

**ARSENIC REMOVAL IN WATER TREATMENT FACILITIES: SURVEY OF
GEOCHEMICAL FACTORS AND PILOT PLANT EXPERIMENTS**

Steven D. Wilson, Walton R. Kelly, Thomas R. Holm

Illinois State Water Survey

Jonathan L. Talbott

Illinois Waste Management and Research Center

ACKNOWLEDGMENTS

The authors thank the IllinoisEPA, Groundwater Section, for providing a municipal map of arsenic concentrations that served as the basis for selecting the municipal supplies for sampling.

IN addition, Dave McMillan, Manager, Planning and Assessment Unit, Groundwater Section, IEPA, assisted in selection of the communities and sent letters to each selected community introducing the project and asking for their cooperation.

The authors thank the following people for their help. Bryan Coulson assisted with contacting water treatment plants and sampling. Joe Karny and Brian Dunneback assisted with sampling. Sofia Lazovsky, Ruth Ann Nichols, Teresa Chow, and Monte Wilcoxon performed many of the chemical analyses. The authors thank the municipalities for permission to collect samples from their water treatment plants and the plant operators for their cooperation in the sampling. The authors especially thank Mr. Scott Seniff, Director of Public Works, Danvers, for his cooperation.

This research was supported by the Midwest Technology Assistance Center for Small Community Water Supplies.

INTRODUCTION

Study Objectives

Groundwater is the main source of drinking water for most small communities in Illinois.

Naturally occurring arsenic (As), a suspected carcinogen, has been found in many aquifers in the state at concentrations greater than 10 µg/L. 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 µg/L, with final implementation of the rule in 2006 for all community and non-transient, non-community water supplies in the United States.

The Illinois Environmental Protection Agency (IEPA) has identified about 50 public water systems that have arsenic concentrations in their finished water that will be out of compliance when the MCL is lowered to 10 µg/L. The IEPA estimate of compliance costs due to added 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. 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).

Water treatment plants remove some arsenic in conventional processes, such as iron (Fe) removal and softening, but these processes are not optimized for arsenic removal. Substantial data exist regarding arsenic levels in community water supplies, especially treated samples. However, data

on both raw and treated samples for a given system are not as readily available. Clearly, understanding the removal efficiency of existing systems will be an important component for proper application of treatment methods. Therefore, the initial objective of this research was to determine the current arsenic-removal efficiency of those community water treatment plants that have significant amounts of arsenic in their raw water. These systems draw water from the various aquifers in Illinois, and by determining the types of treatments and natural chemical conditions that promote the removal of arsenic using conventional treatment, public water supplies may be able to use these results to improve their arsenic removal using conventional treatment methods. Clearly, it would be advantageous to identify treatment processes that economically remove arsenic from potable water. Therefore, the first objective of this study was to identify the factors, including raw water quality and treatment process parameters, that cause effective (and ineffective) arsenic removal at water treatment plants in Illinois.

A second part of the project was to conduct a bench-scale test of arsenic removal by potassium permanganate (KMnO_4) oxidation and manganese greensand filtration at a water treatment plant. Both KMnO_4 oxidation and manganese greensand (MGS) filtration are used in potable water treatment, mostly for Fe and manganese (Mn) removal. Arsenic is probably removed by treatment systems using these processes, even though the systems were not designed for it. Bench-scale studies of arsenic removal by manganese greensand have been performed with varying results. Lauf (1994) performed experiments with a MGS column operated in intermittent regeneration mode and a synthetic influent containing 4 mg/L Fe^{2+} and 200 $\mu\text{g/L}$ As(III). The effluent arsenic concentration was $\sim 5 \mu\text{g/L}$ for ~ 300 bed volumes. The effluent then increased

sharply. Subramanian et al. (1997) performed MGS column experiments in continuous regeneration mode using tap water with added Fe^{2+} and 200 $\mu\text{g/L}$ As(III). For an iron-to-arsenic ratio of 10 the effluent arsenic concentration gradually increased from $\sim 20 \mu\text{g/L}$ to $\sim 50 \mu\text{g/L}$ over several hours of operation. For an iron-to-arsenic ratio of 20 the effluent arsenic concentration remained below 25 $\mu\text{g/L}$ (the Canadian standard) for the course of the experiment. In a test of a full-scale MGS filtration plant the arsenic concentration in untreated groundwater had 66 $\mu\text{g/L}$, while the effluent had less than 5 $\mu\text{g/L}$ (Magyar, 1992).

The third objective of this study was to characterize the arsenic speciation in raw and finished water samples and determine if and how conventional treatment affects arsenic speciation.

Arsenic in groundwater occurs in two chemical forms, or species, As(III) and As(V).

Determining arsenic speciation is important because the chemical and toxicological properties of the two species are quite different and the removal methods for each may be somewhat different.

The determination of arsenic speciation is a difficult task and few prior data are available.

Background

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). Somewhat lower doses 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). Both As(III) and As(V) are strongly adsorbed in the human body (Hindmarsh and McCurdy, 1986). As(III) tends to accumulate in the tissues, whereas As(V) and organic arsenic are rapidly and almost completely eliminated via the kidneys (Bertolero et al., 1987). The MCL for arsenic in drinking water for many years was 50 $\mu\text{g/L}$, but recent research (Smith et al., 1992) has suggested that the cancer risk at 50 $\mu\text{g/L}$ is unacceptably high. A review of the available arsenic- and health-related data prompted the USEPA to lower the MCL to 10 $\mu\text{g/L}$, 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 $\mu\text{g/L}$ are common in groundwater. In some aquifers and under certain conditions, much greater arsenic concentrations can be found, and concentrations above 10 $\mu\text{g/L}$ 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 $\mu\text{g/L}$. Focazio et al. (2000) reported that the median arsenic concentration for all groundwater samples from Illinois was 1 $\mu\text{g/L}$.

Aquifers in Illinois

In Illinois, there are two 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 Wisconsinan glacial episodes. The meltwaters from these glaciations filled the large bedrock channels, or valleys, with sand and gravel that we now utilize as unconsolidated sand and gravel aquifers (Figure 2). Any sand and gravel deposited since the Wisconsinan glacial episode were deposited by rivers along existing river valleys, and are described as recent alluvium. The southern two-thirds of Illinois does have groundwater available in the bedrock, but poor water quality, usually because of high total dissolved solids (TDS) or sulfur, makes these formations unsuitable for water supply and thus they are not considered aquifers.

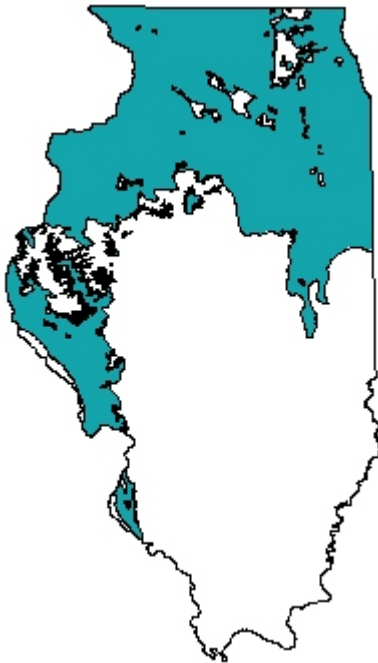


Figure 1. Bedrock Aquifers in Illinois.



Figure 2. Major Sand and Gravel Aquifers in Illinois.

Arsenic Occurrence in Community Wells in Illinois

The IEPA has been analyzing for arsenic in ambient water samples from community wells since the early 1970s. Over 19,000 samples have been analyzed since that time, although many of these are multiple samples from single wells. A recent survey of these records found that 77 of 347 Illinois community groundwater supplies (22%) had at least one sample with arsenic greater than 10 µg/L in the 1990s (NRDC, 2000). This database has recently been updated and was reevaluated for this study.

Approximately two-thirds of the ambient water samples had arsenic concentrations below the detection limit (usually < 2 µg/L), and about 89% had concentrations less than 10 µg/L.

Approximately 2% of the samples had arsenic greater than 50 µg/L. A total of approximately 700 wells representing more than 350 municipalities had at least one sample over 10 µg/L arsenic.

Communities with elevated arsenic concentrations are found throughout the state (Figure 3).

Areas in which many affected wells are not found, such as southern Illinois, are in general areas where there are few communities using groundwater. Almost two-thirds of the affected wells are finished in sand and gravel aquifers, but elevated arsenic concentrations are also found in wells finished in shallow and deep bedrock formations. Aquifer formations are not defined for about 18% of the wells in the database.

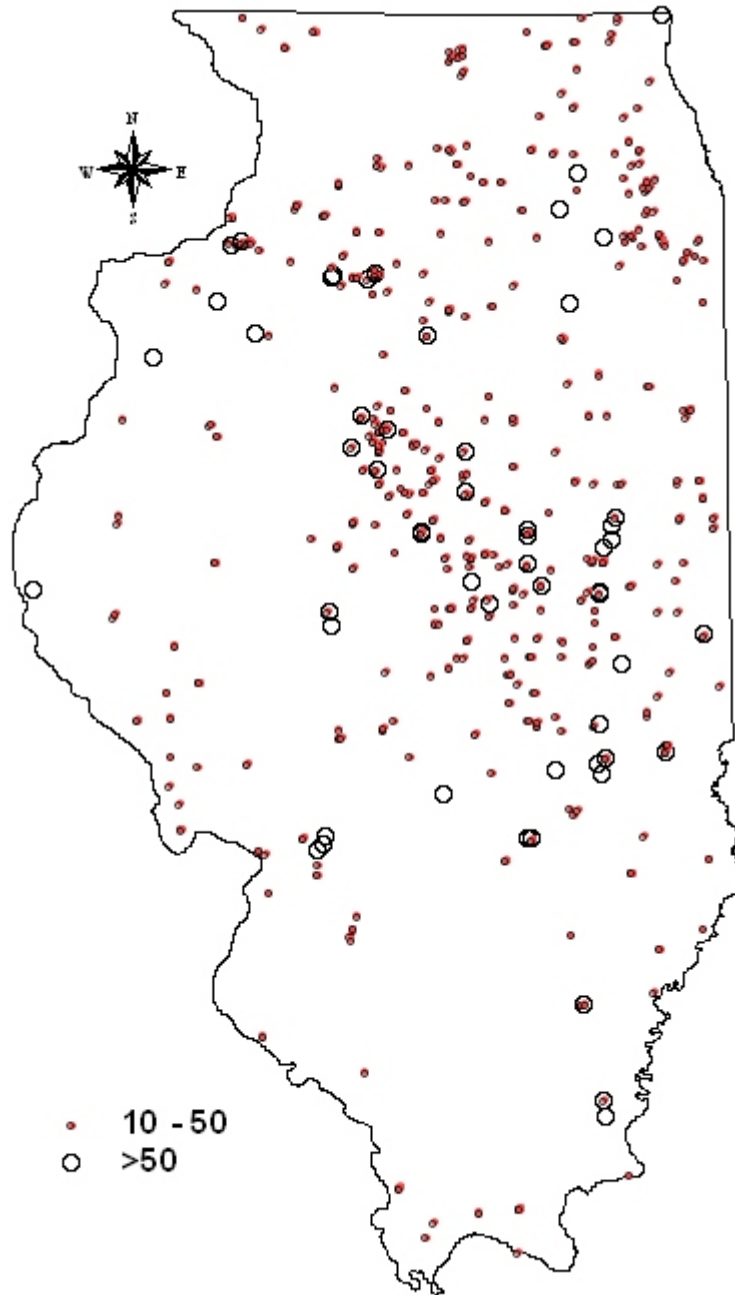


Figure 3. Locations of municipal wells in Illinois with at least one raw water sample having an arsenic concentration of $> 10 \mu\text{g/L}$. Data from the IEPA Ambient Water Quality Database. For wells having more than one occurrence, the most recent sample was used.

Arsenic Chemistry

Arsenic in groundwater occurs in two oxidation states, As(III) (arsenite) and As(V) (arsenate). Arsenious acid (H_3AsO_3) has a pK_a value of 9.2, so in the pH range of most groundwaters there is relatively little of its conjugate base H_2AsO_3^- (Figure 4). The sum of concentrations of H_3AsO_3 and H_2AsO_3^- is denoted As(III). Arsenic acid (H_3AsO_4) has pK_a values of 2.7, 6.8, and 11.5, which are similar to those of phosphoric acid. In the pH range of groundwater the concentrations of H_2AsO_4^- and HAsO_4^{2-} are much greater than those of H_3AsO_4 and AsO_4^{3-} (Figure 5). The sum of concentrations of H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} , and AsO_4^{3-} is denoted As(V). Although methylated forms of arsenic are sometimes found in surface waters, they have only rarely been found in groundwater (Irgolic, 1982; Chatterjee et al., 1995), except in cases of gross contamination by herbicides (Holm et al., 1979). Shraim et al. (2002) did find low concentrations ($< 2 \text{ mg/L}$) of methylated species in groundwater from West Bengal, although the inorganic arsenic concentration in those samples was extremely high ($> 300 \text{ g/L}$).

In most published studies of arsenic speciation, both As(III) and As(V) were found and the less abundant species was at least 2% of the total arsenic (Matisoff et al., 1982; Ficklin, 1983; Welch et al., 1988; Chen et al., 1995; Smedley, 1996; Smedley et al., 1996; Boyle et al., 1998; Yan et al., 2000). In these studies, As(III) was generally predominant under reducing conditions while As(V) was predominant under oxidizing conditions. Korte and Fernando (1991) found only As(III) in shallow wells in an alluvial aquifer in Missouri.

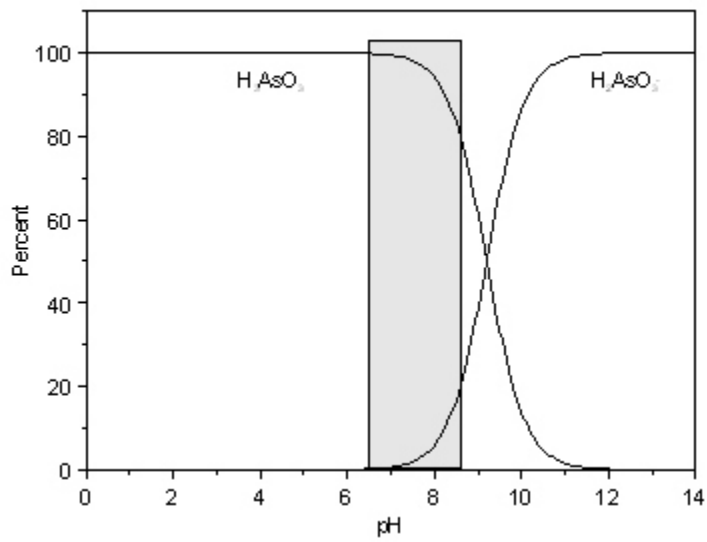


Figure 4. Concentrations of the As(III) species H_3AsO_3 and $H_2AsO_3^-$ at different pH values. The shaded area is the pH range of most groundwaters.

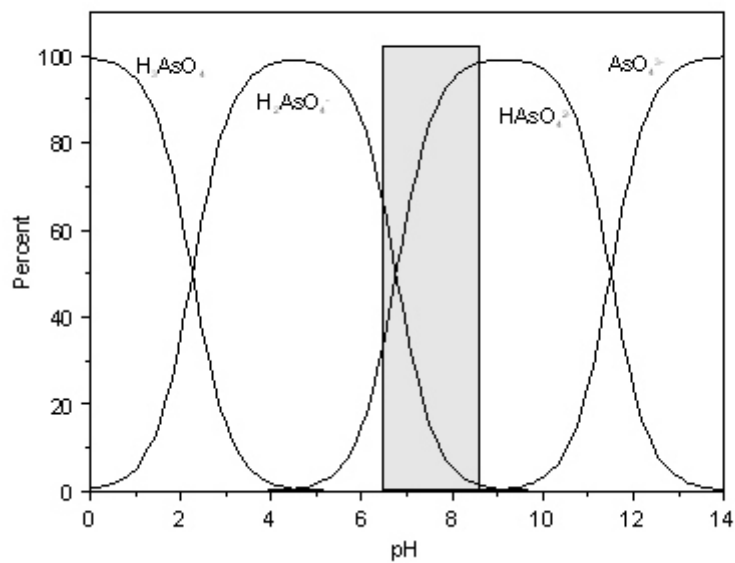


Figure 5. Concentrations of the As(V) species H_3AsO_4 , $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-} at different pH values. The shaded area is the pH range of most groundwaters.

While there are several important arsenic minerals (e.g., arsenopyrite (FeAsS) and orpiment (As_2S_3)), most arsenic in the solid phase is associated with common iron minerals, including iron oxyhydroxides (e.g., FeOOH) and pyrite (FeS_2). Arsenic may be released from these minerals by desorption or reductive dissolution of the arsenic-bearing mineral. The most common cause of widespread arsenic contamination is thought to be release from iron oxyhydroxides, probably due to the reaction of iron oxyhydroxides with organic carbon (Welch et al., 2000). Oxidation of sulfide minerals such as pyrite is also an important source of arsenic, and has been identified as the primary arsenic source in some aquifers in Wisconsin and Michigan (Schreiber et al., 2000).

Both As(III) and As(V) adsorb to particles of the hydrous oxides of iron (Pierce and Moore, 1982) and aluminum (Anderson et al., 1976). That is, under certain conditions addition of iron or aluminum oxide to an As(III) or As(V) solution will reduce the dissolved arsenic concentration even though the solution is undersaturated with respect to known arsenic-containing minerals. Sorption of As(V) depends on the pH. In simple systems with only iron and arsenic, sorption is nearly complete at low pH values and low at high values (Figure 6). The transition region shifts to higher pH values for higher iron to arsenic ratios.

Arsenic sorbs to many common aquifer materials, such as metal oxides and clays, and this is what is thought to limit the mobility of arsenic in most aquifer systems. Hydrous ferric oxide (HFO) sorbs both As(V) and As(III) (Pierce and Moore, 1982). If HFO is subsequently reduced, the sorbed arsenic may be re-released into solution. At neutral pH values As(III) is more mobile than As(V) because it is less strongly adsorbed on most mineral surfaces. Aqueous carbonate,

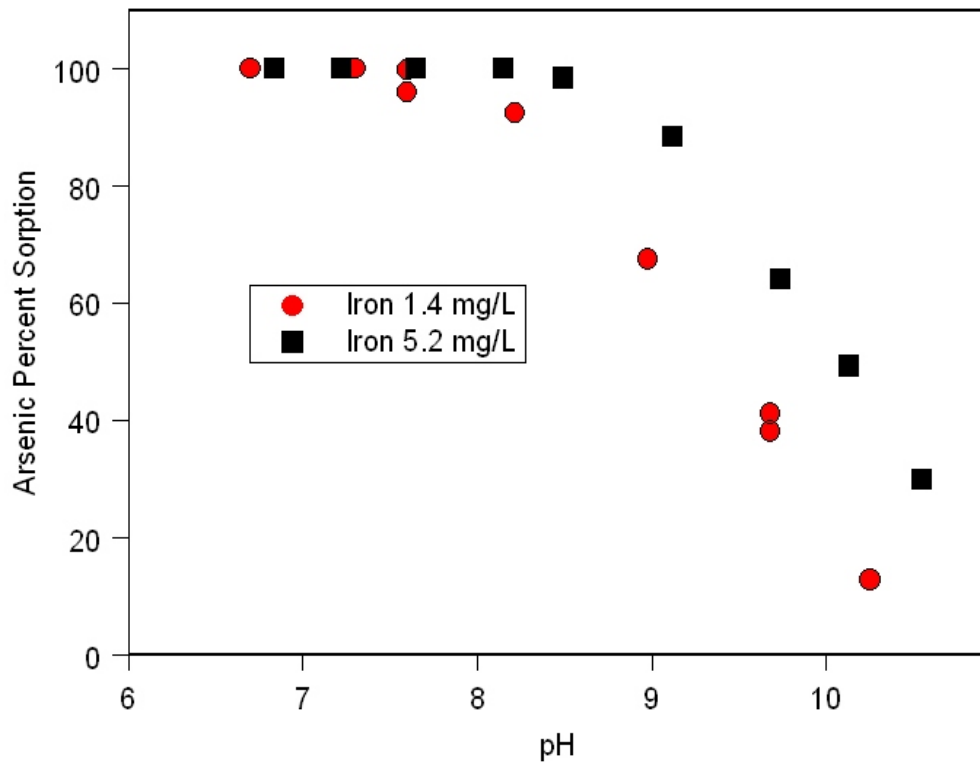


Figure 6. Sorption of As(V) to hydrous ferric oxide as a function of pH for two different iron concentrations. Total arsenic concentration was 38 μ g/L (Holm, 2002).

