Arsenic in midwestern glacial deposits—Occurrence and relation to selected hydrogeologic and geochemical factors

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Conversion Factors, Datum, and Abbreviations

Multiply	By	To obtain
inch (in.)	25.4	millimeter
foot (ft)	0.3048	meter
square mile (mi^2)	2.590	square kilometer

Temperature is given in degrees Farenheit ($^\circ$F), which can be converted to degrees Celsius ($^\circ$C) by use of the following equation:

$$^\circ C = (^\circ F - 32)\ /1.8$$

Vertical coordinate information is referenced to the National Geodetic Vertical Datum of 1929 (NGVD of 1929).

Abbreviated water-quality units used in this report: Chemical concentrations and water temperature are given in metric units. Chemical concentration in water is given in milligrams per liter (mg/L), micrograms per liter (µg/L), or millimoles per liter (mmol/L). Milligrams per liter is a unit expressing the concentration of chemical constituents in solution as weight (milligrams) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to 1 milligram per liter. For concentrations less than 7,000 mg/L, the numerical value is approximately the same as for concentrations in parts per million. Milliequivalents per liter is derived from the mass, in grams, numerically equal to the molecular weight of the substance in a liter of water.

Radioactivity is expressed in picocuries per liter (pCi/L). A picocurie is one-trillionth (1×10^{-12}) the amount of radioactivity represented by a curie (Ci). A curie is the amount of radioactivity that yields 3.7×10^{10} radioactive disintegrations per second. A picocurie yields 2.22 disintegrations per minute.

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Abstract

Ground-water-quality data collected as part of 12 U.S. Geological Survey National Water-Quality Assessment studies during 1996-2001 were analyzed to (1) document arsenic occurrence in four types of glacial deposits that occur in large areas of the Midwest, (2) identify hydrogeologic or geochemical factors associated with elevated arsenic concentrations, and (3) search for clues as to arsenic source(s) or mechanism(s) of mobilization that could be useful for designing future studies.

Arsenic and other water-quality constituents were sampled in 342 monitor and domestic wells in parts of Illinois, Indiana, Ohio, Michigan and Wisconsin. Arsenic was detected (at a concentration ≥ 1 µg/L) in one-third of the samples. The maximum concentration was 84 µg/L, and the median was less than 1 µg/L. Eight percent of samples had arsenic concentrations that exceeded the U.S. Environmental Protection Agency Maximum Contaminant Level (MCL) of 10 µg/L.

Samples were from four aquifer types—confined valley fill, unconfined valley fill, outwash plain, and till with sand lenses. Highest arsenic concentrations were found in reducing waters from valley-fill deposits. In confined valley fill, all waters were reducing and old (recharged before 1953), and almost half of samples had arsenic concentrations greater than the MCL. In unconfined valley fill, redox conditions and ages were varied, and elevated arsenic concentrations were sporadic. In both types of valley fill, elevated arsenic concentrations are linked to the underlying bedrock on the basis of spatial relations and geochemical correlations.

In shallow (<50 ft) till with sand lenses, arsenic was detected in oxic or mixed waters, but concentrations were rarely greater than the MCL. In shallow outwash-plain deposits, arsenic concentrations greater than the MCL were detected in waters that were reducing and young (recharged after 1953).

Although arsenic concentrations were significantly higher in deep wells (>150 ft), all deep wells were from a distinctive aquifer type (confined valley fill). It is not known whether wells at similar depths in other aquifer types would produce waters with similarly high arsenic concentrations.

Correlations of arsenic with fluoride, strontium, and barium suggest that arsenic might be related to epigenetic (Mississippi Valley-type) sulfide deposits in Paleozoic bedrock. Arsenic is typically released from sulfides by oxidation, but in the current study, the highest arsenic concentrations in glacial deposits were detected in reducing waters. Therefore, a link between epigenetic sulfides and elevated arsenic concentrations in glacial deposits would probably require a multi-step process.

Introduction

Arsenic in drinking water has been linked to multiple health problems, including bladder, lung, and skin cancers; cardiovascular disease; diabetes; and neurological dysfunction (National Research Council, 1999). In recognition of the health risks associated with arsenic, the U.S. Environmental Protection Agency (USEPA) decreased the Maximum Contaminant Level (MCL) from 50 to 10 µg/L on October 31, 2001 (U.S. Environmental Protection Agency, 2001a). The new regulation will be enforceable for public-water systems in 2006.

In the United States, highest arsenic concentrations in ground water are generally associated with aquifers in the West, but a recent national data compilation indicates that arsenic concentrations in the Midwest are higher than previously recognized (Welch and others, 2000). In parts of the Midwest, there is no discernible pattern to the distribution of arsenic concentrations in ground water, so occurrences of elevated arsenic concentrations have been described as sporadic (Korte, 1991) or "hot spots" (Dempsey, 2001).

Sources and causes of elevated arsenic concentrations in ground water are difficult to interpret for multiple reasons: (1) Arsenic has both anthropogenic and natural sources. Moreover, arsenic from natural sources can be released by human activities that alter redox conditions in the subsurface. (2) Minerals with which arsenic is associated—pyrite and iron oxides—are ubiquitous trace components of sedimentary bedrock and glacial deposits. Moreover, pyrite can be oxidized to iron oxide. (3) Arsenic can be mobilized under either oxic or anoxic conditions. (4) Arsenic concentrations in the aquifer matrix (solid phase) do not always correlate with arsenic concentrations in ground water (U.S. Geological Survey, 1999; Warner, 2001; Berg and others, 2001).

To unambiguously determine the sources and mechanisms of mobilization of arsenic in ground water, hydrogeologic investigations must incorporate water-quality analysis, mineralogical analysis, and geochemical modeling. The design of such studies can be aided by analysis of available data. During 1991–2001, the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program documented the occurrence and distribution of water-quality constituents in ground water from 51 drainage basins (study units) across the Nation. These data are especially useful for regional water-quality comparisons because consistent methods were used to collect and analyze the data. In addition, the study areas were chosen to be representative of important hydrogeologic and land-use settings.

The long-term research goal, which extends beyond the scope of this study, is to be able to predict which types of glacial deposits are most (and least) vulnerable to elevated arsenic concentrations. In areas where multiple water-producing zones are present, this information would allow drillers to avoid installing wells in zones with a high risk of arsenic contamination. Where avoidance is not possible, agencies responsible for human health could target water-quality monitoring and (or) education about water-treatment options to areas where the sole source of ground water is an aquifer of high risk. The information could also be useful to public-water suppliers faced with meeting the lower arsenic MCL by 2006; in areas with multiple water-producing zones, installing a new well in an aquifer of low risk may be less expensive than upgrading the present water-treatment system.

Purpose and scope

This report summarizes arsenic-related data from NAWQA water-quality studies in Midwestern glacial deposits that were completed during 1996–2001. Arsenic data were collected from 342 wells in selected parts of five Midwestern States. The goals of the report are to document arsenic occurrence in aquifer types that are common to large areas of the Midwest, identify hydrogeologic or geochemical factors with which arsenic concentrations are related, and determine whether occurrence data can provide clues as to the cause of elevated arsenic concentrations in glacial deposits. This preliminary understanding can be revised and refined as additional water-quality data are collected during the next decade of the NAWQA Program.

Description of the study area

Data are from parts of four drainage basins (study units) in the glaciated Midwest—the Lower Illinois River Basin (LIRB) in central Illinois; the Upper Illinois River Basin (UIRB) in northeastern Illinois, northwestern Indiana, and southeastern Wisconsin; the Lake Erie-Lake Saint Clair Drainages (LERI) in southeastern Michigan, and the Great and Little Miami River Basins (MIAM) in southwestern Ohio and southeastern Indiana (fig. 1). A detailed description of the environmental setting of each basin is given in Warner (1998), Arnold and others (1999), Casey and others (1997) and Debrewer and others (2000), respectively. Selected data from these reports are summarized in table 1.

The area is part of the Central Lowlands Physiographic Province, and topography, climate, and land use in the four drainage basins are relatively similar. Topography is flat to gently rolling; most of the relief is associated with river valleys or glacial features. Average annual precipitation is 30 to 42 in. and average annual temperatures are 46 to 55°F. More than 75 percent of the land area in each of the basins is used for agriculture—predominantly corn and soybean rowcrops.

The area is covered by glacial deposits that are typically 50 to 200 ft thick, but they can be more than 400 ft thick in current or former river valleys. The three major types of glacial deposits are coarse-grained stratified sediment, fine-grained stratified sediment, and till (fig. 2a). Coarse-grained stratified sediment is predominantly sand and gravel deposited by glacial meltwaters. Fine-grained stratified sediment is predominantly clay associated with former lakebeds. The most widespread deposit is till, a heterogeneous mixture of clay, silt, sand, and gravel that was deposited directly by the glacier as end moraines (broad, rolling hills) or ground moraine (flat plains). Till is typically fine grained, but it often contains lenses or layers of sand and gravel of varied thickness and extent. The upper 15 to 35 ft of clay-rich tills are commonly fractured (Ruland and others, 1991;
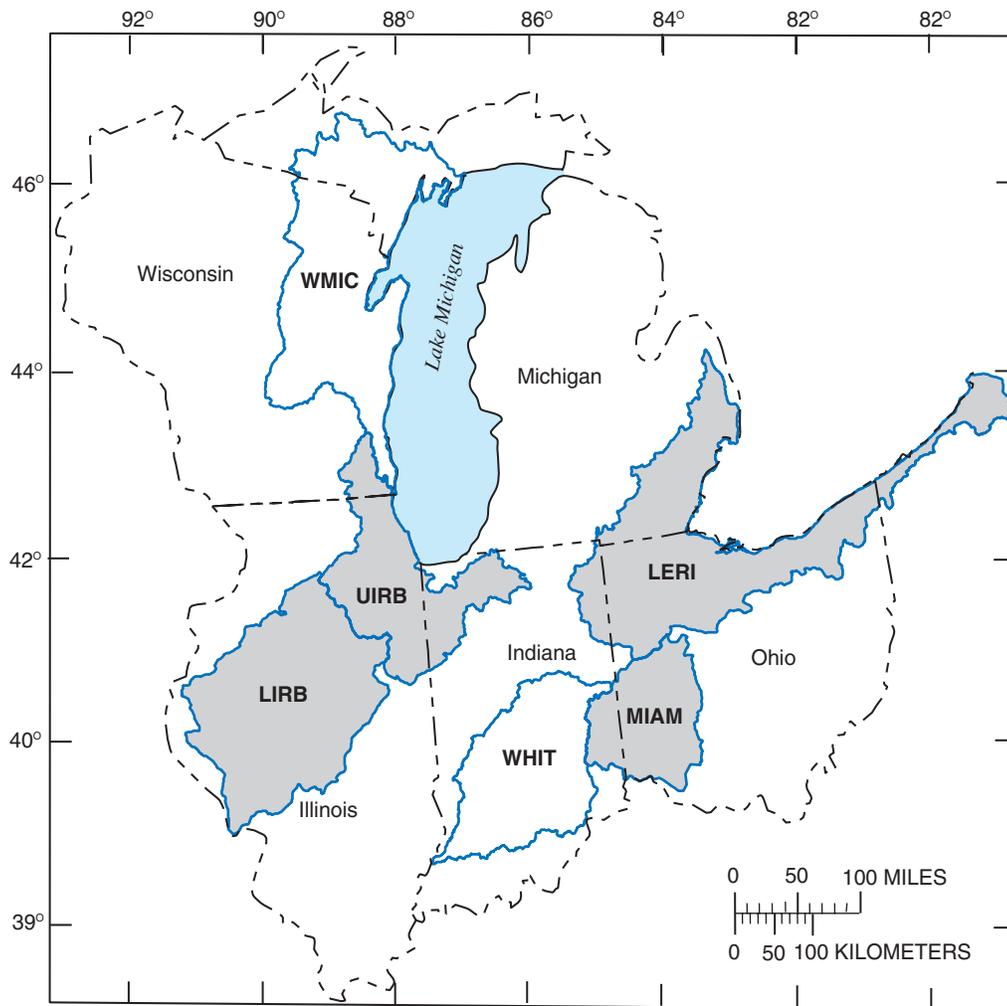
Figure 1.   Location of National Water-Quality Assessment (NAWQA) study units in the glaciated Midwest.

Table 1. Selected characteristics of midwestern drainage basins included in this study.

[mi^2, square miles; in., inches; °F, degrees Farenheit; ft, feet; NGVD, National Geodetic Vertical Datum; Ag, agriculture]

Drainage basin (reference)	Basin size (mi^2)	Physiography[a]		Average annual precipitation (in.)	Average annual temperature (°F)	Land-surface altitude (ft, NGVD of 1929)	Land use (percent of total area)
		Province	Section				
Lower Illinois River Basin (Warner, 1998)	18,000	Central Lowland	Till Plains	35 to 38	50 to 55	Typically 600 to 800	Ag: 87 Urban: 2 Forest: 8
Upper Illinois River Basin (Arnold and others, 1999)	10,949	Central Lowland	Till Plains, Great Lakes	32 to 38	46 to 51	443 to 1,250	Ag: 75 Urban: 17 Forest: 5
Lake Erie-Lake St. Clair Drainages (Casey and others, 1997)	22,300	Central Lowland	Eastern Lake[b]	30 to 34[b]	47 to 50[b]	580 to 1,100	Ag: 75 Urban: 11 Forest: 10
Great and Little Miami River Basins (Debrewer and others,2000)	7,354	Central Lowland	Till Plains	36 to 42	49 to 55	451 to 1,550	Ag: 79 Urban: 13 Forest: 7

[a] From Fenneman and Johnson (1946).

[b] Pertains to northwestern part of the basin, where the ground-water studies were done.

Strobel, 1993; Fleming and others, 1994).

Most domestic or public-supply wells produce water from four types of glacial deposits (fig. 2b): (1) "Till with sand lenses" refers to deposits that produce water from lenses or layers of coarse-grained sediment within clay-rich till. The lenses or layers can be of variable depth, thickness, and lateral extent. (2) "Outwash plain" refers to laterally extensive, sheetlike deposits that are predominantly coarse grained. (3) "Valley fill" is also predominantly coarse-grained sediment, but it occurs as linear deposits associated with current or former rivers. These deposits are subdivided into "unconfined valley fill," where the sediment is predominantly coarse grained, although it can contain lesser amounts of till or fine-grained stratified sediment. "Confined valley fill" refers to a coarse-grained deposit overlain by a thick layer of till or fine-grained stratified sediment. Where valley-fill deposits are coincident with streams, public-supply wells are often located to induce infiltration from surface water.

In the study area, glacial deposits are underlain by Paleozoic sedimentary bedrock, predominantly carbonates and shales with lesser amounts of sandstone (fig. 2c). The bedrock layers are gently dipping. The younger formations subcrop in the Illinois and Michigan structural basins, and the older formations subcrop along the three broad arches that separate the basins (fig. 2d).

