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NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

# The Association of Arsenic With Redox Conditions, Depth, and Ground-Water Age in the Glacial Aquifer System of the Northern United States

Scientific Investigations Report 2007–5036

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

**Front-cover image:** Mixed land uses are spread across this glacial landscape in Dane County, south-central Wisconsin. Water samples from 56 wells throughout Wisconsin were analyzed for the study described in this report. (File photograph from the USGS Wisconsin Water Science Center, Middleton, Wis.)

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DIRK KEMPTHORNE, Secretary

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# FOREWORD

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 to 2001, the NAWQA Program completed interdisciplinary assessments and established a baseline understanding of water-quality conditions in 51 of the Nation's river basins and aquifers, referred to as Study Units (*http://water.usgs.gov/nawqa/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.

Robert M. Hirsch

Associate Director for Water

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## Conversion Factors and Abbreviations

| **Multiply** | **By** | **To obtain** |
|---|---|---|
| | Length | |
| foot (ft) | 0.3048 | meter (m) |
| mile (mi) | 1.609 | kilometer (km) |
| | Volume | |
| liter (L) | 0.2642 | gallon (gal) |
| | Mass | |
| gram (g) | 0.03527 | ounce, avoirdupois (oz) |

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

# The Association of Arsenic With Redox Conditions, Depth, and Ground-Water Age in the Glacial Aquifer System of the Northern United States

By Mary Ann Thomas

## Abstract

More than 800 wells in the glacial aquifer system of the Northern United States were sampled for arsenic as part of U.S. Geological Survey National Water-Quality Assessment (NAWQA) studies during 1991–2003. Elevated arsenic concentrations (greater than or equal to 10 micrograms per liter) were detected in 9 percent of samples.

Elevated arsenic concentrations were associated with strongly reducing conditions. Of the samples classified as iron reducing or sulfate reducing, arsenic concentrations were elevated in 19 percent. Of the methanogenic samples, arsenic concentrations were elevated in 45 percent. In contrast, concentrations of arsenic were elevated in only 1 percent of oxic samples.

Arsenic concentrations were also related to ground-water age. Elevated arsenic concentrations were detected in 34 percent of old waters (recharged before 1953) as compared to 4 percent of young waters (recharged since 1953). For samples classified as both old and methanogenic, elevated arsenic concentrations were detected in 62 percent of samples, as compared to 1 percent for samples classified as young and oxic.

Arsenic concentrations were also correlated with well depth and concentrations of several chemical constituents, including (1) constituents linked to redox processes and (2) anions or oxyanions that sorb to iron oxides.

Observations from the glacial aquifer system are consistent with the idea that the predominant source of arsenic is iron oxides and the predominant mechanism for releasing arsenic to the ground water is reductive desorption or reductive dissolution. Arsenic is also released from iron oxides under oxic conditions, but on a more limited basis and at lower concentrations.

Logistic regression was used to investigate the relative significance of redox, ground-water age, depth, and other water-quality constituents as indicators of elevated arsenic concentrations in the glacial aquifer system. The single variable that explained the greatest amount of variation in the data was redox. Multivariate models that included a redox variable overestimated the percentage of samples with elevated arsenic concentrations because, even though elevated arsenic concentrations were associated with strongly reducing samples, not all strongly reducing samples had elevated arsenic concentrations.

Arsenic concentrations and redox conditions differed among four broad areas of the glacial aquifer system. For the East, Central, and West-Central north areas, there was a trend of increasing arsenic concentrations that corresponded to an increase in reducing conditions. For the West-Central south area, arsenic concentrations in oxic samples were higher than for the other areas, possibly because of high concentrations of orthophosphate, which is linked to desorption of arsenic from iron oxides under oxic conditions.

The observed differences in arsenic concentrations among broad areas of the glacial aquifer system were generally consistent with a conceptual model developed by Smedley and Kinniburg[1], who studied or reviewed studies of widespread arsenic contamination in Bangladesh, India, China, Vietnam, Hungary, Argentina, northern Chile and the Southwestern United States.

## Introduction

The U.S. Environmental Protection Agency (USEPA) recently lowered the Maximum Contaminant Level (MCL) for arsenic from 50 μg/L to 10 μg/L in recognition of the detrimental health effects associated with arsenic in drinking water, including bladder, skin, and lung cancers; diabetes; and neurological dysfunction (National Research Council, 1999). The new MCL went into effect January 2006 for public water-supply systems but not for domestic wells (U.S. Environmental Protection Agency, 2006). Domestic wells are not routinely tested for arsenic in most parts of the country, so homeowners may not know whether their well water has arsenic concentrations greater than the MCL.

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[1] Smedley, P.L., and Kinniburg, D.G., 2002, A review of the source, behaviour, and distribution of arsenic in natural waters: Applied Geochemistry, v. 17, p. 517–568.

Arsenic concentrations in ground water have considerable spatial variability and are difficult to predict on a well-by-well basis; however, the risk of high concentrations is greater in some areas than in others (Smedley and Kinniburg, 2002). If the most susceptible aquifers (or parts of aquifers) could be identified, efforts related to monitoring or education could be targeted to areas of greatest need.

The U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program has been systematically sampling the Nation's ground water since 1991. Between 1991 and 2003, NAWQA analyzed for arsenic and other water-quality properties in 813 samples from the glacial aquifer system in the Northern United States (fig. 1). The samples were selected on the basis of a stratified random design, to be representative of important hydrogeologic settings within the glacial aquifer system. A synthesis of these data provides a large-scale survey of arsenic in ground water, reflecting comparable methods of collection, analysis, and quality control.

The goals of this report are to (1) document arsenic concentrations in samples from the glacial aquifer system; (2) describe relations between arsenic concentrations and redox conditions, well depth, ground-water age, and other water-quality variables; and (3) document variation in arsenic and related factors within the glacial aquifer system.

## Background

Arsenic is relatively abundant in nature. Although arsenic in water can come from anthropogenic sources, most instances of widespread arsenic contamination in ground water are from naturally occurring minerals (Welch, and others, 2000; Smedley and Kinniburg, 2002). Arsenic can occur in multiple minerals, including sulfides (especially pyrite), hydrous metal oxides (especially iron oxides), coal, ironstones, clays, phosphates, silicates, and carbonates. The most important sources of elevated arsenic in ground water are pyrite and iron oxides, partly because of their abundance in aquifers (Smedley and Kinniburg, 2002). Pyrite is an iron sulfide mineral, and arsenic can be present as part of the mineral structure. Iron oxides occur as coatings on mineral grains; arsenic can coprecipitate with iron oxides or sorb to their surface. Pyrite and iron oxides can be enriched in distinct horizons or disseminated throughout the aquifer matrix.

Arsenic concentrations in the aquifer solid phase do not always correspond to arsenic concentrations in ground water; multiple studies have found little or no correlation between the two (Warner, 2001; Welch and others, 2000; Kolker and others, 2003; Smedley and Kinniburg, 2002; Erickson and Barnes, 2005). Most instances of widespread arsenic enrichment in the ground water are in areas where arsenic concentrations in the solid phase are within the range of normal concentrations (Smedley and Kinniburg, 2002).

In ground water, arsenic has two common oxidation states. The predominant form in oxic waters is arsenate, an oxyanion with the +5 oxidation state. In reduced waters, the predominant form is arsenite, an uncharged species with a -3 oxidation state. Because arsenite is uncharged, it is the more mobile in solution. Arsenite is also considered to be the more toxic form.

Because of its two common oxidation states, arsenic can be released from minerals to ground water (mobilized) under either oxic or reducing conditions. Under oxic conditions, arsenic can be mobilized by dissolution of pyrite or by desorption from iron oxides due to an increase in pH or competition with other anions (Welch and others, 2000; Smedley and Kinniburg, 2002). Under reducing conditions, arsenic associated with iron oxides can be mobilized by reductive desorption or reductive dissolution. Reductive desorption occurs when (1) arsenate is reduced to arsenite, which is less strongly sorbed to iron oxides, or (2) the charge on the mineral surface changes and allows arsenate to be desorbed. Reductive dissolution of iron oxides releases arsenic that is part of the mineral structure or sorbed to the surface.

Pyrite and iron oxides are also important sinks for arsenic, so the formation of these minerals can decrease arsenic concentrations in ground water.

## Previous studies

Arsenic concentrations in ground water of the United States were documented by Welch and others (2000) and Ryker (2003). Their dataset included about 30,000 samples from varied aquifers and springs in 48 states; of those, about 11 percent had arsenic concentrations greater than the MCL of 10 µg/L. Highest arsenic concentrations were detected in the West, but concentrations in the Midwest were higher than previously recognized.

In New England, elevated arsenic concentrations in glacial valley-fill deposits and the underlying crystalline bedrock have been linked to desorption related to an increase in pH (Ayotte and others, 2003). Widespread contamination of ground water by arsenic from oxidation of sulfides has been documented in parts of eastern Wisconsin, an area where glacial deposits overlie a Paleozoic sandstone aquifer (Schreiber and others, 2003). Reductive desorption or dissolution of iron oxides was linked to elevated arsenic concentrations in glacial deposits and (or) the underlying bedrock in Ohio (Matisoff and others, 1982), the Midwest (Korte, 1991; Welch and others, 2000; Thomas, 2003), southeastern Michigan (Kolker and others, 2003), central Illinois (Kirk and others, 2004; Kelly and others, 2005), and North Dakota and Minnesota Erikson and Barnes, 2005).

Smedley and Kinniburg (2002) synthesized common features of widespread arsenic contamination in ground water from around the world, including Bangladesh, India, Vietnam, China, Hungary, Argentina, northern Chile, and the Southwestern United States. They developed a conceptual model for widespread arsenic contamination of ground water in low-temperature, nonmineralized areas. In most areas of widespread arsenic contamination, the predominant source of

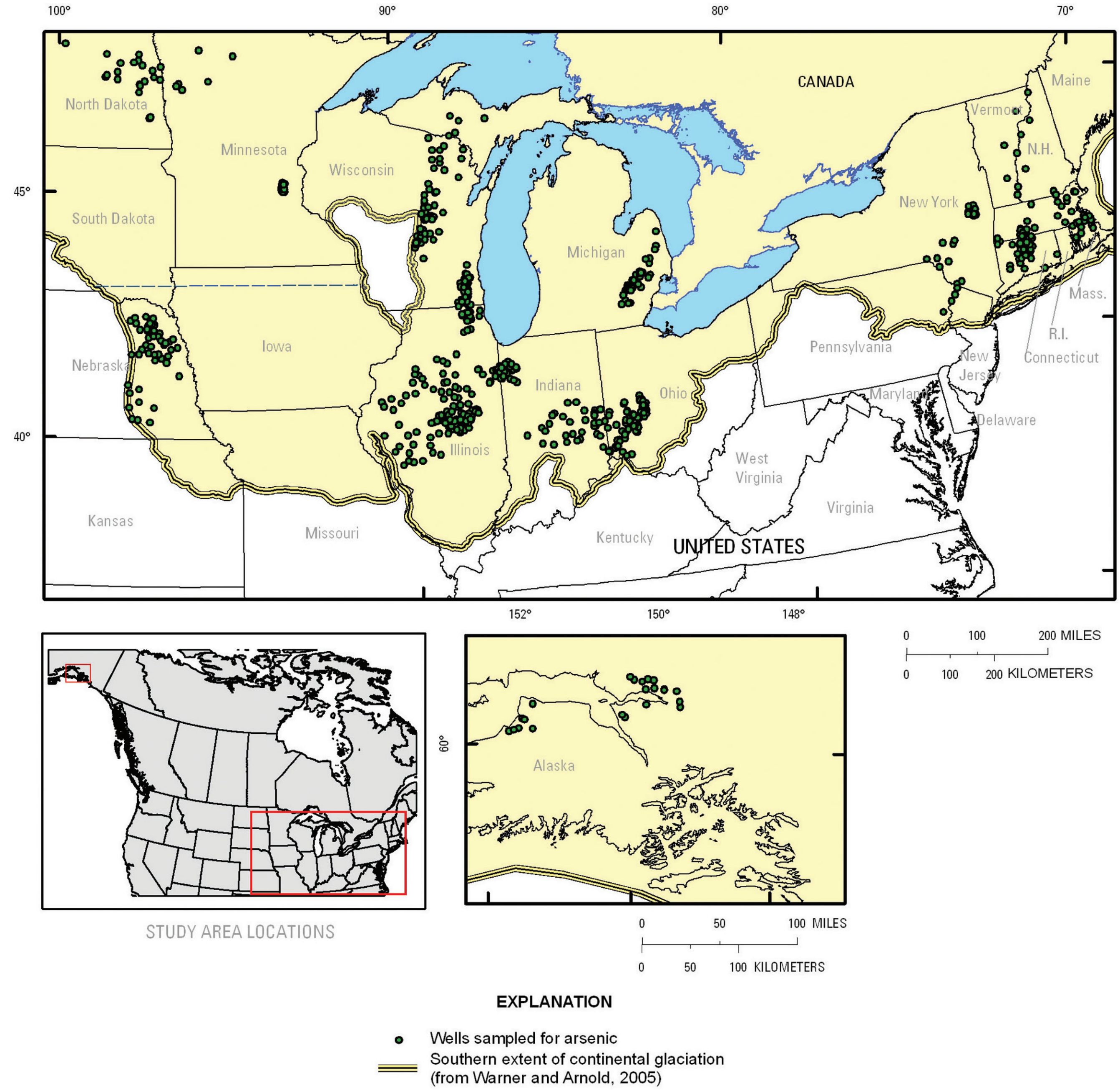


**Figure 1.** Location of wells in the glacial aquifer system sampled for arsenic by the National Water-Quality Assessment Program, 1991–2003.

arsenic is iron oxides. For elevated arsenic concentrations in ground water to develop, a geochemical trigger is needed to release arsenic from minerals. One possible trigger is the onset of strongly reducing conditions, which result from degradation of organic carbon. A confining layer near land surface can help maintain reducing conditions by retarding the transport of oxygen (or other electron acceptor) from the land surface. Arsenic can also be released from iron oxides under oxic conditions due to an increase in pH and (or) competitive sorption by phosphate or other anions. After arsenic is mobilized, it can accumulate in ground water if the rate of flushing is low relative to the rate of mobilization. Therefore, arsenic risk is high in areas of sluggish ground-water flow (in either oxic or reducing conditions).

