

In cooperation with the Illinois Environmental Protection Agency

Arsenic in Illinois Ground Water—Community and Private Supplies

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Introduction

Assessing the distribution of arsenic in ground water from community-water supplies, private supplies, or monitoring wells is part of the process of determining the risk of arsenic contamination of drinking water in Illinois. Lifestyle, genetic, and environmental factors make certain members of the population more susceptible to adverse health effects from repeated exposure to drinking water with high arsenic concentrations (Ryker, 2001). In addition, such factors may have geographic distribution patterns that complicate the analysis of the relation between arsenic in drinking water and health effects. For example, arsenic may not be the only constituent affecting the quality of drinking water in a region (Ryker, 2001); however, determining the extent and distribution of arsenic in ground water is a starting place to assess the potential risk for persons drinking from a community or private supply. Understanding the potential sources and pathways that mobilize arsenic in ground water is a necessary step in protecting the drinking-water supply in Illinois (fig. 1).

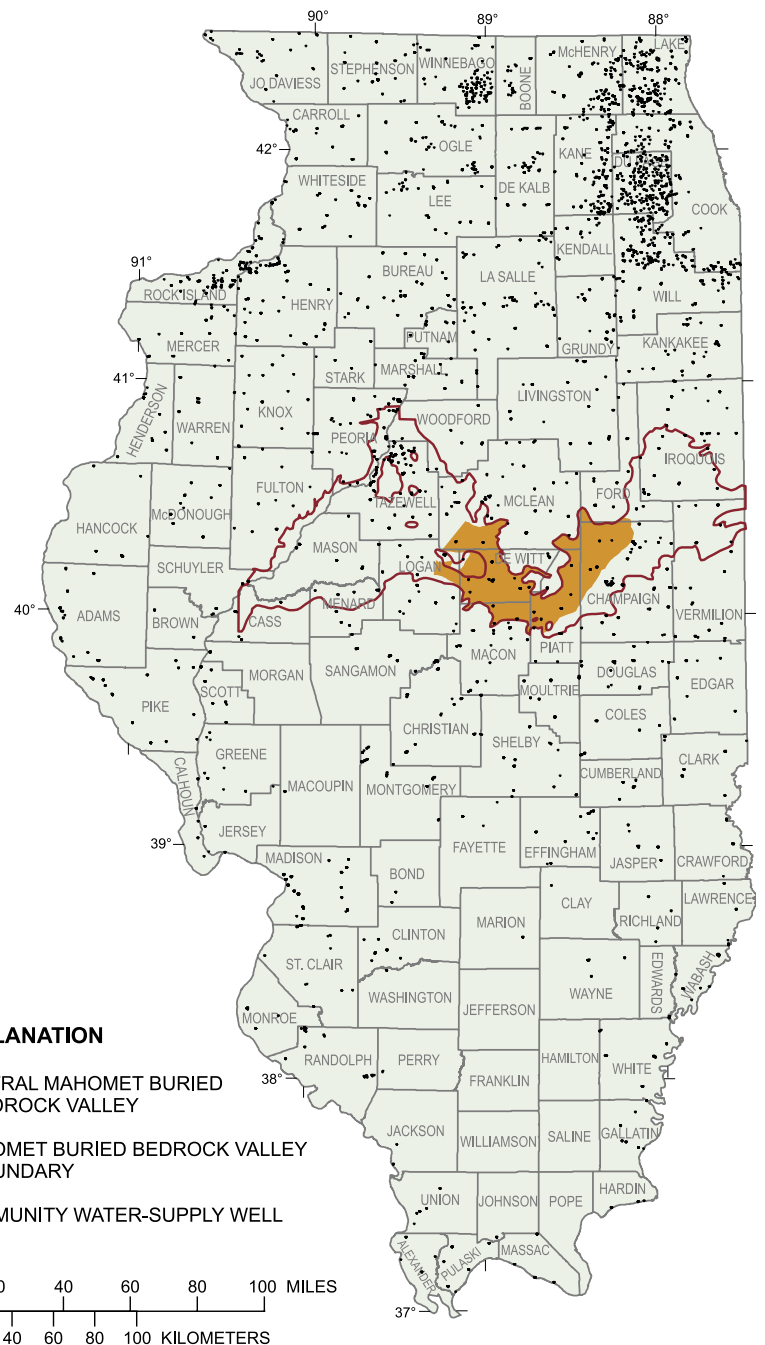


Figure 1. Location of community water-supply wells and the Mahomet Buried Bedrock Valley in Illinois.

Relation Between High Arsenic Concentrations and Health Effects

The metallic element arsenic has a long history as a poison. Albertus Magnus (Albert the Great), in approximately 1250, is the first to have recorded producing pure arsenic (MacRae, 2002), which usually was found in a mixed mineral. It is believed that Napoleon was poisoned with arsenic (Weider and Forshufvud, 1995). In the early 1800s in Italy, there were over a thousand unexplained deaths of young children who died in their living rooms. The deaths were determined to be the result of the release of poisonous arsenic gas from Paris green wallpaper that lined the living rooms and this heavier-than-air gas accumulated at lower levels where young children were more likely to breathe

(King, 2002). Up to the 1940s, arsenic successfully was used to treat syphilis and leprosy. Arsenic was popularized as the poison of choice in many murder-mystery novels and movies, such as *Arsenic and Old Lace*, released in 1944. Today, the threat of arsenic poisoning is real in many parts of the world, such as Bangladesh, India, and China, where in the late 1990s many people consumed or inhaled toxic amounts of arsenic (West Bengal and Bangladesh, 2002). Arsenic in ground water also is a public-health issue in Illinois (fig. 1) and other parts of the Nation. Understanding the distribution, fate, and transport of arsenic in ground water and defining susceptible areas needing further investigation helps water-resource managers assess the risk of arsenic contamination of wells, perhaps, by geographic location and aquifer.

