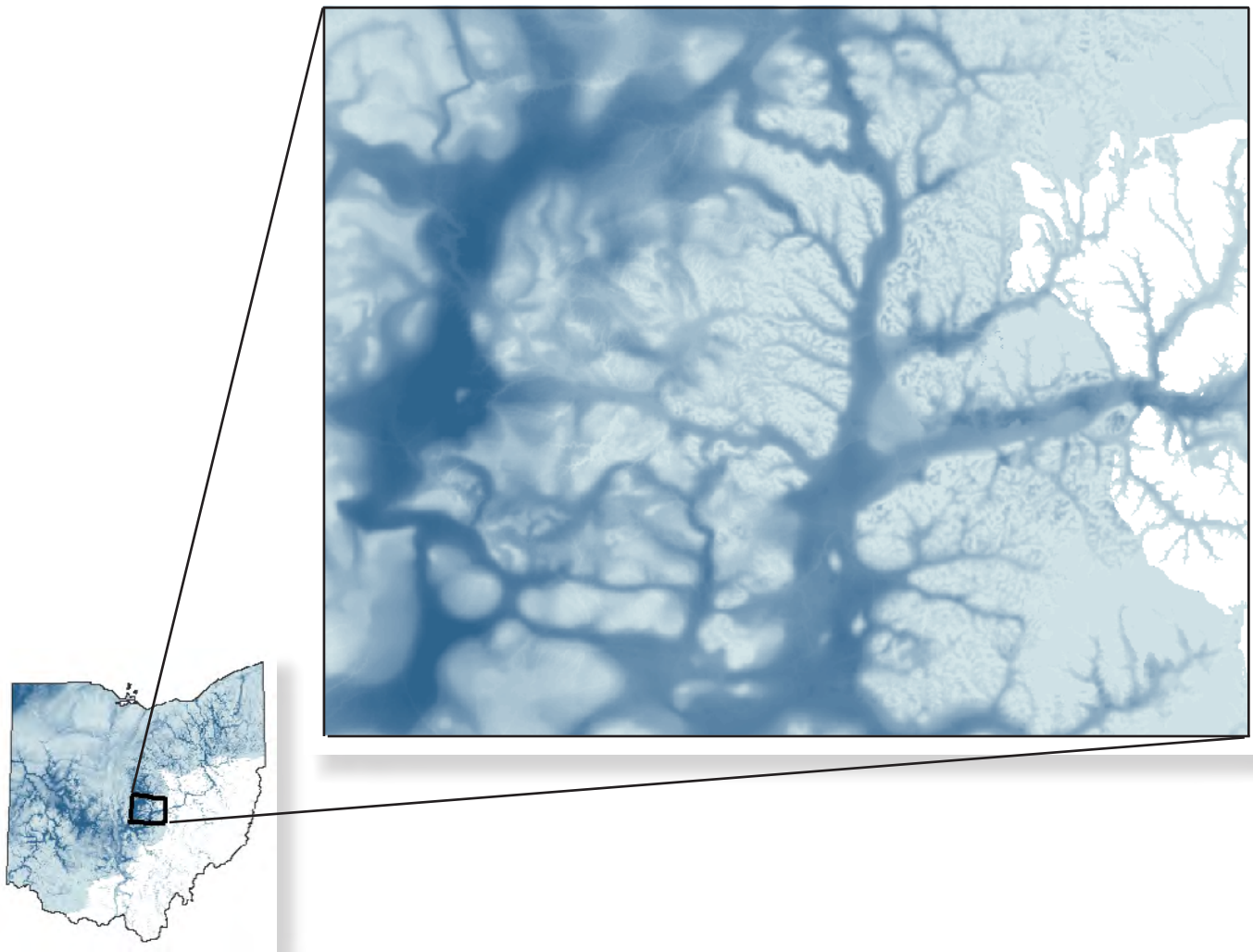


Prepared in cooperation with the Ohio Water Development Authority

Arsenic in Groundwater of Licking County, Ohio, 2012—Occurrence and Relation to Hydrogeology



Scientific Investigations Report 2015–5148

Cover illustration: The design on the cover is based on a geospatial coverage of the thickness of glacial deposits created by the Ohio Department of Natural Resources Division of Geological Survey (2004).

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By Mary Ann Thomas

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Scientific Investigations Report 2015–5148

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

U.S. Department of the Interior
SALLY JEWELL, Secretary

U.S. Geological Survey
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Conversion Factors

Inch/Pound to International System of Units

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)

Datum

Vertical coordinate information is referenced to “mean sea level” in Dove (1960) on which cross-section elevations are based.

Supplemental Information

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ($\mu\text{g}/\text{L}$). Solid-phase concentrations are given in micrograms per kilogram (mg/kg).

Arsenic in Groundwater of Licking County, Ohio, 2012—Occurrence and Relation to Hydrogeology

By Mary Ann Thomas

Abstract

Arsenic concentrations were measured in samples from 168 domestic wells in Licking County, Ohio, to document arsenic concentrations in a wide variety of wells and to identify hydrogeologic factors associated with arsenic concentrations in groundwater. Elevated concentrations of arsenic (greater than 10.0 micrograms per liter [$\mu\text{g/L}$]) were detected in 12 percent of the wells (about 1 in 8). The maximum arsenic concentration of about 44 $\mu\text{g/L}$ was detected in two wells in the same township.

A subset of 102 wells was also sampled for iron, sulfate, manganese, and nitrate, which were used to estimate redox conditions of the groundwater. Elevated arsenic concentrations were detected only in strongly reducing groundwater. Almost 20 percent of the samples with iron concentrations high enough to produce iron staining (greater than 300 $\mu\text{g/L}$) also had elevated concentrations of arsenic.

In groundwater, arsenic primarily occurs as two inorganic species—arsenite and arsenate. Arsenic speciation was determined for a subset of nine samples, and arsenite was the predominant species. Of the two species, arsenite is more difficult to remove from water, and is generally considered to be more toxic to humans.

Aquifer and well-construction characteristics were compiled from 99 well logs. Elevated concentrations of arsenic (and iron) were detected in glacial and bedrock aquifers but were more prevalent in glacial aquifers. The reason may be that the glacial deposits typically contain more organic carbon than the Paleozoic bedrock. Organic carbon plays a role in the redox reactions that cause arsenic (and iron) to be released from the aquifer matrix. Arsenic concentrations were not significantly different for different types of bedrock (sandstone, shale, sandstone/shale, or other). However, arsenic concentrations in bedrock wells were correlated with two well-construction characteristics; higher arsenic concentrations in bedrock wells were associated with (1) shorter open intervals and (2) deeper open intervals, relative to the water level.

The spatial distribution of arsenic concentrations was compared to hydrogeologic characteristics of Licking County.

Elevated concentrations of arsenic (and iron) were associated with areas of flat topography and thick (greater than 100 feet), clay-rich glacial deposits. These characteristics are conducive to development of strongly reducing redox conditions, which can cause arsenic associated with iron oxyhydroxides in the aquifer matrix to be released to the groundwater.

Hydrogeologic characteristics conducive to the development of strongly reducing groundwater are relatively widespread in the western part of Licking County, which is part of the Central Lowland physiographic province. In this area, a thick layer of clay-rich glacial deposits obscures the bedrock surface and creates flat to gently rolling landscape with poorly developed drainage networks. In the eastern part of the county, which is part of the Appalachian Plateaus physiographic province, the landscape includes steep-sided valleys and bedrock uplands. In this area, elevated arsenic concentrations were detected in buried valleys but not in the bedrock uplands, where glacial deposits are thin or absent. The observation that elevated concentrations of arsenic (and iron) were more prevalent in the western part of Licking County is true for both glacial and bedrock aquifers.

In Licking County, thick, clay-rich glacial deposits (and elevated concentrations of arsenic) are associated with two hydrogeologic settings—buried valley and complex thick drift. Most wells in the buried-valley setting had low arsenic concentrations, but a few samples had very high concentrations (30–44 $\mu\text{g/L}$) and very reducing redox conditions (methanogenic and near-methanogenic). For wells in the complex-thick-drift setting, elevated arsenic concentrations are more prevalent, but the maximum concentration was lower (about 21 $\mu\text{g/L}$). Similar observations were made about arsenic concentrations in parts of southwestern Ohio.

The hydrogeologic settings and characteristics associated with arsenic in Licking County also exist in other parts of Ohio. The statewide extent of these characteristics roughly corresponds to areas where elevated concentrations of arsenic are known to exist. This preliminary conceptual model can be tested and revised as additional wells are sampled for arsenic.

Introduction

Arsenic is often a minor component of the rocks and sediments that form the solid framework of an aquifer (the aquifer matrix). Arsenic can be released from the aquifer matrix to the groundwater (mobilized) under certain geochemical conditions. Arsenic is a known human carcinogen; long-term exposure to arsenic in drinking water can cause cancers of the bladder, lung, and skin, and may also be related to cancers of the kidney, liver, and prostate (International Agency for Research on Cancer, 2004; World Health Organization, 2010). Long-term exposure to arsenic has also been linked to cardiovascular disease, Type-2 diabetes, developmental effects, neurotoxicity, and disruptions of the immune system (U.S. Environmental Protection Agency, 2001; Reynolds, 2010; World Health Organization, 2010).

The maximum contaminant level (MCL) for arsenic is 10.0 micrograms per liter ($\mu\text{g/L}$); this is the highest concentration allowed in drinking water from public-water systems (U.S. Environmental Protection Agency, 2009). In this report, the term “elevated arsenic concentrations” refers to arsenic concentrations greater than the MCL. In Ohio, public-water systems are required to monitor for arsenic on a regular basis, and the average annual concentration must meet the MCL. About 17 percent of public-water systems in Ohio had elevated arsenic concentrations prior to treatment (Ohio Environmental Protection Agency, 2010).

In contrast, most private residential (domestic) wells are not routinely tested for arsenic. About 1.8 million Ohioans rely on domestic wells for their water supply (Maupin and others, 2014), and there is limited public awareness of the relatively frequent occurrence of arsenic in Ohio groundwater and (or) the potential threat to human health posed by consuming water with elevated arsenic concentrations. In addition, scientists and managers have a limited understanding of where elevated arsenic concentrations are most likely to occur. Arsenic in groundwater typically appears to be “spotty;” wells in the same neighborhood can have widely varying concentrations. Although it is not possible to predict the arsenic concentration of an individual well, some groundwater settings are more vulnerable to arsenic mobilization than others (Smedley and Kinniburgh, 2002). A better understanding of these vulnerable

hydrogeologic settings, and where they occur in Ohio, would allow well testing and education about water treatment to be focused on areas of greatest need. In 2012, the U.S. Geological Survey in cooperation with the Ohio Water Development Authority, began a project to increase understanding of arsenic in Ohio groundwater, and the work on which this report is based was part of that project.

Purpose and Scope

This report presents results of an investigation of arsenic in groundwater of Licking County, Ohio. The primary goal was to document arsenic concentrations in domestic wells that tap a range of hydrogeologic settings. A second goal was to identify factors associated with elevated arsenic concentrations. A third goal was, to the extent possible, extrapolate results to other parts of the State. The study was based in Licking County because use of domestic wells is relatively widespread, a range of hydrogeologic characteristics are present, and there was an opportunity to collaborate with the Licking County Health Department in a mutually beneficial way.

Water samples from 168 domestic wells in Licking County were collected by homeowners or county sanitarians during March through August of 2012. Samples were analyzed at MASI Laboratories in Columbus, Ohio. All samples were analyzed for arsenic, and 102 samples were also analyzed for iron, manganese, sulfate, nitrate, calcium, and sodium. In November 2012, nine of the wells were resampled and analyzed for arsenic speciation at the USGS National Water Quality Laboratory (NWQL).

Statistical, graphical, and spatial (geographic information system [GIS]) methods were used to document arsenic concentrations and identify factors associated with elevated arsenic concentrations. Information about geology and well construction was compiled from well logs, which were available for 99 of the wells. The GIS coverages from the Ohio Department of Natural Resources were used to identify spatial relations between arsenic concentrations in groundwater and geologic/hydrogeologic characteristics of Licking County. The GIS coverages were also used to extrapolate results from Licking County to other parts of Ohio.



In Ohio, public-supply wells are routinely monitored for arsenic, and about 17 percent (1 in 6) produce water that has elevated arsenic concentrations prior to treatment (Ohio Environmental Protection Agency, 2010).



Domestic (private) wells are used as a source of drinking water by about 1.8 million Ohio residents (Maupin and others, 2014). Many domestic wells are never tested for arsenic.

Background

Arsenic is a component of a wide range of substances, both natural (metal sulfides, metal [oxy]hydroxides, coal, ore deposits, hydrothermal deposits) and manmade (biocides, including wood preservative, glass production, animal feed additives) (Welch and others, 2000; Plant and others, 2003). Most instances of widespread arsenic contamination of groundwater are the result of natural sources of arsenic that exist in the aquifer matrix (Smedley and Kinniburgh, 2002). Minerals in the aquifer matrix often include minor amounts of arsenic, which can be released to the groundwater under certain geochemical conditions. There is a wide range of geochemical conditions under which arsenic can be mobilized, so results of arsenic investigations from other parts of the Nation may not be directly applicable to the geochemical conditions that exist in Ohio groundwater.

In Ohio, elevated concentrations of arsenic are detected in groundwater with reducing redox conditions and circum-neutral or slightly alkaline pH (Matisoff and others, 1982; Petty, 2000; Slattery and others, 2000; Thomas and others, 2005). Redox conditions of groundwater are the result of microbially mediated reactions that involve the exchange of electrons between electron donors (commonly organic carbon) and electron acceptors. Dissolved oxygen is a common electron acceptor, but if it is not available, other electron acceptors are used in a sequential order. If conditions become sufficiently reducing, arsenic associated with iron oxyhydroxides can be released to the groundwater. Iron oxyhydroxides are a relatively common component of an aquifer matrix; they can be dispersed throughout a geologic formation and (or) concentrated in a particular horizon that has been subjected to weathering or contact with oxygenated water. In oxyhydroxides, arsenic can exist within the mineral structure and (or) sorbed onto the mineral surface. Iron oxyhydroxides (and the associated arsenic) are stable in oxic groundwater, but if iron-reducing conditions develop and (or) pH increases, arsenic can be mobilized. Arsenic can also be mobilized by high concentrations of other oxyanions, especially phosphate, which can compete with arsenic for binding sites on aquifer matrix.

Redox reactions, including iron reduction, are enhanced at the interfaces between fine- and coarse-grained sediments (McMahon, 2001). These interfaces can act as mixing zones, where organic acids or humic substances in fine-grained sediments (electron donors) can come in contact with coarse-grained sediments that include iron oxyhydroxides (electron acceptors and a potential source of arsenic).

Smedley and Kinniburgh (2002) concluded that the onset of reducing conditions is one of the most common triggers for mobilizing arsenic in low-temperature, nonmineralized groundwater. Another factor related to the development of high arsenic concentrations is sluggish groundwater flow. After arsenic is released from the solid phase by the onset of reducing conditions, the rate of groundwater flushing should be low enough to allow arsenic to accumulate in the aquifer (Smedley and Kinniburgh, 2002).

Previous Studies

In Ohio, the current (2015) understanding of arsenic in groundwater is based on a patchwork of studies by multiple agencies that fall into three broad categories: water-quality surveys, Test Your Well workshops, and targeted arsenic investigations.

Water-quality surveys.—Arsenic is among the constituents measured as part of water-quality surveys done in selected geographic areas and (or) aquifer types and (or) well types. The Ohio Environmental Protection Agency (Ohio EPA) has documented arsenic concentrations in a network of more than 200 public-supply wells as part of the Ambient Groundwater Program (Ohio Environmental Protection Agency, [n.d.]). A compilation of the arsenic data revealed that elevated arsenic concentrations were detected in each of the State's three major aquifer types but were more prevalent in sand and gravel aquifers than in sandstone or carbonate bedrock aquifers (Slattery and others, 2000; Ohio Environmental Protection Agency, 2000). Elevated arsenic concentrations were associated with iron concentrations indicative of reducing redox conditions. In general, higher arsenic concentrations were associated with public-supply wells that had lower pumping rates/volumes (Ohio Environmental Protection Agency, 2002).

The USGS measured arsenic concentrations as part of water-quality surveys, and results varied widely, depending on the geographic areas and (or) aquifer types sampled. Breen and Dumouchelle (1991) measured arsenic in 82 wells tapping the glacial and carbonate bedrock aquifers in Lucas, Sandusky, and Wood Counties (northwestern Ohio); results indicated that 1 percent of the wells had elevated arsenic concentrations. Dumouchelle (1998) documented water quality in 25 domestic wells tapping the Lockport Dolomite in Darke, Miami, Montgomery, and Preble Counties (southwestern Ohio); results indicated that 68 percent of the wells had elevated arsenic concentrations. A water-quality survey by the National Water-Quality Assessment (NAWQA) program included arsenic determinations for a network of 27 domestic wells tapping the unconfined glacial buried-valley aquifer in the Little and Great Miami River Basins (southwestern Ohio). Results indicated that 7 percent had elevated arsenic concentrations (Shindel and others, 2001). Results of NAWQA water-quality studies in Ohio were included in compilations of arsenic data from the glacial aquifer system of the Midwest (Thomas, 2003) and the northern United States (Thomas, 2007). Jagucki and others (2015) documented water quality in 16 domestic wells tapping glacial and bedrock aquifers in Geauga County (northeastern Ohio); results indicated that 12 percent of the wells had elevated arsenic concentrations.

Samples of soil and stream sediments from Ohio were analyzed for arsenic concentrations as part of the USGS National Geochemical Database (<http://mrddata.usgs.gov/geochemistry/ngs.html>). Venturis and others (2014) used statistical modeling and mapping methods to conclude that the distribution of arsenic in soil and stream sediments varies across the State and is related primarily to the distribution of

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sulfide-bearing bedrock formations; the effects of glaciation are considered to be secondary.

Test Your Well workshops.—The Groundwater Foundation developed guidelines for workshops that allow homeowners to have their well water screened for nitrate by volunteers trained to use a colorimeter (Groundwater Foundation, 2007). The Miami Conservancy District (MCD) modified this design to facilitate testing for arsenic and cosponsored workshops in multiple counties of southwestern Ohio. In addition, they recruited workshop attendees for additional sampling of their wells by MCD. Using these methods, arsenic data were collected from 107 domestic wells in 11 counties of southwestern Ohio. Results indicate that about 20 percent of samples had elevated concentrations (Miami Conservancy District, 2011). A similar type of workshop was held in Union County (west-central Ohio) during 2008; results indicated that 6 of 24 wells (25 percent) had arsenic concentrations greater than the MCL (Christina Burri, Union County Soil and Water Conservation District, written commun., 2008).