High-arsenic environments include deltas or alluvial plains, where large volumes of young sediment have undergone rapid burial and strongly reducing conditions can develop. These environments also tend to have associated fine-grained sediments that can form a confining or semiconfining layer close to land surface. In addition, the land surface is typically flat, low lying and poorly drained, and hydraulic gradients are low. As a result, arsenic is not flushed away faster than it can be mobilized. Inland or closed basins in arid or semiarid areas are also at risk because high pH can develop and lead to arsenic desorption. In addition, the low flushing rates associated with arid or semi-arid environments allow arsenic to accumulate in the ground water.

Data from the glacial aquifer system were not explicitly included in the development of the conceptual model. Therefore, it might be useful to examine the model in light of data from the current study.

## Methods

Data were collected in accordance with NAWQA protocols for study design and site selection (Gilliom and others, 1995; Scott, 1990; Squillace and Price, 1996), well selection or installation (Lapham and others, 1995), sample collection, sample preservation, and quality-assurance/quality-control methods (Koterba and others, 1995; U.S. Geological Survey, variously dated). Ground-water samples were analyzed at the USGS National Water Quality Laboratory for major ions and trace elements (Fishman, 1993; Garbarino, 1999), dissolved organic carbon (Brenton and Arnett, 1993), tritium (Ostlund and Dorsey, 1977), CFCs (Plummer and others, 1993), and $SF_6$ (Busenberg and Plummer, 2000). Tritium-helium-3 was analyzed for at Lamont-Doherty Earth Observation Noble Gas Facility (Ekwurzel and others, 1994). Multiple organic constituents, including volatile organic compounds and pesticides, also were analyzed for as part of NAWQA studies (*http://water.usgs.gov/nawqa*), but results of these analyses are not included in this report.

The laboratory reporting limit for arsenic and several other constituents changed between 1991 and 2003. To account for this, concentrations were censored to the highest common reporting level, which was 1 µg/L for arsenic. Because concentrations of arsenic and several other constituents did not follow a normal statistical distribution, statistical analysis was done by means of nonparametric methods (Helsel and Hirsch, 2002). Median and 75th- percentile values were used to summarize concentrations of water-quality constituents in groups of data. Kruskal-Wallis and Tukey tests were used to determine whether concentrations of constituents were significantly different among groups of samples. Spearman's rho was used to identify significant monotonic correlations between arsenic and other variables. Logistic regression was used to evaluate the relative significance of variables as indicators of elevated arsenic concentrations (Hosmer and Lemeshow, 1989).

## Description of the Study Area

The glacial aquifer system is one of the most important sources of ground water in the Northern United States. Glacial deposits extend across parts of 26 states and were the source of drinking water for 41 million people during 2000 (Warner and Arnold, 2005). For this report, the glacial aquifer system is considered to include unconsolidated deposits above bedrock north of the line of continental glaciation (fig. 1; Warner and Arnold, 2005). Areas where glacial deposits are part of alluvium or flood deposits that extend south of the boundary of continental glaciation are not considered in this report.

A large proportion of glacial deposits is derived from local bedrock or bedrock that is upgradient relative to the direction of movement of the glacial lobes. Bedrock beneath glacial deposits includes sedimentary and crystalline rocks of Precambrian through Tertiary age (fig. 2). The largest proportion of the study area is underlain by Paleozoic and Cretaceous sedimentary bedrock (predominantly carbonates, shale, and sandstone). In the northeastern part of the study area, bedrock is predominantly crystalline (igneous) and metamorphosed sedimentary rock. Crystalline rock also subcrops in part of Wisconsin, Michigan, Minnesota, and Alaska.

Glacial deposits in the study area range in thickness from less than 1 to more than 600 ft (fig. 3). In general, glacial deposits are thinner and less extensive in the eastern part of the study area. Glacial deposits also vary in terms of texture, from clay to boulders. For this report, glacial deposits are referred to as "coarse grained" (predominantly sand or gravel) or "fine grained" (predominantly till or clay). The distribution of coarse- and fine-grained deposits near land surface is shown in figure 3. Sediment texture is not typically uniform with depth, so coarse-grained deposits can underlie fine-grained deposits and vice versa.

Ground water is typically produced from coarse-grained deposits, which can be at land surface or beneath fine-grained deposits. The coarse-grained deposits typically occur as layers, lenses, or linear valley-fill deposits. Sediment texture near land surface and aquifer geometry are related to intrinsic susceptibility, or the ease with which water enters and moves through the glacial aquifer system (Warner and Arnold, 2005). Additional details of the glacial aquifer system are discussed in a later section of this report ("Regional Variation of Arsenic and Redox Conditions Within the Glacial Aquifer System").

Water-quality data collected as part of NAWQA studies are not uniformly distributed across the glacial aquifer system (figs. 1–5). Instead, data are from 26 well networks, each of which includes 20–30 wells. Well locations were determined by a stratified random design (Gilliom and others, 1995). As a result, well networks are representative of hydrogeologic and (or) land-use settings in the glacial aquifer system. Networks of domestic or public-supply wells are representative of hydrogeologic settings that are important in terms of local or regional water supply. Monitor-well networks are installed just below the water table, and the stratification includes land use and hydrogeologic setting.

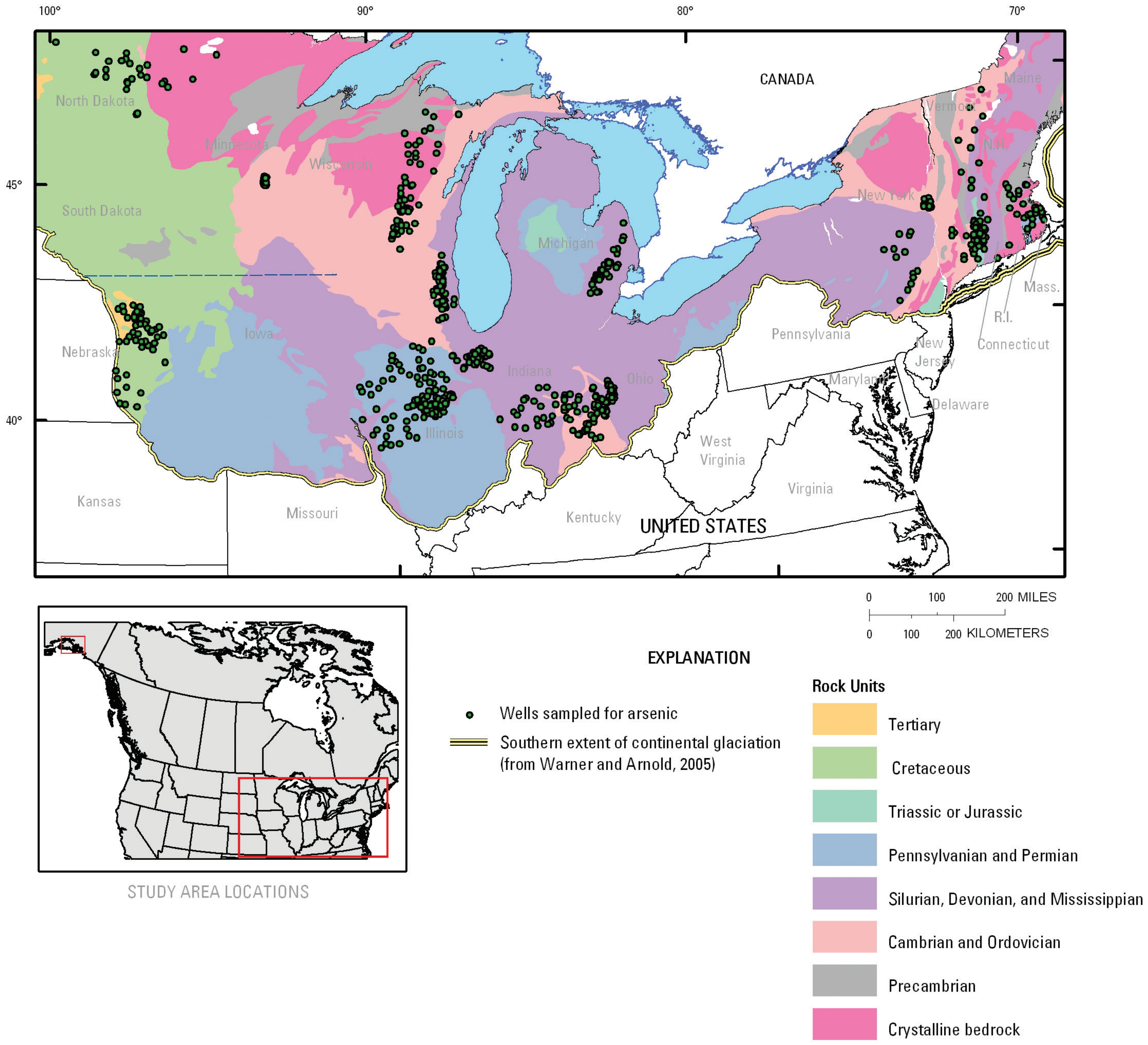


**Figure 2.** Bedrock beneath glacial deposits. (Data not shown for Alaska.)

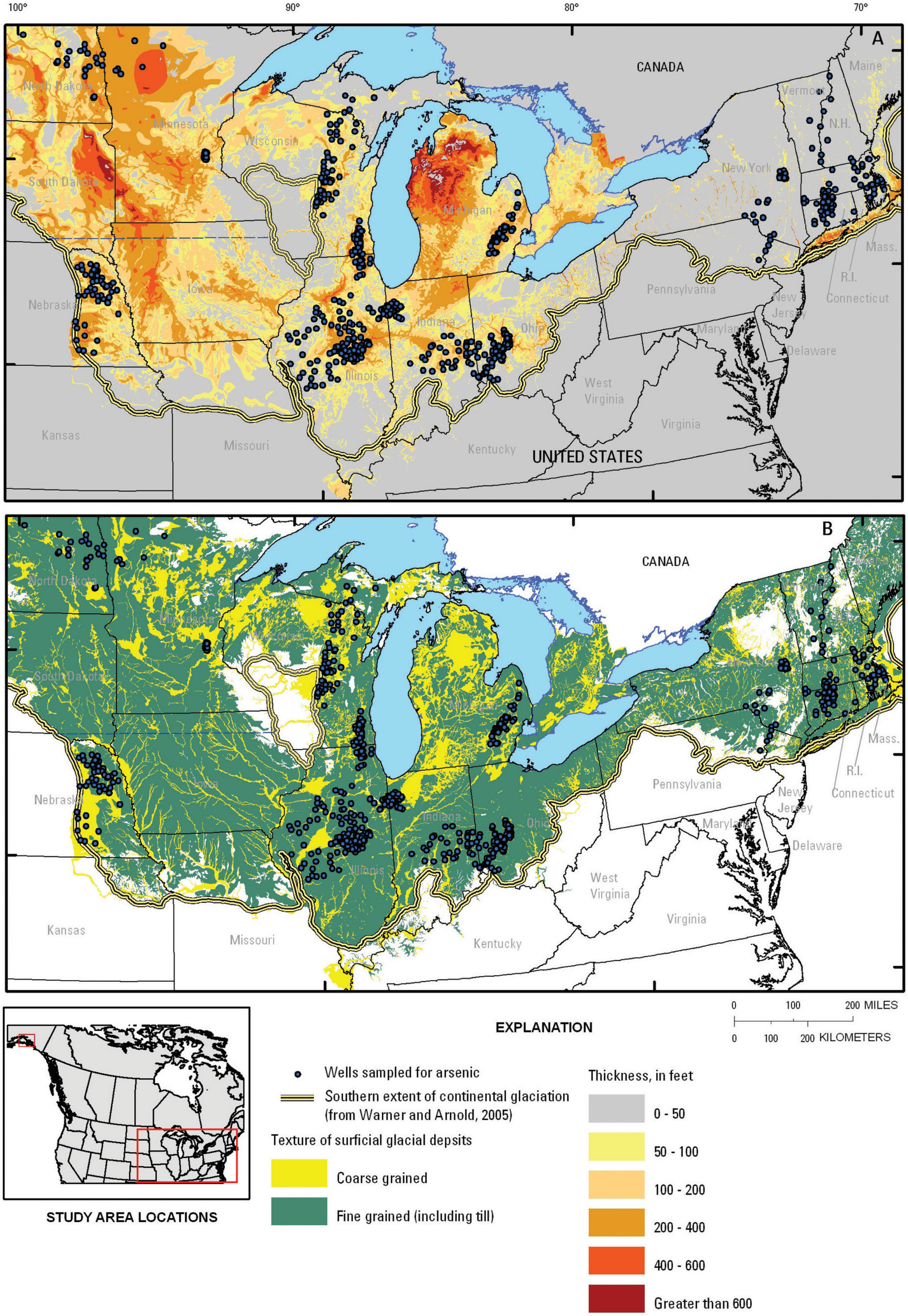


**Figure 3.** Thickness and texture of glacial deposits near land surface. (Data not shown for Alaska.)

# Arsenic Concentrations and Related Factors in the Glacial Aquifer System

This section of the report documents arsenic concentrations and related factors in the glacial aquifer system as a whole, and the analyses include all samples with arsenic determinations. Later sections of the report consider subsets of the data.