Dissolved arsenic is found in ground water across Illi-

nois. The U.S. Environmental Protection Agency (USEPA) drinking-water standard for arsenic has been 50 micrograms per liter ($\mu\text{g/L}$) since 1942 (U.S. Environmental Protection Agency, 2002). In January 2001, the standard for arsenic in drinking water was lowered by USEPA to 10 $\mu\text{g/L}$ and must be implemented at all community-supply facilities by 2006 (U.S. Environmental Protection Agency, 2002; Dawn Shellenberger, U.S. Environmental Protection Agency, written commun., 2002). The cost is substantial for remediating high arsenic concentrations. The Illinois Environmental Protection Agency (IEPA) has estimated that the total cost to reduce arsenic concentrations to below 10 $\mu\text{g/L}$ for 50 selected community-water supplies with elevated arsenic concentrations in Illinois (fig. 2) could reach 40 million dollars, with the highest costs associated with small community supplies (Illinois State Water Survey, 2002). Private wells are not regulated for arsenic concentration.

The purpose of this report, prepared by the U.S. Geological Survey (USGS), in cooperation with the IEPA, is to describe the known distribution of arsenic in ground water in Illinois and to

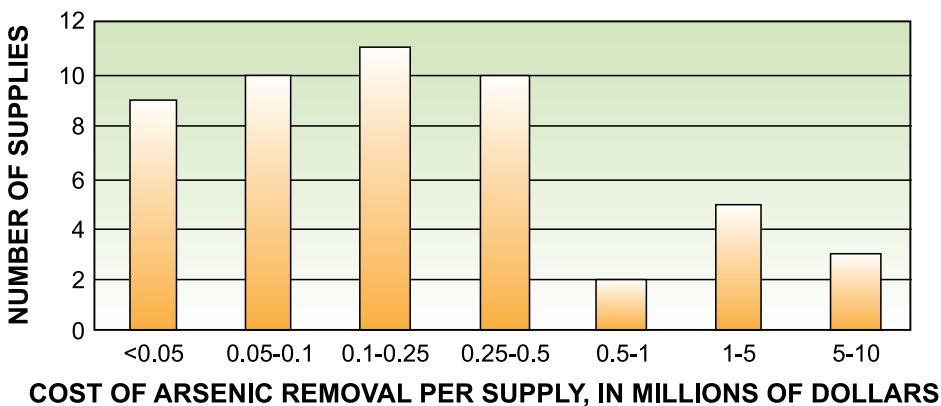


Figure 2. Projected number and cost of remediating arsenic from community-water supplies in Illinois (<, less than) (Modified from Illinois State Water Survey, 2002; oral commun., Rick Cobb, Illinois Environmental Protection Agency, 2002).

