

**ARSENIC IN ILLINOIS GROUNDWATER: IMPLICATIONS FOR  
NON-COMMUNITY PUBLIC WATER SUPPLIES**

by

Steven D. Wilson, Brian Dunneback, and Katie Askren, Groundwater Section  
and  
Brian Kaiser, Public Service Lab

Illinois State Water Survey (ISWS)

## **ACKNOWLEDGMENTS**

The authors thank the Illinois Department of Public Health, Division of Environmental Health, for providing assistance in identifying well logs, facilities, and providing support for the project. Specifically, Jamie Tosetti and Joe Mitchell sent letters to the selected facilities encouraging them to cooperate and provided the results to the facilities after sampling was complete. We also thank the Illinois EPA, Groundwater Section, for providing digital mapping and location information for the non-community facilities which allowed us to map the results.

Sofia Lazovsky and Ruth Ann Nichols performed many of the chemical analyses. The authors thank the facilities for collecting samples and cooperating in this study. This research was supported by the Midwest Technical Assistance Center for Small Community Water Systems (MTAC).

## INTRODUCTION

### Study Objectives

Groundwater is the main source of drinking water for most small community and non-community water supplies in Illinois. Naturally occurring arsenic (As), a suspected carcinogen, has been found in many aquifers in the state at concentrations greater than 10 parts per billion (ppb). In 2001, the U.S. Environmental Protection Agency (USEPA) announced that the maximum contaminant level (MCL) for arsenic would be lowered from 50 to 10 ppb, with final implementation of the rule in 2006 for all community and non-transient, non-community water supplies in the United States. The new arsenic rule will include for the first time non-community, non-transient public water supplies. This change in regulations will affect 450 of the approximately 3950 non-community supplies in Illinois which are regulated by the Illinois Department of Public Health (IDPH) and the Illinois Environmental Protection Agency (IEPA). These facilities, primarily schools and small businesses, may have a difficult time meeting the new standard if the arsenic concentration in their groundwater supply exceeds the acceptable limit because costs for treatment, monitoring and reporting may be prohibitive.

About 250 of the 450 non-community, non-transient facilities in Illinois are schools and have been sampled at least once for arsenic in the last 10-15 years. The other 200 facilities, however, have not been sampled for arsenic as part of an IDPH monitoring program. These facilities occur throughout the state, though the majority are concentrated in the Chicago metropolitan area.

Because few water chemistry data are available for these facilities and because they will be regulated for arsenic starting in 2006, this project was designed to meet the following objectives in support of the IDPH program and in support of those facilities that may be impacted by the new arsenic rule.

*Evaluate the chemical conditions and well construction details of each well to determine what characteristics affect the dissolution of arsenic in groundwater.* Not many wells have been sampled for arsenic in Illinois, and in some cases, the location and well information are lacking. In order to develop an understanding of the characteristics that can be attributed to elevated arsenic concentrations in groundwater, sufficient supporting data must be collected. These data, such as well construction details, source aquifer, and groundwater geochemistry, are essential for developing hypotheses as to what conditions cause elevated arsenic levels in a given well.

*Evaluate the potential costs for those non-community supplies where additional treatment will be required to meet the new USEPA standard for arsenic of 10 ppb.* For community supplies, the IEPA estimate of compliance costs due to added treatment ranges from tens of thousands to millions of dollars, with the costs per person served increasing dramatically as the size of the community served decreases. For example, the USEPA estimates that the per capita costs of a community with 200 people will be ten times the per capita cost of a community with 20,000 people (ISWS, 2003). Non-community supplies are generally very small, fewer than 100 people, and not necessarily in use every day. The analysis by the IEPA suggests that the treatment costs for non-community supplies will be very high on a per capita basis.

*Evaluate the effectiveness of two cost effective arsenic testing kits that could be used by extension, school, and environmental groups to provide a low-cost screening for arsenic in water samples as well as provide an educational tool to promote public awareness of arsenic in groundwater.* There are probably a million or more active private and public groundwater supply wells in Illinois. The need for an accurate, cost-effective method for testing groundwater for arsenic is great. Reliable test kits, even as a screening tool, would be a cost effective alternative for non-community supplies to evaluate their potential for having elevated arsenic levels.

*Contribute to a central database of arsenic data that includes the historical sampling results from the laboratories of the IDPH, IEPA, and ISWS as well as the results of the wells that would be sampled as part of this study.* The Illinois State Water Survey (ISWS) has developed a cooperative partnership with the IEPA and IDPH to combine each agency's groundwater quality data into a central database. The data set, which is continually being developed as new samples are added, is the most complete data set of groundwater arsenic information available for Illinois. Recent projects related to sampling groundwater for arsenic, such as this study, are helping researchers develop an understanding of the factors that may influence arsenic concentrations. This study, in particular, is adding data to the database for some areas of Illinois where little sampling for arsenic has been completed.

## **Background**

In 2001, the ISWS, IDPH, and IEPA produced a white paper that summarized the known information about arsenic in Illinois' groundwater (ISWS, 2003). Based on the data gathered for

that report, little is understood about the variability of arsenic in groundwater and in wells. Some data suggest that arsenic concentrations in groundwater increase with depth (Warner, 2001), while other data suggest that shallower aquifers may have as high or higher concentrations of arsenic (Holm, 1995). New results suggest that there may be differences in well construction that affect the amount of arsenic being withdrawn (ISWS, 2003) or that microbes may play a role in the groundwater chemistry found at a particular well (Kirk et al., 2003).

### Arsenic Toxicity

Arsenic is well known for its acute toxicity. For example, an ingested dose of 70-180 mg of arsenic trioxide ( $As_2O_3$ ) is lethal to humans (Leonard, 1991). Lower doses can produce sub-acute effects in the respiratory, gastrointestinal, cardiovascular, and nervous systems (Jain and Ali, 2000). Chronic exposure to arsenic in drinking water has been linked to serious dermatological conditions, including blackfoot disease (Lu et al., 1991). Epidemiological studies have linked arsenic in drinking water with cancer of the skin, bladder, lung, liver, and kidney (Hindmarsh, 2000) and other ailments (Karim, 2000). The MCL for arsenic in drinking water in the U.S. was 50 ppb for many years, but recent research (Smith et al., 1992) has suggested that the cancer risk at 50 ppb is unacceptably high. A review of the available arsenic- and health-related data prompted the USEPA to lower the MCL to 10 ppb, the same as the World Health Organization's standard.

### Arsenic Occurrence in Groundwater

Arsenic is a minor constituent of some common minerals, and dissolved arsenic concentrations greater than 1 ppb are common in groundwater. In some aquifers and under certain conditions, much greater arsenic concentrations can be found, and concentrations above 10 ppb are not uncommon. Focazio et al. (2000) reviewed analyses of 2,262 public groundwater supply sources and Welch et al. (2000) reviewed analyses of 30,000 groundwater samples from throughout the United States and found that for about 8% and 10% of them, respectively, arsenic concentrations were greater than 10 ppb. Focazio et al. (2000) reported that the median arsenic concentration for all groundwater samples from Illinois was 1 ppb.

### Aquifers in Illinois

In Illinois, there are two primary types of aquifers, unconsolidated sands and gravels, and consolidated bedrock. Most bedrock aquifers in Illinois are found in the northern part of the state (Figure 1) and are either sandstone or limestone, the oldest being Cambrian aged and the youngest Silurian aged. Three major glaciations occurred in Illinois, covering various parts of the state with as much as 400 feet of unconsolidated material above the bedrock. These glacial events are, from oldest to youngest, the pre-Illinoian, Illinoian, and Wisconsin glacial episodes. The meltwaters from these glaciations filled the large bedrock channels, or valleys, with sand and gravel, producing unconsolidated sand and gravel aquifers (Figure 2). Any sand and gravel deposited since the Wisconsin glacial episode were deposited by rivers along existing river valleys, and are described as recent alluvium. The southern two-thirds of Illinois has groundwater available in the bedrock, but the water quality is poor, usually because of high total

dissolved solids (TDS) or sulfur, making these formations unsuitable for water supply and thus they are not considered aquifers.