## Arsenic Concentrations

The frequency distribution of arsenic concentrations is shown in figure 4. The median concentration was less than 1 µg/L. About 9 percent of samples had arsenic concentrations greater than or equal to the USEPA MCL of 10 µg/L. (In this report, arsenic concentrations greater than or equal to 10 µg/L are referred to as "elevated.") About 1 percent of samples had concentrations greater than or equal to 50 µg/L, which was the USEPA MCL prior to January 2006. The maximum arsenic concentration was 340 µg/L. This might be considered an outlier because it was almost 4 times higher than the second-highest concentration of 84 µg/L; however, the maximum concentration was confirmed by analysis of a duplicate sample (Andrews and others, 1998).

Arsenic concentrations were measured in water samples from 813 wells in 18 states. The spatial distribution of arsenic concentrations is shown in figure 5. In most areas, the samples had a wide range of concentrations. There is no evident spatial pattern that links elevated arsenic concentrations to a particular type of bedrock geology (fig. 2) or glacial deposit (fig. 3).

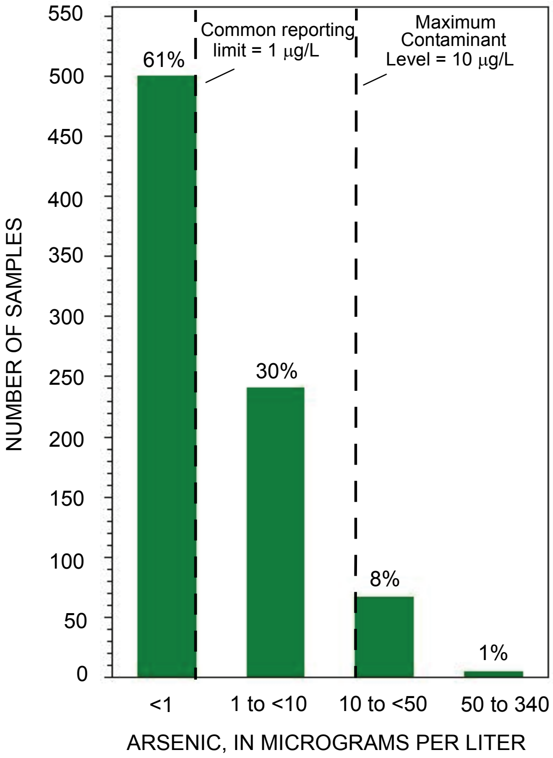


**Figure 4.** Frequency of arsenic concentrations in samples from the glacial aquifer system.

**Table 1.** Concentrations of water-quality constituents used to classify redox conditions of samples from the glacial aquifer system of the Northern United States.

[Modified from Paschke and others, in press; mg/L, milligrams per liter; µg/L, micrograms per liter; "-", constituent concentration not specified]

| Redox classification[1] | Abbreviation used in this report | Oxygen (mg/L) | Nitrate (mg/L as N) | Manganese (µg/L) | Iron (µg/L) | Sulfate (mg/L) |
|---|---|---|---|---|---|---|
| Oxygen reducing | Oxic | ≥0.5 | - | <50 | <100 | - |
| Nitrate reducing | $NO_3$ | <.5 | ≥0.5 | <50 | <100 | - |
| Manganese reducing | Mn | <.5 | <.5 | ≥50 | <100 | - |
| Iron or sulfate reducing[2] | $Fe/SO_4$ | <.5 | < .5 | - | ≥100 | ≥4 |
| Methanogenic[2] | Meth | <.5 | <.5 | - | ≥100 | <4 |

[1] Samples that do not fall into one of these categories are referred to as "mixed or unknown."

[2] These classifications are collectively referred to as "strongly reducing."

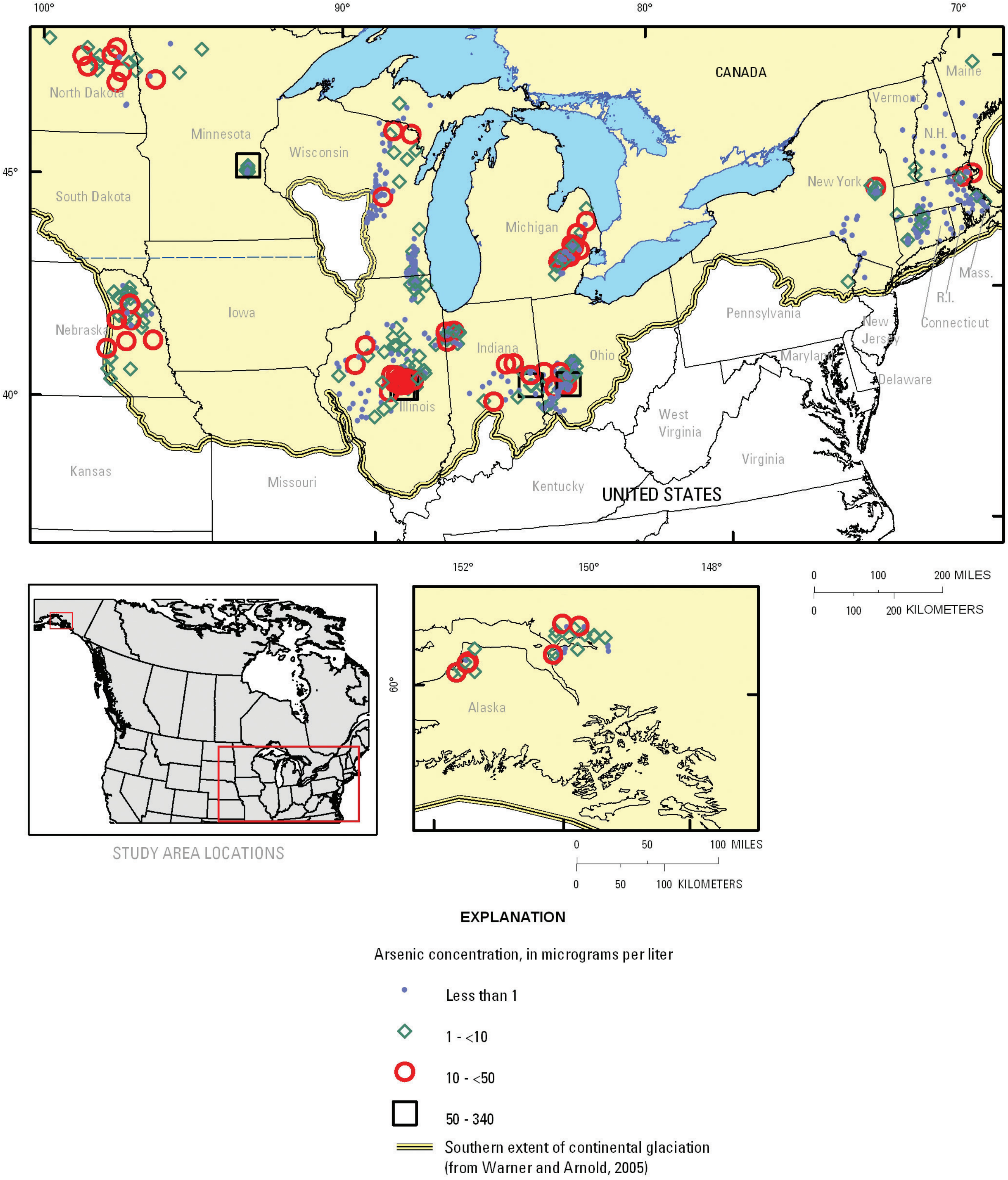


**Figure 5.** Arsenic concentrations in samples from the glacial aquifer system.

## Redox Conditions

Arsenic can be released to (or removed from) the ground water as a result of redox reactions, a term used as a simplification for terminal electron accepting processes (TEAPS). Redox reactions involve the transfer of electrons from an electron donor to an electron acceptor. In ground water, the electron donor is typically organic carbon; however, sulfide minerals and some manufactured organic compounds also can act as electron donors. Electron acceptors include oxygen, nitrate, manganese, ferric iron, sulfate, and carbon dioxide. During the transfer of electrons, organic carbon is oxidized, and the electron acceptors are reduced in sequential reactions that are mediated by microbes. In general, ground-water systems with very low concentrations of organic carbon (or other electron donor) are oxic, whereas systems with high concentrations of organic carbon (or other electron donor) are reducing.

For the current study, redox conditions of ground-water samples were classified on the basis of concentrations of five chemical constituents—dissolved oxygen (DO), nitrate, manganese, ferrous iron, and sulfate (table 1; modified from Paschke and others, in press). This system, adopted by the NAWQA Program, uses concentrations thresholds for five constituents to define five redox categories. Samples that did not correspond to any of the categories were classified as “mixed or unknown.” The term “strongly reducing” is used hereafter as a substitute for “iron reducing or sulfate reducing or methanogenic.”

The fact that the redox classification system does not distinguish between iron-reducing and sulfate-reducing categories is limiting because arsenic concentrations can vary between the two redox conditions. In iron-reducing conditions, arsenic can go into solution as a result of reductive dissolution or desorption from metal oxides. By contrast, in sulfate-reducing conditions, arsenic can be removed from solution as a result of coprecipitation with metal sulfide minerals.

The frequency distribution of redox conditions of samples from the glacial aquifer system is shown in figure 6*A*; 38 percent of samples were oxic, 4 percent were nitrate reducing, 9 percent were manganese reducing, 23 percent were iron or sulfate reducing, 6 percent were methanogenic, and 20 percent were mixed or unknown.

In general, as waters become more reducing, arsenic concentrations were detected more frequently (fig. 6*B*). For example, 1 percent of oxic waters had elevated arsenic concentrations, as compared to 19 percent of iron or sulfate reducing waters and 45 percent of methanogenic waters. In addition, arsenic concentrations were higher in more reducing waters, based on the 75th-percentile values (table in fig. 6).

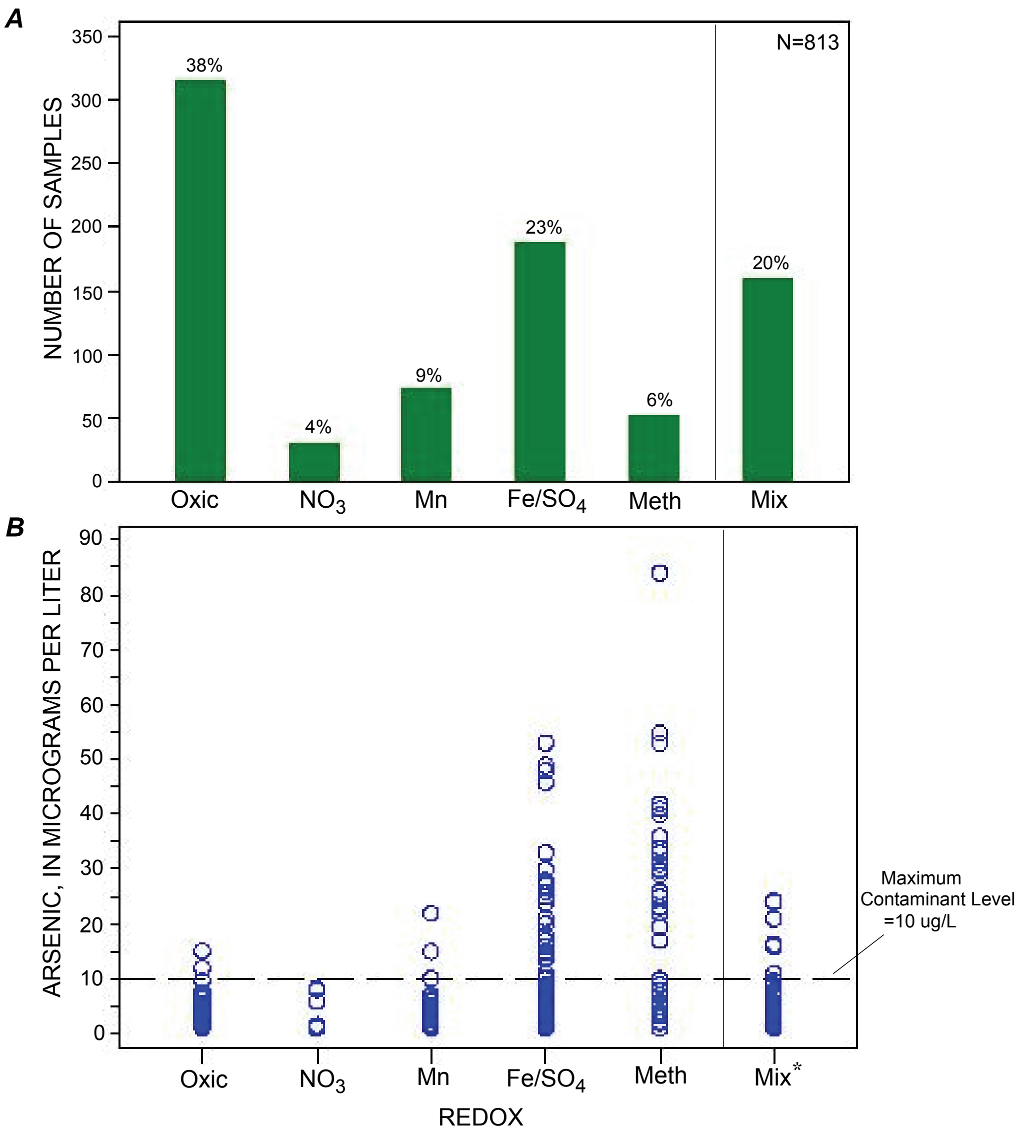
Relations shown in fig. 6 are consistent with the hypothesis that the predominant mechanism for arsenic release is reductive desorption or dissolution. However, a small percentage of the elevated arsenic concentrations were in oxic samples, which suggests that another mechanism releases arsenic to ground water in oxic conditions.