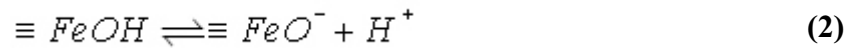
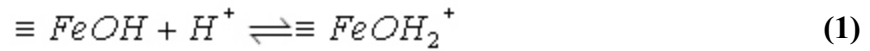
ferrous iron, and organic matter (OM) in groundwater can influence the sorption of arsenic.

Sorption of carbonate at common groundwater concentrations significantly reduces the tendency of arsenic to sorb on HFO, and high concentrations of carbonate could cause the displacement of arsenic (Appelo et al., 2002). Silica and phosphate may also interfere with arsenic sorption or promote arsenic desorption (Manning and Goldberg, 1996; Swendlund and Webster, 1999; Meng et al., 2000; Holm, 2002). Organic matter may influence arsenic sorption to HFO (Redman et al., 2002) and, as a result, increase arsenic mobility in aquifer systems. High concentrations of free sulfide due to sulfate reduction reactions may cause precipitation of sulfide minerals, such as

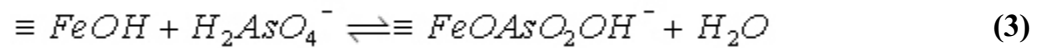
As₂S₃ or FeAsS, removing arsenic from solution (Rittle et al., 1995; Smedley and Kinniburgh, 2002).

Modeling Arsenic Adsorption

Dzombak and Morel (1990) developed a model for the adsorption of metal ions and anions to hydrous ferric oxide (HFO). The model assumes that the HFO surface has hydroxyl groups ($\equiv\text{FeOH}$) that can gain or lose a H⁺ ion (equations 1 and 2).



The net charge of the HFO surface is determined by the relative concentrations of the positive and negative hydroxyl groups. Anions adsorb to HFO by ligand exchange with the surface hydroxyl groups, which also affects the surface charge.



The relative concentrations of dissolved and sorbed anions and charged and uncharged hydroxyl groups is given by mass action equations. For the reaction in equation 3,

$$K = \frac{[\equiv \text{FeOAsO}_2\text{OH}^-]\{C\}}{[\equiv \text{FeOH}][\text{H}_2\text{AsO}_4^-]} \quad (4)$$

where K is the equilibrium constant, square brackets indicate concentrations, and the coulombic term (C) accounts for the interactions between the charged surface and the ions. Because the form of equation 4 is identical to those of more familiar mass action equations, such as acid dissociation, adsorption reactions can be included in chemical equilibrium computer programs. Dzombak and Morel (1990) fit their model to data from many HFO adsorption experiments, including those involving As(V) and As(III). The popular equilibrium program Mineql+ (Schecher and McAvoy, 1994) includes the Dzombak and Morel (1990) model and sorption equilibrium constants.

The data that Dzombak and Morel (1990) fit their model to involved HFO that had been pre-formed and aged to improve reproducibility. However, freshly precipitated HFO has a higher As(V) sorption capacity than pre-formed HFO (Edwards, 1994; Holm, 2002). Holm (2002) found that the Dzombak and Morel (1990) model can successfully model As(V) sorption to freshly precipitated HFO if it is assumed that the iron concentration is ~ 3.8 times the actual iron concentration and that the effects of bicarbonate (HCO_3^-), silica, and phosphate on As(V) sorption to HFO can be modeled to varying degrees of success.

Arsenic Removal at Water Treatment Plants

Few water treatment plants were designed specifically for arsenic removal. However, some arsenic is typically removed at treatment plants designed for iron removal (McNeill and Edwards, 1995) and coagulation (Hering et al., 1997). In both processes, soluble arsenic sorbs to insoluble hydrous ferric or aluminum oxide and gets filtered out.

Many factors affect sorption of arsenic to metal oxides and, therefore, the efficiency of arsenic removal, including the metal to arsenic ratio, the pH, the arsenic oxidation state, and the concentrations of other substances that sorb to (HFO). Higher iron to arsenic ratios favor higher arsenic removal (Wilkie and Hering, 1996). The HFO surface is positively charged and therefore attractive to anions, including $\text{H}_2\text{AsO}_4^-/\text{HAsO}_4^{2-}$ at low pH values and negatively charged and therefore repulsive to anions at high pH values (Dzombak and Morel, 1990). The first pK_a value of arsenious acid is approximately 9.2, so for $\text{pH} < 9.2$, As(III) is not repelled by the negatively charged HFO surface, while the anionic As(V) is. However, under some conditions As(III) is less efficiently removed from water than As(V) (Hering et al., 1996). Several substances that are commonly found in natural water, including bicarbonate (Appelo et al., 2002), silica (Swendlund and Webster, 1999), phosphate (Manning and Goldberg, 1996), and natural organic matter (NOM) (Redman et al., 2002), interfere with arsenic sorption to HFO (Holm, 2002).

All iron removal processes involve oxidizing soluble ferrous iron (Fe^{2+}) to insoluble HFO. Air is used as the oxidant in many water treatment plants, including many in Illinois. Although As(III) is oxidized by dissolved oxygen, the rate of oxidation is slower than that of Fe^{2+} (Hug and Leupin, 2003), so As(III) oxidation by air is likely to be incomplete. Potassium permanganate (KMnO_4) and sodium hypochlorite (NaOCl) are used in some Illinois water treatment plants. Both KMnO_4 (Borho and Wilderer, 1996) and NaOCl (Frank and Clifford, 1986) rapidly oxidize both Fe^{2+} and As(III).

Manganese greensand (MGS) is used for iron removal in some water treatment plants. Greensand contains glauconite, a clay with exchangeable potassium (K^+) ions. MGS is produced by exchanging manganous ions (Mn^{2+}) for the K^+ ions and then treating with $KMnO_4$ to produce a material with a manganese oxide coating. Oxidized MGS is used to treat water with Fe^{2+} and hydrogen sulfide. It acts as both an oxidant and a filter. Laboratory studies have shown that MGS can remove arsenic from Fe-containing water. The removal efficiency depends on the Fe to arsenic ratio and the pH (Subramanian et al., 1997; Anonymous, 1999). A full-scale treatment plant using MGS filtration was constructed in Kelliher, Saskatchewan, to remove iron and hydrogen sulfide from groundwater. When a new well was drilled it was found that the water contained an unacceptably high amount of arsenic. However, the MGS filter reduced the arsenic concentration to below the water quality standard (Magyar, 1992).

Coagulation involves adding one or more chemicals to facilitate the removal of particulate material from water, usually to reduce turbidity. Ferric chloride and alum are used in coagulation. They form hydrous oxides of iron and aluminum which interact with the particulate material and make filtration easier. The metal oxides can also adsorb arsenic, if any is present. Pilot- and full-scale tests of arsenic removal by coagulation have been run (Cheng et al., 1994; Scott et al., 1994). As in the iron removal processes, arsenic removal by coagulation depends on the metal to arsenic ratio, pH, arsenic oxidation state, and concentrations of other substances.

METHODOLOGY

Public Water Supplies

Selection of Community Supplies

In 2001, the IEPA compiled a list of community public water supplies in Illinois that had source (raw) water arsenic concentrations above 10 µg/L, and of those facilities that would potentially exceed the new MCL in their finished (treated) water. More than 150 supplies were identified on the IEPA list. These supplies included cities and towns, mobile home parks, and subdivisions. Fifty-five of these routinely had finished water with arsenic above 10 µg/L. Of these 55, 11 that had wells in the Mahomet Aquifer were previously sampled as part of the study that led to this effort (Holm et al., 2004), and 10 were mobile home parks or subdivisions that we chose not to sample. The remaining were 34 community facilities that made up our initial list of potential sites. One of these was a rural nursing home with a complete treatment system and was therefore included in the list. The selected facilities were prioritized based on the following criteria: the level of arsenic, the number of wells, geographic location, aquifer type, and treatment processes. Because our sampling procedure included sampling both individual wells for raw water quality and a finished water at the treatment plants, facilities with 4 wells or fewer were selected ahead of facilities that used a large number of wells in order to maximize the number of facilities sampled.

The IEPA assisted by reviewing our list of potential sites and then sending letters to the selected facilities describing the project, informing the facility of the importance of the study, asking each to participate, and offering help in answering questions about the project. These voluntary activities by the IEPA were significant in securing participation from the communities sampled. The facilities were contacted to solicit their permission to sample, as well as to gather additional information about their treatment processes, raw water access for sampling, pumping schedules, and availability of personnel to assist on sampling days. Sampling days were scheduled so that several facilities could be sampled in a relatively small area and samples could be returned to the analytical laboratory in a timely manner.

Well records were analyzed for each facility to categorize the aquifer type, well depth, and well status for each well to better identify similarities in results and to assist in identifying factors that may influence arsenic levels and treatment effects.

Sample Collection

Sample Containers and Preservatives

Table 1 lists the sample containers and preservatives used. The containers for arsenic and metals were cleaned by filling with 8% (v/v) HCl, soaking at least 24 hours, and thoroughly rinsing with deionized water.

Special care was taken in collecting and storing groundwater samples for arsenic speciation.

There is no consensus in the literature about preserving arsenic speciation in water samples.

Analyte	Container Material	Preservative ⁴	Holding Time (days)
Arsenic Species ¹	HDPE ²	0.3% HCl	1
Total Arsenic ³	HDPE	0.3% HCl	30
Metals	HDPE	0.2% HNO ₃	180
Anions/Alkalinity	HDPE	None	2
Ammonia-N	HDPE	0.2% H ₂ SO ₄	24
Total Organic Carbon ³	Glass	0.5% H ₂ SO ₄	ASAP ⁵

Notes: ¹0.45 μm filtered samples.

²HDPE high-density polyethylene.

³Unfiltered.

⁴Percent by volume of concentrated high-purity acid.

⁵Holding time not specified for acidified samples.

Although some authors have found that As(III) oxidation was apparently inhibited by acidification (Aggett and Kriegman, 1987; Borho and Wilderer, 1997; Volke and Merkel, 1999), others have found the opposite (Eaton et al., 1998; Cabon and Cabon, 2000). For the present work it was decided that acidification was important because groundwater in Illinois has Fe²⁺ in solution, and Fe²⁺ oxidation might cause some arsenic to be sorbed. We used HCl as a preservative to avoid any oxidation of As(III) by HNO₃ and analyzed the samples as soon as possible after collection to minimize As(III) oxidation.

The preservative was added to the bottles before leaving on a sampling trip. Addition of preservative was performed in a class-100 clean air bench. Powder-free gloves were worn when handling the bottles. Bottle sets, consisting of one bottle for each analyte in Table 1, were

assembled in two-gallon Zip-Lock[®] bags. Some bags also contained an extra bottle for spiking with a mixture of As(III) and As(V).

Sample Collection

Before each sampling trip a multi-probe instrument for real-time measurement of temperature, specific conductance (SpC), pH, oxidation-reduction potential (ORP) using a platinum electrode, and dissolved oxygen (DO) (Mini-Sonde[®], Hydrolab, Austin, TX) was calibrated according to the manufacturer's directions. The treatment plant operators showed the sampling crews the locations of the sampling taps. The Hydrolab[®] flow cell was connected to the raw water tap and the readings were monitored until the values stabilized. The final readings were recorded along with the date, time, and sampling location. The readings were considered to be stable if the change in one minute was less than: temperature 0.1°C, SpC 5% of the initial value, pH 0.02 unit, ORP 5 mV. The readings typically stabilized within 5-10 minutes except for DO, which continued to drift downward. The DO probe responded very slowly to DO concentrations below ~ 1 mg/L, so if the DO reading fell to less than ~0.8 mg/L and was still falling, it was assumed that the DO was undetectable and the sample was then collected. Because of the high flow rates and the time necessary for the readings to stabilize, it was assumed that the well and pump were completely purged prior to sampling. In fact, most of the wells were operating when the sampling crew arrived at the site.

After the values of temperature, etc. were recorded, the flow cell was disconnected from the sampling line. One member of the sampling crew put on a pair of powder-free gloves. This

person was the only one to handle sample bottles. Unfiltered samples were collected for total organic carbon (TOC) and total arsenic. The sample tube was then connected to a 0.45 μ m filter capsule (Gelman) and filtered samples were collected for arsenic species, metals, anions, alkalinity, and ammonia-N ($\text{NH}_3\text{-N}$). The arsenic species sample was immersed in an ice-water bath immediately after collection. After all of the samples were collected the bottles were returned to their Zip-Lock[®] bag and the bag was stored in a cooler with ice. A treated water sample was collected by the same procedure.

Sampling Quality Assurance

Each sampling crew collected one extra arsenic species sample per day. This sample was spiked with a mixture of As(III) and As(V) to check for species stability. In most cases, this was done at the first sampling site of the day. Each day at least one crew collected a set of blanks by pumping deionized water through the sampling tubing and filter capsule with a peristaltic pump.

Chemical Analyses

Total Arsenic and Total Dissolved Arsenic

Arsenic concentrations were determined by inductively coupled plasma mass spectrometry (ICPMS). The arsenic concentrations in unfiltered and filtered samples were operationally defined as the total and total dissolved arsenic concentrations, respectively.

Arsenic Speciation

Arsenic species were determined at the Illinois Waste Management and Research Center (WMRC) in Champaign. Speciation for As(III), As(V), monomethylarsonic acid (MMAA), and dimethylarsinic acid (DMAA) were determined using HPLC-ICPMS (Holm et al., 2004)

Chromatograms obtained from the HPLC-ICPMS system are shown in Figure 7 for both a 40 $\mu\text{g/L}$ standard and a groundwater sample spiked with arsenic species at 5 $\mu\text{g/L}$. As evident from the figure, good separation of all four arsenic species was obtained. Detection limits for all four species in groundwater preserved in HCl were not formally determined but were easily observed

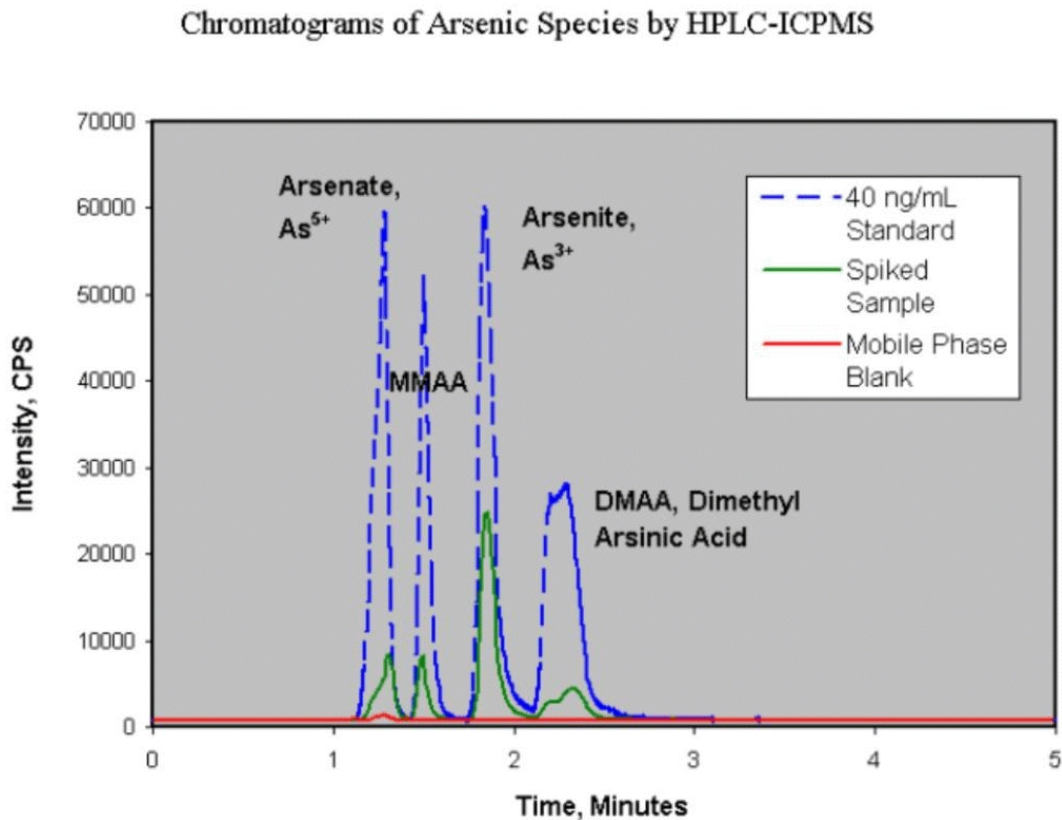


Figure 7. Chromatograms showing separation of As(V), monomethylarsonic acid, As(III), and dimethylarsinic acid by HPLC-ICPMS.

to be $< 0.5 \mu\text{g/L}$ for minimum 2x dilutions of samples, still substantially below the new arsenic MCL of $10 \mu\text{g/L}$.