**Figure 1.** Bedrock Aquifers in Illinois.



**Figure 2.** Major Sand and Gravel Aquifers in Illinois.

#### The Non-Community Well Program at IDPH

The IDPH maintains a database of information for every non-community water supply in Illinois. There are two types of non-community supplies, transient and non-transient. A transient, non-community water supply is one that serves at least 25 people daily, but not necessarily the same people, for at least 60 days a year; for example, a highway rest area. A non-transient, non-community system is one that serves at least 25 people, the same people, for at least 6 months of the year, such as a school or large business. The IDPH routinely samples the non-community



wells for nitrate and coliform bacteria. The program calls for periodic testing of a wider range of constituents for non-transient, non-community water supplies. Lead and copper testing is required in staggered intervals of six months, one year, and every three years as supplies meet compliance criteria. Samples are collected for inorganics, volatile organics, pesticides, and synthetic organics every three years. Arsenic is not regularly tested for, however. A complete description of the IDPH non-community public water supply program can be found at:

[http://www.idph.state.il.us/envhealth/ncpws\\_handbook.htm#your%20responsibilities](http://www.idph.state.il.us/envhealth/ncpws_handbook.htm#your%20responsibilities)

#### Arsenic Occurrence in Non-Community Wells in Illinois

Though arsenic is not one of the constituents listed in the non-community sampling program, some non-community supplies have been tested for arsenic. The IDPH has sampled most of the 250 schools that are non-community water supplies for arsenic within the last 10 years. Only 15 of those samples had detectable arsenic, 5 of which were above 10 ppb.

#### Arsenic Testing Kits

Several colorimetric testing kits to screen water for arsenic have been developed. One of the most extensive evaluations of these kits was completed by Rahman et al. (2002) in Bangladesh and West Bengal, India. They found the kits to be unreliable as a screening tool. They reported that the millions of dollars being spent to screen wells with these kits were being wasted, and that improved laboratory techniques are needed to produce reliable data. However, newer kits claim to detect arsenic at lower levels, which would make them more effective as a screening tool.

With this in mind, we decided to evaluate two test kits for use in Illinois

## METHODOLOGY

### Site Selection

The focus of the project was to sample non-transient, non-community wells that have not been sampled in the past for arsenic, because these facilities will be regulated for arsenic as part of the new rule. However, because one of our objectives was to add these results to the growing database of knowledge about arsenic in groundwater, there were several criteria developed in selecting sites. To be included, the site had to have a well log for their well. In addition, because these facilities are not evenly distributed throughout the state, when more than two sites were in close proximity to each other, only two were sampled. Lastly, if the log indicated that the well was in an unconfined aquifer, or was either dug or bored, that well was not included in the final list. These wells were eliminated because our sampling to date suggested that, in Illinois at least, wells in oxidized zones in the subsurface would likely not have detectable arsenic. However, sampling of several community wells for a study just completed (Wilson et al., 2004) indicates that shallow aquifers can contain arsenic and that these types of facilities should not have been removed from consideration.

Because past experience has indicated that not every facility would have a well log, the strategy employed was to look for well logs for the 200 non-transient, non-community wells first. If 150 of those facilities did not have adequate well logs, then transient facilities would be added until 150 facilities with well logs could be identified. An adequate well log is one that clearly

identifies the location of the well in sufficient detail and includes a geologic log that allows for a determination of what aquifer water is being withdrawn from.

### Well Logs

The ISWS is the repository for water-well logs in Illinois. In the ISWS groundwater files are hundreds of thousands of well records that vary dramatically in content and quality. Initially, ISWS staff went to the IDPH offices and reviewed the files for the 200 potential non-transient facilities. Where a well log was available in those files, it was copied for use in the project. Those that had no log or had a log that was questionable in some way were identified so that a review of the well records at the ISWS could be completed in hopes that the well log was on file there. When a log was found, the log was copied and became part of the project database.

### Soliciting Cooperation

As candidate facilities were identified, the IDPH sent them a letter describing the project and asking for their cooperation in collecting a water sample. Though not required to participate, the facilities were informed of the impending changes in regulations regarding arsenic and offered this chance to have a free water analysis completed. The letters also included information about the sampling procedures and discussed the importance of following the sampling instructions.

### Sample Collection

About a week after a site was sent a letter by IDPH, the Public Service Lab (PSL) at the ISWS sent them a sampling kit in the mail. The standard PSL operating procedure is to send a set of

bottles to the well owner, along with instructions on how to collect the sample and a questionnaire to ask the well owner to provide pertinent information about the well. The ISWS has analyzed over 200,000 water samples dating back to the 1890s and utilizing the well owner as sampler provides an economical alternative to sending staff throughout the state to collect samples.

For this project, two additional bottles were added to the kit sent to well owners. The additional bottles were filled so that analyses could be performed utilizing two colorimetric test kits for arsenic.

#### Laboratory Sample Analysis

The PSL lab supports research by ISWS scientists and also serves the public by providing well owners with a cost effective avenue for getting their well tested for metals and inorganic constituents. Table 1 lists the analytes and standard methods utilized by the PSL.

#### Hach Arsenic Screening Kit

The Hach arsenic test kit is a colorimetric test that measures arsenic levels between 0 to 500 ppb. It was designed to test natural water, drinking water, and groundwater per the instructions that are sent with the kit. The test kit contains a capped reaction vessel, five reagents, a set of test strips, and a set of instructions.

Table 1. PSL Analytes and Methods Description

<b>Metal/ Sample Property</b>	<b>Method Used</b>	<b>Description</b>
Iron (Fe)	US EPA 200.7, Revision 4.4	Inductively Coupled Argon Plasma-Atomic Emission Spectrometry
Manganese (Mn)	US EPA 200.7, Revision 4.4	Inductively Coupled Argon Plasma-Atomic Emission Spectrometry
Calcium (Ca)	US EPA 200.7, Revision 4.4	Inductively Coupled Argon Plasma-Atomic Emission Spectrometry
Magnesium (Mg)	US EPA 200.7, Revision 4.4	Inductively Coupled Argon Plasma-Atomic Emission Spectrometry
Sodium (Na)	US EPA 200.7, Revision 4.4	Inductively Coupled Argon Plasma-Atomic Emission Spectrometry
Nickel (Ni)	US EPA 200.7, Revision 4.4	Inductively Coupled Argon Plasma-Atomic Emission Spectrometry
Barium (Ba)	US EPA 200.7, Revision 4.4	Inductively Coupled Argon Plasma-Atomic Emission Spectrometry
Copper (Cu)	US EPA 200.7, Revision 4.4	Inductively Coupled Argon Plasma-Atomic Emission Spectrometry
Boron (B)	US EPA 200.7, Revision 4.4	Inductively Coupled Argon Plasma-Atomic Emission Spectrometry
Zinc (Zn)	US EPA 200.7, Revision 4.4	Inductively Coupled Argon Plasma-Atomic Emission Spectrometry
Chromium (Cr)	US EPA 200.7, Revision 4.4	Inductively Coupled Argon Plasma-Atomic Emission Spectrometry
Chloride (Cl)	US EPA Method 300.0, Revision 2.1	Ion Chromatography
Nitrate (NO <sub>3</sub> )	US EPA Method 300.0, Revision 2.1	Ion Chromatography
Sulfate (SO <sub>4</sub> )	US EPA Method 300.0, Revision 2.1	Ion Chromatography
Fluoride (F)	SM18, 4500-F-C	Ion-Selective Electrode Method
pH	US EPA Method 150.1	Electrometric
Alkalinity	USGS-1030-85	Electromagnetic titration, mg/L as CaCO <sub>3</sub>
Total Dissolved Solids	SM18, 2540-C	Dried at 180°C
Turbidity	SM18, 2130-B	Nephelometric Method
Color	SM18, 2120-B	Visual Comparison Method
Odor	SM18, 2150-B	Threshold Odor Test
Hardness	SM18, 2340-B	Hardness by Calculation
Arsenic (As)	SM18.3113	Atomic Absorption