## Well Depth and Well Type

The water samples were collected from 411 monitor wells, 277 domestic wells, 104 public-supply wells, and 21 other well types. (Hereafter, the “other” wells are included in the “public-supply” category.) The wells were from 8 to 425 ft deep, and the median depth was 44 ft. For the dataset as whole, the relation between arsenic concentrations and well depth was significant ($p<0.0001$) but weak (Spearman’s $rho=0.24$). When the data were subdivided by well type, arsenic concentrations were correlated with well depth for domestic wells ($p<0.0001$; $rho=0.37$) and public-supply wells ($p<0.0001$; $rho=0.51$) but not for monitor wells ($p=0.32$).

Relations among arsenic concentration, redox condition, and well depth for each well type are shown in figure 7. Of the three well types, monitor wells were shallowest (median depth of 26 ft) and had the lowest percentage of samples with elevated arsenic concentrations (4 percent) and strongly reducing conditions (18 percent). Compared to monitor wells, domestic wells were deeper (median depth of 82 ft) and had a higher percentage of samples with elevated arsenic concentrations (14 percent) and strongly reducing conditions (47 percent).

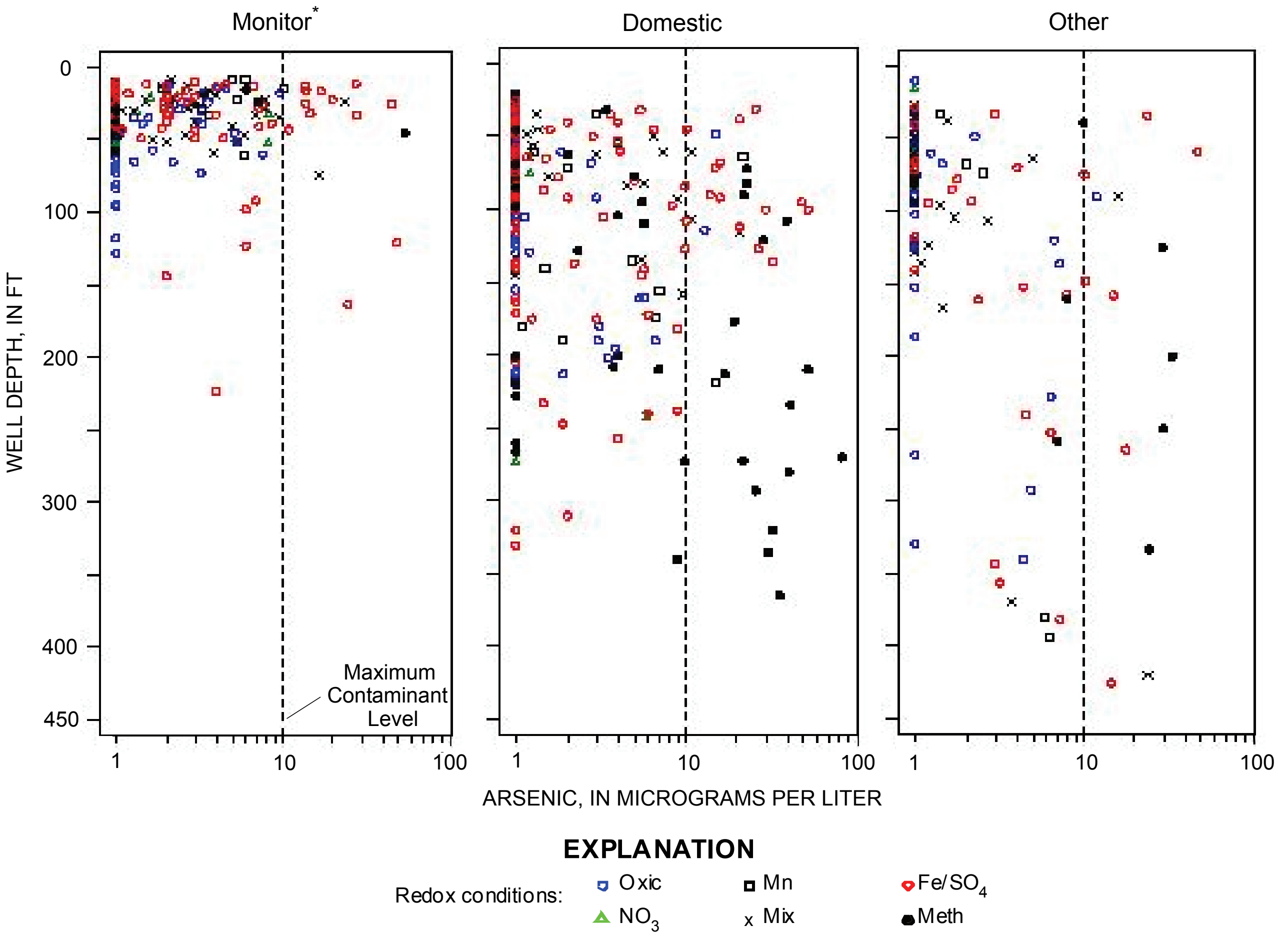
Public-supply wells were similar to domestic wells in terms of median depth (80 ft) but differed in terms of redox conditions; samples from public-supply wells had a lower percentage of strongly reducing conditions and higher percentages of oxic and mixed redox conditions (fig. 7). In general, samples from public-supply wells had redox conditions that were intermediate between those of monitor and domestic wells. Public-supply wells also had longer open intervals and higher discharge rates than domestic (or monitor) wells (fig. 7). The long open intervals and higher discharge rates of public-supply wells can cause mixing of ground water from multiple depths, with differing redox conditions and (or) ground-water ages (Landon and others, 2006). For this reason, further discussion of relations among depth, redox, and ground-water age are limited to the subset of data from monitor and domestic wells.



| Summary statistics | Oxic | $NO_3$ | Mn | $Fe/SO_4$ | Meth | Mix |
|---|---|---|---|---|---|---|
| Number of samples | 311 | 30 | 73 | 188 | 51 | 160 |
| Percentage of samples with arsenic≥10 µg/L[1] | 1 | 0 | 4 | 19 | 45 | 5 |
| Arsenic (µg/L)[1] | | | | | | |
| Median | <1 | <1 | <1 | 2 | 7 | <1 |
| 75th percentile | <1 | <1 | 2.0 | 6.5 | 29 | 2.1 |
| Maximum | 15 | 8 | 22 | 53 | 84 | 340 |

[1] µg/L, micrograms per liter.

**Figure 6.** *A*, Frequency of estimated redox conditions of samples from the glacial aquifer system. *B*, Arsenic concentrations for samples in each redox category.



| Well and sample characteristics | Well type | | |
|---|---|---|---|
| | Monitor | Domestic | Public supply |
| Number of samples | 411 | 277 | 125 |
| Well depth (median, in feet) | 26 | 82 | 80 |
| Open interval (median, in feet) | 5 | 4 | 12 |
| Well discharge (median, in gallons per minute) | 1 | 18 | 376 |
| Percentage of samples with arsenic $\geq$10 µg/L[1] | 4 | 14 | 12 |
| Percentage of samples with redox classification: | | | |
| Oxic | 43 | 32 | 37 |
| Mixed or unknown | 24 | 13 | 22 |
| Strongly reducing | 18 | 47 | 28 |

[1] µg/L, micrograms per liter.

**Figure 7.** Relation of arsenic concentration and redox condition to well depth for the three types of wells sampled. (See table 1 for explanation of redox abbreviations. *Not shown is sample with arsenic concentration of 340 µg/L and mixed redox conditions at 18 feet.)

## Ground-Water Age

Of the 688 samples from monitor or domestic wells, ground-water age was determined for 483. The term “ground-water age” refers to the time since water recharged the ground-water system (or was isolated from the atmosphere). Ages were determined by analysis for one or more of the following environmental tracers: chlorofluorocarbons (CFCs), sulfur hexafluoride ($SF_6$), tritium/helium-3 ($^3H/^3He$), or tritium. CFCs and $SF_6$ are anthropogenic compounds with known inputs, whereas $^3H/^3He$ and tritium methods are based on radioactive decay since the time of a known event (Plummer and others, 1993).

For 219 samples from monitor and domestic wells, age dates were based on CFCs, $SF_6$, or $^3H/^3He$ tracers. The samples were collected over a range of years, so the recharge year was subtracted from the collection year to estimate the age of the sample. Elevated arsenic concentrations (≥10 μg/L) were detected only in samples older than 15 years (fig. 8). Samples less than 5 years old were predominantly oxic (81 percent), and most of the young, oxic waters had arsenic concentrations less than 1 μg/L. As the age of the water increases, redox conditions become more reducing, and arsenic concentrations increase. Samples older than 15 years had elevated arsenic concentrations in 7 to 8 percent of samples.

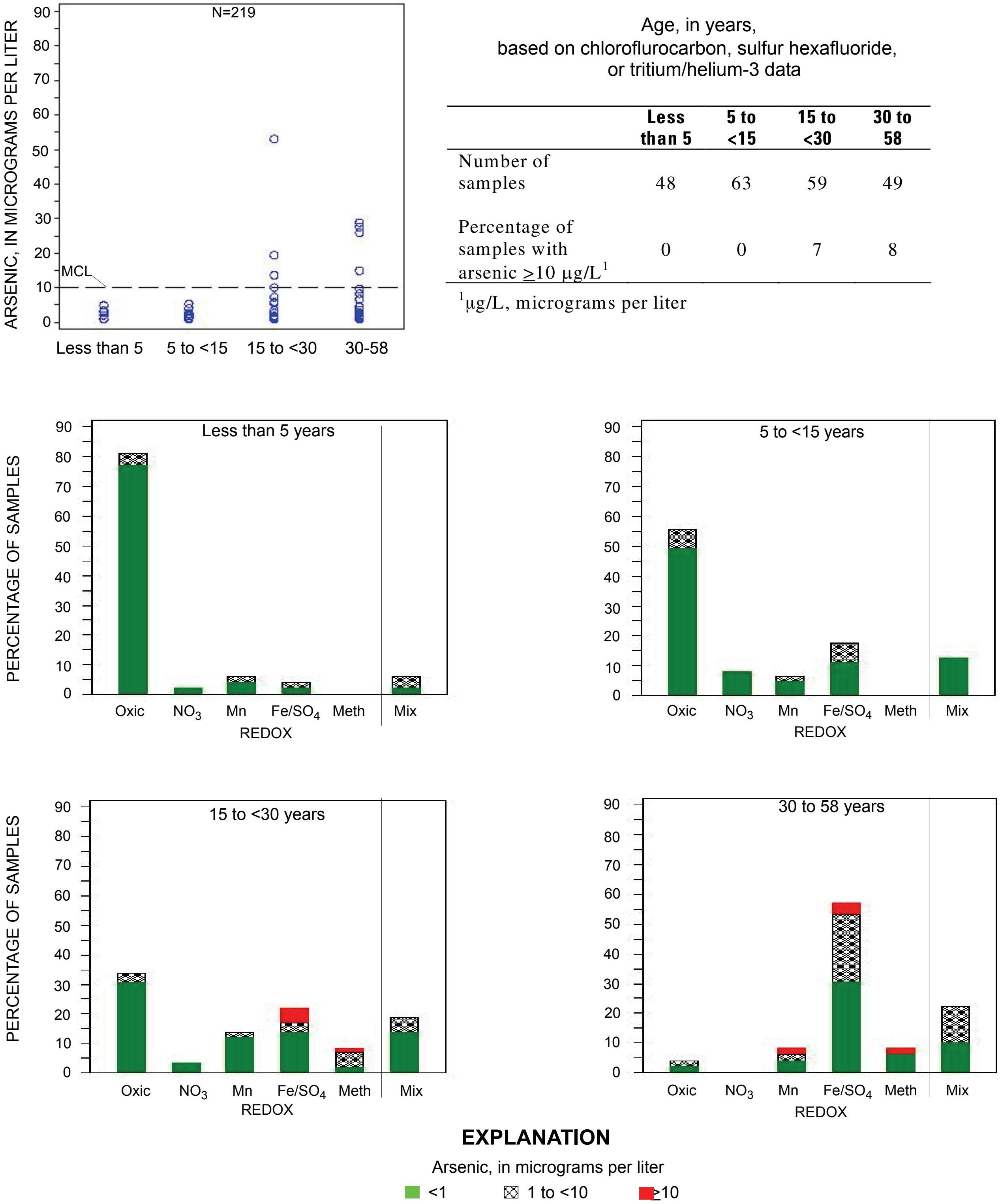
The tritium method was used to determine ages of 264 samples from monitor and domestic wells. The tritium age-dating method differs from the other three methods in that it provides a binary indication of ground-water age—whether a sample was recharged before or after 1953. If measurable tritium (>1 tritium unit) is detected in a sample, it is assumed that at least some fraction of the water was recharged since 1953. For this report, waters recharged before 1953 are referred to as “old” and those recharged since 1953 are referred to as “young.”