Bedrock is a productive source of ground water in some parts of the study area. Silurian-Devonian carbonate rocks in western Ohio, northeastern Indiana, northern Illinois, and southeastern Wisconsin form an important regional aquifer (Arnold and others, 1999; Eberts and George, 2000). In contrast, Mississippian-age sedimentary bedrock in parts of southeastern Michigan cannot be consistently utilized as a source of drinking water because of problems with quantity and (or) quality (Mozola, 1953). For similar reasons, uppermost Mississippian and Pennsylvanian bedrock contributes less than 10 percent of total water use in central Illinois (Warner, 1998).
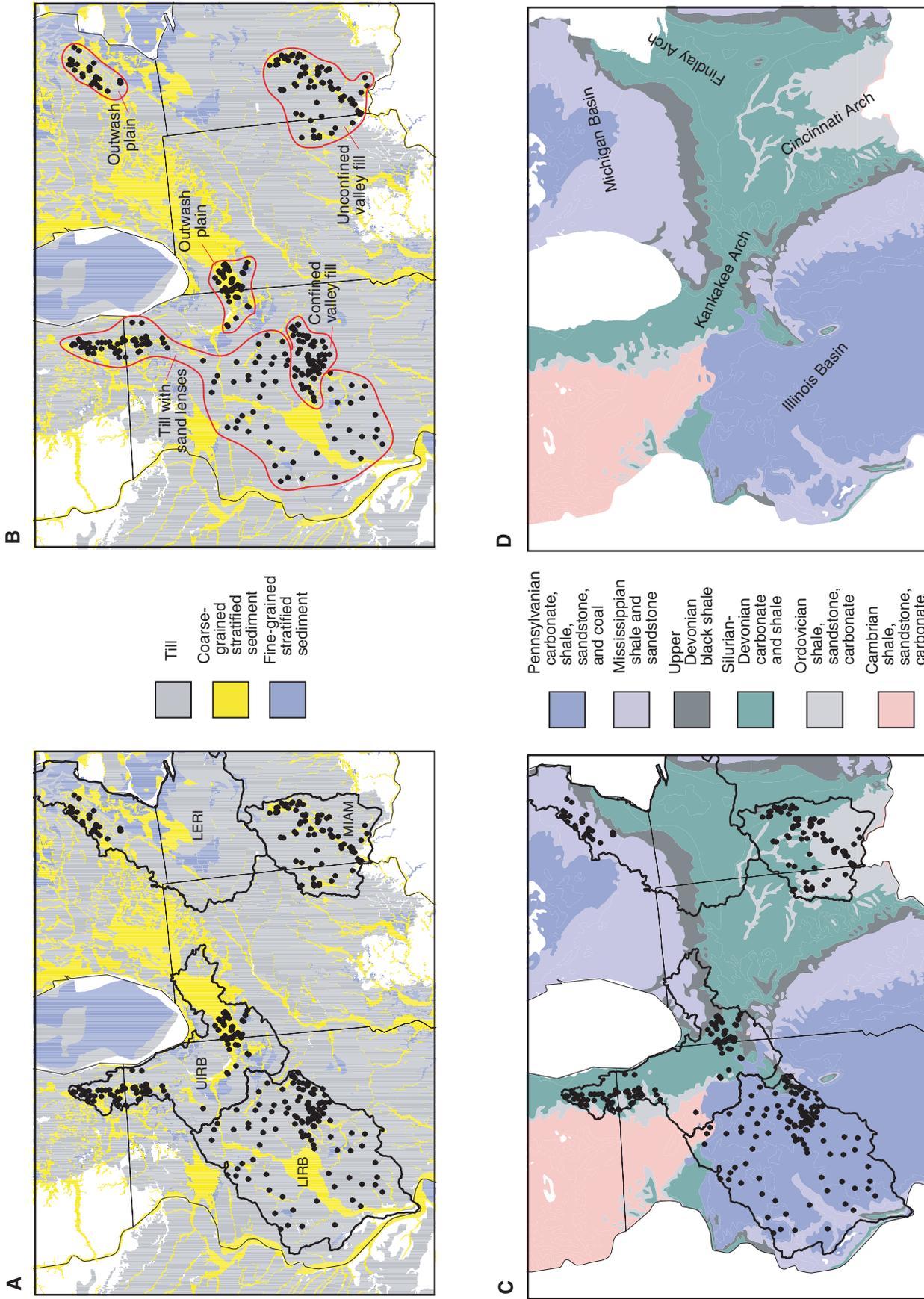
Figure 2. Location of well networks in relation to (A) surficial glacial deposits (Soller and Parkard, 1998), (B) aquifer type (K. Warner, USGS, written commun., 2002), (C) bedrock geology (Schruben and others, 1997), and (D) major geologic structures (Eberts and George, 2000).

Previous studies

Welch and others (2000) presented a thorough summary of the occurrence and geochemistry of arsenic in ground water of the United States. Arsenic is the 20th most common component in the Earth's crust (Welch and others, 2001). Arsenic is associated with various minerals—it is a component of sulfide minerals; it substitutes into the crystalline lattice of silicates; and it sorbs to iron/manganese oxyhydroxides, clays, and organic matter. Presumably, arsenic can be mobilized under conditions in which these materials become unstable (Welch and others, 1988). In ground water, arsenic is commonly present in two oxidation states. Arsenate ($H_nAsO_4^{n-3}$) has a oxidation state of +5 and is the predominant form of arsenic in oxic waters. Arsenite ($H_nAsO_3^{n-3}$) has an oxidation state of –3, and it is the predominant form in reducing waters. Of the two forms, arsenite is more toxic and more mobile in solution.

The current discussion focuses on studies of arsenic in ground water of the Midwest. One of the most frequently cited sources of elevated arsenic concentrations in midwestern ground water are sulfides, such as pyrite. Arsenic-bearing sulfides were deposited in Paleozoic bedrock by large-scale migrations of ore-bearing fluids during late stages of the Ouachita and Appalachian orogenies (Goldhaber and others, 2003). Arsenic concentrations in pyrite are typically 0.02 to 0.5 percent, but they can be much higher (Welch and others, 2000). Glacial deposits derived from sedimentary bedrock also conintain sulfides. For example, pyrite is abundant in till in central Illinois (Warner, 2001), and clasts of pyrite-rich black shale are visible in till of northwestern Ohio and southwestern Michigan (Thomas, 2000b).

Pyrite is unstable under oxic conditions. The most well-studied mechanism of pyrite oxidation is by oxygen, which occurs as a bacterially mediated multistep process. Pyrite can also be oxidized by ferric iron or nitrate (Welch and others, 2000; Appelo and Postma, 1996). The process can be either biotic or abiotic, and it can occur in waters with pH values that are acidic to slightly alkaline (Evangelou and others, 1998; Welch and others, 2000). However, reaction rates vary in response to the reaction pathway.

Pyrite oxidation was the proposed cause of arsenic concentrations greater than 100 µg/L detected in domestic wells in eastern Wisconsin. The wells produce water from the Ordovician bedrock aquifer overlain by glacial deposits. The bedrock contains a sulfide-cemented zone of diagenetic origin, and this zone has been oxidized by oxygen that entered the aquifer by well bores or by a lowered water table that resulted from increased withdrawals in the study area (Schreiber and others, 2003). Lower arsenic concentrations (<100 µg/L) were also found in the same aquifer, but these were interpreted to be due to a mechanism other than pyrite oxidation (Schreiber and others, 2003).

Pyrite oxidation was also the initial working hypothesis for elevated arsenic concentrations in wells in eastern Michigan, where Mississippian bedrock is overlain by glacial deposits. Water-quality and core data were studied to determine whether the relatively high concentration of pyrite in the Mississippian Marshall Sandstone was the source of the arsenic in the ground water (U.S. Geological Survey, 1999; Haack and Treccani, 2000). Little correlation was found between arsenic concentrations in the water and bedrock, and in addition, preliminary geochemical modeling was not consistent with oxidation of pyrite in reducing ground water. As a result, the working hypothesis was expanded to include other mechanisms (U.S. Geological Survey, 1999; Kolker and others, 2003). In a related study, Kim and others (2000) did laboratory experiments using data from the Marshall Sandstone to demonstrate that arsenic can be leached from pyrite by bicarbonate under reducing conditions. Oxidation of black-shale fragments within glacial deposits was proposed as the cause of arsenic in ground water in parts of northeastern Indiana (Yarling, 1992).

A second commonly cited source of arsenic to midwestern ground water is iron/manganese oxyhydroxides. These minerals form by weathering of iron/manganese-bearing minerals, including sulfides. Iron/manganese oxyhydroxides can be disseminated throughout an aquifer or concentrated along particular horizons—such as zones of fluid migration or along unconformities. Iron/manganese oxyhydroxides are widespread in the Midwest, where there are multiple major and minor unconformities in bedrock and glacial deposits. For brevity, the term "iron oxides" will be used as shorthand for "iron/manganese oxyhydroxides."

Arsenic is associated with iron oxides in two ways: (1) It can coprecipitate with iron oxides and become incorporated into the mineral structure. Coprecipitated arsenic will be mobilized by reductive dissolution of the iron oxides. The reductant can be naturally occurring organic carbon, such as peat (McCarthur and others, 2001), or synthetic organic chemicals (Welch and others, 2000). (2) Arsenic can also be sorbed onto the surface of iron oxides. Mobilization of arsenic can occur by reduction of arsenate by microbes (Zobrist and others, 2000) by desorption related to an increase in pH (Schlottman and others, 1998), or by desorption due to competing oxyanions such as phosphate (Welch and others, 2000). Sorbed arsenic will also be released during reductive dissolution of iron oxides.

Matisoff and others (1982) investigated elevated arsenic concentrations in an area of northeastern Ohio where a buried valley dissects a sandstone aquifer overlain by till. The conclusion was that arsenic was released from iron oxides under reducing conditions. One possible reductant could have been methane gas leaking from deep underground storage. Another explanation that may have wider applicability to the glaciated Midwest is that iron oxides, which were initially deposited in subaerial environment, have become unstable in a reducing environment created after a layer of surficial till restricted recharge to the aquifer.

Korte (1991) investigated elevated arsenic concentrations in ground water at sites in Missouri and Ohio and reviewed selected arsenic studies in other parts of the Midwest. He concluded that arsenic is released from iron oxides in response to a change from oxic to reducing conditions caused by sediment deposition. In addition, he proposed that the sporadic nature of

arsenic detections may result because of local variations in redox conditions and that high arsenic concentrations were more likely to occur in low-yield wells in areas with relatively high amounts of clay.

At high pH, arsenic is less strongly sorbed to iron oxides than at low pH. In the western United States, high pH can be related to felsic volcanic rocks (Welch and others, 2000). In relation to sedimentary bedrock, Schlottman (2001) proposed that arsenic desorbs from iron oxides in a sandstone aquifer where high pH is the result of cation exchange in confined, clay-rich zones. Cation exchange between ground water and clay causes concentrations of dissolved sodium to increase while concentrations of dissolved calcium and magnesium decrease. When geochemical equilibrium shifts, dolomite dissolves and concentrations of dissolved bicarbonate (and therefore pH) increase.

Warner (2001) analyzed arsenic in glacial deposits of the Lower Illinois River Basin and reported that (1) arsenic concentrations in the deeper deposits were much higher than in the shallower deposits; (2) most arsenic is in the reduced form (arsenite), and (3) there is no simple relation between arsenic in ground water and the aquifer matrix. The conclusions were that geologic structures are a potential pathway for migration of arsenic from bedrock, as evidenced by a positive correlation between arsenic and chloride.

Breit and others (2001) discussed cycling of arsenic between sulfides and iron oxides (and weathered biotite) in response to changes in geochemical environments caused by fluctuations of sea level, cycles of erosion and burial, and land use. The Breit and others' study site was the Bengal Delta in eastern Bangladesh; but the conclusions may be applicable to the Midwest, which was subjected to multiple cycles of glaciation during Pleistocene and major shifts of geochemical environments during deposition and erosion of Paleozoic (and presumably Mesozoic and Cenozoic) bedrock.

In addition to natural sources, arsenic has various anthropogenic sources, as summarized by Welch and others (2000). During the 1980s and 1990s, the major use of arsenic was as a wood preservative, although that use is being voluntarily phased out. Arsenic compounds are also used in glass production, added to swine and poultry feed, and included in some crabgrass herbicides sold to the public. Prior to 1980, the use of arsenic as an agricultural pesticide was much more widespread than it is today. Elevated arsenic concentrations in soil have been linked to historical uses of arsenic in orchards and other agricultural areas. In such areas, application of phosphate fertilizer could mobilize arsenic sorbed to soil. Arsenic is detected in ground water beneath waste-disposal sites, but the source is not always anthropogenic; arsenic can be released from iron oxides in the aquifer matrix resulting from reducing conditions caused by a contaminant plume.

Methods

Water-quality data were collected from 342 wells in glacial deposits of the Midwest. The wells are part of three types of well networks (listed below) common to NAWQA ground-water studies across the Nation (fig. 3) (Gilliom and others, 1995):

- An Agricultural Land-Use Study (ag) is a network of 20 to 30 monitor wells installed just below the water table in an area overlain by agricultural land use. This report includes data from four agricultural land-use studies (120 wells).

- An Urban Land-Use Study (urb) is a network of 20 to 30 monitor wells installed just below the water table in an area overlain by recent residential/commercial land use. This report includes data from three urban land-use studies (83 wells).

- A Major Aquifer Survey (mas) is a network of 20 to 30 existing (typically domestic) wells in an aquifer that is an important source of drinking water. This report includes data from five major-aquifer surveys (139 wells). Two of the 139 wells are public-supply wells, but the production rates are so low that they are considered comparable to domestic wells for this analysis.

Each well was sampled once. The studies followed NAWQA guidelines for study design, selection or installation of wells, sample collection, quality-assurance protocols, and analytical procedures (table 2).

Table 2. Protocols used for U.S. Geological Survey National Water-Quality Assessment (NAWQA) studies, 1996–2001.

[USGS, U.S. Geological Survey]

Procedure	Reference
Study design and site selection	Gilliom and others (1995); Scott (1990); Squillace and Price (1996)
Criteria for selecting wells Methods for installing monitor wells	Lapham and others (1995)
Well purging Sample collection, filtration, and preservation Equipment decontamination Collection of quality-assurance samples	Koterba and others (1995)
Analysis of water samples: Major ions, nutrients Trace elements Dissolved organic carbon Tritium	USGS Water-Quality Laboratory: Fishman (1993) Fishman (1993); Garbarino (1999) Brenton and Arnette (1993) Ostlund and Dorsey (1977)
Documentation of land use and geology in the vicinity of each well	Koterba (1998)

Figure 3.   National Water-Quality Assessment (NAWQA) well networks in midwestern glacial deposits sampled for arsenic during 1996–2001.

Arsenic concentrations were measured from samples filtered through a 0.45-μm capsule filter. For studies that were done in 1996 to 1999, arsenic concentrations were measured by the graphite furnace atomic-absorption (GFAA) method, with a reporting limit of 1 μg/L. After 1999, arsenic was analyzed by the inductively coupled plasma-mass spectrophotometry (ICP/MS) method, with reporting limits of 0.9 to 0.18 μg/L. For the purpose of data analysis, arsenic data were censored to 1 μg/L, the highest reporting limit. Therefore, the phrase "arsenic was detected" means that the arsenic concentration was equal to or greater than 1 μg/L. The USEPA MCL is based on arsenic concentrations from unfiltered samples. Filtration can remove some particulates with arsenic, so the reported values from some NAWQA (filtered) samples may underestimate arsenic concentrations relative to the MCL.

Water-quality data from the 12 studies were retrieved from USGS National Water Information System databases in Ohio, Michigan, and Illinois. Data were combined into a single dataset and analyzed using graphical methods (histograms, cross plots, and Piper diagrams) and nonparametric statistical methods (Kruskal-Wallis, Tukey, and Spearman's rho tests) (Helsel and Hirsch, 1995).

Information about the environmental setting, well-selection criteria, and water-quality characteristics of each well network were obtained from NAWQA reports (Casey and others, 1997; Warner, 1998; Debrewer and others, 2000; Arnold and others, 1999; Myers and others, 2000; Groschen and others, 2000), NAWQA Web sites (U.S. Geological Survey, 2001a,b,c,d) and journal articles based on NAWQA studies (Thomas, 2000a; Warner, 2001).

Four methods were used to estimate ground-water ages—tritium, tritium-helium, chlorofluorocarbons (CFCs), or sulfur hexafluoride (SF_6) (Plummer and others, 1993). Samples with tritium concentrations <5.7 pCi/L were interpreted to have been recharged before 1953, and samples with concentrations ≥5.7 pCi/L were interpreted to have been recharged after 1953. More precise age-dates were estimated using tritium-helium, CFCs, or SF_6 methods, but to facilitate comparisons among well networks, ground-water ages were censored to the highest reporting level—that of the tritium method. Samples interpreted to have been recharged after 1953 (based on any method) are referred to as "young" waters, and those interpreted to have been recharged before 1953 are referred to as "old."