The initial step is to place a test strip into a slot in the vessel cap. It is important to make sure that the pad on the strip is placed over a small hole in the bottom of the cap so that the gases within the reaction vessel can interact with the pad. After adding 50 mL of the water sample to the reaction vessel, the first reagent, sodium phosphate, is added and mixed with the water. Reagents two and three, which are a mixture of oxone and monopersulfate compound and a mixture of ethylenediaminetetraacetic acid (EDTA), disodium salt, and EDTA tetrasodium salt, respectively, are then added. According to the instructions, the three reagents are added so that “hydrogen sulfide is first oxidized to sulfate to prevent interference, and the oxidizing environment is then neutralized”. The fourth and fifth reagents, sulfamic acid and powdered zinc, respectively, are added to react with the solution and “create strong reducing conditions in which inorganic arsenic is reduced to arsine gas ( $\text{AsH}_3$ ).”

After all the reagents have been mixed in with the sample, the arsine gas reacts with the mercury bromide in the test strip. After a thirty minute reaction period, the test strip is examined for a change in color. The color of the strip ranges from white (no arsenic present) to yellow (low levels of arsenic present) to brown (high levels of arsenic present). Hach includes a color spectrum with the kit for the user to compare with the test strip. The color on the test strip is associated with an arsenic value. The intervals of arsenic value on the provided color spectrum were 0, 10, 30, 50, 70, 300, and 500 ppb.

There are substances which might be present in the sample water that could interfere with the test. The Hach company listed the following ions or substances that possibly interfere: sulfide (at

a concentration greater than 5 ppm), selenium (greater than 1 ppm), antimony (greater than 1 ppb), and tellurium, which the Hach company described as likely to interfere, but was not tested. The Hach test kit is designed to test only for inorganic arsenic. They do provide an alternate methodology that measures both organic and inorganic arsenic, but because only groundwater was sampled, which typically does not contain organic arsenic, the original methodology was used.

### ITS arsenic Screening Kit

The Independent Test Systems (ITS) Low Range arsenic test is similar to the Hach test. In the ITS test, a set of three reagents are added and mixed with the water sample. The resulting gases react with a test strip, and a color change on the strip occurs. The color is compared to a spectrum, from which the arsenic value is determined.

The primary difference between the tests is the reagents used. The first reagent is a mixture of tartaric acid (98.7%), ferrous sulfate (0.7%), and nickel sulfate (0.6%). The second reagent is a mixture of potassium peroxymonopersulfate (42.8%) and inert ingredients (57.2%). This reagent is added to the sample so the test can tolerate hydrogen sulfide (H<sub>2</sub>S) up to a concentration of 2 ppm in the sample. The third reagent is zinc dust, used to react with the solution and create arsine gas. A test strip containing mercuric bromide (HgBr<sub>2</sub>) is placed inside the reaction vessel. After a 12 minute reaction period, the test strip is removed and its color is compared to the provided color spectrum. Similar to the Hach test, colors ranged from white (no arsenic present) to yellow (low values of arsenic present) to brown (high values of arsenic present).

The color spectrum associated with this test differs from the Hach test, in that the ITS spectrum focuses on lower values of arsenic. The value intervals on the ITS spectrum are 4, 6, 8, 10, 12, 14, 16, 18, 20, 30, 40, 50, 60, 70, 80, 100, 140, and 160 ppb.

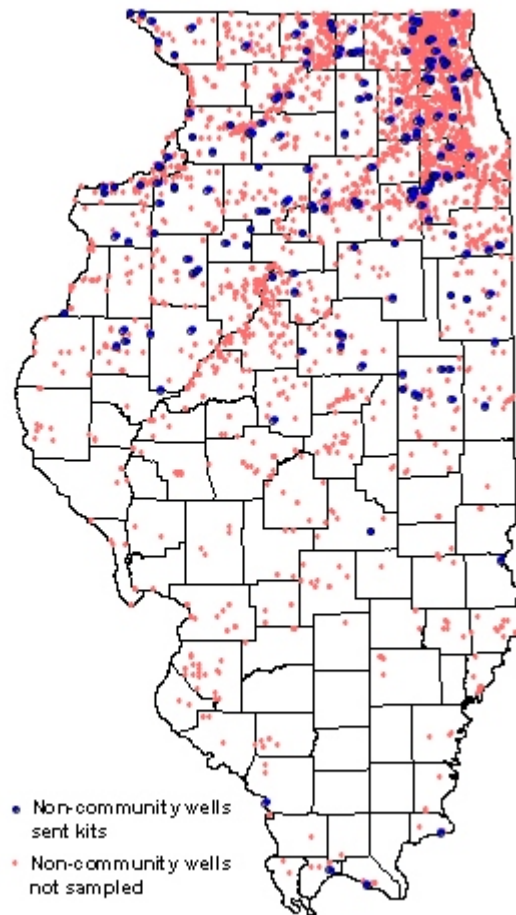


## RESULTS

### Well Selection

Well selection proved to be a difficult task. Only about 10 logs were found at IDPH and about 90 logs were found in the ISWS records for non-transient facilities. After eliminating those facilities whose logs were incomplete or were in shallow or dug or bored wells, 83 wells were included in the final list. In addition, as was discovered when samples began to come in, sometimes a facility had more than one well, but there was only one well log in the IDPH/ISWS files. Because of this, some sample kits were sent to facilities where samples were collected from wells for which no log existed.

In total, 168 kits were mailed out. Eighty-three were mailed to non-transient facilities and 85 to transient facilities. The site locations are shown in Figure 3.



**Figure 3.** Location of all non-community wells in Illinois and those sent sampling kits.

## Well Logs

The process of matching well logs with the samples received was difficult for several reasons. A particularly challenging factor involved the self-reporting of information by well owners. Often the information reported was incomplete, lacking information such as the prior owner's name, drilling date, well depth, and location. In these cases, if the sample could be matched to a well log through records of the current or previous owner's name, information was taken from the well records on file under the assumption that the well sampled corresponded to the well log. Other times, critical information was reported that contradicted our well logs. In cases where the information reported was only slightly different from the information in the well log, such as where only the depth or plot location was different, the well information was taken from the well log with a notation of the difference between the reported information and the information on file. Where there were significant differences between the reported information and the information on file, such as a difference in both location and depth or drilling date and depth, the reported information was generally assumed to be more accurate, especially in cases where the ISWS had some record of a well matching the description provided by the well owner.

Analytical results indicated that some samples were treated even though the instructions clearly asked that they provide untreated samples, as did the letters sent by IDPH to inform them of the project. By evaluating the calcium, magnesium, and fluoride values, it was determined that three samples reported as untreated were actually softened; in these instances, the samples were flagged as having been softened. It is, however, possible that some samples reported as raw were actually treated in ways that we could not detect.

Another significant challenge was a lack of well records for the correct well. For 27 out of the 127 samples, complete geology could not be determined because logs for these wells could not be located. In these cases all well information was taken from well owner's reports, which were sometimes incomplete, and geology was determined based on other nearby well logs.