Precision and Accuracy of the Analysis

Total dissolved arsenic was determined by ICP-MS with a correction for the $^{40}\text{Ar}^{35}\text{Cl}$ interference. For almost all samples for which both As(III) and As(V) were detectable, the relative difference between the total dissolved arsenic concentration and the sum of As(III) and As(V) was less than 10%. The only exceptions were a few samples with less than $1 \mu\text{g/L}$ total arsenic. Figure 8 compares total dissolved arsenic with As(III)+As(V). There was very good

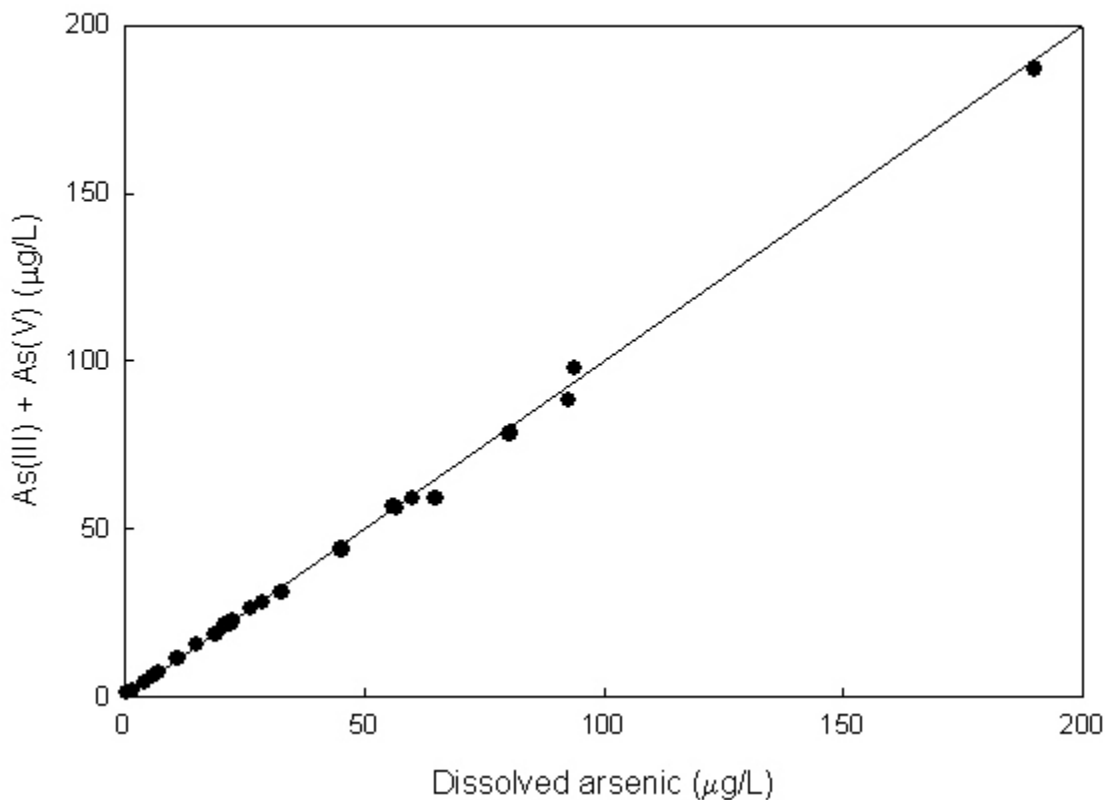


Figure 8. Comparison of sums of arsenic species concentrations determined by HPLC-ICPMS with total dissolved arsenic concentrations.

correlation between total dissolved arsenic and As(III)+As(V) (slope, intercept, and r^2 values were 0.98, 0.03, and 1.00, respectively). Therefore, there was very little bias in the method.

The precision of the speciation analysis was recently assessed by conducting replicate analyses of the same sample (Holm et al., 2004). Seven replicate analyses of a private well water sample spiked at just 0.5 $\mu\text{g/L}$ of both As(III) and As(V) yielded within-run relative standard deviations of 0.5 % and 0.7 %, respectively, for the inorganic arsenic species. These values are well within the data quality objective (DQO) for precision of analysis for the project.

Other Analytical Methods

Other analytes besides arsenic were determined using standard methods (Table 2). One of the project hypotheses was that arsenic speciation and solubility are consistent with the geochemistry of the aquifer. Therefore a comprehensive analysis was performed for all samples. Another hypothesis was that arsenic is removed at community water treatment plants to varying degrees depending on water chemistry and treatment processes. While this hypothesis is not strictly testable, comprehensive chemical analyses of the raw and finished water at the treatment plants were performed to determine any changes in total arsenic concentrations and arsenic speciation to evaluate which processes and operational variables provide the greatest arsenic-removal efficiency.

Analyte	Method	Reference	Laboratory
NH ₃ -N	EPA 350.1	USEPA (1993a)	ISWS
Alkalinity	USGS I-1030-85	USGS (1989)	ISWS
Anions (F ⁻ , Cl ⁻ , SO ₄ ²⁻ , NO ₃ ⁻ , PO ₄ ³⁻)	EPA 300.0	USEPA (1993b)	WMRC
Metals (Ca, Mg, Na, Fe, Mn, P, Si)	EPA 200.8	USEPA (1994)	WMRC
TOC	EPA SW-846/9060	USEPA (1986)	WMRC

Data Analysis

Pearson product moment correlation tests were run to measure the strength of association between arsenic and the other chemical parameters measured. This is a parametric test that assumes the residuals are normally distributed with constant variance and does not require the variables to be assigned as independent and dependent. The statistical software package SigmaStat (SPSS, 2003) was used.

Water Treatment Experiments

Danvers Water Treatment Plant

Water treatment experiments were performed using water from the Danvers, IL, water treatment plant. Danvers has a population of approximately 1,100. The water treatment plant uses water from three wells that withdraw water from the Mahomet Aquifer. The treatment processes are air oxidation, sand filtration, ion exchange softening (33% of flow), chlorination, and fluoridation. The groundwater has 30-40 g/L arsenic, mostly in the As(III) form and 1.5-3.0 mg/L Fe (Table 3). Only 20-25% of the arsenic is removed by the treatment system and the As(III) is almost completely oxidized to As(V). For the measured Fe:As ratio one would expect good arsenic

removal. However, the concentrations of bicarbonate, silica, organic matter, and phosphate are all high enough to interfere with arsenic removal.

In a subsequent visit to the Danvers plant, water samples were taken from Well 3, directly downstream from the sand filter, and after chlorination (finished water). The sampling crew used a membrane filter device to filter some samples. To avoid confusion, “filter” or “filtered” refer to membrane filtration and “sand filter” or “sand filtered” refer to the water treatment plant process. There was little particulate arsenic in the groundwater; filtered and unfiltered concentrations were nearly the same (Table 4). Most (~80%) of the arsenic was As(III). Aeration and sand filtration

Well	Water	pH	As(III) (g/L)	As(V) (g/L)	Na (mg/L)	Mg (mg/L)	Ca (mg/L)	Fe (mg/L)
3	Raw	7.0	32.8	6.2	220	22.7	52.4	1.5
4	Raw	7.0	37.4	3.8	130	35.1	75.8	3.0
5	Raw	7.0	32.6	5.6	165	32.3	69.3	2.1
5	Treated	7.0	<2.0	24.5	165	37.1	57.5	<0.1

Well	Water	Si (mg/L)	P (mg/L)	Cl (mg/L)	TOC (mg/L)	NH ₃ -N (mg/L)	Alkalinity (mg/L as CaCO ₃)
3	Raw	6.9	0.6	49	13	7.1	495
4	Raw	8.1	0.6	29	13	9.4	556
5	Raw	7.7	0.5	41	13	8.3	544
5	Treated	7.9	0.1	39	13	8.4	531

reduced the arsenic concentration by ~30% but the arsenic concentration in the finished water was above the MCL of 10 g/L. There was little oxidation of As(III) due to aeration. The As(III) was oxidized by chlorination.

The inadequate arsenic removal may have been caused by incomplete oxidation of As(III) or interference with sorption to HFO. The water treatment experiments were designed to test both hypotheses.

Table 4. Arsenic concentrations at different points in the Danvers treatment system.			
Sampling point	Arsenic concentration (g/L)		
	Total (unfiltered)	Dissolved (filtered)	As(III)
Well head	37.9	36.3	29.3
After aeration and filtration	25.2	24.7	20.3
Finished water	26.8	26.6	1.6

Arsenic Oxidation Experiments

Manganese greensand was obtained from Hungerford and Terry (Clayton, NJ). A column (1 in. or 2.54 cm dia.) was packed with ~100 cm³ of the material. The MGS was treated twice with 0.01M KMnO₄. The first treatment decolorized the KMnO₄ but the color persisted after the second treatment.

Column experiments were performed with water flowing into the top of the column. In the laboratory experiments water was pumped from a reservoir to the column (Figure 9). In experiments conducted at the Danvers water treatment plant, well water flow was controlled by a flow meter. The flow rate was 100 mL/min., corresponding to a loading rate of 5 gal. per min. per square foot. The larger reservoir contained 0.01M NaHCO₃ and 0.5 mM NaH₂AsO₃, which had approximately the same pH, alkalinity, and As(III) content as the Danvers groundwater. The

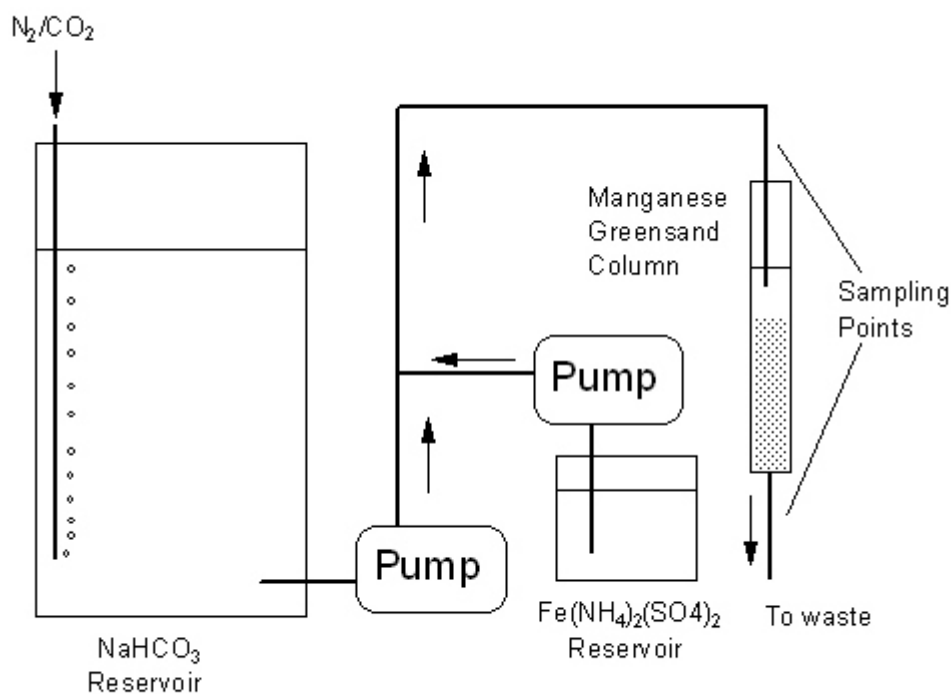


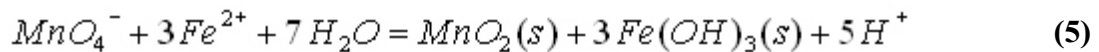
Figure 9. Experimental set-up for the manganese greensand column experiments. Thick lines indicate tubing and arrows indicate flow direction.

solution was sparged with a mixture of N₂ and CO₂ to remove dissolved O₂ and adjust the pH to 7.0 ± 0.05. Sparging for ~30 min. reduced the O₂ concentration to ~0.2 mg/L and further sparging did not cause any more reduction. This is consistent with research on O₂ sparging (Butler et al., 1994). The ferrous iron had to be kept in a separate reservoir because the residual O₂ was sufficient to oxidize the ferrous iron in less than one hour (the experiment lasted about three hours).

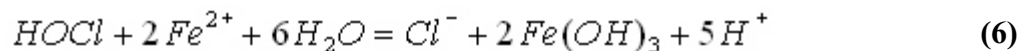
Influent and effluent samples were collected (Figure 9). In-line filtration was used to avoid exposure to air. After each experiment the column was back-washed to remove the HFO and the greensand was treated with KMnO_4 to restore its oxidizing capacity.

Additional oxidation experiments involved KMnO_4 and NaOCl . Freshly collected well water was analyzed for iron using a portable colorimeter (CheMetrics, Calverton, VA). Two series of bottles were prepared with no oxidant (control), and either KMnO_4 or NaOCl equivalent to 1, 2, or 3 times the iron concentration. Fresh well water was added to the bottles and the contents were filtered after a reaction time of ~1 hr. The filtrates were analyzed for dissolved arsenic and As(III) and for iron. Duplicate well water samples were also collected using the same procedure as in the treatment plant survey.

The KMnO_4 dose was estimated from the stoichiometry of the oxidation reaction.



Even though manganese dioxide (MnO_2) is capable of oxidizing As(III) to As(V) (Scott and Morgan, 1995), it was assumed that over the short residence time in a water treatment plant the reaction shown in equation 5 is the only important reaction and therefore the molar ratio of KMnO_4 to Fe^{2+} was 1:3. As for KMnO_4 , the NaOCl dose was estimated from the stoichiometry of the oxidation reaction.



In equation 6, HOCl (hypochlorous acid) is the conjugate acid of hypochlorite (OCl⁻). The pK_a of HOCl is 7.5, so at the pH value of Danvers groundwater (~7.0) the concentration ratio of HOCl to OCl⁻ is about 3.

Arsenic Adsorption Experiments

Coagulation/adsorption was tested as a method to further treat (“polish”) the finished water to get the arsenic concentration below the MCL. Finished water samples were collected from the Danvers plant. Varying amounts of 0.1M Fe(NO₃)₃/0.1M HNO₃ and NaOH equivalent to the HNO₃ was added to the finished water. The samples were filtered and analyzed for arsenic.

Chemical Analyses

Arsenic concentrations were determined by graphite furnace atomic absorption spectrophotometry using palladium as a matrix modifier (Clesceri et al., 1998). Anion exchange was used to determine As(III) (Ficklin, 1983; Edwards, 1998; Fields, 2000). In an acidified solution(0.05% H₂SO₄), As(V) and As(III) are in the anionic H₂AsO₄⁻ and uncharged H₃AsO₃ forms, respectively. The As(V) is retained by the resin, while the As(III) passes through. The effluent was analyzed by atomic absorption. A separate sample was analyzed for As(V)+As(III) and As(V) is calculated by difference.

Iron concentrations were determined by the phenanthroline colorimetric method (Clesceri et al., 1998).

RESULTS

Public Water Supplies

Arsenic Concentrations and Speciation

Raw water samples were collected from 52 wells in 33 communities. Ten of the wells (19%) had arsenic concentrations greater than 50 $\mu\text{g/L}$ and 38 (73%) had concentrations greater than 10 $\mu\text{g/L}$. Twenty-five of the communities had at least one well with arsenic greater than 10 $\mu\text{g/L}$. A total of 43 finished water samples were collected from the 33 communities. Two of the finished waters (Grand Ridge and Jewett) had arsenic concentrations greater than 50 $\mu\text{g/L}$ and 19 (44%) had arsenic greater than 10 $\mu\text{g/L}$. The arsenic in the raw water samples was predominantly As(III); in the 51 wells in which arsenic was detected, As(III) was greater than 70% of the total arsenic in 43 (84%). MMAA and DMAA were not detected in any of the samples.

There appeared to be particulate arsenic in some of the raw water samples. The difference between the unfiltered and 0.45 μm -filtered arsenic concentrations normalized to the unfiltered concentrations was less than 10% for about 71% of the samples, and negative for almost 30% of the samples (Figure 10). Most of the samples with high percentages of particulate arsenic had total arsenic concentrations less than 20 $\mu\text{g/L}$. However, four samples with total arsenic greater than 40 $\mu\text{g/L}$ had between 58 and 91% particulate arsenic: DeWitt County Nursing Home, Manlius 2 and 3, and Ridgway 3.

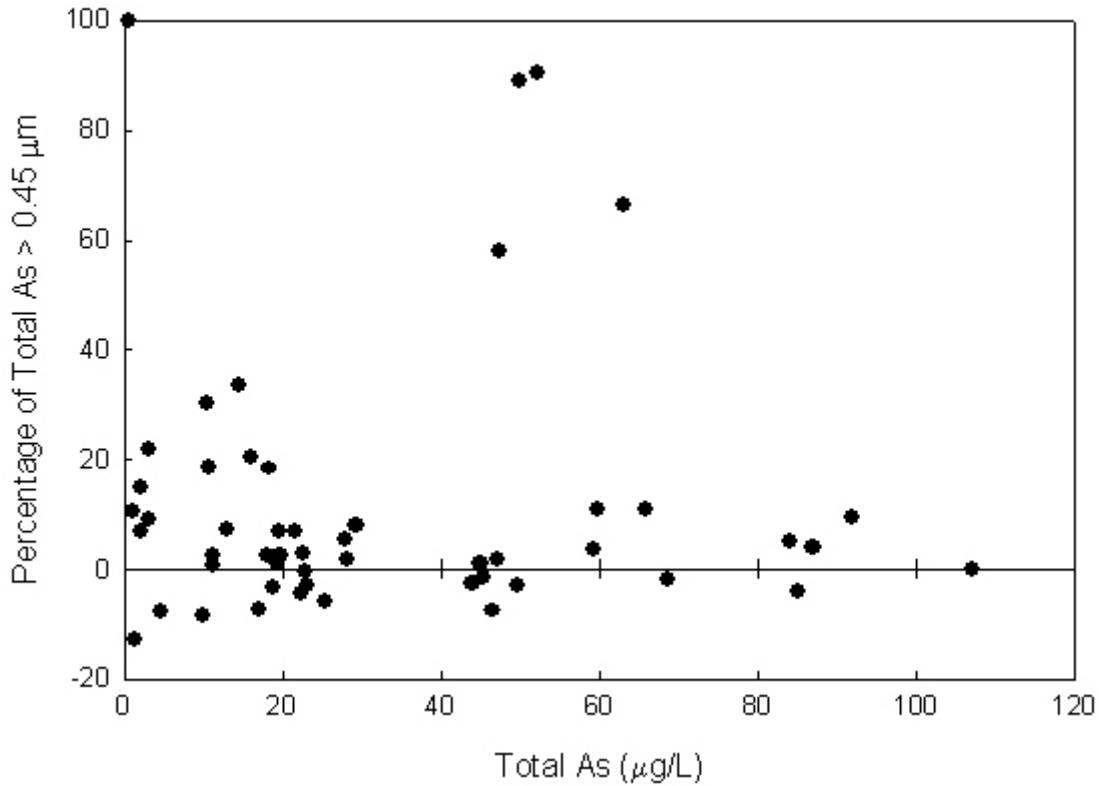


Figure 10. The percentage of particulate arsenic in raw water samples. Particulate arsenic is defined as the difference between concentrations in unfiltered and 0.45 μm -filtered samples.

The wells sampled in this study were finished in several different aquifers. Most of the wells were finished in sand and gravel aquifers, 17 in Illinoian aged (including Glasford) formations, and 22 in pre-Illinoian aged formations, primarily the Mahomet and Sankoty. Eight wells were finished in bedrock, five in Silurian carbonates, two in the St. Peter Sandstone, and one in Cambrian-Ordovician Sandstone. Arsenic concentrations were below 20 $\mu\text{g/L}$ in all of the bedrock wells, with only two exceeding 10 $\mu\text{g/L}$ (Figure 11). Wells in both the Illinoian and pre-Illinoian sand and gravel aquifers had wide ranges of arsenic concentrations.

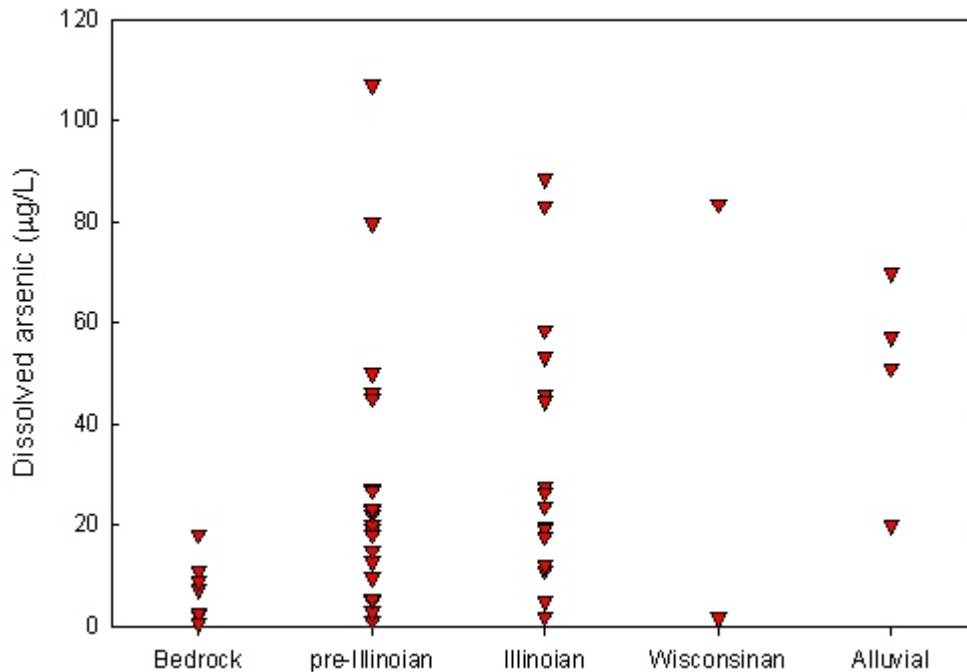


Figure 11. Arsenic concentrations in raw water samples as a function of aquifer type and depositional age.