Estimated redox conditions of each sample were based on concentrations of dissolved oxygen (DO), iron, and sulfate (table 3). Estimating redox conditions with this method is not ideal, but it is practical for regional studies in which hydrogen-ion concentrations or redox couples were not measured. Samples with concentrations of DO ≥1 mg/L and iron <50 μg/L were classified as oxic. Conversely, samples with concentrations of DO <1 mg/L and iron ≥50 μg/L were classified as anoxic. The anoxic waters were further subdivided into post

oxic (iron = 50 to 500 μg/L), iron reducing (iron >500 μg/L and sulfate >0.3 mg/L) and sulfate reducing (iron >500 μg/L and sulfate <0.3 mg/L). A fifth category, referred to as "mixed," was used for samples with characteristics of both oxic and anoxic waters (DO ≥1 mg/L and iron ≥50 μg/L or DO<1 mg/L and iron <50 μg/L). These redox signatures could be due to mixing of different water types in or near the wellbore or to higher turbidity in samples from low-yield monitor wells.

Table 3. Constituent concentrations used to estimate redox condition of ground-water samples from midwestern glacial deposits.

[mg/L, milligrams per liter; μg/L, micrograms per liter; na, not applicable to classification]

Redox classification[a]		Dissolved oxygen (mg/L)	Iron (μg/L)	Sulfate (mg/L)
Oxic		≥1	<50	na
Anoxic	Post oxic	<1	50 to 500	na
	Iron reducing	<1	>500	≥0.3
	Sulfate reducing	<1	>500	<0.3
Mixed oxic and anoxic signatures		≥1	≥50	na
		<1	<50	

[a] Classification modified from Berner, 1981.

Summary of Arsenic Occurrence in Well Networks

Arsenic was detected in one-third of the 342 ground-water samples. The maximum concentration was 84 μg/L, and the median was <1 μg/L. Eight percent of samples exceeded the MCL of 10 μg/L. Arsenic concentrations greater than the MCL were detected in monitor wells and domestic wells alike at depths of 11 to 365 ft. A map of arsenic concentrations (fig. 4) shows no obvious spatial patterns, except for a cluster of high arsenic concentrations in east-central Illinois. In each drainage basin, at least one sample had an arsenic concentration exceeding the MCL.

Selected characteristics of the 12 well networks are described in the following section of the report. The goals are to describe and illustrate the hydrogeologic setting, provide an overview of selected water-quality characteristics, and summarize arsenic detection frequencies in each well network. Comparisons can be made among networks within a basin (figs. 5-8) and among basins (table 4).
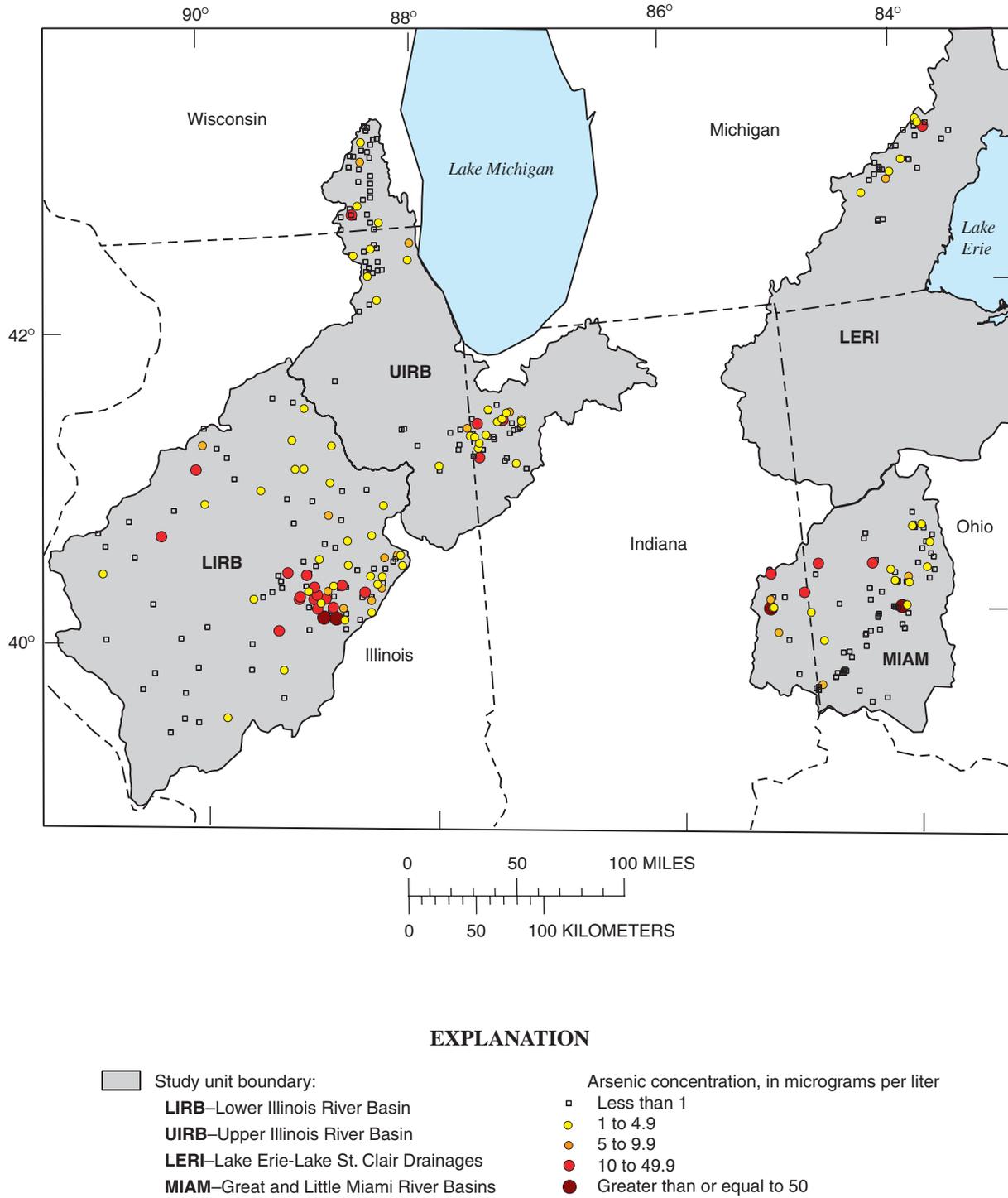
Figure 4. Arsenic concentrations in ground-water samples from National Water-Quality Assessment well networks in midwestern glacial deposits.

Table 4. Selected hydrogeologic characteristics and arsenic summary statistics for each well network.

[ft, feet; µg/L, micrograms per liter; ag, Agricultural Land-Use Study; mas, Major Aquifer Survey; urb, Urban Land-Use Study]

Well network identifier	Wells sampled			Land use	Type of glacial deposit	Bedrock	Arsenic concentrations (µg/L)		Percent exceedances	
	Number and type	Depth (ft)	Date (month/ year)				Med- ian	Max- imum	≥1 µg/L	≥10 µg/L
Lower Illinois River Basin (LIRB)										
LIRBmas2	30 domestic wells	30 to 108 median: 50	7/96 to 11/96	Pre- dominantly agricultural	Till with sand lenses	Pennsylvanian carbonate, shale, sandstone, coal	<1	40	33	10
LIRBag1	27 monitor wells	14 to 59 median: 20	8/97 to 11/97	Agricultural	Till with sand lenses	Pennsylvanian carbonate, shale, sandstone, coal	<1	8	22	0
LIRBag2	30 monitor wells	13 to 59 median: 2	6/97 to 9/97	Agricultural	Till with sand lenses	Pennsylvanian carbonate, shale, sandstone, coal	<1	8	47	0
LIRBmas1	30 domestic wells	200 to 365 median: 245	6/96 to 7/96	Pre- dominantly agricultural	Confined valley fill	Pennsylvanian carbonate, shale, sandstone, coal	9	84	83	47
Upper Illinois River Basin (UIRB)										
UIRBurb	28 monitor wells	14 to 59 median: 29	4/00 to 6/00	Residential	Till with sand lenses	Silurian-Devonian carbonates	<1	11	25	4
UIRBmas2	27 domestic wells	31 to 175 median: 72	3/01 to 5/01	Pre- dominantly residential	Till with sand lenses	Silurian-Devonian carbonates	<1	8	15	0
UIRBag	29 monitor wells	11 to 50 median: 14	6/99 to 9/99	Agricultural	Outwash plain	Silurian-Devonian carbonates	<1	28	38	7
UIRBmas1	22 domestic wells	25 to 70 median: 44	8/00 to 10/00	Pre- dominantly agricultural	Outwash plain	Silurian-Devonian carbonates	<1	26	36	4
Lake Erie-Lake Saint Clair Drainages (LERI)										
LERIurb	30 monitor wells	11 to 68 median: 25	11/96 to 1/97	Residential	Outwash plain	Lower Mississippian shale and sandstone	<1	17	23	3
Great and Little Miami River Basins (MIAM)										
MIAMurb	25 monitor wells	22 to 53 median: 43	10/01 to 11/01	Residential	Unconfined valley fill	Ordovician shale; Silurian carbonates	<1	1	4	0
MIAMag	34 monitor wells	11 to 55 median: 28	7/00 to 8/00	Agricultural	Unconfined valley fill	Silurian carbonates; Ordovician shale	<1	55	35	9
MIAMmas	30 domestic wells	21 to 121 median: 60	5/99 to 7/99	Mixed	Unconfined valley fill	Silurian carbonates; Ordovician shale	< 1	53	27	10

Lower Illinois River Basin

The environmental setting of the Lower Illinois River Basin and the characteristics of the well networks are described in Warner (1998), Groschen and others (2000), and U.S. Geological Survey (2001b).

The Lower Illinois River Basin spans 18,000 mi^2 in central Illinois (fig. 1). The area consists of till plains dissected by the Illinois River and its tributaries. In the northeastern part of the basin, the till is of Wisconsinan age; it is typically 100 to 200 ft thick, and the landscape is characterized by morainal topography (broad, rolling hills). The southeastern section is beyond the limit of Wisconsinan glaciation; the older Illinoian till is thinner (<50 to100 ft), and morainal hills are not common. Thin sand lenses within the till are an important source of water to domestic wells. Subsurface valleys, such as the Mahomet buried valley, contain thick deposits of sand and gravel overlain by more than 100 ft of till. These deposits are one of the major sources of public water supply in the basin.

Beneath the glacial deposits, the uppermost bedrock consists of Pennsylvanian shales and carbonates with interbedded sandstone and coal. Bedrock aquifers supply less than 10 percent of the ground-water use in the basin (Warner, 2001). Relative to geologic structure, the area lies on the northwestern flank of the Illinois structural basin. There is some evidence that major faults and folds affect ground-water quality by providing pathways for upward migration of deep-basin fluids (Panno and others, 1994; Warner, 2001).

Samples were collected in four well networks in the Lower Illinois River Basin during 1996 and 1997 (fig. 5 and table 4). For all networks, land use is predominantly agricultural.

LIRBmas2—This well network was in the southwestern part of the drainage basin, where the till is of Illinoian age, and moraines are not present. The network consisted of 30 domestic wells, about half of which were large-diameter wells (36 in.). The median well depth was 50 ft. Samples were mixed-ion-type waters. Forty-seven percent of samples were oxic (dissolved oxygen concentration $\geq$1 mg/L), and 80 percent were young (interpreted to have been recharged after 1953). Arsenic was detected in 33 percent of samples.The maximum concentrationwas 40 µg/L, and 10 percent of samples had arsenic concentrations greater than the MCL.

LIRBag1—This well network was in the northern part of the basin, where land use is agricultural and the surficial sediment is Wisconsinan till. This well network differs from LIRBag2 in that the area does *not* overlie the Mahomet buried valley. The network consisted of 27 monitor wells with a median well depth of 20 ft. Samples were mixed-cation-bicarbonate-sulfate-type waters. Sixty-three percent of samples were oxic, and 85 percent were young. Arsenic was detected in 22 percent of the samples. The median arsenic concentration was <1 µg/L, and the maximum was 8 µg/L.

LIRBag2—This well network was in the northeastern part of the basin, in an area that overlies the Mahomet buried valley. Land use is agricultural and surficial sediment is Wisconsinan till. The network comprised 30 monitor wells with a median well depth of 28 ft. Samples were mixed-cation-bicarbonate-sulfate-type waters. Fifty-five percent of samples were oxic, and 72 percent were young. Arsenic was detected in 47 percent of samples. The median arsenic concentration was <1 µg/L, and the maximum was 8 µg/L.

LIRBmas1—This well network tapped the Mahomet buried valley. The network consisted of 30 wells (28 domestic wells and 2 public-supply wells) with a median depth of 245 ft. The coarse-grained valley-fill sediment is confined by more than 100 ft of clay-rich till, and water quality is minimally affected by human activities. Samples were mixed-cation-bicarbonate-chloride-type waters. All samples were old and anoxic. Arsenic was detected in 83 percent of wells, and the maximum concentration was 84 µg/L. Almost half of the samples (47 percent) had arsenic concentrations greater than the MCL.

Arsenic concentrations in this well network were significantly higher than in the 11 other networks, based on Kruskal-Wallis and Tukey tests (table 4). In addition, the water quality was relatively uniform and distinct from that of other networks; samples had relatively high concentrations of iron, dissolved organic carbon, alkalinity, and phosphate and low concentrations of dissolved oxygen, nitrate, and sulfate.

A

B

EXPLANATION

△ Monitor well

○ Domestic well

MCL Maximum Contaminant Level

C

[Top number is median; lower number is range (minimum to maximum); ug/L, micrograms per liter; mg/L, milligrams per liter.]

	LIRBmas2	LIRBag1	LIRBag2	LIRBmas1
Well depth	50	28	20	245
(feet)	30 to 108	13 to 59	14 to 59	200 to 365
Arsenic	<1	<1	<1	9
(ug/L)	<1 to 40	<1 to 8	<1 to 8	<1 to 84
Dissolved solids	450	482	451	493
(mg/L)	215 to 1340	317 to 1520	360 to 583	236 to 817
pH	6.8	7.0	7.0	7.2
(standard unit)	6.3 to 7.3	6.6 to 7.5	6.7 to 8.0	7.0 to 7.5
Dissolved oxygen	1.4	2.9	3.0	<1
(mg/L)	0.02 to 6.8	0.3 to 6	0.1 to 7.4	<1 to 0.2
Alkalinity (mg/L as	342	358	355	415
CaCO$_3$)	91 to 659	177 to 577	250 to 636	245 to 580
Chloride	18	8	8	34
(mg/L)	0.5 to 120	0.9 to 34	0.6 to 30	0.2 to 110
Sulfate	44	78	38	<0.1
(mg/L)	0.1 to 450	0.5 to 828	0.17 to 139	<0.1 to 33
Iron	20	20	6	1750
(ug/L)	<3 to 9800	<3 to 3450	<3 to 2826	930 to 3000
Manganese	28	103	58	22
(ug/L)	1 to 1260	7 to 449	2 to 1066	10 to 322
Nitrate	1.3	0.07	0.4	<0.5
(mg/L)	<0.05 to 77	<0.05 to 24	<0.05 to 19	<0.05 to .09
Dissolved organic	0.9	2.7	4.9	7.2
carbon (mg/L)	0.3 to 3.6	0.5 to 12	0.4 to 30	0.6 to 54
Ortho	0.010	<0.010	<0.010	0.15
phosphate	<0.010 to	<0.010 to	<0.010 to	0.03 to 0.70
(mg/L)	0.090	0.040	0.169	

Figure 5. Characteristics of four National Water-Quality Assessment well networks in the Lower Illinois River Basin: (A) simplified diagram of hydrogeologic settings, (B) arsenic concentrations, and (C) median and range of selected water-quality characteristics. (Well network abbreviations are defined in table 4.)

