdenum	.00	.00	.00	.05	**.06**	.00
Nickel	.00	.00	.02	.00	.00	.00
Selenium	.00	.00	.00	.00	.00	.00
Strontium	.00	.00	.00	.00	.00	**.94**
Uranium	.00	.00	.00	.00	.00	**.14**
Vanadium	.00	.00	.00	.00	.00	.00
Zinc	.00	**.21**	**.19**	.00	**.70**	.00

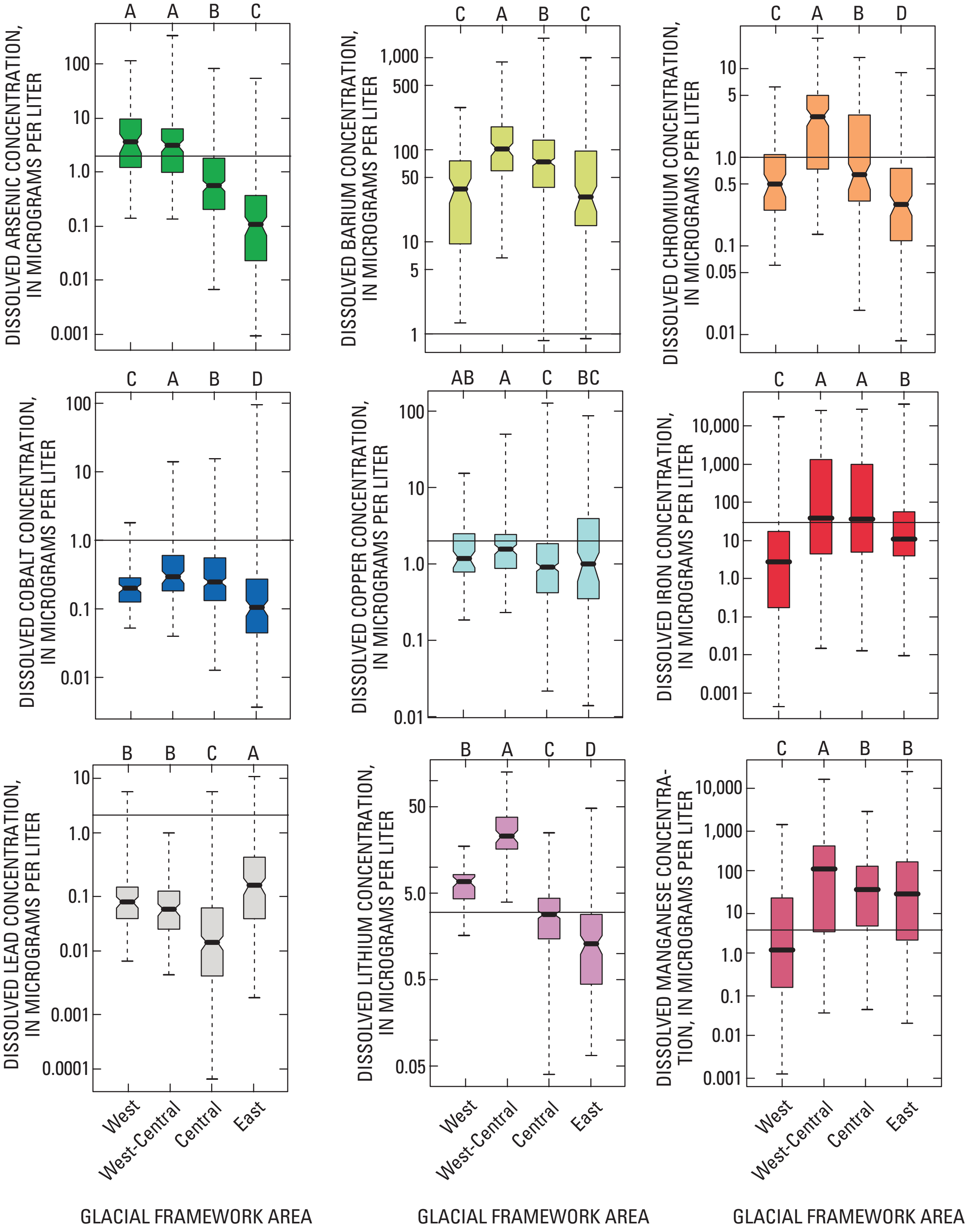
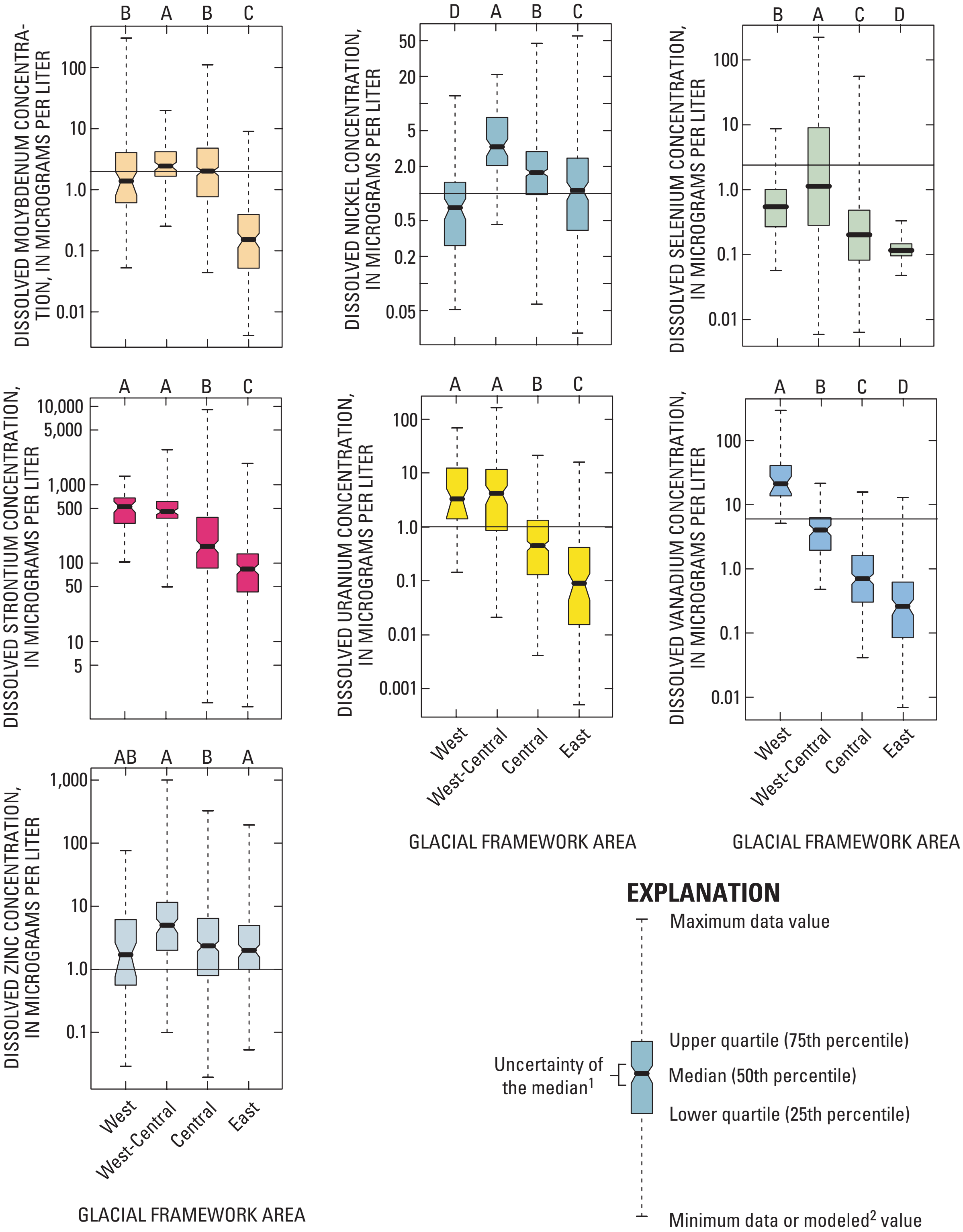


Figure 23. Concentrations of selected elements by glacial framework area for well samples from the glacial aquifer system. Boxes labeled with different letters have significantly different empirical cumulative distribution functions on the basis of Peto and Peto tests. Horizontal line indicates highest reporting level for element.



[1] Based on ±1.57 times the interquartile range divided by the square root of the number of samples. Not included in all boxplots.

[2] Modeled values from Regression on Order Statistics or Kaplan-Meier.

Figure 23. Concentrations of selected elements by glacial framework area for well samples from the glacial aquifer system. Boxes labeled with different letters have significantly different empirical cumulative distribution functions on the basis of Peto and Peto tests. Horizontal line indicates highest reporting level for element.—Continued

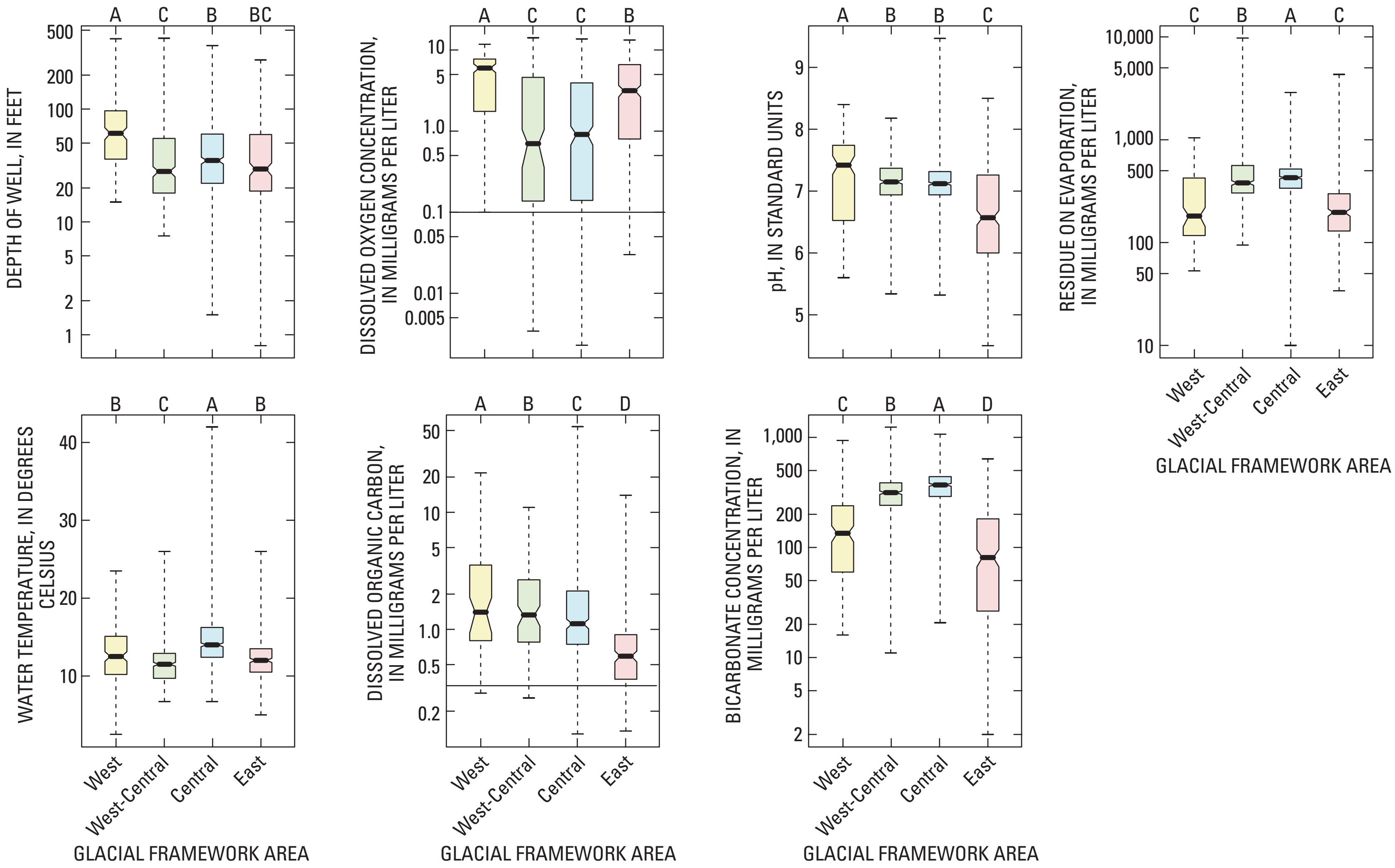


Figure 24. Selected factors by glacial framework area for well samples from the glacial aquifer system. Boxes labeled with different letters have significantly different medians on on the basis of Kruskal-Wallis tests. Horizontal line indicates highest reporting level for element. See figure 23 for explanation of box plots.

Table 8. P-values for pairwise tests of significant differences among selected factors by glacial framework area.

[Blues cells indicate $p < 0.05$; ecdf, empirical cumulative distribution function]

Factor	Paired glacial framework areas					
	East/Central	East/ West-Central	East/West	Central/ West-Central	Central/West	West-Central/ West
	Kruskal-Wallis comparisons between medians					
Well depth	**0.20**	0.00	0.00	0.00	0.00	0.00
pH	.00	.00	.00	**.51**	.00	.00
Temperature	.00	.00	**.28**	.00	.00	.00
Residue on evaporation	.00	.03	**.52**	.03	.00	.00
Bicarbonate	.00	.00	.00	.00	.00	.00
	Peto and Peto comparisons between ecdf					
Dissolved organic carbon	0.00	0.00	0.00	0.00	0.00	0.00
Dissolved oxygen	.00	**.55**	.05	**.55**	.00	.00

higher concentrations of an element to an individual factor. However, it is useful to examine possible relations among specific elements and individual factors, where feasible. In addition, chemical factors are examined in relation to iron, manganese, and selected trace elements and with respect to other factors where relevant. The chemical factors are pH; concentrations of DOC, bicarbonate, dissolved solids (residue upon evaporation), and oxygen; and redox environment.

Water Use

The water-use categories examined in this report are private (domestic) supply, public supply, other (mostly miscellaneous or unknown uses), and monitor wells; the numbers of wells in each of these groups are summarized in table 9. The category “other” was not statistically characterized because of the small number of wells sampled. Finally, the category “drinking-water wells” comprises both private-supply and public-supply wells. Wells providing water for other uses, such as industrial or thermoelectric supply, were not sampled in the glacial aquifer system. Figure 25 shows box plots of well depth, pH, temperature, and concentrations of dissolved oxygen, residue on evaporation, DOC, and bicarbonate by water use. Table 10 shows p-values for Kruskal-Wallis tests of significant differences among these factors by water-use category.

Private and public water-supply wells are significantly deeper (fig. 25) than monitor wells in the study area. The monitor wells were generally installed with openings at or near the water table, and the water-supply wells were generally drilled deeper to avoid land-surface contamination and to maintain a consistent water supply under varying climatic conditions. Although the public-supply wells are significantly deeper than the monitor wells, there was not a significant difference in dissolved oxygen between the two water-use categories of wells. The pH was significantly different among all three categories—highest in private-supply wells and lowest in public-supply wells. The cause of this pH difference between private- and public-supply wells is unknown. However, the public-supply wells were lowest for the four other factors—dissolved solids concentration, organic carbon concentration, bicarbonate concentration, and temperature. For these same four factors, monitor wells were highest.

Arsenic, lithium, and strontium were not significantly different among all water-use categories. Table 11 lists the significance (p-values) of pairwise comparisons with respect to these categories among elements. For this report, a p-value greater than 0.05 indicates that the two categories being compared are not significantly different for a specific element. The p-values for pairwise categorical comparisons of ecdf of arsenic, lithium, and strontium are all higher than 0.05 for all comparisons with respect to category; therefore, concentrations of these elements were considered not significantly different.

Table 9. Summary of glacial aquifer system wells sampled for iron, manganese, and selected trace elements by water use category.

[See table 1 for list of elements. Private supply, non-community water supply; public supply, community water supply; other, industrial or unknown use; monitor, water not used]

Water-use category	Number of wells sampled for iron and manganese	Percentage of all wells sampled for iron and manganese	Number of wells sampled for selected trace elements	Percentage of all wells sampled for selected trace elements
Private supply	463	29	273	32
Public supply	93	5.8	88	10
Other	33	2	24	2.8
Monitor	1,001	63	462	54

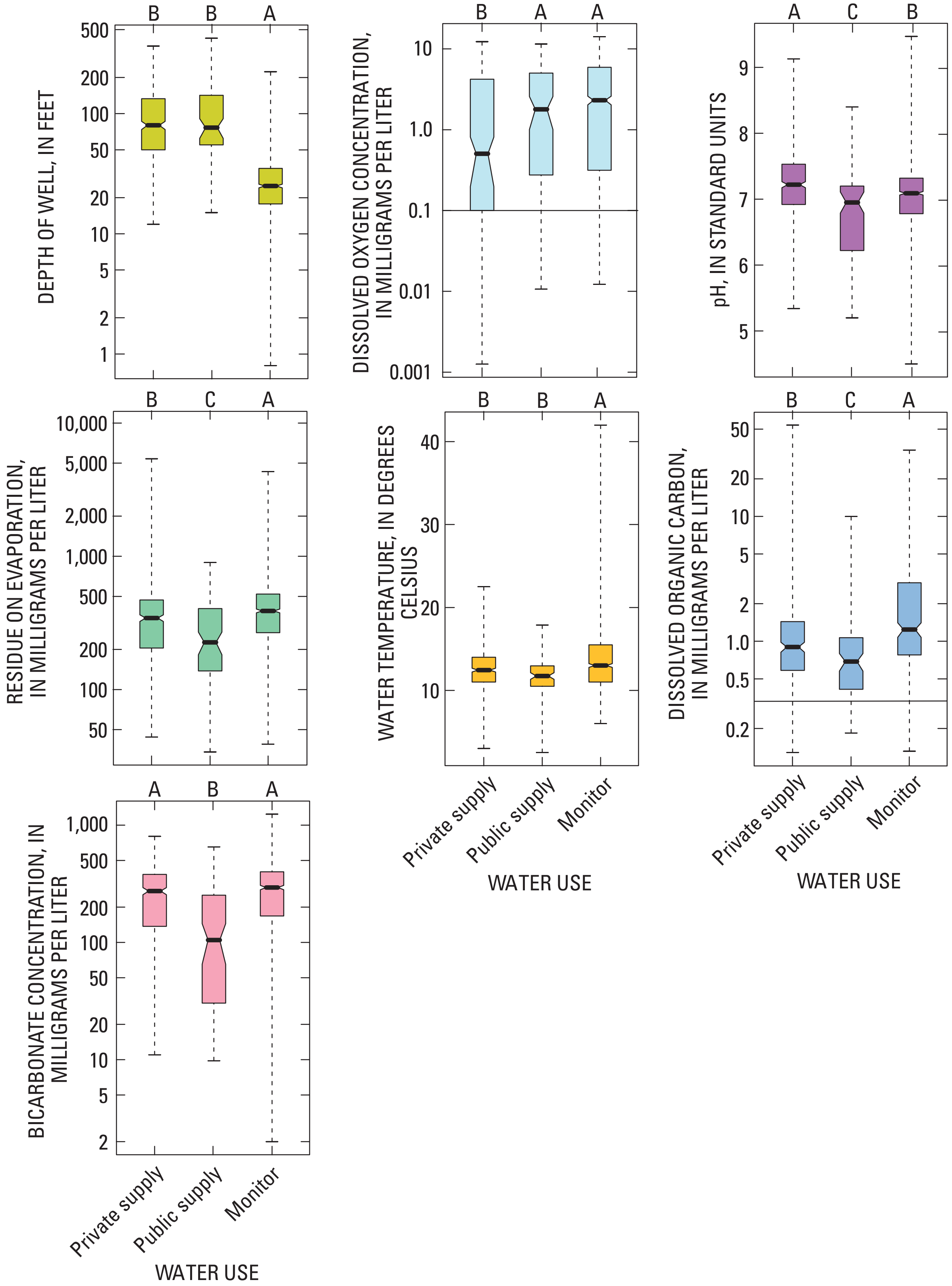


Figure 25. Selected factors by water-use category for well samples from the glacial aquifer system. Boxes labeled with different letters have significantly different medians on the basis of Kruskal-Wallis tests or different empirical cumulative distribution functions on the basis of Peto and Peto tests (dissolved oxygen and organic carbon). Horizontal line indicates highest reporting level for dissolved oxygen or organic carbon. See figure 23 for explanation of box plots.

Table 10. P-values for pairwise tests of significant differences among selected factors by water-use category.

[Blue cells indicate $p < 0.05$; Private supply, non-community water supply; monitor, water not used; public supply, community water supply; drinking supply, combined private supply and public supply wells; ecdf, empirical cumulative distribution function]

Factor	Paired water-use categories			
	Private supply/ monitor	Private supply/ public supply	Public supply/ monitor	Drinking supply/ monitor
	Kruskal-Wallis comparisons between medians			
Well depth	0.00	**0.61**	0.00	0.00
pH	.00	.00	.00	.00
Temperature	.00	.00	.00	.00
Residue on evaporation	.00	.00	.00	.00
Bicarbonate	**.09**	.00	.00	.00
	Peto and Peto comparisons between ecdf			
Dissolved organic carbon	0.00	0.01	0.00	0.00
Dissolved oxygen	.00	.02	**.30**	.00

Table 11. P-values for pairwise Peto and Peto tests of significant differences between empirical cumulative distribution functions of element concentrations with respect to water-use category.

[Blue cells indicate $p < 0.05$; Private supply, non-community water supply; monitor, water not used; public supply, community water supply; drinking supply, combined private supply and public supply wells; ecdf, empirical cumulative distribution function]

Element	Paired water-use categories			
	Private supply/ monitor	Private supply/ public supply	Public supply/ monitor	Drinking supply/ monitor
Arsenic	**0.05**	**0.16**	**0.56**	**0.16**
Barium	**.35**	**.08**	.01	**.07**
Chromium	.00	.00	.00	.00
Cobalt	.00	**.79**	.00	.00
Copper	.00	**.46**	.00	.00
Iron	.00	.00	**.79**	.00
Lead	.00	.00	.00	.00
Lithium	**.92**	**.43**	**.42**	**.68**
Manganese	.00	**.41**	**.12**	.00
Molybdenum	.01	.02	.00	.00
Nickel	.00	**.24**	.00	.00
Selenium	.00	**.17**	.00	.00
Strontium	**.13**	**.92**	**.36**	**.11**
Uranium	.00	**.15**	.03	.00
Vanadium	.04	.00	.00	.00
Zinc	.00	.00	.00	.00

Elements that are significantly different among all the categories are chromium, lead, molybdenum, vanadium, and zinc. Barium concentrations were not significantly different between categories except between monitor wells and public-supply wells. Cobalt was significantly different among all categories except between private- and public-supply wells. Iron was significantly different among all categories except between public-supply and monitor wells. Manganese was significantly different only between private-supply and monitor wells and between drinking-water supply wells and monitor wells. Elements that were significantly different among most categories are plotted in figure 26. Most casings in private-supply wells are polyvinyl chloride (PVC), but a small number are iron or steel as are those in most public-supply wells. Steel alloy contains several trace elements in addition to iron and manganese. Galvanized steel contains a large proportion of zinc. Stainless steel, which is commonly used for well screens, contains chromium, nickel, molybdenum, and vanadium. Wires for electric pumps are usually copper. As the metal casing, screens, or wiring corrodes, these elements are released into the water in and around the well. This study found some indications (see table 11 and fig. 26) that slightly higher iron and copper concentrations may be associated with drinking-water wells than with monitor wells.

