Importance of disinfection on arsenic release in wells. [DNR-172] [2005?]

Importance of Disinfection on Arsenic Release in Wells

W. C. Sonzogni
A. Clary
G. Bowman
J. Standridge

Wisconsin State Laboratory of Hygiene,
University of Wisconsin - Madison

D. Johnson

Wisconsin Department of Natural Resources

M. Gotkowitz

Wisconsin Geological and Natural History Survey

ABSTRACT

Arsenic levels in well water used for drinking is a major problem for many homeowners in Wisconsin, particularly for those living in the northeast part of the state where groundwater often intersects arsenic laden mineral deposits. Levels can exceed recommended safe (from a health standpoint) levels, often by large amounts. It has been previously reported that oxidation of arsenic containing mineral deposits by air (oxygen) can lead to elevated arsenic levels. Additionally, it is thought that reduction of oxide minerals associated with microbial processes, such as reduction of arsenic-rich iron oxides by iron bacteria within biofilms, can play an important role in the dissolution of arsenic. Anecdotal evidence suggests that well disinfection treatments (e.g., chlorination), often performed to control microbes in wells, may also be playing a role in arsenic release. This could be caused by the oxidizing strength of the disinfectant or other factors. However, the effect on arsenic levels from disinfection practices is poorly understood. Consequently, studies were conducted to gain more information on the effect of different disinfection practices, particularly the effect of different chlorination treatments. These studies included an assessment of (1) a test well subjected to different disinfection treatments studies (sequentially over time), (2) a survey of a large number of wells with arsenic problems, (3) the effect of biofilm (biological encrustation) treatment with an acid surfactant followed by low dose chlorination and (4) the leaching of arsenic from scale or pipe encrustations. Results of these studies showed that disinfection practices generally caused a temporary increase in well water arsenic (probably from the disintegration or dissolution of biofilms/encrustations). However, once flushed (several well volumes pumped out), arsenic levels generally decreased. There was no indication that any of the disinfection practices evaluated caused sustained increases in arsenic in the well water. The well survey showed that certain well drilling

techniques, such as wash-rotary drilling and Bradenhead grouting, were associated with lower arsenic levels in wells. Whether the aquifer was confined or unconfined did not seem to affect arsenic levels. Based on the overall result of the study, acid surfactant treatment of wells, followed by low dose chlorination, is the recommended treatment approach in most situations. The acid surfactant treatment is recommended because of its effectiveness in controlling biofilms, which are believed to play an important role in the dissolution of mineral arsenic in many situations. Clearly, the chemical and hydrologic characteristics of a well can be complex and very site specific, but some general approaches to disinfection that minimize arsenic levels in drinking water are emerging.

INTRODUCTION

One of the more perplexing groundwater problems currently facing Wisconsin is the high concentration of arsenic found in many northeastern Wisconsin drinking water wells. High levels of arsenic in drinking water pose a relatively large risk to human health, including increasing the odds of developing skin and internal cancers, cardiovascular diseases, peripheral neuropathy and diabetes (Abernathy et al. 1999; Chowdhury et al. 2000; Karim 2000; Matschullat 2000; Morales et al. 2000; National Research Council 1999; Steinmanus et al. 2000; Tondel et al. 1999). Because of these concerns, the U.S. Environmental Protection Agency (U.S. EPA) recently enacted a nation-wide drinking water standard for arsenic of 10 μg/L (the old limit was 50 μg/L). Even the new 10 μg/L limit is thought by some to be too lenient to provide adequate public health protection.

Many Wisconsin private wells exceed this new limit (Burkel 1993). In Outagamie, Winnebago, and Brown counties in Wisconsin, approximately one out of three drinking water

wells sampled have total arsenic concentrations of 5 µg/L or greater. This area has been designated as an Arsenic Advisory Area by the Wisconsin Department of Natural Resources (WDNR) and the Wisconsin Department of Health and Family Services (WDHFS).

The cause of elevated arsenic in northeastern Wisconsin wells has been investigated for several years, and elsewhere for an even longer period (Matisoff et al. 1982). The main source in northeastern Wisconsin appears to be the oxidation of naturally occurring sulfide-bearing mineralized zones within a confined sandstone aquifer, resulting in the release of arsenic (Schreiber et al. 2000). The oxidation can be initiated by the induction of air in the drilling process (air rotary drilling), exposure of minerals to air through fluctuations in water levels within the borehole due to cycling of the pump, or exposure through oscillations of the water table level due to drought or from the mining of water. It may also be a result of microbial oxidation of various elements. The role of oxidizing bacteria may be significant in highly impacted wells (>100 µg/L arsenic), because these bacteria can potentially produce Fe(III), which can act as an oxidant of sulfides under low pH (Schreiber et al. 2003). Thus, the introduction of air during the well drilling process can initiate arsenic release.