Upper Illinois River Basin

The environmental setting of the Upper Illinois River Basin and the characteristics of the well networks are described in Arnold and others (1999) and U.S. Geological Survey (2001d).

The Upper Illinois River Basin spans 10,950 mi^2 in northern Illinois, northwestern Indiana, and southeastern Wisconsin. The surficial sediment consists of till, outwash, and lesser amounts of lakebed clays. Glacial deposits are of Wisconsinan age and are typically 50 to 200 ft thick. In relation to geologic structure, the basin is along the Kankakee Arch, in the area between the Michigan and Illinois structural basins.

In the study area, the uppermost bedrock consists of Silurian-Devonian carbonates and shale. Roughly equal amounts of ground water are withdrawn from the glacial and bedrock aquifers. Since 1986, withdrawals from bedrock aquifers have declined, and withdrawals from the glacial aquifer have increased (Arnold and others, 1999).

Four ground-water studies were done in the UIRB from 1999 to 2001. Two of the well networks produced water from outwash-plain aquifers in predominantly agricultural areas, and the other two produced water from till with sand lenses in predominantly residential areas (fig. 6).

UIRBurb—This well network comprised 28 monitor wells with a median depth of 29 ft. The surficial sediment is predominantly till, and wells were installed in sand lenses within the till. The study area was north of the Chicago metro area, where land use is recent residential and commercial. Samples were mixed-cation-bicarbonate-chloride-type waters. Sixty-four percent of the samples (14 of 22) were oxic, and 85 percent (17 of 20) were young. Arsenic was detected in 25 percent of samples. The maximum concentration was 11 µg/L. Four percent of samples exceeded the MCL.

UIRBmas2—This well network comprised 27 domestic wells with a median depth of 72 ft. The network was in the same aquifer type as UIRBurb–surficial sediment consisting of till with interbedded sand lenses. Samples were mixed-cation-bicarbonate-chloride-type waters. Twenty-six percent of samples were oxic, and 63 percent (12 of 19) were young. Arsenic was detected in 15 percent of samples, and the maximum arsenic concentration was 8 µg/L.

UIRBag—This well network consisted of 29 monitor wells with a median depth of 14 ft. The surficial sediment is sand and gravel, which forms a shallow outwash-plain aquifer. Land use is agricultural, and large areas are irrigated (Arnold and others, 1999). Samples were mixed-ion-type waters. Fifty-five percent of samples were oxic, and 92 percent (23 of 25) were young. Arsenic was detected in 38 percent of samples. Seven percent of samples exceeded the MCL. The maximum arsenic concentration was 28 µg/L.

UIRBmas1—This well network comprised 22 domestic wells with a median depth of 44 ft. The network was co-located with UIRBag; the surficial sediment is sand and gravel, and land use is agricultural. Samples were mixed-cation-bicarbonate-sulfate-type waters. Eighteen percent of samples were oxic, and 55 percent were young. Arsenic was detected in 36 percent of samples. The maximum concentration was 26 µg/L. Four percent of samples exceeded the MCL.

A

Northwest   UIRBurb UIRBmas2   Southeast

DEPTH, IN FEET

Till with sand lenses

Outwash plain (sand and gravel)   UIRBag UIRBmas1

Silurian-Devonian carbonates

Not to scale

EXPLANATION

Monitor well network

Domestic well network

B

DISSOLVED ARSENIC, IN MICROGRAMS PER LITER

MCL

UIRBurb   UIRBmas2   UIRBag   UIRBmas1

EXPLANATION

△   Monitor well

○   Domestic well

MCL   Maximum Contaminant Level

C

[Top number is median; lower number is range (minimum to maximum); µg/L, micrograms per liter; mg/L, milligrams per liter.]

	Till with sand lenses		Outwash plain	
	UIRBurb	UIRBmas2	UIRBag	UIRBmas1
Well depth (feet)	29 / 14 to 59	72 / 31 to 175	14 / 11 to 50	44 / 25 to 70
Arsenic (µg/L)	<1 / <1 to 11	<1 / <1 to 8	<1 / <1 to 28	<1 / <1 to 26
Dissolved solids (mg/L)	582 / 324 to 976	440 / 286 to 870	243 / 78 to 686	260 / 113 to 588
pH (standard units)	7.0 / 6.5 to 7.6	7.2 / 6.9 to 7.7	7.2 / 5.9 to 8.4	7.4 / 6.9 to 8.7
Disolved oxygen (mg/L)	3.7 / 0.5 to 10.5	0.9 / 0.05 to 6.3	2.9 / 0.05 to 7.5	0.4 / 0.02 to 7
Alkalinity (mg/L as CaCO$_3$)	343 / 258 to 483	328 / 247 to 441	142 / 17 to 342	150 / 53 to 405
Chloride (mg/L)	89 / 0.3 to 316	40 / 1 to 210	4 / 0.1 to 147	10 / 1 to 42
Sulfate (mg/L)	48 / <0.3 to 152	41 / <0.1 to 100	23 / 0.4 to 233	49 / <0.3 to 157
Iron (µg/L)	<10 / <10 to 2674	745 / <10 to 2133	10 / <10 to 5590	600 / <10 to 6778
Manganese (µg/L)	21 / <1 to 389	37 / 0.3 to 729	90 / <1 to 1418	76 / 8 to 545
Nitrate (mg/L)	0.36 / <0.05 to 12	<0.05 / <.05 to 4	2.4 / <0.05 to17	0.05 / <0.05 to 10
Dissolved organic carbon (mg/L)	1.2 / 0.6 to 7.2	0.8 / 0.4 to 34	2.1 / 0.5 to 22	1.4 / 0.3 to 260
Ortho phosphate (mg/L)	<0.010 / <0.010 to 0.034	<0.0180 / <0.018 to 0.046	0.017 / <0.010 to 0.487	0.021 / <0.010 to 0.137

Figure 6.   Characteristics of four National Water-Quality Assessment well networks in the Upper Illinois River Basin: (A) simplified diagram of hydrogeologic setting, (B) arsenic concentrations, and (C) median and range of selected water-quality characteristics. (Well network abbreviations are defined in table 4.)

Lake Erie-Lake Saint Clair Drainages

The environmental setting of the drainage basin and the characteristics of the well networks are described in Casey and others (1997), Myers and others (2000), Thomas (2000a, 2000b), and U.S. Geological Survey (2001a).

The Lake Erie-Lake Saint Clair drainage basin spans a 22,300-mi^2 area in parts of Ohio, Michigan, Indiana, Pennsylvania, and New York. One of the major areas of ground-water withdrawals is southeastern Michigan and northwestern Ohio. Glacial deposits are typically 100 to 200 ft thick, and water is produced from outwash-plain aquifers and till with sand lenses. Bedrock is Lower Mississippian shale and sandstone (Coldwater, Sunbury, and Bedford Shales; Berea Sandstone). The bedrock is not a reliable source of ground water because of quantity and (or) quality problems (Mozola, 1953). In terms of geologic structure, the area is along the eastern flank of the Michigan structural basin.

LERIurb—This well network was in an area of recent residential development on the far outskirts of the Detroit metropolitan area. The surficial sediment is sand and gravel deposited as outwash plains (fig. 7). The well network consisted of 30 monitor wells with a median depth of 25 ft. Samples were mixed-cation-bicarbonate-chloride-type waters. Fifty-seven percent of samples were oxic, and 97 percent of samples were young. Arsenic was detected in 23 percent of samples, and the maximum concentration was 17 µg/L. Three percent of samples exceeded the MCL for arsenic.

A
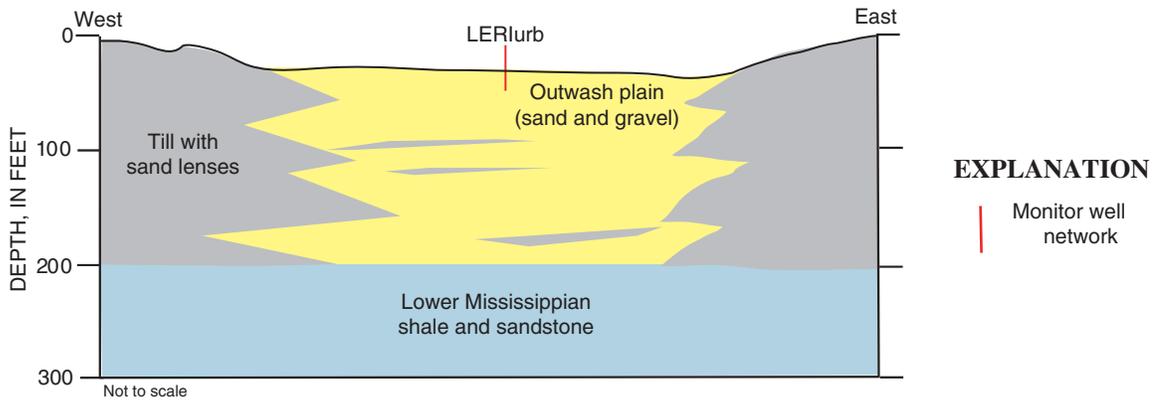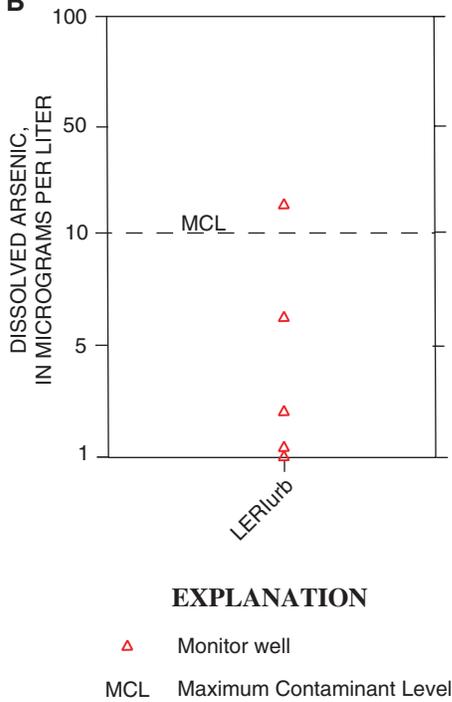
West   LERIurb   East

Outwash plain
(sand and gravel)

Till with
sand lenses

DEPTH, IN FEET

Lower Mississippian
shale and sandstone

Not to scale

EXPLANATION

Monitor well
network

B

DISSOLVED ARSENIC,
IN MICROGRAMS PER LITER

MCL

LERIurb

EXPLANATION

△   Monitor well

MCL   Maximum Contaminant Level

C

[Top number is median; lower number is range (minimum to maximum); μg/L, micrograms per liter; mg/L, milligrams per liter.]

	LERIurb
Well depth (feet)	25 11 to 68
Arsenic (μg/L)	<1 <1 to 17
Dissolved solids (mg/L)	458 82 to 1840
pH (standard unis)	7.1 6.5 to 8.5
Dissolved oxygen (mg/L)	1.7 0.1 to 8.6
Alkalinity (mg/L as CaCO$_3$)	279 55 to 877
Chloride (mg/L)	70 2 to 800
Sulfate (mg/L)	33 0.3 to 60
Iron (μg/L)	10 <3 to 28,000
Manganese (μg/L)	30 <1 to 985
Nitrate (mg/L)	0.7 <0.05 to 18
Dissolved organic carbon (mg/L)	1 0.5 to 34
Ortho phosphate (mg/L)	<0.010 <0.010 to 0.02

Figure 7. Characteristics of the National Water-Quality Assessment well network in the Lake Erie-Lake St. Clair Drainages: (A) simplified diagram of hydrogeologic setting, (B) arsenic concentrations, and (C) median and range of selected water-quality characteristics. (Well network abbreviations are defined in table 4.)

Great and Little Miami River Basins

The environmental setting of the drainage basin and the characteristics of the well networks are described in Debrewer and others (2000) and U.S. Geological Survey (2001c).

The Miami River Basin spans a 7,350-mi^2 area of southwestern Ohio and southeastern Indiana. The area is characterized by gently dipping sedimentary bedrock overlain by glacial till that is typically 0 to 100 ft thick. The bedrock is dissected by deep valleys that were part of the preglacial Teays River drainage system. The valleys typically contain 150 to 250 ft of fill consisting of glacial sediment—predominantly sand and gravel with varied amounts of till—which forms a regional aquifer system. The upper part of the aquifer system is vulnerable to surface contamination, and the lower part is variably confined. The valley-fill aquifer system supplies water to more than 1.6 million people in the basin (Debrewer and others, 2000).

In areas not underlain by valley fill, ground water is produced from till with sand lenses or from the underlying bedrock. Silurian carbonates subcrop in the northern part of the basin, and Ordovician shale interbedded with limestone subcrops in the southern part. In relation to geologic structure, the Miami River Basin lies along the Cincinnati Arch, in between the Illinois and Appalachian structural basins.

Three NAWQA ground-water studies were done during 1999–2001. All well networks were in the shallow parts of the valley-fill aquifer (fig. 8).

MIAMurb—This well network consisted of 25 monitor wells installed just below the water table in areas where the valley fill is overlain by recent residential or commercial land use. The median well depth is 43 ft. Waters were mixed-cation-bicarbonate-chloride type. Seventy-one percent (17 of 24) of samples were oxic, and all were young. Arsenic was detected in 4 percent of samples, and the maximum concentration was 1 µg/L. Arsenic concentrations in this well network were significantly lower than in the other 11 networks, based on results of Kruskal-Wallis and Tukey tests with a confidence interval of 95 percent (table 4).

MIAMag—This well network consisted of 34 monitor wells in areas where the valley fill is overlain by agricultural land use. The median well depth was 28 ft. At eight sites, pairs of shallow and deep monitor wells were installed adjacent to each other. Samples were calcium-magnesium-bicarbonate-sulfate-type waters. Fifty-six percent (18 of 32) were oxic, and 97 percent (31 of 32) were young. Arsenic was detected in 35 percent of samples. The maximum arsenic concentration was 55 µg/L. Nine percent of samples exceeded the MCL for arsenic.

MIAMmas—This well network consisted of 30 domestic wells that produce water from the shallow part of the valley fill. The median well depth was 60 ft. Samples were calcium-magnesium-bicarbonate type waters. Forty-seven percent of samples were oxic, and 97 percent (28 of 29) of samples were young. Arsenic was detected in 27 percent of samples; 10 percent exceeded the MCL. The maximum arsenic concentration was 53 µg/L.

A

B

EXPLANATION

△   Monitor well

○   Domestic well

MCL   Maximum Contaminant Level

C

[Top number is median; lower number is range (minimum to maximum); µg/L, micrograms per liter; mg/L, milligrams per liter.]

	MIAMurb	MIAMag	MIAMmas
Well depth	43	28	60
(feet)	22 to 53	11 to 55	21 to 121
Arsenic	<1	<1	<1
(µg/L)	<1 to 1	<1 to 55	<1 to 53
Dissolved solids	510	418	448
(mg/L)	374 to 868	295 to 790	<10 to 614
pH	7.0	7.1	6.8
(standard units)	6.3 to 7.5	6.7 to 9.5	6.7 to 7.2
Dissolved oxygen	3.2	2.9	0.1
(mg/L)	0.07 to 8	0.1 to 14	<0.1 to 10
Alkalinity (mg/L as	342	283	309
CaCO$_3$)	223 to 396	99 to 528	245 to 397
Chloride	67	18	28
(mg/L)	22 to 289	2 to 37	4 to 110
Sulfate	44	42	47
(mg/L)	28 to 107	<0.3 to 226	16 to 94
Iron	<10	<10	145
(µg/L)	<10 to 2185	<10 to 3510	<10 to 3910
Manganese	2	22	34
(µg/L)	0.1 to 386	<1 to 601	<1 to 414
Nitrate	2.6	4	0.4
(mg/L)	<0.02 to 10	<0.05 to 18	<0.05 to 15
Dissolved organic	0.6	0.9	1.0
carbon (mg/L)	0.2 to 2.1	<0.3 to 2.9	0.5 to 2.3
Ortho	<0.02	<0.01	0.01
phosphate	<0.020 to	<0.010 to	<0.010 to
(mg/L)	0.031	0.278	0.067

Figure 8. Characteristics of three National Water-Quality Assessment well networks in the Great and Little Miami River Basins: (A) simplified diagram of hydrogeologic setting, (B) arsenic concentrations, and (C) median and range of selected water-quality characteristics. (Well network abbreviations are defined in table 4.)