For many elements (fig. 26), concentrations were higher in monitor wells than in the set of glacial wells as a whole or drinking-water supply wells—private or public. These elements are chromium, cobalt, molybdenum, nickel, selenium, uranium, and vanadium. One possible reason why the shallow monitor wells [mean depth 30 feet (ft)] had higher concentrations than the drinking-water wells (mean depth 104 ft) is that DOC was significantly higher in monitor wells. Dissolved organic carbon is inversely correlated to well depth (Kendall's $\tau = -0.19$, $p = 0$) and is discussed in section "Dissolved Organic Carbon and Bicarbonate" (page 52) with respect to element concentrations. Alternatively, surficial materials or soils may have larger soluble amounts of these elements in minerals or other solid phases than the deeper aquifer material tapped by drinking-water wells, and the concentrations of these elements in ground water may reflect that availability in the matrix. Zinc is the only element that was lower in monitor wells than in glacial aquifer system wells overall or in drinking-water wells.

Chromium, molybdenum, and vanadium were significantly lower in public-supply wells than in other wells, including private-supply wells. Only lead was higher in public-supply wells than in other wells. However, that relation is tenuous because of the small sample size and the relatively large number of censored values (40 of 85 samples) in the public-supply well subset.

Well Depth

Iron was not significantly related to well depth (Kendall's $\tau = 0.09$ and $p < 0.001$). Iron would be expected to increase with well depth because dissolved oxygen typically declines with depth in glacial aquifers (relations with dissolved oxygen are discussed in section "Dissolved Oxygen" on page 54), and coincidentally, the geochemical environment is typically more reducing at depth and conducive to dissolving ferrous iron. Manganese, another element whose water solubility is affected by dissolved oxygen, had a slight correlation with well depth (Kendall's $\tau = -0.11$ and $p < 0.001$). However, manganese was inversely correlated with depth—it decreased slightly as well depth increased. The relation between well depth and redox condition is common and is discussed in section "Oxidation-Reduction Environment" (page 55), of this report. Figure 27 shows the relation of selected elements to well depth. Only the six elements that have a significant correlation with depth are shown in figure 27. A significant correlation is defined here as having an absolute value of Kendall's $\tau \geq 0.1$ and $p < 0.05$.

Kendall's τ and p-values for regressions of trace elements on well depth are listed in table 12. Most elements had little or no relationship to well depth—concentrations of barium, chromium, copper, lead, molybdenum, selenium, uranium, and vanadium were independent of well depth. Arsenic, lithium, and zinc had significant, but weak, direct relationships to well depth—they increased slightly as well depth increased. Similar to that of manganese, cobalt and nickel had weak inverse relationships to well depth—their concentrations decreased slightly with increased well depth.

Network Type and Land Use

Land use (agricultural or urban) and network type (LUS and MAS wells) are closely related because the LUS wells are predominantly monitor wells installed by the NAWQA Program and the MAS wells are primarily preexisting private- or public-supply wells. Land-use survey wells comprise 981 of the glacial wells sampled for iron and manganese. The iron distributions, as described previously, show important differences between LUS wells and MAS wells. Wells sampled by network and land use are summarized in table 13. The median manganese concentration for all wells was 34 µg/L, for LUS wells combined was 36 µg/L, and for MAS wells was 33 µg/L. The range of the medians for individual study-unit networks was 0.1 µg/L (estimated by ROS) to 445 µg/L—four orders of magnitude. The variability in manganese concentrations is larger among well networks (geospatially) than between network types—LUS or MAS wells—and likely reflects both differences in manganese content of aquifer material and factors that may mobilize manganese.

The land uses where shallow monitor wells were sampled for trace elements include agriculture (612 wells in 30 networks), urban (areas of residential or light commercial land use less than about 30 years old, comprising 347 wells in 14 networks), and forest (18 wells) and reference wells (4). Reference wells associated with a specific LUS network are intended to represent nearby relatively undeveloped areas that were expected to have consistent land-use management for the

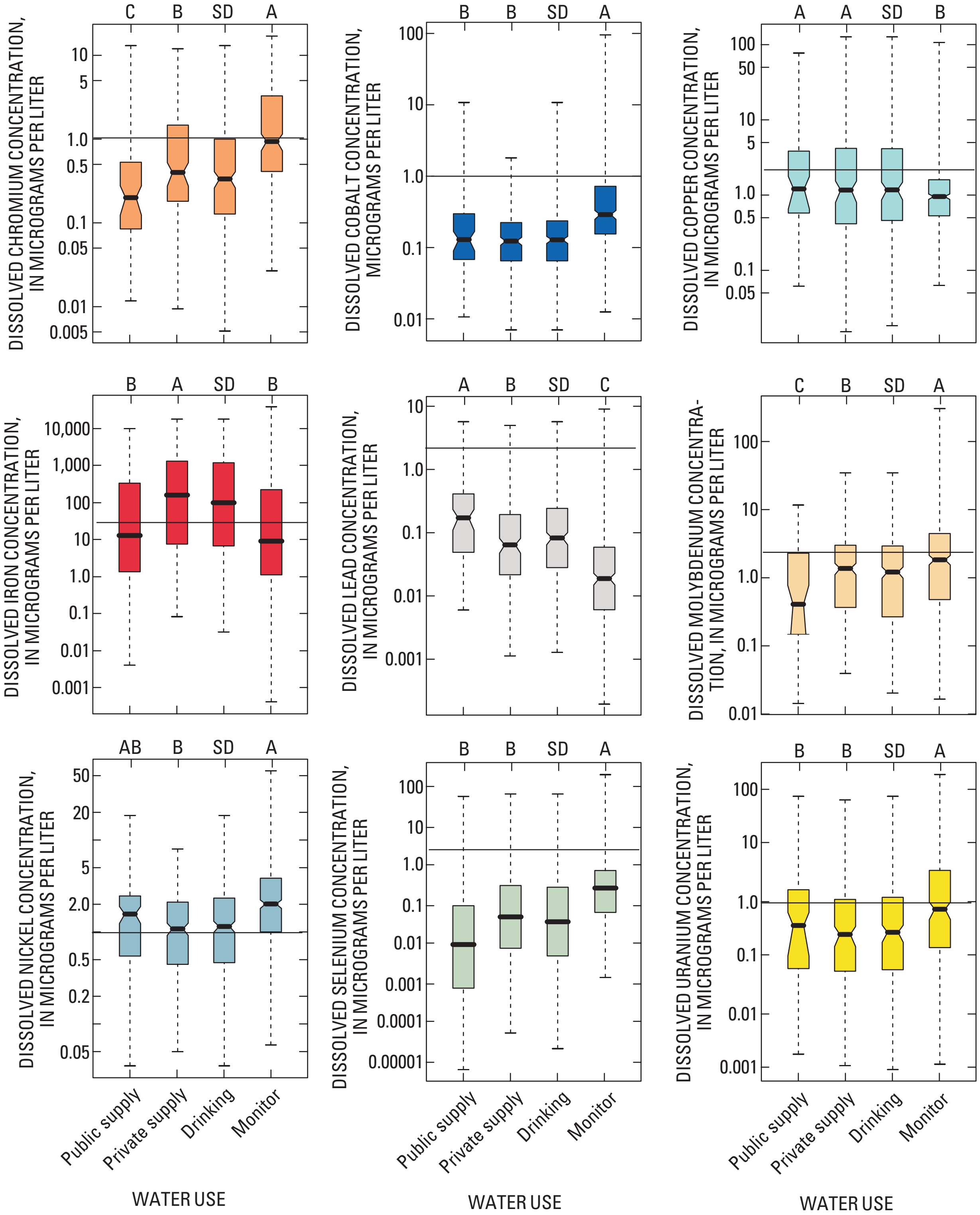


Figure 26. Concentrations of selected elements by water-use category for well samples from the glacial aquifer system. Boxes labeled with different single letters (A, B, or C) have significantly different empirical cumulative distribution functions (ecdf) on the basis of Peto and Peto tests. Drinking water wells, a category composed of private-supply and public-supply wells, were only compared to monitor wells. "SD" indicates a significant difference between ecdf of drinking-water wells and monitor wells. Horizontal line indicates highest reporting level for element. See figure 23 for explanation of box plots.

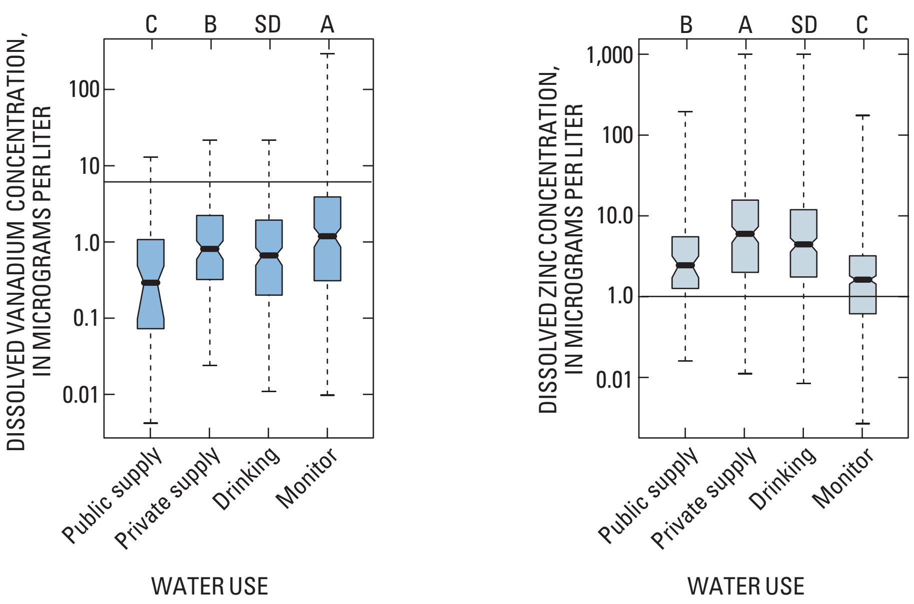


Figure 26. Concentrations of selected elements by water-use category for well samples from the glacial aquifer system. Boxes labeled with different single letters (A, B, or C) have significantly different empirical cumulative distribution functions (ecdf) on the basis of Peto and Peto tests. Drinking water wells, a category composed of private-supply and public-supply wells, were only compared to monitor wells. "SD" indicates a significant difference between ecdf of drinking-water wells and monitor wells. Horizontal line indicates highest reporting level for element. See figure 23 for explanation of box plots.—Continued

foreseeable future. However, data from forest and reference wells were not statistically characterized as groups because few wells were sampled.

Figure 28 shows box plots of well depth, dissolved oxygen, pH, residue on evaporation, temperature, DOC, and bicarbonate by network type and land use. Table 14 lists p-values of Kruskal-Wallis tests of significant differences among these factors by land-use/network type. MAS wells (mostly private- and public-supply wells) are generally deepest (fig. 28). There is no significant difference in well depth between agricultural and urban land-use wells. Urban land-use wells had significantly lower pH than agricultural or MAS wells. Temperature was lowest in MAS wells. This was expected because MAS wells are significantly deeper as a group. Bicarbonate concentration was significantly higher in agricultural wells, but there was no difference in concentration between urban land-use wells and MAS wells. Dissolved solids concentration was highest in agricultural wells. That relation may be a factor for the many trace elements that were statistically higher in agricultural wells as discussed in the following paragraphs. Dissolved oxygen concentrations were highest in the two groups of land-use wells and significantly lower in the MAS wells. Again, this is because the MAS wells are deeper than the land-use wells in general.

Figure 29 shows box plots of selected elements that were significantly different with respect to network type or land use or both. Many trace elements were similar between the two network types—LUS and MAS. Similar to the concentrations of iron, the concentrations of lead, and zinc were higher in the MAS wells relative to the LUS wells (fig. 29). However, chromium, cobalt, molybdenum, nickel, selenium, uranium, and vanadium were higher in the LUS wells relative to the MAS wells. This is the same set of trace elements that were highest in monitor wells relative to private- and public-supply wells. The LUS wells subset overlaps substantially with the monitor wells subset because most of the LUS wells are monitor wells. Dissolved organic carbon concentration was highest in agricultural land-use wells and lowest in MAS wells (fig. 28). Dissolved organic carbon may be related to the higher levels of these seven elements in LUS wells.

The median iron concentration for all glacial aquifer wells was 15 µg/L, for LUS wells it was 7.8 µg/L, and for MAS wells it was 140 µg/L. Box plots in figure 29 show the iron concentrations for these groups of well samples. The LUS wells have a lower median iron concentration than the glacial aquifer system as a whole but the range in concentration is similar. The MAS wells had a significantly higher median but a smaller range in concentrations. Reasons for this difference may be related to the construction of these wells. Private-supply and public-supply wells generally are constructed deeper than monitor wells to avoid land-surface contamination and to ensure a more stable supply of water under varying climatic conditions. Deeper wells tend to have less dissolved oxygen (described in detail in a following section "Dissolved Oxygen" on page 54), thus more reducing conditions and hypothetically, higher iron concentrations.

As described previously (see page 21), manganese is apparently preferentially dissolved in glacial aquifer system ground water relative to iron, on the basis of average lithospheric and soil ratios. However, iron concentrations were significantly higher in MAS wells than in LUS wells and in glacial aquifer wells as a whole (fig. 29). Manganese concentrations were similar among the various networks and land-use categories of wells (fig. 29). Because zinc also had significantly higher concentrations in MAS wells, it is possible that relatively high iron and zinc concentrations indicate the effect of well casing materials on samples from MAS wells. Some MAS wells, primarily public-supply wells, are constructed from steel and galvanized steel parts that could leach iron and zinc. Most private-supply wells and almost all the LUS wells are constructed of PVC.

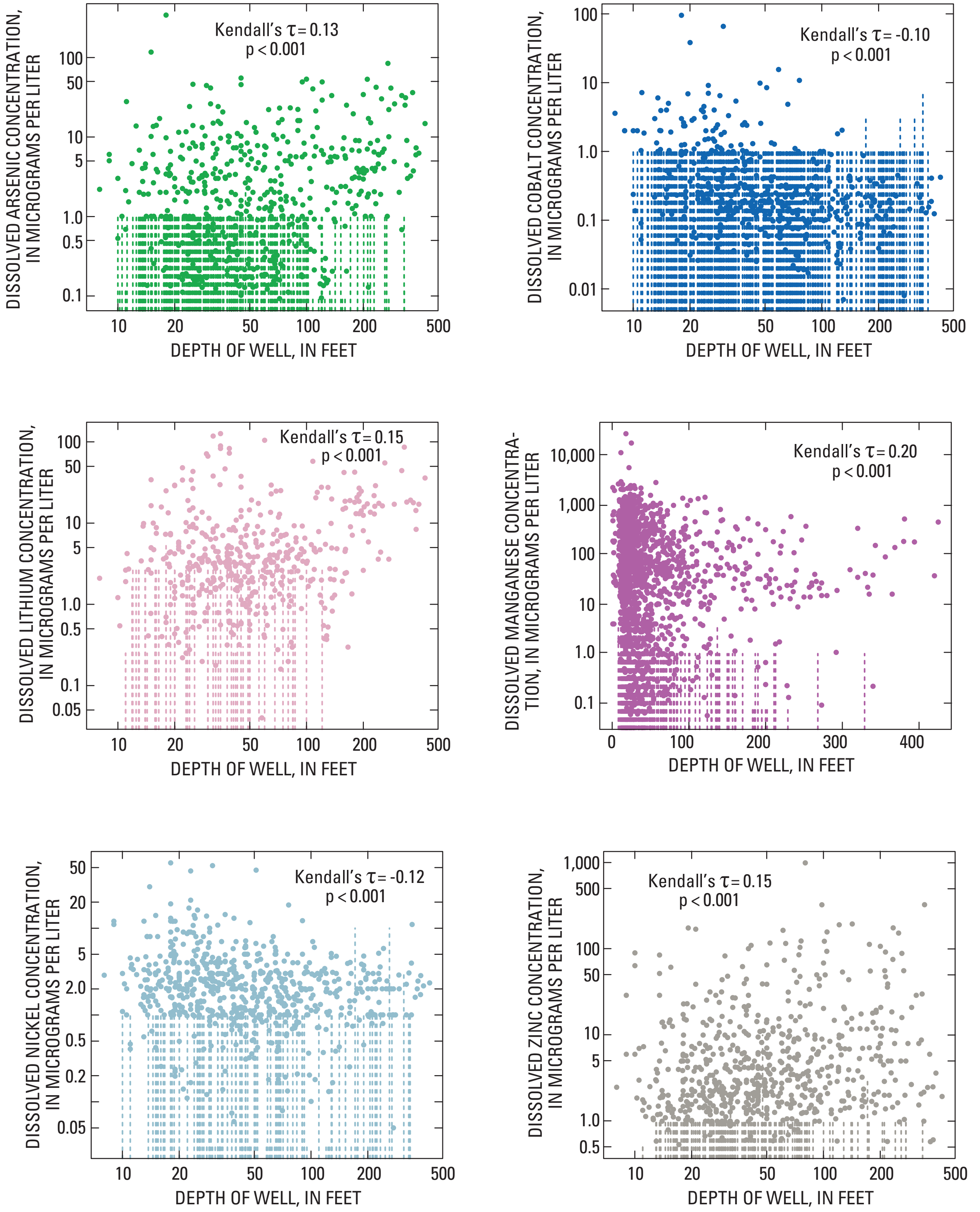


Figure 27. The relation between concentrations of selected elements and well depth for well samples from the glacial aquifer system. For censored results (those results below detection) the "true concentration" lies somewhere in the interval between zero and the reporting level, therefore, vertical dashed lines indicate censored element results.

Table 12. Nonparametric regression correlation coefficients (Kendall's tau) and associated p-values for the relations between selected element concentrations and well depth in samples from wells in the glacial aquifer system.

[Green cells indicate tau equal to or greater than 0.1; blue cells indicate $p < 0.05$; gray cells indicate tau equal to or less than -0.1]

Element	Tau	P-value
Arsenic	**0.13**	0.00
Barium	.04	.12
Chromium	-.04	.12
Cobalt	**-.10**	.00
Copper	.01	.82
Iron	.09	.00
Lead	.03	.19
Lithium	**.15**	.00
Manganese	**-.11**	.00
Molybdenum	.01	.60
Nickel	**-.12**	.00
Selenium	-.01	.75
Strontium	.07	.02
Uranium	-.04	.05
Vanadium	.03	.35
Zinc	**.15**	.00

With the lone exception of lead, all these elements were higher in agricultural land-use wells than in urban land-use wells. Although the difference is likely related to dissolved solids concentrations, the reason that these elements and dissolved solids were higher in agricultural areas than in urban areas is not readily apparent and there is no apparent reason to attribute the higher concentrations to agricultural land-use practices. However, as noted previously, DOC was higher in agricultural land-use wells than in urban wells and may be a factor in the higher trace element concentrations. Also, in the West-Central and West areas, irrigation may indirectly increase dissolved solids and trace elements in shallow ground water (Ayotte and others, 2007). Molybdenum, uranium, and vanadium were also higher in the subset of monitor wells. Although lead may have had higher concentrations in urban wells than in agricultural wells, the subset of urban wells has too many censored values (186 of 207, or 90 percent of samples) to draw any inference. Table 15 lists the p-values for Peto and Peto tests of significant differences between ecdf of elements with respect to network type and land use.

Agricultural and urban wells had the fewest significant differences in comparisons of element concentration ecdf. There are only 9 elements (of 16) that were significantly different between agricultural land-use wells and urban land-use wells. Arsenic, copper, lithium, manganese, molybdenum, selenium, strontium, uranium, and vanadium had substantial variations between agricultural and urban land uses (table 15). All these element concentrations were higher in agricultural wells than in urban wells. Land-use survey wells as a group have the most significant differences in element ecdf from MAS wells. Only lithium and manganese were not significantly different between LUS wells and MAS wells.

pH

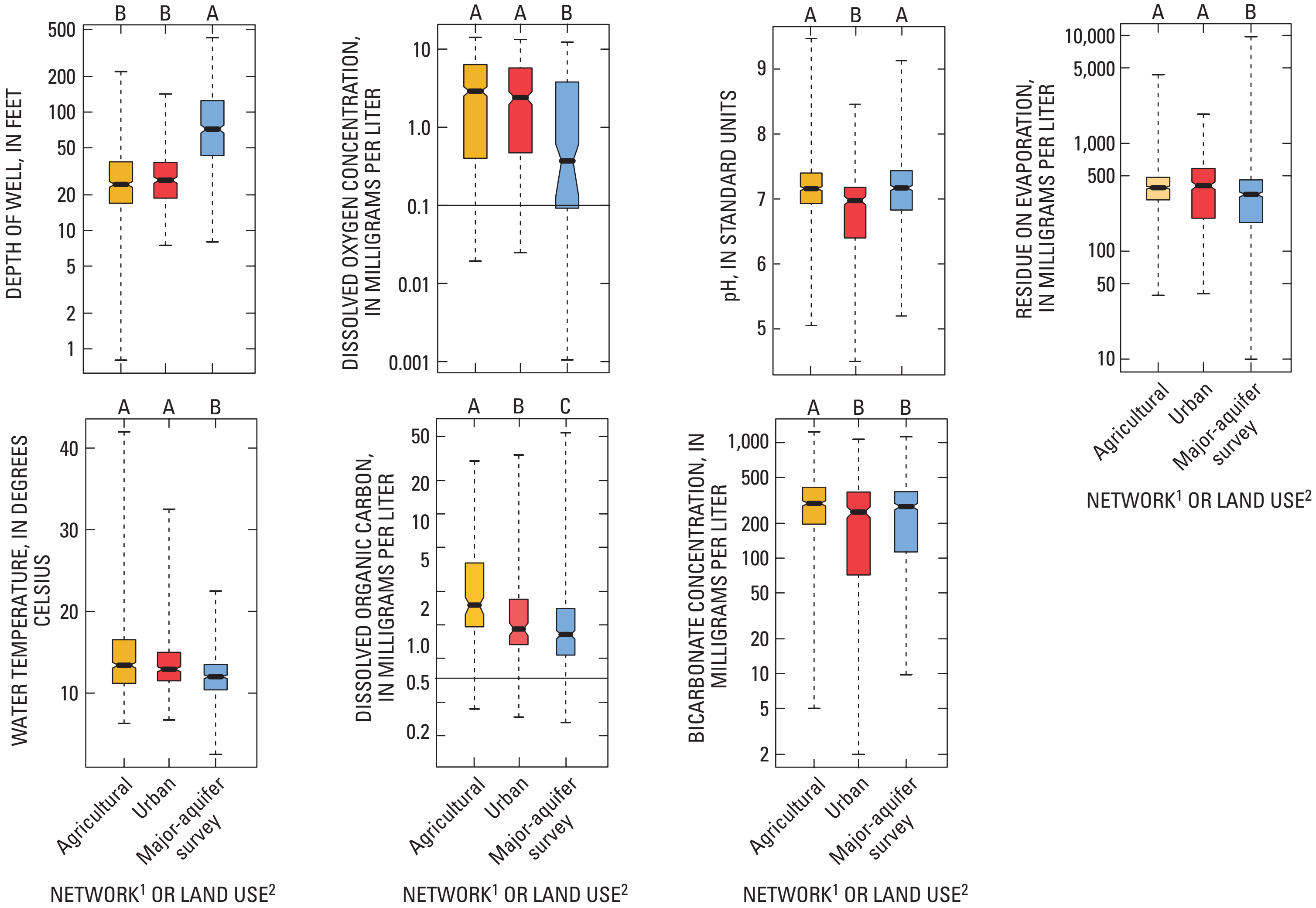
In general, most of the elements discussed here are more soluble under low pH conditions than neutral (7.0) or high pH conditions. The tendency to form oxyanions, such as arsenate/arsenite, molybdate, selenate, or vanadate, for example, complicates this because the chemical behavior of many oxyanions is quite different from that of hydrated free ion species (Stumm and Morgan, 1996). Negatively charged hydrated oxyanions such as arsenate will sorb to positively charged solids more effectively at low pH (Dzombak and Morel,

Table 13. Summary of glacial aquifer system wells sampled for iron, manganese, and selected trace elements by network type and land use.