Targeted arsenic investigations.—A limited number of studies have been done specifically for the purpose of investigating the source and distribution of elevated arsenic concentrations in domestic wells. The first investigation of this type in Ohio was done by researchers at Case Western Reserve University (Matisoff and others, 1982). The goal was to determine the source of arsenic detected in two school wells in an area of northeastern Ohio. After several potential anthropogenic sources were considered and eliminated, the source was determined to be naturally occurring arsenic released from iron hydroxides by the onset of reducing conditions, which were attributed to a thick layer of till that impedes recharge of oxygenated water or possibly to the release of methane from an underground storage facility.

The Ohio Department of Health investigated arsenic in domestic wells in parts of Perry, Vinton, and Jackson Counties (southeastern Ohio). Results indicated that elevated arsenic concentrations were detected in wells tapping a similar hydrogeologic setting—upper Mississippian sandstone immediately underlying valley-fill deposits (Petty, 2000).

Multiple studies have been done in parts of southwestern Ohio. The Ohio Department of Health, in cooperation with the U.S. Environmental Protection Agency (EPA), investigated the source of arsenic detected in domestic wells in the vicinity of a waste site in Preble County, Ohio. Investigators sampled more than 500 domestic wells and concluded that the arsenic

contamination was not related to the waste site but was a result of geologic materials. Highest arsenic concentrations were detected in wells greater than 100 feet (ft) deep within or along margins of buried valleys (Ohio Department of Health, 1999).

The USGS and the Miami Conservancy District investigated factors associated with elevated arsenic in a three-county area of southwestern Ohio (Thomas and others, 2005). A network of 57 domestic wells tapping a range of hydrogeologic settings and aquifer types were sampled. Elevated arsenic concentrations were detected in strongly reducing groundwater in glacial deposits as well as carbonate bedrock aquifers. The highest arsenic concentrations were in methanogenic groundwater in glacial buried-valley deposits. A followup study in southwestern Ohio included detailed analysis of solid phase and groundwater samples at two sites in a small watershed in southwestern Ohio (Thomas and others, 2008). Results of solid-phase (sediment and bedrock) analysis indicate that the highest arsenic concentrations were in the vicinity of unconformities, including (1) the boundary between glacial deposits and Paleozoic bedrock, and (2) paleosols in the glacial deposits. Analysis of the groundwater indicated that depth-related shifts in redox conditions caused dramatic variations in arsenic concentrations at a single site.

Methods

The water-quality data for this study were collected and analyzed by several different methods (table 1). A private lab in Columbus, Ohio, analyzed samples from 168 wells for arsenic; 102 of the samples were also analyzed for six other water-quality constituents. Of the 168 samples, 125 were collected by homeowners and 43 were collected by county sanitarians. Because methods of collection and analysis were similar, the data were combined into a single dataset that is referred to as the “primary water-quality dataset.” In addition, nine wells were resampled by USGS personnel and analyzed for arsenic species and other constituents at the USGS NWQL. For the most part, the speciation data and primary water-quality data were analyzed separately due to the collection and analysis differences listed in table 1. Water quality data are presented in table 2 (at the back of this report or the Excel file can be accessed at <http://dx.doi.org/10.3133/sir20155148>).



Most of the water samples were collected by well owners and analyzed for arsenic at a local private laboratory. Bottles and instructions for collecting samples were provided to well owners as part of Test Your Well workshops.



Table 1. Methods used for collection and analysis of water-quality data, Licking County, Ohio, 2012.

[$\mu\text{g/L}$, microgram per liter; SM, standard method; mg/L , milligram per liter; EPA, U.S. Environmental Protection Agency method; As, arsenic; USGS, U.S. Geological Survey]

Number of samples	Sample collection		Sample analysis					
	Collected by	Date	Laboratory	Sample type	Constituents	Reporting limit	Analytical method	Method reference
Primary water-quality data								
125	Well owners who attended Test Your Well workshops	June–August, 2012	MASI Laboratories, Columbus, Ohio	Unfiltered	Arsenic	3 $\mu\text{g/L}$	SM3113B	http://standardmethods.org/
					Sulfate	5.0 mg/L	SM4500 $\text{SO}_4\text{-E}$	
					Nitrate	0.10 mg/L	SM4500 $\text{NO}_3\text{-F}$	
					Iron	80 $\mu\text{g/L}$	EPA 200.7	
43	Licking County Health Department sanitarians	March–August, 2012	U.S. Environmental Protection Agency, 1994.	Manganese	30 $\mu\text{g/L}$			
				Calcium	2 mg/L			
				Sodium	10 mg/L			
Arsenic speciation data								
9	U.S. Geological Survey personnel	November, 2012	U.S. Geological Survey, National Water Quality Laboratory, Denver, Colorado	Filtered	Arsenate	0.4 $\mu\text{g/L}$ as As	I-2195-05	Garbarino and others, 2006.
					Arsenite	0.2 $\mu\text{g/L}$ as As		
					Monomethylarsonate	3.2 $\mu\text{g/L}$ as As		
					Dimethylarsinate	0.6 $\mu\text{g/L}$ as As		

Collection and Analysis of Primary Water-Quality Data

A total of 125 water samples were collected during three Test Your Well workshops held in June, July, and August of 2012. Workshop attendees were given labeled bottles and instructions for collecting unfiltered water samples. The instructions included guidance about collecting untreated water, purging the tap prior to filling the bottles, and keeping the samples chilled. The bottles did not include a preservative, so samples had to be returned during specified hours and were preserved by acidification upon arrival at the lab. In addition, 43 water samples were collected by sanitarians from the Licking County Health Department during routine well-inspection activities between March and August, 2012. Methods used for sample collection were similar to those provided to homeowners.

A total of 168 water samples (125 collected by homeowners and 43 collected by sanitarians) were analyzed at MASI Laboratories in Columbus, Ohio. All samples were analyzed for arsenic, and 102 samples were also analyzed for iron, manganese, sulfate, nitrate, calcium, and sodium. Nitrate was analyzed within 48 hours of sample collection, and the other constituents were analyzed within 7 days of collection. These water-quality data are included in table 2.

Collection and Analysis of Arsenic Speciation Data

After compiling arsenic results from the private laboratory, nine wells were selected for resampling to determine arsenic speciation. The criteria for well selection were (1) the arsenic concentration from the primary dataset was greater than 10.0 $\mu\text{g/L}$, (2) a well log was on file at ODNR, and (3) well owners were willing to participate in the study. The nine wells were sampled during November, 2012, by USGS personnel using documented methods for well purging, determination of field parameters, sample collection, preservation, and quality assurance (U.S. Geological Survey, variously dated). Samples were analyzed at the USGS NWQL for concentrations of arsenic species, major ions, trace metals, nutrients, and dissolved organic carbon (table 1). Determinations of pH, specific conductance, temperature, dissolved oxygen, and alkalinity were made at the time of sample collection. The complete dataset is available on the USGS National Water Information System (NWIS) (<http://nwis.waterdata.usgs.gov/usa/nwis/qwdata>). For two wells, sulfate concentrations from the NWQL were substituted for those from the private laboratory in table 2 because the lower detection limits were necessary to estimate redox conditions (see “Redox Conditions Estimated From Concentrations of Iron, Manganese, Sulfate, and Nitrate” section).

Quality Assurance

MASI Laboratories was certified by the Ohio EPA to analyze samples from public-supply wells, and at the time of this study (2012), the Licking County Health Department used MASI Laboratories to analyze water samples collected during routine well inspections. A USGS lab-evaluation process was used to verify that analytical results from MASI Laboratories would meet the data-quality objectives of this study (<http://bqs.usgs.gov/>). MASI Laboratories met the criteria of the evaluation process.

A total of 22 quality-control (QC) samples were used to assess variability and bias of the water-quality data collected during the course of this study. Results of the QC samples are presented in tables 3, 4, and 5 (all at the back of this report). During Test Your Well workshops in the summer of 2012, 10 QC samples were submitted to MASI Laboratories along with samples collected by homeowners (table 3). The samples included a trip blank, five replicates, and four standard reference samples. Results of the trip blank did not indicate contamination during transport or analysis. Arsenic concentrations for pairs of replicate samples differed by 18 percent or less. Arsenic concentrations determined for standard reference samples differed from the most probable values (MPVs) by 31 percent or less. The MPV is the median concentration determined by multiple laboratories. The results showed no clear bias; two of the results were less than the MPV, and two were greater.

During collection of the speciation dataset in November 2012, three QC samples were submitted to the NWQL (table 4). The samples included an equipment blank (and a source-solution blank), a field blank (and a source-solution blank), and a replicate sample analyzed for arsenic speciation. Concentrations of arsenic species for replicate samples differed by 3 percent or less. Results of the equipment blank did not indicate contamination related to the sampling equipment. In the field blank, arsenic was detected at a concentration of 0.0575 µg/L. This concentration is not considered to be problematic because it is less than the reporting level of 0.08 µg/L (U.S. Geological Survey National Water Quality Laboratory, 2015).

For most wells, arsenic concentrations in the speciation dataset are different from those in the primary dataset. The cause is not known, but it may be related to differences in sampling date, type of sample (filtered vs. unfiltered), method of collection, or analytical method (table 1). In addition, processing errors in the field or laboratory could have contributed to the different results. To investigate further, additional QC samples were collected in April 2013, during the data-analysis phase of this study (table 5). Four pairs of replicate samples

were submitted to MASI Laboratories, and results indicated that arsenic concentrations for pairs of replicate samples differed by 30 percent or less. In addition, five unfiltered split samples were submitted to MASI Laboratories and the USGS NWQL to evaluate analytical differences between the labs. Results indicated that arsenic concentrations in the laboratory split samples differed by -7–81 percent. Four of the five samples analyzed at MASI Laboratories had higher results than the samples analyzed at NWQL. The cause of these differences is not known.

A different type of quality assurance was used to assess whether samples collected by homeowners had been affected by water treatment (even though homeowners were instructed to collect untreated water). Water softening by cation exchange is the most common form of water treatment in Ohio and is also used as a form of pretreatment for other processes used to treat arsenic, such as reverse osmosis and anion exchange. During cation exchange, calcium displaces sodium on the solid media, and as a result, calcium concentrations in the water decrease and sodium concentrations increase. Therefore, high sodium/calcium ratios in water can be indicative of the effects of water softening. Four out of 102 samples were suspected of being softened because (1) sodium/calcium ratios were very high (98–133), and (2) calcium was not detected above the minimum reporting level of 2 milligrams per liter (mg/L). In comparison, the other 98 samples had sodium/calcium ratios of 0.05–18 and calcium concentrations of 9–139 mg/L. Cation exchange has little effect on arsenic concentrations because arsenic exists in groundwater as a neutral or negatively-charged compound; however, cation exchange decreases iron and manganese concentrations, which were used to estimate redox conditions of water. Therefore, iron and manganese concentrations of softened samples were excluded from the dataset, but arsenic concentrations were not. None of the samples indicated treatment by reverse osmosis or anion exchange on the basis of iron, manganese, nitrate, and sulfate concentrations. The 66 samples that were not analyzed for additional water-quality constituents could not be screened for evidence of water treatment.

Overall, it is likely that the methods used for sample collection and analysis added some variability and (or) uncertainty to the water-quality results. This uncertainty was taken into consideration during data analysis by grouping arsenic concentrations into broad concentration classes (of <3 µg/L, 3–10.0 µg/L, 10.1–29.9 µg/L, and 30–44 µg/L). The effect of the analytical variability on estimation of redox conditions is likely minimal because redox categories are defined by (1) broad concentration classes and (2) a combination of at least two constituents.

Data Analysis

Two types of data were collected as part of this study: water-quality data and well-log data (table 6). The water-quality data includes arsenic concentrations for 168 wells, concentrations of 6 additional water-quality constituents for 102 wells, and arsenic species for 9 wells. Well logs, which were available for 99 wells, were used as a source of information about aquifer and well characteristics. Arsenic concentrations, additional water-quality constituents, and well logs were available for 68 wells.

Relations among the variables were investigated using robust non-parametric statistical methods. The Kruskal-Wallis test was used to compare arsenic concentrations among groups of samples. The Spearman’s rho test was used to identify monotonic correlations between continuous variables. Test results with a *p*-value less than 0.05 were considered to be statistically significant. The number of samples used for each individual statistical test varied depending on availability of the different types of data.

In addition, GIS coverages from the Ohio Department of Natural Resources (ODNR) (<http://geospatial.ohiodnr.gov/gis-home>) were used to assess spatial relations between water quality and selected geologic/hydrogeologic characteristics of Licking County. The same coverages were used to extrapolate results from Licking County to the rest of the Ohio. All of the variables used for data analysis are included in table 2.

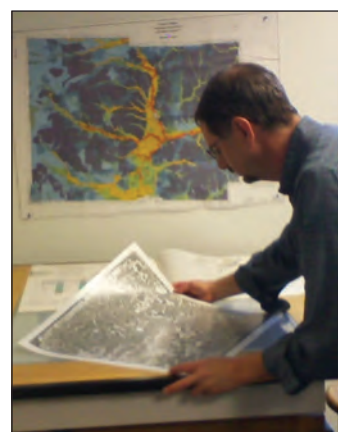
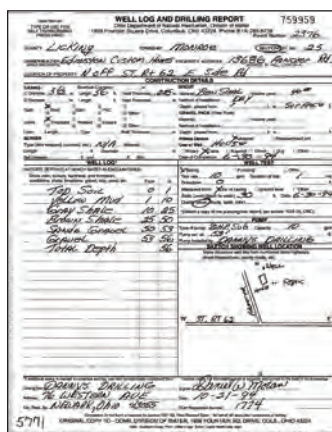
Table 6. Variables used for analysis of arsenic data from Licking County, Ohio, 2012.

Analysis variables	Number of samples
Arsenic concentrations	168
Six additional water-quality constituents	¹ 102
Well log variables	² 99
Arsenic concentrations, 6 additional water-quality constituents, and well logs	68
Arsenic species	9

Geospatial coverages:

- Bedrock geology of Ohio (Slucher and others, 2006).
- Unconsolidated aquifers of Ohio (Ohio Department of Natural Resources, 2000).
- Drift thickness of Ohio (Ohio Department of Natural Resources, Division of Geological Survey, 2004).
- Pollution potential of Licking County (Ohio Department of Natural Resources, 1995).

¹Nitrate concentration was not available for 1 sample.
²Well depths and water levels were known for 100 wells.



Information from well logs and geologic maps/coverages was used to help understand results of the water analyses.

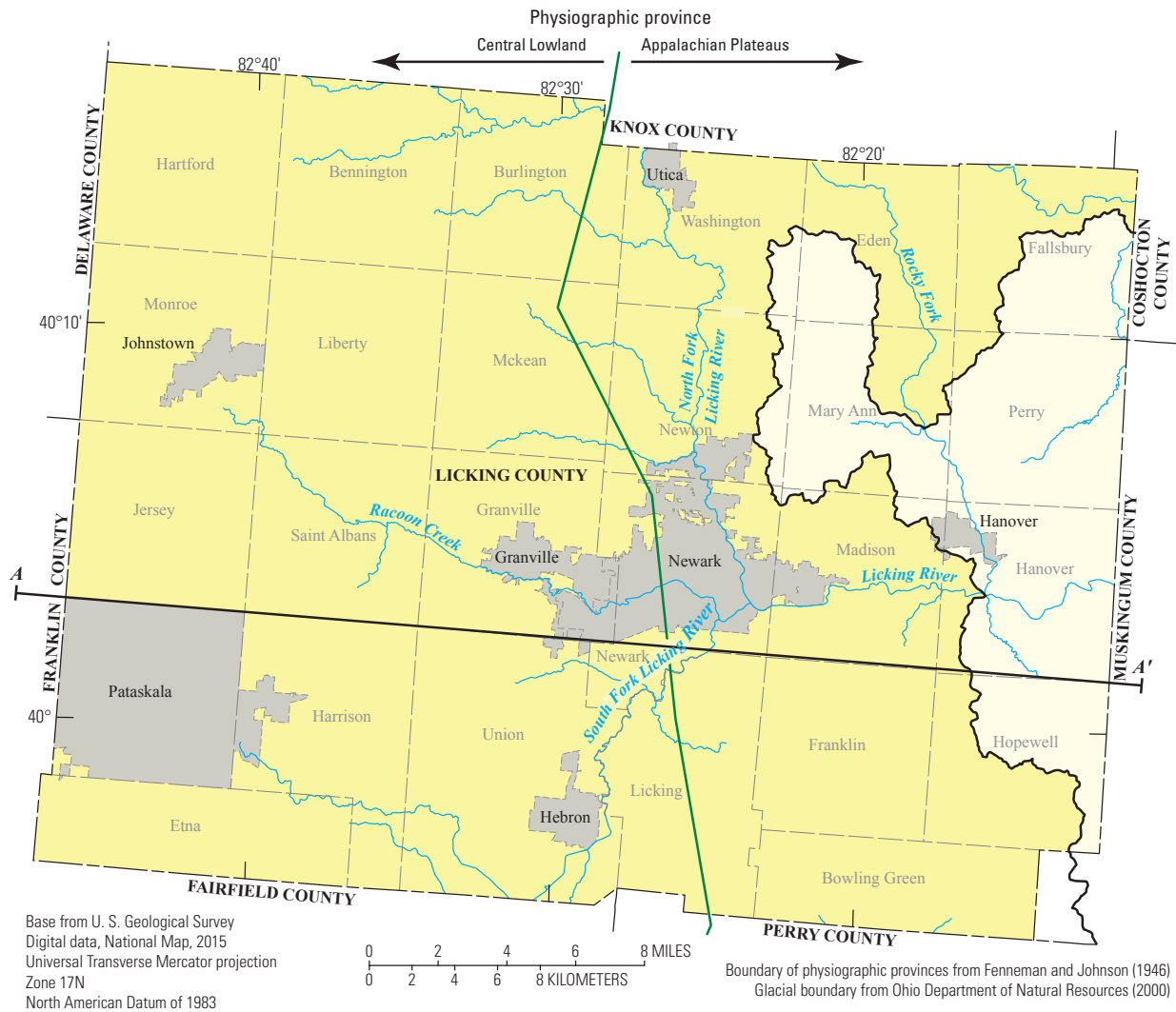
Description of Study Area

Licking County is in central Ohio on the eastern outskirts of the Columbus metropolitan area (fig. 1). The county includes a mix of urban and rural land uses, and the population during 2010 was 166,492 (U.S. Census Bureau, 2012).