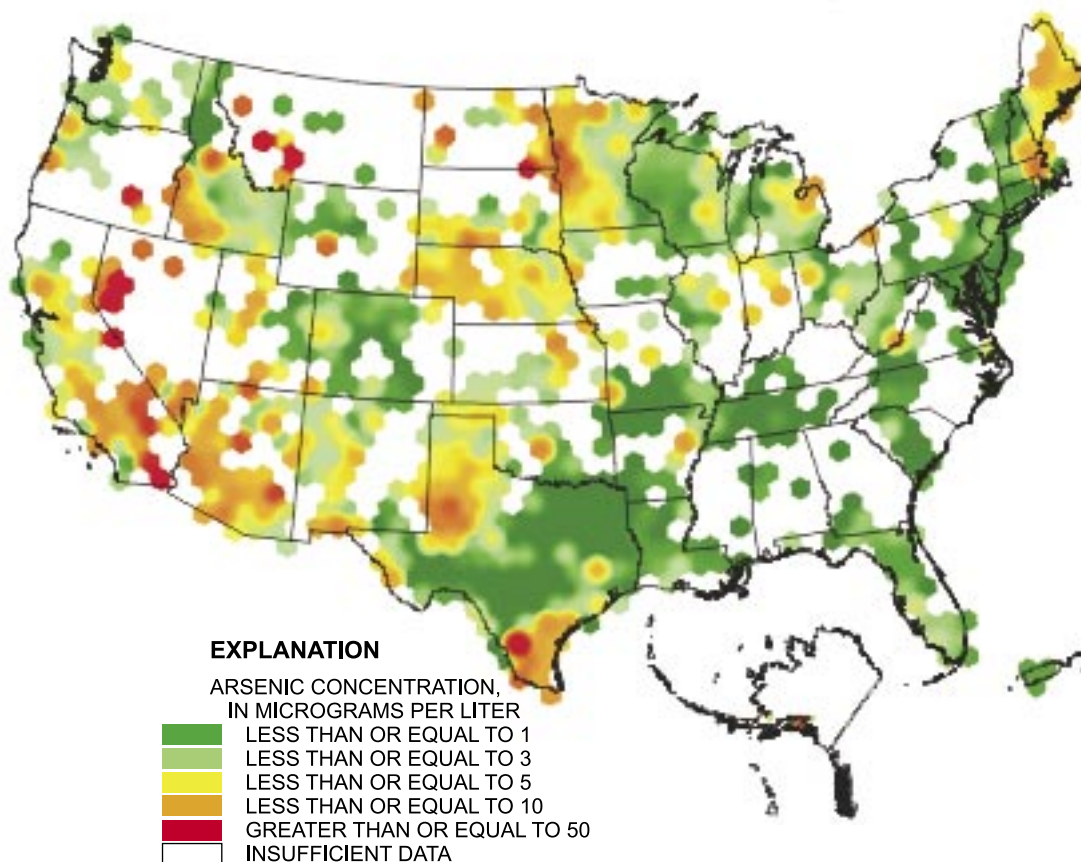


Figure 3. Areas of equal arsenic concentrations in ground water, United States (from Ryker, 2001). In 2001, the U.S. Geological Survey database included trace-element data from 31,000 wells and springs.

describe use of a geostatistical technique to estimate arsenic concentrations in areas where little or no data are available. In addition, potential sources of arsenic in Illinois are described. In Illinois, the most abundant data on arsenic in ground water are from community supplies (fig. 1). Assessment of the spatial distribution of arsenic in community supplies and comparison to other water-quality data available from private supplies can allow inferences to be made about the extent and distribution of arsenic in private supplies.

Because arsenic is common in ground water in Illinois, the patterns and correlations of arsenic with other constituents can be used to identify areas of concern, highlight potential indicators of high arsenic concentrations, and determine where additional research is needed to understand the fate and transport of arsenic in ground water. In addition, the study of community-water supplies will help the owners of private, unregulated wells make informed decisions on whether to have their well tested for arsenic.

Arsenic Concentrations on a National and Regional Scale

Elevated arsenic concentrations (above drinking-water standards) are a national and regional concern. An environmental research program by the USGS (Ryker, 2001) compiled arsenic analyses from 31,000 wells and springs in 49 States for the national map (fig. 3). Scientists with the USGS and State agencies collected and analyzed these data mainly from

private wells, monitoring wells, and community-supply wells. These samples were collected for studies on the quality of the Nation's potable ground-water resources. The data set contains no explicit information on the rural population that does not use ground water from public supply. The national map includes arsenic concentrations in drinking-water data from monitoring and research programs in the United States. Monitoring of community-supply systems is required for compliance with State and Federal water-quality standards. The national map data set provides an important basis for estimating how many community-supply systems have arsenic concentrations above the present standard, or what proportion of the urban population obtains water from community-supply systems with arsenic concentrations above the drinking-water standard (Ryker, 2001).

More than 99 percent of the Nation's rural population relies on ground water for drinking water. Approximately 50 percent of community supplies in Illinois are from ground water; approximately 90 percent of private supplies are from ground water. Because private wells are unregulated, no national regulatory database is available to fill this data gap on rural private wells.

Additional data often are available at statewide or local scales for more specific comparison. Although the national map shows that Illinois has three areas with arsenic concentrations at or above 5 µg/L in ground water (central, northeastern, and northwestern Illinois), larger areas with appreciably higher arsenic concentrations are present in other parts of the Nation.

Arsenic Concentrations in Ground Water in Illinois

Known Distribution

The most extensive data set of arsenic concentrations in ground water in Illinois has been collected by the IEPA as part of compliance monitoring programs. Approximately 8,200 samples collected by IEPA from 2,771 community-water supplies in Illinois provide a detailed picture of the arsenic distribution in most of the aquifers underlying Illinois. The USGS National Water-Quality Assessment (NAWQA) program has collected data from 225 monitoring and private wells screened in the glacial and alluvial aquifer system. The glacial and alluvial aquifer system, as defined in this report,

includes all aquifers above bedrock (fig. 4). In the central Mahomet Buried Bedrock Valley (fig. 1), the aquifer of concern is the deep portions of the glacial and alluvial aquifer system (Mahomet aquifer) (fig. 4). NAWQA samples are collected for studies of the quality of the Nation's surface- and ground-water resources. This program uses a nationally consistent network design, sampling program, and methods of data analyses for low levels of over 300 chemical constituents. The Illinois State Water Survey (ISWS) also collects arsenic data for studies in the State. In a study by the ISWS, in cooperation with the Illinois Waste Management and Research Center, the variability of arsenic concentrations with depth is being studied in the glacial and alluvial aquifer system in central Illinois. In another study, approximately 30 small community-water supplies are being sampled for arsenic and arsenic species concentrations by the ISWS. In addition, 150 non-community wells are being sampled for arsenic and other chemical constituents. All these programs and studies provide useful information, but it also is important to combine the available data sets. IEPA and USGS provide data on arsenic concentrations in community and private wells.