Arsenic concentrations for individual wells are plotted on a map of Illinois in Figure 12. Wells with concentrations greater than 10 µg/L were found throughout the state. Interestingly, of the seven wells sampled south of the Mahomet Aquifer region, six had arsenic greater than 50 µg/L (two of the Ridgway wells plot on top of one another). Four of these wells were finished in alluvial aquifers and a fifth was finished in a Wisconsinan aquifer. The IEPA data also seem to indicate that a relatively large percentage of wells in these shallow aquifers have arsenic concentrations greater than 50 µg/L (Figure 3).

Geochemistry

Complete results of the Pearson product tests are shown in the Appendix A. Using all the data, arsenic was determined to be positively correlated with TOC, iron, NH₃-N, HCO₃⁻, sodium,

chloride, and phosphorus, and negatively correlated with ORP and well depth. When the wells were separated according to aquifer, there were generally fewer significant correlations; this is partly due to having smaller data sets. The pre-Illinoian wells had the most correlations, with arsenic being positively correlated with TOC, iron, $\text{NH}_3\text{-N}$, HCO_3^- , sodium, chloride, and phosphorus.

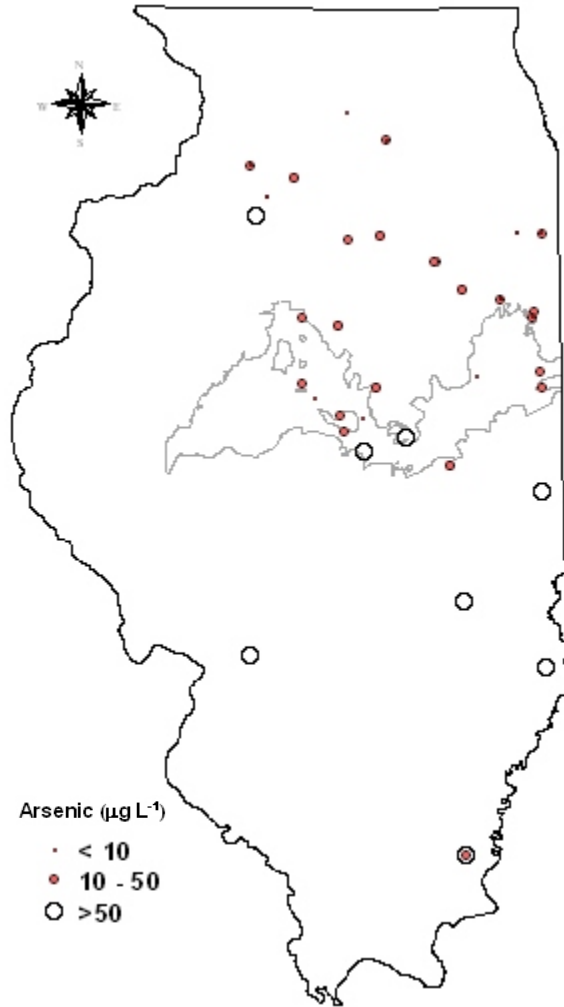


Figure 12. Dissolved arsenic concentrations in raw water samples. The areal extent of the Mahomet Aquifer is outlined.

Arsenic concentrations in the Mahomet Aquifer are related to other redox-sensitive parameters, primarily sulfate, $\text{NH}_3\text{-N}$, TOC, and bicarbonate (Holm et

al., 2004). For example, arsenic and sulfate tend to be mutually exclusive, i.e., if one is present the other generally is not detected. This relationship was also generally observed for the wells sampled in this study, with a few exceptions (Figure 13). This relationship was not identified by the Pearson test because it is not a linear relation. Complete chemical results are found in Appendix B. This relationship was least apparent for the bedrock wells, which had relatively high sulfate concentrations compared to most of the sand and gravel wells. Arsenic is plotted

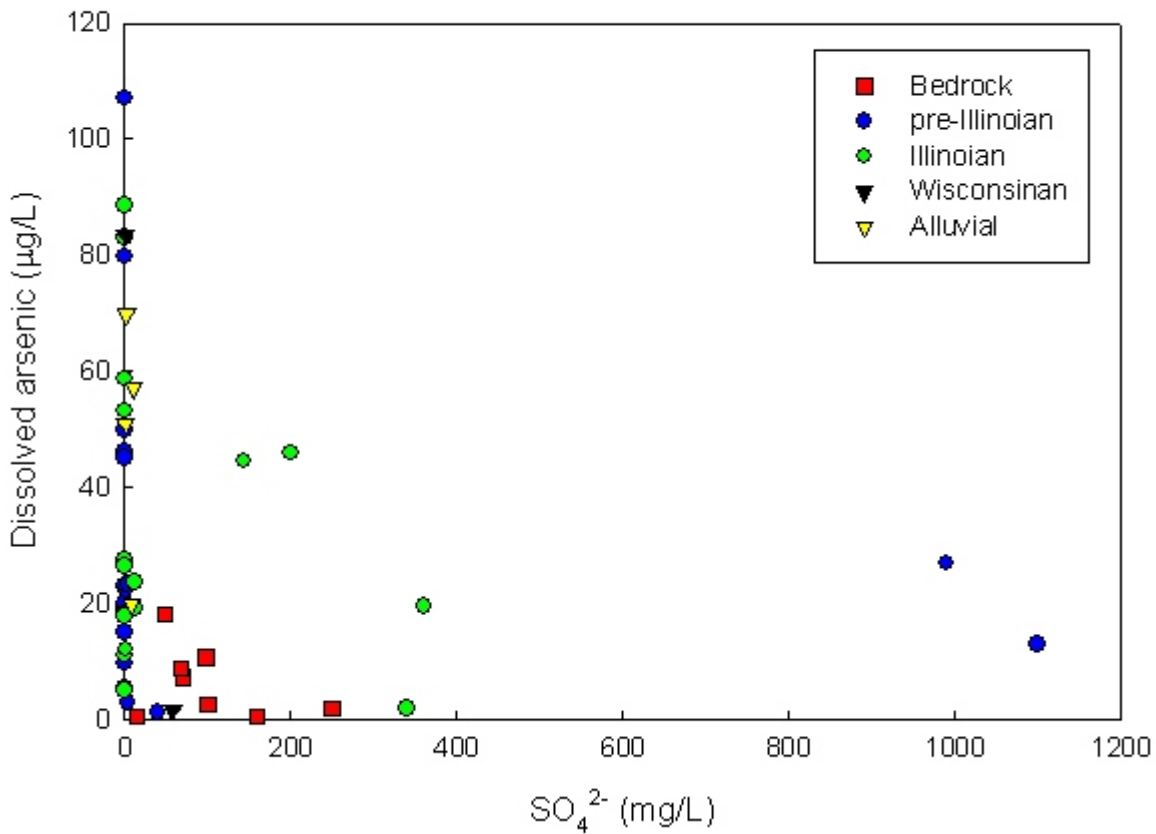


Figure 13. Dissolved arsenic concentrations as a function of sulfate concentrations in raw water samples.

against other redox sensitive parameters ($\text{NH}_3\text{-N}$, TOC, iron, manganese, bicarbonate, and ORP) in Figure 14. While arsenic concentrations tended to increase with increasing concentrations of all of these parameters except Mn and ORP, there was considerable scatter in the data.

Treatment Relationships

The predominant arsenic species in raw groundwater at most facilities was As(III). In most samples As(III) accounted for over 90% of the dissolved arsenic. However, in most treated waters As(V) accounted for almost 100% of the dissolved arsenic (Figure 15). All facilities

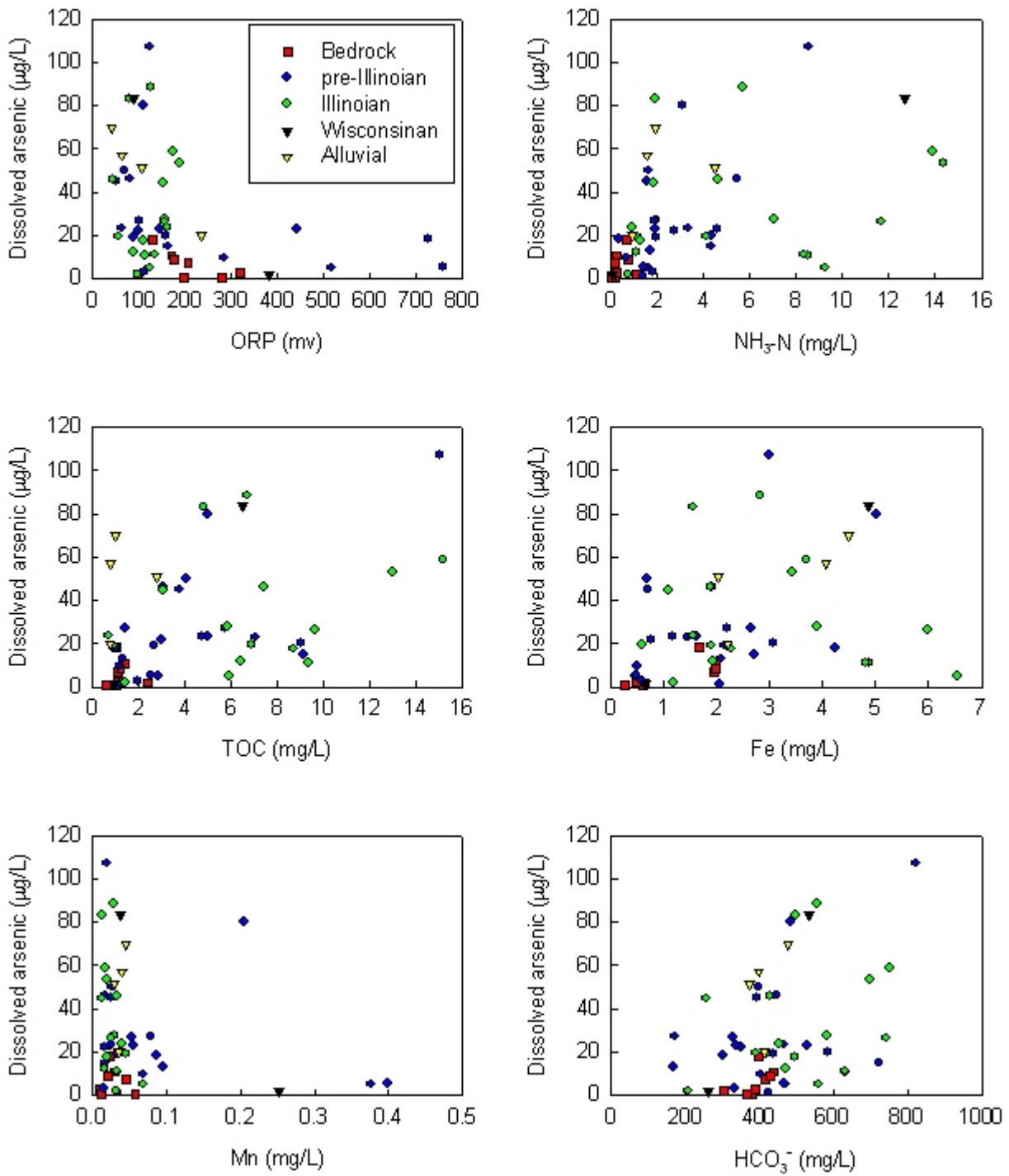


Figure 14. Dissolved arsenic concentrations as functions of various constituent concentrations in raw water samples.

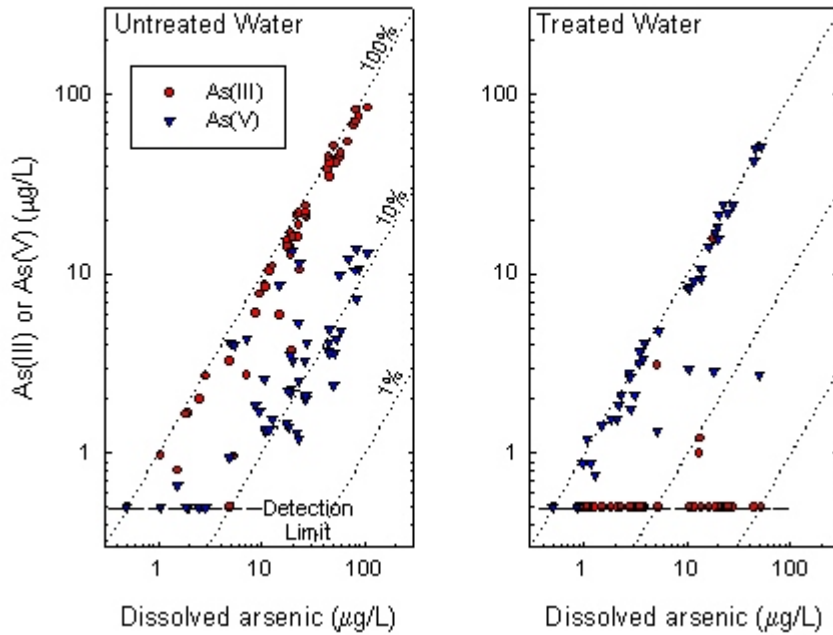


Figure 15. Arsenic species in untreated and treated groundwater.

added chlorine for disinfection, but the amount of chlorine was apparently inadequate for As(III) oxidation at a few facilities because As(III) accounted for 100% of the dissolved arsenic at four facilities and ~ 10% at two others.

Because arsenic removal depends on sorption of arsenic to HFO, we divided the data into three groups on the basis of the iron to arsenic ratio. The lowest arsenic concentrations in treated waters were generally found for the systems with the highest iron to arsenic ratios, the highest arsenic concentrations were found for the lowest ratios, and intermediate concentrations were found for intermediate ratios regardless of the total arsenic concentration in untreated water (Figure 16). There was some overlap, but the iron to arsenic ratio was a fairly good predictor of final arsenic concentration. For communities unfortunate enough to have high arsenic or low iron

concentrations in their raw water, addition of iron may help to reduce arsenic concentrations in their treated water.

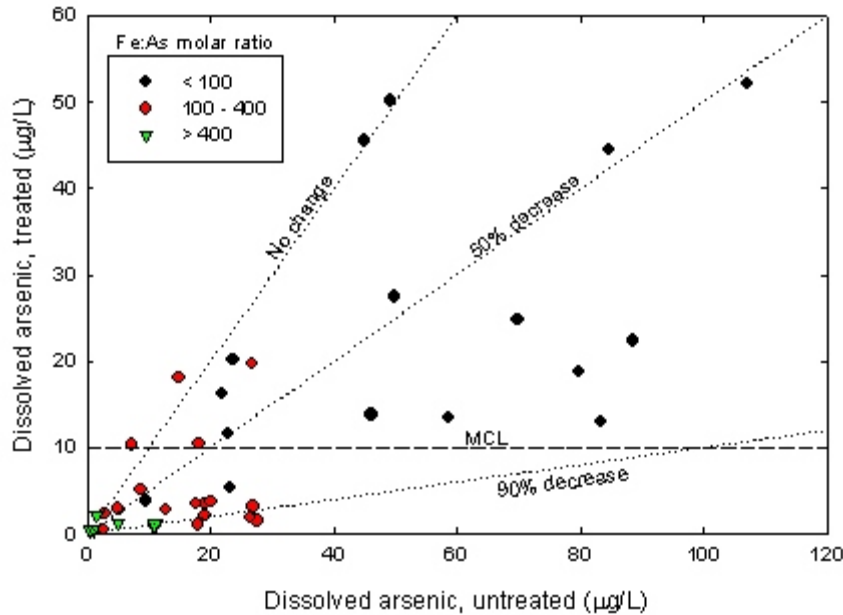


Figure 16. Arsenic in treated water as a function of concentration in raw water for different iron to arsenic ratios.

All of the water treatment plants in the present work had iron in their raw water and they dealt with the iron either by removing it or by adding polyphosphate to inhibit “red water” formation. Some of the water treatment plants remove iron by aeration while others add chlorine or KMnO_4 before or in place of aeration (preoxidation). Figure 17 shows the dissolved (0.45 µm filtered) arsenic concentration in treated water as a function of the dissolved concentration in untreated well water. The dissolved concentration is the theoretical minimum concentration that could be achieved by nearly complete removal of particulate material. For most of the facilities that do not remove iron there was no reduction in dissolved arsenic; the dissolved arsenic concentrations in

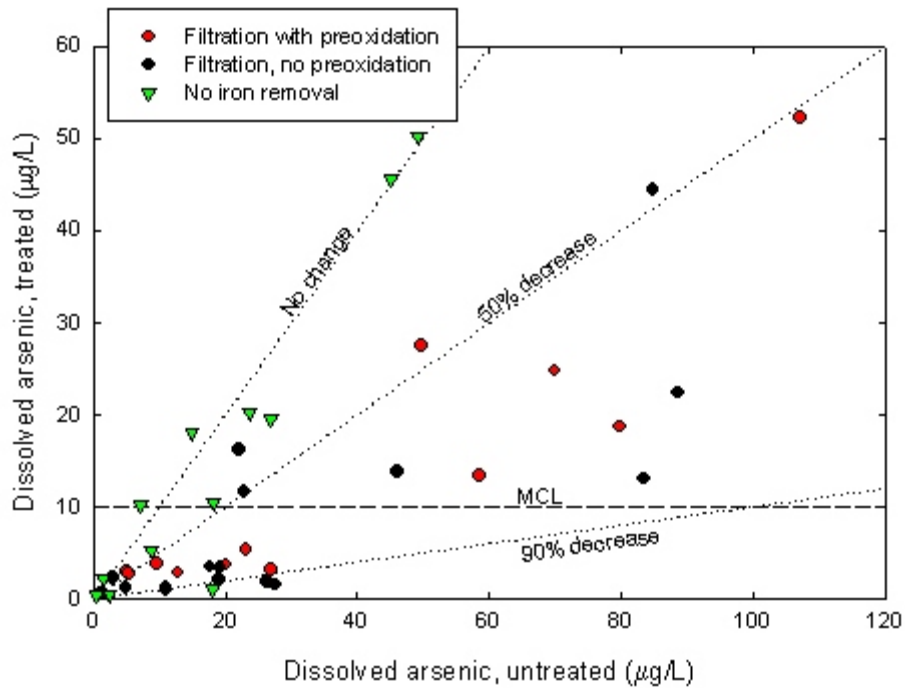


Figure 17. Dissolved arsenic concentrations in treated water as a function of untreated water concentration and for different methods of iron removal (0.45 µm filtered).

the treated-water samples were nearly the same as in the well-water samples. For five of these facilities, the finished-water dissolved arsenic concentrations were less than 10 µg/L because the raw water had less than 10 µg/L. For two of these facilities there were significant reductions in dissolved arsenic (50% and 90%). However, the dissolved iron concentrations also decreased at these facilities, probably because the polyphosphate addition was insufficient to keep all of the soluble iron from oxidizing to HFO. The dissolved arsenic reduction was probably caused by sorption to the HFO.