The hydrogeology of Licking County has been described by Dove (1960), Forsyth (1966), Hartzell (1982), Angle (1995), Siegrist and others (1997), Froelking and Szabo (1998), and Froelking and Pachell others (2006). The geologic and hydrogeologic characteristics of Licking County have

been mapped by the ODNR (<http://geospatial.ohiodnr.gov/gis-home>).

Most of Licking County is within the Muskingham River watershed. The principal stream is the Licking River, which is formed by the confluence of the North Fork Licking River, South Fork Licking River, and Raccoon Creek (fig. 1). The water supply for Newark is from the North Fork Licking River, but all other public-water systems in the county rely on groundwater. About 40 percent of the population have domestic water supply wells that tap bedrock formations and (or) unconsolidated glacial deposits (Siegrist and others, 1997).



EXPLANATION

- Glaciated region
- Unglaciaded region
- Glaciated region boundary
- Physiographic province boundary
- Line of section

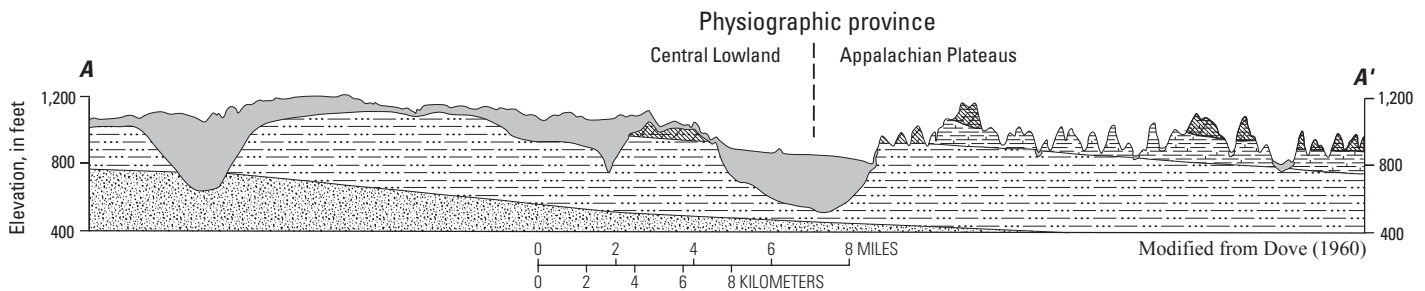


Figure 1. Location of the study area in Licking County, Ohio, 2012. A—A' indicates the approximate location of the cross section in figure 2.

The boundary between two major physiographic provinces is near the middle of Licking County (figs. 1 and 2) (Fenneman and Johnson, 1946). The western part of the county is in the Central Lowland physiographic province, where a thick layer of glacial deposits obscures the underlying bedrock and the land surface is gently undulating plains. Surface drainage networks are poorly developed, and most of the rivers (except Raccoon Creek) occupy shallow, narrow valleys (Dove, 1960). The eastern part of the county is in the Appalachian Plateaus physiographic province, where much of the landscape consists of steep-sided valleys with bedrock uplands. Thick glacial deposits exist in the buried valleys, but glacial deposits are thin or absent in the bedrock uplands.

The bedrock of Licking County consists of Devonian- to Pennsylvanian-age sedimentary formations that dip gently to the east (Slucher and others, 2006) (fig. 2). The oldest formations—Sunbury Shale, Berea Sandstone, and Bedford Shale—subcrop near the western boundary of the county. The Berea

Sandstone is considered a good aquifer but is not frequently used for domestic supply because of its depth (Dove, 1960). The Mississippian-age Cuyahoga Formation is present over most of the county and is considered to be the most productive aquifer (Dove, 1960). The formation is a relatively complex mix of sandstone, shale, siltstone, and conglomerates that is generally more coarse-grained in the east. In parts of central and eastern Licking County, the Cuyahoga Formation is overlain by the Logan Formation, which consists of interbedded sandstone, shale, siltstone, and conglomerates. In easternmost Licking County, the Logan Formation is unconformably overlain by Pottsville and Allegheny Formations of Pennsylvanian age. The lithology is interbedded sandstone, shale, siltstone, and conglomerate. The Allegheny Formation also includes thin beds of limestone, coal, and flint. These formations are considered to be a poor aquifer, largely because of the thickness and (or) position relative to the water table (Dove, 1960).



System	Formation	Lithology
Quaternary	Glacial deposits	Unconsolidated till, silt, clay, sand, gravel, and bolders.
Pennsylvanian	Allegheny	Sandstone, shale, siltstone, conglomerate. Some thin beds of limestone, coal, flint.
	Pottsville	
Mississippian	Logan	Interbedded sandstone, shale, siltstone, conglomerate.
	Cuyahoga	Sandstone, shale, siltstone, conglomerate. Generally coarser-grained towards the east.
	Sunbury shale	Brown to black shale.
Devonian	Berea Sandstone ¹	Fine-grained sandstone.
	Bedford shale ¹	Red or blue shale.

¹Classified as Mississippian by Dove (1960); later re-classified as Devonian (Slucher and others, 2006).

Figure 2. Geology of Licking County, Ohio. Approximate location of cross section A—A' is shown on figure 1.



Domestic wells in Licking County produce water from glacial deposits or bedrock (or both). Minor amounts of arsenic in these geologic materials can be released to the groundwater under certain geochemical conditions.

Glacial deposits overlie bedrock in much of the county (fig. 3A). The most widespread type of glacial deposit is till (unsorted clay, silt, sand, and gravel), which may include lenses of sand and gravel. Fines (clay and silt) with lenses of sand and gravel are present in valleys in the southern and eastern parts of the county. Sand and gravel, with minor fines, are present in valleys in the northern and central parts of the county.

Glacial deposits are 0 to 596 ft thick (fig. 3B). The easternmost part of the county is unglaciated, although glacial deposits occur in valleys beyond the limit of glacial advance. The thickest glacial deposits are in two north-south trending valleys cut into bedrock by the preglacial Teays River system. These are referred to as “buried valleys” because they eventually filled with glacial sediments. The buried valley in the western part of the county is filled with predominantly fine-grained sediment; it has no current stream and is not visible from land surface. The buried valley near the center of the county partially corresponds to the location of the current Licking River; this buried valley has a larger fraction of sand and gravel, but fines are also present.

The glacial deposits of Ohio have been grouped into hydrogeologic settings largely on the basis of lithology and drift thickness (Ohio Department of Natural Resources, 2000). In Licking County, the predominant hydrogeologic settings are buried valley, complex thick drift, ground moraine, thin upland, and alluvial (fig. 3C). In addition, a small patch of Illinoian end moraine is present in the eastern part of the county but is not considered to be one of the predominant hydrogeologic settings.

In Licking County, wells produce water from glacial deposits and (or) bedrock at depths of about 40–400 ft. Well yields vary from less than 10 to more than 500 gallons per minute (Hartzell, 1982). The best water supplies are available from thick deposits of sand and gravel, especially those at land surface and (or) in contact with current rivers. In areas where surficial glacial deposits consist of till or fines, water can be produced from sand and gravel lenses or layers within the finer-grained sediment. If sufficient sand and gravel are not present in glacial deposits, wells can be drilled to the underlying bedrock. Most wells in upland areas in the central and eastern parts of the county are in bedrock. Some areas of the county use bedrock and glacial wells almost equally (Angle, 1995).



Western Licking County is overlain by thick layer of glacial deposits, which creates a flat to gently-rolling land surface (above). Over much of eastern Licking County, the layer of glacial deposits overlying bedrock is much thinner, and the topography is more rugged (right). These factors can influence the chemical quality of the groundwater.



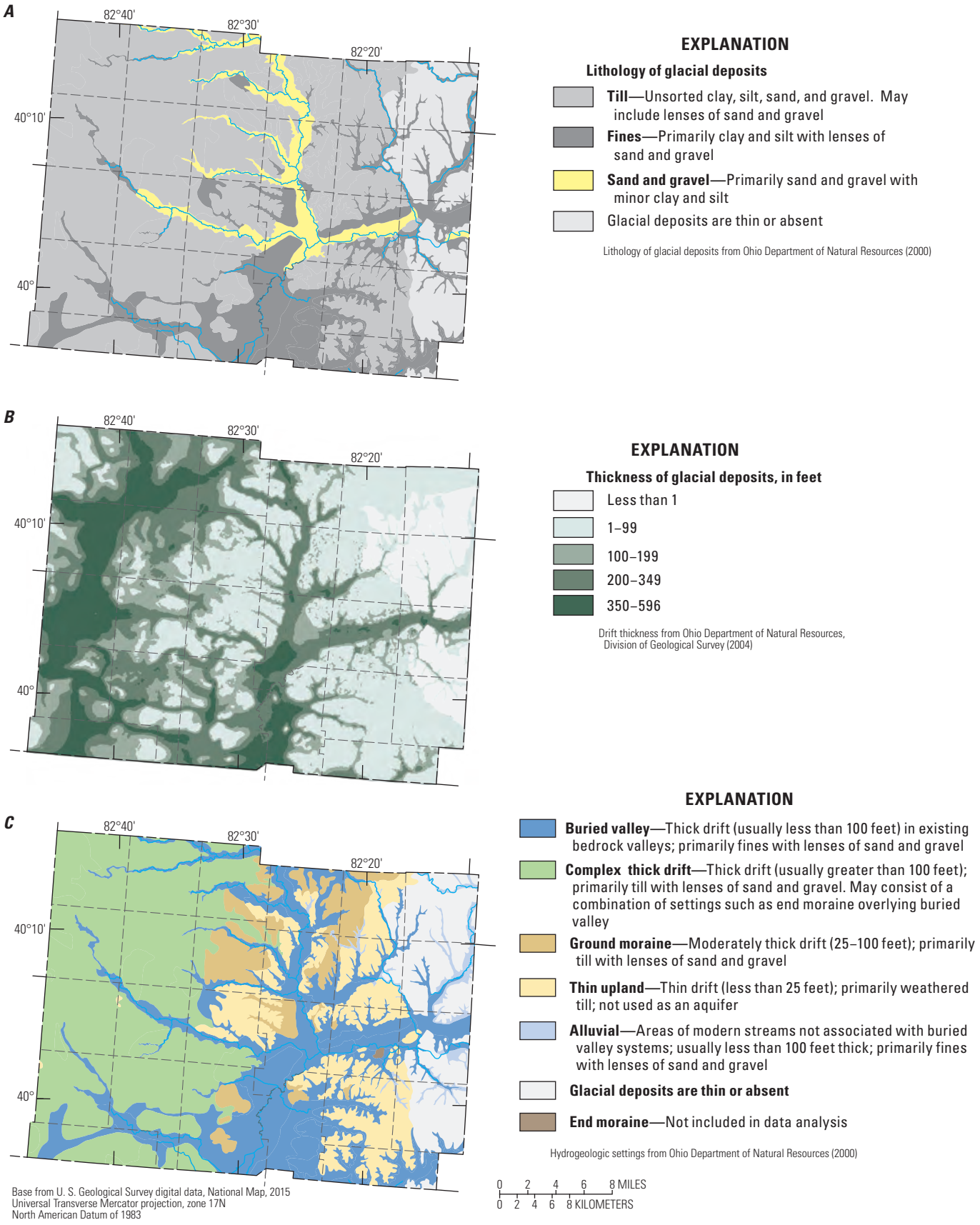
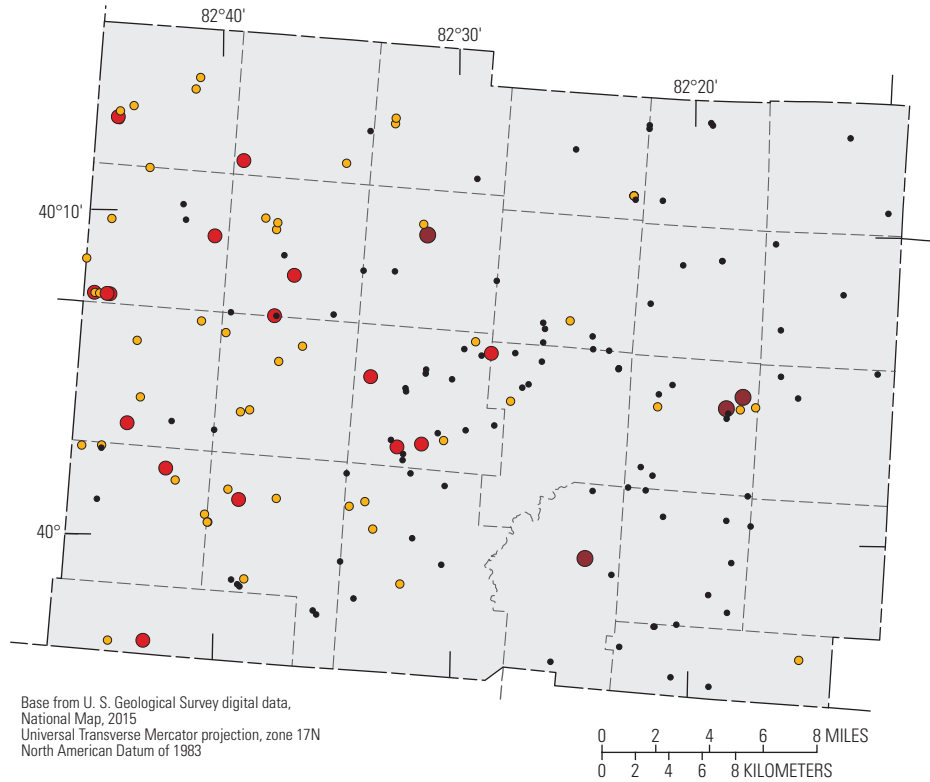


Figure 3. Characteristics of glacial deposits of Licking County, Ohio. *A*, Lithology. *B*, Drift thickness. *C*, Hydrogeologic settings.

Arsenic Concentrations

Arsenic concentrations were determined for water samples from 168 domestic wells in Licking County, and concentrations ranged from less than 3 µg/L to 43.8 µg/L (fig. 4). The maximum contaminant level (MCL) for arsenic is

10.0 µg/L, and almost 1 in 8 samples (12 percent) had concentrations greater than the MCL. In this report, “elevated arsenic concentrations” refers to concentrations greater than the MCL. The spatial distribution of the data (fig. 4) shows that elevated arsenic concentrations are more prevalent and widespread in the western part of the county than in the eastern part.



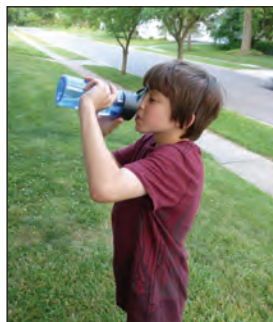
EXPLANATION

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

- Less than 3
- 3–10.0
- 10.1–29.9
- 30–44

Number of samples	168
Percentage with arsenic concentrations:	
<3 ug/L (lower detection limit)	58
3–10.0 ug/L	30
>10.0 ug/L (maximum contaminant level)	12
Arsenic concentrations, in µg/L	
Median	<3
75th percentile	6
Maximum	43.8

Figure 4. Arsenic concentrations from 168 domestic wells in Licking County, Ohio, 2012.



Almost 1 in 8 domestic wells had arsenic concentrations greater than the maximum contaminant level of 10 µg/L. In general, elevated arsenic concentrations were more widespread and prevalent in the western half of Licking County than in the eastern half.

Arsenic Species

In groundwater, arsenic primarily occurs as two inorganic species—arsenite (As^{3+}) and arsenate (As^{5+}). In general, As^{3+} is considered to be more toxic to humans than As^{5+} . The As^{5+} is usually the predominant species in oxic redox conditions, and As^{3+} is usually the predominant species in reducing redox conditions. At pH values typical of groundwater, As^{5+} exists in solution as a negatively charged ion ($HAsO_4^{2-}$ or $HAsO_4^-$). In contrast, As^{3+} exists as an uncharged species (H_3AsO_3) which makes it more difficult to remove from water; treating water to remove As^{3+} can require multiple steps (U.S. Environmental Protection Agency, 2003). Although arsenic speciation is important to know when purchasing a water-treatment system, this type of analysis was not available from the private laboratory. Therefore, in November, 2012, a subset of nine wells with elevated arsenic concentrations was resampled by USGS

personnel, and filtered samples were analyzed at the NWQL for arsenic species and other constituents (table 1).

Four arsenic species were analyzed—two inorganic species (arsenate and arsenite) and two organic species (dimethylarsinate and monomethylarsonate) (table 7). The organic species were not detected above the minimum reporting levels. Arsenite (As^{3+}) was the predominant species in all samples. The percentage of As^{3+} was estimated relative to the sum of As^{3+} and As^{5+} , and values ranged from 55 to 92 percent, with a median of 80 percent.

For most samples, the sum of the two inorganic species was greater than total arsenic concentration; however, this was not considered to be a problem because the data are used in a qualitative way to identify the predominant arsenic species. Differences between arsenic concentrations in the primary and speciation datasets are briefly discussed in the “Quality Assurance” section.

Table 7. Arsenic species from nine domestic wells, Licking County, Ohio, 2012.

[Arsenic and arsenic species were analyzed from filtered samples at U.S. Geological Survey National Water Quality Laboratory; mm/dd/yy, month/day/year; $\mu\text{g/L}$, microgram per liter; As, arsenic; <, less than]

Well identifier	Date (mm/dd/yy)	Arsenic ($\mu\text{g/L}$)	Arsenite (As^{3+}) ($\mu\text{g/L as As}$)	Arsenate (As^{5+}) ($\mu\text{g/L as As}$)	Dimethylarsinate ($\mu\text{g/L as As}$)	Monomethylarsonate ($\mu\text{g/L as As}$)	Percentage of As^{3+} relative to ($As^{3+}+As^{5+}$)
LI-40	11/06/12	20.2	16.9	3.9	<.6	<3.2	81
LI-37	11/06/12	20.6	15.8	4.1	<.6	<3.2	79
LI-43	11/07/12	7.1	5.1	.7	<.6	<3.2	88
LI-32	11/07/12	67.5	67.2	6.3	<1.8	<9.6	91
LI-31	11/07/12	51.7	51.2	4.2	<1.2	<6.4	92
LI-36	11/08/12	31.0	21.8	10.6	<1.2	<6.4	67
LI-49	11/08/12	22.0	21.7	3.3	<.6	<3.2	87
LI-33	11/09/12	12.7	8.5	3.8	<.6	<3.2	69
LI-38	11/09/12	31.0	17.3	14.2	<1.2	<6.4	55



The effectiveness of water treatment methods to remove arsenic depends on the type (species) of arsenic present in the water. Nine of the wells were resampled for analysis of arsenic species at the USGS National Water Quality Laboratory.

Factors Related to Arsenic Concentrations

Three types of information were used to investigate factors related to arsenic concentrations in the groundwater of Licking County: (1) water-quality constituents indicative of redox conditions, (2) aquifer and well characteristics from well logs, and (3) GIS coverages of the spatial distribution of hydrogeologic characteristics across the county.