TIME STRATIGRAPHY			GENERAL ROCK STRATIGRAPHY		HYDROSTRATIGRAPHY	
Quaternary System	Pleistocene Series	Holocene	Recent deposits		Glacial and alluvial aquifer system	Local aquifers and confining units not described in this report
		Wisconsinan	Wedron and Mason Groups			
		Illinoian	Winnebago and Glasford Formations			
		Pre-Illinoian	Banner Formation			
		Mahomet Sand Member	Sankoty Sand Member		Deep glacial drift aquifer (greater than 200 feet below land surface)	Mahomet aquifer

Figure 4. Relation of time stratigraphy, general rock stratigraphy, and hydrostratigraphy of glacial deposits in central Illinois (modified from Willman and Frye, 1970; Hansel and Johnson, 1996; and Warner, 2001).

Concentrations of total (dissolved and suspended) arsenic samples collected from community supplies and concentrations of dissolved arsenic in samples collected from monitoring and private wells may not be comparable. Two major issues concerning these data sets are: (1) the difference in pumping volumes; (2) the difference in filtering procedures; samples from community-supply wells are unfiltered, whereas samples from monitoring and private wells are filtered. Because community-supply wells generally pump larger amounts than

monitoring or private wells, water flows from a larger area in an aquifer (capture zone) to community-supply wells; therefore, resulting arsenic concentrations may differ even when community-supply, and monitoring or private wells are close to each other (Ohio Environmental Protection Agency, 2002). The filtering issue is well documented (Horowitz and others, 1996). Comparing arsenic concentrations from filtered and unfiltered samples is complicated by the adsorption of arsenic to clay particles and colloids within the water sample.

Filtration will remove these particles and the adsorbed arsenic, decreasing the apparent concentration of arsenic in the sample. Turbidity is a rough estimate of the amount of particles in a water sample. When it is low, few particulates are present in samples, and dissolved and total arsenic concentrations should be similar. Turbidity in both the community- and private-supply samples was low, so comparing arsenic concentrations in ground water from these two well types should not be biased because of turbidity.

Arsenic concentrations in ground water usually are the result of the interaction between water and geologic materials. The geochemical environment in the aquifer is one of the biggest factors affecting arsenic concentrations. Factors such as ground-water age, depth to water, and land use affect the fate and transport of constituents introduced by humans, but have limited effects on the concentration of arsenic in ground water. Arsenic data from community and private supplies were compared in Illinois and other parts of the country (Warner, 2001; Bruce and Oelsner, 2001). Comparison of arsenic concentrations in private supplies (filtered) and arsenic concentrations in community-water supplies (unfiltered) in the deep por-

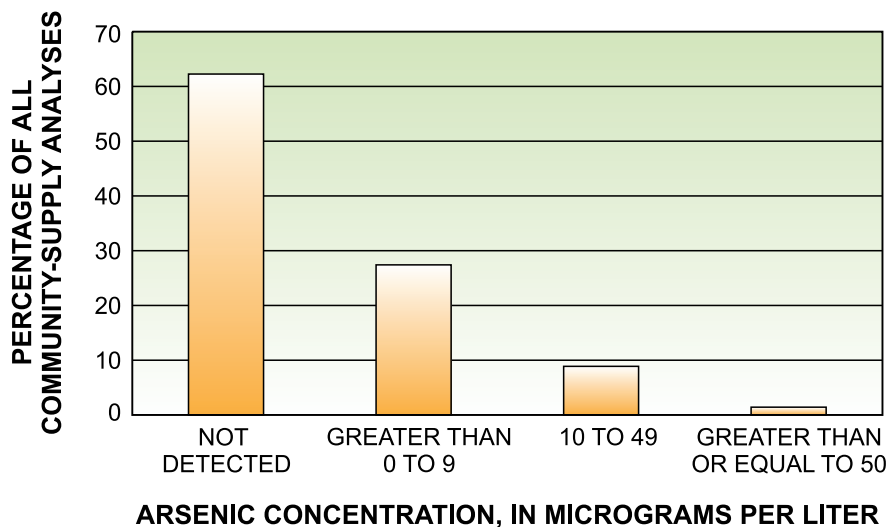


Figure 5. Arsenic concentrations in community-supply well samples in Illinois, 1978-2001.

tions of the glacial and alluvial aquifer system in Illinois were similar for a data set containing less than 100 samples (Warner, 2001). The deep portions of the glacial and alluvial aquifer system are defined as the deep glacial drift aquifer (fig. 4) by Warner (2001). In the deep portions of the glacial and alluvial aquifer system, filtered arsenic concentrations for ground-water

samples from private wells ranged from less than 1.0 to 84 $\mu\text{g/L}$, with a median concentration of 1.5 $\mu\text{g/L}$; whereas the range of unfiltered arsenic concentrations for ground water from community-water supplies ranged from less than 1 to 110 $\mu\text{g/L}$, with a median of 1.0 $\mu\text{g/L}$ (Warner, 2001). A study comparing filtered private and unfiltered community

supplies in the High Plains aquifer in central Colorado did not show a statistical difference in arsenic concentration (Bruce and Oelsner, 2001). The median concentration in the High Plains aquifer from private and community supplies was 2.04 and 1.55 $\mu\text{g/L}$, respectively. On a national basis, arsenic concentrations in samples not from community-supply wells tended to be higher than concentrations in samples from community-supply samples (Welch and others, 1999).