### Sample Data

127 samples were returned to the ISWS Public Service Laboratory of the 168 kits sent out and all were analyzed. Of the 83 kits sent to non-transient facilities, 74 were returned. Of the 85 kits sent to transient facilities, only 53 were returned. This is not unexpected because the transient supplies are sometimes seasonal, small rural businesses, or parks and recreation areas that haven't been involved in any regulatory monitoring. The non-transient supplies are typically larger and more established businesses that already are involved in a sampling program with the IDPH.

Of the 127 samples, it was determined that 38 had been subjected to some form of treatment. These samples either had information listed on their return questionnaire that indicated a type of treatment, or treatment was determined by sample analysis. Table 2 lists the types and number of treated samples.

Treatment affects the chemical composition of a sample. For the data collected for this study, the 38 treated samples were omitted from the geochemical analysis, but left in for evaluating geology and well depth. They are important in identifying facilities that may need additional treatment,

even if they currently have some treatment in place. It should be noted, however, that treatment such as softening and iron filtering likely remove arsenic from the water. Thus, it is possible that the arsenic concentrations in the groundwater, not the tap water, are higher than the results indicate. Three samples, in particular, were softened prior to the sampling point and their arsenic levels were still greater than 40 ppb. The source water for these samples may have had higher arsenic concentrations before being softened.

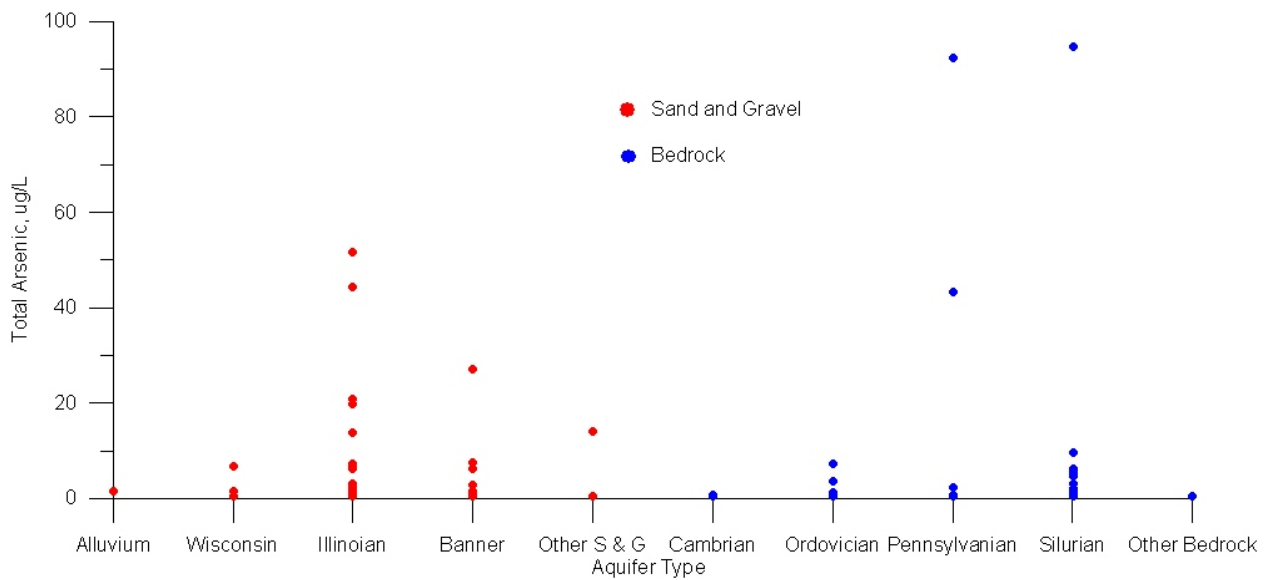
Type of Treatment	Number of Samples
None	89
Chlorination	7
Chlorination, Softener	3
Iron Filter	3
Iron Filter, Softener	3
Reverse Osmosis	1
Softener	20
UV light, Filter, Softener	1

Table 2. Samples by type of treatment.

### Geology

The geologic unit the wells were finished in was determined for all but one sample. There were 89 bedrock samples, 37 sand and gravel samples, and one undetermined sample. Where well logs were not available, the well owner provided a depth for the well. In these cases, the ISWS well logs were reviewed and other well logs were found in the immediate vicinity of the sampled

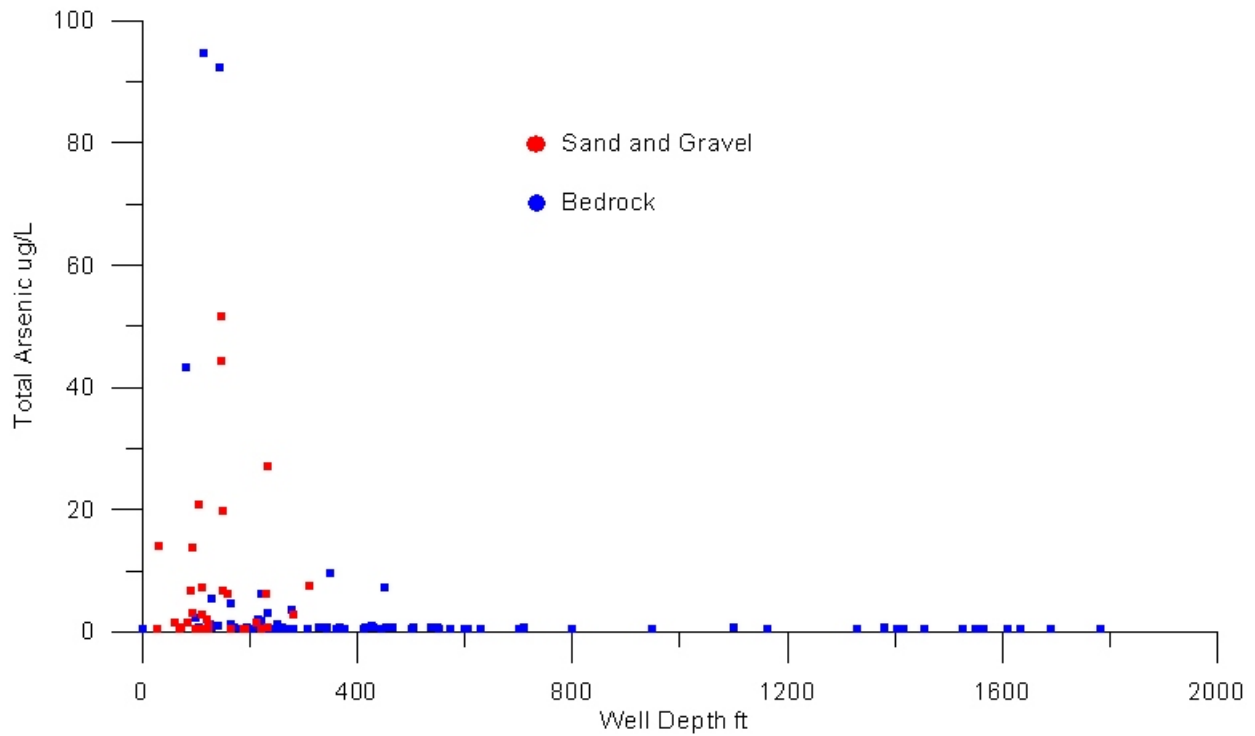
well. Using those data and the given depth, a geologic profile was developed that allowed for the determination of the formation the well was likely finished in. For the one sample that was not determined, the depth indicated the well was finished near the contact between the bedrock and sand and gravel, making it impossible to determine which unit the well was actually finished in. Figure 4 shows the arsenic results for each geologic type. Alluvium, Wisconsin, Illinoian, and Banner are sand and gravel aquifer types. Cambrian, Ordovician, Pennsylvanian, and Silurian are bedrock aquifer types. The “other” samples are those where it was possible to determine whether the well was in bedrock or sand and gravel, but it was not possible to determine the specific geologic unit because of geologic complexity in the area or a lack of nearby well logs.