Geochemical Conditions of Groundwater

Redox conditions and pH are the two most important geochemical controls on arsenic concentrations in groundwater (Smedley and Kinniburgh, 2002). In parts of southwestern Ohio, elevated arsenic concentrations were detected in groundwater with strongly reducing redox conditions and circumneutral to slightly alkaline pH (Thomas and others, 2005). To investigate whether arsenic is mobilized in

similar geochemical conditions in Licking County, 102 of the 168 water samples were analyzed for water-quality constituents used to estimate redox conditions of the groundwater. In this section of the report, redox conditions are estimated using two methods, and the results are compared. It was not practical to determine pH of samples in the primary dataset; however, the nine samples in the speciation dataset had pH values of 6.9–7.8 (median of 7.2), which is circumneutral to slightly alkaline.

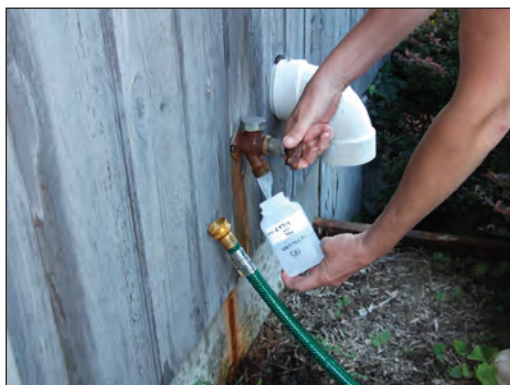
McMahon and Chapelle (2008) developed a method for estimating redox conditions of groundwater using concentrations of five water-quality constituents: dissolved oxygen, nitrate, manganese, iron, and sulfate. For the current study, it was not practical to analyze samples for dissolved oxygen because the measurement should be made at the time of sample collection, using equipment not available to homeowners or county sanitarians. Therefore, for this report, estimates of redox are based on concentrations of four constituents—iron, manganese, sulfate, and nitrate. The modified system is shown in table 8.

Table 8. Framework used to estimate redox conditions from concentrations of iron, manganese, sulfate, and nitrate in groundwater, Licking County, Ohio, 2012.

[Modified from McMahon and Chapelle (2008); NO₃, nitrate as nitrogen; mg/L, milligram per liter; Mn, manganese; µg/L, microgram per liter; Fe, iron; SO₄, sulfate; --, not applicable; ≥, greater than or equal to; <, less than]

Redox Category	Estimated redox condition	Water-quality criteria			
		NO ₃ (mg/L)	Mn (µg/L)	Fe (µg/L)	SO ₄ (mg/L)
Not strongly reducing	Oxic or suboxic	<0.5	<50	<100	--
	NO ₃ reducing	≥0.5	<50	<100	--
	Mn reducing	<0.5	≥50	<100	--
	Mixed ¹	≥0.5	--	≥100	--
Strongly reducing	Fe or SO ₄ reducing	<0.5	--	≥100	≥0.5
	Methanogenic	<0.5	--	≥100	<0.5

¹Other types of mixed redox are possible, but this was the only type detected in this study.



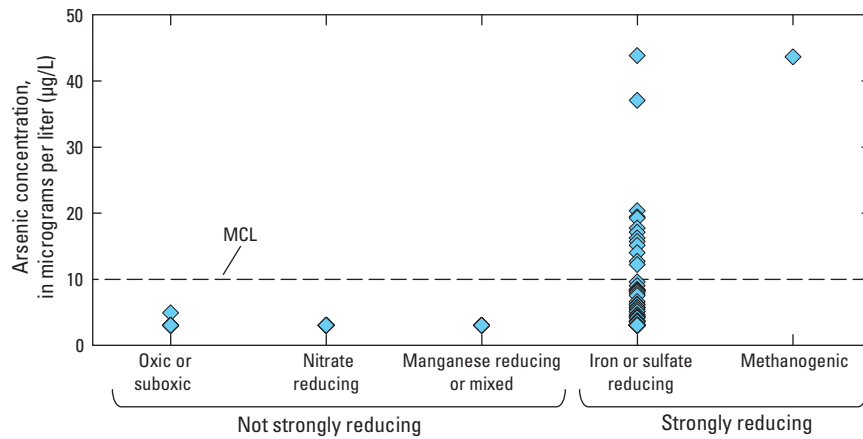
Staining of household surfaces is caused by high-iron groundwater, which is found in many parts of Licking County. More than 18 percent of the high-iron samples had elevated concentrations of arsenic.

Redox Conditions Estimated From Concentrations of Iron, Manganese, Sulfate, and Nitrate

A total of 101 samples had sufficient data to estimate redox conditions by using the modified redox framework (fig. 5). Most (75 percent) samples were iron- or sulfate-reducing, and one sample was methanogenic. In this report, these redox conditions are categorized as “strongly reducing.” All samples with elevated concentrations of arsenic were strongly reducing; however, not all strongly reducing samples had elevated arsenic concentrations. Of the strongly reducing samples, 18 percent had arsenic concentrations greater than the MCL of 10.0 µg/L.

About 24 percent of the samples were estimated to be oxic, suboxic, nitrate-reducing, manganese-reducing, or mixed, and are categorized as “not strongly reducing.” None of the samples in this category had elevated arsenic concentrations; 4.9 µg/L was the maximum arsenic concentration for a sample that was not strongly reducing.

As shown in table 8, methanogenic waters differ from iron- or sulfate-reducing waters in terms of sulfate concentrations; both types of water have high iron concentrations, but methanogenic waters have sulfate concentrations less than 0.5 mg/L (McMahon and Chapelle, 2008). The reporting level for sulfate at the private lab was 5 mg/L, and the two samples with the maximum arsenic concentrations had sulfate concentrations less than 5 mg/L; therefore, it was not possible to determine if the redox conditions were methanogenic. However, the same two wells were resampled for analysis of arsenic speciation at the NWQL, where the reporting limit for sulfate was 0.09 mg/L; so sulfate concentrations from the NWQL were substituted into the primary dataset for two wells with arsenic concentrations of about 44 µg/L. One of the samples had a sulfate concentration of less than 0.09 mg/L and was classified as methanogenic. The second sample had a sulfate concentration of 4.45 mg/L and was classified as iron- or sulfate-reducing; however, in the “Hydrogeologic Settings” section, this sample will be referred to as “near-methanogenic.”



Estimated redox conditions	Not strongly reducing			Strongly reducing	
	Oxic or suboxic	Nitrate reducing	Manganese reducing or mixed	Iron or sulfate reducing	Methanogenic
Number of samples ¹	7	10	7	76	1
Percentage of arsenic concentrations >10.0 µg/L	0	0	0	18	1 of 1
Arsenic concentrations, in µg/L	Median	<3	<3	3.7	--
	75th percentile	<3	<3	8.2	--
	Maximum	4.9	<3	43.6	43.8

¹Concentrations of nitrate, manganese, iron, and sulfate were known for 101 wells.

Figure 5. Arsenic concentrations in relation to redox conditions estimated from concentrations of iron, manganese, sulfate, and nitrate—Licking County, Ohio, 2012. [MCL, Maximum Contaminant Level]

Redox Conditions Estimated From Iron Concentrations

A simplified method for estimating redox conditions is to consider only iron concentrations. The EPA established a secondary MCL (SMCL) of 300 µg/L for iron because concentrations greater than that cause iron staining of plumbing and household fixtures (U.S. Environmental Protection Agency, 2009); therefore, 300 µg/L is used as the boundary between two simplified redox categories: “low iron” and “high iron.”

Iron concentrations, which were available for 102 wells, ranged from less than 80 µg/L (the minimum reporting level) to 6,560 µg/L, with a median of 767 µg/L. Most samples (71 percent) had high iron concentrations (fig. 6). Elevated arsenic concentrations were detected only in high-iron samples; however, not all high-iron samples had elevated arsenic concentrations. About 19 percent of samples with iron concentrations greater than 300 µg/L also had arsenic concentrations greater than 10.0 µg/L. Low concentrations of iron were detected in 29 percent of samples, none of which had elevated arsenic concentrations. The maximum arsenic concentration for a low-iron sample was 4.9 µg/L.

Comparison of Methods for Estimating Redox Conditions

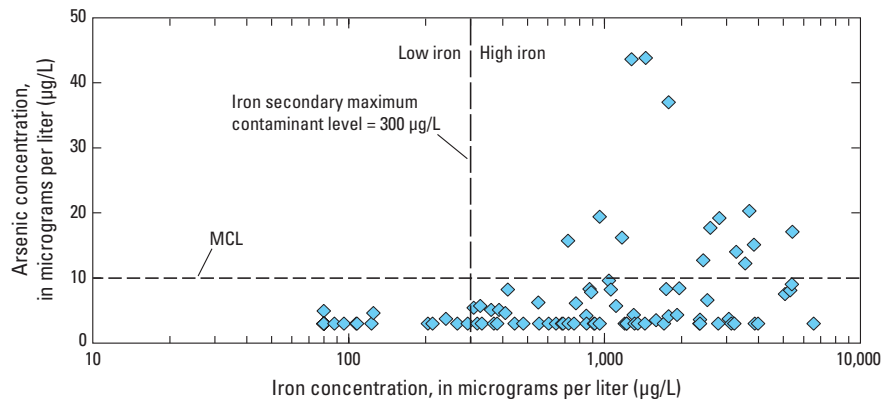
The two methods of estimating redox conditions led to similar conclusions: elevated arsenic concentrations were detected only in strongly reducing or high-iron samples; 18 percent of strongly reducing and 19 percent of high-iron samples had arsenic concentrations greater than 10.0 µg/L. In

contrast, not strongly reducing or low-iron samples had arsenic concentrations less than 4.9 µg/L.

An advantage to categorizing redox conditions using iron concentrations is the relatively wide applicability of the method. If a water analysis is not available, iron staining of household fixtures (by untreated water) can provide a visual clue that the water is strongly reducing and therefore, the arsenic concentration may be greater than the MCL of 10.0 µg/L. Based on data from the current study, elevated arsenic concentrations may exist in almost 1 in 5 wells (19 percent) that have iron concentrations high enough to cause staining.

A drawback to estimating redox conditions using only iron concentrations is that it is not possible to identify samples with mixed or methanogenic redox conditions. In general, mixed redox conditions are more likely to be detected in public-supply wells than domestic wells, which is because public-supply wells are often pumped at relatively high rates and (or) have relatively long screened or open intervals and are therefore more likely to produce water from multiple horizons that may have different redox conditions (Eberts and others, 2013).

An advantage of estimating redox using four water-quality constituents, instead of one, is that methanogenic redox conditions can be identified. Results of an arsenic study in southwestern Ohio indicated that the highest arsenic concentrations were associated with methanogenic groundwater (Thomas and others, 2005, 2008). The presence of methane in domestic wells can be a safety concern for homeowners because, if not properly vented, methane from groundwater could accumulate in confined spaces (wells or basements) and pose a risk of explosion or asphyxiation.



	Low iron ≤300 µg/L	High iron >300 µg/L
Number of samples ¹	30	72
Percentage with arsenic concentrations >10.0 µg/L	0	19
Arsenic concentrations, in µg/L	Median	<3
	75th percentile	<3
	Maximum	43.8

Figure 6. Arsenic concentrations in relation to redox conditions estimated from iron concentrations—Licking County, Ohio, 2012. [MCL, Maximum Contaminant Level]

¹Iron concentrations were known for 102 wells.

Aquifer and Well Characteristics From Well Logs

Well logs (drillers logs) include information about geology, well construction, and well yield. Of the 168 wells sampled for this study, 99 well logs were available from the ODNR Well Log Database (<http://soilandwater.ohiodnr.gov/search-file-well-logs>). In addition, the well depth and water level were available for one well that did not have a well log.

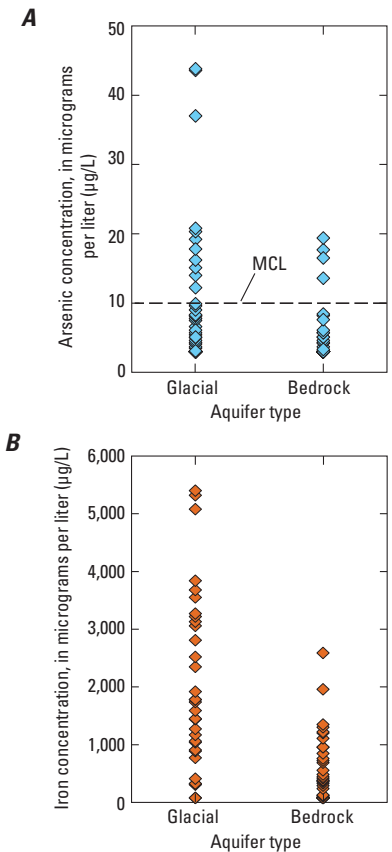
Aquifer Type

The type of aquifer tapped by the well was noted on 97 well logs. Forty-six wells tapped glacial deposits (referred to as glacial wells) and 51 wells tapped bedrock (bedrock wells). Two wells that tapped both aquifers are not included in the total. Elevated arsenic concentrations were detected in each aquifer type but were more prevalent in glacial aquifers than in bedrock aquifers (fig. 7A). Twenty-four percent of glacial wells had arsenic concentrations greater than 10.0 µg/L, as compared to 8 percent of bedrock wells. The maximum arsenic concentration for glacial wells was 43.8 µg/L, as compared

to 19.4 µg/L for bedrock wells. Results of the Kruskal-Wallis test indicated that the difference in arsenic concentrations was statistically significant (chi-square = 13.8478, *p* = 0.0002, *n* = 97).

Glacial and bedrock wells also differed in terms of iron concentrations (fig. 7B). Iron concentrations and aquifer type were available for 68 wells. High-iron waters were more prevalent in glacial wells (94 percent) than in bedrock wells (63 percent). The median iron concentration for glacial wells was four times higher than for bedrock wells, and results of the Kruskal-Wallis test indicate that the difference is statistically significant (chi-square = 20.4711, *p* < 0.0001, *n* = 68). The difference in iron concentrations (and redox conditions) is likely due to the presence of more labile organic carbon in the younger glacial deposits than in the older Paleozoic bedrock. Organic carbon acts as an electron donor in the redox-related processes that mobilize arsenic from iron oxyhydroxides.

Some well logs also included information about the type of bedrock tapped by the well. Bedrock lithology (shale, sandstone, sandstone and shale, or other) was indicated on 48 well logs. The relation between arsenic concentrations and bedrock lithology will be discussed in the “Bedrock Geology” section of this report.



	Arsenic	
	Glacial	Bedrock
Number of samples ¹	46	51
Percentage with arsenic concentrations >10.0 µg/L	24	8
Arsenic concentrations, in µg/L	Median	5.2
	75th percentile	9.9
	Maximum	43.8

¹Aquifer type was known for 97 wells.

	Iron	
	Glacial	Bedrock
Number of samples ²	33	35
Percentage with iron concentrations >300 µg/L	94	63
Iron concentrations, in µg/L	Median	1,760
	75th percentile	3,130
	Maximum	5,400

²Aquifer type and iron concentrations were known for 68 wells.

Figure 7. Comparison of glacial and bedrock aquifers, Licking County, Ohio, 2012. A, Arsenic concentrations. B, Iron concentrations. [MCL, Maximum Contaminant Level]

Well Characteristics

Well logs include information about well construction and well yield, including well depth, water level, top of the open interval, length of the open interval, date of construction, and results of aquifer tests (pump rate, drawdown of the water level, and duration of the test), which can be used to calculate specific capacity—a rough indicator of well yield. Summary statistics for 10 well characteristics were computed for glacial

and bedrock wells (table 9). In addition, the Spearman's rho test was used to investigate whether any of the variables were correlated with arsenic concentrations. For bedrock wells, two variables had statistically significant ($p < 0.05$) relations to arsenic concentrations: (1) the length of the open interval, and (2) the top of the open interval above/below the water level. Since these relations are only relevant to bedrock wells, they will be discussed in the "Bedrock Geology" section of this report.

Table 9. Well-log variables, summary statistics, and results of a statistical test for correlation with arsenic concentrations in groundwater, Licking County, Ohio, 2012.

[**Bold** text indicates that correlation with arsenic concentration is statistically significant based on the p -value < 0.05 ; <, less than; ft, foot; gpm/ft, gallon per minute per foot of drawdown]

Aquifer type	Number of wells	Range	Median	Result of Spearman's rho test for correlation with arsenic concentration	
				Spearman's correlation coefficient	p -value
Well depth, ft below land surface					
Glacial	46	42–327	115	0.06208	0.6819
Bedrock	51	37–400	160	-0.06584	0.6462
Water level, ft below land surface					
Glacial	46	1–155	44	0.13670	0.3650
Bedrock	49	1–200	65	-0.07527	0.6072
Top of open interval, ft below land surface					
Glacial	43	39–311	107	0.14916	0.3398
Bedrock	50	25–255	100	0.13383	0.3542
Top of open interval, ft below water level					
Glacial	43	-20–197	53	0.06274	0.6894
Bedrock	49	-58–128	30	0.36383	0.0102
Length of open interval, ft					
Glacial	43	<1–48	3	-0.27033	0.0796
Bedrock	50	<1–293	41	-0.32972	0.0194
Date of construction, year					
Glacial	45	1956–2012	1994	-0.00743	0.9587
Bedrock	51	1957–2012	1998	-0.26620	0.0771
Pump rate, gallons per minute					
Glacial	45	5–50	12	-0.05303	0.7294
Bedrock	48	4–45	15	-0.22307	0.1275
Drawdown, ft					
Glacial	39	<1–150	10	0.20648	0.2073
Bedrock	43	<1–175	20	0.18630	0.2316
Test duration, hours					
Glacial	40	1–22	2	-0.14398	0.3754
Bedrock	47	0–24	1	0.12679	0.3958
Specific capacity ¹ , gpm/ft					
Glacial	39	0.05–300	1	-0.22243	0.1735
Bedrock	43	0.08–200	1.05	-0.25803	0.0948

¹Computed as pump rate/drawdown.

Hydrogeologic Characteristics of Licking County

In this section of the report, the spatial distribution of arsenic concentrations is compared to hydrogeologic characteristics of Licking County, including topography, thickness and lithology of glacial deposits, hydrogeologic settings, and bedrock geology (Ohio Department of Natural Resources, [n.d.]).