[See table 1 for list of elements]

Network type or land use	Number of wells sampled for iron and manganese	Percentage of all wells sampled for iron and manganese	Number of wells sampled for selected trace elements	Percentage of all wells sampled for selected trace elements
Major-aquifer survey	609	38	380	45
Land-use survey[1]	981	62	467	55
Agriculture	612	38	253	30
Urban	347	22	207	24
Forest	18	1.1	3	0.4
Reference	4	0.2	4	.5

[1] Land-use survey category includes wells in the agriculture, urban, forest, and reference categories.



[1] Network types are major-aquifer survey or land-use survey.

[2] Land-use surveys are agricultural or urban.

Figure 28. Selected factors by network type or land use for well samples from the glacial aquifer system. Boxes labeled with different letters have significantly different medians on the basis of Kruskal-Wallis tests. Horizontal line indicates highest reporting level for dissolved oxygen or organic carbon. See figure 23 for explanation of box plots.

Table 14. P-values for pairwise tests of significant differences among selected factors by network type or land use.

[Blues cells indicate $p < 0.05$; major-aquifer survey, network of major aquifer wells; land-use survey, combined urban and agricultural wells; ecdf, empirical cumulative distribution function]

Factor	Paired network types or land uses			
	Agricultural/ Urban	Agricultural/ Major-aquifer survey	Urban/ Major-aquifer survey	Land-use survey/Major-aquifer survey
	Kruskal-Wallis comparisons between medians			
Well depth	**0.12**	0.00	0.00	0.00
pH	.00	**.69**	0.00	.00
Temperature	**.06**	.00	0.00	.00
Residue on evaporation	**.96**	.00	0.00	.00
Bicarbonate	.00	.00	**.23**	.02
	Peto and Peto comparisons between ecdf			
Dissolved organic carbon	0.00	0.00	0.02	0.00
Dissolved oxygen	**.54**	.00	.00	.00

1990) and be taken out of solution. Many elements had lower concentrations in low pH (less than 6.0) water than in neutral- or near neutral pH (6.5–7.5) water. Kendall's τ values for the relations of iron and manganese to pH are both 0.0 and the value is only significant for manganese. Relationships of trace elements to pH are shown in figure 30 for those elements with p-values less than 0.05. The Kendall's τ coefficients are shown on the graphs and in table 16 for all elements. The elements that do show significant correlations ($\tau \geq 0.1$ and p-values < 0.05) are arsenic, lithium, molybdenum, strontium, uranium, and vanadium. All the significant correlations are direct—implying that the element concentrations increase as the pH increases. For oxyanions, such as arsenate and molybdate, this is consistent with sorption reactions in which sorption of the negative oxyanion decreases as the pH increases. The other elements have a $\tau \cong 0$ or a p-value greater than 0.05 or both with respect to pH.

The relations of element concentrations to pH are complex because of the dependence of pH on other variables such as glacial framework area. In the previous discussion of glacial framework areas, it was shown that ground-water pH was significantly different among all glacial framework areas in pairwise comparisons except between Central and West-Central framework areas. The median pH of the New England Coastal Basins wells, in the East framework area, was 5.9, and the median pH for all glacial wells was 7.4. The mean residue on evaporation for New England Coastal Basins wells was 192 mg/L; for all glacial wells, the mean residue on evaporation was 416 mg/L. The low pH is coincidental with relatively dilute ground water that may have had less contact or travel time in glacial sediments containing smaller amounts of carbonate minerals that could buffer the pH. The mean calcium concentration for the New England Coastal Basins wells was 14 mg/L, and for all glacial wells, the mean calcium concentration was 71 mg/L. These relatively lower calcium and trace elements concentrations in the low pH category reflect dilute ground water in the Northeastern United States; thus, this area had lower overall concentrations of major and trace elements despite the significantly lower pH.

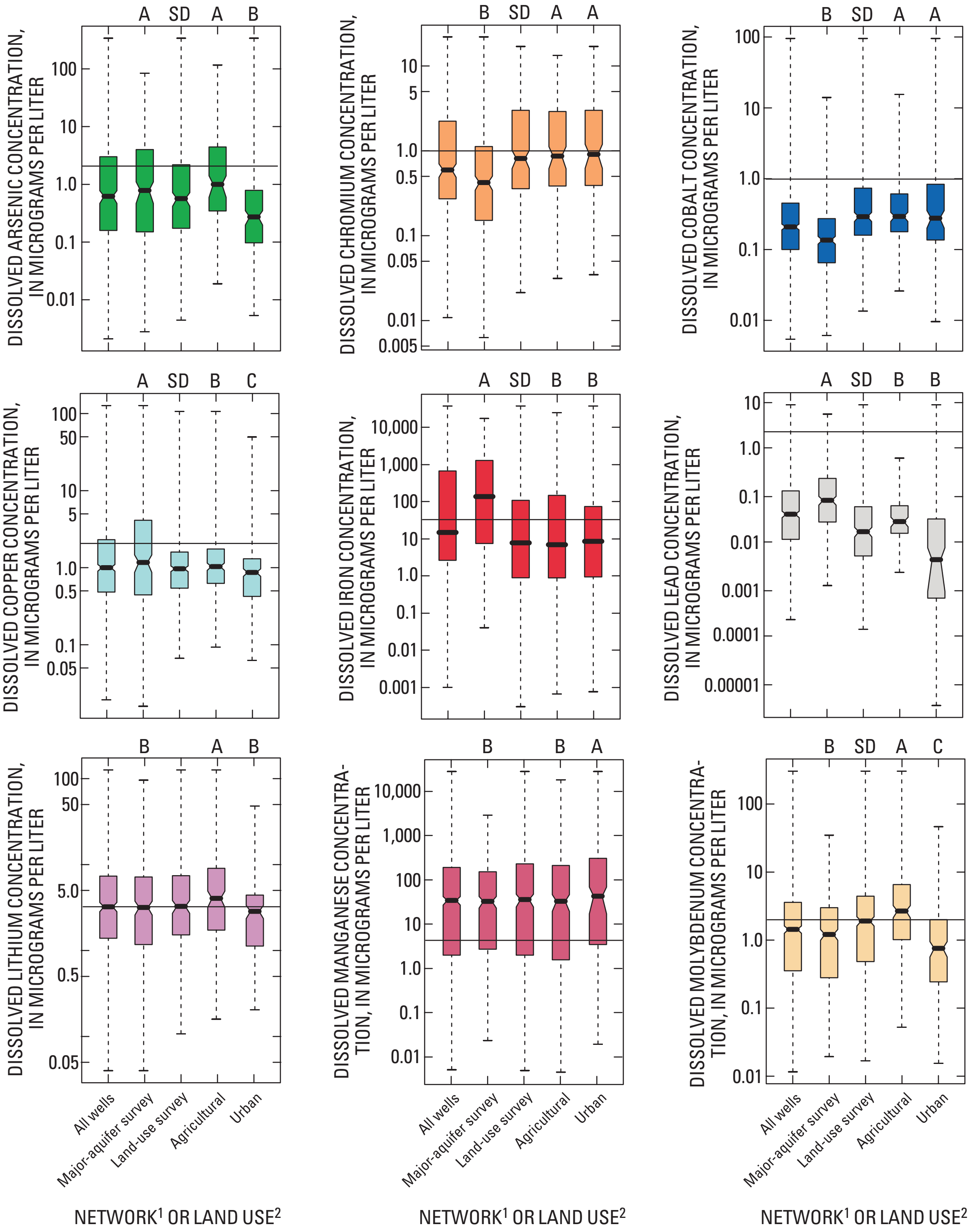
Dissolved Organic Carbon and Bicarbonate

Dissolved organic carbon, as discussed previously, was significantly higher in shallow wells, particularly in agricultural land-use monitor wells. Higher DOC is also associated with significantly higher concentrations of chromium, cobalt, molybdenum, nickel, selenium, uranium, and vanadium (fig. 31). Table 17 lists the Kendall's τ for nonparametric regressions of element concentrations on DOC. As indicated in the table, all elements except copper, lead, selenium, and zinc are significantly and directly correlated with DOC. Arsenic, barium, manganese, molybdenum, and strontium have the strongest correlations. This could be caused by the nature of chemical interactions between the elements and DOC, or DOC and these elements may be higher because of some other unmeasured factor possibly related to well depth.

Bicarbonate (alkalinity) is the primary anion in most glacial aquifer water and accounts for a substantial amount of the variability in overall chemistry in the glacial aquifer (Arnold and others, 2008). Nonparametric regression Kendall's τ and p-values are listed in table 18. All element concentrations, except copper, lead, and zinc are significantly and directly related to the concentration of bicarbonate in the aquifer.

Dissolved Solids

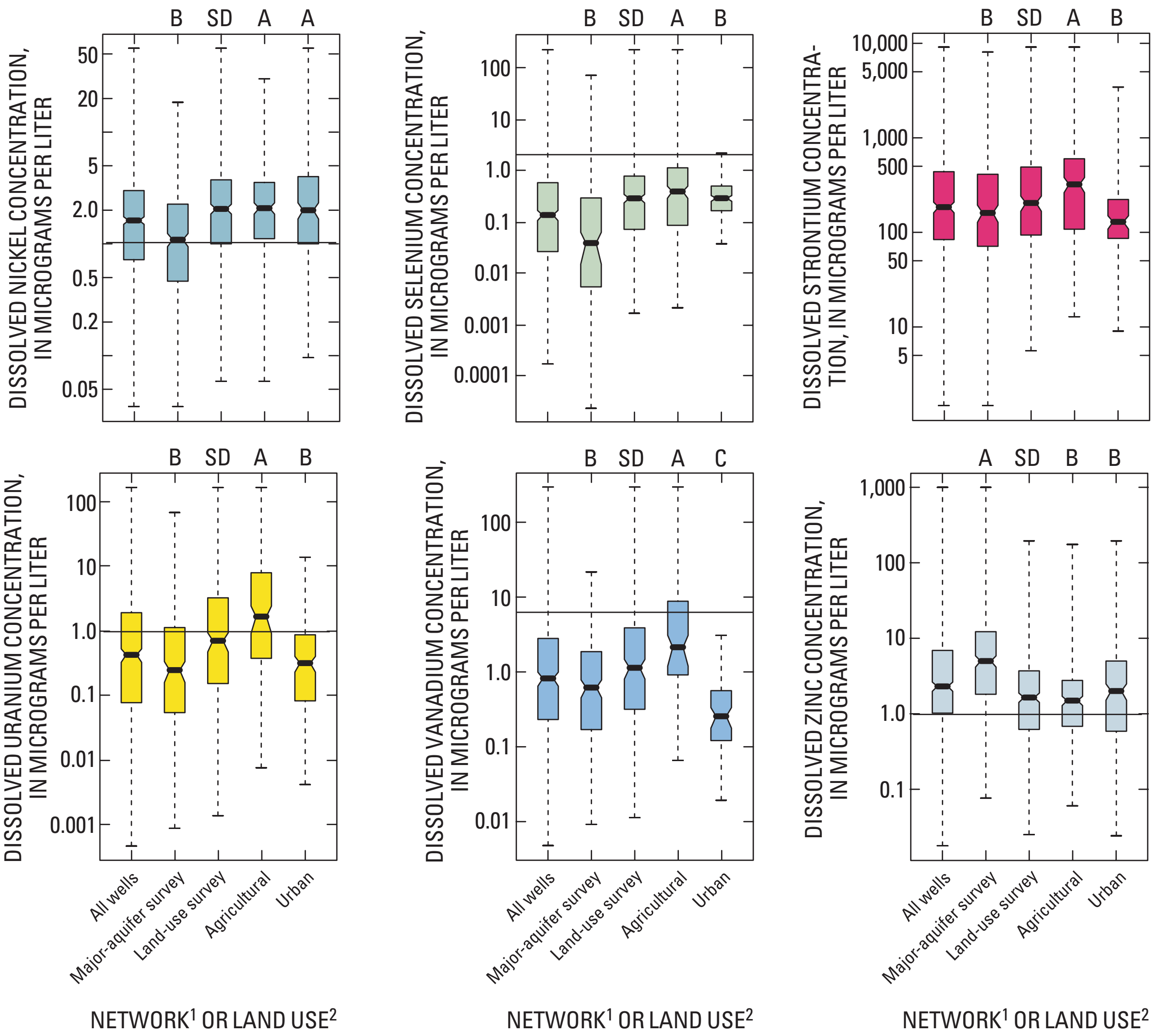
The concentration of dissolved solids, as residue on evaporation at 180 degrees Celsius (˚C), is directly related to that of iron, manganese, and trace elements. The nonparametric regression Kendall's τ and p-values are listed in table 19. Only copper, iron, lead, and zinc are not directly and significantly related to dissolved solids. Why that is the case is not readily apparent. It would be expected that all dissolved elements would be directly related to dissolved solids. However, copper, lead, and zinc were also not significantly related to bicarbonate, as discussed previously. Figure 32 shows graphs of the elements that are significantly correlated to residue on evaporation.



[1] Network types are major-aquifer survey or land-use survey.

[2] Land-use surveys are agricultural or urban.

Figure 29. Concentrations of selected elements by network type and land use for well samples from the glacial aquifer system. The category “All wells” is included for comparison of the entire set of wells sampled to the network type and land use subsets and was not tested for significant differences. Boxes labeled with different letters (A, B, or C) have significantly different empirical cumulative distribution functions (ecdf) on the basis of Peto and Peto tests. The category land-use survey wells, combined urban and agricultural wells, was only compared to major-aquifer survey wells and “SD” indicates a significant difference in ecdf between major-aquifer surveys and land-use surveys. Horizontal line indicates highest reporting level for element. See figure 23 for explanation of box plots.



1 Network types are major-aquifer survey or land-use survey.
2 Land-use surveys are agricultural or urban.

Figure 29. Concentrations of selected elements by network type and land use for well samples from the glacial aquifer system. The category "All wells" is included for comparison of the entire set of wells sampled to the network type and land use subsets and was not tested for significant differences. Boxes labeled with different letters (A, B, or C) have significantly different empirical cumulative distribution functions (ecdf) on the basis of Peto and Peto tests. The category land-use survey wells, combined urban and agricultural wells, was only compared to major-aquifer survey wells and "SD" indicates a significant difference in ecdf between major-aquifer surveys and land-use surveys. Horizontal line indicates highest reporting level for element. See figure 23 for explanation of box plots.—Continued

Dissolved Oxygen

Dissolved oxygen concentration could be expected to decrease with well depth. As indicated in the discussion on well depth, the Kendall's τ correlation coefficient for dissolved oxygen with depth was not different from zero even though deeper wells tend to have little to no dissolved oxygen. Figure 33 shows the relations between dissolved oxygen and selected elements. The graphs for iron and manganese in figure 33 indicate that there are significant relationships between these elements and dissolved oxygen.

In the data collected, only the data for dissolved oxygen are useful for comparing the redox behavior of iron and manganese. This is because iron and manganese concentrations could not be separated into redox categories on the basis of the scheme used for the other elements. In that scheme (discussed in the "Oxidation-Reduction Environment" section), the concentrations of dissolved iron and manganese were used to determine the redox categories. Therefore, no independent data besides that for dissolved oxygen are available for determining redox effects on iron and manganese concentrations. A Kendall's τ of -0.38 ($p \cong 0$) for the relation

Table 15. P-values for pairwise Peto and Peto tests of significant differences in empirical cumulative distribution functions of element concentrations with respect to network type or land use for wells in the glacial aquifer system.

[Blue cells indicate $p < 0.05$; major-aquifer survey, network of major aquifer wells; land-use survey, combined urban and agricultural wells]

Element	Paired network types or land use			
	Agricultural/ Urban	Agricultural/ Major-aquifer survey	Urban/ Major-aquifer survey	Land-use survey/ Major-aquifer survey
Arsenic	0.00	**0.12**	0.00	0.03
Barium	**.10**	**.16**	.01	.02
Chromium	**.52**	.00	.00	.00
Cobalt	**.80**	.00	.00	.00
Copper	.00	.04	.00	.00
Iron	**.21**	.00	.00	.00
Lead	**.36**	.00	.00	.00
Lithium	.00	.02	**.09**	**.42**
Manganese	.01	**.95**	.01	**.26**
Molybdenum	.00	.00	.02	.00
Nickel	**.68**	.00	.00	.00
Selenium	.00	.00	**.15**	.00
Strontium	.00	.00	**.08**	.04
Uranium	.00	.00	**.47**	.00
Vanadium	.00	.00	.00	.00
Zinc	**.07**	.00	.00	.00

of iron with dissolved oxygen and a τ of -0.39 ($p \cong 0$) for the relation of manganese with dissolved oxygen were determined on the basis of these data (table 20). Although the correlation coefficients are similar, close examination of the graphs of the iron and manganese relations to dissolved oxygen in figure 33 shows that, with respect to oxygen, the two elements behave somewhat differently. Hem (1962; 1963) described slightly different redox behavior for iron and manganese. The difference is likely due to the slightly higher (more positive) redox potential for dissolved manganese reduction of IV to II (Stumm and Morgan, 1996) and possibly to kinetic differences between iron and manganese in redox reaction (Hem, 1963).

Oxidation-Reduction Environment

Iron and manganese concentrations are especially affected by redox conditions but many trace elements also are “redox sensitive.” For this report, the term “redox sensitive” is used to indicate an element that occurs dissolved in near neutral pH (between pH 5 and 9) ground water under more than one common oxidation state and where one or more oxidation states are more soluble than others. Iron and manganese both fall into this category because the reduced (II) oxidation state of either of these elements is more soluble under the range of natural ambient geochemical conditions for the glacial aquifer system than the oxidized state. However, when a substantial amount of dissolved sulfide is present, precipitation of iron sulfides a can effectively limit the dissolved iron concentrations. Microbial activity is not discussed here even though processes that oxidize or reduce trace elements and thus remove or add them to ground water are dominated by microbial mediation (Stumm and Morgan, 1996). No data were collected by the NAWQA Program to assess microbial effects on trace element concentrations. The redox sensitive trace elements discussed in this report are arsenic, chromium, cobalt, copper, molybdenum, selenium, uranium, and vanadium. They are included primarily because of their common multiple oxidation states and the propensity of several to form oxyanions (such as AsO_4^{3-} and MoO_4^{2-}) that are commonly controlled by redox conditions.

Arsenic is commonly recognized as redox sensitive (Thomas, 2003, 2007) even though it is found at concentrations that exceed drinking-water standards as both oxidized (AsV) and reduced (AsIII) states (Smedley and Kinniburgh, 2002). In the glacial aquifer system, high concentrations of arsenic can occur under reducing conditions in the form of arsenite (AsO_3^{3-}; Thomas, 2003, 2007).

Redox, as used in this report, is classified into six categories on the basis of a scheme developed by Chapelle and others (1995) as modified by Paschke and others (2007) that uses threshold concentrations of selected indicator dissolved constituents, such as iron and manganese, and dissolved oxygen that are commonly available (table 21). The categories assigned by Chapelle and others (1995) through a decision tree are simplified for this discussion. The categories, listed in decreasing oxidation potential, are “oxic” (oxygen reducing)—dissolved oxygen concentration is greater than or equal to 0.5 mg/L; “NO_3” (nitrate reducing)—dissolved oxygen is less than 0.5 mg/L and nitrate concentration is greater than or equal to 0.5 mg/L; “Mn” (manganese reducing)—dissolved oxygen and nitrate are both less than 0.5 mg/L, manganese concentration is greater than or equal to 50 µg/L, and iron concentration is greater than or equal to 100 µg/L; “Fe/SO_4”—(iron or sulfate reducing) dissolved oxygen and nitrate are both less than 0.5 mg/L, dissolved iron concentration is greater than or equal to 100 µg/L, and sulfate concentration is greater than or equal to 4 mg/L (or the reporting level for sulfate); and, “methanic” (carbon dioxide reducing)—dissolved oxygen and nitrate are both less than 0.5 mg/L, dissolved iron is greater than or equal to 100 µg/L

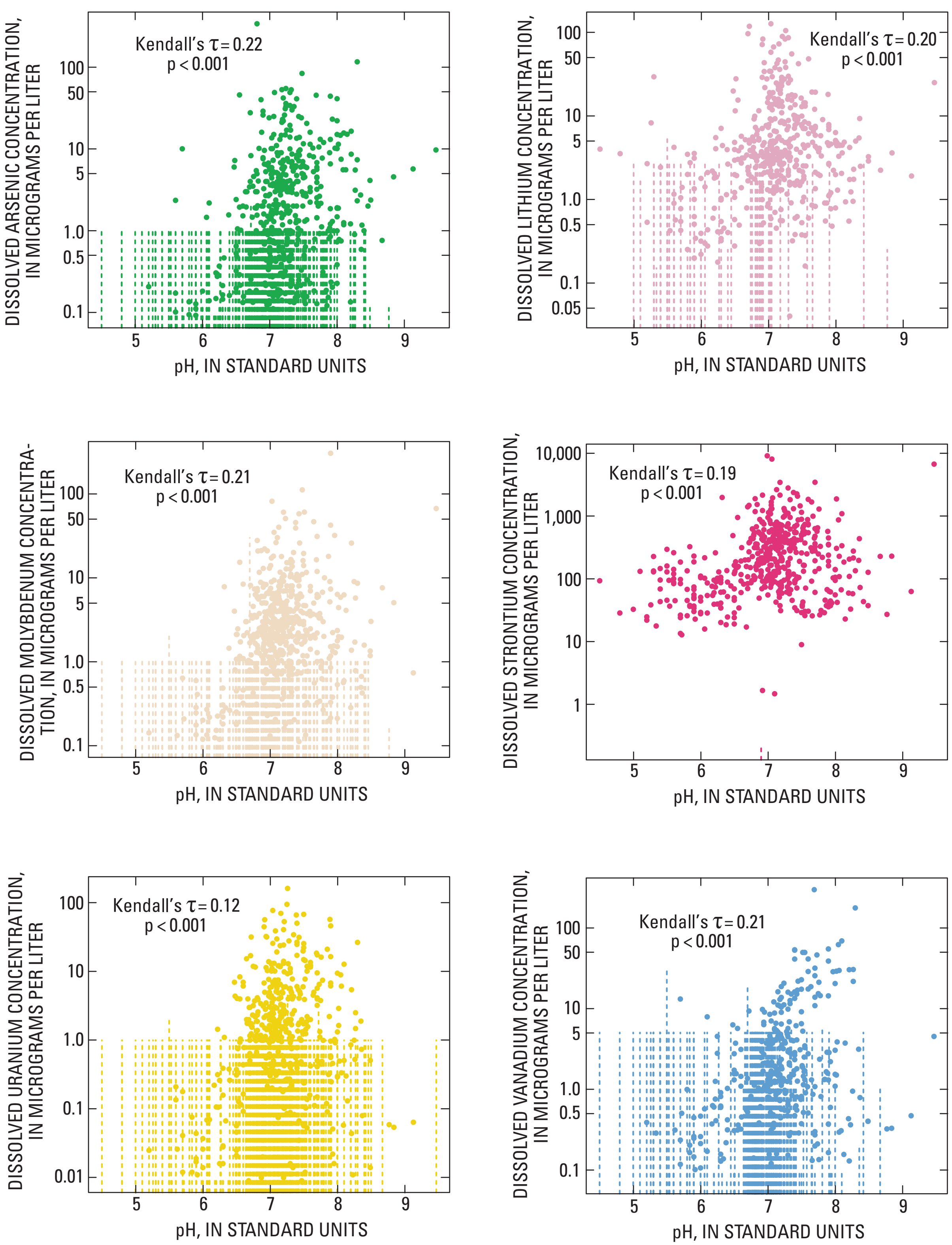


Figure 30. The relation between the concentrations of selected elements and pH for wells sampled in the glacial aquifer system. For censored results (those results below detection) the "true concentration" lies somewhere in the interval between zero and the reporting level, therefore, vertical dashed lines indicate censored element results.

Table 16. Nonparametric regression correlation coefficients (Kendall's tau) and associated p-values for the relations between selected element concentrations and pH in samples from wells in the glacial aquifer system.