Relation of Arsenic to Selected Hydrogeologic Factors

Relations between arsenic concentrations and selected hydrogeologic characteristics were investigated using the Kruskal-Wallis and Tukey tests (Helsel and Hirsch, 1995).

Arsenic concentrations were compared among groups of data, and p-values <0.05 indicate that differences are statistically significant with a 95-percent confidence level. Results are summarized in table 5.

Table 5.   Results of Kruskal-Wallis and Tukey tests with a 95-percent confidence level, midwestern glacial deposits.

[ft, feet; network abbreviations are defined in table 4]

Hydrogeologic factor	Subgroup	Number of samples in each subgroup	Comparison of median arsenic concentrations among subgroups		
			Significantly lower	No significant difference	Significantly higher
Well network	LIRBmas2	30		X	
	LIRBag1	30		X	
	LIRBag2	27		X	
	LIRBmas1	30			X
	UIRBurb	28		X	
	UIRBmas2	27		X	
	UIRBag	29		X	
	UIRBmas1	22		X	
	LERIurb	30		X	
	MIAMurb	25	X		
	MIAMag	34		X	
	MIAMmas	30		X	
Well depth	<50 ft	233		X	
	50 to 150 ft	77		X	
	>150 ft	32			X
Well type	Monitor (30–70 ft deep)	78		X	
	Domestic (30–70 ft deep)	70		X	
Land use	Agricultural	120			X
	Residential	83	X		
Aquifer type	Till with sand lenses	142		X	
	Outwash plain	81		X	
	Unconfined valley fill	89		X	
	Confined valley fill	30			X

Well depth

Land surface can be a source of anthropogenic contaminants and (or) oxygenated recharge, so the depth of a well below land surface can affect water quality. In general, samples from shallower wells are younger, more oxic, and more likely to be affected by anthropogenic contaminants than those from deeper wells; however, exceptions are numerous because of complexities of ground-water flowpaths.

In the current study, well depths were 11 to 365 ft, and arsenic concentrations exceeding the MCL were detected over the entire range (fig. 9). To facilitate statistical comparisons, wells were classified as shallow (<50 ft), intermediate-depth (50 to 150 ft), or deep (>150 ft). No significant difference in arsenic concentrations was found between shallow and intermediate-depth wells (p=0.68). Arsenic concentrations in deep wells were significantly higher (p<0.0001) than in the two groups of shallower wells. However, most deep wells (30 of 32) were from one network (LIRBmas1) in a distinctive aquifer type (confined valley fill); it is not known whether wells at similar depths in other aquifer types would produce waters with similarly high arsenic concentrations.

Well type

Monitor wells, domestic wells, and public-supply wells can differ in terms of construction, pumping rate, and size of the contributing area, and these differences can affect the quality of the water produced. Korte (1991) proposed that low-yield domestic wells should have higher arsenic concentrations than high-yield public-supply wells. Michael Slattery (Ohio Environmental Protection Agency, oral commun., 2001) investigated arsenic concentrations in public-supply wells in Ohio and observed an inverse relation between arsenic concentrations and the number of people served, an approximate surrogate for pumping rate.

In the current study, arsenic concentrations above the MCL were detected in both monitor and domestic wells (fig. 9). For the dataset as a whole, arsenic concentrations were significantly higher in domestic wells, but this was largely due to LIRBmas1, a network of deep domestic wells with unusually high arsenic concentrations. For a subset of wells with depths between 30 and 70 ft (78 monitor and 70 domestic wells), there was no significant difference in arsenic concentrations by well type (p=0.97).

EXPLANATION

△   Monitor well

○   Domestic well

MCL   Maximum Contaminant Level
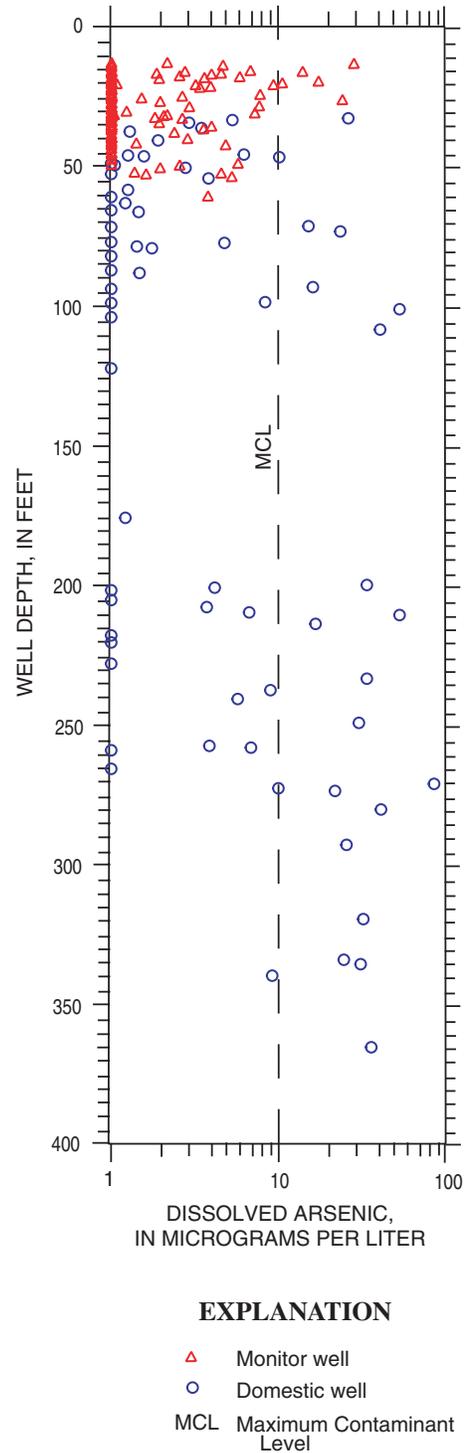
Figure 9.   Relation between arsenic concentration and well depth in midwestern glacial deposits.

Aquifer type

Well networks were in four types of aquifers within glacial deposits—till with sand lenses, outwash plain, unconfined valley fill, and confined valley fill. Within aquifer types, arsenic concentrations generally showed a similarity in terms of maximum concentrations and frequency of exceedance of the MCL (fig. 10 and table 4).

Till with sand lenses

Five well networks (LIRBag1, LIRBag2, UIRBurb, UIRBmas2, LIRBmas2) sampled water from till with sand lenses. The first four networks were in Wisconsinan till; the maximum arsenic concentrations were 8 to 11 µg/L, and 0 to 4 percent of samples exceeded the MCL (fig. 10).

The fifth well network was in Illinoian till. The maximum arsenic concentration was 40 µg/L, and 10 percent of samples exceeded the MCL. The elevated arsenic concentrations were detected in three samples of old water from deeper wells (72-108 ft). All young, shallow waters had arsenic concentrations less than or equal to 5 µg/L.

Outwash plain

Three well networks sampled outwash-plain aquifers (UIRBag, UIRBmas1, and LERIurb). Maximum arsenic concentrations were 17 to 28 µg/L, and 3 to 7 percent of samples had arsenic concentrations greater than the MCL. At depths of less than 50 ft, maximum arsenic concentrations in outwash were twice as high as those in till with sand lenses.
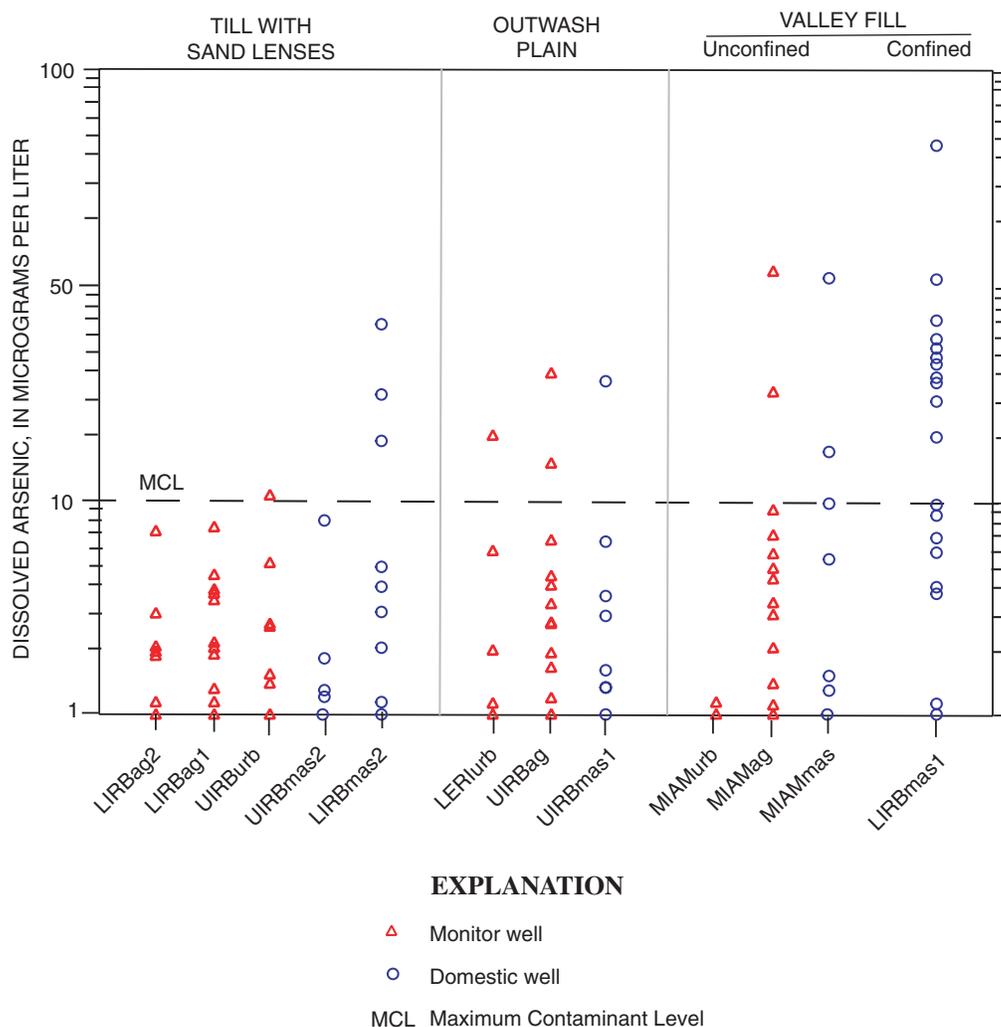
Figure 10.   Arsenic concentrations in four types of midwestern glacial deposits. (Well network abbreviations are defined in table 4.)

Valley fill

Highest arsenic concentrations (>50 µg/L) were detected in valley-fill aquifers. In unconfined valley fill, water-quality characteristics, ages, and redox conditions were variable, and detections of elevated arsenic concentrations were sporadic. In contrast, water quality in confined valley fill was relatively uniform, and detections of elevated arsenic concentrations were widespread.

Unconfined valley fill—Three networks were in unconfined valley fill—MIAMurb, MIAMag, and MIAMmas. Arsenic concentrations in MIAMag and MIAMmas were generally similar in terms of maximum arsenic concentrations (53 and 55 µg/L) and in frequency of detections greater than the MCL (9 to10 percent). In contrast, arsenic concentrations in MIAMurb were significantly lower than in all other networks. The maximum arsenic concentration was 1 µg/L, and 96 percent of samples had concentrations less than that.

Confined valley fill—One well network (LIRBmas1) produced water from confined valley fill. Arsenic concentrations in samples from this aquifer were significantly greater than those of any of the other three aquifer types. The maximum arsenic concentration was 84 µg/L, and 47 percent of samples had arsenic concentrations exceeding the MCL. The wells were also significantly deeper than those in the other aquifer types.

Bedrock geology

Over most of the study area, bedrock is 50 to 200 ft below land surface. A large percentage of glacial sediment is derived from local bedrock; therefore, bedrock mineralogy may affect arsenic concentrations in the glacial aquifers. In addition, regional discharge from the bedrock into valley-fill deposits can affect water quality in the vicinity of major river valleys (Panno and others, 1994; Feulner and Hubble, 1960).

All of the well networks overlie Paleozoic sedimentary bedrock (fig. 11). Well networks in the Lower Illinois River Basin are underlain by Pennsylvanian shale and carbonates with lesser amounts of sandstone and coal. Lower Mississippian shale and interbedded sandstone underlie the well networks in the Lake Erie-Lake Saint Clair Drainages. Silurian carbonates underlie wells in the Upper Illinois River Basin and the northern Miami River Basin. The southern half of the Miami River Basin is underlain by Ordovician shale with interbedded limestone.

Each bedrock formation contains potential sources of arsenic in the form of sulfides and (or) iron oxides. Sulfides are common in Paleozoic sedimentary bedrock of the Midwest, as documented by Heyl (1968). Greatest concentrations occur as epigenetic (Mississippi Valley-type) deposits in carbonates, shales or sandstones. These sulfides (along with fluorite, barite and celestite) occur along major geologic fault systems, especially at their intersection with domes or arches. A map by Heyl (1968) shows epigenetic sulfides in bedrock formations of northwestern and southwestern Ohio, northern Illinois, southern Wisconsin, northeastern Michigan, and much of Indiana. The same map shows diagenetic sulfides in central Illinois. In addition, syngenetic sulfides are disseminated throughout black shales, which subcrop in Ohio, Indiana, Michigan, and Illinois (fig. 11).

Iron oxides are also a common component of sedimentary bedrock. Where iron or manganese-bearing minerals (including sulfides) are exposed to weathering or oxygenated ground water, they can be converted to iron oxides. Iron oxides can be disseminated throughout a formation or concentrated along a horizon, such as an erosional unconformity.

For most of the study area, there was no clear spatial relation between bedrock subcrops and arsenic concentrations in ground water; a range of arsenic concentrations is associated with each type of bedrock (fig. 11). One exception is in the Miami River Basin, where arsenic concentrations in valley fill may be linked to Silurian carbonates, based on several observations: (1) Arsenic concentrations are significantly higher in the northern part of the basin, underlain by Silurian carbonates, than in the southern part, underlain by Ordovician shale (fig. 11; Miami Conservancy District, 2001). (2) Arsenic concentrations in valley fill correlate with strontium, a constituent linked to Silurian carbonates (Fuelner and Hubble, 1960). (3) Arsenic concentrations as high as 31 µg/L have been reported in domestic wells tapping Silurian carbonates (Bendula, 1996; Dumouchelle, 1998; Shindel and others, 2003).

Land use

Land use can have a major effect on the quality of shallow ground water. Human activities can affect water quality directly (by contributing chemicals to ground water as point or nonpoint sources) or indirectly (by altering redox conditions of the ground water).