**Figure 4.** Arsenic concentrations in water samples as a function of aquifer.

## Well Depth

The wells ranged from 28 feet to 1783 feet. Figure 5 shows the relationship between well depth and arsenic concentration. The sand and gravel wells show no trend with depth, but for the bedrock, wells over 450 feet deep had very little arsenic.

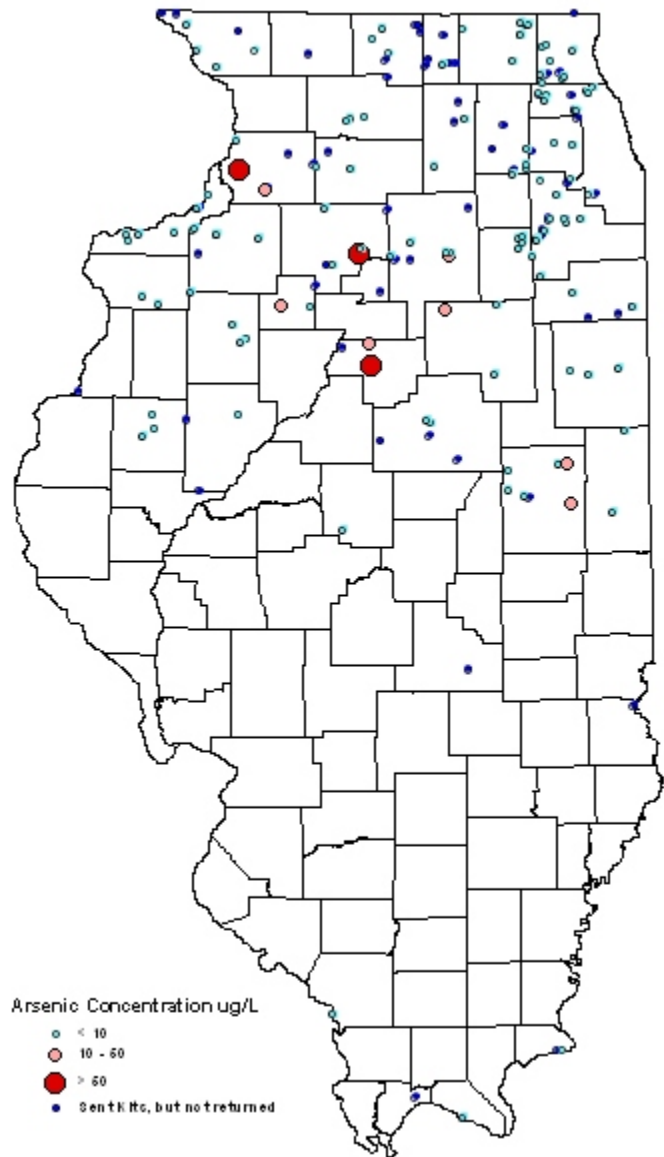


**Figure 5.** Arsenic concentrations as a function of well depth.

## Arsenic Data Summary

The distribution of arsenic for the 127 samples is shown in Figure 6. There were three samples with arsenic concentrations greater than 50 ppb and seven samples with arsenic concentrations between 10 ppb and 50 ppb. Table 3 is a summary of the arsenic relationships by various factors. The data indicate that transient supplies, as well as sand & gravel wells, are more likely to have

elevated arsenic concentrations. Recent research has also indicated that elevated arsenic is more commonly found in sand and gravel aquifers (Holm et al., 2004; Wilson et al., 2004). However, the 43 transient wells sampled only represent a little over 1% of all transient supplies in the state. Even though there was no preference given to the chosen supplies except that a well log with geology was assumed to be available (pseudo-random), the



**Figure 6.** Arsenic concentrations and distribution of samples.

sample size is too small to represent the entire group of transient supplies. In addition, there is no physical relationship between transient and non-transient facilities that would be obvious as a factor in determining the amount of arsenic.

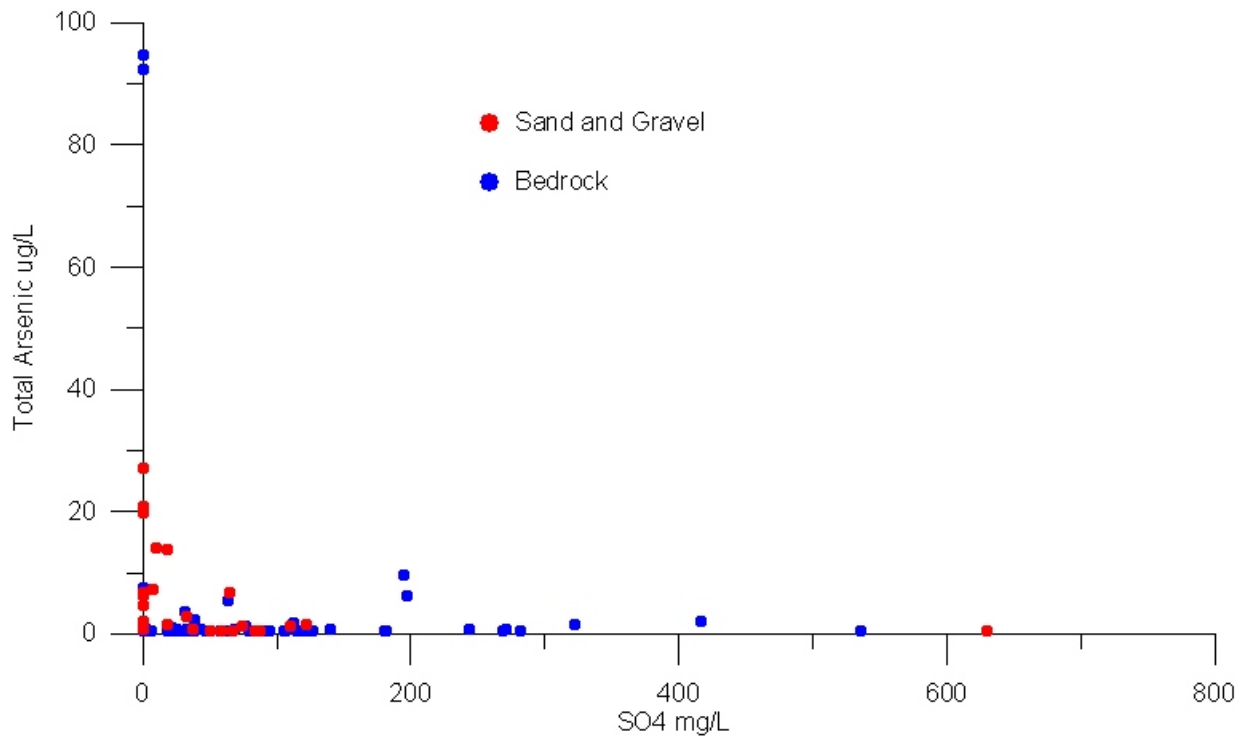
	Number	# < DL*	% < DL	# > 10 ppb	% > 10 ppb
All Samples	127	79	63%	10	9%
Facility Type	127				
Non-Transient	74	56	76%	1	1%
Transient	53	23	43%	9	17%
Geology	126**				
Bedrock	89	67	75%	3	3%
Sand & Gravel	37	12	32%	7	19%
Treatment	127				
No treatment	89	53	60%	7	8%
Treatment	38	26	68%	3	8%
* DL = Detection Limit					
** For one sample, geology could not be determined					

**Table 3.** Summary of factors and their relationship to arsenic concentrations.

### Geochemistry

Only the 89 untreated samples were used in this analysis. Figure 7 shows the arsenic concentrations as a function of sulfate concentrations. ISWS researchers have seen a similar relationship between sulfate and arsenic in recent water quality sampling projects (Kirk et al., 2003; Holm et al., 2004; Wilson et al., 2004). Sulfate and arsenic seem to be mutually exclusive and the data from this study support that result. Additional comparisons between arsenic and various chemical parameters are shown in Figure 8. The nitrate graph also shows a mutually exclusive relationship. Senn and Hemmond (2002) have found the same relationship between arsenic and nitrate in anoxic surface water. They found that bacteria use nitrate to oxidize ferrous iron and As(III) to hydrous ferric oxides and As(V). In these oxidized states, they form arsenic sorbing particulate complexes that effectively bind the arsenic and take it out of solution.