Topography

The topography of Licking County was presented in a generalized form by Ohio Department of Natural Resources

(1995). Land surface slopes of less than 6 percent are relatively widespread in the west, where a thick layer of glacial deposits overlies the bedrock surface. In the east, low slopes are generally limited to stream valleys; in upland areas, where glacial deposits are thin or absent, slopes can be more than 18 percent. In Licking County, elevated arsenic concentrations roughly correspond to areas of low topographic relief (fig. 8). Topographic relief is one of the primary drivers of subsurface groundwater flow, and flat topography is often associated with low hydraulic gradients and sluggish rates of groundwater flow.

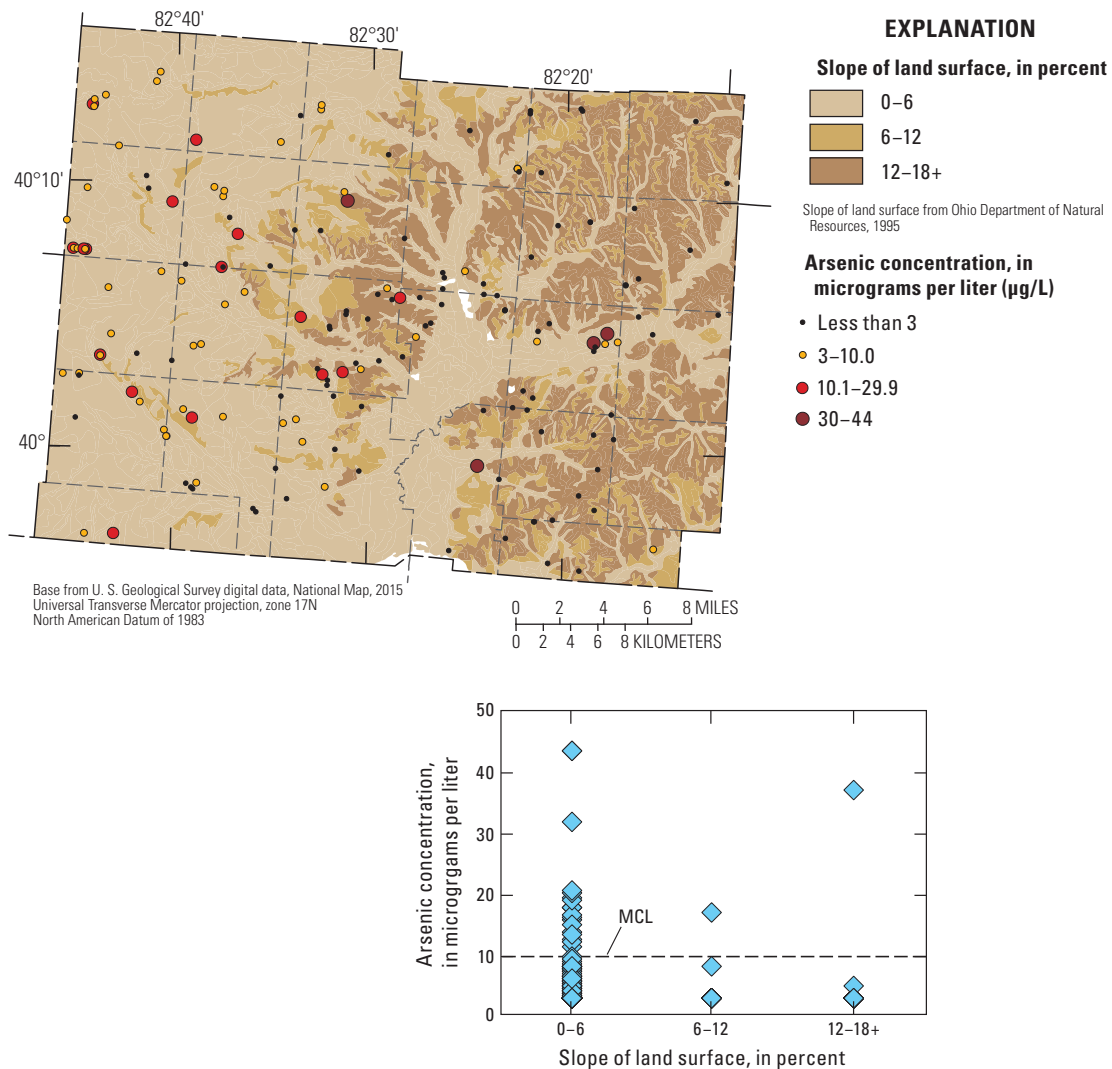


Figure 8. Distribution of arsenic concentrations in Licking County, Ohio (2012) in relation to topography. [MCL, Maximum Contaminant Level]

Lithology of Glacial Deposits

Glacial deposits of Licking County can be grouped into three general categories: fines (predominantly clay or silt with lenses of sand and gravel), till (unsorted mixture of clay, silt, sand, and gravel with or without lenses of sand and gravel), and sand and gravel (predominantly sand and gravel with minor fines) (Ohio Department of Natural Resources, 2000).

In Licking County, elevated arsenic concentrations were associated with till or fines (fig. 9). In general, till and fines are clay-rich deposits that are often associated with low rates of groundwater recharge and (or) flow.

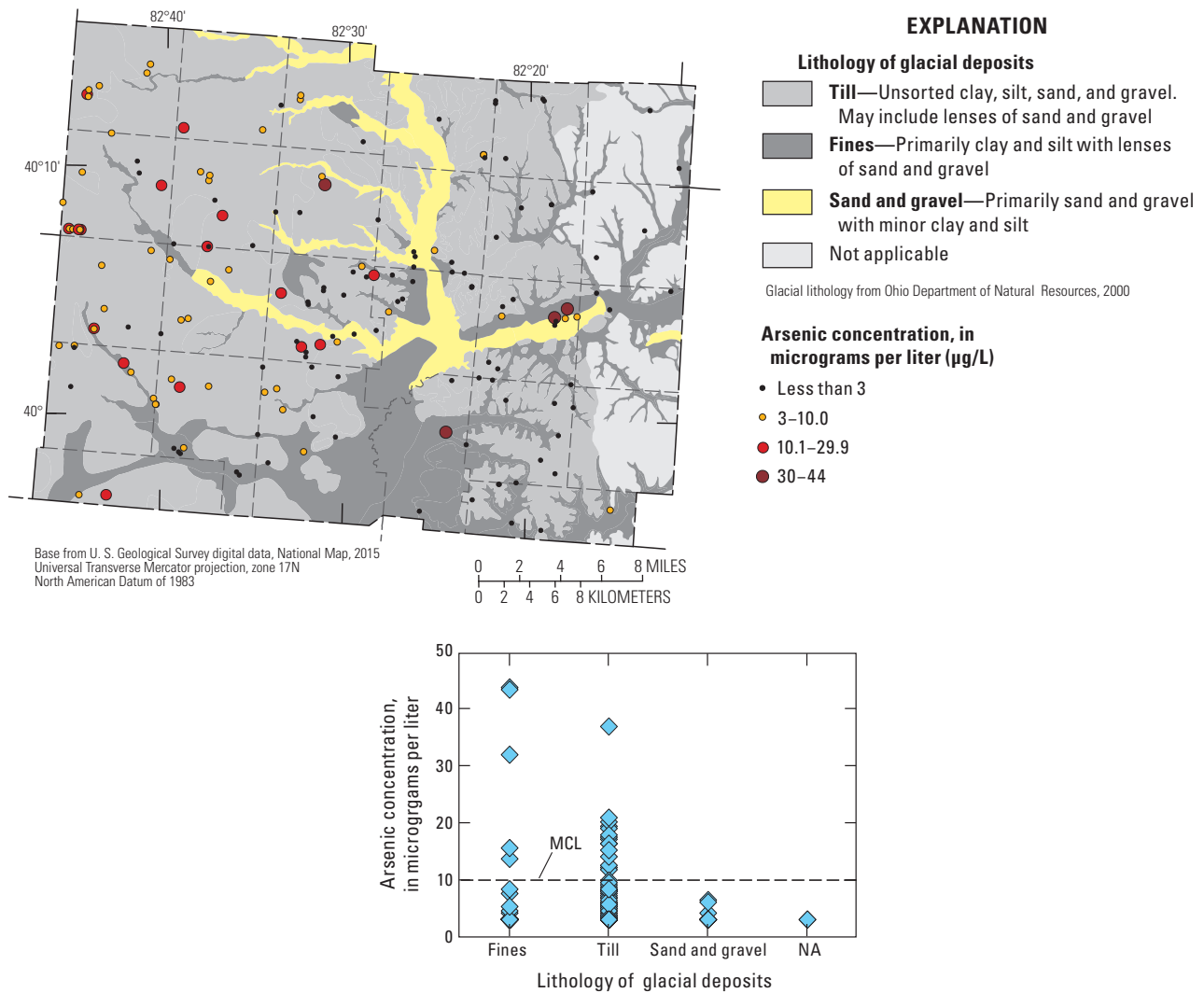


Figure 9. Distribution of arsenic concentrations in Licking County, Ohio (2012) in relation to lithology of glacial deposits. [NA, glacial deposits are thin or absent; MCL, Maximum Contaminant Level]

Drift Thickness

Drift thickness refers to the thickness of the layer of glacial deposits overlying bedrock. In Licking County, drift thickness varies from 0 to 596 ft (Ohio Department of Natural Resources, Division of Geological Survey, 2004). As shown on the generalized map of figure 10, thick glacial deposits are widespread in the western part of the county but are limited to buried valleys in the east. In Licking County, elevated arsenic concentrations generally correspond to areas where glacial deposits are thicker than 100 ft.

The hydrogeologic characteristics associated with elevated arsenic concentrations—low topographic relief (fig. 8) and a thick layer of low-permeability glacial deposits (figs. 9 and 10)—are more prevalent in the western part of Licking County, which is within the Central Lowland physiographic province (figs. 1 and 2). These characteristics are generally conducive to the development of reducing groundwater. The redox condition of groundwater is a balance between the

supply of dissolved oxygen (and other electron acceptors) as compared to the supply of organic carbon (and other electron donors). In general, a thick layer of low-permeability glacial deposits promotes reducing conditions in the subsurface by (1) retarding the movement of dissolved oxygen from the land surface to the aquifer, and (2) providing a source of organic carbon, which serves as an electron donor in redox reactions. If redox conditions become sufficiently reducing, arsenic can be released from iron oxyhydroxides in the aquifer matrix to the groundwater. In addition, a low-relief and low-permeability land surface is conducive to low rates of recharge and sluggish rates of groundwater flow. The observations from Licking County are generally consistent with the conceptual model of Smedley and Kinniburgh (2002), which states that high concentrations of arsenic can develop where (1) the onset of reducing conditions causes arsenic to be mobilized from the aquifer matrix, and (2) low rates of groundwater flushing allow the released arsenic to accumulate in the aquifer.

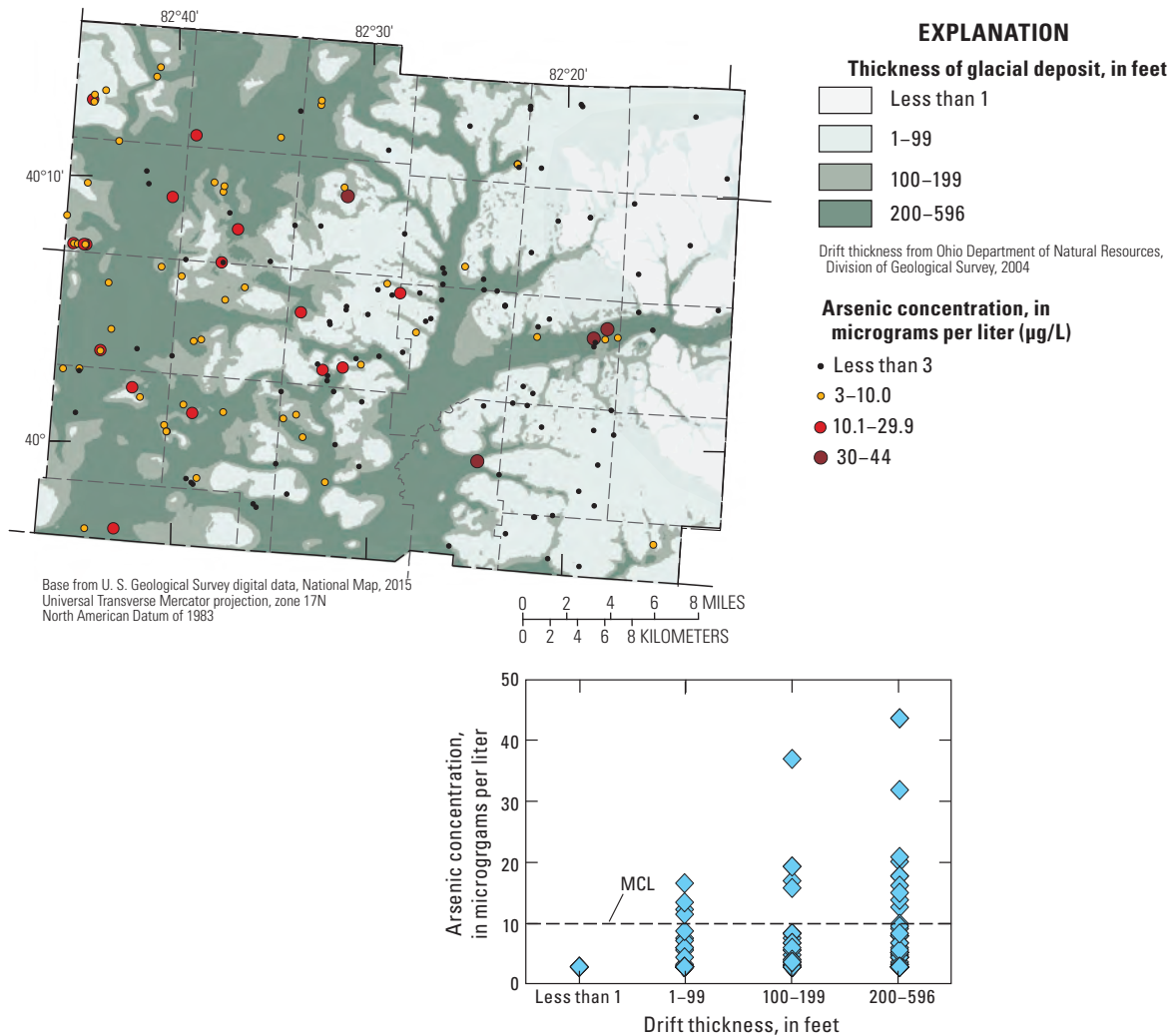


Figure 10. Distribution of arsenic concentrations in Licking County, Ohio (2012) in relation to drift thickness. [MCL, Maximum Contaminant Level]

Hydrogeologic Settings

Unconsolidated glacial deposits of Ohio have been mapped as 10 hydrogeologic settings, 5 of which are present over substantial areas of Licking County: buried valley, complex thick drift, ground moraine, thin upland, and alluvial (fig. 3C) (Ohio Department of Natural Resources, 2000). Elevated arsenic concentrations are generally associated with two of the hydrogeologic settings—buried valley and complex thick drift (fig. 11A). Buried-valley settings are present in previously existing bedrock valleys; streams overlie some, but not all, buried valleys. Complex-thick-drift settings may consist of a combination of hydrogeologic settings, such as end moraine overlying a buried valley. Both settings are characterized by (1) predominantly low-permeability sediment (fines and till) that may contain lenses of sand and gravel, and (2) drift thickness greater than 100 ft. Because the buried-valley and complex-thick-drift hydrogeologic settings are both partly defined on the basis of drift thickness, the extent of drift thicker than 100 ft (fig. 10) is somewhat similar to the combined extent of the two hydrogeologic settings (fig. 11A).

Even though elevated arsenic concentrations are associated with buried-valley and complex-thick-drift settings, the statistical distribution of arsenic concentrations differs between the two settings. Arsenic concentrations measured in wells in relation to the hydrogeologic setting extracted from the GIS coverage are shown in figure 11B. In buried-valley settings, most arsenic concentrations are low (less than 3 µg/L), but a few samples have very high concentrations (30–44 µg/L). For the complex-thick-drift setting, elevated arsenic concentrations were more prevalent, but all concentrations were less than 21 µg/L.

Two samples with elevated arsenic concentrations are associated with the ground moraine hydrogeologic setting, rather than the buried-valley or complex-thick-drift setting (figs. 11A and 11B). Ground moraine is defined as primarily till that is 25–100 ft thick (Ohio Department of Natural Resources, 2000); however, well logs for these two wells indicate that the glacial deposits are 121 and 131 ft thick and therefore meet the definition of buried-valley or complex-thick-drift settings.

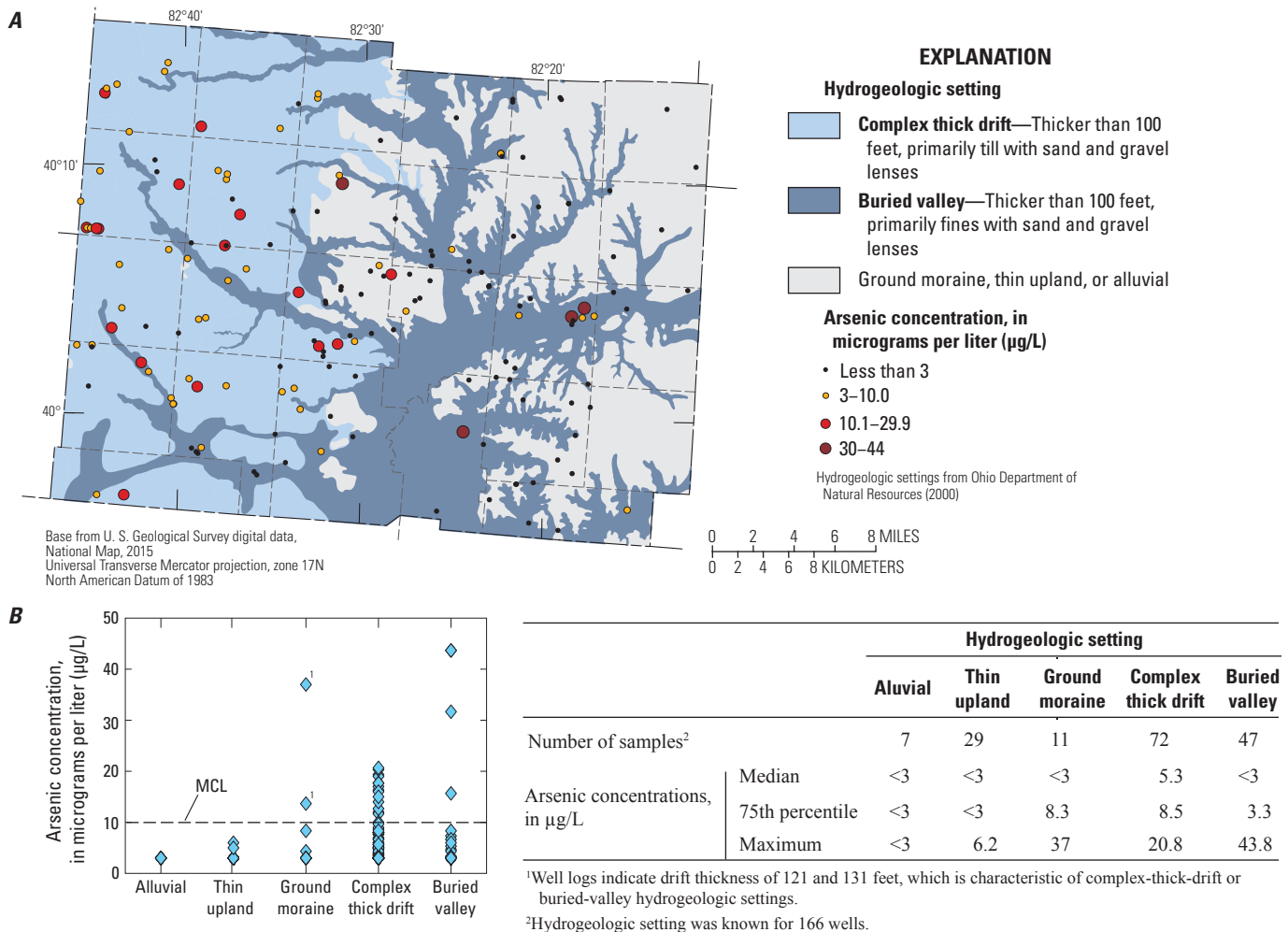


Figure 11. Arsenic concentrations in relation to hydrogeologic settings of Licking County, Ohio, 2012. A, Spatial relations (see fig. 3 for more detailed map and definitions of hydrogeologic settings). B, Statistical relations. [MCL, Maximum Contaminant Level]

The data from figure 11 are subdivided by aquifer type on figure 12. Even though hydrogeologic settings are defined by characteristics of the glacial deposits, relations between arsenic concentrations and hydrogeologic settings are relatively similar for glacial aquifers (fig. 12A), bedrock aquifers

(fig. 12B), and for wells for which the aquifer type is unknown because no well log was available (fig. 12C). This similarity may indicate that arsenic concentrations in bedrock aquifers are at least partly related to characteristics of the overlying glacial deposits.