Among monitor wells (N=203), arsenic concentrations in agricultural areas were significantly higher than those in residential areas (p=0.0029). However, this result does not account for differences in glacial or bedrock geology among the monitor-well networks. For example, for the Miami River Basin, the network of monitor wells in residential areas had significantly lower arsenic concentrations that the network of wells in agricultural areas. However, the two well networks also differ in terms of the type of bedrock underlying the valley fill, and there is some evidence that this affects arsenic concentrations.
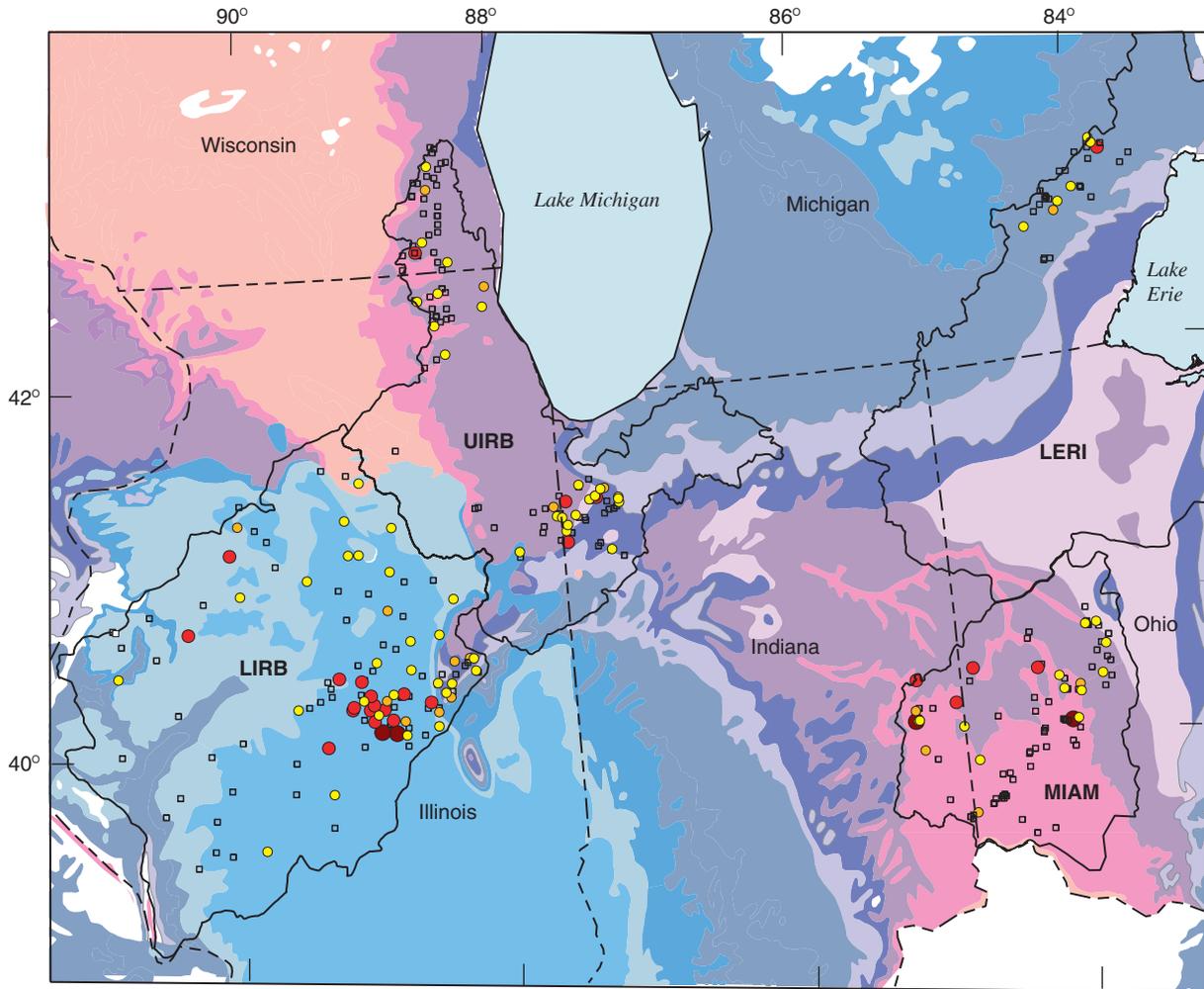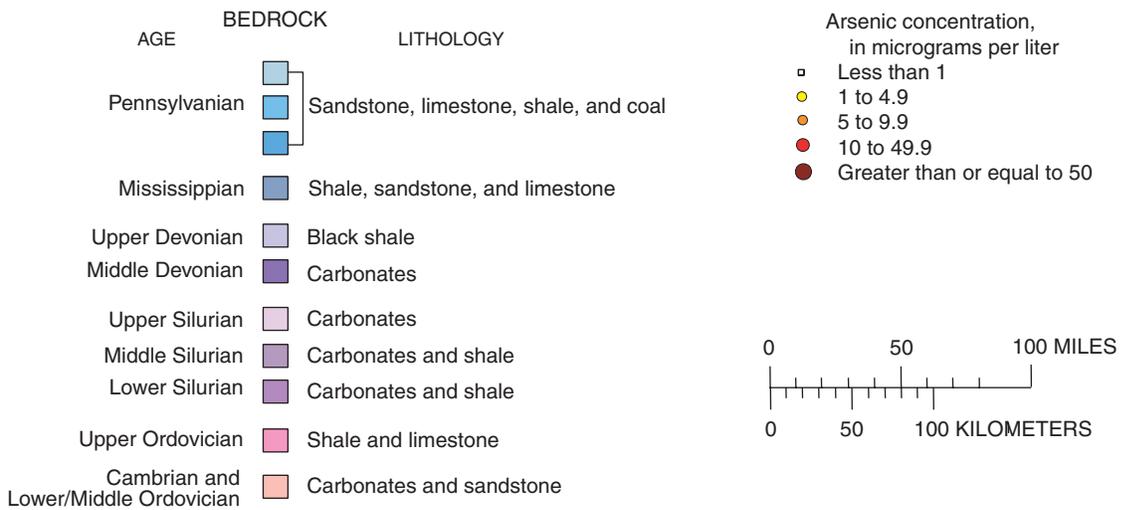
Figure 11.   Arsenic concentrations in relation to bedrock geology (from Schruben and others, 1991).

Relation of Arsenic to Selected Water-Quality Properties and Constituents

Relations between arsenic and other water-quality constituents can provide clues as to the source and (or) mechanism of mobilization of arsenic in ground water. Spearman's rho, a nonparametric test for monotonic relations between variables, was used to identify constituents correlated with arsenic at a 95-percent confidence level (table 6). Correlations in the entire dataset were strongly affected by the well network in confined valley fill, which had unusually high concentrations of arsenic and other water-quality constituents in comparison to the other 11 well networks. For this reason, statistical tests were done for the entire dataset (N=342) and for each of the four aquifer types.

Redox-sensitive constituents

In general, arsenic was inversely related to dissolved oxygen (DO) and nitrate, and directly related to ammonia, manganese, and iron (table 6). These correlations indicate that elevated arsenic concentrations are associated with reducing conditions. In confined valley fill, correlations between arsenic and DO, nitrate, ammonia, and manganese were not significant because all waters were reducing.

Iron

Arsenic and iron were significantly correlated for the entire dataset and each aquifer type. Iron is soluble under reducing conditions, so a correlation between arsenic and iron would be expected in waters where arsenic had been released from iron oxides under reducing conditions. Ninety-six percent (25 of 26) of samples with arsenic concentrations exceeding the MCL had iron concentrations >500 µg/L. However, not all samples with elevated iron concentrations also had elevated arsenic concentrations. Arsenic was also detected in samples with low iron concentrations (<50 µg/L), but in these samples, arsenic concentrations were relatively low—88 percent (22 of 25) were <5 µg/L.

Table 6.   Results of Spearman rho test for correlations between arsenic and selected chemical constituents for midwestern glacial deposits.

[N, number of samples in each group; HS, correlation is highly significant (p<.0001); S, correlation is significant (p<0.05); '-': correlation is inverse; blank space, correlation is not significant (p≥0.05); nm, constituent not measured]

Chemical constituent		All data N=342	Till N=142	Outwash plain N=81	Unconfined valley fill N=89	Confined valley fill N=30
Redox-sensitive constituents	Dissolved oxygen	-HS	-S	-S	-S	
	Nitrate	-HS	-S	-HS	-S	
	Ammonia	HS	HS	S	HS	
	Manganese	HS	S	HS	S	
	Iron	HS	S	HS	HS	S
	Sulfate	-S		S		
pH		S			S	S
Phosphate		HS				
Dissoved organic carbon		HS	S	S	HS	
Alkalinity					S	
Chloride		-S	-S		-S	HS
Sodium minus chloride		HS	S		S	
Radon		-HS	-S	-HS	-S	
Barium		HS	S		S	HS
Fluoride		HS	S	S	HS	
Silica		S			HS	-HS
Strontium		S			HS	nm

Sulfate

For the entire dataset, arsenic and sulfate were inversely correlated (table 6). Under sulfate-reducing conditions, sulfate is removed from solution as it is reduced to sulfide. An inverse relation between arsenic and sulfate, along with elevated iron concentrations, is consistent with high arsenic concentrations in sulfate-reducing waters. Some authors have suggested that arsenic should not occur in sulfate-reducing waters because sulfide minerals should precipitate and fix arsenic within its crystal lattice (Korte, 1991; Zobrist, 2000). In the current study, however, three of the four aquifer types had at least one sample with an elevated arsenic concentration in sulfate-reducing conditions.

In contrast, arsenic and sulfate are directly correlated in outwash-plain deposits (table 6). Such a relation might be expected if arsenic were released by pyrite oxidation. However, in outwash-plain deposits, elevated arsenic concentrations are in iron-reducing conditions, which are not conducive to pyrite oxidation.

Estimated redox condition

The redox condition of each sample was estimated on the basis of concentrations of dissolved oxygen, iron, and sulfate (table 3). Arsenic concentrations greater that the MCL were detected in at least one sample from each category except for post oxic (fig. 12). Iron or sulfate reducing waters were more likely to have elevated arsenic concentrations than those that were oxic or mixed waters. Of the 9 percent of samples classified as sulfate reducing, about half had elevated arsenic concentrations.
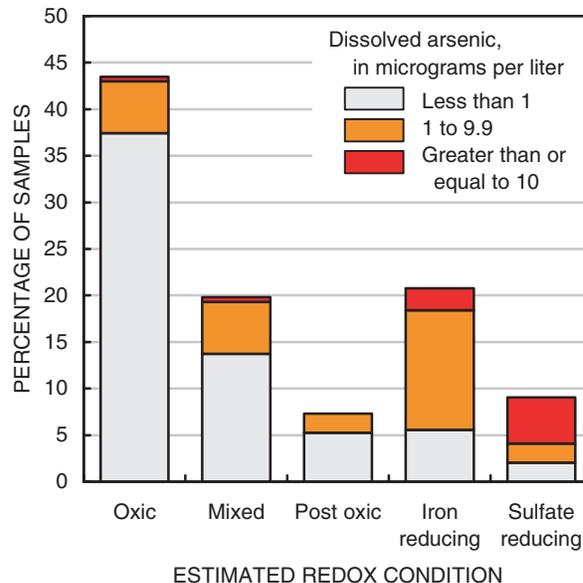
Figure 12.   Arsenic concentrations in five redox categories in midwestern glacial deposits.

The relations between concentrations of arsenic, iron, sulfate, and redox conditions are further illustrated in fig. 13. Elevated arsenic concentrations were detected in waters with (1) iron concentrations >500 µg/L and no detectable sulfate (sulfate reducing conditions), (2) iron concentrations >500 µg/L and intermediate to high sulfate conditions (iron-reducing or mixed redox conditions), and (3) iron concentrations <50 µg/L and intermediate to high sulfate concentrations (oxic or mixed redox conditions).
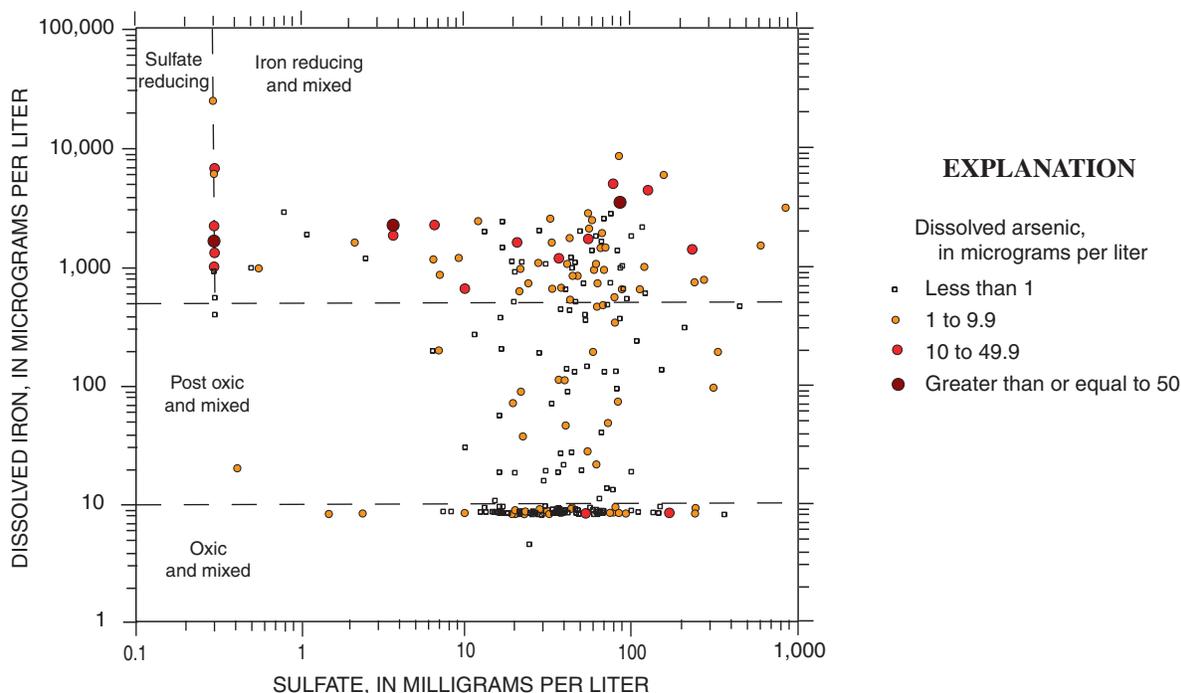
Figure 13.   Relations between iron, sulfate, arsenic, and estimated redox conditions in midwestern glacial deposits.