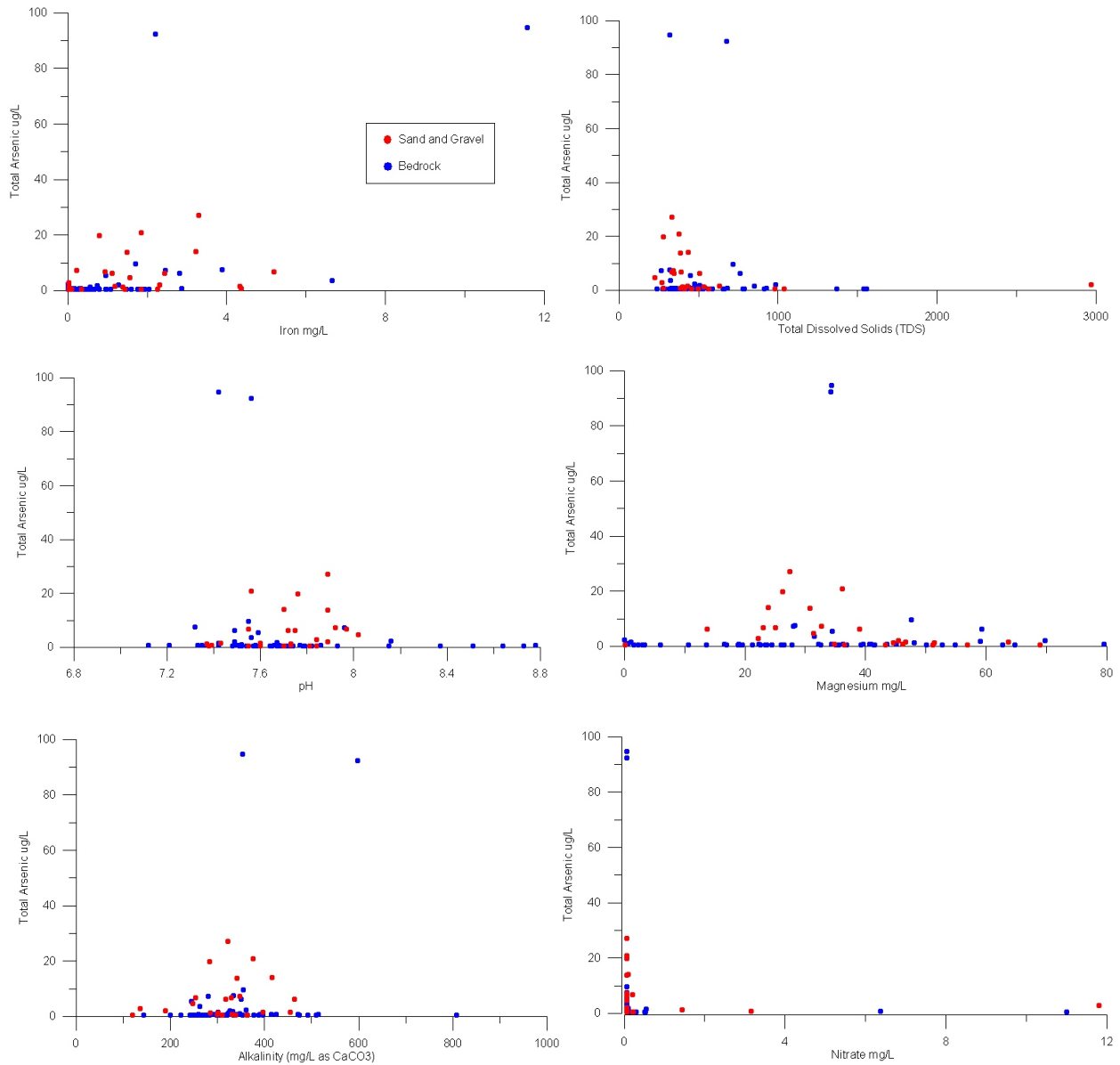




**Figure 7.** Arsenic concentration as a function of sulfate concentration.

### Data Quality

Analytical data for these samples are considered to be of reliable accuracy. Any samples that did not meet the QA/QC standards required by the lab were returned for verification. These quality control standards require that the relative percent ion balance difference and the relative percent difference between calculated and measured values for total dissolved solids in a sample be less than fifteen percent. These values do not necessarily reflect inaccuracies in the measurement of arsenic levels. After re-analysis, only 3 samples still did not meet QA/QC standards, an error of less than 3%. These samples were included in the analysis.



**Figure 8.** Arsenic concentration as a function of various chemical parameters.

## Test Kits

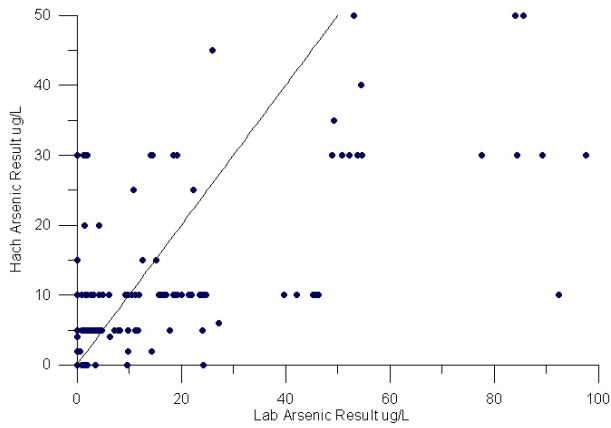
The results from the Hach and ITS test kits were compared to the results from the samples submitted to the PSL lab. The laboratory results were considered the control data for comparison purposes.

In addition to the samples submitted as part of this study, samples collected in other ongoing studies submitted for laboratory analysis were tested with the two kit methods as well. This report includes those additional samples. More samples provided the opportunity for a more comprehensive set of data to review. In total, 169 samples were tested with the Hach kit and 167 samples with the ITS kit. In two cases, there was not enough sample collected for testing with both kits, so the Hach kit was the only one used.

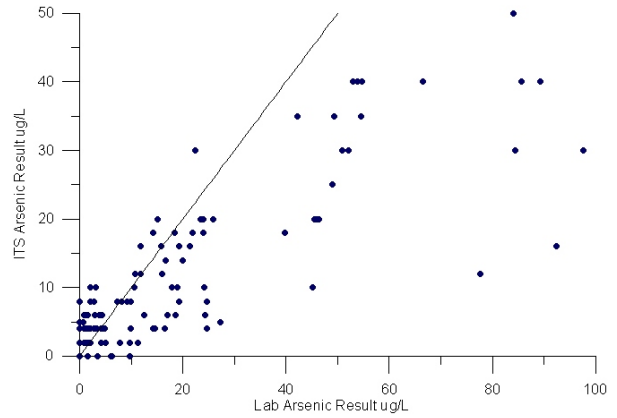
To determine the accuracy of the test kit results, the mean error and the variance of the data were measured. The mean error of the Hach test kit was 9.4 parts per billion (ppb) and for the ITS test kit was 7.3 ppb. The mean square error of the test kits were 263 and 208 for the Hach and ITS kits, respectively, indicating there were large errors associated with some of the samples.