There was some reduction in dissolved arsenic at all iron-removal plants. The dissolved arsenic concentration in treated water was less than 10 µg/L for raw-water concentrations up to ~30

$\mu\text{g/L}$. There were no apparent differences in dissolved arsenic reduction between facilities that used preoxidation and those that did not.

The reduction in dissolved arsenic was 80-100% for almost all samples with up to $30 \mu\text{g/L}$ in the raw water (Figure 18). A few plants with high arsenic concentrations pulled the regression line down to 66%. For most of the non-iron-removal plants the change in dissolved arsenic was $\sim 0 \pm 4 \mu\text{g/L}$, which is probably the combined uncertainty of sampling and analysis. There was essentially no decrease in arsenic concentrations at Grand Ridge, whose treatment consists of the addition of polyphosphate and chlorination.

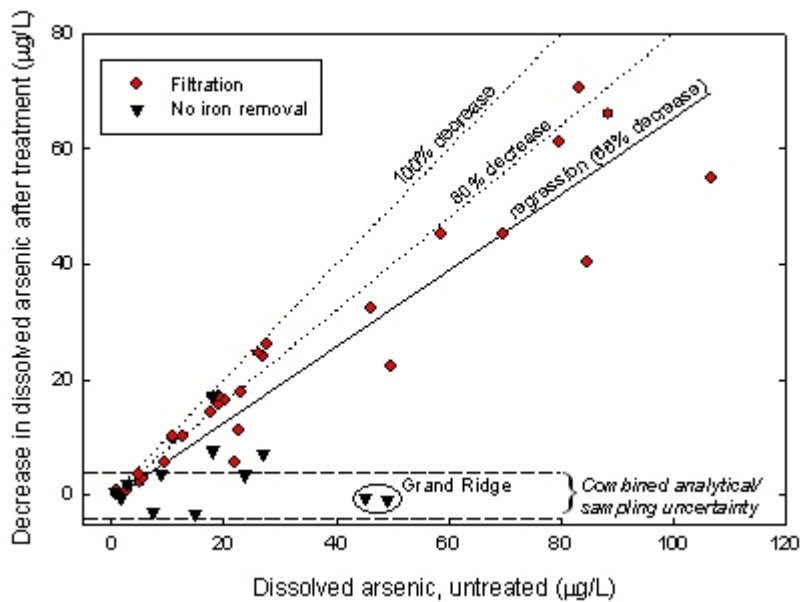


Figure 18. Percent decrease in dissolved arsenic concentration due to filtration. Regression does not include Grand Ridge wells.

Figure 19 shows the total (unfiltered) arsenic concentrations in treated water as a function of untreated well-water concentrations. Total arsenic concentrations reflect the combined efficiency of adsorption and filtration. There was some arsenic removal at all iron removal plants but one, although there was no apparent difference in arsenic removal between plants that used preoxidation and those that did not (Figure 19). There was no arsenic removal at the facilities that did not remove iron. Although this may seem intuitively obvious, it is important to remember that these treatment plants were designed to deal with iron, not arsenic.

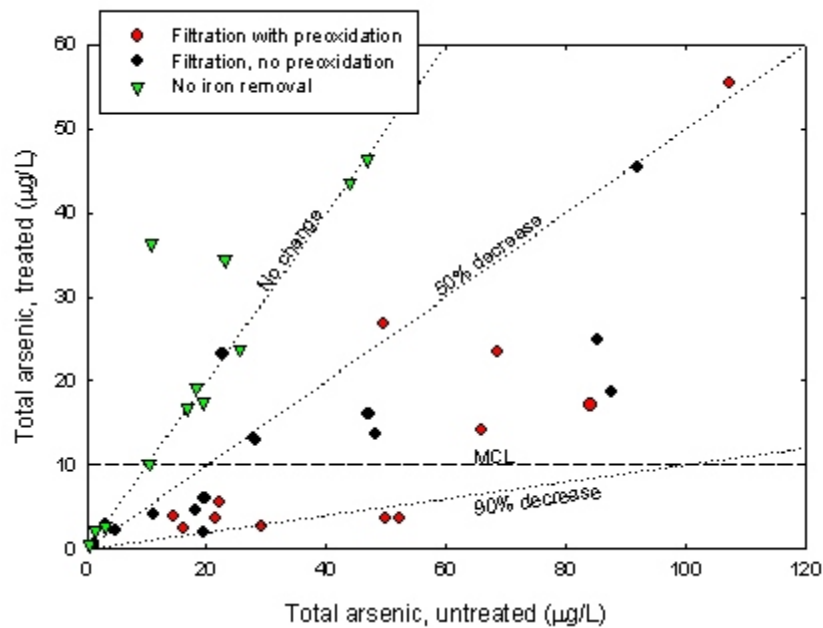


Figure 19. Total arsenic concentrations in treated water as a function of untreated water concentration and for different methods of iron removal.

The data for all facilities but two are plotted in Figures 16, 17, and 19. Dwight and Ashkum have two and three wells, respectively, and the raw waters were blended before treatment. For both

facilities the raw-water total arsenic concentrations in the wells were quite different so we assumed that a valid comparison of raw-water and finished-water arsenic concentrations was impossible. For Ashkum the raw-water concentrations were 45.0, 2.2, and 2.1 $\mu\text{g/L}$, while for Dwight the concentrations were 18.9 and 45.3 $\mu\text{g/L}$. Five other facilities had two or more wells and blended the raw waters before treatment, but we considered the arsenic concentrations to be similar. For example, the raw-water concentrations in the Ohio samples were 25.5 and 23.0 $\mu\text{g/L}$. Nine facilities had two or more wells but both raw and treated samples were collected for each well. Seventeen facilities had only one well.

Arsenic removal at some water treatment plants may not have been as efficient as it could have been. At the iron removal plants the finished water had gone through the sand filter for iron removal. However, the sampling crew performed additional filtration through a 0.45 μm filter. Those samples the crew filtered are referred to as filtered samples. Finished water samples that were not filtered through the 0.45 μm filter are referred to as unfiltered samples. For some facilities the arsenic concentrations in the unfiltered finished water samples were above the MCL but the concentrations in the filtered samples were below the MCL (Figure 20). Improvements in filtration at these facilities may improve arsenic removal and may even allow some facilities to satisfy the new MCL.

Besides the iron to arsenic ratio, the other parameters that may affect arsenic removal are the pH and concentrations of bicarbonate, phosphate, silica, and organic carbon. The data suggest that pH affects arsenic removal at varying ratios of iron to arsenic. For the lowest ratios the arsenic

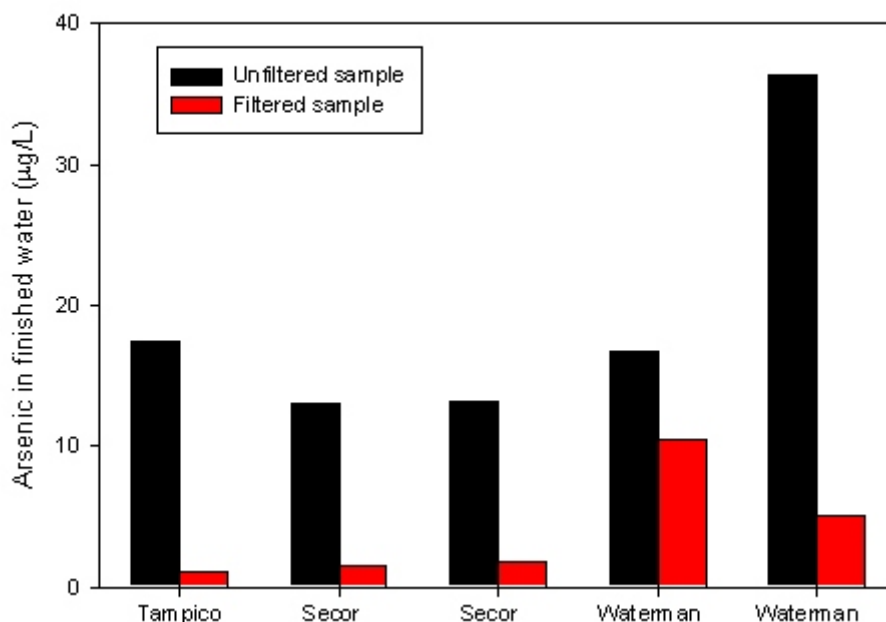


Figure 20. Arsenic concentrations in filtered and unfiltered samples of finished water at selected treatment plants. Secor and Waterman alternate wells which changes their finished water quality depending on which wells are being utilized.

removal generally decreases with pH in qualitative agreement with controlled sorption experiments. For the highest ratios arsenic removal is essentially independent of pH, which is also consistent with experiments. For intermediate ratios there is no apparent dependence on pH.

Arsenic removal efficiencies generally decreased with increasing concentrations of phosphate (Figure 21). Although the correlation for phosphate was rather weak and there were a few outliers, the trend was consistent with controlled experiments. On the other hand, it was hard to discern any effect of alkalinity, silica, or organic carbon on arsenic removal, even though these substances are also expected to compete with arsenic and reduce its tendency to sorb to HFO (Figure 21).

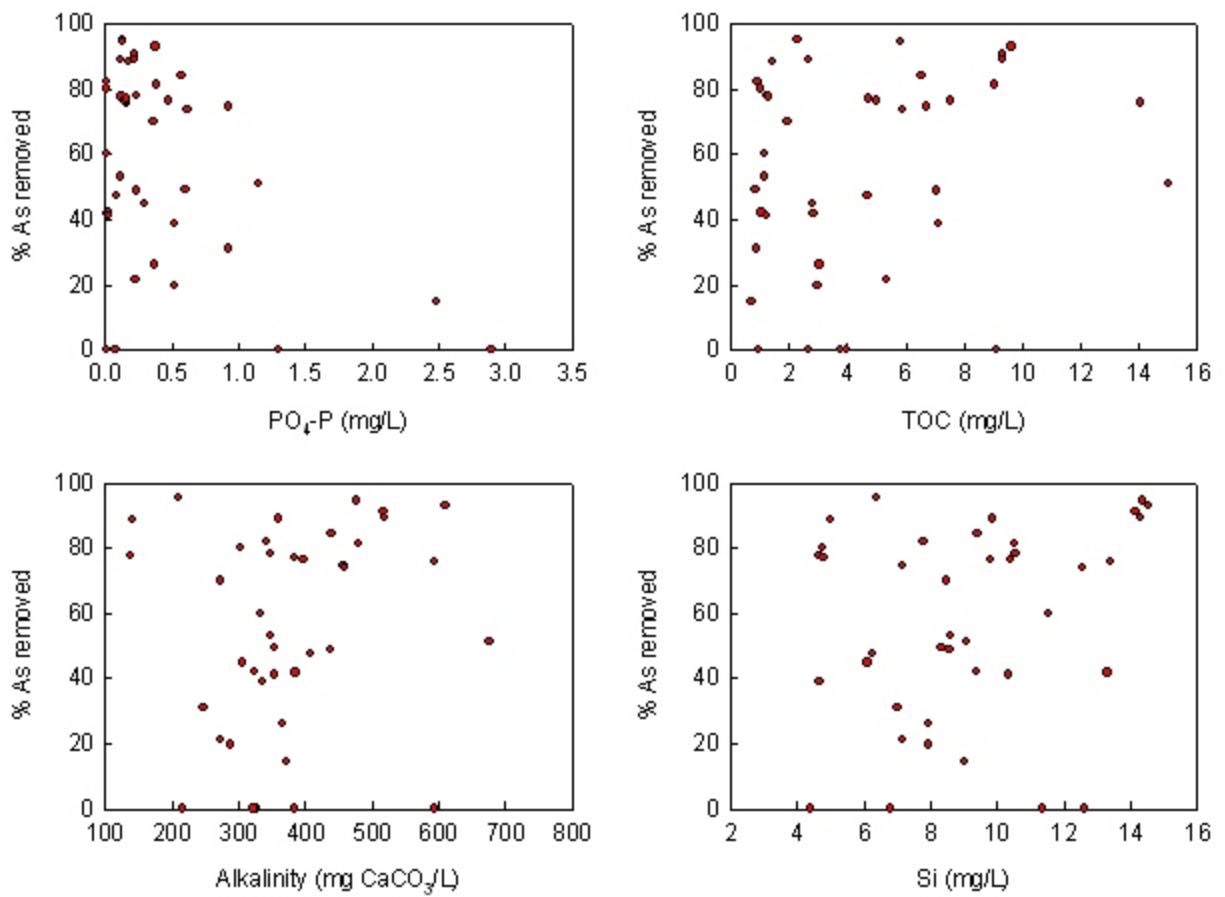


Figure 21. Arsenic removal efficiency plotted as a function of Phosphate, Total Organic Carbon, Alkalinity, and Silica concentrations.

Water Treatment Experiments

Manganese Greensand Column Experiments

In the laboratory experiments only total arsenic concentrations in filtered and unfiltered samples were determined (i.e., no speciation). Although the arsenic concentration in the effluent was always less than in the influent, it was above the MCL and usually increased with time (Figure 22). There was no detectable iron in any filtered effluent sample, so the column still had some oxidizing capacity at the end of each experiment. (The iron concentration in filtered influent samples was the expected value, so there was no oxidation in the short time before the water reached the column.) There was no detectable iron in unfiltered effluent samples, so the precipitated HFO particles were efficiently trapped by the greensand column packing.

In the column experiment performed at the water treatment plant the results were similar to those obtained in the laboratory (Figure 23). The effluent arsenic concentrations varied with time, but were above the MCL in all samples. In most cases the arsenic concentrations in filtered and unfiltered samples collected at the same time were nearly the same, so there was little particulate arsenic. The total dissolved arsenic and As(III) concentrations in effluent samples were the same, so there was little As(III) oxidation in the column.

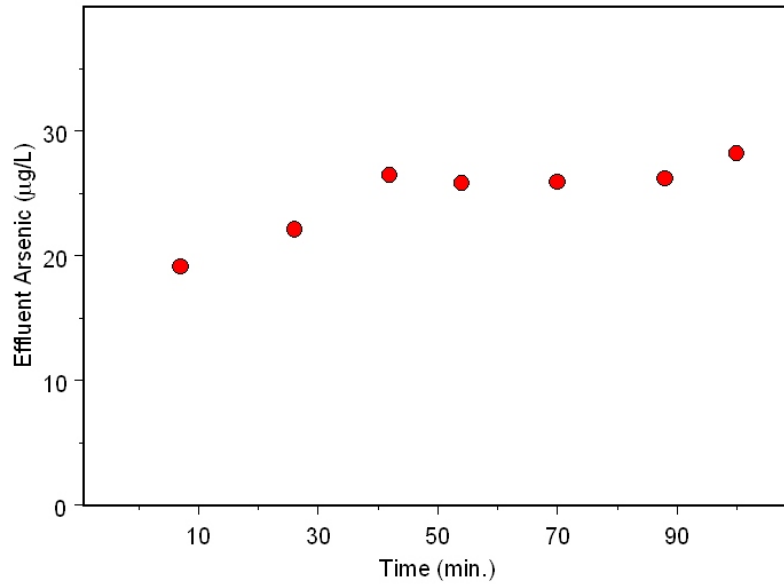


Figure 22. Effluent arsenic concentrations in a laboratory manganese greensand experiment. The influent contained 40 µg/L arsenic.

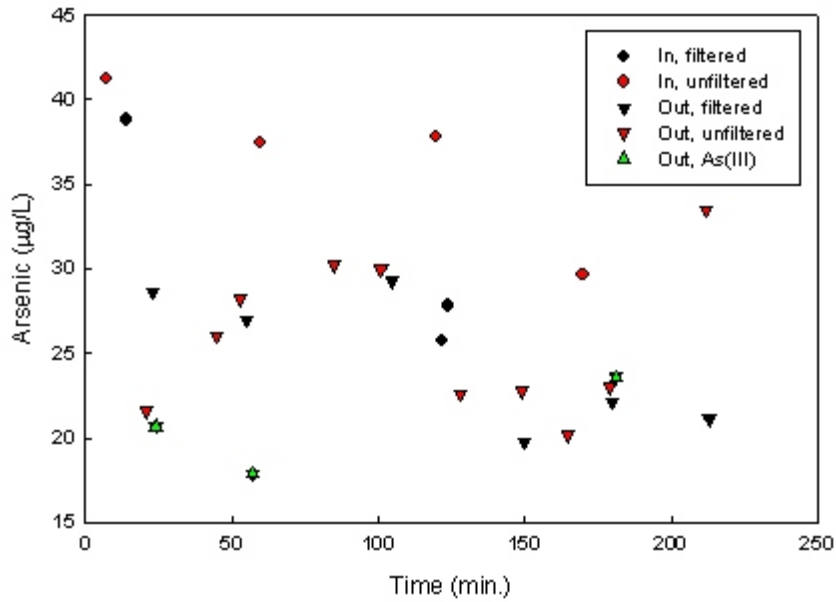


Figure 23. Influent and effluent arsenic concentrations in a manganese greensand experiment performed at the Danvers water treatment plant.

Batch Oxidation Experiments

The iron concentration in the raw well water was 1.65 mg/L or ~ 30 μM . The equivalent KMnO_4 dose was 10 μM or 1.6 mg/L. Increasing doses of KMnO_4 produced lower total dissolved arsenic concentrations, although the arsenic concentration produced by 4.8 mg/L KMnO_4 was still above the MCL (Table 5). For the lowest dose there was ~ 14 $\mu\text{g/L}$ remaining As(III) and ~ 2 $\mu\text{g/L}$ for the higher doses. All KMnO_4 doses completely oxidized the dissolved Fe^{2+} to HFO.

The NaOCl dose that was equivalent to 29.5 μM iron was ~ 15 μM or 1.2 mg/L. The two lowest NaOCl doses had little effect on total dissolved arsenic and the highest dose caused a slight reduction. All dissolved arsenic concentrations in the NaOCl treated samples were well above the MCL. The As(III) concentrations for the two lowest doses were approximately the same, while the highest NaOCl dose decreased the As(III) concentration by $\sim 50\%$. There were small amounts of unoxidized Fe^{2+} for the two lowest NaOCl doses.

Besides the samples with KMnO_4 or NaOCl added, two other sets of duplicate samples were collected. One set was immediately acidified with HNO_3 just as for the samples that were collected from the other treatment plants. These samples were meant to serve as a reference for all other samples. The other set had nothing added. These samples were meant to serve as a control for the oxidation experiment. There was clearly a problem with the control samples. One replicate had almost 150% as much arsenic as the duplicate groundwater samples while the other had less than 50%. The samples were discarded before they could be reanalyzed. Nevertheless, it is still possible to compare treated samples with the acid-preserved groundwater samples.

Oxidant	Dose (mg/L)	Fe (mg/L)	Total Dissolved As (g/L) ^b	As(III) (g/L)	Comment
None	– ^a	1.65	45.2, 45.6	– ^c	Initial sample
KMnO ₄	1.6	<0.05	32.8, 32.4	14.0, 13.7	
KMnO ₄	3.2	<0.05	21.8, 21.0	1.6, 2.0	
KMnO ₄	4.8	<0.05	18.5	1.7	
NaOCl	1.7	0.2	42.9, 45.9	30.8, 32.2	
NaOCl	2.4	0.1	45.5, 45.4	33.9, 30.8	
NaOCl	4.8	<0.05	40.0	24.4	
None	--	0.8	45.2, 45.6	--	Control

Notes: ^aNo oxidant added.