Arsenic concentrations were significantly higher in old-water samples than in young-water samples (fig. 9). Of the 203 young-water samples, 5 percent had elevated arsenic concentrations. Of the 61 old samples, 43 percent of had elevated arsenic concentrations. Young and old waters also differed in terms of redox conditions (fig. 9). For young waters, the highest proportion of samples (33 percent) were oxic and had arsenic concentrations less than 1 μg/L. For old waters, less than 10 percent were oxic. Most old waters (66 percent) were strongly reducing. Of the old and strongly reducing samples, 60 percent had elevated arsenic concentrations.

The two types of age data were combined by categorizing age dates from CFCs, $SF_6$, and $^3H/^3He$ methods according to whether the recharge year was before or after 1953. For this combined dataset, elevated arsenic concentrations were detected in 4 percent of young-water samples and 34 percent of old-water samples (fig. 10).

Relations between depth, redox and age are not simple (fig. 10). As a generalization, old and reducing water is more prevalent at greater depths. However, elevated arsenic concentrations can be detected in samples from a range of depths because (1) old waters can occur at shallow depths, (2) old, deep waters can be oxic, and (3) young, shallow waters can be reducing. For example, the maximum arsenic concentration of 340 μg/L was detected in a sample that was young water from a shallow well (18 ft), and the redox condition was categorized as mixed.

The percentages of samples with elevated arsenic, by redox and age categories are shown in figure 11. For young and old waters alike, the percentage of samples with elevated arsenic concentrations was greater in more reducing conditions, but the trend is more pronounced for old waters. For example, 17 percent of young and methanogenic samples had elevated arsenic concentrations, as compared to 62 percent of old and methanogenic samples.

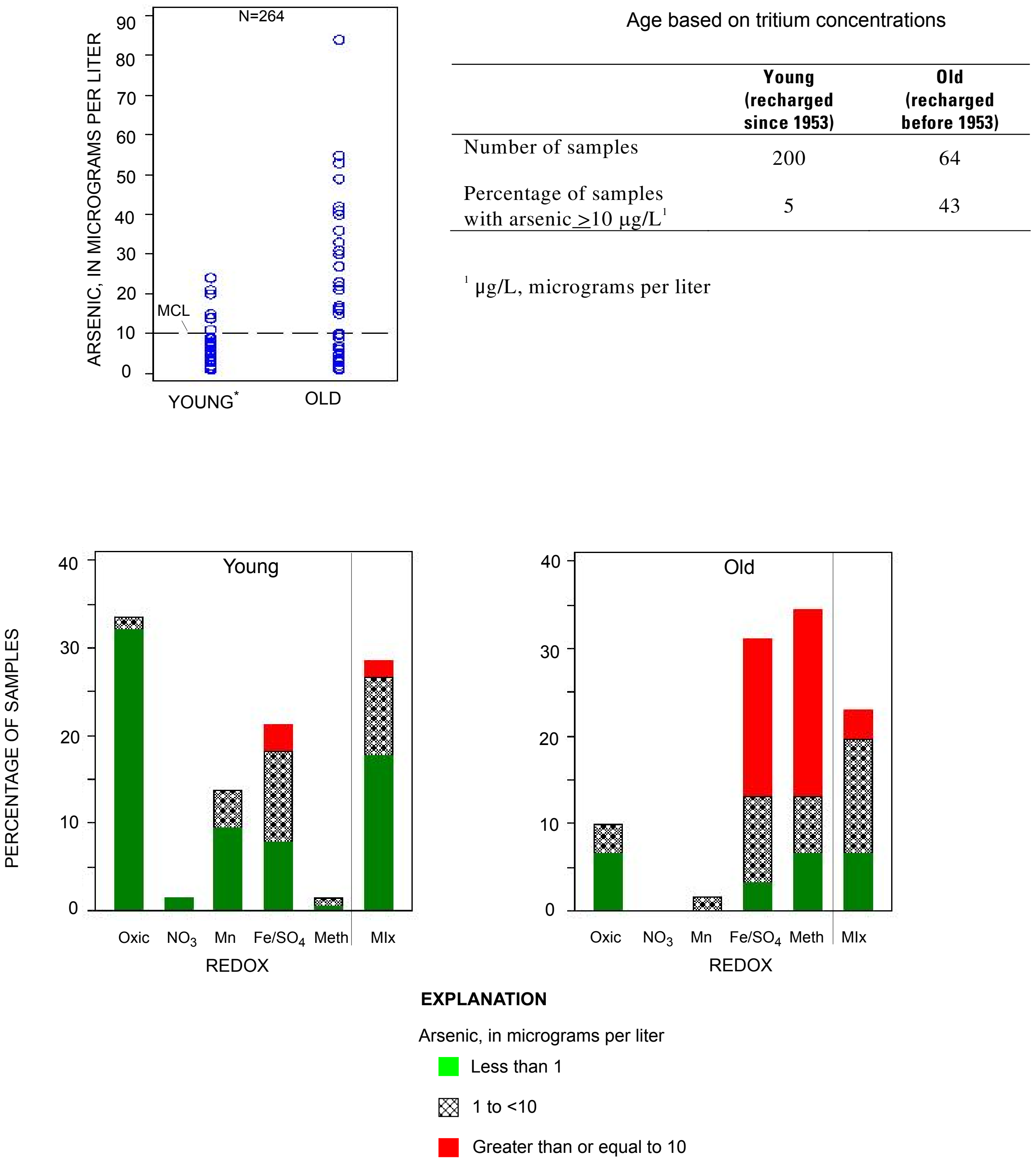


Age, in years,
based on chloroflurocarbon, sulfur hexafluoride,
or tritium/helium-3 data

| | Less than 5 | 5 to <15 | 15 to <30 | 30 to 58 |
|---|---|---|---|---|
| Number of samples | 48 | 63 | 59 | 49 |
| Percentage of samples with arsenic ≥10 µg/L[1] | 0 | 0 | 7 | 8 |

[1] µg/L, micrograms per liter

**Figure 8.** Relation of arsenic concentrations to estimated ground-water age determinations from chlorofluorocarbons, sulfur hexafluoride, or tritium/helium-3 methods. (See table 1 for explanation of redox abbreviations. MCL is Maximum Contaminant Level.)

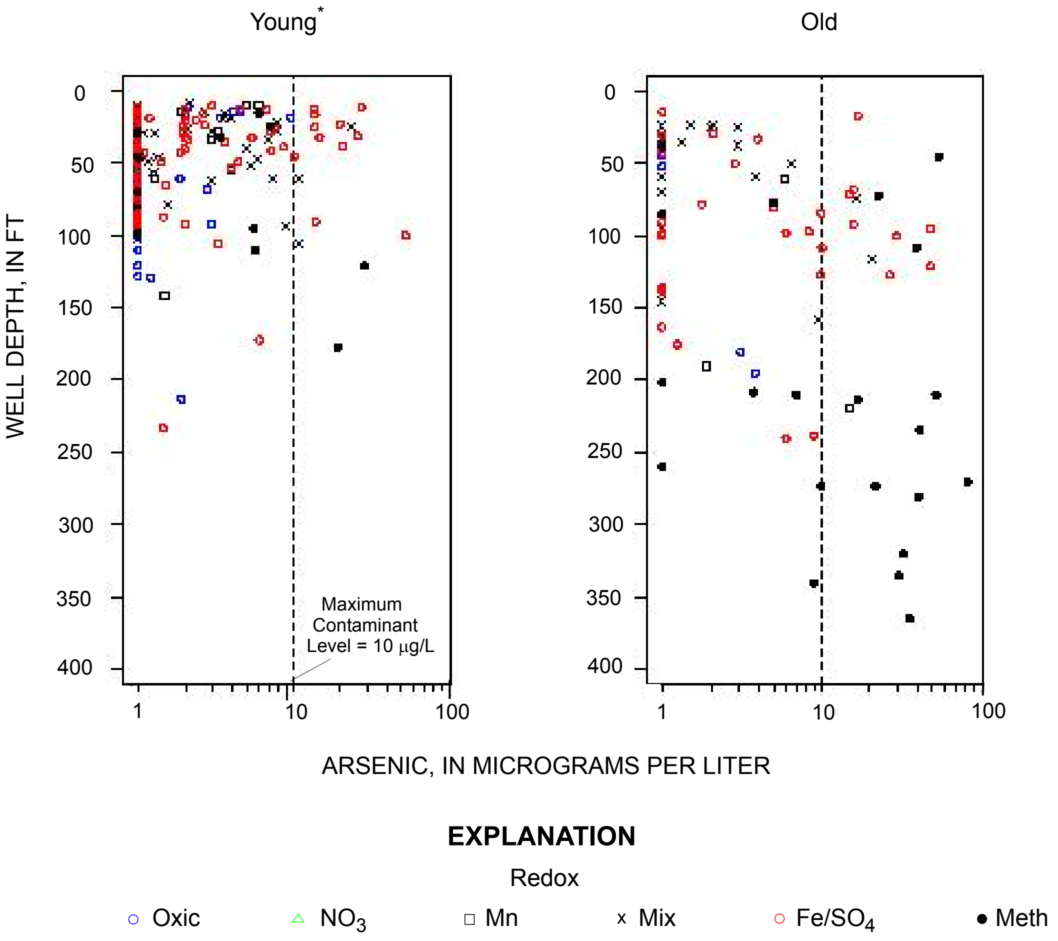


Age based on tritium concentrations

| | **Young (recharged since 1953)** | **Old (recharged before 1953)** |
|---|---|---|
| Number of samples | 200 | 64 |
| Percentage of samples with arsenic ≥10 μg/L[1] | 5 | 43 |

[1] μg/L, micrograms per liter

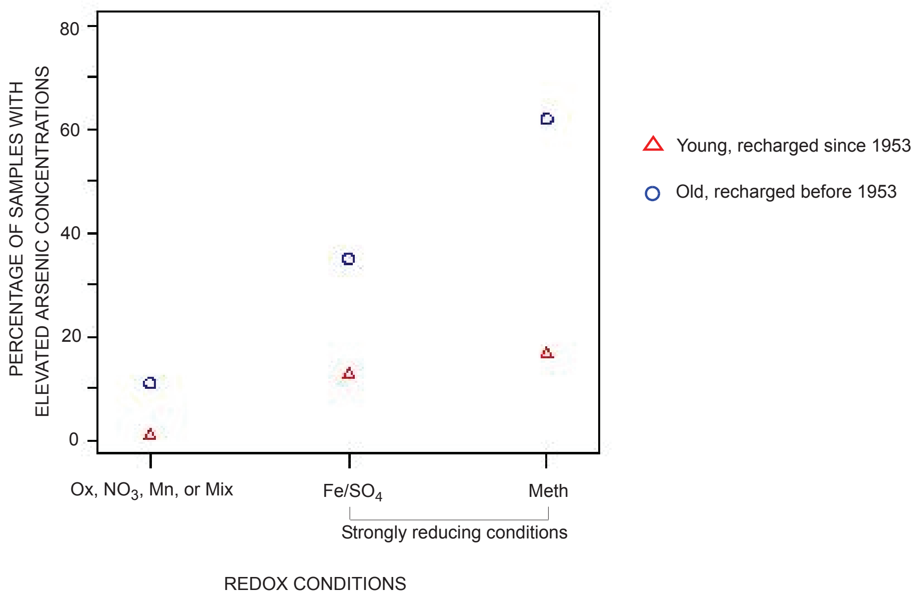
**Figure 9.** Relation of arsenic concentrations to estimated ground-water age determinations from tritium concentrations. (See table 1 for explanation of redox abbreviations. MCL is Maximum Contaminant Level. *Not shown is sample with arsenic concentration of 340 μg/L.)



| | Young (recharged since 1953) | Old (recharged before 1953) |
|---|---|---|
| Number of samples | 403 | 80 |
| Percentage of samples with arsenic ≥10 µg/L[1] | 4 | 34 |

[1] µg/L, micrograms per liter

**Figure 10.** Relation of arsenic concentration and redox condition to well depth for young and old waters. (See table 1 for explanation of redox abbreviations. *Not shown is sample with arsenic concentration of 340 µg/L and mixed redox conditions at 18 feet.)



| | **Ox, $NO_3$, Mn, or Mix** | **Fe/$SO_4$** | **Meth** |
|---|---|---|---|
| | **Young (N=403)** | | |
| Number of samples | 306 | 85 | 12 |
| Percentage of samples with arsenic ≥10 µg/L | 1 | 13 | 17 |
| | **Old (N=80)** | | |
| Number of samples | 28 | 31 | 21 |
| Percentage of samples with arsenic ≥10 µg/L | 11 | 35 | 62 |

**Figure 11.** Percentage of samples with elevated arsenic concentrations for young and old waters in three redox categories. (Elevated arsenic concentration, greater than or equal to 10 micrograms per liter. See table 1 for explanation of redox abbreviations.)