[Green cells indicate tau equal to or greater than 0.1; blue cells indicate $p < 0.05$]

Element	Tau	P-value
Arsenic	**0.22**	0.00
Barium	-.01	.61
Chromium	.04	.11
Cobalt	-.05	.03
Copper	-.08	.00
Iron	-.00	.95
Lead	-.05	.02
Lithium	**.20**	.00
Manganese	-.07	.00
Molybdenum	**.21**	.00
Nickel	-.06	.01
Selenium	.03	.12
Strontium	**.19**	.00
Uranium	**.12**	.00
Vanadium	**.21**	.00
Zinc	-.02	.32

and sulfate concentration is less than 4 mg/L. Two additional categories are included here: "mixed" and "unknown." Mixed samples are those that have conflicting concentrations (for example, dissolved oxygen greater than 0.5 mg/L and iron concentration greater than 100 µg/L). Samples in the category "unknown" are those that have insufficient data available (unclassifiable), such as samples that are missing a dissolved oxygen value and have an iron concentration less than the detection limit. More than 80 percent of the samples in the mixed category had measured dissolved oxygen that, by itself, would have put those samples in the oxic category. The category "unknown" is not discussed further.

Figure 34 shows box plots of selected factors by redox category. Table 22 lists the p-values for pairwise tests of significant differences in medians of these factors by redox category. With respect to well depth, the methanic category wells are significantly deeper than all other categories. Next deepest are the wells in the Fe/SO_4 category. The other categories vary less and the differences among them are not as great as with the two most strongly reducing categories. There is little variation or significant differences among the redox categories with respect to pH or temperature. Some redox reactions, such as sulfide oxidation, generate hydrogen ions, whereas others consume them; however, there seems to be little indication in the glacial aquifer that there are important effects of redox on pH or vice versa. Alternatively, pH changes could be obscured by alkalinity buffering and(or) carbonate mineral dissolution. Bicarbonate concentration has more significant variation than pH among redox categories and it is highest in the methanic category, followed by the Fe/SO_4 and mixed categories. The production of methane can both consume CO_2 or bicarbonate or generate either, depending on the reaction and microorganisms involved (Stumm and Morgan, 1996). Dissolved organic carbon has a roughly similar pattern among redox categories as bicarbonate concentration and was highest in the methanic category. There were small differences among the redox categories with respect to residue on evaporation, but some differences in medians are significant.

As described previously (page 21; fig. 10), there is a correlation between iron and manganese concentrations in the glacial aquifer system because the two elements are geochemically similar and are redox sensitive. One reason the correlation may not be as robust as might be expected is that wells in the lirbsus1 MAS network have a median manganese concentration less than the median manganese concentration for the glacial aquifer system in spite of having the highest median iron concentration. Lirbsus1 is in the confined portion of the

Table 17. Nonparametric regression correlation coefficients (Kendall's tau) and associated p-values for the relations between selected element concentrations and dissolved organic carbon concentration in samples from wells in the glacial aquifer system.

[Green cells indicate tau equal to or greater than 0.1; blue cells indicate $p < 0.05$]

Element	Tau	P-value
Arsenic	**0.23**	0.00
Barium	**.22**	.00
Chromium	**.19**	.00
Cobalt	**.15**	.00
Copper	-.01	.82
Iron	**.18**	.00
Lead	-.04	.09
Lithium	**.19**	.00
Manganese	**.23**	.00
Molybdenum	**.28**	.00
Nickel	**.18**	.00
Selenium	.04	.12
Strontium	**.26**	.00
Uranium	**.14**	.00
Vanadium	**.19**	.00
Zinc	.06	.01

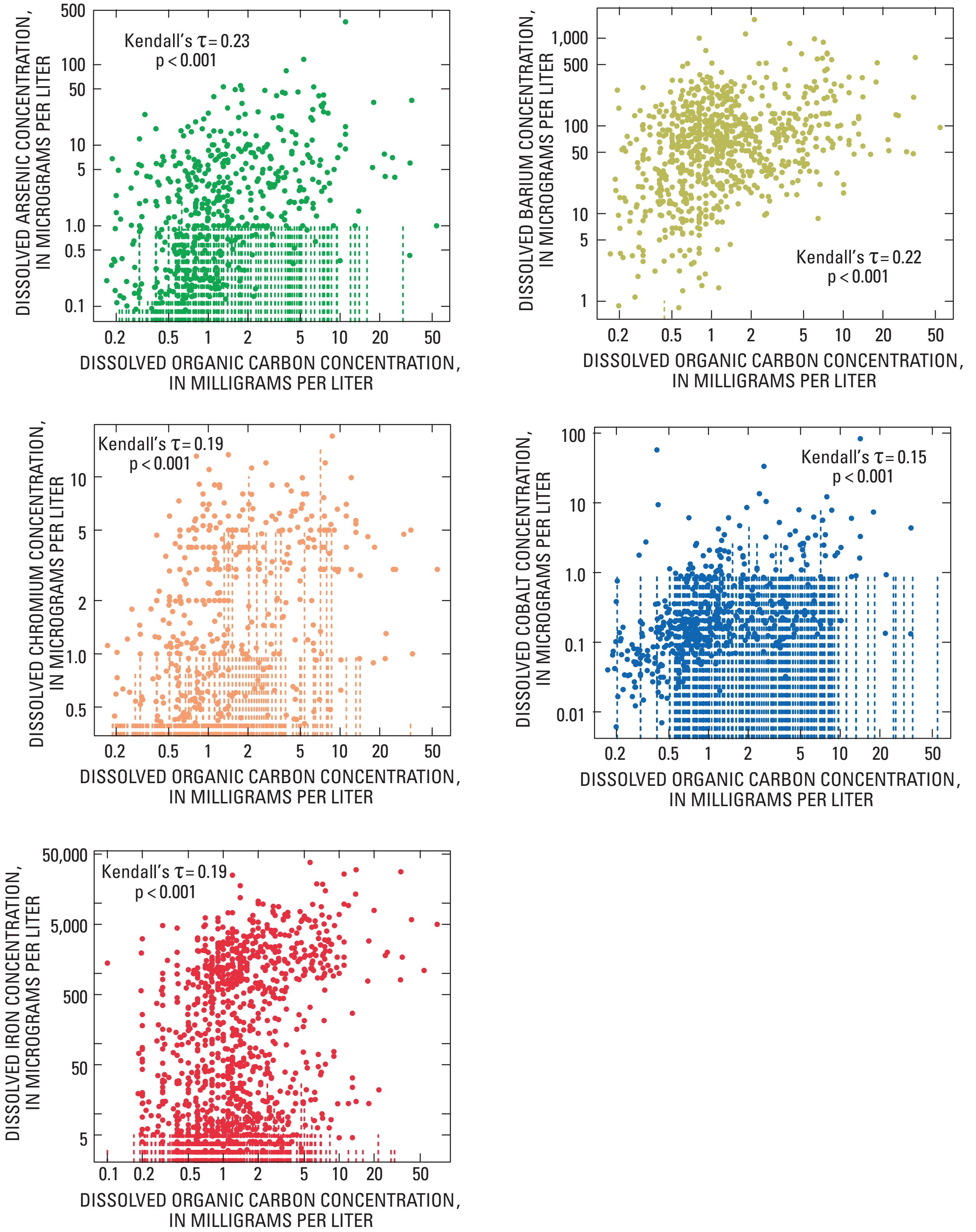


Figure 31. The relation between concentrations of selected elements and the concentration of dissolved organic carbon for wells sampled in the glacial aquifer system. For censored results (those results below detection) the "true concentration" lies somewhere in the interval between zero and the reporting level, therefore, vertical dashed lines indicate censored element result.

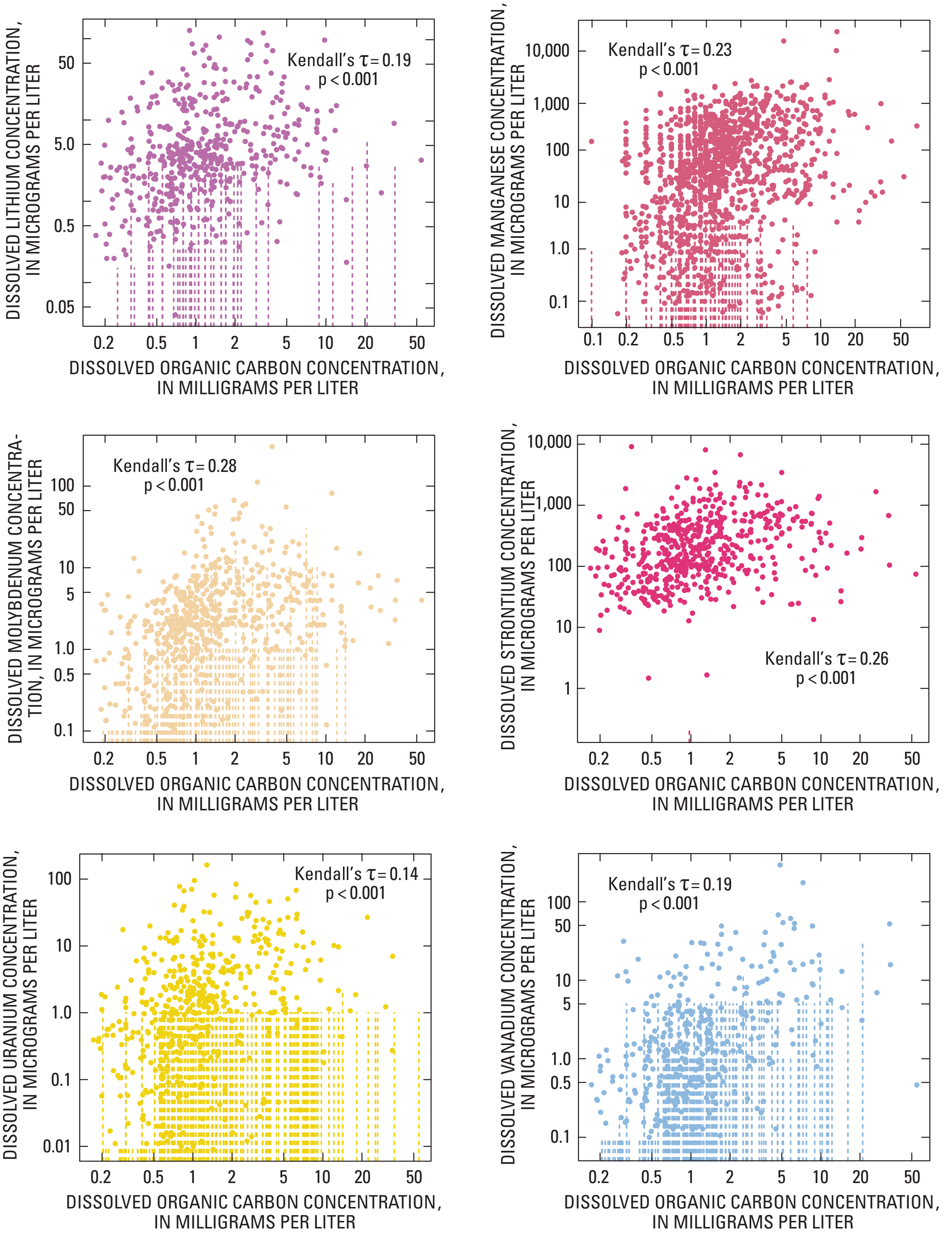


Figure 31. The relation between concentrations of selected elements and the concentration of dissolved organic carbon for wells sampled in the glacial aquifer system. For censored results (those results below detection) the "true concentration" lies somewhere in the interval between zero and the reporting level, therefore, vertical dashed lines indicate censored element result.—Continued

Table 18. Nonparametric regression correlation coefficients (Kendall's tau) and associated p-values for the relations between selected element concentrations and bicarbonate concentration in samples from wells in the glacial aquifer system.

[Green cells indicate tau equal to or greater than 0.1; blue cells indicate $p < 0.05$]

Element	Tau	P-value
Arsenic	**0.20**	0.00
Barium	**.35**	.00
Chromium	**.27**	.00
Cobalt	**.13**	.00
Copper	-.02	.50
Iron	**.15**	.00
Lead	-.06	.01
Lithium	**.40**	.00
Manganese	**.14**	.00
Molybdenum	**.35**	.00
Nickel	**.20**	.00
Selenium	**.11**	.00
Strontium	**.39**	.00
Uranium	**.24**	.00
Vanadium	**.22**	.00
Zinc	.06	.01

Mahomet aquifer in central Illinois, and most wells in the network are in the methanic redox category. Of the 69 glacial aquifer system wells in the methanic category, 25 are in the lirbsus1 network—36 percent of that category.

The distribution by redox category of wells sampled for trace elements is listed in table 23 and figure 35 shows box plot summaries of the distributions of barium and other selected elements with respect to redox categories. Barium is not a redox-sensitive element (it has only one common oxidation state in water). There are few significant differences among barium distributions for most of the categories, as would be expected for an element that is not redox sensitive. However, the barium distribution in the methanic redox category does appear to be significantly different from distributions in the other categories. This is likely, at least in part, because of the relatively large number of lirbsus1 wells in this category. As discussed previously, the geochemical environment in this aquifer is anoxic—lirbsus1 has the highest median iron of all glacial aquifer networks. Sulfate is readily reduced to sulfide through bacterial mediation (Kirk and others, 2004), thereby limiting the amount of sulfate in solution in much of the aquifer. Most of these wells are categorized as 'methanic' on the basis of high dissolved iron and low sulfate concentrations. However, dissolved hydrogen gas concentrations collected in all lirbsus1 wells in 2007 indicated that the predominant terminal electron-accepting process is sulfate reduction (dissolved H_2 concentrations of 4–6 nanomoles per liter). Kirk and others (2004) found that there is substantial methane produced in this aquifer. Lower sulfate concentrations enable dissolved barium to remain at a substantially higher concentration than it would be otherwise, assuming that there is a source of barium in the aquifer matrix. The saturation index of barite ($BaSO_4$) in the lirbsus1 well samples ranges from -0.02 (saturated) to -2.0 (very undersaturated). The solubility of barite likely limits the amount of barium in natural water (Hem, 1985). The four samples near barite saturation had measured sulfate concentrations of 6.6, 9.0, 21, and 33 mg/L). The remaining 26 samples, except for 3 with measurable sulfate (2.1, 2.5, and 7.1 mg/L), were very undersaturated, had no detectable sulfate, and had relatively high barium concentrations (greater than 100 µg/L, which is the mean concentration of barium in all glacial wells). Thus, even though barium itself is not redox sensitive, the anion in barite is controlled by redox and therefore does affect the barium concentration in at least one glacial aquifer network. Strontium is not affected by redox conditions as the p-values for the Peto and Peto tests in table 24 indicate. Ten of 15 pairwise comparisons show

Table 19. Nonparametric regression correlation coefficients (Kendall's tau) and associated p-values for the relations between selected element concentrations and residue on evaporation in samples from wells in the glacial aquifer system.

[Green cells indicate tau equal to or greater than 0.1; blue cells indicate $p < 0.05$]

Element	Tau	P-value
Arsenic	**0.16**	0.00
Barium	**.31**	.00
Chromium	**.19**	.00
Cobalt	**.14**	.00
Copper	.06	.01
Iron	.07	.00
Lead	-.03	.24
Lithium	**.37**	.00
Manganese	**.12**	.00
Molybdenum	**.29**	.00
Nickel	**.24**	.00
Selenium	**.12**	.00
Strontium	**.43**	.00
Uranium	**.27**	.00
Vanadium	**.17**	.00
Zinc	.09	.00

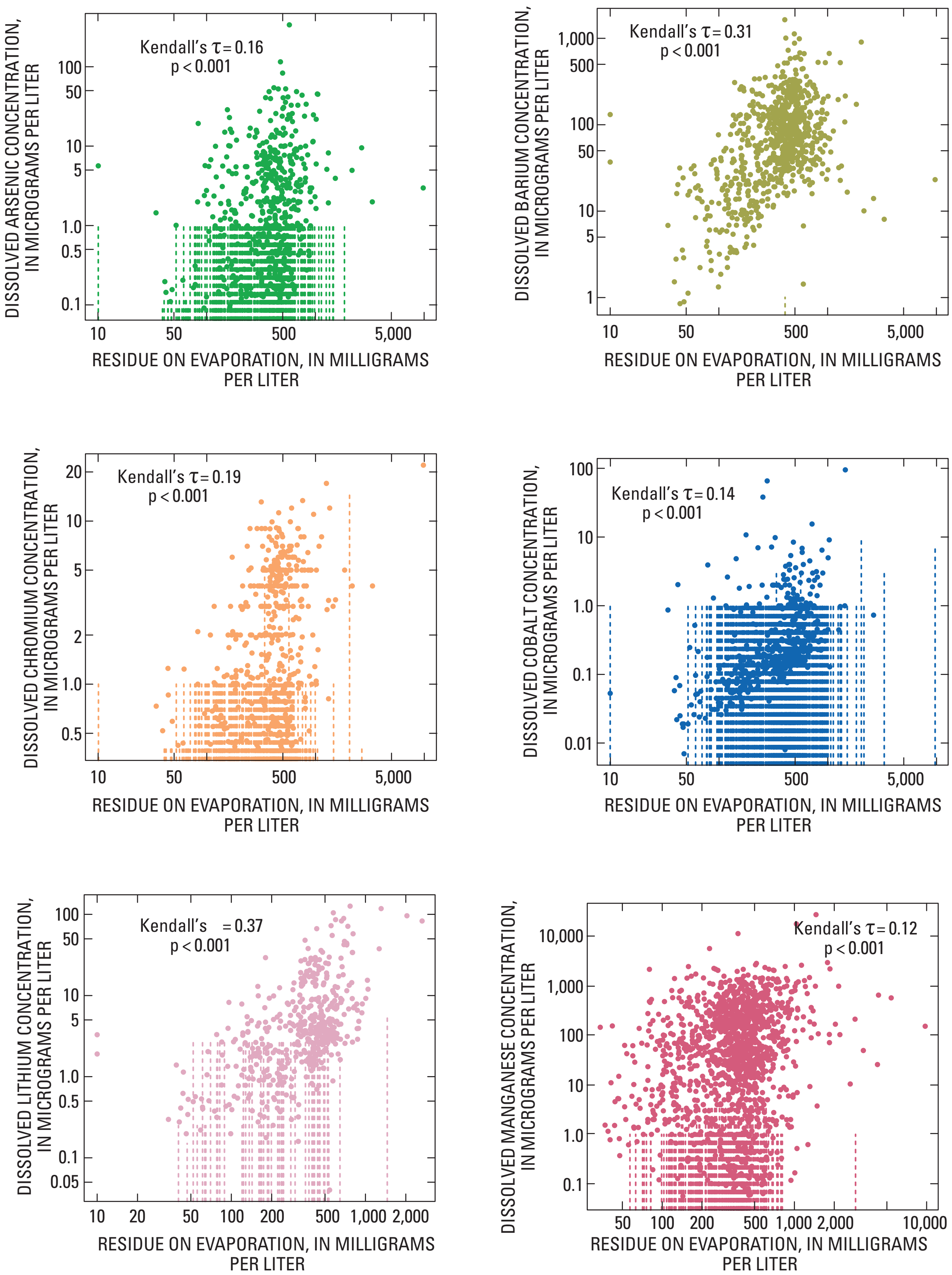


Figure 32. The relation between concentrations of selected elements and residue on evaporation for wells sampled in the glacial aquifer system. For censored results (those results below detection) the "true concentration" lies somewhere in the interval between zero and the reporting level, therefore, vertical dashed lines indicate censored element results.

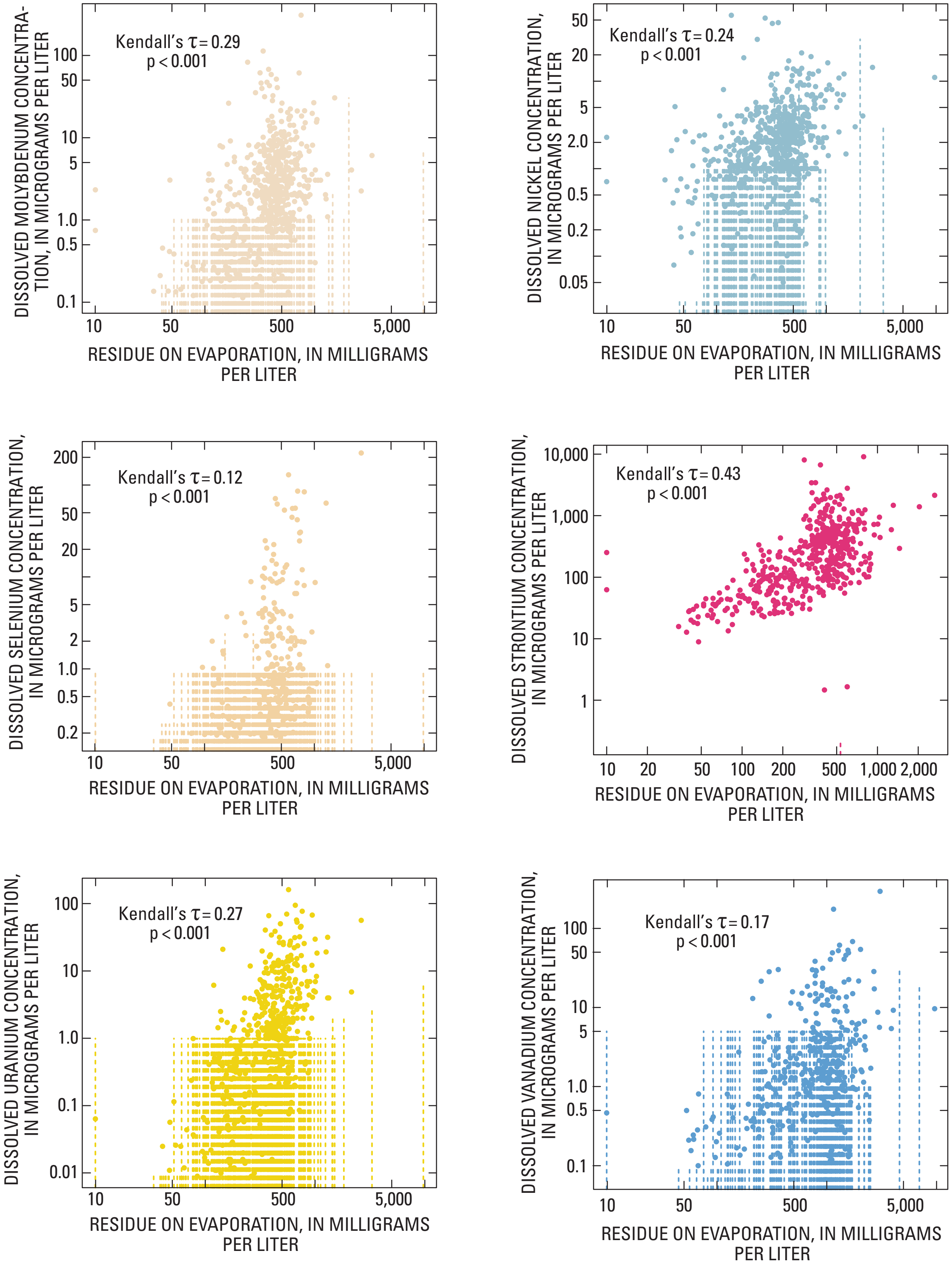


Figure 32. The relation between concentrations of selected elements and residue on evaporation for wells sampled in the glacial aquifer system. For censored results (those results below detection) the "true concentration" lies somewhere in the interval between zero and the reporting level, therefore, vertical dashed lines indicate censored element results.—Continued