The IEPA collected arsenic data at 2,771 community-water supply wells (prior to treatment) in various aquifers in Illinois from 1978 through 2001. Some wells were sampled multiple times. Arsenic was not detected in 60 percent of samples (5031 of 8180 samples; fig. 5).

Table 1. Comparison of arsenic concentrations in ground water from private and monitoring wells within the glacial and alluvial aquifer system, all routinely sampled community-supply wells, and community-supply wells within the glacial and alluvial aquifer system. (NAWQA, National Water-Quality Assessment; IEPA, Illinois Environmental Protection Agency; $\mu\text{g/L}$, micrograms per liter; <, less than)

	NAWQA program wells in the glacial and alluvial aquifer system	All IEPA routine samples from community supplies in all aquifers	All IEPA routine samples from community-supply wells in the glacial and alluvial aquifer system
Number of analyses	268	2036	886
Minimum concentration ($\mu\text{g/L}$)	< .2	< 1	< 1
Maximum concentration ($\mu\text{g/L}$)	128	100	100
25 percent of analyses above this concentration ($\mu\text{g/L}$)	< .2	< 1	< 1
75 percent of analyses above this concentration ($\mu\text{g/L}$)	3.9	2	6
Median concentration ($\mu\text{g/L}$)	.5	< 1	< 1
Percent arsenic detections	58	43	47
Percent above 10 $\mu\text{g/L}$	14	11	19

As previously discussed, community-supply well samples are collected routinely or as part of special studies within the IEPA (table 1). Routine samples (2,036 samples in the data set) are samples collected by the community-supply well operator before any treatment for compliance. Samples for arsenic generally are collected every 5 years unless there are compliance issues requiring more sampling. Special studies can include a wide variety of programs from ambient monitoring to compliance. Of the community- and private-supply samples, 11 and 14 percent, respectively, exceeded the 10 µg/L arsenic standard. The highest arsenic concentrations and most frequent detections in samples from community-supply wells were from the deep portions of the glacial and alluvial aquifer system underlying central Illinois (Mahomet aquifer) (fig. 4).

With large water-quality data sets (for example, the community-supply data set from IEPA), there can be statistical bias because of the number of samples in any given year and the laboratory methods used for analysis. The largest number of samples from community-water supplies in Illinois was collected

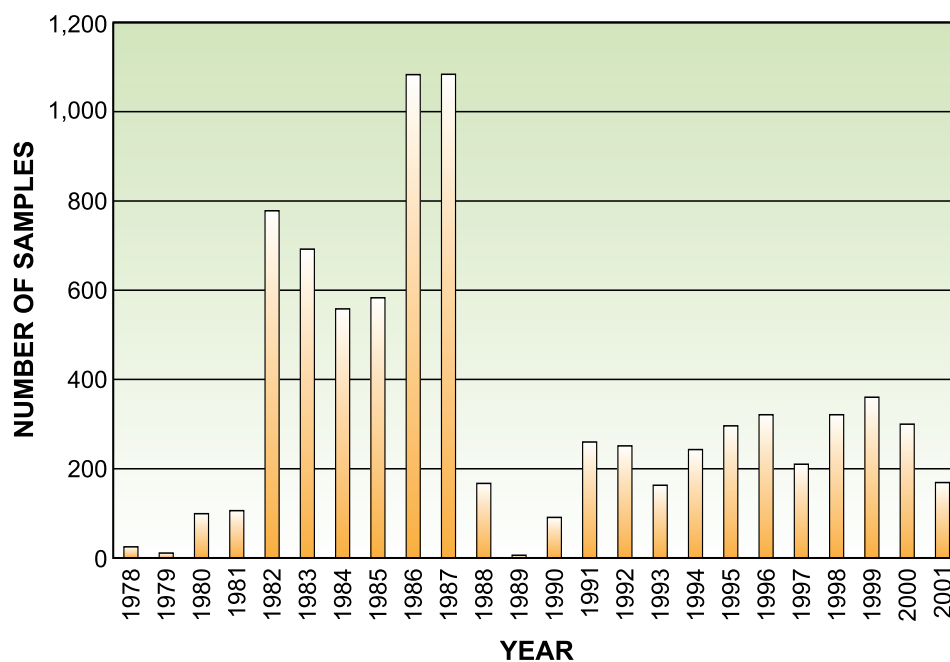


Figure 6. Sampling program for community-supply wells in Illinois, 1978-2001

each year from 1982 to 1987 (fig. 6) after the implementation of the Clean Water Act in 1980. The percentage of samples each year with concentrations greater than or equal to 10 µg/L and less than 50 µg/L remained relatively constant at 9 percent across these years, and samples greater than 50 µg/L ranged from 1 to 2 percent over this time period. Laboratory reporting levels (Irl) have ranged from 0.001 to 5 µg/L. Generally, the lower reporting levels are for more recent samples because analytical machines and methods with higher precision were used in more recent years. If all the samples were screened to the highest reporting level of 5 µg/L, then only 15 percent of all wells would have arsenic detections.