## Other Water-Quality Properties

Spearman's rho, a nonparametric test for monotonic correlation, was used to investigate possible correlations between arsenic and 30 other water-quality properties and constituents: pH, dissolved oxygen, alkalinity, major ions (calcium, magnesium, sodium, potassium, iron, manganese, chloride, bromide, sulfate, silica, fluoride, and dissolved solids), nutrients (nitrate, ammonia, and orthophosphate), trace elements (aluminum, barium, chromium, cobalt, copper, molybdenum, nickel, selenium, uranium, and zinc), dissolved organic carbon (DOC), and radon.

A total of 12 constituents had correlations with arsenic that were statistically significant ($p<0.0001$), with Spearman's rho values of at least 0.33 (table 2). Ammonia, molybdenum, iron, fluoride, strontium, lithium, silica, orthophosphate, and DOC were directly correlated with arsenic, whereas dissolved oxygen, nitrate, and radon were inversely correlated with arsenic.

Correlations of arsenic with iron, ammonia, DOC, nitrate, and dissolved oxygen are consistent with the observation that arsenic is associated with reducing conditions. Orthophosphate, silica, molybdenum, and fluoride are anions or oxyanions that sorb to iron oxides, as does arsenic (Smedley and Kinniburg, 2002). Radon is a radioactive gas with a short half-life that is associated with young waters, so the inverse correlation with arsenic is consistent with the observation that arsenic is generally higher in older waters. It is unclear why strontium and lithium were correlated with arsenic.

**Table 2.** Results of Spearman's rho tests for the 12 water-quality constituents that have the best correlations with arsenic in the glacial aquifer system of the Northern United States.

[p<0.0001 and rho≥0.33]

| Type of correlation | Water-quality constituent | Number of samples | Spearman's rho | p-value |
|---|---|---|---|---|
| Direct | Ammonia | 677 | 0.46 | <0.0001 |
| | Molybdenum | 646 | 0.45 | < .0001 |
| | Iron | 685 | 0.43 | < .0001 |
| | Fluoride | 675 | 0.41 | < .0001 |
| | Strontium | 406 | 0.40 | < .0001 |
| | Lithium | 365 | 0.40 | < .0001 |
| | Silica | 687 | 0.36 | < .0001 |
| | Orthophosphate | 666 | 0.34 | < .0001 |
| | Dissolved organic carbon | 650 | 0.33 | < .0001 |
| Inverse | Dissolved oxygen | 676 | -0.40 | < .0001 |
| | Nitrate | 677 | -0.39 | < .0001 |
| | Radon | 497 | -0.35 | < .0001 |

## Relative Significance of Factors Related to Arsenic

The relative significance of redox, ground-water age, well depth, and concentrations of the above mentioned 12 constituents as indicators of elevated arsenic concentrations was investigated by use of logistic regression. Logistic regression is a statistical method suitable for analysis of censored data (data that include values marked as less than the reporting limit), and it has been successfully used to investigate nitrate in ground water (Tesoriero and Voss, 1997; Nolan, 2001; Rupert, 2003). The method differs from linear regression in that linear regression predicts a response, whereas logistic regression predicts the probability of a response. For this study, logistic regression was used to model the probability of detecting arsenic at a concentration greater than or equal to 10 µg/L. The goal was not to create a predictive equation for its own sake, but to use the predictive capability of logistic regression to investigate the relative significance of factors related to arsenic in the glacial aquifer system.

As a first step, univariate logistic regression was used to test the significance of individual variables as indicators of elevated arsenic concentrations. Univariate models were judged on the basis of the Likelihood Ratio and its associated probability (p-value) (Hosmer and Lemeshow, 1989). The Likelihood Ratio is also a measure of the goodness-of-fit of a model, with a higher value indicating a better model (Tesoriero and Voss, 1997). A positive slope coefficient indicates a direct relation between the explanatory variable and the probability of detecting elevated arsenic concentrations, whereas a negative slope indicates an inverse relation between the two. The univariate analysis was done for the subset of data from monitor and domestic wells with ground-water age determinations (N=483).

The redox variable was a better indicator of elevated arsenic than the age or depth variables (table 3). Of the variables related to concentrations of other water-quality constituents, the ones with the highest Likelihood Ratios were ammonia, molybdenum, fluoride, and orthophosphate.

As a second step, multivariate logistic regression was used to investigate the simultaneous influence of variables that are individually significant. Variables from the best-fitting univariate models were used to build a multivariate model by means of combined forward and backward selection methods (Hosmer and Lemeshow, 1989). Whether an added variable improved a model was determined by the whether the Likelihood Ratio and Wald's statistic had a p-value <0.05 (Hosmer and Lemeshow, 1989).

The predictive ability of the univariate redox model was improved by adding either age or depth variables, but not both. Age improved the predictive ability of the redox model more than depth did, but less than variables based on concentrations of molybdenum, ammonia, or fluoride did. Several combinations of the variables from table 3 created multivariate models that were relatively similar in terms of Likelihood Ratios and Wald's statistics.

Another way to evaluate multivariate logistic regression models is to compare predicted conditions to observed conditions. Often, a logistic regression model is created using one dataset and tested using a second dataset. An alternative is jackknifing, a method whereby each observation is omitted, one at a time; each observation is then classified as an "event" or "nonevent" using the model that omits that particular

**Table 3.** Variables that are the best indicators of elevated arsenic concentrations in the glacial aquifer system of the Northern United States, based on results of univariate logistic regression.

[N, number of samples. See text for description of Likelihood Ratio, p-value, and sign of regression coefficient.]

| Name | Description | Type | N | Likelihood ratio | p-value | Sign of regression coefficient |
|---|---|---|---|---|---|---|
| Redox_var3 | Simplified redox classification:<br>1=iron or sulfate reducing;<br>2=methanogenic;<br>3=other redox conditions | Nominal | 483 | 68.6 | <0.0001 | Positive |
| Fe_var | Iron >100 ug/L | Binary | 483 | 65.5 | <.0001 | Positive |
| $NH_4$_var | Ammonia >0.15 mg/L | Binary | 479 | 64.4 | <.0001 | Positive |
| Redox_var2 | Strongly reducing (iron or sulfate reducing or methanogenic) 0=no 1=yes | Binary | 483 | 59.7 | <.0001 | Positive |
| DO | Dissolved oxygen concentration, in mg/L | Continuous | 477 | 53.2 | <.0001 | Negative |
| Age_var | Recharged before 1953 0=no 1=yes | Binary | 483 | 51.5 | <.0001 | Positive |
| Depth | Well depth, in ft | Continuous | 483 | 49.1 | <.0001 | Positive |
| Mo_var | Molybdenum > 5 µg/L 0=no 1=yes | Binary | 449 | 46.9 | <.0001 | Positive |
| F_var | Fluoride > 0.03 mg/L 0=no 1=yes | Binary | 481 | 47.8 | <.0001 | Positive |
| Ba | Barium concentration, in µg/L | Continuous | 452 | 42.0 | <.0001 | Positive |
| $PO_4$_var | Orthophosphate > 0.05 mg/L 0=no 1=yes | Binary | 478 | 21.9 | <.0001 | Positive |
| Sr | Strontium concentration, in µg/L | Continuous | 254 | 18.4 | <.0001 | Positive |

observation (SAS Institute, 1995). A SAS procedure that approximates jackknifing was used to evaluate the predictive accuracy of multivariate models (SAS Institute, 1995).

The model with the best predictive accuracy included three variables: redox, depth, and molybdenum concentrations. Using a probability cutpoint of 0.50, this three-variable model had an overall correct prediction rate of 99 percent. However, this rate may be misleading. All multivariate models that included the redox variable had a low rate of false-negative predictions and a high rate of false-positive predictions. For the three-variable model based on redox, depth, and molybdenum, the false negative rate was 4 percent, indicating that the model accurately predicted where elevated arsenic did not occur. This is consistent with the observation that elevated arsenic concentrations were uncommon in samples that were not strongly reducing. Most samples (about 90 percent) did not have elevated arsenic concentrations, so an accurate rate of predicting nonevents led to a high rate of overall correct predictions. On the other hand, the three-variable model had a much higher rate of false-positive predictions (26 percent), indicating that it overestimated the occurrence of elevated arsenic concentrations. This is consistent with the observation that, although arsenic was associated with strongly reducing conditions, not all strongly reducing samples had elevated arsenic concentrations.

# Regional Variation of Arsenic and Redox Conditions Within the Glacial Aquifer System

The previous section of the report was an analysis of arsenic and related factors in the glacial aquifer system as a whole. The goal of this section is to document and compare arsenic concentrations and redox conditions among different parts of the glacial aquifer system. The analysis is limited to data from monitor and domestic wells.

## Regional Framework of the Glacial Aquifer System

Warner and Arnold (2005) developed a regional framework to facilitate comparison of water-quality data among parts of the glacial aquifer system. Four framework areas were defined on the basis of physiography and origin of glacial lobes (fig. 12). The goal was to identify areas with similar geologic source material. Mineralogical or geochemical differences among the areas have not been documented, so these areas were presented as preliminary divisions that are subject to revision (Warner and Arnold, 2005).

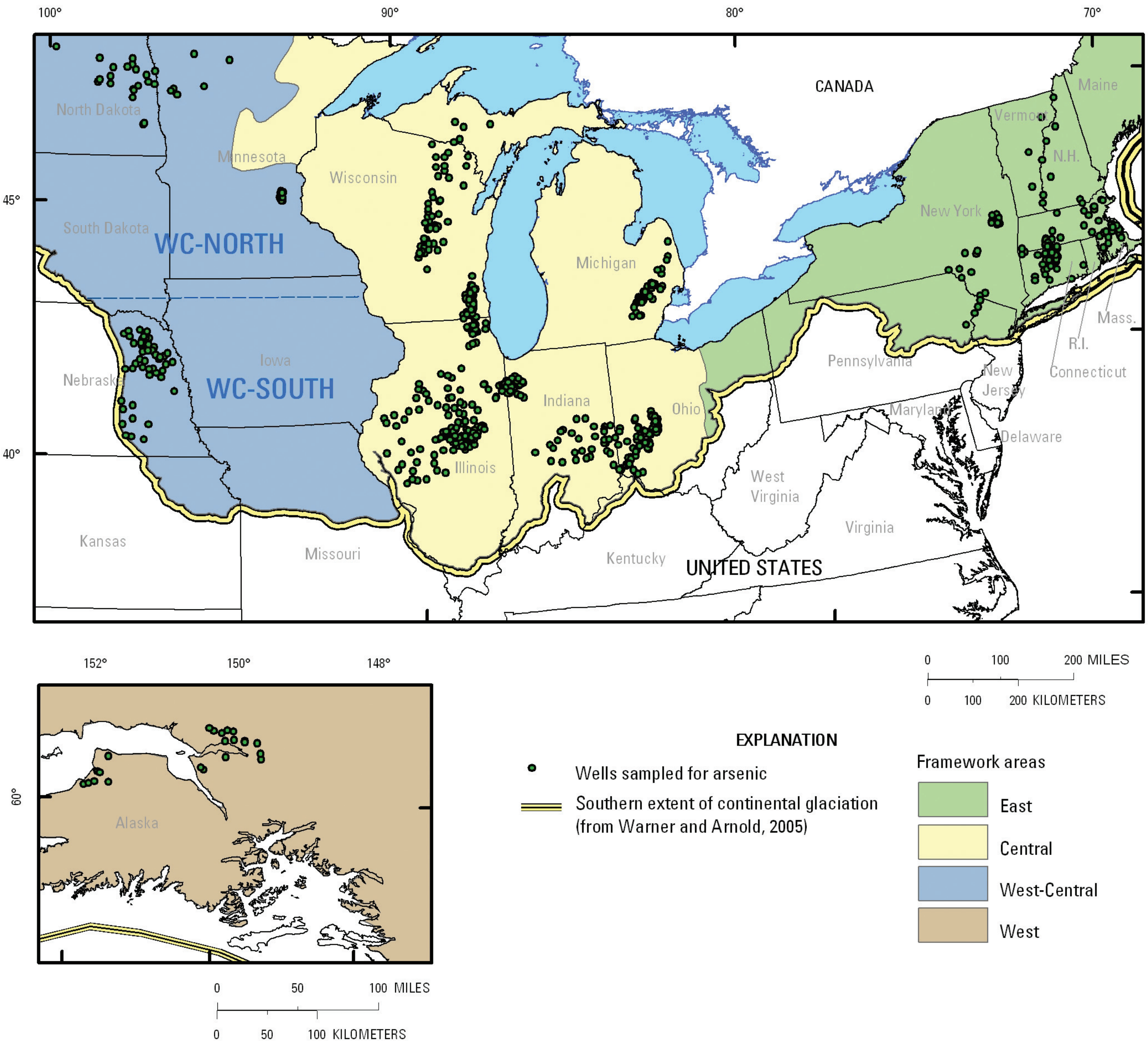
For the East area, data are from 118 monitor and domestic wells in Connecticut, Massachusetts, New Hampshire, Vermont, New York, and eastern Pennsylvania. This is part of the Appalachian Highlands physiographic division, and bedrock is predominantly crystalline and metamorphosed sedimentary rock. The glacial sediment was deposited by the latest advance (Wisconsin) of the Laurentide ice sheet. Much of the water used for public supply comes from glacial valley-fill deposits (Ayotte and others, 2003). The valley fill typically has three facies: two coarse-grained facies plus an intervening layer of finer-grained deposits (Randall, 2001). Uplands are covered by a layer of till with an average depth of 25 ft (Randall, 2001). In most areas, coarse-grained outwash is limited to valleys and is less than 200 ft thick (fig. 3).