Ground-water age

Ages were estimated for 89 percent of samples, as described in the methods section of the report. Arsenic concentrations were significantly higher in old waters (recharged before 1953) than young waters (recharged after 1953), based on results of a Kruskal-Wallis and Tukey tests (p<0.0001). Similar results (p=0.0003) were obtained when samples from- from the confined valley-fill aquifer were excluded from the dataset. The correlation between arsenic concentration and ground-water age is probably partly related to redox conditions—old waters are more likely to be reducing than young waters. However, the relation between the two variables was not straightforward (fig. 14). For example, in outwash-plain deposits, highest arsenic concentrations were associated with waters that were young and reducing.
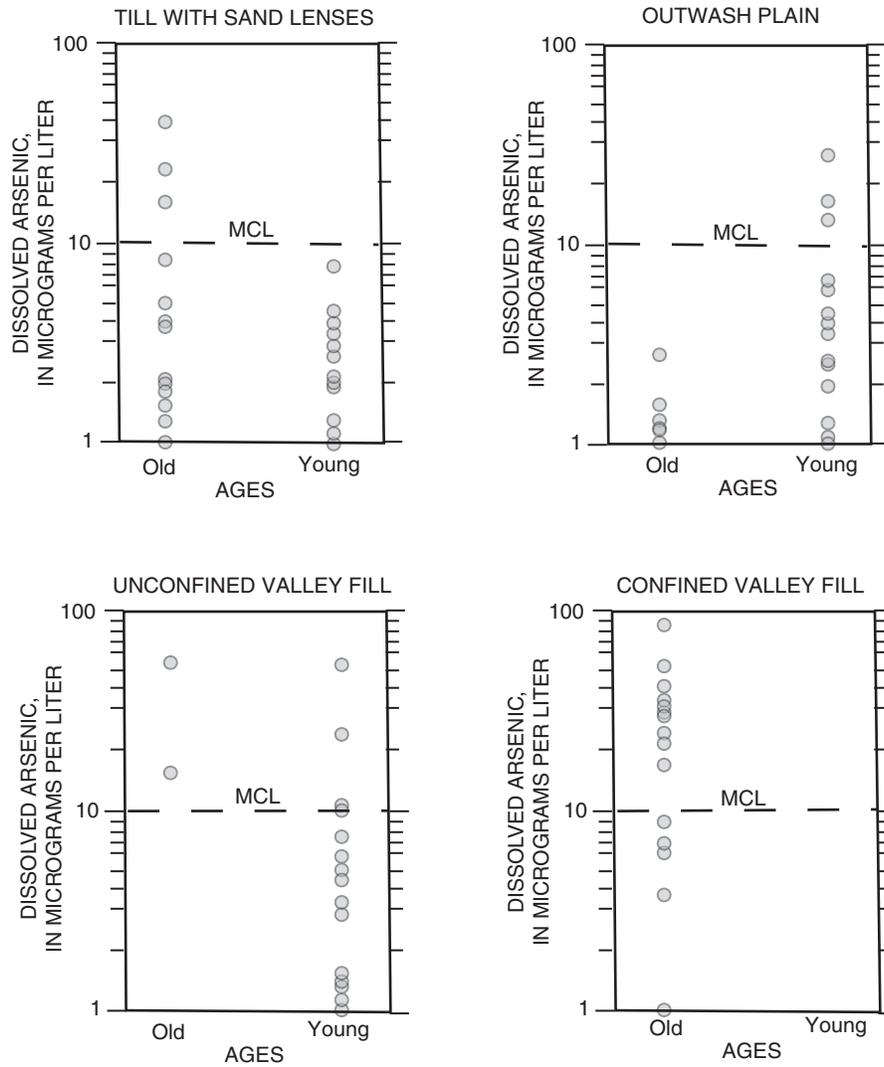
Figure 14. Ground-water ages and arsenic concentrations in four types of midwestern glacial deposits. ("Old" waters are estimated to have been recharged prior to 1953, and "young" waters are estimated to have been recharged after 1953; MCL, Maximum Contaminant Level.)

Other properties and chemical constituents

pH

Arsenic can desorb from iron oxides at high pH. Welch and others (2000) determined that a highly significant direct relation was present between arsenic and pH in a national dataset of more than 29,000 ground-water samples. Alternatively, arsenic and pH can be inversely related in waters affected by pyrite oxidation (Schreiber and others, 2002). In the current study, a significant direct relation between pH and arsenic was found in the entire dataset and in unconfined and confined valley fill (table 6). Most pH values were circumneutral, but one sample had an unusually high pH (9.5) and an elevated arsenic concentration (10 μg/L).

Phosphate

Phosphate can mobilize arsenic by displacing it from binding sites on iron oxides. The national dataset of Welch and others (2000) showed a highly significant relation between arsenic and phosphate. In the current study, there was no significant relation between arsenic and phosphate in the four aquifer types (table 6). The correlation between arsenic and phosphate was highly significant for the entire dataset, probably because confined valley fill had unusually high concentrations of both arsenic and phosphate (fig. 5).

Dissolved organic carbon

Organic carbon is a common electron donor and therefore could be associated with arsenic released from iron oxides under reducing conditions. Dissolved organic carbon (DOC) showed a significant correlation with arsenic in entire dataset and for three of the four aquifer types. The exception was confined valley fill; however, in this aquifer type, arsenic and DOC concentrations were both unusually high (fig. 5).

Alkalinity

Microbial reduction of iron oxides is coupled with oxidation of organic carbon; therefore, arsenic released by reductive dissolution of iron oxides could be correlated with alkalinity (Schreiber and others, 2002). A significant relation between arsenic and alkalinity was found for unconfined valley fill.

Chloride

Warner (2001) noted a direct correlation between arsenic with chloride in LIRBmas1, a network of deep wells in confined valley fill. This aquifer is minimally affected by human activities, and elevated concentrations of chloride and arsenic were attributed to inflow of deeper ground water from bedrock. In contrast, a significant inverse correlation between arsenic and chloride was found for the entire dataset and for two aquifer types—till with sand lenses and unconfined valley fill (table 6). Chloride is a widespread anthropogenic contaminant, and an inverse relation between arsenic and chloride in these relatively shallow wells suggests that the source of arsenic is not related to human activities.

Sodium minus chloride

Schlottman and others (1998) showed that arsenic was correlated with cation exchange and pH in ground water from a sandstone aquifer in central Oklahoma. Cation exchange (in millimoles per liter Na) was estimated by subtracting chloride (millimoles per liter) from sodium (millimoles per liter). The assumption is that values close to zero indicate the source of sodium is primarily sodium chloride (either anthropogenic or natural), and positive values are the result of release of sodium from clays by cation exchange.

In the current study, cation exchange correlated with arsenic concentrations in the entire dataset and in two aquifer types—till with sand lenses and unconfined valley fill (table 6). Cation exchange is expected to increase with increasing clay content and (or) residence time in the subsurface. In addition, cation exchange can result from mixing of waters with different compositions. The relation was not significant in confined valley fill, but concentrations of arsenic and cation exchange were both unusually high.

Radon

Warner (2001) documented an inverse correlation between arsenic and radon in the glacial deposits in central Illinois. A similar inverse relation was found for the entire dataset and for three of the four aquifer types (table 6).

Barium

Warner (2001) noted a direct correlation between arsenic and barium in the glacial deposits in central Illinois. A similar relation was found for the entire dataset and for three of the four aquifer types (table 6). Barium concentrations in ground water are often controlled by the solubility of barite (Hem, 1985). Barite ($BaSO_4$) is one of the minerals commonly associated with epigenetic sulfides in the central United States (Heyl, 1968). Under sulfate-reducing conditions, barium can remain in solution as sulfate concentrations decrease. (In the current study, a significant inverse relation between barium and sulfate was found for the entire dataset and two aquifer types.) Therefore, a correlation between arsenic and barium may be a reflection of the observation that highest arsenic concentrations occur in sulfate-reducing waters (figs. 12, 13).

Fluoride

A direct correlation between arsenic and fluoride was found for the entire dataset and for three of the four aquifer types. Fluoride is a constituent of fluorite (CaF_2) and apatite ($Ca_5(CL,F,OH)(PO4)_3$). A correlation between fluoride and arsenic could be related to the observations that (1) fluorite occurs with epigenetic sulfide minerals in sedimentary bedrock in the study area (Heyl, 1968), or (2) fluoride forms strong complexes with ferric oxides (Hem, 1985). The relation was not significant for confined valley fill, but concentrations of fluoride and arsenic were both unusually high in this aquifer type.

Silica

A direct correlation between arsenic and silica was found for the entire dataset and for unconfined valley fill. In contrast, silica and arsenic were inversely related in confined valley fill. Most silica is derived from weathering of silicate minerals, and the primary factors that control silica concentrations in solution are dissolution kinetics, adsorption, and precipitation of secondary minerals (Hem, 1985). A direct relation between arsenic and silica be the result of dissolution kinetics; in other words, arsenic concentrations are generally higher in older waters, where greater dissolution of silicate minerals has occurred. The inverse correlation between arsenic and silica in confined valley fill may be related to precipitation of secondary minerals.

Strontium

A highly significant relation between arsenic and strontium was found in unconfined valley fill of southwestern Ohio. Strontium is a component of celesite ($SrSO_4$) and strontianite ($SrCO_3$). Celestite is associated with epigenetic sulfides (Heyl, 1968), and in northwestern Ohio, elevated strontium concentrations in ground water were the best indicator of sulfide mineralization in Silurian carbonate bedrock (Deering and others, 1983). In addition, ground-water discharge from Silurian carbonates has been linked to elevated strontium concentrations in valley fill of southwestern Ohio (Fuelner and Hubble, 1960).

The relation between arsenic and strontium differs among the three well networks in unconfined valley fill (fig. 15). For MIAMag and MIAMmas, most of the samples with elevated strontium (>1,000 µg/L) also have elevated arsenic concentrations (≥10 µg/L). These elevated concentrations occur in the northern half of the basin, in the vicinity of the subcrop of the Silurian carbonate bedrock (fig. 11). In contrast, concentrations of both strontium and arsenic are significantly lower in the MIAMurb network. Most of these wells are in areas underlain by Ordovician bedrock, which contains little or no celestite (Fuelner and Hubble, 1960) and does not contribute appreciable amounts of recharge to the valley-fill deposits (Dumouchelle, 1998).
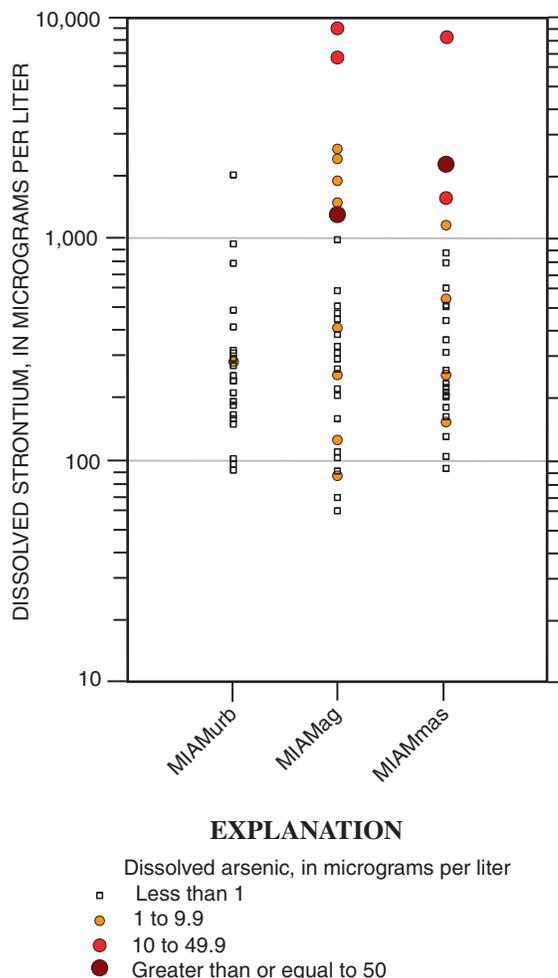
Figure 15. Strontium and arsenic concentrations in well networks of the Great and Little Miami River Basins. (Well network abbreviations are defined in table 4.)

Observations About Arsenic in Midwestern Glacial Deposits

There were no simple relations between arsenic concentrations in ground water and any single hydrogeologic factor such as well type, well depth, aquifer type, or bedrock geology. Elevated arsenic concentrations (≥10 µg/L) were detected in both monitor and domestic wells, at a range of depths (11–365 ft), in all four types of glacial deposits, and in areas underlain by various types of bedrock (Silurian-Devonian carbonates, Mississippian shale and sandstone, and Pennsylvanian carbonates, shale, and sandstone). In addition, relations between arsenic and other chemical constituents were complex; elevated arsenic concentrations were detected in oxic and anoxic waters, old and young waters, and waters with wide ranges of pH (6.7 to 9.5),

alkalinity (99 to 580 mg/L as $CaCO_3$), iron (<10 to 7,400 µg/L) and sulfate (<0.3 to 226 µg/L).

The lack of simple relations between arsenic concentrations and hydrogeologic or geochemical factors is probably partly related to the fact that the current study includes data from multiple aquifers that vary in terms of mineralogy, characteristics of ground-water flow, and distribution of redox conditions.

A second complicating factor is that arsenic can be mobilized in both oxic and reducing waters. Many aquifers include both types of water, so presumably, arsenic can be mobilized by at least two different processes in the same aquifer. In oxic ground water, oxidation of sulfides is expected to be a principal-mechanism of arsenic mobilization. The process is expected to be more common in young, shallow waters because common oxidants such as oxygen and nitrate are most abundant near land surface. In reducing ground water, arsenic can be released from iron oxides by desorption or reductive dissolution. It is expected that arsenic mobilized under reducing conditions would be detected more frequently with increasing depth because reducing conditions are more widespread in deeper parts of ground-water-flow systems. However, reductive dissolution of iron oxides can also occur at shallow depths, where weathered sediment is exposed to localized reducing conditions due to natural factors (upward migration of deeper ground water, or high amounts of organic carbon associated with wetlands) or human activities (inefficient septic systems, landfills, or waste lagoons).

Correlations of arsenic with barium, fluoride and strontium suggest a link between elevated concentrations of arsenic in ground water and epigenetic (Mississippi-Valley type) sulfide mineralization. Barite ($BaSO_4$), fluorite (CaF_2), and celestite ($SrSO_4$) are minerals associated with epigenetic sulfide deposits in Paleozoic bedrock of the Midwest (Heyl, 1968). In northwestern Ohio, trend-surface maps of barium, fluoride, and strontium in shallow ground water reflect the geographic distribution of Mississippi Valley-type mineralization in Silurian carbonate bedrock (Deering, 1983). Goldhaber and others (2003) proposed that some local occurrences of arsenic in Paleozoic bedrock aquifers are related to deposition of arsenic-rich pyrite by the large-scale migration of brines associated with Mississippi Valley-type deposits.

Arsenic is typically released from sulfides by oxidation; but in the current dataset, elevated arsenic concentrations were in reducing waters, which are not conducive to pyrite oxidation. Therefore, if the ultimate source of arsenic in ground water were epigenetic sulfides, the history of mobilization would have to include multiple steps, such as (1) oxidation of sulfides and release of iron and arsenic, (2) deposition of iron oxides and coprecipitation or sorption of arsenic, (3) a shift from oxic to reducing conditions, possibly related to burial, and (4) release of arsenic from iron oxides by reductive dissolution or desorption. Similar scenarios have been proposed by others, including Matissoff and others (1982), Korte (1991) and Breit and others (2001).

Despite the complexity of the dataset (and the hydrogeologic and geochemical systems that it represents), several generalizations can be made about the distribution of arsenic concentrations in ground water in the four types of glacial deposits (fig. 16). The observations presented here can be tested and refined as additional arsenic data are collected in the glacial deposits. Geochemical modeling and analysis of aquifer mineralogy are necessary to conclusively identify processes responsible for mobilizing arsenic.

Till with sand lenses—At shallow depths (< 50 ft), this aquifer type had lower arsenic concentrations than outwash plain or unconfined valley-fill deposits (fig. 16). The maximum concentration was 11 µg/L, and only 1 percent of samples had an arsenic concentration greater than the MCL. In addition, this aquifer type had the highest percentage of arsenic detections in oxic or mixed waters.

The relatively frequent occurrence of low concentrations of arsenic in oxic or mixed waters might be related to the hydrogeology of surficial till. Clay-rich tills are typically fractured at shallow depths. Above the water table, fractures are lined with iron and manganese oxides, but below the water table, sediment is uniformly gray and lacks evidence of oxidation. Recharge of water containing oxygen (or nitrate) through these fractures is expected to cause pyrite oxidation along the fracture faces in the unsaturated zone. As surfaces become armored by iron oxides, the rate of pyrite oxidation decreases (Appelo and Postma, 1996). Presumably, a significant drop in the water table could cause pyrite in the saturated zone to be oxidized. Alternatively, a significant rise in the water table could cause iron oxides in the unsaturated zone to be reduced. As the water table fluctuates, arsenic could presumably cycle between ground water and the solid phase.

In deeper wells (≥50 ft), arsenic was detected in waters with a range of redox conditions, but concentrations greater than the MCL were in iron- or sulfate-reducing waters. These three samples were from LIRBmas2, a network of domestic wells in Illinoian till. It is not known whether these high concentrations are related to the till composition to the greater well depths and more reducing conditions.