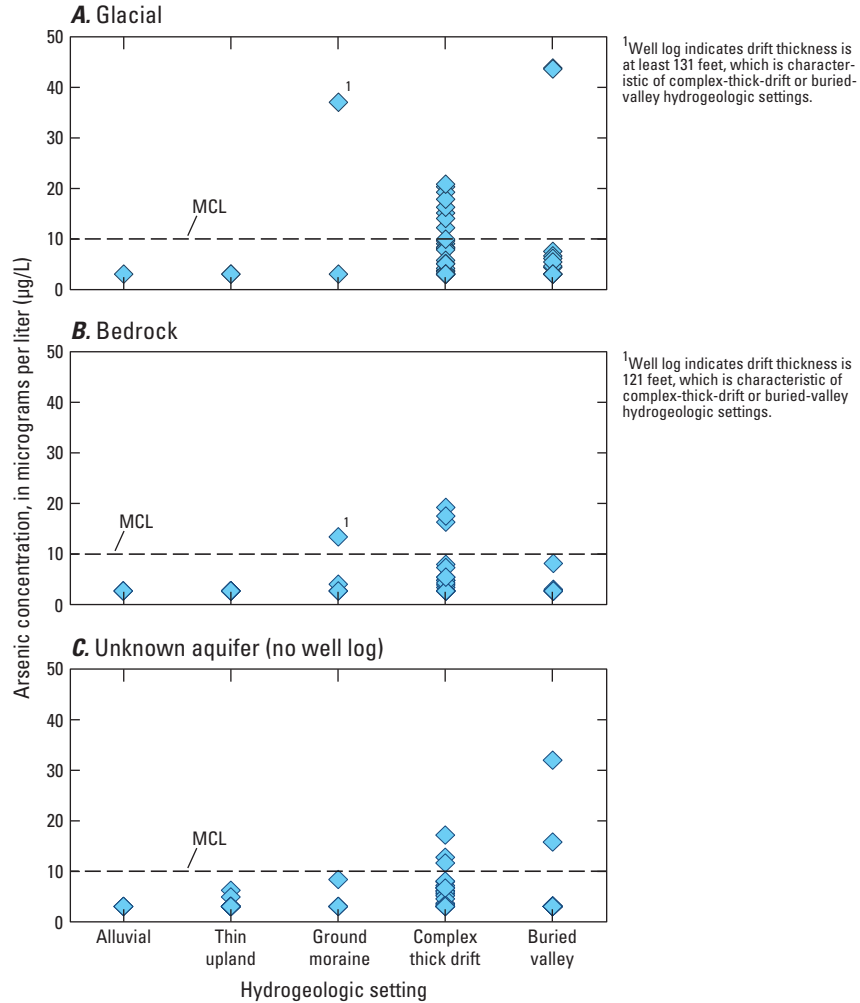


Figure 12. Arsenic concentrations in relation to hydrogeologic settings, Licking County, Ohio, 2012. A, Glacial wells. B, Bedrock wells. C, Unknown-aquifer wells. [MCL, Maximum Contaminant Level]

In Licking County, elevated concentrations of arsenic were generally more prevalent in glacial wells than in bedrock wells. Glacial aquifers can have widely varying hydrogeologic characteristics, and arsenic is more prevalent in some types of glacial deposits than in others.



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The redox conditions of samples associated with the hydrogeologic settings are shown on figure 13. All samples from the complex-thick-drift setting are classified as iron- or sulfate-reducing (fig. 13A). Redox conditions in the buried-valley setting are more varied, and the highest arsenic concentrations were associated with methanogenic (or near-methanogenic) redox conditions. These observations are similar

to observations from arsenic studies in southwestern Ohio (Thomas and others, 2005; Thomas and others, 2008). It is interesting to note that samples associated with complex-thick-drift and buried-valley hydrogeologic settings have relatively similar iron concentrations (fig. 13B) but very different sulfate concentrations (fig. 13C).

A

	Alluvial	Thin upland	Ground moraine	Complex thick drift	Buried valley
Number of samples ¹	6	17	9	36	33
Redox classification (percent)					
Not strongly reducing	33	59	33	0	27
Iron or sulfate reducing	67	41	67	100	67
Methanogenic or near-methanogenic	0	0	0	0	6

¹Hydrogeologic setting and iron or sulfate concentrations were known for 101 wells.

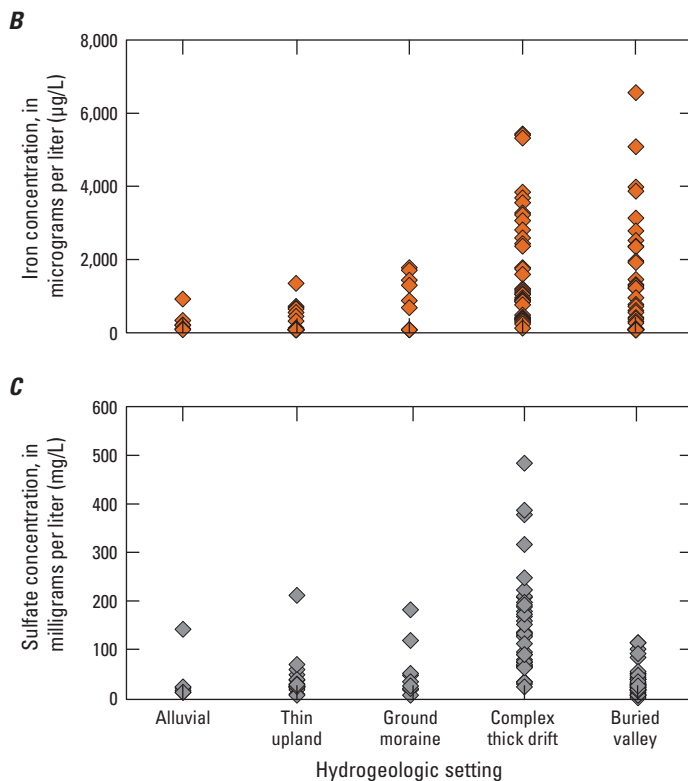


Figure 13. Redox conditions in hydrogeologic settings, Licking County, Ohio, 2012. *A*, Redox conditions estimated by using nitrate, manganese, iron, and sulfate concentrations. *B*, Iron concentrations. *C*, Sulfate concentrations.

In Licking County, the two wells with the highest arsenic concentrations (43.6 and 43.8 $\mu\text{g/L}$) were associated with the buried-valley setting in the east-central part of the county (fig. 11A). For one well, the redox condition was estimated to be methanogenic. For the second well, the redox condition was estimated to be “near-methanogenic” (as discussed in the “Estimation of Redox Conditions From Concentrations of Iron, Manganese, Sulfate, and Nitrate” section). A third well that taps buried-valley deposits less than 2 miles to the northeast produces water with methanogenic redox conditions and an average arsenic concentration of 69 $\mu\text{g/L}$. This well was not sampled as part of the current study (and is not shown on fig. 9), but it was the site of an EPA pilot study of arsenic-removal methods for use in small public-water systems (U.S. Environmental Protection Agency, 2011).

These three wells, with arsenic concentrations of 44–69 $\mu\text{g/L}$ and methanogenic or near-methanogenic redox conditions, are in an area of predominantly fine-grained glacial deposits in the buried valley between the municipalities of Newark and Hanover (figs. 1 and 11A). The glacial geology of this area was studied in detail to gain insight into the processes that led to Pleistocene drainage reversals (Frolking and Pachell, 2006). During the Late Wisconsinan, a west-flowing tributary of the Teays River system was blocked by glacial ice advancing from the northeast, which caused ponding of the river water and led to deposition of a thick layer of dense, laminated lakebed (lacustrine) silt. The Late Wisconsinan lacustrine silt overlies Illinoian sand and gravel deposits.

It is possible that this type of setting may be especially conducive to arsenic mobilization. The layer of laminated lacustrine silt would presumably be conducive to the development of reducing conditions in an underlying aquifer by inhibiting recharge of oxygenated water. In addition, lacustrine sediment is typically rich in organic matter, which serves as an electron donor in redox reactions that mobilize arsenic. The underlying deposits—Illinoian sand and gravel—may be rich in iron oxyhydroxides (and associated arsenic) as a result of weathering during the interglacial period. This idea is

generally consistent with observations from a study in southwestern Ohio, where the highest solid-phase concentrations of arsenic, iron, and other metals in glacial sediments were in paleosols near the boundary of Illinoian and Wisconsinan deposits (Thomas and others, 2008).

In Licking County, the boundary between Wisconsinan lacustrine deposits (presumably rich in organic carbon) and weathered Illinoian paleosol (presumably rich in iron oxyhydroxides and associated arsenic) may have geochemical conditions favorable for arsenic mobilization. A water well that taps that particular horizon may be vulnerable to contamination from naturally occurring arsenic; however, this hypothesis needs to be tested.

Bedrock Geology

Bedrock in Licking County is a complex mix of interbedded shales, sandstones, siltstones, and limestones of Devonian to Pennsylvanian age (Slucher and others, 2006). The spatial distribution of arsenic concentrations in bedrock wells is shown in figure 14. Four of the 51 bedrock wells had elevated arsenic concentrations, and all are in the subcrop of the Cuyahoga and Logan Formations in western Licking County. The western part of the county is also where topography and glacial characteristics are conducive to arsenic mobilization, as discussed in the “Topography, Lithology of Glacial Deposits, and Drift Thickness” section. Therefore, it is difficult to determine if higher arsenic concentrations in bedrock wells are related to the composition of the bedrock, the characteristics of the overlying glacial deposits, or both. The relations illustrated in figure 12B—higher arsenic concentrations in bedrock wells overlain by complex-thick-drift and buried-valley settings—may indicate that a thick (greater than 100 ft) layer of till or fines could be conducive to development of reducing conditions, and mobilization of arsenic, in the underlying bedrock. This idea may warrant further investigation in future studies.

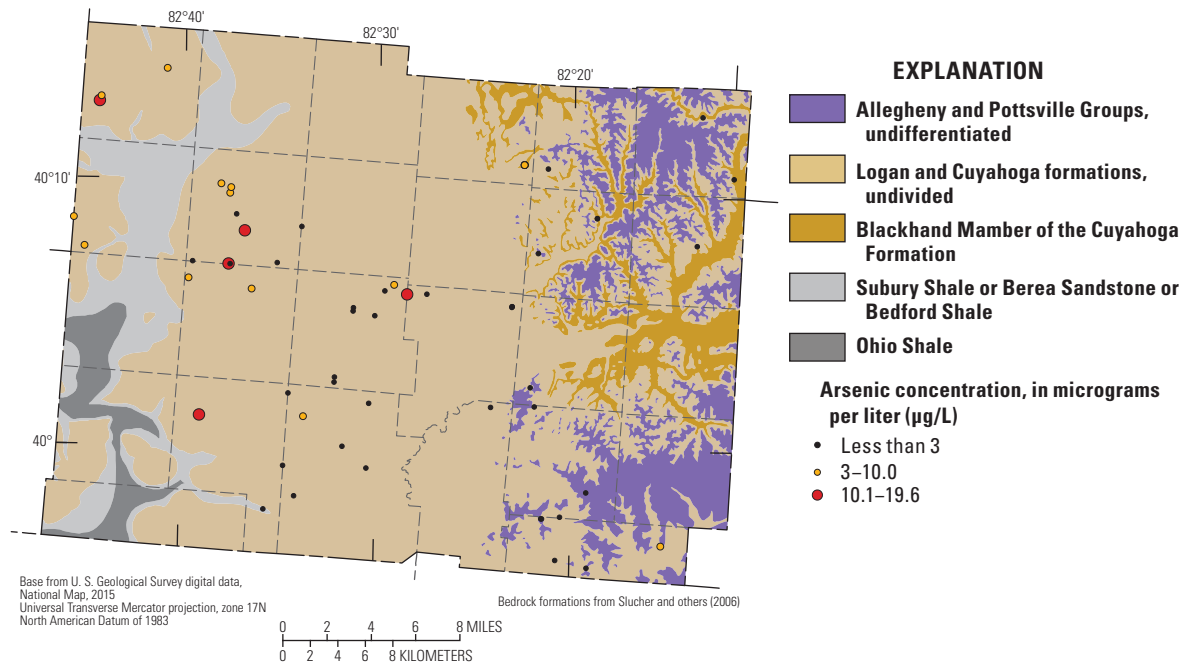
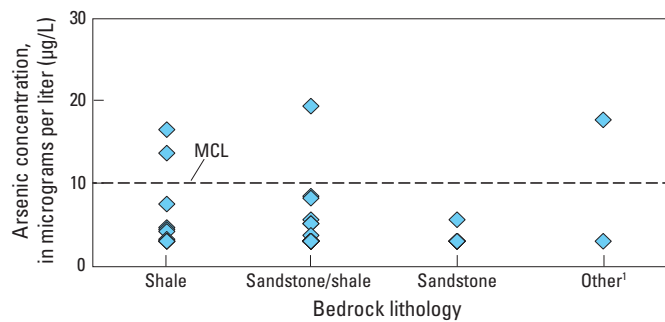


Figure 14. Distribution of arsenic concentrations in bedrock wells in relation to bedrock formations, Licking County, Ohio, 2012.

Bedrock Lithology

Information about bedrock lithology was available from 48 well logs. Bedrock wells were subdivided into four groups: shale, sandstone and shale, sandstone, and other. Arsenic concentrations in sandstone wells were generally lower than in the other categories (fig. 15); however, results of the Kruskal-Wallis test indicate that differences in median concentrations among the groups are not statistically significant (chi-square = 6.5552; $p = 0.0875$; $n = 48$).



	Bedrock lithology			
	Shale	Sandstone/ shale	Sandstone	Other ¹
Number of samples ²	11	25	10	2
Percentage with arsenic concentrations >10.0 µg/L	18	4	0	50
Arsenic concentrations, in µg/L	Median	<3	<3	-
	75th percentile	7.6	3.7	<3
	Maximum	16.5	19.4	5.7

¹Includes sandstone/shale/limestone and blue rock.

Figure 15. Relation between arsenic concentrations and bedrock lithology from well logs, Licking County, Ohio, 2012. [MCL, Maximum Contaminant Level]

Well Construction Characteristics of Bedrock Wells

As discussed in the “Well Characteristics” section, arsenic concentrations in bedrock wells were correlated with two well-construction characteristics compiled from well logs (table 9).

Length of open interval.—The term “open interval” is used to refer to a well screen or an uncased section of the borehole. The length of the open interval was estimated by subtracting the top of the open interval (or the bottom of the casing) from the bottom of the open interval (or the bottom of the well). For bedrock wells, open intervals ranged from <1 to 293 ft, with a median of 41 ft (fig. 16A; table 9). Results of the Spearman’s rho test indicate that the length of the open interval was negatively correlated with arsenic concentrations (Spearman’s correlation coefficient = -0.32972; *p*-value = 0.0194; *n* = 50). A negative correlation coefficient indicates shorter open intervals were associated with higher arsenic concentrations. Elevated arsenic concentrations were detected only in bedrock wells with open intervals less than 40 ft long.

For glacial wells, open intervals ranged from <1 to 48 ft, with a median of 3 ft (table 9). Elevated arsenic concentrations were detected only in glacial wells with open intervals <10 ft, and the correlation coefficient was negative, but the correlation with arsenic concentrations was not statistically significant (Spearman’s correlation coefficient = -0.27033; *p*-value = 0.0796; *n* = 43).

Long open intervals can allow mixing of water from multiple parts of an aquifer that have different water-quality characteristics (Eberts and others, 2013). The correlation of longer open intervals with lower arsenic concentrations is consistent with the idea that high-arsenic water is from a relatively thin horizon of the aquifer. If this were true, a long open interval could allow high-arsenic water from a thin horizon to be diluted by inflow of low-arsenic water from other parts of the aquifer. The idea that high-arsenic water may originate in a thin horizon of the aquifer is consistent with observations from a study in southwestern Ohio (Thomas and others, 2008). Solid-phase analysis of samples from a 100-ft core of carbonate bedrock indicated that, with one exception, all bedrock samples had very low concentrations of arsenic (less than or equal to 2 milligrams per kilogram [mg/kg]). The only exception was a sample from a thin (less than 5 ft) horizon, just below glacial/bedrock boundary, where the arsenic concentration was 42 mg/kg. The same horizon was also rich in iron and other metals.