The Central area includes data from 443 monitor and domestic wells in Ohio, Indiana, Illinois, Michigan, and Wisconsin. This is part of the Interior Plains and Laurentian Upland physiographic divisions. Most of the area is underlain by Paleozoic shales, carbonates, and sandstone, but crystalline rocks underlie the northwestern part of the Central area (fig. 2). Glacial sediments were deposited by the Great Lakes lobes of the Laurentide ice sheets. With the exception of Western Illinois, glacial deposits at land surface are of Wisconsinan age. Older glacial deposits underlie Wisconsinan deposits in many areas, especially in deep buried valleys. Glacial deposits in upland areas are about 50 to 150 ft thick, and coarse-grained outwash deposits are more than 400 ft thick in some areas (fig. 3).

The West-Central area includes data are from 105 monitor and domestic wells in Minnesota, North Dakota, and Nebraska. The area is part of the Interior Plains physiographic division. Cretaceous sedimentary bedrock underlies most the area, except for the northwestern part, where crystalline bedrock subcrops (fig. 2). The glacial deposits were from Northwest Provenance lobes of the Laurentide ice sheet. The layer of till in upland areas is about 100 to 200 ft thick, and coarse-grained outwash deposits are more than 400 ft thick in some areas (fig. 3).

The West area includes data from 22 domestic wells in Alaska. The area is part of the Pacific Mountain System, and bedrock is predominantly volcanic and sedimentary. Glacial sediment is of Wisconsinan age and was deposited by the Corderillan ice sheet.

For this report, a modified framework was used (fig. 12). Data from the West area were not considered because of the small number of samples. In addition, the West-Central area was subdivided by age of the glacial deposits. In the northern part of the West Central (WC-north) area, glacial deposits at land surface are Wisconsinan. Data are from 59 monitor and domestic wells in the North Dakota and Minnesota. In the southern part (WC-south), glacial deposits are older (pre-Illinoian). Data are from 46 monitor and domestic wells in Nebraska.



| Framework areas[1] | Physiographic division[2] | Bedrock | Ice sheet | Lobes | Framework areas used in this report | Age of glacial deposits near land surface |
|---|---|---|---|---|---|---|
| East | Appalachian Highlands | Crystalline; sedimentary | Laurentide | | East | Wisconsinan |
| Central | Interior Plains; Laurentian upland | Sedimentary; crystalline | Laurentide | Great Lakes | Central | Wisconsinan |
| West-Central | Interior Plains | Sedimentary; cyrstalline | Laurentide | Northwest Province | WC-north<br>WC-south | Wisconsinan<br>Pre-Illinoian |
| West | Pacific Mountain System | Crystalline; sedimentary | Cordilleran | | - | - |

[1] Warner and Arnold (2005).

[2] Fenneman (1946.)

**Figure 12.** Framework areas of the glacial aquifer system. (Framework areas from Warner and Arnold, 2005.)

## Comparison of Arsenic and Related Factors Among Framework Areas

Results of Kruskal-Wallis and Tukey tests indicate that arsenic concentrations were significantly different ($p<0.0001$) among samples from the four framework areas considered in this report: East, Central, WC-north, and WC-south (fig. 13). Arsenic concentrations were lowest in the East area. None of the samples had elevated arsenic concentrations, and the median was less than 1 µg/L. Arsenic concentrations in the Central area were significantly higher than those in the East; 9 percent of samples had elevated arsenic concentrations, although the median was still less than 1 µg/L. Arsenic concentrations were significantly higher in the two West-Central areas than in the Central area. For the WC-north area, 14 percent of samples had elevated arsenic concentrations, and the median was 2 µg/L. For the WC-south area, 11 percent of samples had elevated arsenic concentrations, and the median was 3.2 µg/L. Arsenic concentrations were not statistically different among the two WC areas; however, the percentage of elevated concentrations was higher in the WC-north area, whereas the median concentration was higher in the WC-south area (fig. 13).

The framework areas also differed in terms of redox conditions (fig. 13). The percentage of strongly reducing samples increased from the East (15 percent) to the Central (33 percent) to the WC-north areas (47 percent). For these three areas, the increase in elevated arsenic concentrations corresponds to an increase in strongly reducing conditions (fig. 14). Plots of median DOC and ammonia concentrations show a similar trend (fig. 14). Organic carbon acts as an electron donor in redox reactions, and higher amounts of organic carbon are typically associated with more reducing conditions. Ammonia can also be derived from reduction of organic matter. The trends illustrated in fig. 14 are consistent with the idea that reductive desorption or dissolution from iron oxides is one of the most common mechanisms of arsenic mobilization in the glacial aquifer system. In the WC-south area, three of the four samples with elevated arsenic concentrations were strongly reducing, so reductive desorption or dissolution of arsenic from iron oxides is also probably an active mechanism for mobilizing arsenic in all four of the framework areas of the glacial aquifer system.

A second mechanism for mobilizing arsenic may be active in the WC-south area. For the WC-south area, the percentage of oxic samples was similar to that for the East area, but arsenic concentrations in oxic samples were much higher in the WC-south than the East (or Central or WC-north) (fig. 15). However, the majority of oxic samples in the WC-south area had midrange arsenic concentrations (1–9.9 µg/L) rather than elevated concentrations (equal to or greater than 10 µg/L) (fig. 15).

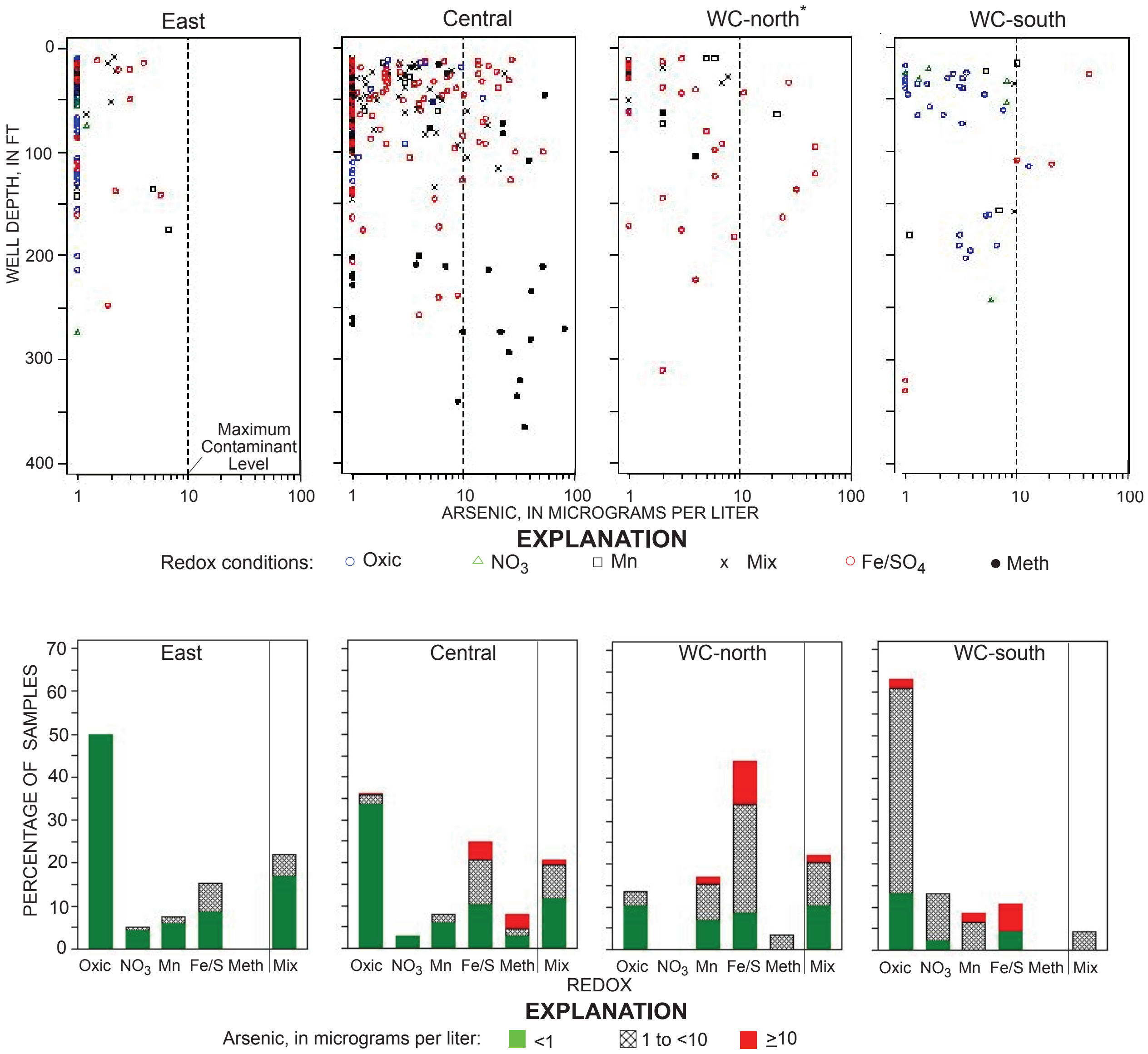
Under oxic conditions, arsenic can be released to ground water by desorption from iron oxides as a result of increased pH or by competition for sorption sites by other anions, especially phosphate (Smedley and Kinniburg, 2002). For the WC-south area, concentrations of orthophosphate are significantly higher than in the other areas, and these high concentrations might be linked to the higher arsenic concentrations in oxic samples. The link between arsenic and pH in oxic samples is not as clear; however, there is some evidence that pH and phosphate interact to affect sorption of arsenic to iron oxides (Smedley and Kinniburg, 2002).

## Relation to Conceptual Model for High-Arsenic Environments

Smedley and Kinniburg (2002) observe that, in most areas with widespread elevated arsenic concentrations, the arsenic content of the solid phase is within a normal range (1 to 20 mg/kg). For the current study, there are not sufficient mineralogical data to determine whether regional differences in arsenic concentrations of the ground water are related to the arsenic content of the aquifer matrix.

Smedley and Kinniburg (2002) propose two general requirements for the widespread development of elevated arsenic concentrations in ground water. One requirement is for a geochemical trigger to release arsenic from the aquifer matrix to the ground water. The two most important geochemical triggers are (1) development of strongly reducing conditions at near-neutral pH, which leads to release of arsenic from iron oxides by reductive desorption or dissolution, and (2) development of high pH (or competition with phosphate), which leads to desorption of arsenic from iron oxides. The second requirement is for arsenic to accumulate in the ground water faster than it is flushed away. Sluggish ground-water flow is often associated with flat, low-lying topography and thick accumulations of young, fine-grained sediment.

For the current study, the observed differences among the framework areas appear to be generally consistent with Smedley and Kinniburg’s conceptual model (2002). For example, arsenic concentrations were lowest in the East framework area. In the East, DOC concentrations in ground water are low, and strongly reducing conditions are not widespread; therefore, conditions are not conducive to arsenic release by reductive desorption or dissolution (fig. 14). Neither are geochemical conditions conducive to arsenic mobilization under oxic conditions because pH and concentrations of orthophosphate are low (fig. 15). Hydrogeology of the East area is also less conducive to arsenic accumulation in the ground water: the topographic relief is greater, and glacial deposits are generally thinner and more coarse-grained than in the Central and West-Central region (fig. 3; Randall, 2001). The observation that arsenic concentrations were relatively low in glacial deposits of the East framework area is consistent with findings of Ayotte and others (2003). In New England, elevated arsenic concentrations were associated with bedrock aquifers, especially calcareous bedrock, but were much lower in glacial deposits.



| Well or sample characteristics | East | Central | WC-north | WC-south |
|---|---|---|---|---|
| Number of samples | 118 | 443 | 59 | 46 |
| Well depth (median, in feet) | 30 | 39 | 29 | 45 |
| Arsenic concentration (median, in µg/L[1]) | <1 | <1 | 2.0 | 3.2 |
| Percentage of samples with: | | | | |
| Arsenic ≥10 µg/L[1] | 0 | 9 | 14 | 11 |
| Oxic conditions | 50 | 36 | 14 | 63 |
| Strongly reducing conditions[2] | 15 | 33 | 47 | 11 |

[1] µg/L, micrograms per liter

[2] Strongly reducing conditions are iron or sulfate reducing or methanogenic.

**Figure 13.** Arsenic in relation to redox and well-depth relations for framework areas of the glacial aquifer system. (See table 1 for explanation of redox abbreviations.)