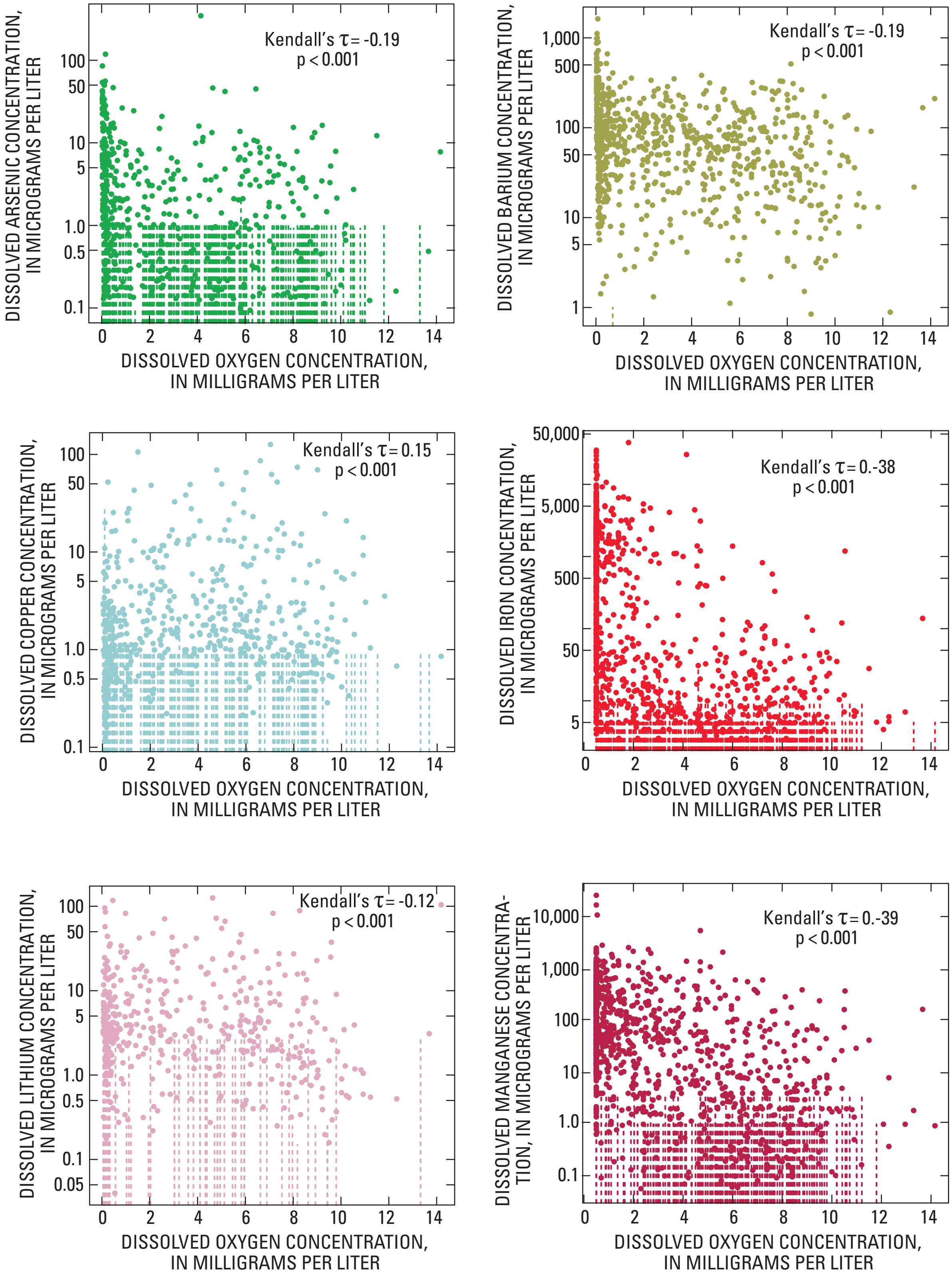


Figure 33. The relation between concentrations of selected elements and the concentration of dissolved oxygen for wells sampled in the glacial aquifer system. For censored results (those results below detection) the "true concentration" lies somewhere in the interval between zero and the reporting level, therefore, vertical dashed lines indicate censored element results.

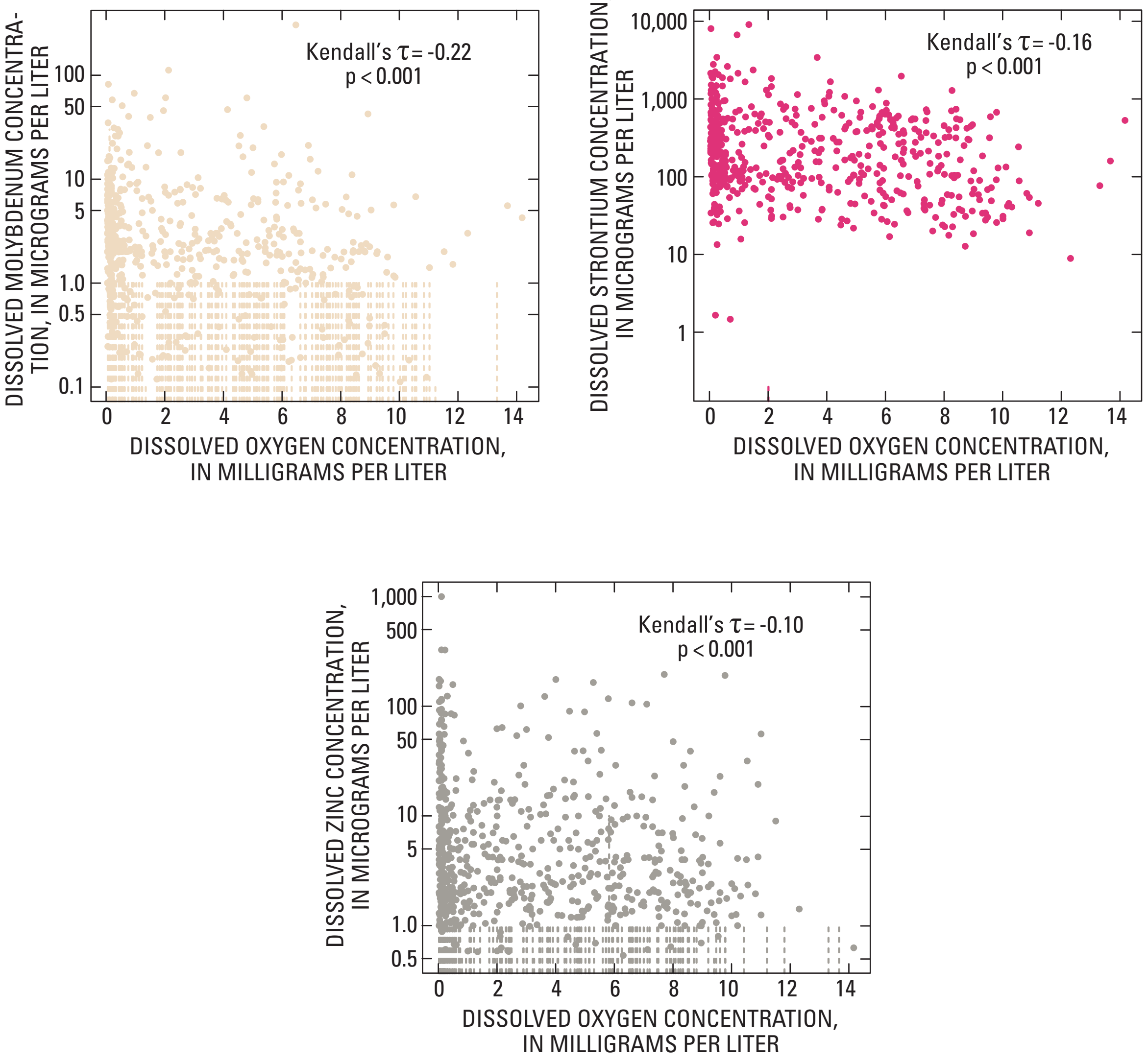


Figure 33. The relation between concentrations of selected elements and the concentration of dissolved oxygen for wells sampled in the glacial aquifer system. For censored results (those results below detection) the "true concentration" lies somewhere in the interval between zero and the reporting level, therefore, vertical dashed lines indicate censored element results.—Continued

no significant differences among the Sr distributions with respect to redox category. The lirbsus1 network samples were not analyzed for strontium, and therefore only eight samples constitute the methanic redox category.

Arsenic, chromium, cobalt, copper, molybdenum, selenium, uranium, and vanadium are considered to be redox sensitive elements. Figure 35 shows box plots for the element concentrations that are apparently significantly different by redox category regardless of whether they are considered redox sensitive. On the basis of the sum of significant differences between ecdf using the Peto and Peto test, the relative importance of redox category to trace element concentrations is

Cu > As > Co = Se > Ba = Cr = Mo > Ni = U > Sr = Pb > Li = V > Zn.

Copper has 13 out of 15 pairwise ecdf comparisons that are significantly different and zinc has 3. Zinc is last indicating that the other metals are more redox sensitive than it and this is in agreement with conventional notions that it is not redox sensitive. That uranium (6 significantly different out of 15 redox ecdf comparisons) and vanadium (4 of 15) appear to be relatively insensitive to redox was not expected. Most of the remaining elements; cobalt, selenium, barium, chromium, and molybdenum, have 8 or 7 significant differences in pairwise ecdf comparisons among redox categories so the exact order in the above list may not be relevant. The p-values and box plots indicate that there are a few significant differences in the element concentrations among the six redox categories. Barium, nickel, lithium and zinc ions have only one common oxidation state in water. The

Table 20. Nonparametric regression correlation coefficients (Kendall’s tau) and associated p-values for the relations between selected element concentrations and dissolved oxygen concentration in samples from wells in the glacial aquifer system.

[Gray cells indicate tau equal to or less than -0.1; blue cells indicate $p < 0.05$; green cells indicate tau equal to or greater than 0.1]

Element	Tau	P-value
Arsenic	**-0.19**	0.00
Barium	**-.19**	.00
Chromium	-.00	.93
Cobalt	-.06	.01
Copper	**.15**	.00
Iron	**-.38**	.00
Lead	.03	.20
Lithium	**-.12**	.00
Manganese	**-.39**	.00
Molybdenum	**-.22**	.00
Nickel	-.03	.21
Selenium	.09	.00
Strontium	**-.16**	.00
Uranium	.00	.89
Vanadium	.08	.01
Zinc	**-.10**	.00

fact that barium, nickel, and lithium exhibit redox sensitivity at all, and for barium and nickel greater sensitivity than elements that are considered redox sensitive, is unexpected. The “sensitivity” of barium can be explained by its sulfate-related chemistry. Sulfate is highly redox sensitive (see page 60). Nickel and lithium may have associations with other redox sensitive ions or minerals but characterizing those relationships is beyond the scope of this report. The arsenic concentrations shown in the box plot for the methanic category are highest (fig. 35). Reduced arsenite (AsIII) may be more soluble in the glacial aquifer system than the oxidized (AsV) species (Thomas, 2007). Most other redox category arsenic distributions are significantly different. The cobalt plot in figure 35 and the p-values in table 24 do not show substantial differences. Chromium does show one outstanding difference—the methanic category has the highest concentrations. This result may reflect the influence of the lirbsus1 well network, which has the highest chromium median in the glacial wells, on the relatively small subset of samples in the methanic category. There were 47 samples analyzed for chromium in the methanic category, and 31 of these (66 percent) are from several Lower Illinois River Basin networks—all of which have median chromium concentrations higher than the median for all glacial wells. Whether redox conditions are affecting the chromium concentrations in these wells is not certain, but its apparent redox sensitivity is consistent with the higher solubility of chromium (III or II) than that of oxidized chromium (VI). These results may also be an artifact of the small subset of chromium samples in the methanic category (table 23).

Molybdenum concentrations (fig. 35) are significantly different between redox categories, but show only slight variations among the categories. The p-values for the pairwise group comparisons in table 24 confirm this—there are fewer pairwise comparisons that indicate significant differences than do not. The lack of significant differences among the six redox categories for nickel (table 24) is in agreement with nickel’s generally understood redox behavior—it has only one oxidation state as an aqueous ion. Strontium is similar in that it shows no pattern with respect to redox category. Uranium would theoretically be expected to be less soluble under reducing conditions; however, table 24 indicates that uranium in the methanic category is significantly different from uranium in all other categories. Though not shown in figure 35 because of the lack of significant differences among redox categories, uranium concentration is lowest in the methanic category. However, concentrations in the oxic category for uranium were not significantly different from those in any other category, except methanic.

The selenium concentrations in the Fe/SO_4 category (fig. 35) appear to be substantially different from those in the

Table 21. Concentration thresholds of constituents used to classify redox conditions of well samples from the glacial aquifer system.

[mg/L, milligram per liter; µg/L, microgram per liter; ≥, greater than or equal to; ns, not specified; <, less than]

Redox category[1]	Abbreviations used in this report	Oxygen, in mg/L	Nitrate, in mg/L	Manganese, in µg/L	Iron, in µg/L	Sulfate, in mg/L
Oxygen reducing	Oxic	≥ 0.5	ns	< 50	< 100	ns
Nitrate reducing	NO_3	< .5	≥ 0.5	< 50	< 100	ns
Manganese reducing	Mn	< .5	< .5	≥ 50	< 100	ns
Iron or sulfate reducing	Fe/SO_4	< .5	< .5	ns	≥ 100	≥ 4
Methanogenic	Methanic	< .5	< .5	ns	≥ 100	< 4

[1] Redox categories based on Paschke and others, 2007.

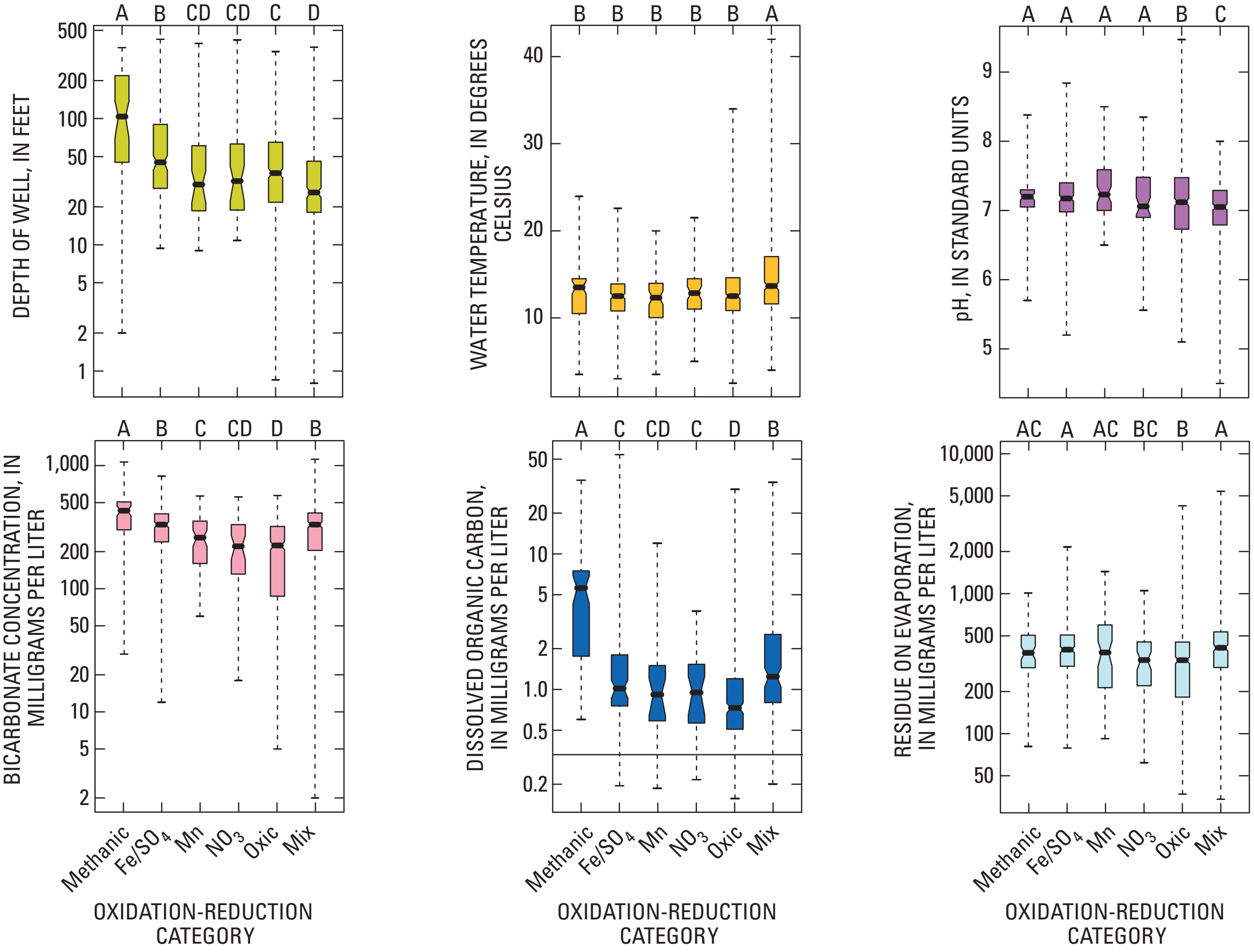


Figure 34. Selected factors by redox category for wells sampled in the glacial aquifer system. Boxes labeled with different letters have significantly different medians on the basis of Kruskal-Wallis tests or, for dissolved oxygen concentrations, significant differences between empirical cumulative distribution functions on the basis of Peto and Peto tests. Horizontal line indicates highest reporting level for dissolved oxygen. See figure 23 for explanation of box plots.

other categories; however, selenium was not commonly detected. In fact, the methanic category for selenium had insufficient detections (less than 20 percent for the category) to be significant and is not shown in the figure. Arsenic, chromium, molybdenum, and selenium can exist dissolved as oxyanions that are, in part, dependent on redox conditions. Because only total dissolved metals were measured by the analytical procedures, the effect of oxyanions with respect to redox category cannot be fully addressed here.

The implications of these redox results are that, even though these elements commonly exist in different oxidation states, with the exception of copper, arsenic, iron, and manganese concentrations, redox apparently does not substantially affect many concentrations of the total dissolved elements in the glacial aquifer system. Alternatively, the analytical data collected (total dissolved element) or the range of redox conditions sampled is insufficient to discriminate redox sensitivity of these elements on the basis of the redox categories as used in this report.

Elements and Environmental Factors in a Human-Health Context

The occurrence and distribution of the elements are discussed in this section with respect to the environmental factors with which they are associated. This is a step to an assessment of the potential human-health implications of the occurrence of these elements in ground water. Table 25 lists the regulated and unregulated elements with their associated MCL or HBSL, when available.

Table 22. P-values for pairwise tests of significant differences in selected factors by redox category.

[Blue cells indicate $p < 0.05$; redox categories: Meth, methanic; $FeSO_4$; iron/sulfate reducing; Mn, manganese reducing; NO_3, nitrate reducing; O_2, oxygen reducing; mix, mixed redox indicators; ecdf, empirical cumulative distribution function]

Factor	Meth/ $FeSO_4$	Meth/ Mn	Meth/ NO_3	Meth/ O_2	Meth/ mix	$FeSO_4$/Mn	$FeSO_4$/NO_3	$FeSO_4$/O_2	$FeSO_4$/mix	Mn/NO_3	Mn/O_2	Mn/mix	NO_3/O_2	NO_3/mix	O_2/mix
	Kruskal/Wallis comparisons between medians														
Well depth	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	**0.97**	**0.48**	**0.06**	**0.39**	**0.09**	0.00
pH	**.92**	**.36**	**.46**	**.16**	.00	**.22**	**.50**	.02	.00	**.17**	.01	.00	**.57**	**.09**	.00
Temperature	**.28**	**.21**	**.99**	**.83**	.01	**.39**	**.37**	**.25**	.00	**.18**	**.14**	.00	**.78**	.01	.00
Residue on evaporation	**.50**	**.61**	**.12**	.01	**.31**	**.66**	.00	.00	**.62**	**.15**	.01	**.65**	**.69**	.00	.00
Bicarbonate	.00	.00	.00	.00	.00	.00	.00	.00	**.54**	**.30**	.01	.03	**.30**	.00	.00
	Peto and Peto comparisons between ecdf														
Dissolved organic carbon	0.00	0.00	0.00	0.00	0.00	0.01	**0.09**	0.00	0.02	**0.47**	**0.28**	0.00	0.03	0.00	0.00

Table 23. Summary of glacial aquifer system wells sampled for iron, manganese, and selected trace elements in each redox category.

[See table 1 for list of elements]

Redox category	Number of wells sampled for iron and manganese	Percentage of all wells sampled for iron and manganese	Number of wells sampled for selected trace elements	Percentage of all wells sampled for selected trace elements
Mixed[1]	347	22	193	23
Oxic	527	33	313	37
NO_3	54	3.4	26	3.1
Mn	61	3.8	28	3.3
Fe/SO_4	279	18	117	14
Methanic	69	4.3	47	5.5
Unknown[2]	253	16	123	14

[1] "Mixed" are wells with conflicting redox-related data.

[2] "Unknown" are wells with insufficient data to determine the category.

Water-use data provide information about the potential for human exposure to elements through drinking-water consumption. Ground water from private-supply wells usually is consumed with little or no treatment; however, it is used by smaller numbers of people (typically one family per well) than ground water from public-supply wells (typically thousands of people per well). Ground water from public-supply wells may be treated before it is consumed, potentially reducing concentrations. Ground-water data from monitor wells are not directly relevant to human health because this water is not consumed, but contamination in monitor wells can be both a contributor to, and a predictor of, future contamination in deeper aquifers used for drinking-water sources. The concentrations from monitor wells are compared with human-health benchmarks in this report for context only.

The USEPA does not regulate private wells—only local public health agencies may have authority over private wells, and that authority varies by State. Only a small number of wells included in this study—93 of the 1,590 wells sampled for iron and manganese (and 88 wells of the subset of 847 wells sampled for trace elements)—are public-supply wells. However, none of the samples collected by the USGS for the NAWQA program are part of the USEPA regulatory program.

Assessing the implications of these element concentrations for human health is complicated because many of these elements are micronutrients (essential trace elements). Of all the elements discussed in this report, only arsenic, barium, lead, manganese, molybdenum, nickel, selenium, strontium, and uranium concentrations approach or exceed, their respective benchmark (table 26). The following paragraphs combine a screening level assessment by element with the patterns of environmental factors that are most likely to influence the element.

- Antimony concentration may have been greater than the MCL of 6 µg/L in only one well in the glacial aquifer system (in the Red River of the North Basin study unit). The reporting level for that analysis was 7 µg/L, so the actual concentration may have been higher than the MCL. Antimony was below detection in 79 percent of samples analyzed. The small number of detections indicates it may not be a human-health issue but also precludes any further interpretation of antimony occurrence in the glacial aquifer.

- Arsenic is included in the potential health implications of multiple trace elements occurring together (see section "Multiple Trace Elements in Wells"). Arsenic had a BQ greater than 1 in 72 wells (8.6 percent) and a BQ greater than or equal to 0.1 in 339 wells (41 percent). Arsenic occurrence is significantly related to well depth, has no significant relation to water use from wells, was significantly higher in agricultural and MAS wells than in urban wells, is significantly related to pH, bicarbonate concentration, DOC concentration, and dissolved solids and is strongly affected by redox condition (inversely related to dissolved oxygen and highest in strongly reducing environments). A separate report discussing arsenic in the glacial aquifer system of the Northern United States was recently released (Thomas, 2007). The results presented in this report are consistent with Thomas' (2007) conclusions.

- Barium was detected in all but one sample analyzed and at relatively high concentrations compared to other trace elements, but never exceeded the HBSL. Barium is not related to water use or well depth, is not significantly related to land use or well network type, is not related to pH, but is significantly and directly related to bicarbonate, DOC, and dissolved solids. It also is inversely related to dissolved oxygen and was significantly higher in strongly reducing conditions. However, this last result may reflect the dominance of one well network in the category of most strongly reducing conditions.