A false positive, as discussed below, is a test kit result that indicated a positive value for arsenic, but the lab result was below the detection limit for arsenic. Similarly, a false negative is a test kit result that indicated there was no arsenic in the sample, but the lab result indicated an arsenic concentration that was above the detection limit. For the Hach kits, there were 17 false positives ranging from 2 to 30 ppb, and 16 false negatives with a high value of 24.3 ppb. For the ITS kits,

there were 28 false positives ranging from 2 to 8 ppb, and 5 false negatives with a high value of 9.7 ppb. The results of the Hach and ITS test kits are shown in Figures 9 and 10, respectively. Ideally, if all lab and test kit results matched correctly, the points would fall on the solid line on each graph.



**Figure 9.** Arsenic results, Lab vs. Hach Kit



**Figure 10.** Arsenic results, Lab vs. ITS Kit

## DISCUSSION

### Well Selection/Well Logs

Having both a location and a well log for each site was important for mapping the data and for identifying the correct aquifer as the source of water for the well. We found, however, that not all of our matching efforts were successful. In several cases, we identified a well at the correct location and having the correct well owner, only to find out that the well being sampled was not the well that we had a log for. We were able to gather the necessary location and aquifer information for all samples but one by the end of the study. There were also two situations where the water was blended from more than one well, but because the wells were utilizing the same aquifer, this was not considered a problem.

### Sample Collection

Of the 168 kits mailed out, 127 were returned with samples. About 90% of the non-transient facilities returned a sample but only 62% of the transient facilities did so. This was disappointing, but not unexpected because the study was dependent on volunteer responses. The transients are sometimes seasonal businesses, they are not going to be regulated by the new arsenic rule, and they tend to have shorter “life-spans” than do the non-transient facilities. Facilities that had not returned samples were called and the response was very poor from the transient facilities. In several cases, the phone number on file was disconnected.

### Geology/Well Depth

In this study, more than two-thirds of the samples were from bedrock aquifers. The data make it clear that the shallower aquifers, especially unconsolidated sands and gravels, are more likely to have elevated arsenic. For the bedrock samples, the shallower Pennsylvanian and Silurian aquifers were the only units to show elevated arsenic. This result is interesting and somewhat unexpected because bedrock core samples indicate that the amount of arsenic solids is typically higher than in sand and gravel sediments (Warner, 2001). Upwelling of groundwater from deeper bedrock to shallower sands and gravels has been postulated as one likely mechanism responsible for the elevated arsenic found in previous studies (Warner, 2001; Holm et al., 2004; Wilson et al., 2004). The data collected here suggest that though there may be less solid phase arsenic available in the unconsolidated materials, chemical and microbial conditions are more likely to produce elevated arsenic in the shallower units than in the deeper bedrock aquifers. Recent ambient arsenic sampling in community bedrock wells in Illinois (Wilson et al., 2004) also found very little arsenic.

The fact that all of the samples that were greater than 500 feet below land surface had arsenic at levels below 2 ppb is significant. Even though conditions are reducing in these deep aquifers, all of the necessary conditions to promote arsenic dissolution are not in place. Some recent research (Kirk et al., 2003) indicates that bacteria may be important to these systems and the role of microbes needs to be further studied.

## Geochemistry

The relationships between arsenic and other geochemical parameters in this study are similar to the relationships found in several recently completed studies in Illinois (Holm et al., 2004; Wilson et al., 2004). Arsenic in groundwater is found under strongly reducing conditions, typically where sulfate is absent. Kirk et al. (2003) concluded that arsenic concentrations were only elevated where sulfate had been exhausted and was no longer available as an electron acceptor. Active sulfate reduction produces sulfide, which would limit arsenic concentrations in solution by precipitation of arsenic sulfide minerals or coprecipitation with other sulfide minerals. Once sulfate has been eliminated, methanogenesis becomes the dominant metabolism and because there is no precipitation pathway, arsenic can build up in solution. There was also evidence that nitrate influences dissolved arsenic concentrations. In the Holm et al. (2004) and Wilson et al. (2004) studies, nitrate was low in all samples, so this relationship was not evident.

Because these samples were collected by the well owners and samples may have been in transit for several days before analysis, these data may not be as reliable as samples collected by researchers and analyzed soon after sampling. These results are consistent with the results of Wilson et al. (2004) and a more complete description of the geochemistry with respect to arsenic mobilization can be found there.

## Test Kits

Since the goal of the testing was to evaluate how well these kits might be used as a screening tool, the number of false negatives is the most important attribute. The Hach kit “missed” a

value as high as 24.3 ppb. The ITS kit “missed” a result as high as 9.7 ppb. There were many fewer false negatives with the ITS kit, but there were many more false positives, suggesting the ITS kits are overly sensitive to arsenic concentration. By most measures, the ITS kits provided more consistent results when compared with the Hach kit, but overall, both kits were disappointing. The Hach kit can not be recommended as a screening tool because of the number of samples with arsenic that the testing determined had no arsenic. Conversely, the ITS kit had so many false positives that there would be no relative savings of time or resources by using this kit to screen samples for laboratory analyses.

The visual method of testing for arsenic is subjective, relying on the tester’s ability to distinguish color differences. So many factors can influence the results on a particular day, such as a sunny day versus a cloudy day, sunlight versus artificial lighting, etc. When sampling occurs over many months, as was the case in this study, keeping the conditions constant is unlikely and some of the inconsistencies in results are likely because of these differences.

#### The Economics of Small System Arsenic Treatment

The testing completed for this study suggests that only a few non-community, non-transient systems in Illinois are going to be affected by the new arsenic rule. Though we only sampled 74 of the likely 450 non-community, non-transient systems in Illinois, the IDPH has also already tested about 250 schools that fall into this category. Of the 250 schools sampled, there were fifteen that had detectable arsenic, and only five of those had arsenic levels above 10 ppb.



However, for the few systems that are impacted, added costs for meeting the new standard are a concern.

For community supplies, the IEPA estimate of compliance costs due to added centralized treatment for these systems is from tens of thousands to millions of dollars, with the costs per person served increasing dramatically as the size of the community served decreases. In recent years, there has been a significant amount of research completed to identify cost-effective point-of-entry (POE) and point-of-use (POU) treatment methods for the removal of arsenic. These research studies indicate that for small systems, POU treatment methods will be much more cost effective per connection (USEPA, 2000; Kommineni et al., 2003) . The research varies somewhat on where the breakeven point would be, (i.e., 100 connections versus 500 connections versus 1000 connections), but in regard to non-community supplies, all sites would have connections well below 100.

The USEPA report Arsenic Treatment Technology Evaluation Handbook for Small Systems (USEPA, 2003) identifies both POE and POU options for small systems. The POU options identified are activated alumina and iron-based sorbent sorption processes and reverse osmosis (RO). The USEPA identifies the costs as being similar, but the RO system requires more operator skill (USEPA, 2003).

For groundwater systems, like those sampled for this study, there is an issue regarding whether arsenic is present as arsenic (III) or arsenic (V). Holm et al. (2004) and Wilson et al. (2004)

found that arsenic in groundwater in Illinois is predominantly As(III), generally more than 80% of the total arsenic is found as As(III). Adsorptive media processes, like the activated alumina mentioned above, remove both As(III) and As(V), but the RO system only removes As(V) (Gilles, 2001). Therefore, in order for an RO system to be effective, the water being treated would have to be oxidized prior to the RO unit to be effective.