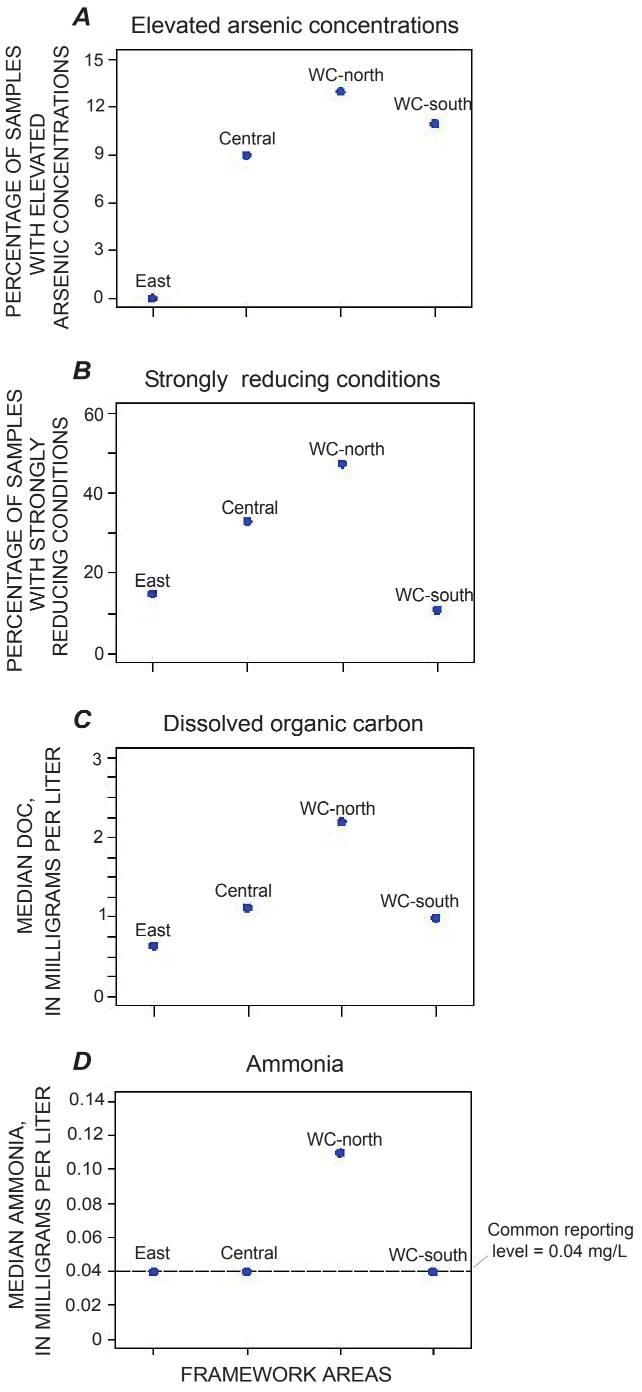


**Figure 14.** Comparison of arsenic concentration and redox-related characteristics among framework areas of the glacial aquifer system: *A*, Percentage of samples with elevated arsenic concentrations (≥ 10 µg/L). *B*, Percentage of samples with strongly reducing conditions. *C*, Median concentrations of dissolved organic carbon. *D*, Median concentrations of ammonia.

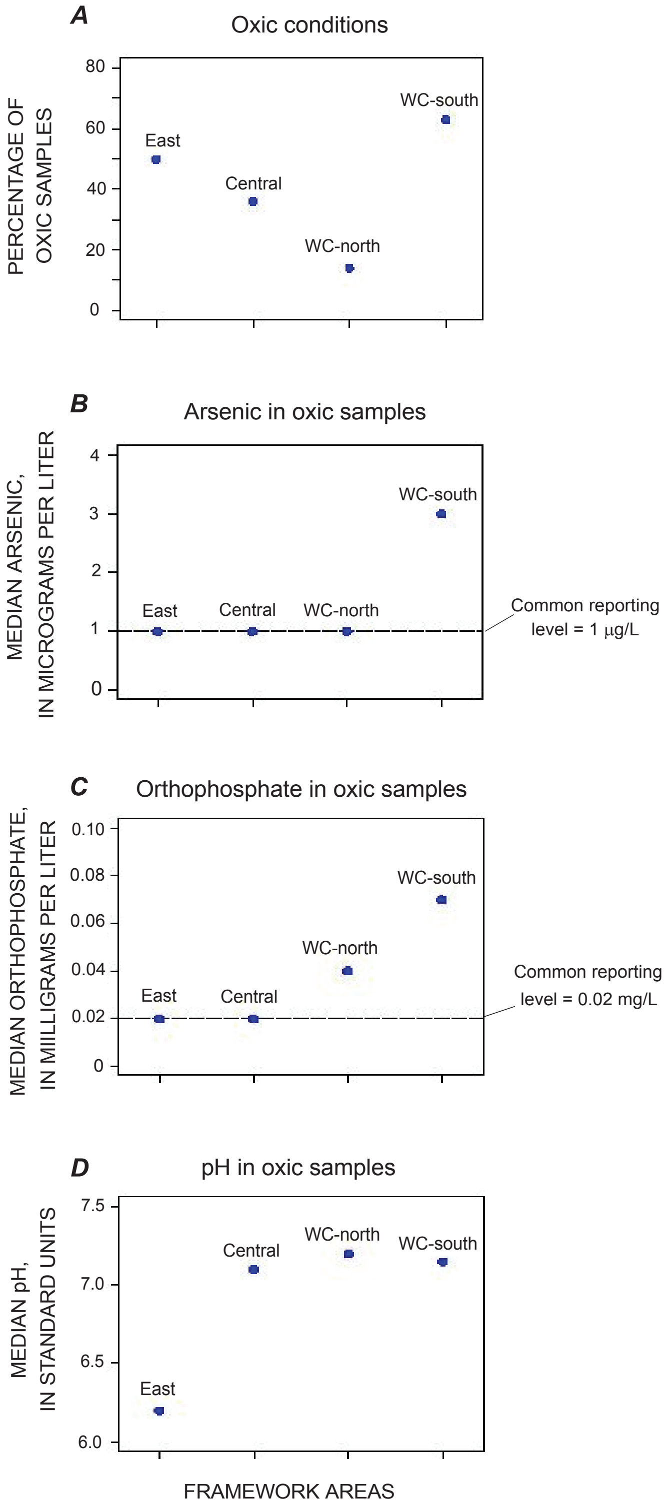


**Figure 15.** Comparison of oxic samples among framework areas of the glacial aquifer system: *A*, Percentage of oxic samples. *B*, Median arsenic concentrations in oxic samples. *C*, Median orthophosphate concentrations in oxic samples. *D*, Median pH in oxic samples.

In the Central and WC-north areas, DOC concentrations were higher and reducing conditions were more prevalent than in the East area (fig. 14). In these area, glacial deposits are thicker, and fine-grained sediment is more common (not only near land surface but also as confining or semiconfining layers at depth). Erikson and Barnes (2005) investigated arsenic in glacial aquifers of North Dakota, Minnesota, Iowa, and South Dakota, and they linked elevated arsenic concentrations to the relatively high content of organic carbon and fine-grained sediment in Late Wisconsinan till from the Northwest Provenance glacial lobes.

In the WC-south area, glacial deposits are thick and fine-grained sediment is prevalent, but DOC concentrations were lower and reducing conditions were less prevalent (fig. 14). These observations could be related to the fact that glacial deposits are older (pre-Illinoian) and more heavily weathered. In the WC-south area, there is evidence that an additional mechanism mobilizes arsenic: desorption from iron oxides under oxic conditions due to competition with phosphate, possibly in combination with moderately high pH (fig. 15).

## Summary and Conclusions

Arsenic concentrations were measured in 813 water samples from the glacial aquifer system of the Northern United States as part of USGS National Water-Quality Assessment studies during 1991–2003. Samples were collected from monitor, domestic, and public-supply wells that were 8 to 425 ft deep. Arsenic was detected (at a concentration greater than or equal to 1 µg/L) in 39 percent of samples. Arsenic concentrations were elevated (greater than or equal to 10 µg/L) in 9 percent of samples.

Elevated arsenic concentrations were associated with strongly reducing conditions. Of the samples classified as iron reducing or sulfate reducing, arsenic concentrations were elevated in 19 percent. Of the methanogenic samples, arsenic concentrations were elevated in 45 percent. In contrast, concentrations of arsenic were elevated in only 1 percent of oxic samples.

Elevated arsenic concentrations also were associated with older ground water. For the subset of data with ground-water-age determinations, arsenic concentrations were elevated in 34 percent of old samples (recharged before 1953) as compared to 4 percent of young samples (recharged since 1953). For samples classified as both old and methanogenic, arsenic concentrations were elevated in 62 percent of samples, as compared to 1 percent for samples classified as young and oxic.

Arsenic concentrations were correlated with concentrations of several other chemical constituents, including (1) constituents linked to redox processes (dissolved oxygen, nitrate, ammonia, iron, and dissolved organic carbon) and (2) anions or oxyanions that sorb to iron oxides (orthophosphate, silica, fluoride, and molybdenum.

Observations from the glacial aquifer system are consistent with the idea that the predominant source of arsenic is iron oxides and the predominant mechanism for releasing arsenic to the ground water is reductive desorption or reductive dissolution. Arsenic is also released from iron oxides under oxic conditions, but on a more limited basis and at lower concentrations.

Logistic regression was used to investigate the relative significance of redox, ground-water age, depth, and other water-quality constituents as indicators of elevated arsenic concentrations in the glacial aquifer system. The single binary variable that explained the greatest amount of variation in the data was related to redox conditions. The best multivariate logistic regression models included a redox variable, but in general, these models overestimated the occurrence of elevated arsenic. This is consistent with the observation that, although arsenic was associated with strongly reducing conditions, not all samples with strongly reducing conditions had elevated arsenic concentrations. On the other hand, the redox-based multivariate models reliably predicted where elevated arsenic did not occur. This is consistent with the observation that elevated arsenic concentrations were uncommon in samples that were not strongly reducing.

Comparisons of arsenic concentrations and redox conditions were made among four broad areas of the glacial aquifer system—East (Connecticut, Massachusetts, New Hampshire, Vermont, New York, and Pennsylvania), Central (Ohio, Indiana, Illinois, Michigan, and Wisconsin), West-Central north (North Dakota and Minnesota) and West-Central south (Nebraska). Arsenic concentrations were lowest in the East area, higher in the Central area, and highest in the West-Central north (WC-north) and West-Central south (WC-south) areas.

For the East, Central, and WC-north areas, the increase in arsenic concentrations corresponds to an increase in strongly reducing conditions. In the East area, 15 percent of samples were strongly reducing, and none had elevated arsenic concentrations. For the Central area, 33 percent of samples were strongly reducing and 9 percent had elevated arsenic concentrations. For the WC-north area, 47 percent of samples were strongly reducing and 14 percent had elevated arsenic concentrations. There is a similar increase from East to Central to WC-north areas for median concentrations of dissolved organic carbon (DOC), the predominant electron donor in redox reactions.

The WC-south area differed from the other areas; the median DOC concentration and the percentage of strongly reducing samples was relatively low, but the percentage of samples with elevated arsenic concentrations was relatively high. In addition, arsenic concentrations in oxic samples were higher than in the other areas. The higher arsenic concentrations in oxic samples in WC-south compared to the East could be the result of higher concentrations of orthophosphate and higher pH, both of which are linked to desorption of arsenic from iron oxides under oxic conditions.

The observed differences in arsenic concentrations among broad areas of the glacial aquifer system were generally consistent with a conceptual model developed by Smedley and Kinniburg, who studied or reviewed studies of widespread arsenic contamination in Bangladesh, India, China, Vietnam, Hungary, Argentina, northern Chile and the Southwestern United States.

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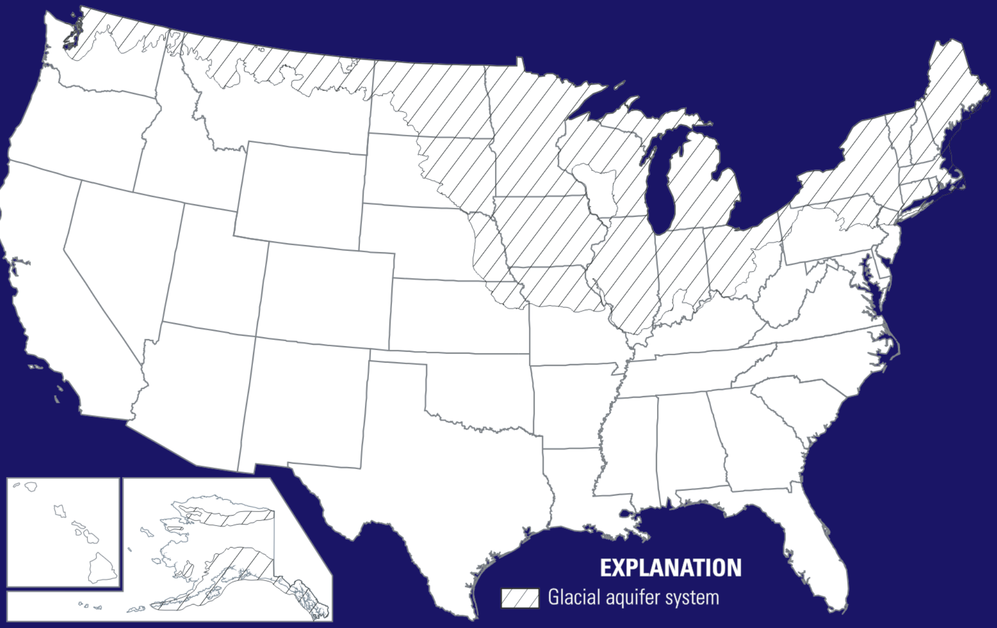

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