^bThe double entries indicate duplicate treatments.

^cNot analyzed.

Iron Addition for Polishing Tap Water

Addition of 4.5 mg/L iron reduced the dissolved arsenic concentration to approximately 1 g/L, and larger additions reduced it to undetectable levels (Table 6). The second coagulation experiment (Table 7) used smaller increments of added iron. The first iron addition of 0.9 mg/L

Iron Added (mg/L)	Arsenic (g/L)
0	36.2
4.5	1.2
9.0	<0.5
13.5	<0.5
18.0	<0.5
22.5	<0.5

reduced the dissolved arsenic concentration almost to the MCL and 1.8 mg/L iron reduced arsenic to less than 4 g/L, which is well below the MCL.

Table 7. Iron addition to tap water, 0-8.1 mg/L	
Iron Added (mg/L)	Arsenic (g/L)
0	27.4
0.9	11.0
1.8	3.8
2.7	1.9
3.6	1.2
4.5	1.2
6.3	1.4
8.1	0.9

DISCUSSION

Public Water Supplies

Distribution of Arsenic

The sampled community wells were selected because previous samples from these communities had arsenic concentrations greater than the new MCL. Therefore, the fact that about three-fourths of the wells had arsenic concentrations greater than 10 µg/L was not unexpected, and should not lead to the conclusion that most public water supplies in Illinois have arsenic contamination.

Sand and gravel aquifers appear to be more vulnerable to arsenic contamination than bedrock aquifers. Most of the bedrock wells sampled had arsenic less than 10 µg/L, and none exceeded 20 µg/L. It should be noted that only eight bedrock wells were sampled, only three of which could be defined as deep bedrock (greater than Silurian age). It is possible that other bedrock aquifers might have elevated arsenic. Studies in the Mahomet Aquifer in central Illinois suggest that in certain areas bedrock discharge into the sand and gravel aquifer may be introducing elevated arsenic, although the bedrock units themselves are not aquifers (Warner, 2001; Holm et al., 2004). Still, because the wells in this study were selected based on previously elevated arsenic levels, the fact that so few bedrock wells were selected and most of those had concentrations less than the MCL suggest that arsenic is not a major concern in most bedrock aquifers in Illinois.

If the Mahomet Aquifer is designated as the dividing line between north and south in Illinois, elevated arsenic concentrations were primarily found in wells sampled in the southern half of the state (Figure 12). Most of the wells sampled were in the Mahomet (or aquifers overlying the Mahomet) and north of the Mahomet. All of the bedrock wells were north of the Mahomet. Only one well north of the Mahomet had arsenic greater than 50 µg/L. In contrast, 6 of 7 wells sampled south of the Mahomet had arsenic concentrations greater than 50 µg/L. These wells included all of the wells in alluvial aquifers and one of the two wells finished in Wisconsinan deposits. Figure 3 also indicates that for those wells with elevated arsenic, nearly all of those south of the Mahomet Aquifer have As concentrations over 50 µg/L. It is unclear if these high arsenic values are an artifact of sample selection or represent geologic or geochemical conditions favoring elevated arsenic in solution. More detailed sampling in the southern part of the state is warranted.

Arsenic Geochemistry

There have been a number of studies of arsenic in aquifers throughout the world. Arsenic has been observed to correlate with different parameters depending on hydrogeological and geochemical conditions. The most extensive studies on the source and fate of arsenic in groundwater have been done in the shallow aquifers in Bangladesh and eastern India. The polluted groundwater is coming from organic-rich deltaic sediments, with highest concentrations in deeper, more reduced sections of the aquifers.

Investigators have reported different chemical correlations with arsenic. Arsenic and iron have been found to be associated in the solid phase (Nickson et al., 1998; Nickson et al., 2000; McArthur et al., 2001; Harvey et al., 2002), and sometimes in solution (Nickson et al., 1998; Nickson et al., 2000; Dowling et al., 2002) but sometimes not (Nickson et al., 1998; Nickson et al., 2000; McArthur et al., 2001). In most cases, arsenic was correlated with HCO_3^- (Nickson et al., 1998; Nickson et al., 2000; McArthur et al., 2001; Harvey et al., 2002). The correlation with HCO_3^- was determined to be due to reductive dissolution of iron oxyhydroxides coupled with oxidation of abundant organic matter in the sediments. The arsenic, either adsorbed to or co-precipitated with FeOOH , is released into solution, and HCO_3^- is produced from the oxidation of the organic carbon.

While it is clear that there must be some relation between iron and arsenic, we did not observe that they were correlated in solution. There may be several reasons for this, as suggested by (McArthur et al., 2001): (1) dissolved Fe may also come from weathering of minerals in addition to FeOOH ; (2) the Fe/As ratio in dissolving FeOOH is variable; and (3) Fe may be removed from solution into Fe minerals such as vivianite ($\text{Fe}_3(\text{PO}_4)_2$), siderite (FeCO_3), or pyrite.

In Bangladeshi samples, arsenic was also observed to be correlated with $\text{NH}_3\text{-N}$, methane (CH_4), dissolved organic carbon (DOC), and Ca (Dowling et al., 2002; Harvey et al., 2002). Arsenic was not found where DO or nitrate were present (Nickson et al., 1998; Nickson et al., 2000).

(Ravenscroft et al., 2001) and (Harvey et al., 2002) observed that arsenic and SO_4^{2-} tended to be mutually exclusive, and SO_4^{2-} was absent from the samples collected by (Dowling et al., 2002).

We observed that arsenic was weakly correlated with $\text{NH}_3\text{-N}$ and TOC. Although we did not measure CH_4 , it seems reasonable it would be correlated with arsenic and methane has been detected in many Illinoian and pre-Illinoian glacial deposits. (Meents, 1960) reported that the source of the CH_4 was degradation of organic matter, either in the sand or buried soils, peats, and organic-rich silts associated with interglacial stages, which are also typically abundant in Illinois glacial deposits.

The mutual exclusivity of arsenic and SO_4^{2-} (and Fe and SO_4^{2-}) was used by (Ravenscroft et al., 2001) as evidence that pyrite oxidation was not the source of arsenic in Bangladeshi groundwater. We observed that arsenic concentrations were significantly greater in samples that had low concentrations of SO_4^{2-} indicating that pyrite oxidation was not the source of arsenic. In addition, elevated concentrations of $\text{NH}_3\text{-N}$ and lower ORP values were found in these samples, suggesting strongly reducing conditions (Figure 14). All of the samples with arsenic greater than $25 \mu\text{g/L}$ had ORP values below 200 mv (Figure 14).

Sulfate-reducing conditions should reduce the solubility of arsenic by promoting the precipitation of arsenic-containing sulfide solid phases. More strongly reducing conditions, however, could produce greater arsenic concentrations in solution. Kirk et al. (2003) sampled wells in the Mahomet Aquifer and detected significant volumes of methane in many wells that had elevated arsenic. Based upon these and other observations, they concluded that arsenic concentrations were only elevated where SO_4^{2-} had been exhausted and was no longer available as an electron acceptor. If SO_4^{2-} is present and SO_4^{2-} reduction is active, arsenic concentrations are low because

any arsenic entering solution is probably removed by precipitation as an arsenic sulfide mineral or by coprecipitation with other sulfide minerals. After SO_4^{2-} has been eliminated, methanogenesis becomes the dominant metabolism and arsenic, in the absence of a precipitation pathway, builds up in the groundwater. In addition, based upon the relationship between arsenic, hydrogen gas, and other redox sensitive species, Kirk et al. (2003) suggested that some degree of iron reduction may be occurring in zones dominated by both methanogens and SO_4^{2-} reducers.

Holm et al. (2004) suggested that the availability of OM may be driving the reducing conditions that cause depletion of SO_4^{2-} in the Mahomet Aquifer. Low levels of SO_4^{2-} tended to occur where TOC concentrations were high. Kirk et al. (2003) observed that wells with significant methane only occurred where TOC exceeded 2 mg/L, while those with TOC below this level had significant concentrations of SO_4^{2-} . All of the wells we sampled that had arsenic greater than 40 $\mu\text{g/L}$ had TOC levels greater than 2 mg/L (Figure 14). The rate at which terminal electron acceptors are used up in pristine groundwater environments is often limited by the supply of organic substrates (Chapelle, 1993; Postma and Jakobsen, 1996). Hence, areas richer in OM are more likely to have exhausted the supply of SO_4^{2-} allowing accumulation of arsenic.

Relatively elevated concentrations of HCO_3^- suggest CO_2 production due to OM oxidation during reductive dissolution of ferric oxyhydroxides. Samples with elevated arsenic tended to also have elevated HCO_3^- (Figure 14). In addition to driving reductive iron dissolution, organic ligands may bind with arsenic in solution and also decrease the amount of adsorption of arsenic (Redman et al., 2002).

One reason why the correlations between arsenic and other chemical parameters are weaker in public wells than domestic wells (see Holm et al., 2004) is that public wells typically have much longer well screens and are pumped at much greater rates. Aquifers typically exhibit considerable chemical heterogeneity, especially vertically. Water with high concentrations of arsenic may occur in a small area, but vigorous pumping of wells with long screens mixes waters with different chemical signatures. Thus any geochemical correlations with respect to arsenic may be dampened.

Water Treatment Experiments

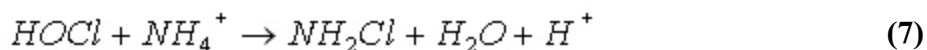
The manganese greensand column reduced the dissolved arsenic concentration by an amount similar to that achieved by the existing treatment system. The dissolved iron was completely oxidized, but there was little oxidation of As(III). The existing treatment system was also ineffective in oxidizing As(III). Thus, the similarity is not surprising. Subramanian et al. (1997) achieved similar reductions in dissolved arsenic with a MGS column. However, they used tap water with added iron and As(III), not groundwater and did not say whether the tap water was chlorinated or not. They did not determine arsenic speciation in the treated effluent.

The MGS column was used in the “intermittent mode.” That is, the MGS was treated with KMnO_4 and then untreated water was pumped through the column. The column would have to be taken off line for regeneration. An MGS column can also be used in “continuous mode,” in which KMnO_4 is added to water and then the mixture is pumped through the column. The MGS

removes the excess permanganate. The results of the batch oxidation experiment suggest that a somewhat better arsenic removal could have been achieved in continuous mode with a KMnO_4 dose of 4.8 mg/L. However, this finished water would still have had arsenic above the MCL.

KMnO_4 addition improved arsenic removal, which implies that part of the explanation for poor arsenic removal at the Danvers facility is the lack of As(III) oxidation. However, even a large excess of KMnO_4 failed to reduce the dissolved arsenic concentration below the MCL. Adding small amounts of iron reduced the arsenic concentration in finished tap water below the MCL. Therefore, incomplete adsorption is also a likely explanation for poor arsenic removal.

Iron oxidation was incomplete for the two lowest NaOCl doses and As(III) oxidation was incomplete for all NaOCl doses. As(III) oxidation was incomplete for the lowest KMnO_4 dose. The NaOCl doses were based on dissolved iron concentrations. However, for a total chlorine concentration less than the $\text{NH}_3\text{-N}$ concentration, ammonium (NH_4^+) reacts with hypochlorite to form monochloramine (Fair et al., 1968):



The $\text{NH}_3\text{-N}$ concentration was ~7 mg/L or 0.5 mM, which was roughly 30 times the dissolved iron concentration and 10 times the highest NaOCl dose. The groundwater also contained a fairly high concentration of NOM (13 mg/L as carbon). Aqueous chlorine (HOCl/OCl^-) (Richardson et al., 2002) and permanganate (Myllykangas et al., 2002) are both known to react with NOM. The extent of Fe^{2+} , NH_4^+ , NOM, and As(III) oxidation depends on the relative rates of reaction with

permanganate and chlorine. Clearly, future batch oxidation experiments should include determination of both iron and $\text{NH}_4\text{-N}$.

SUMMARY AND RECOMMENDATIONS

Public Water Supplies

Warner (2001), who wrote one of the first papers about arsenic in Illinois glacial aquifers, suggested that the source of arsenic in the Mahomet sand and gravel aquifer in central Illinois was bedrock. This conclusion was partially based on solids testing that revealed higher levels of arsenic in the bedrock than the sand and gravel in the aquifer above it. While limited samples collected by the ISWS show elevated arsenic levels along the bedrock walls in the central Mahomet aquifer, thus potentially a bedrock source, other studies of arsenic in Illinois groundwater suggest that the bedrock is not a major source of arsenic (Holm et al., 2004); this study). The source of the arsenic is likely in the aquifer near the well. In fact, our private well sampling (Holm et al., 2004) suggests that it is local, near-well conditions that determine the dissolution of arsenic and that there are possibly microbial controls that drive these changes (Kirk et al., 2003).

Six of the seven sampled wells that had arsenic over 50 µg/L were in southern Illinois in alluvial or Wisconsin-aged sand and gravel aquifers. This was surprising because most available data suggested that these shallow aquifers are generally low in arsenic. Conditions in these particular aquifers, however, were sufficiently reducing to increase arsenic solubility. Southern Illinois has not been studied extensively in the past because there are not many groundwater supplies, compared to the northern half of Illinois, except along the Mississippi River. More study of the

aquifers in southern Illinois is needed to better evaluate these differences. In addition, because shallow aquifers have been thought to be low in arsenic in Illinois, many of the shallow aquifers in the northern half of Illinois have been ignored by researchers. The water quality in these aquifers, which provide water supply to hundreds of thousands of private wells, needs to be better characterized.

As Holm et al. (2004) found, arsenic and sulfate tend to be mutually exclusive; i.e., raw water samples with arsenic concentrations above the MCL had little or no sulfate while water with detectable sulfate generally had low concentrations of arsenic. Sulfate measurement may be a useful screening tool for determining the likely presence of arsenic; if sulfate is detected, it is unlikely that there is significant arsenic in solution. There are commercially available field kits for detecting sulfate that are reliable. Using these kits may prove beneficial in the installation of new wells as well as existing ones. Sulfate measurements would also be valuable at treatment plants to indicate changes in redox conditions. For facilities with more than one well, where the individual wells have different arsenic chemistry, this knowledge may help the operator when rotating wells and determining alternative treatment plans to accommodate the change in chemistry.

As(III) accounted for most of the dissolved arsenic in the raw groundwater samples. Conversely, almost all of the arsenic in finished water in most facilities was As(V), although As(V) was only 5-50% at a few of the facilities. Because of the cost of new treatment, the potential for varying arsenic concentrations with time, and the uncertainty of a one-time sample, resampling of those

plants with As(III) in their finished water would be a first step to confirm the arsenic speciation.

Oxidation is clearly inadequate if finished water has any As(III), and improved oxidation of those waters that have As(III) should lead to improved arsenic removal overall. There are several methods available that may help these facilities that are discussed below.

Particulate arsenic made up more than 40% of the total arsenic in some raw samples. Where that occurred, the total arsenic was higher than 50 µg/L, but the dissolved arsenic concentration was at or below 50 µg/L. Resampling of these facilities would be helpful to confirm the particulate levels found in the one-time samples. For these facilities, better filtration, either through better control of their sand filter systems or the addition of a secondary filter, may help them reduce the arsenic level in their finished water. Possible solutions include replacing the existing sand filter media, increase the frequency of filter back-flushing, and adding a membrane filter to polish the finished water.

The iron to arsenic ratio was a rough indicator of arsenic removal efficiency. Facilities with the highest Fe:As ratio had the most arsenic removal. The addition of iron at some facilities may be a viable, cost effective treatment option to enhance the removal of arsenic. Additional bench-scale tests under varying conditions, to further the initial results of this work of the effects iron addition as discussed below, would be the next recommended step.

Almost all of the facilities with over 1 mg/L of P had poor arsenic removal (<50%). If the phosphate is interfering with arsenic adsorption to HFO, adding iron to increase HFO may improve arsenic removal.

Water Treatment Experiments

The bench-scale tests were successful in evaluating several hypotheses regarding the removal of arsenic and changes in arsenic chemistry. The results show that arsenic concentrations can change in the short term, which has implications on the validity of one-time sampling.

Potassium permanganate addition can be effective in arsenic removal, but it appears that to maximize the removal of arsenic, the amount added needs to be adjusted for the groundwater conditions. Prechlorination was ineffective in these experiments likely due to interference with ammonia in the water. The addition of iron significantly increased the efficiency of arsenic removal.

In an experiment at the Danvers water treatment plant, the arsenic level in their well water varied between 30 and 40 $\mu\text{g/L}$ over a three and a half hour period. Other researchers have found arsenic levels to vary in community wells with time and it is likely that arsenic levels would be found to vary in other municipal supply wells (Root et al., 2003). In addition to variability found in short term sampling (hours), researchers have found significant variability, as much as 50%, on a longer scale (weeks and months) that could influence management decisions (OhioEPA, 2003). Collecting time series samples to examine short term and long term temporal variability is

essential to understanding what conditions cause these changes. Results would help determine how often samples should be collected and if quarterly or less frequent sampling is adequate in determining health risk.

When KMnO_4 was added to the Danvers water at 1.6 mg/L, 100% of the iron was removed, but only about 60% of the As(III) was oxidized, about the same as the existing air oxidation, and only 25% of the arsenic was removed. Doubling the amount of KMnO_4 resulted in about 95% oxidation of As(III) and about 50% arsenic removal. Poor oxidation of As(III) may help explain the poor arsenic removal at Danvers because more extensive oxidation coincided with more efficient removal of arsenic. Inadequate KMnO_4 addition may explain why there were no apparent differences in As removal between plants with similar treatment that added KMnO_4 and those that did not. It appears that all plants may benefit from adding KMnO_4 regardless of what their current treatment is. Bench scale tests at these facilities would be fairly inexpensive and would answer questions about how beneficial KMnO_4 addition could be for facilities that need to remove additional arsenic from their wells.

Up to 4.8 mg/L of NaOCl was added to Danver's groundwater, but this proved to be ineffective both in oxidizing As(III) (less than 50% conversion of As(III) to As(V)) and in removing arsenic (less than 10% removal). The amount of NaOCl added was based on the soluble iron concentration. However, the ammonia-N concentration was roughly 30 times the iron concentration and NaOCl reacted with the ammonia/ammonium. This probably explains the poor As(III) oxidation. More testing is needed with NaOCl to determine if higher doses would be

effective in oxidizing As(III). Operators should also consider their ammonia levels when calculating the NaOCl dose to add in treatment for arsenic removal.

Iron was added to Danvers tap water with very encouraging results. Adding about 1 mg/L of iron, then filtering the resulting HFO through a 0.2 micron filter reduced the arsenic concentration from about 30 $\mu\text{g/L}$ to about 11 $\mu\text{g/L}$. Adding 2 mg/L iron and then filtering reduced the arsenic concentration to 4 $\mu\text{g/L}$. As mentioned in the results, the control samples (no added iron) were discarded because the measured arsenic in the duplicate samples did not meet our data quality standards. We would expect a 0.2 micron filter to reduce the arsenic concentration to below 30 $\mu\text{g/L}$ based on what was found with the 0.45 micron filters used in sampling, but not down to the levels found with iron addition. In addition, there was better arsenic removal when more iron was added (2 mg/L versus 1 mg/L), which indicates the additional iron was responsible for the additional reduction in arsenic. These experiments should be repeated with both a larger sample set and a wider range of iron doses.