- Beryllium may have exceeded its MCL of 4 µg/L in only one well sample (Red River of the North Basin)—the laboratory reporting level was 7 µg/L for that analysis. Beryllium was below detection in 98 percent of samples analyzed. The low number of detections indicates it may not be a human-health issue but also precludes any further interpretation of occurrence.

- Cadmium was not detected widely, only 70 samples (12 percent) out of a total of 560 samples analyzed

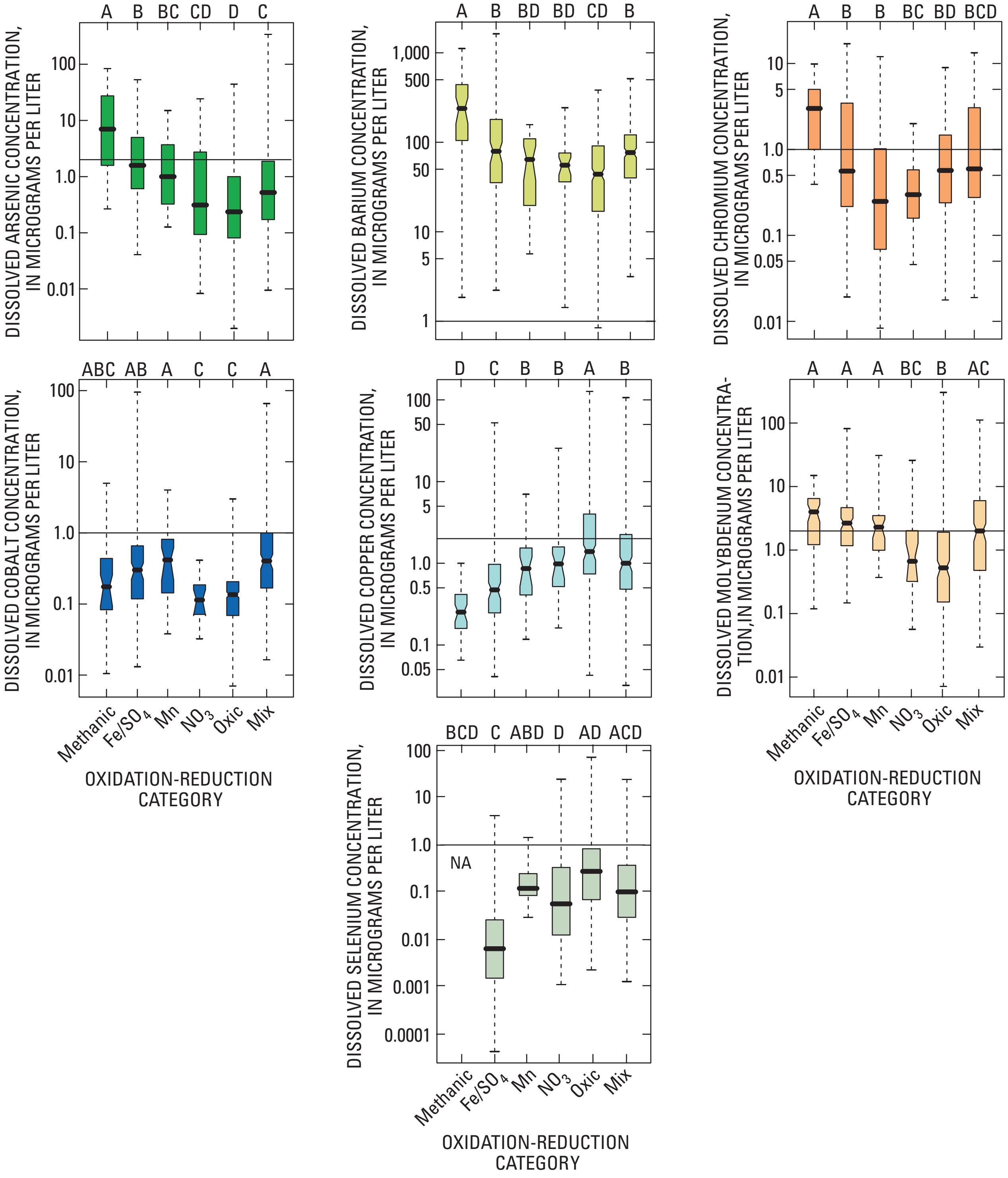


Figure 35. Concentrations of selected elements by redox category for wells sampled in the glacial aquifer system. Boxes labeled with different letters have significantly different empirical cumulative distribution functions on the basis of Peto and Peto tests. Horizontal line indicates highest reporting level for element. “NA” indicates insufficient data to plot. See figure 23 for explanation of box plots.

Table 24. P-values for pairwise Peto and Peto tests of significant differences in empirical cumulative distribution functions of element concentrations by redox category.

[Blue cells indicate $p < 0.05$; redox categories: Methanic, methanogenic; Fe/SO_4, iron/sulfate reducing; Mn, manganese reducing; NO_3, nitrate reducing; Oxic, oxygen reducing; mix, mixed redox indicators]

Arsenic	**Fe/SO_4**	**Mn**	**NO_3**	**Oxic**	**Mix**
Methanic	0.00	0.00	0.00	0.00	0.00
Fe/SO_4		**.27**	.01	.00	.00
Mn			**.20**	.00	**.05**
NO_3				**.27**	**.73**
Oxic					.00

Molybdenum	**Fe/SO_4**	**Mn**	**NO_3**	**Oxic**	**Mix**
Methanic	**0.30**	**0.17**	0.00	0.00	**0.12**
Fe/SO_4		**.40**	.00	.00	**.16**
Mn			.00	.00	**.84**
NO_3				**.17**	**.05**
Oxic					.00

Barium	**Fe/SO_4**	**Mn**	**NO_3**	**Oxic**	**Mix**
Methanic	0.00	0.00	0.00	0.00	0.00
Fe/SO_4		**.11**	**.10**	.00	**.69**
Mn			**.90**	**.28**	**.12**
NO_3				**.29**	**.09**
Oxic					.00

Nickel	**Fe/SO_4**	**Mn**	**NO_3**	**Oxic**	**Mix**
Methanic	**0.18**	**0.86**	**0.69**	**0.98**	0.00
Fe/SO_4		**.33**	**.57**	.02	.00
Mn			**.77**	**.97**	.00
NO_3				**.58**	.01
Oxic					.00

Chromium	**Fe/SO_4**	**Mn**	**NO_3**	**Oxic**	**Mix**
Methanic	0.00	0.00	0.00	0.00	0.00
Fe/SO_4		**.72**	**.10**	**.28**	**.14**
Mn			**.22**	**.24**	**.19**
NO_3				.01	.01
Oxic					**.38**

Selenium	**Fe/SO_4**	**Mn**	**NO_3**	**Oxic**	**Mix**
Methanic	**0.20**	**0.24**	**0.07**	0.00	0.04
Fe/SO_4		.00	.00	.00	.00
Mn			**.57**	.04	**.84**
NO_3				**.17**	**.69**
Oxic					.00

Cobalt	**Fe/SO_4**	**Mn**	**NO_3**	**Oxic**	**Mix**
Methanic	**0.26**	**0.13**	**0.48**	**0.08**	0.01
Fe/SO_4		**.27**	.02	.00	.00
Mn			.01	.00	**.43**
NO_3				**.48**	.00
Oxic					.00

Strontium	**Fe/SO_4**	**Mn**	**NO_3**	**Oxic**	**Mix**
Methanic	**0.57**	**0.69**	**0.67**	**0.68**	**0.84**
Fe/SO_4		**.81**	.03	.00	.00
Mn			**.08**	.02	.02
NO_3				**.96**	**.62**
Oxic					**.24**

Copper	**Fe/SO_4**	**Mn**	**NO_3**	**Oxic**	**Mix**
Methanic	0.00	0.00	0.00	0.00	0.00
Fe/SO_4		.01	.00	.00	.00
Mn			**.75**	.01	**.39**
NO_3				.04	**.79**
Oxic					.00

Uranium	**Fe/SO_4**	**Mn**	**NO_3**	**Oxic**	**Mix**
Methanic	0.00	0.00	0.01	0.00	0.00
Fe/SO_4		**.05**	**.49**	**.72**	**.08**
Mn			.04	**.07**	**.46**
NO_3				**.48**	**.13**
Oxic					**.06**

Lead	**Fe/SO_4**	**Mn**	**NO_3**	**Oxic**	**Mix**
Methanic	**0.08**	**0.48**	**0.77**	**0.20**	**0.94**
Fe/SO_4		.00	.01	.00	.04
Mn			**.60**	**.87**	**.15**
NO_3				**.26**	**.60**
Oxic					.00

Vanadium	**Fe/SO_4**	**Mn**	**NO_3**	**Oxic**	**Mix**
Methanic	0.03	**0.05**	**0.17**	**0.72**	**0.17**
Fe/SO_4		**.16**	**.93**	.01	**.36**
Mn			**.22**	.05	**.11**
NO_3				**.21**	**.72**
Oxic					.03

Lithium	**Fe/SO_4**	**Mn**	**NO_3**	**Oxic**	**Mix**
Methanic	**0.77**	**0.56**	**0.53**	**0.58**	**0.86**
Fe/SO_4		**.71**	.01	.00	**.07**
Mn			.02	.01	**.12**
NO_3				**.67**	**.16**
Oxic					**.10**

Zinc	**Fe/SO_4**	**Mn**	**NO_3**	**Oxic**	**Mix**
Methanic	**0.38**	**0.08**	**0.14**	0.00	0.03
Fe/SO_4		**.17**	**.30**	.01	**.18**
Mn			**.68**	**.81**	**.51**
NO_3				**.78**	**.75**
Oxic					**.24**

Table 25. Selected element drinking-water standards and Health-Based Screening Levels, in micrograms per liter.

[MCLs are U.S. Environmental Protection Agency Maximum Contaminant Levels; HBSLs are U.S. Geological Survey Health-Based Screening Levels; --, not available]

Element	Human-health benchmark[1]	
	Benchmark value	Type
Antimony (Sb)	6	MCL
Arsenic (As)	10	MCL
Barium (Ba)	2,000	MCL
Beryllium (Be)	4	MCL
Cadmium (Cd)	5	MCL
Chromium (Cr)	100	MCL
Cobalt (Co)	--	--
Copper (Cu)	1,300	Action Level
Iron (Fe)	--	--
Lead (Pb)	15	Action Level
Lithum (Li)	--	--
Manganese (Mn)	300	HBSL
Molybdenum (Mo)	40	HBSL
Nickel (Ni)	100	HBSL
Selenium (Se)	50	MCL
Silver (Ag)	100	HBSL
Strontium (Sr)	4,000	HBSL
Thallium (Tl)	2	MCL
Uranium (U)	30	MCL
Vanadium (V)	--	--
Zinc (Zn)	2,000	HBSL

[1] Maximum Contaminant Levels values current as of August 2006 (U.S. Environmental Protection Agency, 2006a, accessed at *http://www.epa.gov/waterscience/criteria/drinking/dwstandards.pdf*). Health-Based Screening Levels values current as of April 10, 2008, (Toccalino and others, 2008, accessed at *http://water.usgs.gov/nawqa/HBSL/*).

had detectable concentrations of cadmium, but another 70 samples had estimated concentrations. Only one well (Red River of the North Basin) may have exceeded the cadmium MCL of 4 µg/L. That analysis is censored at 7 µg/L—the actual concentration may have been at or above the MCL. The low number of detections indicates it may not be a human-health issue but also precludes any further interpretation of occurrence.

- Chromium can exist as a trivalent (CrIII) or hexavalent ion (CrVI). The hexavalent form is much more toxic but is not as soluble in water as trivalent chromium and generally is found only at anthropogenically contaminated areas. Chromium (III plus VI) was detected in 52 percent of samples analyzed, although no sample exceeded the MCL for total chromium. Chromium was significantly different in each framework area—highest in the West-Central area and lowest in the East area. It was significantly higher in monitor wells than in drinking-water wells as a group and lowest in public-supply wells. While it is not significantly related to well depth, chromium was significantly lower in MAS wells than in LUS wells. Chromium has no significant relation to pH, but it did increase with increased bicarbonate, DOC, and dissolved solids concentrations. It is not significantly related to dissolved oxygen concentration although it was significantly higher in the most strongly reduced redox-categories and lowest in the most oxic.

- Cobalt was detected in 53 percent of samples analyzed. Cobalt has no available drinking-water benchmark (table 25). Similar to patterns of barium and chromium, cobalt was significantly different in all framework areas—highest in the West-Central area and lowest in the East area. Cobalt was significantly higher in monitor wells than in drinking-water supply wells, decreased with increasing well depth, and was significantly higher in LUS wells (both urban and agricultural) than in MAS wells. Cobalt concentrations are not related to pH; however, they increased with increased concentrations of bicarbonate and dissolved solids. Cobalt has no significant relation to dissolved oxygen concentration but was lowest in the most strongly oxic redox categories. It is considered a redox-sensitive element but it does not have a simple pattern among the redox categories.

- Copper and lead can be released from plumbing to tap water. Recent studies have indicated that alternatives to the use of chlorine for disinfection of drinking water, such as chloramine (monochloramine—NH_2Cl), can enhance the solubility of copper and lead in plumbing (Switzer and others, 2006). Copper was detected in 66 percent of samples analyzed but no sample exceeded the action level. Copper concentrations did not vary as significantly among the framework areas as most other elements but were slightly higher in West-Central wells and lowest in Central wells. Concentrations also did not vary as widely among water-use categories but were lowest in monitor wells—unlike the pattern for most other trace elements. It has no important relation to well depth. It was slightly, but significantly, higher in MAS wells than in LUS wells and was lowest in urban wells. It is not related to pH or to bicarbonate, DOC, or dissolved solids concentrations. It is the only element that is directly correlated to dissolved oxygen concentration and is the most redox sensitive element of those examined in this report. It was significantly different in most redox categories—

Table 26. Summary of benchmark quotients for well samples.

[Listed in descending order of percentage of wells sampled with a benchmark quotient greater than or equal to 0.1]

Element	Number of wells sampled	Samples with benchmark quotient greater than or equal to 0.1		Samples with benchmark quotient greater than 1	
		Number	Percentage of wells sampled	Number	Percentage of wells sampled
Manganese	1,590	827	52	290	18
Arsenic	833	339	41	71	8.5
Molybdenum	847	198	23	14	1.6
Uranium	832	162	19	20	2.4
Strontium	552	157	28	3	.5
Barium	847	118	14	0	0
Selenium	833	46	5.5	11	1.3
Nickel	847	33	3.9	0	0
Lead	847	19	2.2	0	0
Chromium	839	12	1.4	0	0
Thallium	480	4	.8	0	0
Zinc	847	4	.5	0	0
Cadmium	847	3	.4	0	0
Beryllium	847	1	1.2	0	.0

lowest in the most strongly reducing category and highest in the most strongly oxic category.

- Iron was detected in 68 percent of samples analyzed but had the largest concentration (maximum, 38,100 µg/L; mean, 820 µg/L) and interquartile range (680 µg/L) of the all elements discussed. It varied widely by framework area—highest in the West-Central and Central areas and lowest in the West area. It was significantly higher in private water-supply wells than in either public-supply wells or monitor wells. It does not appear to be related to well depth and was higher in MAS wells than all LUS wells. Iron is not related to pH, but increased with increased bicarbonate and DOC concentrations, but not dissolved solids. It is strongly inversely correlated to dissolved oxygen concentration. It is considered strongly redox sensitive; however, that sensitivity could not be examined in detail with the available data.

- Lead, similar to copper, has an action level that is not to be exceeded at the tap (15 µg/L). It was detected in only 26 percent of samples analyzed, and the action level was not exceeded in any of the wells sampled. However, two samples from the Red River of the North study unit may have exceeded the action level of 15 µg/L. In these two samples from private wells, the reporting level was 30 µg/L. Lead was significantly different among the framework areas, but unlike most elements was highest in the East area and lowest in the Central area. It was highest in public-supply wells and lowest in monitor wells. It does not have a relation to well depth. It was highest in MAS wells and lowest in urban land-use wells. Lead is not related to pH or bicarbonate, dissolved solids, or dissolved oxygen concentrations, but did increase with increased DOC concentration. It is not considered redox sensitive, and the data do not indicate significant variation with respect to redox category.

- Lithium was detected at moderate concentrations, compared to the other elements, in 90 percent of samples analyzed. It has no drinking-water benchmark (table 25). Lithium varied significantly and substantially among the framework areas—highest in the West-Central area and lowest in the East area. There was little significant difference in concentrations among the water-use categories, but lithium did increase significantly with increased well depth. It varied slightly, but significantly, among land-use but not network type. It was highest in agricultural wells and lowest in urban wells. Lithium increased significantly with pH, but has no relation to bicarbonate concentration. It did, however, increase significantly with increased DOC and dissolved solids concentrations. It correlates inversely to dissolved oxygen although it is not considered a redox sensitive element. Lithium shows no significant variation with respect to redox categories.

- Manganese concentrations were greater than its HBSL of 300 µg/L in more samples (290) than any other element (table 26). Because manganese was detected in 86 percent of samples analyzed, and the high percentage of manganese concentrations greater than the HBSL, manganese is discussed further in the next section "Manganese' on page 74. It was highest in the West-Central area and lowest in the West area. Manganese was significantly different between private-supply and monitor wells and between drinking water-supply wells and monitor wells, but not between public-supply and monitor wells or public-supply and private-supply wells. It increased with increased well depth but varied only slightly among land uses. It was highest in urban wells and was not significantly different between network types. Manganese has no relation to pH; however, it increased with increased bicarbonate, DOC, and dissolved solids concentrations. Like iron, manganese is strongly inversely related to dissolved oxygen. Also similar to iron, it is considered redox sensitive; however, redox sensitivity, aside from the relation to dissolved oxygen could not be examined in detail with the available data.

- Molybdenum was detected in 72 percent of samples analyzed and exceeded the HBSL of 40 µg/L in only 5 samples. Molybdenum varied among framework areas—highest in the West-Central area and lowest in the East area. It varied significantly among water-use categories—highest in monitor wells and lowest in private-supply wells. It is not related to well depth. It was highest in agricultural land-use wells and lowest in urban wells. It increased with increased pH and bicarbonate, DOC, and dissolved solids concentrations. It decreased with increased dissolved oxygen concentration. It is considered a redox-sensitive element and varied significantly among redox categories—highest in the most strongly reducing and lowest in the oxic category, a pattern consistent with inverse correlation with dissolved oxygen.

- Nickel concentrations did not exceed the HBSL of 100 µg/L—the highest concentration was 56 µg/L. Nickel was detected in 82 percent of samples and varied significantly among all framework areas—highest in the West-Central area and lowest in the West area. The variations are not all significant, but nickel was highest in monitor wells and lowest in private-supply wells. Nickel concentrations decreased with increased well depth. It was higher in land-use wells than in MAS wells. It is not related to pH or DOC concentrations but did increase with increased bicarbonate and dissolved solids concentrations. It is not considered redox sensitive and shows no significant relation to dissolved oxygen and only slight differences among redox categories.

- Selenium concentrations exceeded the MCL of 50 µg/L in 11 samples. Three of these wells are private wells in the West-Central framework area, the rest are monitor wells in various land-use areas. Overall, selenium was detected in only 30 percent of samples analyzed. Selenium was significantly different among all framework areas—highest in the West-Central area and lowest in the East area. It was highest in monitor wells and significantly lower in private- and public-supply wells. It has no relation to well depth. It was highest in agricultural land-use wells and significantly lower in urban land-use wells and MAS wells. It is not related to pH or DOC concentrations, but increased slightly with increased bicarbonate and dissolved solids concentrations. It is considered redox sensitive; however, it has no significant relation to dissolved oxygen. It varied somewhat among redox categories—highest in the oxic category and lowest in the Fe/SO_4 reducing category—there were insufficient samples to completely characterize the methanic category for selenium.

- Silver was analyzed in 861 samples, but only one sample—in the Connecticut River Basin study unit—had a measurable concentration (0.38 µg/L). One other sample had an estimated concentration of 0.15 µg/L, but all other results for silver were below the reporting level and thus far below the MCL. The low number of detections indicates it may not be a human-health issue but also precludes any further interpretation of occurrence.

- Strontium was detected in all but one sample analyzed and at relatively high concentrations compared to most other elements. Five samples had concentrations greater than the HBSL of 4,000 µg/L. Strontium was highest in the West and West-Central framework areas and lowest in the East area, had no significant variation among water-use categories, and is not related to well depth. It was slightly but significantly higher in agricultural land-use wells than in urban wells or MAS wells. Strontium increased with increased pH and bicarbonate, DOC, and dissolved solids concentrations. This pattern is expected because of the similarity of its chemical behavior to that of calcium. Also like calcium, strontium is not considered redox sensitive; however, is has a significant inverse correlation to dissolved oxygen. It did not vary substantially with redox category.

- Thallium was detected in less than 14 percent of samples analyzed. No sample exceeded the MCL of 2 µg/L. The low number of detections indicates it may not be a human-health issue but also precludes any further interpretation of occurrence.

- Uranium was detected in less than two-thirds of samples analyzed and at low concentrations relative to those for other elements; however, it exceeded the MCL of 30 µg/L in three samples. Uranium concentration varied significantly among most framework areas—highest in the West and West-Central areas and lowest in the East area. Monitor wells had significantly higher uranium concentrations than the water-supply wells. Uranium is unrelated to well depth. It was highest in agricultural land-use wells and lowest in urban land use wells and MAS wells. It increased with pH and bicarbonate, DOC, and dissolved solids concentrations. Carbonate/bicarbonate ions form important soluble uranium complexes, and this behavior is consistent. Uranium is redox sensitive and would be expected to be directly correlated with dissolved oxygen; however, for the glacial aquifer, there is no significant relation between uranium and oxygen, nor significant differences among redox categories. Uranium is discussed in detail in another glacial aquifer system report (Ayotte and others, 2007).

- Vanadium was detected in 62 percent of samples analyzed and at relatively low concentrations. It has no drinking-water benchmark (table 25). Vanadium varied significantly and simply among the framework areas—highest in the West and decreasing monotonically to the East, where it was lowest. It was highest in monitor wells and lowest in public-supply wells. It is not related to well depth. It was highest in agricultural land-use wells than other land-use/network type groups and lowest in urban land-use wells. Vanadium increased with increased pH and bicarbonate, DOC, and dissolved solids concentrations. It is considered somewhat redox sensitive but has no relation to dissolved oxygen concentration and did not vary substantially among redox categories.

- Zinc was detected in 79 percent of samples analyzed; however, no well sample was greater than the HBSL of 2,000 µg/L. Similar to copper, zinc had limited variability among framework areas. It varied significantly among all water uses—highest in private-supply wells and lowest in monitor wells. It increased with increased well depth. It was higher in MAS wells than in land-use wells. It is not related to pH or bicarbonate, DOC, or dissolved solids concentrations. Zinc is not considered redox-sensitive but does have a significant inverse relation to dissolved oxygen concentration. It did not vary significantly among redox categories.