The glacial and alluvial aquifer system, which is the primary aquifer system used for community-water supplies in Illinois, had the greatest number of arsenic samples. Almost 50 percent of the community-supply wells in Illinois are open to this aquifer system (fig. 7). Similar ranges and arsenic detections are present for samples taken from either community-supply (less than 1.0-100 µg/L) or private/monitoring (less than 0.2-128 µg/L) wells open to this aquifer system (table 1).

Estimated Distribution

Possible arsenic sources may be determined by establishing a relation between arsenic

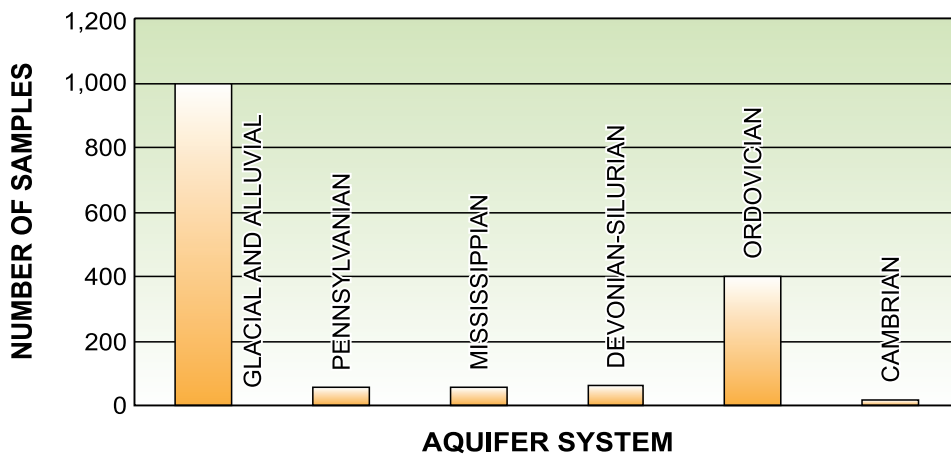


Figure 7. Number of community-supply samples analyzed for arsenic by aquifer system in Illinois.

concentration and concentrations of other chemical constituents and/or physical properties (such as well depth). The relation of arsenic with depth is not straightforward. Arsenic sources may be at various depths and geochemical conditions affecting arsenic mobilization also vary with depth. A study by the USGS in the central Mahomet Buried Bedrock Valley in Illinois (fig. 1) found arsenic concentrations and frequency of detection to be highest in the deep glacial drift aquifer (fig. 4) (median depth of 256 feet) compared to the shallow drift aquifer (fig. 4) (median depth of 33 feet) (Warner, 2001). A comparison of private supplies in this same area found concentrations to be similar for comparable depths (Warner, 2001). In contrast, the ISWS found, in general, higher arsenic concentrations in samples from the shallow portions than in

the deep portions of the glacial and alluvial aquifer system in Tazewell County (Illinois State Water Survey, 2002). This result is based on 590 samples collected by the Tazewell County Health Department and interpolated well-depth information.

In Illinois, many groundwater supplies are hard (hardness as CaCO_3 greater than 120 milligrams per liter (mg/L); Heath, 1984). Therefore, most community and some private supplies treat the drinking water to remove calcium and magnesium, as well as iron, manganese, and other constituents. The removal of these constituents from drinking water also may reduce arsenic concentrations because arsenic adsorbs to iron and manganese oxides (Illinois State Water Survey, 2002). Data from 1,449 community-water supplies that utilize the glacial and alluvial aquifer system were analyzed for arsenic,

iron, and manganese concentrations. Co-kriging, a geostatistical method, was used to estimate arsenic concentrations in ground water across the State by interpolating between data points with known arsenic, iron, and manganese concentrations (figs. 8a, b). More information on these methods can be found in Isaaks and Srivastava (1989) and Kitanidis (1997).

Where the estimates are based on relatively few data points (compared to other parts of the State), there is more uncertainty in the estimated arsenic concentrations (fig. 8b). The geostatistical methods provide a good estimate when compared to known arsenic concentrations but tend to underestimate the highest concentrations and tend slightly to underestimate the variability of the concentrations (the multiple R^2 coefficient of determination was 0.64 between measured and estimated values). The darker shaded areas on figure 8a indicate the highest estimated arsenic concentrations in association with iron and manganese. These areas also may indicate where community and some private supplies likely are treating for iron and manganese, which may remove some of the arsenic. The area of high arsenic, iron, and manganese