Because arsenic removal was enhanced by iron addition, it is possible that other solutes, such as phosphorous, are competing for HFO sorption sites, thus reducing the capacity for arsenic removal. In these cases, the addition of iron would likely increase the amount of arsenic removed. More testing is needed to determine the effects of iron addition.

REFERENCES

- Aggett, J., and Kriegman, M. (1987). Preservation of arsenic(III) and arsenic(V) in samples of sediment interstitial water. *Analyst 112*: 153-157.
- Anderson, M. A., Ferguson, J. F., and Gavis, J. (1976). Arsenate adsorption on amorphous aluminum hydroxide. *J. Coll. Interf. Sci. 54*(3): 391-399.
- Anonymous (1999). Arsenic Removal from Water Using Manganese Greensand: Laboratory Scale Batch and Column Studies. Las Crusces, NM, New Mexico State U.: 101.
- Appelo, C. A. J., Van der Weiden, M. J. J., Tournassat, C., and Charlet, L. (2002). Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. *Environmental Science & Technology 36*(14): 3096-3103.
- Bertolero, F., Pozzi, G., Sabbioni, E., and Saffiotti, U. (1987). Cellular Uptake and Metabolic Reduction of Pentavalent to Trivalent Arsenic as Determinants of Cytotoxicity and Morphological Transformation. *Carcinogenesis 8*(6): 803-808.
- Borho, M., and Wilderer, P. (1996). Optimized Removal of Arsenate(III) by Adaptation of Oxidation and Precipitation Processes to the Filtration Step. *Water Science & Technology 34*(9): 25-31.
- Borho, M., and Wilderer, P. (1997). A Reliable Method for Preservation and Determination of Arsenate(III) Concentrations in Groundwater and Water Works Samples. *Aqua (Oxford) 46*(3): 138-143.

- Boyle, D. R., Turner, R. J. W., and Hall, G. E. M. (1998). Anomalous arsenic concentrations in groundwaters of an island community, Bowen Island, British Columbia. *Environmental Geochemistry & Health* 20(4): 199-212.
- Butler, I. B., Schoonen, M. A. A., and Rickard, D. T. (1994). Removal of Dissolved Oxygen from Water - a Comparison of 4 Common Techniques. *Talanta* 41(2): 211-215.
- Cabon, J. Y., and Cabon, N. (2000). Determination of arsenic species in seawater by flow injection hydride generation in situ collection followed by graphite furnace atomic absorption spectrometry - Stability of As(III). *Analytica Chimica Acta* 418(1): 19-31.
- Chapelle, F. H. (1993). Ground-Water Microbiology & Geochemistry. New York, John Wiley & Sons, Inc.
- Chatterjee, A., Das, D., Mandal, B. K., Chowdhury, T. R., Samanta, G., and Chakraborti, D. (1995). Arsenic in Ground Water in Six Districts of West Bengal, India - the Biggest Arsenic Calamity in the World .1. Arsenic Species in Drinking Water and Urine of the Affected People. *Analyst* 120(3): 643-650.
- Chen, S. L., Yeh, S. J., Yang, M. H., and Lin, T. H. (1995). Trace element concentration and arsenic speciation in the well water of a Taiwan area with endemic blackfoot disease. *Biological Trace Element Research* 48(3): 263-274.
- Cheng, R., Liang, S., Wang, H., and Beuhler, M. (1994). Enhanced coagulation for arsenic removal. *Jour. AWWA* 86(9): 79-90.
- Clesceri, L. S., Greenberg, A. E., and Eaton, A. D. (1998). Standard Methods for the Examination of Water and Wastewater, 20th ed. Washington, D.C., A.P.H.A., A.W.W.A., W.E.F.

- Dowling, C. B., Poreda, R. J., Basu, A. R., Peters, S. L., and Aggarwal, P. K. (2002).
Geochemical study of arsenic release mechanisms in the Bengal Basin groundwater.
Water Resources Research 38(9): 12-1 - 12-18.
- Dzombak, D. A., and Morel, F. M. M. (1990). Surface Complexation Modeling: Hydrous Ferric Oxide. New York, Wiley.
- Eaton, A., Wang, H. C., and Northington, J. (1998). Analytical chemistry of arsenic in drinking water. Denver, CO, American Water Works Assoc. Res. Found.
- Edwards, M. (1994). Chemistry of arsenic removal during coagulation and Fe-Mn oxidation. *J. Am. Water Works Assoc.* 86(9): 64-78.
- Fair, G. M., Geyer, J. C., and Okun, D. A. (1968). Water and Wastewater Engineering. Volume 2. Water Purification and Wastewater Treatment and Disposal. New York, Wiley.
- Ficklin, W. H. (1983). Separation of arsenic(III) and arsenic(V) in ground waters by ion-exchange. *Talanta* 30: 371-373.
- 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.
- Frank, P., and Clifford, D. (1986). Arsenic(III) oxidation and removal from drinking water. Washington, USEPA: 69.
- Harvey, C. F., Swartz, C. H., Badruzzaman, A. B. M., Keon-Blute, N., Yu, W., Ali, M. A., Jay, J., Beckie, R., Niedan, V., Brabander, D., Oates, P. M., Ashfaque, K. N., Islam, S.,

- Hemond, H. F., and Ahmed, M. F. (2002). Arsenic mobility and groundwater extraction in Bangladesh. *Science* 298(5598): 1602-1606.
- Hering, J. G., Chen, P. Y., Wilkie, J. A., and Elimelech, M. (1997). Arsenic Removal From Drinking Water During Coagulation. *Journal of Environmental Engineering-ASCE* 123(8): 800-807.
- Hering, J. G., Chen, P.-Y., Wilkie, J. A., and Elimelech, M. (1996). Arsenic removal from drinking water during coagulation. *Journal of Environmental Engineering*: 800-807.
- Hindmarsh, J. T. (2000). Arsenic, its clinical and environmental significance. *Journal of Trace Elements in Experimental Medicine* 13(1): 165-172.
- Hindmarsh, J. T., and McCurdy, R. F. (1986). Clinical and Environmental Aspects of Arsenic Toxicity. *Crc Critical Reviews in Clinical Laboratory Sciences* 23(4): 315-347.
- Holm, T. R. (2002). Effects of carbonate/bicarbonate, silica, and phosphate on arsenic sorption to hydrous ferric oxide. *J. Am. Water Works Assoc.* 94(4): 174-181.
- Holm, T. R., Anderson, M. A., Iverson, D. G., and Stanforth, R. S. (1979). Heterogeneous Interactions of Arsenic in Aquatic Systems. Chemical Modeling in Aqueous Systems. E. A. Jenne. Washington, DC, ACS. **93**: 711-736.
- 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.
- Hug, S. J., and Leupin, O. (2003). Iron-catalyzed oxidation of arsenic(III) by oxygen and by hydrogen peroxide: pH-dependent formation of oxidants in the Fenton reaction. *Environmental Science & Technology* 37(12): 2734-2742.

- Irgolic, K. (1982). Speciation of Arsenic in Water Supplies. Washington, USEPA.
- 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.
- Korte, N. E., and Fernando, Q. (1991). A review of arsenic(III) in groundwater. *Crit. Rev. Environ. Control* 21: 1-39.
- Lauf, G. F. (1994). Arsenic removal using potassium permanganate generated greensand. Proc. - Water Qual. Technol. Conf. (1995) (Pt. 1). Denver, AWWA: 255-266.
- 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.
- Magyar, J. (1992). Kelliher arsenic removal study. Regina, Saskatchewan Environment and Public Safety.

- Manning, B. A., and Goldberg, S. (1996). Modeling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals. *Soil Sci. Soc. Am. J.* 60: 121-131.
- Matisoff, G., 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 Wat.* 20(4): 446-456.
- McArthur, J. M., Ravenscroft, P., Safiulla, S., and Thirlwall, M. F. (2001). Arsenic in groundwater: Testing pollution mechanisms for sedimentary aquifers in Bangladesh. *Water Resources Research* 37(1): 109-117.
- McNeill, L., and Edwards, M. (1995). Soluble arsenic removal at water treatment plants. *Jour. AWWA* 87(4): 105-113.
- Meents, W. F. (1960). Glacial-Drift Gas in Illinois. Urbana, IL, Illinois State Geological Survey: 58.
- Meng, X., Bang, S., and Korfiatis, G. (2000). Effects of silicate, sulfate, and carbonate on arsenic removal by ferric chloride. *Wat. Res.* 34(4): 1255-1261.
- Myllykangas, T., Nissinen, T. K., Rantakokko, P., Martikainen, P. J., and Vartiainen, T. (2002). Molecular size fractions of treated aquatic humus. *Water Research* 36(12): 3045-3053.
- Nickson, R., McArthur, J., Burgess, W., Ahmed, K. M., Ravenscroft, P., and Rahman, M. (1998). Arsenic poisoning of Bangladesh groundwater. *Nature* 395(6700): 338-338.
- Nickson, R. T., McArthur, J. M., Ravenscroft, P., Burgess, W. G., and Ahmed, K. M. (2000). Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. *Applied Geochemistry* 15(4): 403-413.

- NRDC (2000). Arsenic and Old Laws. A Scientific and Public Health Analysis of Arsenic Occurrence in Drinking Water, Its Health Effects, and EPA's Outdated Arsenic Tap Water Standard. Washington, Natural Resources Defense Council.
- OhioEPA (2003). 2002 305(b) Report: Ohio's Ground Water Quality. O. E. P. Agency, Ohio EPA: 78 pgs.
- Pierce, M. L., and Moore, C. B. (1982). Adsorption of arsenite and arsenate on amorphous iron hydroxide. *Wat. Res.* 16: 1247-1253.
- Postma, D., and Jakobsen, R. (1996). Redox zonation: Equilibrium constraints on the Fe(III)/SO₄-reduction interface. *Geochimica Et Cosmochimica Acta* 60(17): 3169-3175.
- Ravenscroft, P., McArthur, J. M., and Hoque, B. A. (2001). Geochemical and palaeohydrological controls on pollution of groundwater by arsenic. Fourth International Conference on Arsenic Exposure and Health Effects, San Diego, CA, Elsevier Science Ltd., Oxford.
- Redman, A. D., Macalady, D. L., and Ahmann, D. (2002). Natural organic matter affects arsenic speciation and sorption onto hematite. *Environmental Science & Technology* 36(13): 2889-2896.
- Richardson, S. D., Simmons, J. E., and Rice, G. (2002). Disinfection byproducts: The next generation. *Environmental Science & Technology* 36(9): 198A-205A.
- Rittle, K. A., Drever, J. I., and Colberg, P. J. S. (1995). Precipitation of arsenic during bacterial sulfate reduction. *Geomicrobiology Journal* 13(1): 1-11.
- Root, T. L., Bahr, J., and Gotkowitz, M. (2003). Arsenic in groundwater in southeastern Wisconsin: sources of arsenic and mechanisms controlling arsenic mobility. Geological Society of America Annual Meeting, Seattle, WA.

- Schecher, W., and McAvoy, D. (1994). MINEQL+: A Chemical Equilibrium Program for Personal Computers. Users Manual, Version 3.0. Hallowell, ME, Environmental Research Software.
- Schreiber, M. E., Simo, J. A., and Freiberg, P. G. (2000). Stratigraphic and geochemical controls on naturally occurring arsenic in groundwater, eastern Wisconsin, USA. *Hydrogeology Journal* 8(2): 161-176.
- Scott, K., Green, J., Do, H., and McLean, S. (1994). Arsenic removal by coagulation. *J. AWWA* 86(9): 114-126.
- Scott, M. J., and Morgan, J. J. (1995). Reactions at oxide surfaces .1. oxidation of As(III) by synthetic birnessite. *Environmental Science & Technology* 29(8): 1898-1905.
- Shraim, A., Sekaran, N. C., Anuradha, C. D., and Hirano, S. (2002). Speciation of arsenic in tube-well water samples collected from West Bengal, India, by high-performance liquid chromatography-inductively coupled plasma mass spectrometry. *Applied Organometallic Chemistry* 16(4): 202-209.
- Smedley, P. L. (1996). Arsenic in rural groundwater in Ghana. *J. African Earth Sciences* 22: 459-470.
- Smedley, P. L., Edmunds, W. M., and Pelig-Ba, K. B. (1996). Mobility of arsenic in groundwater in the Obuasi gold-mining area of Ghana: some implications for human health. Environmental Geochemistry and Health. J. D. Appleton, R. Fuge and G. J. H. McCall. London, Geological Society. **Special Pub. 113**: 163-181.
- Smedley, P. L., and Kinniburgh, D. G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry* 17(5): 517-568.

- 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.
- Subramanian, K. S., Viraraghavan, T., Phommavong, T., and Tanjore, S. (1997). Manganese greensand for removal of arsenic in drinking water. *Water Qual. Res. J. Canada* 32(3): 551-561.
- Swendlund, P. J., and Webster, J. G. (1999). Adsorption and polymerisation of silicic acid on ferrihydrite, and its effect on arsenic adsorption. *Water Research* 33: 3414-3422.
- Volke, P., and Merkel, B. (1999). Using of a new field analysis method to investigate the stability of arsenic and its inorganic species in aquatic systems. *Acta Hydrochimica et Hydrobiologica* 27(4): 230-238.
- 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., Lico, M. S., and Hughes, J. L. (1988). Arsenic in ground water of the western United States. *Ground Water* 26: 333-347.
- 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.
- Wilkie, J. A., and Hering, J. G. (1996). Adsorption of Arsenic Onto Hydrous Ferric Oxide - Effects of Adsorbate/Adsorbent Ratios and Co-Occurring Solutes. *Colloids & Surfaces A-Physicochemical & Engineering Aspects* 107: 97-110.

Yan, X. P., Kerrich, R., and Hendry, M. J. (2000). Distribution of arsenic(III), arsenic(V) and total inorganic arsenic in porewaters from a thick till and clay-rich aquitard sequence, Saskatchewan, Canada. *Geochimica et Cosmochimica Acta* 64(15): 2637-2648.

APPENDIX A.

Pearson product moment correlation results. The pairs of variables with positive correlation coefficients and P values below 0.050 tend to increase together. For the pairs with negative correlation coefficients and P values below 0.050, one variable tends to decrease while the other increases. For pairs with P values greater than 0.050, there is no significant relationship between the two variables.

	All Wells		Bedrock		pre-Illinoian		Illinoian		Alluvial	
	(n = 52)		(n = 8)		(n = 21)		(n = 17)		(n = 4)	
	r	P	r	P	r	P	r	P	r	P
ORP	-0.348	0.015	-0.468	0.243	-0.396	0.104	0.100	0.712	-0.990	0.010
TOC	0.425	0.002	-0.036	0.932	0.617	0.003	0.231	0.373	0.137	0.863
Sulfate	-0.159	0.260	-0.385	0.347	-0.112	0.629	-0.211	0.416	-0.385	0.615
Fe	0.345	0.012	0.775	0.024	0.435	0.049	-0.198	0.445	0.752	0.248
Mn	-0.164	0.247	0.010	0.982	-0.177	0.443	-0.494	0.044	0.511	0.489
NH ₃ -N	0.436	0.001	0.275	0.509	0.650	0.001	0.163	0.531	0.304	0.696
HCO ₃ ⁻	0.378	0.006	0.529	0.178	0.437	0.047	0.206	0.427	0.389	0.611
well depth	-0.334	0.018	-0.258	0.537	-0.349	0.121	-0.286	0.266	-0.872	0.128
Spec Cond	0.141	0.339	-0.219	0.602	0.406	0.094	-0.121	0.656	0.703	0.297
pH	0.194	0.187	0.616	0.104	0.082	0.747	0.122	0.652	0.140	0.860
Fluoride	0.205	0.150	0.155	0.714	0.276	0.226	0.251	0.332	-0.717	0.283
Chloride	0.340	0.014	-0.194	0.645	0.582	0.006	0.519	0.033	-0.082	0.918
Na	0.430	0.001	-0.315	0.447	0.568	0.007	0.381	0.132	-0.256	0.744
Mg	-0.170	0.227	0.224	0.595	-0.155	0.503	0.037	0.887	0.109	0.891
Ca	-0.272	0.051	-0.079	0.852	-0.215	0.350	-0.303	0.237	0.187	0.813
Si	-0.084	0.555	0.774	0.024	-0.235	0.306	-0.247	0.340	-0.094	0.906
P	0.348	0.012	0.099	0.816	0.469	0.032	0.044	0.866	0.791	0.209

APPENDIX B.

Municipality	Well #	Date	Depth (ft)	Aquifer Age	Temp (C)	Sp Cond (µS/cm)	pH	ORP (mv)	DO (mg/L)
Alhambra	4	03/13/03	91	Illinoian	14.58	987.2	7.14	126	<0.5
Armington	2	04/16/03	251	Pre-Illinoian	15.68	1010	7.31	285	<0.6
Ashkum	2	04/02/03	147	Illinoian	12.70	758.1	7.09	153	NA
Ashkum	3	04/02/03	215	Bedrock	12.64	976.7	7.01	98	<0.3
Ashkum	4	04/02/03	120	Illinoian	11.87	1040	7.38	98	<0.3
Birds	1	03/12/03	82	Alluvial	13.62	629.4	7.38	106	5.77
Chrisman	5	03/10/03	92	Wisconsinan	13.07	863.9	7.06	90	<0.5
Deland	6	04/04/03	82	Illinoian	12.65	1516	6.43	174	<0.4
Deland	7	04/04/03	79	Illinoian	12.92	1456	6.47	190	<0.4
DeWitt Co NH	+	04/04/03	320;330	Pre-Illinoian	15.65	1401	6.95	145	<0.5
Downs	1	04/15/03	105	Illinoian	13.51	1628	6.62	114	0.35
Downs	2	04/15/03	119	Illinoian	13.02	1631	6.68	136	0.23
Dwight	7	04/01/03	147	Illinoian	12.92	1430	7.88	58	<0.7
Dwight	8	04/01/03	157	Illinoian	12.97	1559	7.76	44	<0.6
Grand Ridge	1	03/31/03	162	Pre-Illinoian	12.82	598.3	7.87	69	<0.5
Grand Ridge	3	03/31/03	190	Pre-Illinoian	12.27	594.3	7.95	52	<0.5
Grant Park	3	03/31/03	330	Bedrock	12.30	865.3	6.80	171	<0.5
Grant Park	4	03/31/03	504	Bedrock	12.45	791.6	6.78	207	<0.7
Hoppeston	5	04/14/03	104	Illinoian	NA	NA	NA	NA	NA
Hopedale	5	03/11/03	205	Pre-Illinoian	13.02	600.1	7.19	90	<0.6
Jewett	3	03/12/03	138	Pre-Illinoian	7.21	1888	6.85	125	<1.0
Kempton	2	04/14/03	238	Pre-Illinoian	NA	NA	NA	NA	NA
Kempton	4	04/14/03	238	Pre-Illinoian	NA	NA	NA	NA	NA
Manlius	2	04/03/03	268	Pre-Illinoian	12.56	678.4	6.94	516	<0.4
Manlius	3	04/03/03	285	Pre-Illinoian	12.55	671.4	6.90	758	<0.4
Manteno	6	04/02/03	280	Bedrock	13.15	920	6.54	320	<0.7
Manteno	9	04/02/03	300	Bedrock	12.19	1066	6.55	281	<0.5
Maroa	1	03/13/03	85	Illinoian	13.10	912.8	7.46	80	<0.5
Metamora	7	04/15/03	418	Pre-Illinoian	12.05	1497	7.40	159	9.99
Ohio	4	04/03/03	404	Pre-Illinoian	12.12	478.8	7.39	102	<0.4
Ohio	5	04/03/03	434	Pre-Illinoian	10.61	491.5	7.23	442	<0.5
Paxton	7	04/14/03	340	Pre-Illinoian	12.57	NA	NA	NA	NA
Ridgway	1	03/12/03	85	Alluvial	15.63	637.2	7.14	64	<1.0
Ridgway	2	03/12/03	85	Alluvial	15.73	724.1	7.12	41	<1.4
Ridgway	3	03/12/03	101	Alluvial	16.40	625.6	7.10	235	<1.5
Rochelle	4	04/01/03	1450	Bedrock	11.67	604.8	6.91	197	<0.5
Rossville	+	03/10/03	127;135	Illinoian	13.56	632.9	7.14	162	<0.5
Sadorus	2	04/21/03	112	Illinoian	12.91	1163	7.04	111	<0.3
Sadorus	3	04/21/03	116	Illinoian	11.31	1116	7.06	89	<0.25
Secor	1	04/15/03	156	Illinoian	13.26	1437	6.69	156	0.44
Secor	2	04/15/03	158	Illinoian	12.86	1813	6.63	156	0.29
Sheffield	6	04/03/03	216	Pre-Illinoian	13.14	699.3	7.25	111	<0.5
Tampico	1	04/03/03	173	Pre-Illinoian	11.67	449.7	6.85	725	<0.5
Tampico	2	04/03/03	53	Wisconsinan	12.36	559	7.00	382	<0.5
Tonica	4	03/31/03	205	Pre-Illinoian	13.00	1070	7.69	64	<0.5
Wapella	2	03/11/03	79	Illinoian	12.71	815.4	6.53	124	<0.5
Waterman	2	04/01/03	400	Bedrock	11.34	710.6	7.20	129	1.56
Waterman	3	04/01/03	400	Bedrock	12.33	1110	7.00	176	<0.5
Watseka	6	04/02/03	160	Pre-Illinoian	12.79	503.9	7.28	112	<0.35
Watseka	7	04/02/03	133	Pre-Illinoian	13.30	708.1	7.05	82	<0.4
Watseka	8	04/02/03	176	Pre-Illinoian	13.98	543.7	7.24	100	<0.5
Waynesville	6	03/11/03	162	Pre-Illinoian	13.83	963.5	6.80	163	<0.9

+: water from 2 wells combined upstream from sampling point. NA: not analyzed.