Top of open interval below/above the water level.—The depth to the top of the open interval, relative to the water level, was computed by subtracting the water level (in feet below land surface) from the top of the open interval (in feet below land surface). This variable was correlated with arsenic concentrations for bedrock wells only (Spearman’s correlation coefficient = 0.36382; *p*-value = 0.0102; *n* = 49) (fig. 16B and table 9). The positive correlation coefficient indicates that higher arsenic concentrations in bedrock wells are generally associated with greater depths (relative to the water level); however, it is interesting to note that one of the four bedrock wells with elevated arsenic concentrations (16.5 µg/L) was from a very shallow (40 ft) shale well and the top of the open interval was only 21 ft below the water level. Additional water-quality data are not available for this well, so redox conditions are unknown. Additional studies may be warranted to investigate whether well construction characteristics can affect the concentration of arsenic in the produced water.

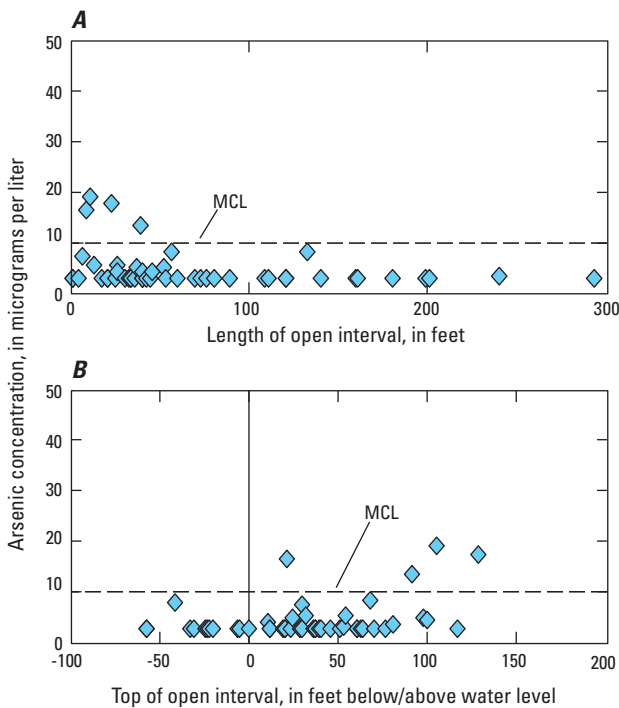


Figure 16. Arsenic concentrations in bedrock wells in relation to well-construction characteristics, Licking County, Ohio, 2012. *A*, Length of the open interval. *B*, Top of the open interval, in feet above/below water level. Summary statistics and results of Spearman’s rho test are shown in table 6. [MCL, Maximum Contaminant Level]



One aspect of well construction is determining which part of groundwater system is tapped to produce water. Different parts of the groundwater system can have different chemical characteristics, so well construction/design can sometimes have an effect on the quality of the water produced from a well (Eberts and others, 2013).

Preliminary Extrapolation of Results From Licking County to Other Parts of Ohio

In Licking County, elevated arsenic concentrations were detected in areas where glacial deposits are thicker than 100 ft (fig. 10) and in buried-valley or complex-thick-drift hydrogeologic settings (fig. 11). Similar hydrogeologic characteristics exist in other parts of Ohio, and it is possible that

groundwater in these areas also has elevated arsenic concentrations (greater than the MCL of 10.0 µg/L).

The statewide distribution of hydrogeologic characteristics associated with elevated arsenic concentrations in groundwater of Licking County is shown in figure 17A: (1) buried-valley and complex-thick-drift hydrogeologic settings, and (2) drift thickness greater than 100 ft. The combined extent of these characteristics, shown in figure 17B, can be considered an initial estimate of areas where groundwater may be vulnerable to contamination by natural sources of arsenic.

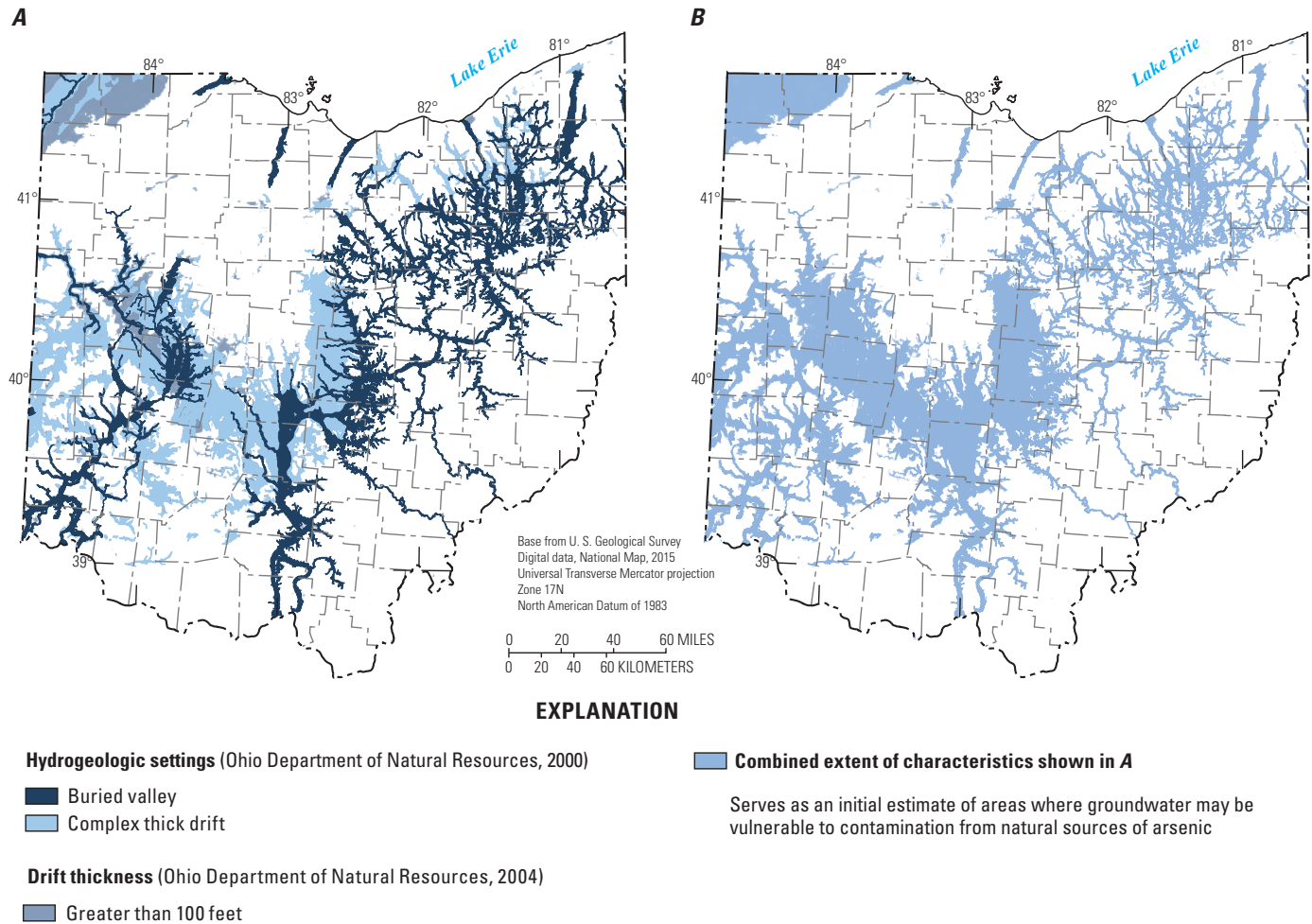


Figure 17. Preliminary extrapolation of results from Licking County, Ohio, 2012. *A*, Characteristics associated with elevated arsenic concentrations (greater than 10.0 micrograms per liter) in groundwater of Licking County, Ohio, 2012. *B*, Combined extent of the characteristics shown in *A*. *C*, Approximate location of targeted arsenic investigations in domestic wells. *D*, Arsenic concentrations in public-supply wells of the Ohio Environmental Protection Agency ambient groundwater network, measured in 2013.

As an initial test of this hypothesis, the extent of the potentially vulnerable areas was compared to the location of known elevated arsenic concentrations. Figure 17C shows the approximate location of the targeted arsenic investigations discussed in the “Previous Studies” section. These studies were done in areas where elevated arsenic concentrations in domestic wells were interpreted to be from natural sources. Figure 17D shows arsenic concentrations in public-supply

wells sampled during 2013 as part of the Ohio EPA ambient groundwater program (Ohio Environmental Protection Agency, 2013). For both maps, there is a relatively good spatial correspondence between detections of elevated arsenic concentrations and the potentially vulnerable areas. This preliminary conceptual model can be tested and refined as additional wells are sampled for arsenic and other water-quality constituents.

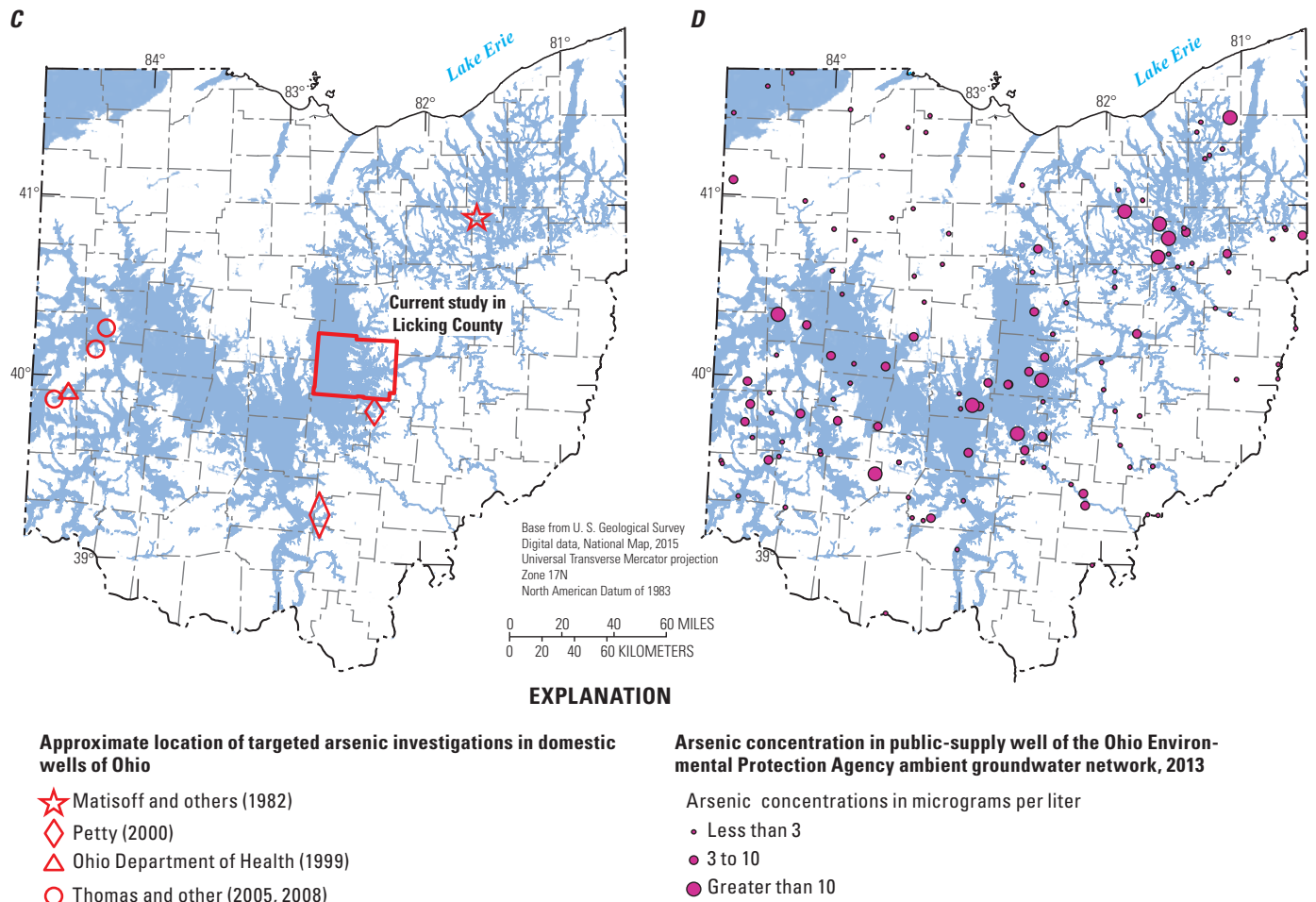


Figure 17. Preliminary extrapolation of results from Licking County, Ohio, 2012. A, Characteristics associated with elevated arsenic concentrations (greater than 10.0 micrograms per liter) in groundwater of Licking County, Ohio, 2012. B, Combined extent of the characteristics shown in A. C, Approximate location of targeted arsenic investigations in domestic wells. D, Arsenic concentrations in public-supply wells of the Ohio Environmental Protection Agency ambient groundwater network, measured in 2013.—Continued

Summary

Rocks and sediments of the aquifer matrix often include minor amounts of arsenic, which can be released to the groundwater under certain geochemical conditions. In groundwater of Ohio and other parts of the Midwest, evidence indicates that arsenic associated with metal oxyhydroxides is mobilized in groundwater with strongly reducing redox conditions and circumneutral to slightly alkaline pH.

Consumption of drinking water with elevated arsenic concentrations (greater than 10.0 micrograms per liter [$\mu\text{g/L}$]) is linked to multiple cancers and other serious health problems, but most domestic wells are never tested for arsenic. Understanding which parts of the groundwater system are likely to have elevated arsenic concentrations would allow well testing and education about water treatment to be targeted to areas of greatest need.

During March–August of 2012, arsenic concentrations were measured in water samples from 168 domestic wells in Licking County, Ohio. Samples were collected by well owners and county sanitarians and were analyzed at a local private laboratory. Methods of sample collection and analysis probably introduced some variability/uncertainty into the water-quality dataset, but this was taken into account by grouping the data into broad concentration classes for analysis. Elevated arsenic concentrations (greater than 10.0 $\mu\text{g/L}$) were detected in 12 percent of the samples (about one in eight). The maximum concentration of about 44 $\mu\text{g/L}$ was detected in two wells in the same township.

In groundwater, arsenic occurs as two inorganic species—arsenite (As^{3+}) and arsenate (As^{5+}). Nine of the wells with elevated arsenic concentrations were resampled and analyzed for arsenic speciation at the U.S. Geological Survey National Water Quality Laboratory. Results indicated that As^{3+} was the predominant species. The percentage of arsenic in the nine samples ranged from 55–92 percent. Arsenite is generally considered to be more toxic to humans than As^{5+} . In addition, As^{3+} is more difficult to remove from water because it occurs as an uncharged species (whereas As^{5+} occurs as a negatively charged ion). Removing high concentrations of As^{3+} from drinking water can require multiple treatment steps.

A subset of 102 samples were also analyzed for concentrations of iron, manganese, sulfate, and nitrate, which were used to estimate redox conditions. Elevated arsenic concentrations were detected only in samples classified as “strongly reducing” or “high iron.” About 18 percent strongly reducing samples, and 19 percent of high-iron samples, had arsenic concentrations greater than 10.0 $\mu\text{g/L}$.

The water-quality data were analyzed in relation to aquifer and well-construction characteristics compiled from drillers logs, which were available for 99 wells. Wells in Licking County produce water from two types of aquifers—unconsolidated glacial deposits and the interbedded sandstone and shale bedrock. Elevated concentrations of arsenic were detected in both types of wells, but were more prevalent in glacial wells

(24 percent) than in bedrock wells (8 percent). The reason may be that the younger glacial deposits typically contain more organic carbon than the Paleozoic bedrock. Organic carbon acts as an electron donor in redox reactions that can mobilize arsenic (and iron) from oxyhydroxides in the aquifer matrix. Arsenic concentrations were not significantly different for different types of bedrock (sandstone, shale, sandstone/shale, or other).

The relation between arsenic concentrations and well characteristics was investigated for glacial and bedrock wells separately. Variables compiled from well logs included well depth, water level, length of the open interval, top of the open interval below the land surface, top of the open interval above or below the water level, date of construction, and aquifer-test variables (pump rate, drawdown of the water level, and duration of the test), which were used to calculate specific capacity—a rough indicator of well yield. Results of a non-parametric statistical test indicated that higher arsenic concentrations in bedrock wells were associated with (1) shorter open intervals and (2) deeper open intervals, relative to the water level. Additional study may be warranted to investigate the relation between well construction characteristics and the concentration of arsenic in the produced water.

The spatial distribution of the water-quality data was compared to hydrogeologic characteristics mapped by the Ohio Department of Natural Resources. Elevated concentrations of arsenic (and iron) were associated with low topographic relief and a thick (greater than 100 feet) layer of clay-rich glacial deposits. In general, these characteristics are conducive to the development of redox conditions that are sufficiently reducing to mobilize arsenic from iron oxyhydroxides in the aquifer matrix.

Hydrogeologic characteristics conducive to the development of strongly reducing conditions are relatively widespread in the western part of Licking County, which is part of the Central Lowland physiographic province. In this area, a thick layer of clay-rich glacial deposits obscures the bedrock surface and creates a flat to gently rolling landscape with poorly developed drainage networks. The eastern part of the county is in the Appalachian Plateaus physiographic province, where topographic relief is greater and much of the landscape consists of steep-sided valleys and bedrock uplands. In this area, elevated arsenic concentrations were detected in buried valleys but not in the bedrock uplands, where glacial deposits are thin or absent. The observation that elevated concentrations of arsenic (and iron) were more prevalent in the western part of Licking County is true for both glacial and bedrock aquifers.

In Licking County, thick, clay-rich glacial deposits (and elevated concentrations of arsenic) are associated with two hydrogeologic settings—buried valley and complex thick drift. In the complex-thick-drift hydrogeologic setting, all samples were strongly reducing, 18 percent had elevated arsenic concentrations, and the maximum arsenic concentration was about 21 $\mu\text{g/L}$. In the buried-valley hydrogeologic setting, wells had a wide range of arsenic concentrations; most were <10.0 $\mu\text{g/L}$, but a few samples had very high arsenic

concentrations (30–44 µg/L) and very reducing conditions (methanogenic or near-methanogenic). The two samples with the highest arsenic concentrations (44 µg/L) and the most reducing redox conditions (methanogenic and near-methanogenic) were detected in the glacial buried valley in the east-central part of the county, where a thick layer of dense, laminated Wisconsinan lakebed silt overlies Illinoian sand and gravel deposits.

The hydrogeologic settings and characteristics associated with arsenic in Licking County also exist in other parts of Ohio. The statewide extent of these characteristics roughly corresponds to areas where elevated concentrations of arsenic are known to exist. This preliminary conceptual model can be tested and revised as additional wells are sampled for arsenic.