Kommineni (2003) recently completed a detailed study of costs associated with POU systems. They calculated monthly costs for an RO system to be about \$50/ month and for an adsorption system to be about \$38/month. They divided the initial installation and equipment costs over only 3 years to calculate complete cost recovery; the equipment will likely last much longer than this. They also assumed \$300 a year for maintenance, sampling, and reporting, which would not likely be an additional expense for the non-transient systems that already have a sampling program in place. Eliminating that cost and assuming a longer depreciation for the installation and equipment reduces their estimated monthly cost by more than 50%. Kommineni et al. (2003) also compared centralized versus POU adsorption costs based on the number of service connections. For 20 connections, the centralized treatment would cost \$120 per household per month versus \$38 for POU (likely less than this as mentioned above). For 80 connections, the costs were \$50 and \$32, respectively. In their analysis, the centralized system became the less expensive option at 200 service connections, and that was due to the costs of administration, monitoring, and reporting.

For some systems that only have a few drinking water outlets at their facilities, an additional option may be to provide bottled water. The current water system would be suitable for purposes other than drinking and cooking, so bottled water/water coolers may be a reasonable alternative for some systems.

## SUMMARY

Based on the arsenic sampling conducted for this study, along with the samples on file at the IDPH, there does not appear to be a significant arsenic problem in non-transient, non-community wells in Illinois. Of the 89 non-transients systems tested, only 9% had arsenic greater than 10 ppb. Fewer than 3% of the samples the IDPH has tested had arsenic above 10 ppb. There are over 3000 transient, non-community wells in Illinois, however, and our limited sampling found 17% of the 53 samples we collected to have arsenic greater than 10ppb. Though not currently regulated, many of these facilities provide drinking water to individuals.

Results from this study are in agreement with findings from recently concluded research on arsenic occurrence in Illinois (Holm et al., 2004; Wilson et al., 2004). Arsenic in Illinois groundwater appears to be much more of a problem in shallower sand and gravel aquifers that are typically confined and under reducing conditions. Where arsenic is found in bedrock aquifers, it is generally near the top of the bedrock where surface and unconsolidated aquifers have the potential to interact.

The samples that were treated in this study had similar numbers in regard to arsenic with those that were not treated. Previous analyses from the PSL lab and the IEPA have shown that where arsenic is present, treatment such as softening and iron filtering can remove a significant amount of arsenic from water, sometimes more than 40% (Wilson et al., 2002). This suggests that for the samples that were treated in this study, some may have higher arsenic levels in their source

water. Because the arsenic rule is in regard to drinking water, however, those facilities with arsenic greater than 10 ppb in their tap water will have to provide additional treatment to lower their arsenic concentrations, whether they currently have any treatment or not. An alternative for some supplies may be to use softening or iron filtering, since those processes are known to reduce the level of arsenic in water.

The push to look at cost-effective arsenic treatment methods nationwide by the USEPA has provided small systems with hope for dealing with their arsenic problems in an affordable way. For most non-community public water supplies, POU systems or using bottled water appear to be the most cost-effective solutions. Both are affordable and can be implemented easily on most current systems.

## REFERENCES

- Focazio, M. F., Welch, A. H., Watkins, S. A., Helsel, D. R., and Horn, M. A. (2000). A retrospective analysis on the occurrence of arsenic in ground-water resources of the United States and limitations in drinking-water-supply characterizations. Washington, D.C., U. S. Geological Survey: 21.
- Gilles, G., Odom, S., and Mathis, J. (2001). POU an affordable arsenic treatment for small systems. *Water Technology Magazine*. September 2001
- Hindmarsh, J. T. (2000). Arsenic, its clinical and environmental significance. *Journal of Trace Elements in Experimental Medicine* 13(1): 165-172.
- Holm, T. R. (1995). Ground-water quality in the Mahomet aquifer, McLean, Logan, and Tazewell Counties. Champaign, IL, Illinois State Water Survey: 42.
- Holm, T. R., Kelly, W. R., Wilson, S. D., Roadcap, G. R., Talbott, J. L., and Scott, J. S. (2004). Arsenic Geochemistry and Distribution in the Mahomet Aquifer, Illinois. I. W. M. a. R. Center. Champaign, IL, Illinois Waste Management and Research Center: 145.
- ISWS (2003). Arsenic in Illinois Groundwater. Arsenic Information. Champaign, Illinois State Water Survey. 2003: Arsenic Fact sheet developed jointly by the ISWS, IEPA, and IDPH.
- Jain, C. K., and Ali, I. (2000). Arsenic: Occurrence, toxicity and speciation techniques [Review]. *Water Research* 34(17): 4304-4312.
- Karim, M. (2000). Arsenic in groundwater and health problems in Bangladesh. *Water Research* 34(1): 304-310.

- Kirk, M., Park, J., Jin, Q., Sanford, R. A., Fouke, B. W., and Bethke, C. M. (2003). Microbial control on arsenic concentration in groundwater from a glacial aquifer system. Geological Society of America Annual Meeting, Seattle, WA.
- Kommineni, S., Narasimhan, R., and Durbin, H. (2003). Point-of-Use/Point-of-Entry Treatment for Arsenic Removal: Operational Issues and Costs. Public Water System Compliance Using Point-of-Use and Point-of-Entry Treatment Technologies, Orlando, FL, NSF.
- Leonard, A. (1991). Arsenic. Metals and their compounds in the environment. E. Merian. Weinheim, VCH: 751-774.
- Lu, F. J., Hsieh, H. P., Yamauchi, H., and Yamamura, Y. (1991). Fluorescent humic substances-arsenic complex in well water in areas where blackfoot disease is endemic in Taiwan. *Appl. Organomet. Chem.* 5: 507-512.
- Rahman, M. M., Mukherjee, D., Sengupta, M. K., Chowdhury, U. K., Lodh, U., Chanda, C. R., Roy, S., Selim, M., Quamruzzman, Q., Milton, A. H., Shahidullah, S. M., Rahman, M. D., and Chakraborti, D. (2002). Effectiveness and Reliability of Arsenic Field Testing Kits: Are the Million Dollar Screening Projects Effective or Not? *Envir. Sci. & Technol.* 36(No. 24): 5385-5394.
- Senn, D. B., and Hemond, H. F. (2002). Nitrate controls on iron and Arsenic in an Urban Lake. *Science* 296(5577): 2373-2376.
- Smith, A. H., Hopenhaynrich, C., Bates, M. N., Goeden, H. M., Hertzpicciotto, I., Duggan, H. M., Wood, R., Kosnett, M. F., and Smith, M. T. (1992). Cancer risks from arsenic in drinking water. *Environ. Health Persp.* 97: 259-267.

USEPA (2000). Technologies and Costs for Removal of Arsenic from Drinking Water. *Office of Water EPA 815-R-00-028*.

USEPA (2003). Arsenic Treatment Technology Evaluation Handbook for Small Systems. *Office of Water EPA 816-R-03-014*: 126 pages.

Warner, K. L. (2001). Arsenic in glacial drift aquifers and the implication for drinking water - lower Illinois river basin. *Ground Wat. 39*(3).

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 [Review]. *Ground Water 38*(4): 589-604.

Wilson, S. D., Kelly, W. R., Roadcap, G. R., Holm, T. R., Skowron, L., Kaiser, B., Talbott, J. L., and Scott, J. S. (2002). Arsenic in Illinois Groundwater: Current Research Efforts at the Illinois State Water Survey. Water 2002, Champaign, IL.

Wilson, S. D., Kelly, W. R., Holm, T. R., and Talbott, J. L. (2004). Arsenic Removal in Water Treatment Facilities: Survey of Geochemical Factors and Pilot Plant Experiments. Contract Report. Champaign, IL, Illinois State Water Survey.