Municipality	Well #	As(III)	MMAA	As(V)	DMAA	As(III) + %		Diss'd As	Total	Susp'd
						As(V)	As(III)		As	As
Alhambra	4	74.98	< 1	10.61	< 10	85.59	87.6	88.52	85.14	-3.38
Armington	2	7.73	< 1	1.74	< 1	9.47	81.6	9.58	14.46	4.88
Ashkum	2	38.40	< 1	3.71	< 5	42.11	91.2	44.50	44.96	0.46
Ashkum	3	1.66	< 1	< 1	< 1	1.66	100.0	1.98	2.13	0.15
Ashkum	4	1.65	< 1	< 1	< 1	1.65	100.0	1.87	2.20	0.33
Birds	1	42.75	< 1	3.64	< 8	46.39	92.2	51.08	49.58	-1.50
Chrisman	5	70.52	< 1	13.93	< 4	84.45	83.5	83.48	86.92	3.44
Deland	6	47.30	< 1	4.87	< 10	52.17	90.7	58.60	65.82	7.22
Deland	7	41.56	< 1	4.30	< 6	45.86	90.6	53.20	59.78	6.58
DeWitt Co NH	+	16.07	< 1	5.27	< 3	21.35	75.3	22.80	33.70	25.55
Downs	1	8.56	< 1	1.32	< 1	9.88	86.7	10.97	11.25	0.28
Downs	2	8.44	< 1	1.36	< 1	9.80	86.1	11.00	11.28	0.28
Dwight	7	12.80	< 1	2.31	< 3	15.11	84.7	19.45	18.85	-0.60
Dwight	8	34.70	< 1	5.00	< 5	39.70	87.4	45.90	45.28	-0.62
Grand Ridge	1	51.40	< 1	2.39	< 8	53.79	95.6	49.94	46.48	-3.46
Grand Ridge	3	44.86	< 1	4.14	< 10	49.00	91.5	45.10	43.96	-1.14
Grant Park	3	8.65	< 1	2.60	< 2	11.25	76.9	10.72	9.91	-0.82
Grant Park	4	2.72	< 1	4.34	< 1	7.05	38.5	7.22	10.35	3.13
Hoopeston	5	14.31	< 1	3.57	< 1	17.88	80.0	19.16	19.69	0.53
Hopedale	5	16.82	< 1	2.16	< 2	18.99	88.6	19.14	19.37	0.23
Jewett	3	84.48	< 1	13.18	< 14	97.66	86.5	107.06	107.12	0.06
Kempton	2	23.94	< 1	2.01	< 2	25.95	92.3	26.96	29.28	2.32
Kempton	4	11.01	< 1	1.54	< 1	12.55	87.7	12.83	16.11	3.28
Manlius	2	< 1	< 1	4.18	< 1	4.18	0.0	5.00	52.06	47.06
Manlius	3	0.96	< 1	3.97	< 1	4.94	19.5	5.44	49.78	44.34
Manteno	6	1.99	< 1	< 1	< 1	1.99	100.0	2.53	3.24	0.72
Manteno	9	< 1	< 1	< 1	< 1	< 4	ND	< 1	0.57	0.57
Maroa	1	82.00	< 1	7.22	< 12	89.22	91.9	83.08	91.74	8.66
Metamora	7	15.97	< 1	3.29	< 2	19.26	82.9	20.08	21.56	1.48
Ohio	4	21.98	< 1	2.13	< 4	24.11	91.17	26.9	25.46	-1.44
Ohio	5	18.77	< 1	1.21	< 3	19.99	93.93	23.1	22.96	-0.10
Paxton	7	0.97	< 1	< 1	< 1	0.97	100.00	1.1	1.19	0.13
Ridgway	1	44.76	< 1	9.99	< 8	54.75	81.76	57.1	59.24	2.16
Ridgway	2	54.38	< 1	12.18	< 10	66.56	81.70	69.8	68.60	-1.24
Ridgway	3	3.74	< 1	13.33	< 1	17.06	21.91	19.8	47.28	27.48
Rochelle	4	< 1	< 1	< 1	< 1	< 4	ND	< 1	< 1	
Rossville	+	10.45	< 1	11.48	< 1	21.93	47.64	23.6	23.02	-0.62
Sadorus	2	15.17	< 1	1.47	< 2	16.63	91.19	17.7	18.13	0.44
Sadorus	3	10.38	< 1	1.35	< 1	11.73	88.46	12.0	12.98	0.96
Secor	1	20.58	< 1	4.13	< 2	24.71	83.27	27.6	28.08	0.48
Secor	2	21.38	< 1	3.25	< 2	24.63	86.80	26.3	27.84	1.50
Sheffield	6	67.10	< 1	10.54	< 12	77.64	86.43	79.8	84.06	4.26
Tampico	1	14.15	< 1	2.25	< 3	16.40	86.27	18.1	19.45	1.34
Tampico	2	0.80	< 1	0.66	< 1	1.47	54.84	1.6	1.37	-0.18
Tonica	4	21.78	< 1	2.53	< 2	24.31	89.59	23.2	22.24	-0.94
Wapella	2	3.27	< 1	0.95	< 1	4.22	77.40	4.9	4.97	0.07
Waterman	2	14.60	< 1	1.40	< 3	16.00	91.25	18.2	16.95	-1.21
Waterman	3	6.00	< 1	1.88	< 1	7.88	76.14	8.7	10.73	1.98
Watseka	6	2.70	< 1	< 1	< 1	2.70	100.00	2.9	3.15	0.29
Watseka	7	41.60	< 1	3.60	< 4	45.20	92.04	46.1	47.02	0.92
Watseka	8	21.10	< 1	1.30	< 2	22.40	94.2	22.00	22.66	0.66
Waynesville	6	5.88	< 1	8.69	< 1	14.57	40.4	14.94	18.32	3.38

+: water from 2 wells combined upstream from sampling point. ND: not determined.

Municipality	Well #	Al	Na	Mg	Ca	Fe	Mn	Si	P	NH ₃ -N
Alhambra	4	0.001	150	27.9	50.9	2.82	0.029	7.14	0.924	5.70
Armington	2	< 0.001	8.84	34.3	68.6	0.501	0.069	11.5	< 0.02	0.66
Ashkum	2	0.004	74.9	24.9	51.5	1.09	0.013	8.26	0.282	1.86
Ashkum	3	0.002	94.1	38.6	68.8	0.636	0.010	4.74	0.048	1.11
Ashkum	4	0.001	100	35.5	73.9	1.18	0.033	6.19	0.051	0.73
Birds	1	< 0.001	56.7	22.3	52.8	2.03	0.030	6.12	0.302	4.47
Chrisman	5	< 0.001	84.7	31.6	59.2	4.87	0.037	9.44	0.579	12.7
Deland	6	< 0.001	63.3	55.6	98.7	3.70	0.018	14.2	0.150	13.9
Deland	7	0.001	60.9	50.9	92.9	3.43	0.020	12.6	0.184	14.4
DeWitt Co NH	+	< 0.001	110	31.9	64.7	1.44	0.025	8.57	0.236	4.60
Downs	1	< 0.001	53.5	41.1	89.7	4.88	0.034	14.3	0.220	8.51
Downs	2	< 0.001	55.9	43.6	91.8	4.81	0.033	14.1	0.217	8.33
Dwight	7	< 0.001	150	44.4	86.5	0.595	0.045	4.87	0.503	4.10
Dwight	8	< 0.001	170	35.0	64.6	1.88	0.033	4.45	0.533	4.63
Grand Ridge	1	0.002	96.2	14.3	22.7	0.685	0.027	4.34	0.079	1.62
Grand Ridge	3	0.003	93.7	15.7	22.5	0.698	0.025	4.38	0.081	1.57
Grant Park	3	0.006	16.3	47.5	106	1.97	0.031	10.8	0.052	0.26
Grant Park	4	0.002	13.9	42.3	91.8	1.95	0.045	10.3	0.430	0.16
Hoopeston	5	< 0.001	33.0	33.7	64.2	1.89	0.045	7.78	< 0.02	1.16
Hopedale	5	0.001	22.8	37.2	65.3	2.15	0.033	9.84	0.114	1.94
Jewett	3	< 0.001	350	32.9	65.1	2.99	0.020	9.09	1.153	8.55
Kempton	2	< 0.001	220	73.1	140	2.65	0.079	5.02	0.178	1.95
Kempton	4	< 0.001	230	78.7	160	2.08	0.096	4.66	0.126	1.71
Manlius	2	< 0.001	19.8	35.0	84.6	0.455	0.376	13.3	< 0.02	1.58
Manlius	3	< 0.001	15.9	32.5	81.8	0.479	0.398	13.9	< 0.02	1.41
Manteno	6	0.002	19.9	51.0	103	0.489	0.010	5.14	< 0.02	0.22
Manteno	9	< 0.001	43.9	52.9	110	0.255	0.013	4.75	< 0.02	0.03
Maroa	1	< 0.001	87.0	43.5	61.4	1.55	0.013	6.28	0.084	1.92
Metamora	7	< 0.001	82.5	38.3	63.6	3.07	0.038	10.5	0.387	4.35
Ohio	4	< 0.001	54.4	18.2	35.3	2.20	0.054	6.96	0.244	1.87
Ohio	5	0.007	43.0	21.0	42.9	1.17	0.056	7.32	0.209	1.93
Paxton	7	< 0.001	27.1	30.7	80.4	2.05	0.035	8.60	0.117	1.39
Ridgway	1	< 0.001	16.4	34.5	75.7	4.07	0.040	8.43	0.768	1.58
Ridgway	2	< 0.001	22.9	36.2	78.0	4.48	0.046	8.20	0.773	1.90
Ridgway	3	< 0.001	32.8	33.5	71.4	2.20	0.036	8.37	0.268	0.95
Rochelle	4	0.002	8.80	36.8	68.4	0.612	0.058	5.97	< 0.02	0.15
Rossville	+	0.001	25.8	43.9	69.3	1.55	0.040	9.00	2.490	0.92
Sadorus	2	< 0.001	85.0	24.3	56.7	2.28	0.020	10.5	0.162	1.27
Sadorus	3	< 0.001	72.7	25.1	58.9	1.94	0.017	10.3	0.149	1.11
Secor	1	< 0.001	20.1	45.7	94.3	3.90	0.030	14.3	0.136	7.06
Secor	2	< 0.001	34.6	59.7	110	5.99	0.025	14.5	0.377	11.7
Sheffield	6	0.004	53.5	29.0	64.2	5.02	0.204	9.80	0.480	3.08
Tampico	1	< 0.001	4.54	24.5	58.1	4.23	0.086	11.2	0.135	0.36
Tampico	2	< 0.001	9.73	33.7	70.6	0.642	0.251	6.81	< 0.02	0.05
Tonica	4	0.003	140	29.1	39.8	1.61	0.026	4.78	0.165	3.35
Wapella	2	< 0.001	31.7	44.9	97.4	6.56	0.069	12.6	0.618	9.25
Waterman	2	0.003	13.6	47.1	73.3	1.66	0.023	9.39	0.024	0.69
Waterman	3	< 0.001	55.5	53.8	96.5	1.98	0.021	10.3	0.025	0.72
Watseka	6	< 0.001	57.5	14.1	36.1	0.599	0.015	8.50	0.363	1.80
Watseka	7	0.003	65.9	26.6	58.0	1.92	0.017	7.93	0.374	5.44
Watseka	8	0.004	63.9	14.8	37.5	0.762	0.017	7.95	0.523	2.74
Waynesville	6	0.001	66.6	59.7	101	2.71	0.018	11.4	1.306	4.33

+: water from 2 wells combined upstream from sampling point.

Municipality	Well #	TOC	Fluoride	Chloride	Nitrate	Sulfate	PO₄	alkal'ty	HCO₃	lab pH
Alhambra	4	6.7	0.980	60.9	< 0.2	0.321	0.287	457	558	7.59
Armington	2	1.2	< 0.25	2.02	1.14	< 0.25	< 0.25	333	406	7.89
Ashkum	2	3.1	0.386	32.3	0.435	143	< 0.25	210	256	7.81
Ashkum	3	2.4	0.584	23.6	< 0.25	250	< 0.25	251	306	7.76
Ashkum	4	1.4	0.811	28.1	< 0.25	340	< 0.25	171	209	7.94
Birds	1	2.8	0.214	26.4	< 0.2	0.270	< 0.2	307	374	7.81
Chrisman	5	6.5	0.459	40.4	< 0.2	< 0.2	< 0.2	439	536	7.38
Deland	6	15.2	0.597	13.0	< 0.25	< 0.25	< 0.25	617	752	7.24
Deland	7	13.0	0.630	19.2	0.313	< 0.25	< 0.25	572	698	7.27
DeWitt Co NH	+	7.0	0.523	79.0	< 0.25	< 0.25	< 0.25	435	531	7.67
Downs	1	9.3	0.544	11.4	< 0.25	< 0.25	< 0.25	519	633	7.39
Downs	2	9.3	0.529	11.4	< 0.25	< 0.25	< 0.25	518	632	7.43
Dwight	7	6.9	0.498	56.6	< 0.25	360	0.504	321	392	8.23
Dwight	8	7.4	0.544	110	< 0.25	200	< 0.25	351	428	8.11
Grand Ridge	1	4.0	1.138	3.59	< 0.25	< 0.25	< 0.25	326	397	8.10
Grand Ridge	3	3.8	1.125	3.83	< 0.25	< 0.25	< 0.25	322	393	8.17
Grant Park	3	1.4	0.268	16.3	0.773	98.0	< 0.25	358	437	7.31
Grant Park	4	1.1	0.472	10.2	< 0.25	69.7	< 0.25	340	415	7.40
Hoopeston	5	0.93	0.475	3.33	< 0.25	13.7	< 0.25	343	419	7.76
Hopedale	5	2.7	0.343	2.73	< 0.2	< 0.2	< 0.2	359	438	7.68
Jewett	3	15.0	0.429	220	< 0.2	< 0.2	0.404	677	825	7.43
Kempton	2	1.4	0.405	18.7	< 0.25	990	< 0.25	141	172	7.72
Kempton	4	1.3	0.447	18.3	< 0.25	1100	< 0.25	139	170	7.68
Manlius	2	2.8	< 0.25	7.17	< 0.25	< 0.25	< 0.25	386	471	7.69
Manlius	3	2.5	< 0.25	7.11	< 0.25	< 0.25	< 0.25	384	468	7.72
Manteno	6	1.1	0.527	63.3	< 0.25	100	< 0.25	318	388	7.47
Manteno	9	1.0	0.264	93.3	< 0.25	160	< 0.25	302	369	7.48
Maroa	1	4.8	0.426	65.5	< 0.2	< 0.2	< 0.2	409	498	7.85
Metamora	7	9.0	0.404	14.8	< 0.25	< 0.25	< 0.25	480	585	8.05
Ohio	4	5.7	0.683	1.29	< 0.25	< 0.25	< 0.25	271	330	7.92
Ohio	5	5.0	0.583	1.06	0.401	< 0.25	< 0.25	278	339	7.87
Paxton	7	1.2	0.269	0.93	< 0.25	39.8	< 0.25	348	425	7.78
Ridgway	1	0.8	0.258	8.08	< 0.2	11.0	< 0.2	327	399	7.58
Ridgway	2	1.0	0.243	6.63	< 0.2	2.34	< 0.2	392	478	7.61
Ridgway	3	0.8	0.303	9.71	2.28	8.65	< 0.2	340	415	7.62
Rochelle	4	0.6	< 0.25	7.31	0.322	13.8	< 0.25	313	382	7.64
Rossville	+	0.7	0.898	3.58	< 0.2	11.8	0.409	372	453	7.59
Sadorus	2	8.7	0.426	6.92	< 0.25	< 0.25	< 0.25	407	496	7.75
Sadorus	3	6.4	0.413	6.10	< 0.25	1.16	< 0.25	388	473	7.77
Secor	1	5.8	0.462	1.66	< 0.25	< 0.25	< 0.25	477	582	7.46
Secor	2	9.6	0.499	2.25	< 0.25	< 0.25	< 0.25	610	744	7.38
Sheffield	6	5.0	0.563	0.84	0.684	< 0.25	< 0.25	398	485	7.80
Tampico	1	1.0	< 0.25	0.46	< 0.25	< 0.25	< 0.25	248	302	7.77
Tampico	2	0.9	< 0.25	17.2	9.76	57.8	< 0.25	216	264	7.72
Tonica	4	4.7	0.952	120	< 0.25	4.31	< 0.25	384	468	8.02
Wapella	2	5.9	0.443	18.6	< 0.2	< 0.2	< 0.2	459	560	7.10
Waterman	2	1.1	0.451	15.7	1.903	47.9	< 0.25	325	397	7.80
Waterman	3	1.2	0.301	120	< 0.25	68.2	< 0.25	353	431	7.70
Watseka	6	1.9	0.506	2.46	< 0.25	3.82	0.504	273	333	7.92
Watseka	7	3.1	0.255	22.5	< 0.25	< 0.25	< 0.25	367	448	7.77
Watseka	8	3.0	0.412	9.09	< 0.25	0.570	0.756	289	352	7.91
Waynesville	6	9.1	1.04	6.64	< 0.2	< 0.2	0.645	593	724	7.33

+: water from 2 wells combined upstream from sampling point.