References Cited

- Angle, M.P., 1995, Ground water pollution potential of Licking County: Ohio Department of Natural Resources, Division of Water, Ground Water Pollution Potential Report 31, 165 p.
- Breen, K.J., and Dumouchelle, D.H., 1991, Geohydrology and quality of water in aquifers in Lucas, Sandusky, and Wood Counties, northwestern Ohio: U.S. Geological Survey Water-Resources Investigations Report 91-4024, 234 p.
- Brenton, R.W., and Arnett, T.L., 1993, Methods of analysis by the U.S. Geological Survey National Water-Quality Laboratory—Determination of dissolved organic carbon by UV-promoted persulfate oxidation and infrared spectrometry: U.S. Geological Survey Open-File Report 92-480, 12 p.
- Dove, G.D., 1960, Water resources of Licking County, Ohio: Ohio Division of Water Bulletin 36, 96 p.
- Dumouchelle, D.H., 1998, Selected ground-water quality data of the Lockport Dolomite in Darke, Miami, Montgomery, and Preble Counties, Ohio: U.S. Geological Survey Open-File Report 98-655, 13 p.
- Eberts, S.M., Thomas, M.A., and Jagucki, M.L., 2013, The quality of our Nation's waters—Factors affecting public-supply-well vulnerability to contamination—Understanding observed water quality and anticipating future water quality: U.S. Geological Survey Circular 1385, 120 p. [Also available at <http://pubs.usgs.gov/circ/1385/>.]
- Fenneman, N.M., and Johnson, D.W., 1946, Physical divisions of the United States: U.S. Geological Survey, scale 1:7,000,000.
- Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water-Quality Laboratory—Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93-125, 217 p.
- Forsyth, J.L., 1966, Glacial map of Licking County, Ohio: Ohio Division of Geological Survey Report of Investigations 59, map (scale 1:62,500) with text.
- Frolking, T.A., and Pachell, M.A., 2006, Glacial Lake Licking—Late-glacial drainage diversion and the formation of Bland Hand Gorge, Licking County, Ohio: Ohio Journal of Science, v. 106, no. 3, p. 103–111.
- Frolking, T.A., and Szabo, J.P., 1998, Quaternary geology along the eastern margin of the Scioto Lobe in Central, Ohio: Ohio Department of Natural Resources, Division of Geological Survey, Guidebook 16, 40 p.
- Garbarino, J.R., Kanagy, L.K., and Cree, M.E., 2006, Determination of elements in natural-water, biota, sediment, and soil samples using collision/reaction cell inductively coupled plasma-mass spectrometry: U.S. Geological Survey Techniques and Methods, book 5, chap. B1, 88 p.
- Groundwater Foundation, 2007, Test your well, a manual for safe water tomorrow through pollution prevention today: The Groundwater Foundation, 80 p.
- Hartzell, G.W., 1982, Ground-water resources of Licking County: Ohio Department of Natural Resources, Division of Water, map (scale 1:62,500).
- International Agency for Research on Cancer (IARC), 2004, Summaries and evaluations—Arsenic in drinking-water (Group 1): Lyon, International Agency for Research on Cancer, IARC Monographs on the Evaluation of Carcinogenic Risk to Humans, v. 84, p. 39, accessed July 30, 2015, at <http://www.inchem.org/documents/iarc/vol84/84-01-arsenic.html>.
- Jagucki, M.L., Kula, S.P., and Mailot, B.E., 2015, Ground-water quality in Geauga County, Ohio—Status, including detection frequency of methane in water wells, 2009, and changes during 1978–2009: U.S. Geological Survey Scientific Investigations Report 2015-5032, 116 p. [Also available at <http://pubs.usgs.gov/sir/2015/5032/>.]
- Matisoff, Gerald, Khourey, C.J., Hall, J.F., Varnes, A.W., and Strain, W.H., 1982, The nature and source of arsenic in northeastern Ohio ground water: Ground Water, v. 20, no. 4, p. 446–456.
- Maupin, M.A., Kenny, J.F., Hutson, S.S., Lovelace, J.K., Barber, N.L., and Linsey, K.S., 2014, Estimated use of water in the United States in 2010: U.S. Geological Survey Circular 1405, 56 p. [Also available at <http://dx.doi.org/10.3133/cir1405>.]

- McMahon, P.B., 2001, Aquifer/aquitard interfaces—Mixing zones that enhance biogeochemical reactions: *Hydrogeology Journal*, v. 9, p. 34–43.
- McMahon, P.B., and Chapelle, F.H., 2008, Redox processes and water quality of selected principal aquifer systems: *Ground Water*, v. 46, no. 2, p. 259–271.
- Miami Conservancy District, 2011, A study of arsenic levels in private wells in the Great Miami River Basin: accessed May 20, 2011, at <http://www.miamiconservancy.org/water/documents/ArsenicLevelsIntheGMRWatershedstudy110324final.pdf>.
- Ohio Department of Health, 1999, Health Consultation No. 4, Lewisburg Drum Sites Lewisburg, Preble County, Ohio: CERCLIS no. OH0001954791, July 9, 1999, Prepared for the Agency for Toxic Substances and Disease Registry, 14 p.
- Ohio Department of Natural Resources, [n.d.], Statewide Aquifer Mapping Program: Ohio Department of Natural Resources, Division of Soil and Water Resources, accessed February 26, 2015, at <http://soilandwater.ohiodnr.gov/maps/statewide-aquifer-maps>.
- Ohio Department of Natural Resources, 1995, Ground water pollution potential—Licking County (Hydrologic category, theme ID 2797): accessed February 26, 2015, at <http://geospatial.ohiodnr.gov/data-metadata/search-by-category>.
- Ohio Department of Natural Resources, 2000, Unconsolidated aquifers of Ohio (Hydrologic category, theme ID 2101): accessed February 26, 2015, at <http://geospatial.ohiodnr.gov/data-metadata/search-by-category>.
- Ohio Department of Natural Resources, Division of Geological Survey, 2004, Shaded drift-thickness map of Ohio: Ohio Department of Natural Resources, Division of Geological Survey Map SG-3 2004, item no. CDRMSG3, scale 1:5,000,000.
- Ohio Environmental Protection Agency, [n.d.], Obtaining laboratory certification: accessed February 24, 2015, at <http://epa.ohio.gov/Portals/28/documents/labcert/Obtaining%20Laboratory%20Certification.pdf>.
- Ohio Environmental Protection Agency, 2000, 2000 305(B) Report, Ohio's ground water quality: Division of Drinking and Ground Waters, p. 33–37.
- Ohio Environmental Protection Agency, 2002, 2002 305(B) Report, Ohio's ground water quality: Division of Drinking and Ground Waters, p. 67–75.
- Ohio Environmental Protection Agency, 2010, An overview of groundwater quality in Ohio: Ohio 2010 Integrated Report, Section N, 15 p.
- Ohio Environmental Protection Agency, 2013, Inorganic ambient data—Arsenic: accessed April 2015 at <http://www.epa.ohio.gov/ddagw/gwqcp.aspx#115414902-access-data>.
- Petty, Rebecca, 2000, Investigation of arsenic in private water systems in Jackson, Vinton, and Perry Counties, Ohio [abs.], in 45th Annual Midwest Ground Water Conference, Columbus, Ohio: p. 64.
- Plant, J.A., Kinniburgh, D.G., Smedley, P.L., Fordyce, F.M., and Klinck, B.A., 2003, Arsenic and selenium, in Holland, H.D., and Turekian, K.K., eds., *Treatise on geochemistry*: Amsterdam, Elsevier, v. 9, p. 17–66.
- Reynolds, K.A., 2010, Evolving risk assessment of arsenic contamination in Groundwater: *Water Conditioning and Purification*, v. 52, no. 12, p. 60–62, accessed April 2013 at <http://archive.wcponline.com/pdf/December%20On%20Tap.pdf>.
- Siegrist, H., Ricker, K.T., and Brown, L.C., 1997, Water resources of Licking County: Ohio State University Extension Fact Sheet, AEX-480.45-97, 5 p.
- Shindel, H.S., Mangus, J.P., and Trimble, L.E., 2001, Water resources data, Ohio, water year 2002: U.S. Geological Survey Water-Data Report OH-00-2, 440 p.
- Slattery, M., Kenah, C., Slattery, L., and Musser, K., 2000, Occurrence and release of groundwater arsenic in public-water supply wells in Ohio [abs.], in 45th Annual Midwest Ground Water Conference, Columbus, Ohio: p. 63.
- Slucher, E.R., Swinford, E.M., Larsen, G.E., Schumacher, G.A., Shrake, D.L., Rice, C.L., Caudill, M.R., Rea, R.G., and Powers, D.M., 2006, Bedrock geologic map of Ohio: Ohio Division of Geological Survey Map BG-1, version 6.0, scale 1:500,000.
- Smedley, P.L., and Kinniburgh, D.G., 2002, A review of the source, behaviour, and distribution of arsenic in natural waters: *Applied Geochemistry*, v. 17, no. 5, p. 517–568.
- Thomas, M.A., 2003, Arsenic in midwestern glacial deposits—Occurrence and relation to selected hydrogeological and geochemical factors: U.S. Geological Survey Water-Resources Investigations Report 03-4228, 36 p. [Also available at <http://pubs.usgs.gov/wri/wri034228/>].
- Thomas, M.A., 2007, The association of arsenic with redox conditions, depth, and ground-water age in the glacial aquifer system of the Northern United States: U.S. Geological Survey Scientific Investigations Report 2007-5036, 26 p. [Also available at <http://pubs.usgs.gov/sir/2007/5036/>].

- Thomas, M.A., Diehl, S.F., Pletsch, B.A., Schumann, T.L., Pavey, R.R., and Swinford, E.M., 2008, Relation between solid-phase and dissolved arsenic in the ground-water system underlying northern Preble County, Ohio: U.S. Geological Survey Scientific Investigations Report 2008–5205, 56 p. [Also available at <http://pubs.usgs.gov/sir/2008/5205/>.]
- Thomas, M.A., Schumann, T.L., and Pletsch, B.A., 2005, Arsenic in ground water in selected parts of southwestern Ohio, 2002–03: U.S. Geological Survey Scientific Investigations Report 2005–5138, 30 p. [Also available at <http://pubs.usgs.gov/sir/2007/5036/>.]
- U.S. Census Bureau, 2012, Ohio—2010 Summary population and housing characteristics: CPH-1_37, 613 p., accessed June 2015 at <http://www.census.gov/prod/cen2010/cph-1-37.pdf>.
- U.S. Environmental Protection Agency, 2001, Fact sheet—Drinking water standard for arsenic: EPA 815-F-00-015, accessed February 26, 2015, at http://water.epa.gov/lawsregs/rulesregs/sdwa/arsenic/regulations_factsheet.cfm.
- U.S. Environmental Protection Agency, 2003, Arsenic treatment technology evaluation handbook for small systems: Office of Water, EPA 816-R-03-014, 126 p.
- U.S. Environmental Protection Agency, 2009, National Primary Drinking Water Regulations: 816-F-09-004, accessed February 26, 2015, at www.epa.gov/ogwdw000/consumer/pdf/mcl.pdf.
- U.S. Environmental Protection Agency, 2011, Arsenic removal by full-scale greensand system at Licking Valley High School, Letter report to Tom Sorg: Contract No. EP-C-05-057, Task Order No. 0004.
- U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1–A9, accessed January 23, 2007, at <http://pubs.er.usgs.gov/usgspubs/twri/twri09>.
- U.S. Geological Survey National Water-Quality Laboratory, 2015, Current and historical detection and reporting level information for parameter codes matching ‘01000’: accessed April 10, 2015, at <http://nwql.cr.usgs.gov/usgs/ltmdl/ltmdl.cfm?st=p&ss=01000>.
- Venteris, E.R., Basta, N.T., Bigham, J.M., and Rea, Ron, 2014, Modeling spatial patterns in soil As to estimate natural baseline concentrations: *Journal of Environmental Quality*, v. 43, no. 3, p. 936–946.
- Welch, A.H., Westjohn, D.B., Helsel, D.R., and Wanty, R.B., 2000, Arsenic in ground water of the United States—Occurrence and geochemistry: *Ground Water*, v. 38, no. 4, p. 589–604.
- World Health Organization (WHO), 2010, Exposure to arsenic—A major public health concern: accessed July 2015 at <http://www.who.int/ipcs/features/arsenic.pdf?ua=1>.

Tables 2–5

Table 2. Water-quality and hydrogeologic data for 168 domestic wells in Licking County, Ohio, 2012.

Table 2 is an Excel file that can be accessed at <http://dx.doi.org/10.3133/sir20155148>.

Table 3. Results of quality-control samples from Licking County, Ohio analyzed by a private lab during Test Your Well workshops, 2012.

[All samples are unfiltered; mm/dd/yy, month/day/year; µg/L, microgram per liter; mg/L, milligram per liter; ND, no difference; --, no data; NA, not applicable; -, negative]

Sample type	Sample type identifier	Date (mm/dd/yy)	Arsenic (µg/L)	Nitrate (mg/L)	Manganese (µg/L)	Iron (µg/L)	Sulfate (mg/L)	Sodium (mg/L)	Calcium (mg/L)
Blank	Blank water ¹	ND	-0.001	0.0025	0.013	1.237	0	0.004	0.001
	29658	07/10/12	<3.0	<0.10	<30	<80	<5	<5	<2
	Relative percent difference		ND	ND	ND	ND	ND	ND	ND
Replicates	29659	07/09/12	19.2	<0.10	46	2,810	158	130	19.5
	29660	07/09/12	16.7	<0.10	45	2,720	158	131	19.5
	Relative percent difference		14	ND	2	4	ND	0.8	ND
Replicates	44990	08/14/12	<3	--	--	--	--	--	--
	44982	08/14/12	<3	--	--	--	--	--	--
	Relative percent difference		-	--	--	--	--	--	--
Replicates	44980	08/14/12	4.9	--	--	--	--	--	--
	44982	08/14/12	4.1	--	--	--	--	--	--
	Relative percent difference		18	--	--	--	--	--	--
Replicates	44966	08/14/12	<3	--	--	--	--	--	--
	44976	08/14/12	<3	--	--	--	--	--	--
	Relative percent difference		-	--	--	--	--	--	--
Replicates	44983	08/14/12	33.3	--	--	--	--	--	--
	44984	08/14/12	33.8	--	--	--	--	--	--
	Relative percent difference		1.5	--	--	--	--	--	--
Standard reference sample	² T-171	NA	3.5	--	--	--	--	--	--
	44990	08/14/12	<3	--	--	--	--	--	--
	Relative percent difference		>-15	--	--	--	--	--	--
Standard reference sample	² T-183	NA	4.5	--	--	--	--	--	--
	44980	08/14/12	4.9	--	--	--	--	--	--
	Relative percent difference		9	--	--	--	--	--	--
Standard reference sample	² T-193	NA	3.44	--	--	--	--	--	--
	44966	08/14/12	<3	--	--	--	--	--	--
	Relative percent difference		>-14	--	--	--	--	--	--
Standard reference sample	² T-201	NA	24.4	--	--	--	--	--	--
	44983	08/14/12	33.3	--	--	--	--	--	--
	Relative percent difference		31	--	--	--	--	--	--

¹Blank water (lot 4101271) used in preparation of field blank was obtained from U.S. Geological Survey National Water Quality Laboratory.

²Standard reference samples obtained from U.S. Geological Survey National Water Quality Laboratory.

Table 4. Results of arsenic-speciation quality-control samples from Licking County, Ohio analyzed by the U.S. Geological Survey National Water Quality Laboratory, 2012.

[All samples are filtered; mm/dd/yy, month/day/year; hh, hour, mm, minute; µg/L, microgram per liter; As: as arsenic; ND, no difference; --, no data;

Sample type	Sample type identifier	Date (mm/dd/yy)	Time (hhmm)	Arsenic (µg/L)	Arsenate (As ⁵⁺) (µg/L as As)	Arsenite (As ³⁺) (µg/L as As)	Dimethyl-arsinate (µg/L as As)	Monomethyl-arsenate (µg/L as As)
Equipment blank	Blank water ¹	11/05/12	1614	<0.04	--	--	--	--
	Li-40-OAQ	11/05/12	1604	<0.04	--	--	--	--
	Relative percent difference		--	ND	--	ND	--	--
Field blank	Blank water ¹	11/07/12	1716	<0.04	<0.3	<0.4	<0.6	<3.2
	Li-31-OAQ	11/07/12	1706	² 0.0575	<0.3	<0.4	<0.6	<3.2
	Relative percent difference		--	--	ND	ND	ND	ND
Replicates	Li-49	11/08/12	1100	--	3.25	21.74	<0.6	<3.2
	Li-49-WGQ	11/08/12	1401	--	3.32	21.63	<0.6	<3.2
	Relative percent difference		--	ND	3	0.5	--	--

¹Water used in preparation of blanks was obtained from U.S. Geological Survey National Water Quality Laboratory (lot 127459).²Less than the laboratory reporting level.

Table 5. Results of quality-control samples from Licking County, Ohio analyzed at private lab and U.S. Geological Survey National Water Quality Laboratory, 2013.

[All samples are unfiltered; mm/dd/yy, month/day/year; µg/L, microgram per liter]

Sample type	Sample type identifier	Date (mm/dd/yy)	Arsenic (µg/L)
Replicates	¹ 44969	04/22/13	44.6
	¹ 44971	04/22/13	33.4
	Relative percent difference		29
Replicates	¹ 44977	04/22/13	18.8
	¹ 44979	04/22/13	25.4
	Relative percent difference		30
Replicates	¹ 44986	04/22/13	64.1
	¹ 44987	04/22/13	56.7
	Relative percent difference		12
Replicates	¹ 44991	04/22/13	40.1
	¹ 44993	04/22/13	34.0
	Relative percent difference		16
Laboratory split	² Li-31-1459	04/23/13	39.9
	¹ 44991, 44993	04/23/13	37.0
	Relative percent difference ³		-7
Laboratory split	² Li-31-1400	04/23/13	51.0
	¹ 44986, 44987	04/23/13	60.4
	Relative percent difference ³		29
Laboratory split	² Li-38-1100	04/22/13	29.8
	¹ 44969, 44971	04/22/13	39.0
	Relative percent difference ³		27
Laboratory split	² Li-38-1159	04/22/13	9.3
	¹ 44977, 44979	04/22/13	22.1
	Relative percent difference ³		81
Laboratory split	² Li-36-1459	04/22/13	5.7
	¹ 44967	04/22/13	8.5
	Relative percent difference ³		39

¹Unfiltered sample analyzed at private lab.

²Unfiltered sample analyzed at U.S. Geological Survey National Water Quality Laboratory.

³Computed using average of the two replicate samples analyzed by the private lab.

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