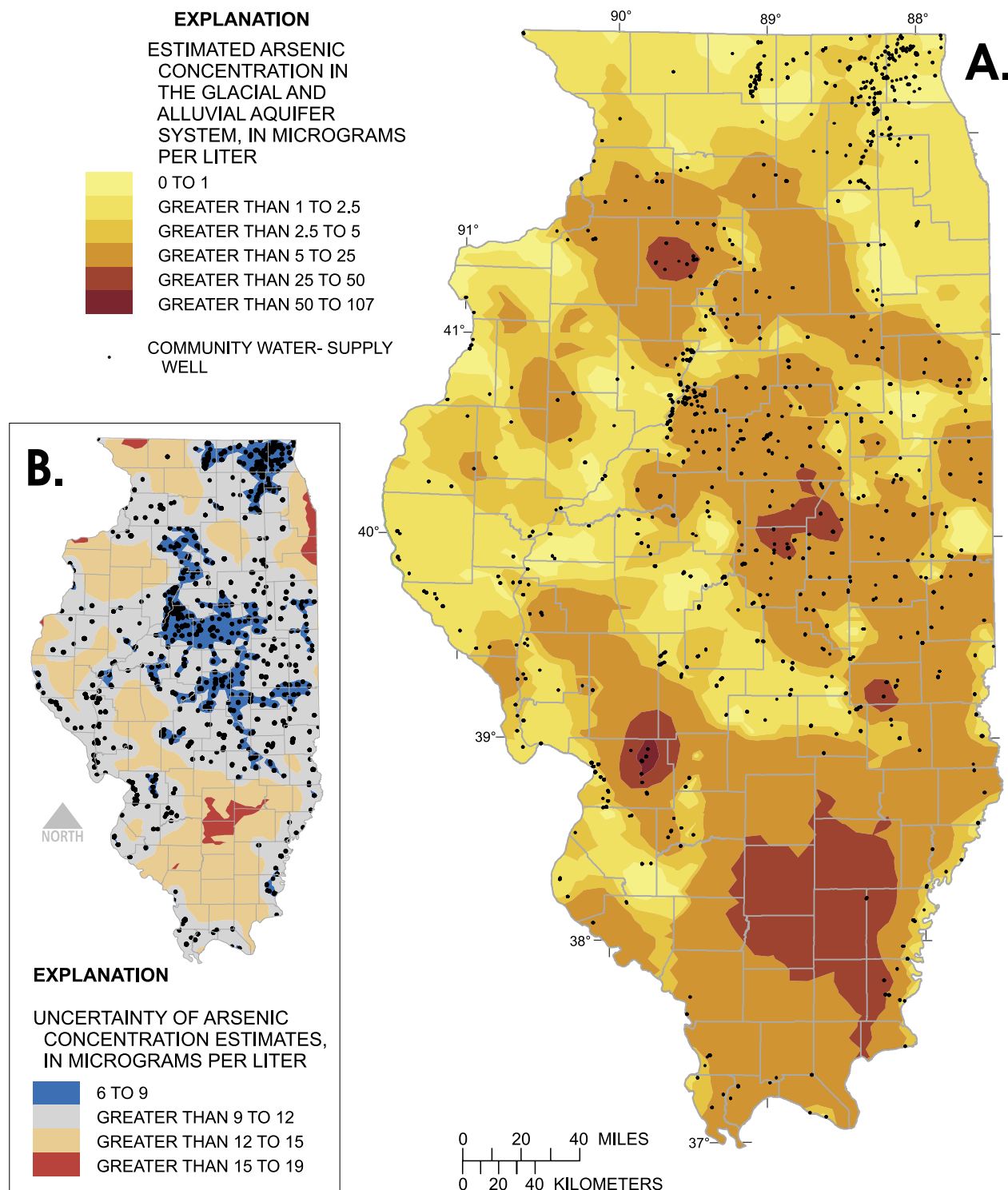


Figure 8. (A) Estimated arsenic concentrations in association with iron and manganese and (B) uncertainty of arsenic concentration estimates, Illinois.

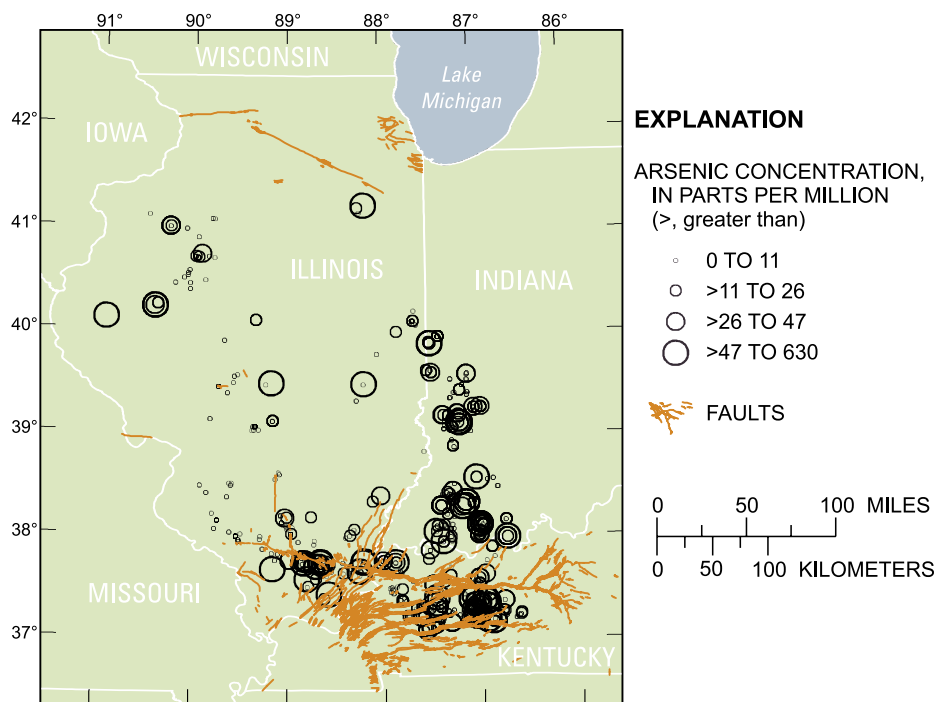


Figure 9. Arsenic concentrations in coal from Illinois, Indiana, and Kentucky (from Goldhaber and others, 2002).

concentrations in central Illinois is associated with part of the Mahomet Buried Bedrock Valley (fig. 1). Water-quality data from private and monitoring wells also indicated high arsenic concentrations in this area.