Manganese

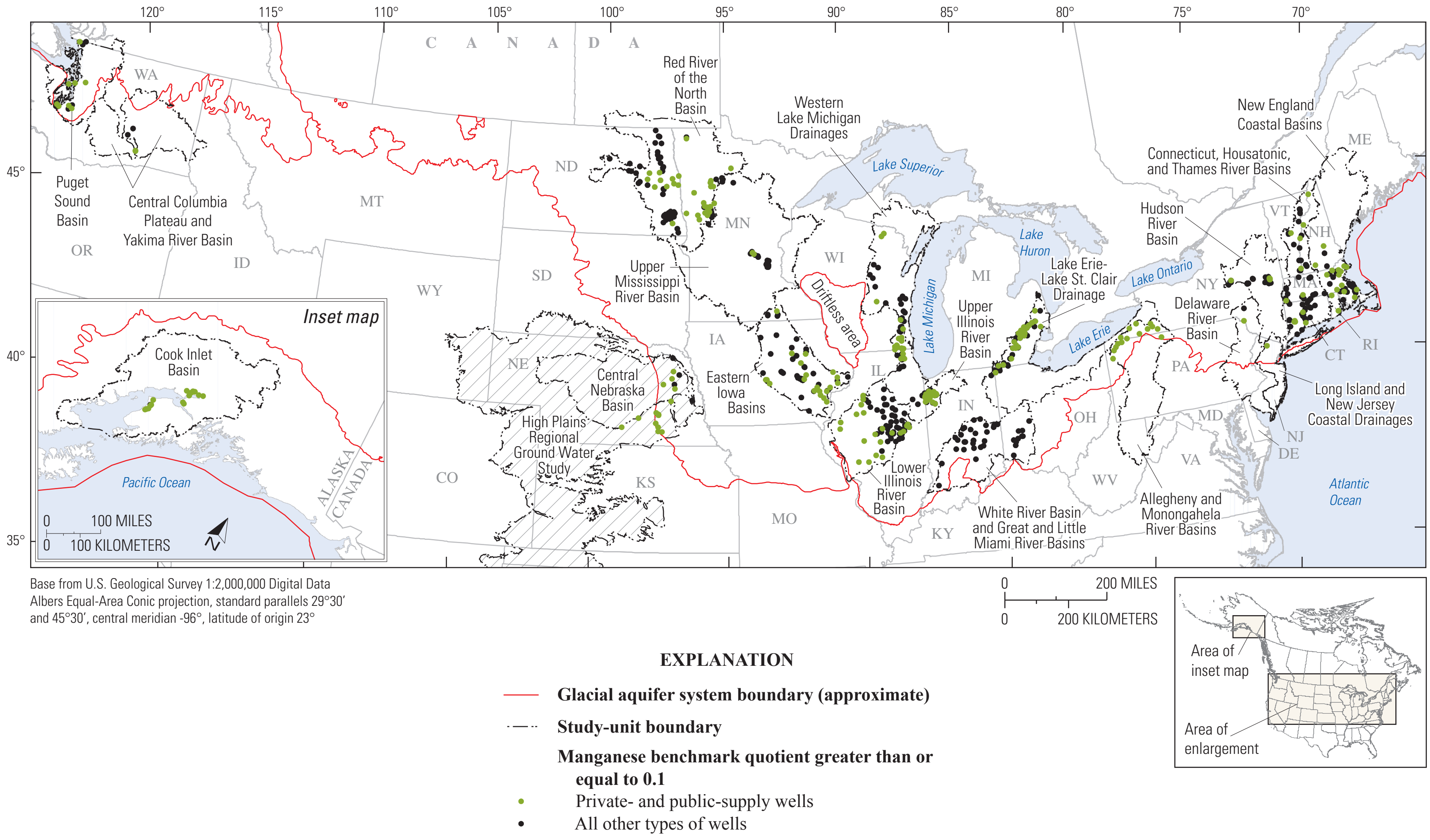
Manganese was detected in 1,349 of the 1,590 wells analyzed only for iron and manganese (85 percent). Manganese was detected in 761 in of the 847 wells sampled for the suite of trace elements (90 percent). The slightly higher detection rate is a result of lower detection levels for the manganese analyses associated with the suite of trace elements, especially those analyzed after 1997. A total of 827 samples (52 percent) had a BQ for manganese greater than or equal to 0.1 (fig. 36), and 290 samples (19 percent) had a BQ greater than 1 (fig. 37) of the 1,590 wells sampled for just iron and manganese. A total of 390 (46 percent) wells sampled for the suite of trace elements had manganese BQs greater than or equal to 0.1, and 103 (12 percent) had a manganese BQ greater than 1. A possible explanation why the wells sampled for manganese and iron had a larger proportion of manganese BQs or greater than 1 (and 0.1) than the wells sampled for the suite of trace elements is shown in figure 3 and table 6. The relative proportion of wells sampled differs for the Central and West-Central glacial framework areas between the set of wells sampled for iron and manganese and the set sampled for the suite of trace elements. The West-Central area had higher concentrations of manganese than Central area wells (fig. 23) and the West-Central area had a relatively larger portion of wells in the West-Central area than the Central area for wells sampled only for iron and manganese.

A BQ of 0.1 corresponds to a manganese concentration of 30 µg/L, and all laboratory reporting levels were much lower than this concentration. The USEPA Secondary MCL (SMCL) for manganese (U.S. Environmental Protection Agency, 2004a)) is 50 µg/L. Finally, of the larger set of sampled wells with manganese, 532, or 33 percent of all samples, were between BQs of 0.1 and 1. Therefore, 1 in 5 wells were at or above the manganese HBSL, and 1 in 3 of those that were below the HBSL had a manganese concentration at a level of potential concern.

By glacial framework area, the 290 wells that had a manganese BQ greater than 1 were distributed as follows: 58 of 329 (18 percent) were East area wells, 76 of 651 (12 percent) were Central wells, 152 of 443 (34 percent) were West-Central wells, and 4 of 167 (2 percent) were West-area wells. By water–use category, the wells that had a manganese BQ greater than 1 were distributed as follows: 233 of 1,001 (23 percent) were monitoring wells, 43 of 463 (9.3 percent) were private-supply wells, 12 of 93 (13 percent) were public-supply wells, and, 2 of 33 (6.1 percent) were other use wells. There was no significant relation between well depth and manganese BQ in part because there is no relation between water use and well depth. By network type, 88 of 609 (14 percent) of MAS wells had a manganese BQ greater than 1. LUS wells had a higher rate (202 of 981, or 20 percent) of BQs greater than 1.

Multiple Trace Elements in Wells

Of the wells sampled for the suite of trace elements, 196 had at least one trace element or manganese BQ greater than 1. Only one well had 3 elements (arsenic, molybdenum, and uranium) with BQs greater than 1—a monitoring well on agricultural land in Washington State (Central Columbia



Base from U.S. Geological Survey 1:2,000,000 Digital Data
Albers Equal-Area Conic projection, standard parallels 29°30′
and 45°30′, central meridian -96°, latitude of origin 23°

EXPLANATION

— **Glacial aquifer system boundary (approximate)**

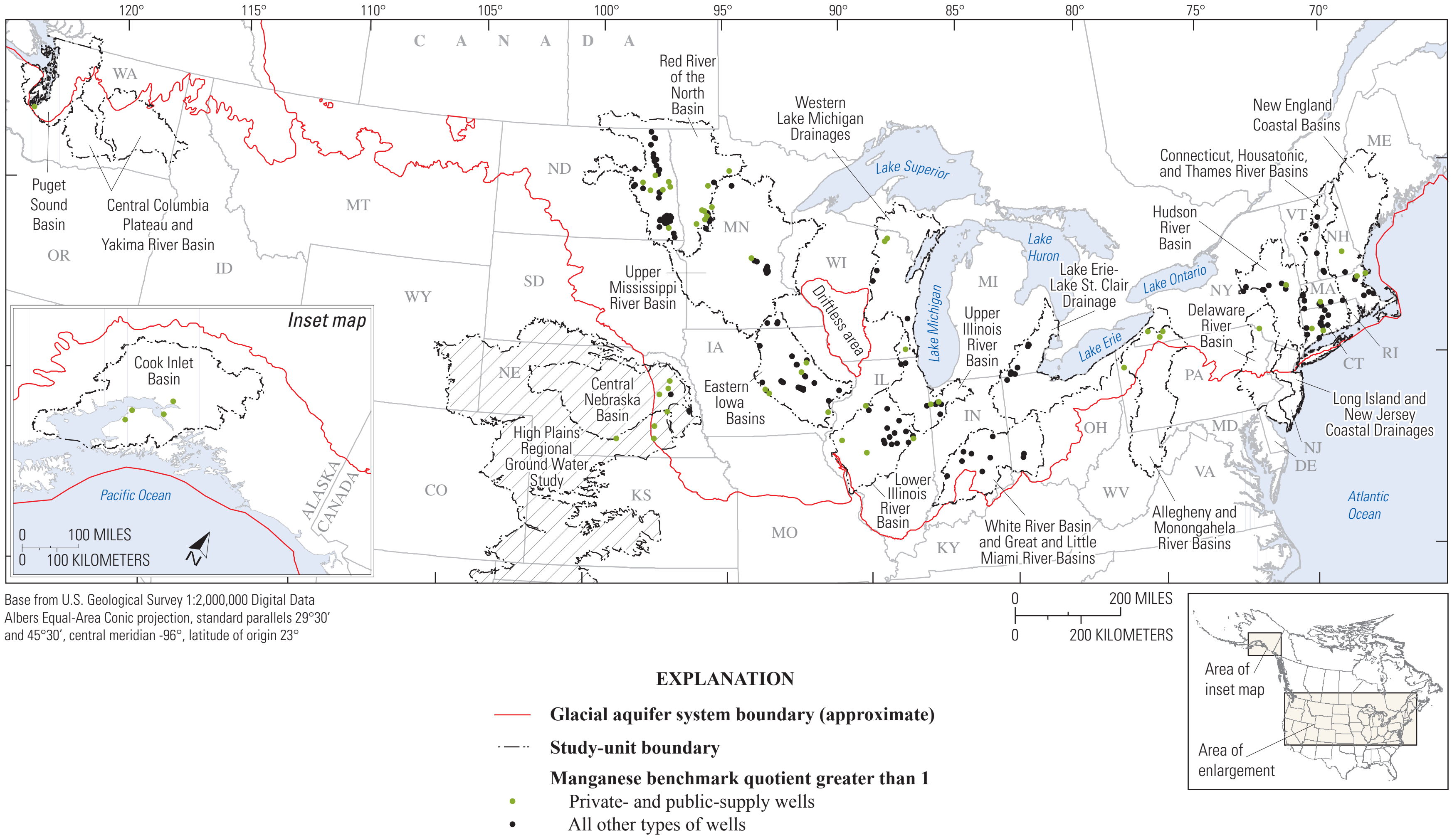
-·- **Study-unit boundary**

Manganese benchmark quotient greater than or equal to 0.1

● Private- and public-supply wells

● All other types of wells

Figure 36. The distribution of study wells in the glacial aquifer system with manganese benchmark quotients greater than or equal to 0.1.



Base from U.S. Geological Survey 1:2,000,000 Digital Data
Albers Equal-Area Conic projection, standard parallels 29°30′ and 45°30′, central meridian -96°, latitude of origin 23°

Figure 37. The distribution of study wells in the glacial aquifer system with manganese benchmark quotients greater than 1.

Plateau Basin study unit). There were 29 wells that had 2 elements with BQs greater than 1. These wells were distributed among the glacial framework areas as follows: 15 in the West-Central area (11 percent), 8 in the Central area (1.8 percent), 4 in the West area (4.5 percent), and 2 in the East area (1 percent). Of those wells with 2 BQs greater than 1, 17 are monitor wells (3.7 percent), 9 are private-supply wells (3.3 percent), and 3 are public-supply wells (3.4 percent).

Furthermore, of the 29 wells that had 2 elements with BQs greater than 1: 23 wells had arsenic, 18 had manganese, 5 had molybdenum, 5 had uranium, 4 had selenium, and 3 had strontium BQs greater than 1. For these wells the most common coincident elements with BQs greater than 1 were arsenic and manganese. Of the wells that were sampled for the suite of trace elements, 166 had just one element BQ greater than 1 (fig. 38). Of these, 88 samples had manganese—19 wells (10 percent) are in the East glacial framework area, 40 wells (9.2 percent) are in the Central area, 28 wells (20 percent) are in the West-Central area, and 1 well (1 percent) is in the West area. Of these 88 wells, 64 are monitor wells, 15 are private-supply wells, 8 are public-supply wells, 1 is in the “other” use category. Among the well samples with only 1 BQ greater than 1, 48 of the BQs were for arsenic—17 are from the West area, 3 are from the West-Central area, 2 are from the East area, and 26 are from the Central area (14 from lirbsus1); also, 19 were from monitor wells, 21 were from private-supply wells, 5 were from public-supply wells, and 3 were from wells in the category “other.”

Of the wells that were sampled for trace elements and had just one element BQ greater than 1, 15 had uranium BQs greater than 1. The distribution of these wells among glacial framework areas is as follows: 12 are in the West-Central area and 3 are in the West area. Of these, 10 are monitor wells, 2 are private-supply wells, and 3 are public-supply wells. Of the wells that were sampled for trace elements and had just one element BQ greater than 1, 8 had molybdenum BQs greater than 1; these 8 are monitor wells in the Central framework area.

Of the wells that had just one element BQ greater than 1, 7 had selenium BQs greater than 1. Of these wells, none were in the East framework area, 1 was in the Central area, 6 were West-Central area, and none were in the West area. Among water-use categories, 4 are monitor wells, 2 are private-supply wells, and 1 is a public-supply well. In summary, the West-Central area generally had the largest percentage of well samples with BQs greater than 1.

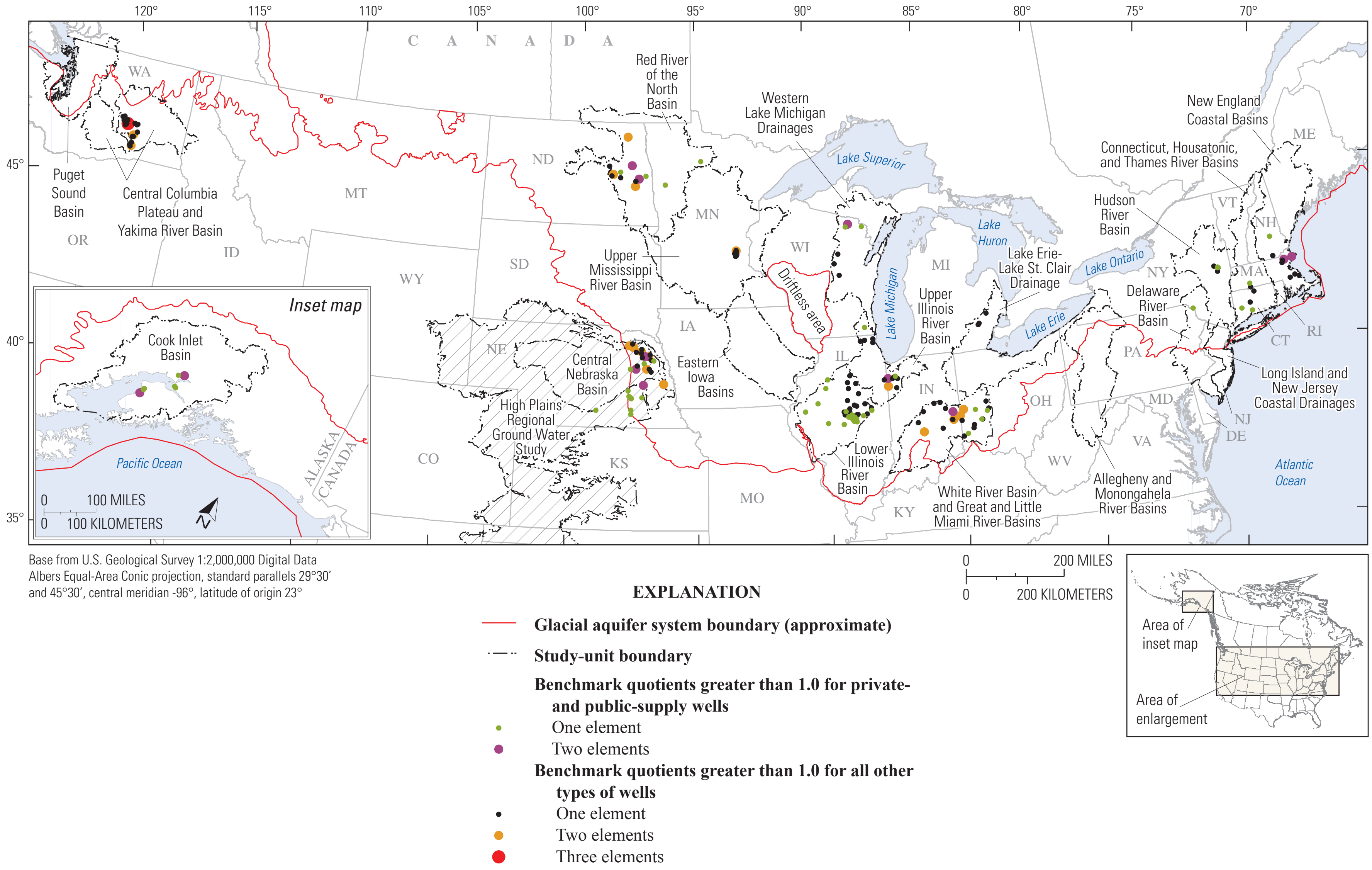
There were 665 wells that had BQs that were at a level of concern or greater (table 26). No well samples had such levels for antimony, chromium, copper, or silver. One monitor well in central Nebraska had 7 elements with BQs at or greater than the level of concern. Eleven wells—2 private-supply and 9 monitor—had 6 elements with BQs at or higher than the level of concern. Twenty-seven wells—4 private-supply, 4 public-supply, and 19 monitor—had 5 elements with such BQs.

Elements in Relation to Hydrochemical Regions and Transferability of Results

The development of hydrochemical regions in the glacial aquifer system by Arnold and others (2008) offers the opportunity for transferability of these results. There are far more wells for which major-ion analyses and ancillary environmental information are available than the set of wells discussed in this report. Relations developed among trace elements and the hydrochemical groups, or with alkalinity or other major group-defining factors, would potentially allow extrapolation of the results of this report to other areas of the glacial aquifer system that were not represented by the sample data. All elements except copper, iron, lead, and zinc were significantly related to bicarbonate (alkalinity), and those concentrations increased with increased alkalinity. Because bicarbonate (alkalinity) is a major component in the hydrochemical regions devised by Arnold and others (2008), it would follow that these elements should be closely correlated to the regions.

Hydrochemical regions (Arnold and others, fig. 39, 2008) were developed to statistically characterize geographic patterns of major ions and define general regions of similar water quality in the glacial aquifer system. The hydrochemical regions were based on major ion concentrations at the wells sampled and extrapolated to other areas by using combinations of environmental and hydrologic characteristics related to these concentrations (table 27). The hydrochemical regions have unique water-quality and physical characteristics that also may reflect distributions of trace elements, iron, and manganese in the glacial aquifer system. The generalities resulting from that extrapolation process will aid the transfer of the results in this report to unsampled areas in the glacial aquifer system that have the environmental data used to determine the hydrochemical regions. Barium, iron, lithium, manganese, molybdenum, and strontium varied significantly (95 percent confidence) among the two or more hydrochemical regions that were determined in a geospatial model (Arnold and others, 2008). Table 28 summarizes by hydrochemical region the distributions of glacial aquifer system wells that were sampled for iron, manganese, and trace elements.

Figure 40 shows box plots of selected environmental factors by hydrochemical region. Well depth is substantially different only between the Western Agricultural and Grassland Region (WAGR) and the Mountain and Coastal Forested Region (MCFR); however, there is little difference among most of the regions with respect to well depth. Table 29 lists the p-values for pairwise tests between regions by environmental factor. pH was highest in the Northern and Great Lakes Forested Region (NGLFR) and the WAGR and substantially lower in the MCFR—indicating the influence of well networks in the Northeastern United States in this region. As described previously, bicarbonate concentration was the largest among major ions across all the regions and showed wide variability; concentrations in each region were



Base from U.S. Geological Survey 1:2,000,000 Digital Data
Albers Equal-Area Conic projection, standard parallels 29°30′ and 45°30′, central meridian -96°, latitude of origin 23°

Figure 38. The distribution of study wells in the glacial aquifer system with benchmark quotients for one or more elements, aside from manganese, greater than 1.

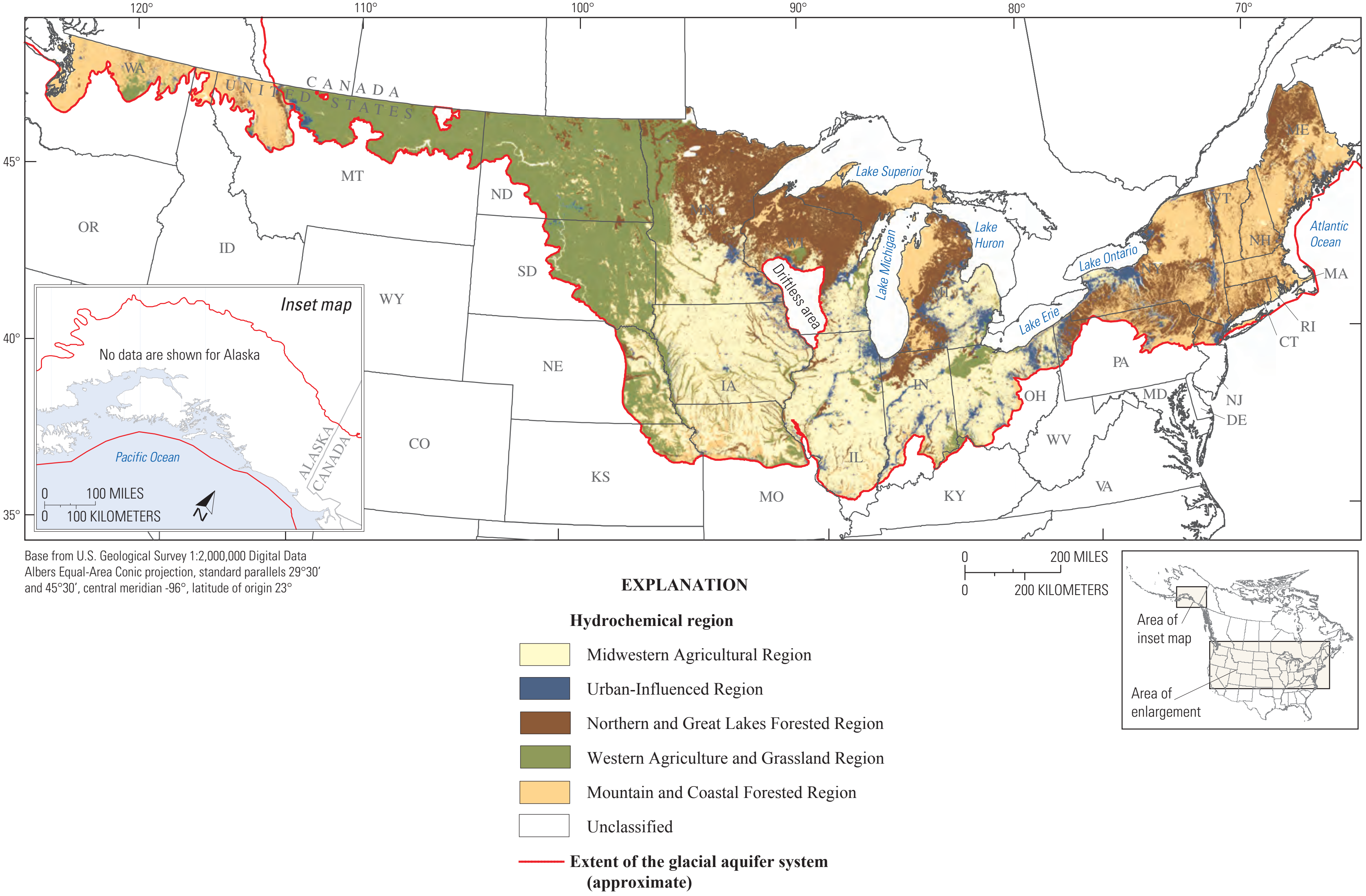


Figure 39. The location and extent of hydrochemical regions from Arnold and others (2008).

Table 27. Environmental and hydrologic characteristics considered in the hydrochemical region geospatial model.