Outwash plain—Most of the ground-water samples from this aquifer type were from relatively shallow (<50 ft) wells. At these depths, arsenic concentrations greater than the MCL were detected more frequently in outwash-plain deposits (4 of 72 samples) than in till with sand lenses (1 of 98 samples). In outwash-plain deposits, samples with arsenic concentrations exceeding the MCL were young, iron-reducing waters (figs. 14, 16). Reducing conditions in young, shallow waters may be the result of high concentrations of organic carbon from natural or anthropogenic sources. McCarthur and others (2001) proposed that the distribution of peat was the primary factor controlling elevated arsenic concentrations in ground water in Bangladesh. Outwash plains are commonly pitted with small lakes and wetlands, which contain elevated concentrations of organic carbon. In the LERIurb well network, the two samples with the highest arsenic concentrations were from shallow wells near wetlands. In addition, Devonian black shale subcrops near the well
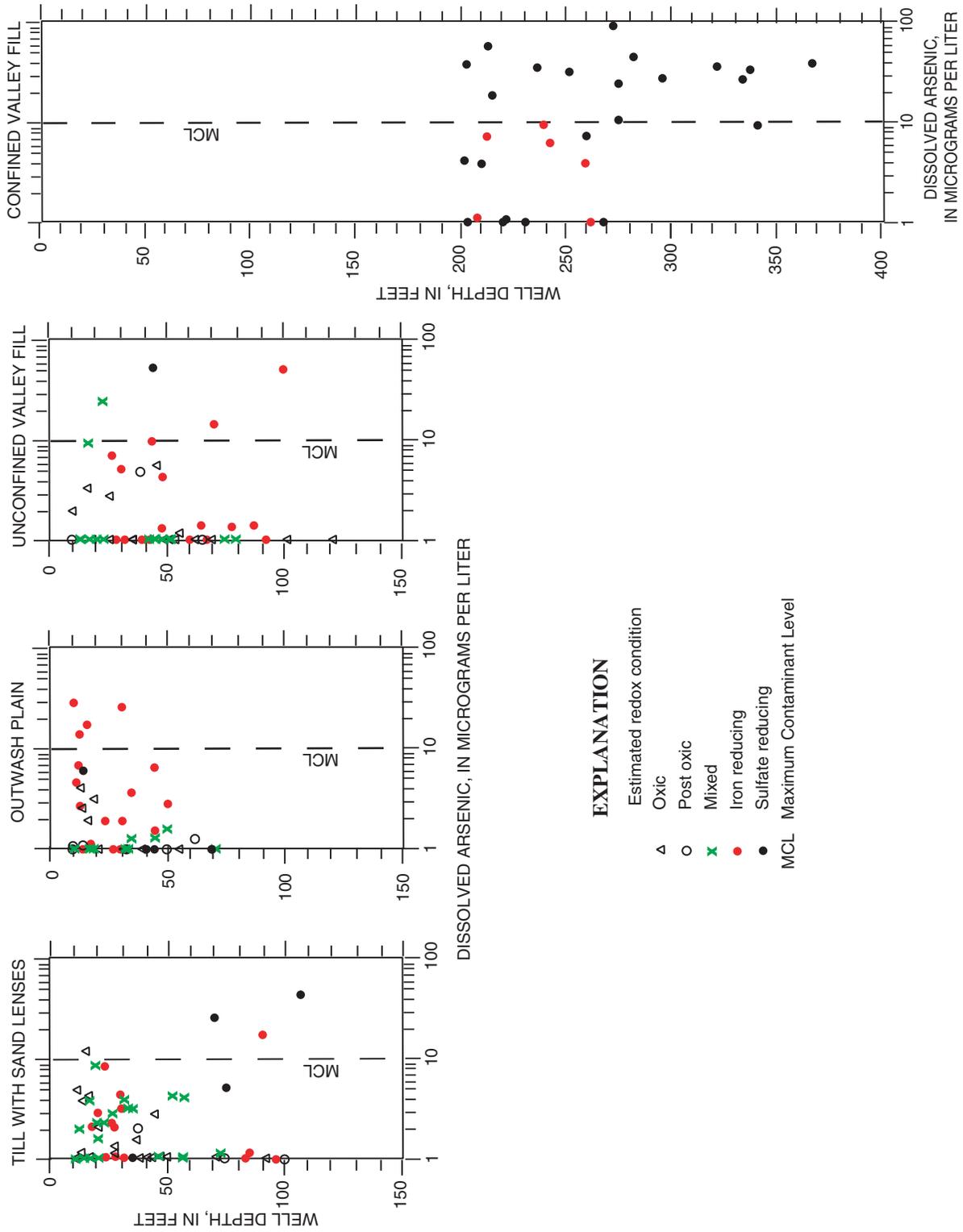
Figure 16.   Arsenic concentrations and redox conditions in relation to well depth in four types of midwestern glacial deposits.

networks (fig. 11) and could serve as an electron donor where it is incorporated into the glacial deposits.

The direct relation between arsenic and sulfate (table 6) suggests an influence of pyrite oxidation. However, highest arsenic concentrations were detected in reducing conditions, which are not conducive to pyrite oxidation. It is possible that pyrite oxidation has affected water quality but is not directly attributable to the highest arsenic concentrations in outwash-plain aquifers.

Valley fill—Highest arsenic concentrations were detected in reducing waters from valley-fill deposits (fig. 16). Elevated arsenic concentrations in alluvial or deltaic deposits have been documented elsewhere, including northeastern Ohio (Matissoff and others, 1982), northern Missouri, southern Iowa, and central Ohio (Korte, 1991), and Bangladesh (McCarthur and others, 2001). The authors of these studies concluded that the source of arsenic was iron oxides on alluvial sediment, and that burial of the deposits produced the reducing conditions that led to the release of arsenic from iron oxides to ground water. McCarthur and others (2001) proposed that any alluvial or deltaic depositional environment with marshes and swamps is vulnerable to arsenic contamination of ground water.

In the current study, arsenic concentrations in valley-fill deposits also appear to be affected by the bedrock into which the valleys are incised. In confined valley fill in east-central Illinois, arsenic was correlated with chloride from the underlying Pennsylvanian bedrock (Panno and others, 1994; Warner, 2001). In unconfined valley fill in southwestern Ohio, arsenic can be linked to the Silurian carbonate bedrock on the basis of two observations: (1) arsenic is correlated with strontium, the source of which is the carbonate bedrock (Fuelner and Hubble, 1960), and (2) arsenic concentrations are significantly higher in the northern part of the basin, where the carbonate bedrock subcrops. However, these geochemical relations do not indicate the source of the arsenic, or how it was mobilized. For example, arsenic could have been transported from bedrock to the valley fill by advection, or alternatively, inflow of reduced ground water from the bedrock could have mobilized arsenic sorbed to iron oxides in the valley fill.

Of the 12 well networks in the current study, there were two end-members in terms of arsenic concentrations, and both were in valley-fill deposits (fig. 10). However, there was a sharp contrast in the hydrogeologic settings and water quality of the two endmembers. The highest arsenic concentrations were in a network of 30 deep (>200 ft) domestic wells in confined valley fill in east-central Illinois. The maximum arsenic concentration was 84 µg/L, and almost half of the samples had concentrations exceeding the MCL. Water quality was relatively uniform; all samples were old, anoxic, and had relatively high concentrations of iron, pH, dissolved organic carbon, alkalinity, and phosphate, all of which have been related to elevated arsenic concentrations in other studies (Welch and others, 2000). The ground water was interpreted to be minimally influenced by human activities but affected by inflow of deeper ground water from bedrock (Panno and others, 1994; Warner, 2001).

In contrast, the lowest arsenic concentrations were in a network of 25 shallow (22 to 53 ft) monitor wells in residential areas overlying unconfined valley fill in southwestern Ohio. The maximum arsenic concentration was 1 µg/L. Waters were young and predominantly oxic. The valley fill is incised into Ordovician shale bedrock, which contributes negligible amounts of ground-water flow to the valley fill (Dumouchelle, 1998). Elevated chloride concentrations were also detected in samples from this network and were probably the result of human activities at land surface.

The other two well networks in unconfined valley-fill deposits (MIAMag and MIAMmas) had water-quality characteristics and hydrogeologic settings intermediate between those just described. The water quality showed evidence of being affected by land surface (pesticides, nitrate) and deeper ground water (strontium, fluoride, silica). One sample from a shallow well near a spring had elevated concentrations of arsenic, elevated pH, and high cation exchange. It is possible that mixing of deep and shallow waters caused cation exchange, increased the pH, and mobilized arsenic by a mechanism similar to the one proposed by Schlottman and others (1998).

Summary and Conclusions

Glacial deposits are a major source of ground water to domestic and public-supply wells in the Midwest. Arsenic concentrations exceeding the USEPA Maximum Contaminant Level of 10 µg/L have been detected in midwestern glacial deposits, but it is not known which parts of the glacial aquifers in the region are most (or least) likely to produce water with elevated arsenic concentrations. Ground-water-quality data collected as part of 12 USGS National Water-Quality Assessment studies during 1996–2001 were analyzed to (1) document arsenic occurrence in four types of glacial deposits that are present in large areas of the Midwest, (2) identify hydrogeologic or geochemical factors associated with elevated arsenic concentrations, and (3) search for clues as to arsenic source(s) or mechanism(s) of mobilization that could be useful for designing future studies.

Arsenic and other water-quality constituents were sampled for in 342 monitor and domestic wells in parts of Illinois, Indiana, Ohio, Michigan, and Wisconsin. Arsenic was detected (at a concentration ≥1 µg/L) in one-third of the samples. The maximum concentration was 84 µg/L, and the median was less than 1 µg/L. Eight percent of samples had arsenic concentrations that exceeded the MCL of 10 µg/L.

There were no simple relations between arsenic and any single hydrogeologic factor such as well type, well depth, or surficial or bedrock geology. Elevated arsenic concentrations (≥10 µg/L) were detected in domestic and monitor wells over the entire range of depths sampled (11 to 365 ft). No significant difference in arsenic concentrations was found between shallow wells (<50 ft) and intermediate-depth wells (50 to 150 ft). Arsenic concentrations were significantly higher in deep wells

(>150 ft), but all deep wells were from a distinctive aquifer type (confined valley fill). It is not known whether wells at similar depths in other aquifer types would produce waters with similarly high arsenic concentrations.

Over most of the area, no spatial trend was found between arsenic and the type of sedimentary bedrock that subcrops beneath the glacial deposits. The exception was in southwestern Ohio, where unusually low arsenic concentrations were detected in the area underlain by Ordovician shale, and higher concentrations were detected in the area underlain by Silurian carbonates.

In general, arsenic was inversely related to dissolved oxygen and nitrate and directly related to ammonia, manganese, and iron. These correlations indicate that arsenic is associated with reducing waters. Arsenic was also detected in oxic and mixed waters, but concentrations were not as high as those in iron- or sulfate-reducing waters. Ninety-six percent (25 of 26) of the arsenic concentrations exceeding the MCL were in samples with iron concentrations >500 µg/L. Sulfate-reducing waters accounted for a relatively small part of the dataset (9 percent), but half of the sulfate-reducing waters had elevated concentrations of arsenic.

In general, old waters (recharged before 1953) had higher arsenic concentrations than young waters (recharged after 1953). This result is probably partly related to redox conditions—old waters are more likely to be reducing than young waters. However, highest arsenic concentrations in outwash-plain deposits were associated with waters that were young and reducing.

Correlations of arsenic with fluoride, strontium, and barium suggest that arsenic might be related to epigenetic (Mississippi Valley-type) sulfide deposits in Paleozoic bedrock. However, arsenic is released from sulfides by oxidation, whereas the highest concentrations of arsenic in glacial deposits were detected in reducing waters. Therefore, a link between epigenetic sulfides and elevated arsenic concentrations in glacial deposits would probably require a multi-step process.

The lack of simple relations between arsenic concentrations and hydrogeologic or geochemical variables in this analysis may result in part from including data from multiple aquifers that vary in terms of mineralogy, characteristics of ground-water flow, and distribution of redox conditions. A second complicating factor is that arsenic can be mobilized under either oxic or reducing conditions, and most aquifers include waters of both types; so, presumably, arsenic can be mobilized by at least two different processes in the same aquifer.

Despite the complexity of the data from the current study, several generalizations can be made about the distribution of arsenic in the four types of glacial deposits sampled.

Till with sand lenses. At shallow depths (<50 ft), this aquifer type had lower arsenic concentrations than outwash-plain or unconfined valley-fill deposits. The maximum concentration was 11 µg/L, and only 1 percent of samples had an arsenic concentration greater than the MCL. In addition, this aquifer type had the highest percentage of arsenic detections in oxic or mixed waters.

The relatively frequent occurrence of low concentrations of arsenic in shallow, oxic or mixed waters might be related to the hydrogeology of surficial till. Clay-rich tills are typically fractured at shallow depths. Recharge of water containing oxygen (or nitrate) through these fractures is expected to cause pyrite oxidation along the fracture faces; but as surfaces become armored by iron oxides, the rate of pyrite oxidation decreases. In deeper wells (≥50 ft), arsenic was detected in waters with a range of redox conditions, but concentrations greater than the MCL were in iron- or sulfate-reducing waters.

Outwash plain—Most of the samples from this aquifer type were from relatively shallow (<50 ft) wells. Arsenic concentrations exceeding the MCL were in young, iron-reducing waters. Reducing conditions in young, shallow waters may be the result of high concentrations of organic carbon from natural or anthropogenic sources.

Valley fill—Highest arsenic concentrations were detected in reducing waters from valley-fill deposits. Elevated arsenic concentrations in alluvial or deltaic deposits have been documented elsewhere; the investigators concluded that the source of arsenic was iron oxides and that burial of the alluvial sediment produced the reducing conditions that led to the release of arsenic from iron oxides to ground water.

In addition, arsenic concentrations appear to be affected by the bedrock into which the valleys are incised, based on geochemical correlations and spatial relations. In the confined valley-fill aquifer in east-central Illinois, arsenic correlated with chloride from the underlying Pennsylvanian bedrock. In the unconfined valley-fill aquifer in southwestern Ohio, arsenic is linked to the Silurian carbonate bedrock. However, these relations do not indicate the source of the arsenic, or how it was mobilized. For example, arsenic could have been transported from bedrock to the valley fill by advection, or alternatively, inflow of reduced ground water from the bedrock could have mobilized arsenic sorbed to iron oxides in the valley fill.

Of the 12 well networks in the current study, the two end members in terms of arsenic concentrations were both in valley-fill deposits. There was also a sharp contrast in the hydrogeologic settings and water quality of these two end members. The highest arsenic concentrations were in a network of 30 deep domestic wells (>200 ft) in confined valley fill in east-central Illinois. The maximum arsenic concentration was 84 µg/L, and almost half of the samples had concentrations exceeding the MCL. Water quality was relatively uniform; all samples were old, anoxic, and had relatively high concentrations of iron, pH, dissolved organic carbon, alkalinity, and phosphate. The ground water is minimally influenced by human activities but is affected by inflow of deeper ground water from bedrock.

In contrast, the lowest arsenic concentrations were in a network of 25 shallow monitor wells (22 to 53 ft) in residential areas overlying the unconfined valley-fill aquifer in southwestern Ohio. The maximum arsenic concentration was 1 µg/L. Waters were young and predominantly oxic. The valley-fill aquifer is incised into Ordovician shale bedrock, which contributes negligible amounts of ground-water flow to the glacial aquifer. Elevated chloride concentrations were also detected in

samples from this network, and were probably the result of human activities at land surface.

The other two well networks in unconfined valley-fill deposits had water-quality characteristics and hydrogeologic settings intermediate between those just described; water quality showed indications of being affected by land surface (pesticides and nitrate) and by deeper ground water (strontium, fluoride and silica).

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