Potential Sources of Arsenic in Illinois

In most of Illinois, arsenic sources are natural. Three potential sources considered here for high arsenic concentrations in Illinois are: 1) dissolution from geologic material; 2) mobilization of adsorbed or coprecipitated arsenic; and/or 3) bedrock recharge.

The dissolution and mobilization of arsenic from geologic materials will occur if there is a source of arsenic in the geologic materials and if the geochemical conditions are conducive to arsenic transport. There are geographically extensive geologic and geochemical conditions that produced widespread arsenic enrichments in the earth's crust in the formation of arsenic-rich pyrite (Goldhaber and others, 2002). These bedrock deposits usually are in contact with overlying glacial sediments and structural features in the bedrock may provide conduits for arsenic transport. Another source of arsenic is dark shale and coal containing pyrite. Some coal deposits in Illinois,

Indiana, and Kentucky contain high arsenic concentration (fig. 9).

Geochemical rock analyses done on the glacial deposits and underlying bedrock in the Central Mahomet Buried Bedrock Valley indicate that the highest arsenic concentrations are in the organic-rich bedrock underlying the valley. This organic-rich bedrock usually is shale or dark limestone. The sand and gravel making up the deep portions of the glacial and alluvial aquifer system had the lowest arsenic concentration of the sedi-

ments above the bedrock. The till overlying the aquifer in this area had arsenic concentrations higher than the sand and gravel, but substantially less than the organic-rich bedrock (Jeff Catalano, U.S. Geological Survey, written commun., 1999). Thus, there is an arsenic source in the geologic materials of the sediments and bedrock composing the aquifers, but the organic-rich bedrock has the highest concentration of arsenic.

The second possible source for the high arsenic concentrations considered here is the mobilization of coprecipitated arsenic. Consideration of this possible source is based on the premise that during glacial peri-

ods, waters with high arsenic concentration were in contact with clay within the till and the arsenic adsorbed onto these clay particles. As the glacial materials were buried, the geochemical environment became more reducing and the arsenic associated with the iron oxides and hydroxides was mobilized.

The third possible source for high arsenic concentrations considered here is bedrock recharge. This possible source was proposed by Panno and others (1994). Most of the work on arsenic in ground water in Illinois primarily has been in the deep portions of the glacial and alluvial aquifer system, where high arsenic concentrations are present in some areas and depths. In Piatt County in central Illinois (fig. 1), there are many bedrock structural features, such as faults and folds, which could provide direct pathways for ground water to flow from the deep bedrock to the deep portions of the glacial and alluvial aquifer system. Arsenic concentrations in the deep portions of the glacial and alluvial aquifer system increase along the ground-water-flow path just west of Piatt County (Warner, 2001). Ground water from the bedrock may be recharging the aquifer with arsenic or may be altering geochemical conditions so that arsenic is mobilized in this area.

Summary and Conclusions

Dissolved arsenic is found in ground water across Illinois. Determining the extent and distribution of arsenic in ground water is a starting place to assess the potential risk for persons drinking from a community or private supply. Understanding the potential sources and pathways that mobilize arsenic in ground water is necessary in protecting the drinking-water supply in Illinois.

Arsenic was not detected in 60 percent of samples from community supplies considered in this study. The highest arsenic concentrations and most frequent detections in samples from community-supply wells were from the deep portions of the glacial and alluvial aquifer system underlying central Illinois (Mahomet aquifer). Of the community- and private-supply samples, 11 and 14 percent, respectively, exceeded the 10 $\mu\text{g}/\text{L}$ arsenic standard; but, private-supply wells are not regulated for arsenic concentrations in ground water.

Arsenic sources may be at various depths and geochemical conditions affecting arsenic mobilization also vary with depth. Estimates of arsenic,

iron, and manganese have been extrapolated from measured concentrations. An area of high estimated arsenic concentration in ground water in central Illinois appears to be associated with the Mahomet Buried Bedrock Valley. Where the estimates are based on relatively few data points (compared to other parts of the State), there is more uncertainty in the estimated arsenic concentrations. The geostatistical methods provide a good estimate when compared to known arsenic concentrations but tend to underestimate the highest concentrations and tend slightly to underestimate the variability of the concentrations.

In most of Illinois, arsenic sources are natural. Limited geochemical rock analyses done on the glacial deposits and underlying bedrock in the Central Mahomet Buried Bedrock Valley indicate that the highest arsenic concentrations are in the organic-rich bedrock underlying the valley. Understanding the fate and transport of arsenic from the source to a community-supply well will need to involve simulation of the ground-water flow and chemical conditions of the glacial and alluvial aquifer system.

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