[Modified from Arnold and others, 2008]

Environmental or hydrologic characteristic
Normal (1980–97) average annual precipitation, in centimeters
Normal (1980–97) average annual temperature, in degrees Celsius
Land surface slope, in percent
1990s land cover
Vertical soil permeability, in inches per hour
Soil clay content, in percent of material less than 2 millimeter in size
Texture of surficial deposits
Type of surficial deposit
Estimated annual natural ground-water recharge potential, in inches per year

significantly different from those in the other four. Bicarbonate was highest in the Midwestern Agricultural Region (MAR) and lowest in the MCFR. Bicarbonate concentration had more variation and more significant differences among regions than pH and therefore may be a better indicator of the buffering capacity of ground water. The ability of bicarbonate to maintain a near-neutral (7.0 ± 0.5 standard units) or slightly above neutral (between 7.5 and 8.5) pH can limit the solubility of many trace elements and affect the sorption of oxyanions containing trace elements (such as arsenic, chromium, selenium, molybdenum, and vanadium).

Dissolved oxygen concentration also varied substantially and somewhat significantly among regions (fig. 40). It was highest in the MCFR wells, slightly lower in the NGLFR wells, and much lower in the MAR, Urban-Influenced Region (UIR), and WAGR wells. As discussed previously, dissolved oxygen concentration can have a substantial effect on the concentrations of dissolved trace elements—generally those that are considered redox sensitive, but others as well. Although temperature was significantly different among all regions, the magnitude of the variation is not likely to be a cause for substantial variations in dissolved trace elements. Temperature was highest in the MAR, which includes many of the southernmost well networks (in Illinois and Indiana), and lowest in the NGLFR, which has many of the northernmost well networks (in Minnesota and Wisconsin)—well temperature reflects climate. DOC and, to a slightly lesser extent, residue on evaporation, have a similar pattern that also is exhibited by at least seven trace elements.

Figure 41 shows box plots of the concentrations of selected trace elements by hydrochemical region. P-values for Peto and Peto tests of significant differences between ecdfs are listed in table 30. The pattern exhibited by a series of elements—arsenic, lithium, molybdenum, selenium, strontium, uranium, and vanadium—is similar to that of DOC. The concentrations of the elements in this group were highest in the WAGR and progressively lower in the MAR, the UIR, the NGLFR, and the MCFR. Of these elements, arsenic, selenium, and uranium—all highest in the WAGR—may present potential health issues in drinking water. Barium, cobalt, and zinc had similar DOC-related patterns with some significant variations.

Another important aspect of the relations among element concentrations and hydrochemical regions is that neither iron nor manganese had as much variability or significant differences among regions as the trace elements. Iron and manganese had the largest ranges in concentrations across the glacial aquifer system and had large variations within and among well networks. However, dissolved oxygen concentration was highest in the MCFR (fig. 41), and iron and manganese were lowest in the MCFR.

Table 28. Summary of glacial aquifer system wells sampled for iron, manganese, and selected trace elements by hydrochemical region.

[See table 1 for list of elements. Hydrochemical regions from Arnold and others, 2008]

Hydrochemical region	Number of wells sampled for iron and manganese	Percentage of all wells sampled for iron and manganese	Number of wells sampled for selected trace elements	Percentage of all wells sampled for selected trace elements
Midwestern agricultural region (MAR)	480	30	266	31
Urban-influenced region (UIR)	269	17	156	18
Northern and Great Lakes forested region (NGLFR)	314	20	128	15
Western agricultural and grasslands region (WAGR)	229	14	116	14
Mountain and coastal forested region (MCFR)	255	16	139	16
Unclassifiable	43	3	42	5

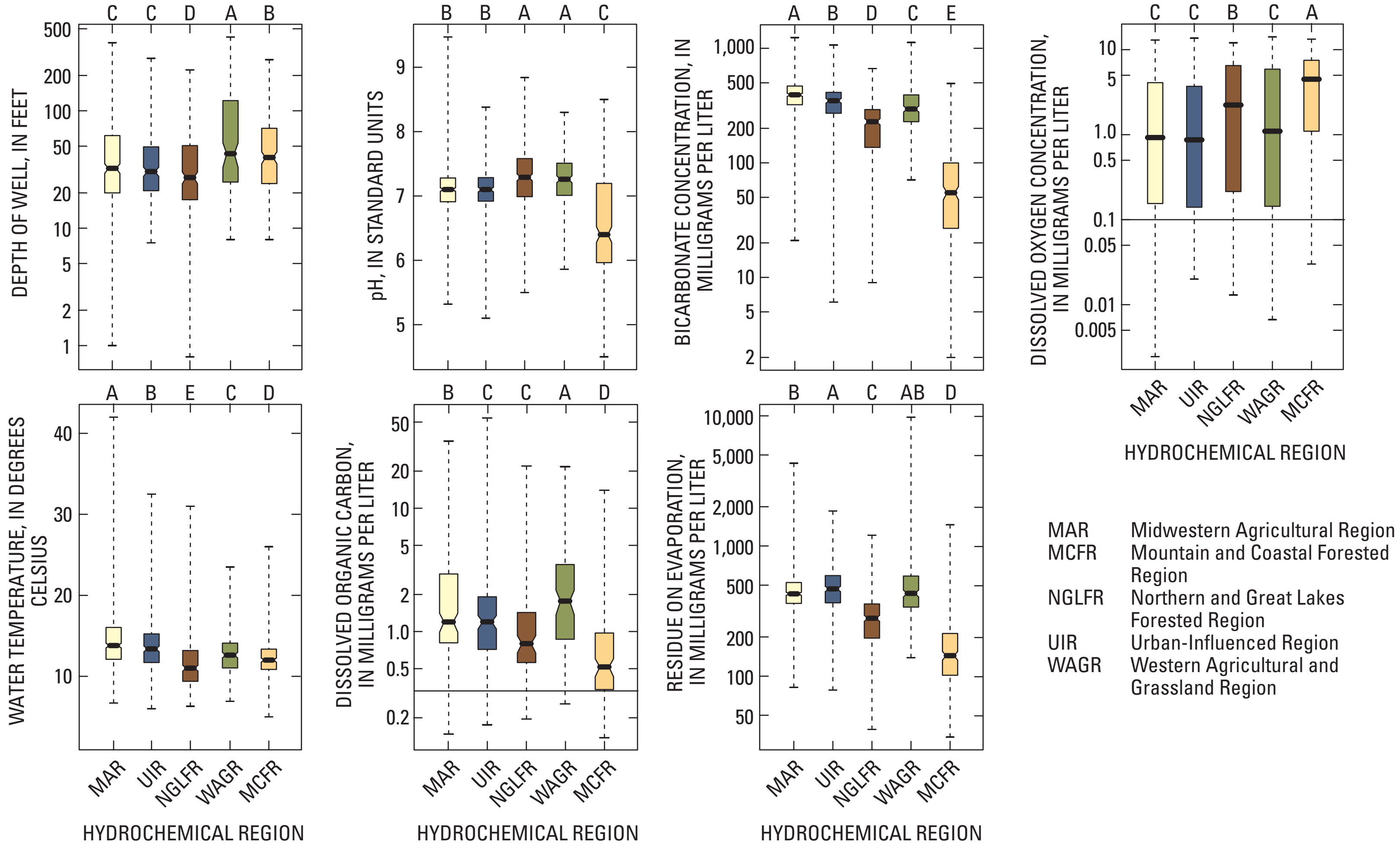


Figure 40. Selected factors by hydrochemical region for wells sampled in the glacial aquifer system. Boxes labeled with different letters have significantly different medians on the basis of Kruskal-Wallis tests or different empirical cumulative distribution functions on the basis of Peto and Peto tests (dissolved oxygen and organic carbon). Horizontal line indicates highest reporting level for dissolved oxygen or organic carbon concentration. See figure 23 for explanation of box plots.

Table 29. P-values for pairwise tests of significant differences among selected factors by hydrochemical region.

[Blue cells indcate p < 0.05; MAR, Midwestern Agricultural Region; UIR, Urban-Influenced Region; NGLFR, Northern and Great Lakes Forested Region; WAGR, Western Agriculture and Grassland Region; MCFR, Mountain and Coastal Forested Region; ecdf, empirical cumulative distribution function]

Factor	Paired hydrochemical regions									
	MAR/UIR	MAR/NGLFR	MAR/WAGR	MAR/MCFR	UIR/NGLFR	UIR/WAGR	UIR/MCFR	NGLFR/WAGR	NGLFR/MCFR	WAGR/MCFR
	Kruskal-Wallis comparisons between medians									
Well depth	**0.25**	0.00	0.00	0.01	0.02	0.00	0.00	0.00	0.00	0.04
pH	**.75**	.00	.00	.00	.00	.00	.00	**.50**	.00	.00
Temperature	.01	.00	.00	.00	.00	.00	.00	.00	.00	.02
Residue on evaporation	.01	.00	**.93**	.00	.00	**.08**	.00	.00	.00	.00
Bicarbonate	.00	.00	.00	.00	.00	.02	.00	.00	.00	.00
	Peto and Peto comparisons between ecdf									
Dissolved organic carbon	0.00	0.00	0.02	0.00	**0.75**	0.00	0.00	0.00	0.00	0.00
Dissolved oxygen	**.61**	.00	**.38**	.00	.00	**.24**	.00	.01	.00	.00

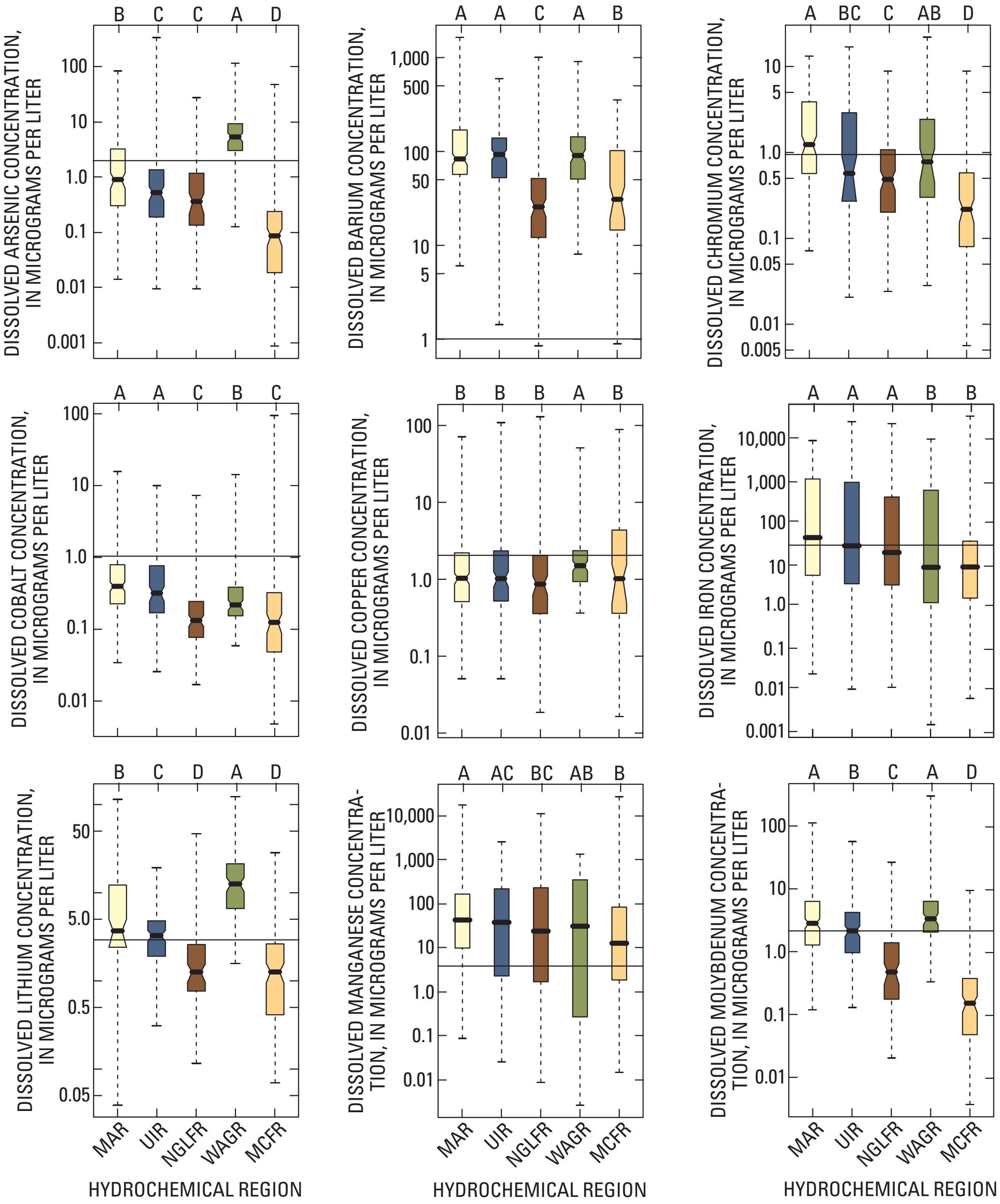


Figure 41. Concentrations of selected elements by hydrochemical region for wells sampled in the glacial aquifer system. Boxes labeled with different letters have significantly different empirical cumulative distribution functions on the basis of Peto and Peto tests. Horizontal line indicates highest reporting level for element. See figure 23 for explanation of box plots.

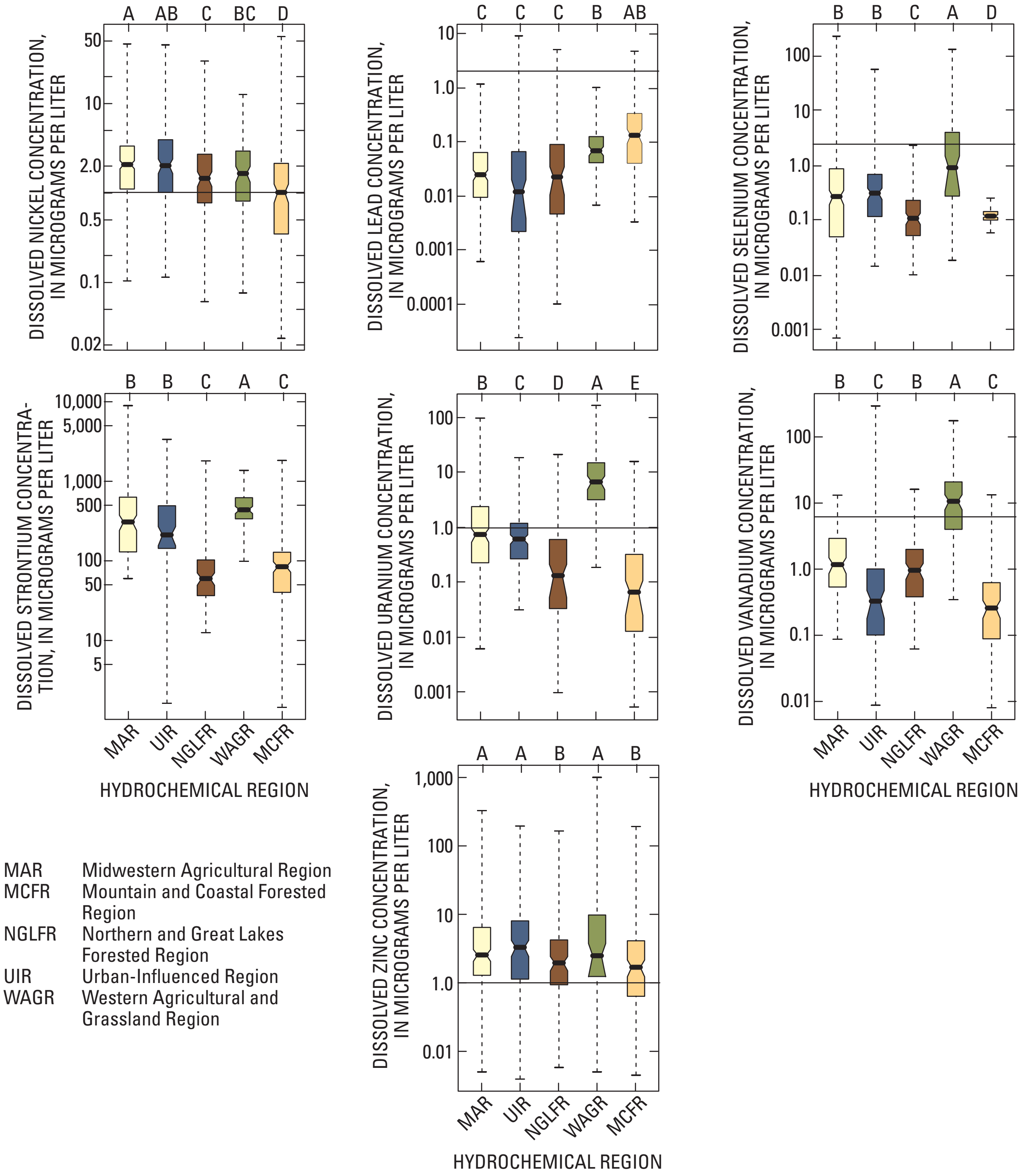


Figure 41. Concentrations of selected elements by hydrochemical region for wells sampled in the glacial aquifer system. Boxes labeled with different letters have significantly different empirical cumulative distribution functions on the basis of Peto and Peto tests. Horizontal line indicates highest reporting level for element. See figure 23 for explanation of box plots.—Continued

Table 30. P-values for pairwise Peto and Peto tests of significant differences in empirical cumulative distribution functions of element concentrations with respect to hydrochemical regions.

[Blue cells indcate $p < 0.05$; UIR, Urban-Influenced Region; NGLFR, Northern and Great Lakes Forested Region; WAGR, Western Agriculture and Grassland Region; MCFR, Mountain and Coastal Forested Region; MAR, Midwestern Agricultural Region]

Arsenic	UIR	NGLFR	WAGR	MCFR
MAR	0.01	0.00	0.00	0.00
UIR		**.21**	.00	.00
NGLFR			.00	.00
WAGR				.00

Barium	UIR	NGLFR	WAGR	MCFR
MAR	**0.44**	0.00	**0.61**	0.00
UIR		.00	**.75**	.00
NGLFR			.00	.04
WAGR				.00

Chromium	UIR	NGLFR	WAGR	MCFR
MAR	0.04	0.00	**0.17**	0.00
UIR		**.06**	**.47**	.00
NGLFR			.01	.00
WAGR				.00

Cobalt	UIR	NGLFR	WAGR	MCFR
MAR	**0.41**	0.00	0.00	0.00
UIR		.00	.01	.00
NGLFR			.00	**.61**
WAGR				.00

Copper	UIR	NGLFR	WAGR	MCFR
MAR	**0.27**	**0.41**	0.00	**0.64**
UIR		**.12**	.02	**.77**
NGLFR			.00	**.33**
WAGR				.02

Iron	UIR	NGLFR	WAGR	MCFR
MAR	**0.89**	**0.11**	0.00	0.00
UIR		**.23**	.01	.00
NGLFR			.04	.00
WAGR				**.79**

Lead	UIR	NGLFR	WAGR	MCFR
MAR	**0.17**	**0.08**	0.00	0.00
UIR		**.54**	.01	.00
NGLFR			.01	.00
WAGR				**.06**

Lithium	UIR	NGLFR	WAGR	MCFR
MAR	0.01	0.00	0.00	0.00
UIR		.00	.00	.00
NGLFR			.00	**.43**
WAGR				.00

Manganese	UIR	NGLFR	WAGR	MCFR
MAR	**0.37**	0.04	**0.08**	0.00
UIR		**.38**	**.21**	.01
NGLFR			**.42**	**.09**
WAGR				**.69**

Molybdenum	UIR	NGLFR	WAGR	MCFR
MAR	0.00	0.00	**0.09**	0.00
UIR		.00	.00	.00
NGLFR			.00	.00
WAGR				.00

Nickel	UIR	NGLFR	WAGR	MCFR
MAR	**0.74**	0.00	0.04	0.00
UIR		.02	**.22**	.00
NGLFR			**.44**	.01
WAGR				.00

Selenium	UIR	NGLFR	WAGR	MCFR
MAR	**0.19**	0.00	0.00	0.00
UIR		.00	.00	.00
NGLFR			.00	.01
WAGR				.00

Strontium	UIR	NGLFR	WAGR	MCFR
MAR	**0.15**	0.00	0.00	0.00
UIR		.00	.00	.00
NGLFR			.00	**.07**
WAGR				.00

Uranium	UIR	NGLFR	WAGR	MCFR
MAR	0.02	0.00	0.00	0.00
UIR		.00	.00	.00
NGLFR			.00	.00
WAGR				.00

Vanadium	UIR	NGLFR	WAGR	MCFR
MAR	0.00	**0.10**	0.00	0.00
UIR		.00	.00	**.19**
NGLFR			.00	.00
WAGR				.00

Zinc	UIR	NGLFR	WAGR	MCFR
MAR	**0.47**	0.01	**0.76**	0.00
UIR		.01	**.84**	.00
NGLFR			.03	**.62**
WAGR				.01

Summary and Conclusions

A series of wells (1,590) in the glacial aquifer system of the Northern United States was sampled by the U.S. Geological Survey National Water-Quality Assessment Program and analyzed for dissolved iron and manganese, among other constituents. A subset of these wells (847) also was sampled and analyzed for a suite of trace elements. Because analytical data contained many results below detection (laboratory reporting level), a statistical technique, Regression on Order Statistics, was used to model the distributions of the element concentrations. The distributions of iron, manganese, and selected trace element concentrations have little regional pattern; however, most elements have significant variations among glacial framework areas. The distributions are characterized with respect to use of water from the wells, land use, network (well type), redox category, and pH in addition to glacial framework areas and hydrochemical regions.

Some trace elements were detected so rarely (antimony, beryllium, cadmium, silver, and thallium) that it was not possible to characterize their distributions in the glacial aquifer system. Strontium and barium were the most commonly detected of the elements analyzed and generally had the highest median concentrations. Iron and manganese were frequently detected and had the next highest median concentrations. Median concentrations of the remaining elements have the following relation: lithium > zinc > nickel > molybdenum > copper > vanadium > arsenic > chromium > uranium > cobalt > selenium > lead > antimony > beryllium > cadmium > thallium > silver.

The relations to selected environmental factors, including well depth, water use, and land use or network type, and chemical factors, including pH, dissolved oxygen, bicarbonate, and dissolved solids concentrations, were examined both with respect to the two sets of factors and to element concentrations. Many element concentrations are related to several of these factors. Some of these patterns were expected, such as the increase in dissolved iron and manganese with increased well depth, but others were not, such as the positive correlation of the concentrations of many elements with agricultural land use. pH had little significant effect on most element concentrations.

Trace element distributions were characterized with respect to redox category, as described in previous studies, to determine the effects of redox environment on their occurrence and distribution. There are significant relations between dissolved oxygen and dissolved iron and manganese because iron and manganese are strongly redox-sensitive. Because the iron and manganese concentrations were used to determine the redox categories, based on these data, no further insight into the variations of iron and manganese with respect to redox could be obtained. Many other trace elements that are generally recognized as redox sensitive did not have robustly similar relations to redox categories. Some selected trace elements had distinct concentration distributions for particular redox categories, but most did not. This is attributed to a variety of factors, such as (1) incomplete characterization of redox environments—there may be limited usefulness to commonly collected chemical data to determine the redox status of a well sample—and (2) the elements are not as redox sensitive as are iron and manganese.

Manganese was one of the most frequently detected elements with concentrations most frequently greater than the Health-Based Screening Level of 300 micrograms per liter. A total of 290 well samples, or 18 percent of wells sampled for manganese, had a manganese concentration that was greater than 300 micrograms per liter. Of those wells that had concentrations greater than the Health-Based Screening Levels for manganese, 43 were private-supply wells and 12 were public-supply wells. For this report, the number of people that were supplied drinking water by the wells with high manganese is not known.

The transferability of the results of this report is limited, in part, due to the large variability in concentrations across the glacial aquifer system and the lack of associations between trace element concentrations and environmental factors. Some potential for limited transferability is assumed on the basis of hydrochemical regions developed in another study. A series of seven elements—arsenic, lithium, molybdenum, selenium, strontium, uranium, and vanadium—share a distribution pattern among hydrochemical regions that may be useful for transferability of results to unsampled wells.

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