In the affected aquifer, alteration of iron-sulfide mineralization appears to be followed by precipitation of goethite, an iron oxide. The iron oxide weathering products of sulfide mineralization have been found to have higher associated arsenic concentrations than the iron-sulfide mineralization (Gotkowitz et. al. 2004). Under reducing conditions, as might occur in confined portions of the aquifer, iron-reducing bacteria may contribute to low- to moderate-levels of arsenic release in wells by reducing these arsenic-bearing iron (hydr)oxides present in the St. Peter aquifer (Gotkowitz et al. 2004).

This study was prompted by several field observations. The first was that some wells constructed according to WDNR recommendations to minimize borehole interactions of air, water and sulfides (with 80 feet of casing and wash rotary drilling) still developed unacceptable arsenic levels. The second observation was that chlorine added to wells as a bacterial disinfectant often resulted in an increase in the arsenic levels in the well water. It stands to reason that chlorine, a strong oxidizing agent, could also cause oxidative breakdown of sulfide minerals. Thus, the purpose of this study was to evaluate whether alternate disinfection techniques could minimize arsenic release.

The evaluation was done in four phases. In the first phase of this study, three disinfection processes were evaluated on a single test well. The test well, which had an existing iron and sulfur bacteria infestation (i.e., biofilms were present), was treated by low dose chlorination, acid surfactant/minimal chlorination and high dose (shock) chlorination. Note that the term "biofilm" is often used to describe microbes growing in association with a solid surface. In a well it can be in the form of an encrustation on pipes or other surfaces.

Phase two of the study involved identifying wells from the Arsenic Advisory Area that represented different construction techniques. Well owners were surveyed about their disinfection practices and requested to submit samples for arsenic and bacteria analysis. The results were analyzed for insights on the effect of well construction, and the effect of subsequent disinfection processes, on arsenic levels in the well water.

In the third phase of the study, the use of an acid surfactant followed by minimal chlorination to disinfect wells was evaluated with respect to the impact of this strategy on eliminating biofilms without excessive use of chlorine (which might lead to additional arsenic release via chemical oxidation). Note that biofilms can occur in many forms, including

biological encrustations. Oxidation of iron, sulfur, manganese and other elements is the process by which some microbes, such as iron bacteria, can obtain their energy to grow. This oxidation can cause chemical precipitation (as can other factors). The encrustations can help protect microbes, including protecting them or physically separating them from disinfectants such as chlorine. These encrustations or masses are also difficult to sample.

Acid surfactant/chlorine treatment has recently shown promise as a means of treating water well biofilms (including treating iron and sulfur bacteria associated with biofilms). Water well biofilms, which at a minimum can cause taste and odor problems, are often difficult to treat with chlorination alone. Nevertheless, repeated high dose (shock) chlorination treatment is still commonly used by well drillers to control biological growths (Oliphant et al. 2002). Acids, such as sulfamic acid (NH_2SO_3H), are effective at killing or disrupting bacteria and help dissolve the encrustation. This aids chemical penetration. The surfactant also helps penetration into the biofilm or aquifer materials (which may harbor biofilms), in part due to its ability to disperse clays. It may also solubilize some cations by forming soluble complexes (depending on the composition of the surfactant). Therefore, treating wells with (iron and sulfur bacteria related) biofilms with an acid surfactant, and then following the acid surfactant treatment with a low dose of chlorine, may be a better alternative to chlorine to treat biofilms while reducing or minimizing arsenic release. Several private wells with iron and sulfur bacteria infestations were tested following this treatment, not only for the amount of arsenic released, but also for the effectiveness of the treatment on the biofilm.

Finally, in the fourth phase, some crude experiments were run to shed some light on the speculation that deposits of minerals in household plumbing (commonly called scale) could be a

source of arsenic in water at the tap. These experiments involved exposing some distribution pipe scale to chlorine bleach under different conditions, and then checking for arsenic release.

It should be stated that the original intent of this project, to test whether steam could be used to disinfect wells and concomitantly reduce (relative to chlorine disinfection) arsenic buildup, was not carried out. Because of changes in Wisconsin Department of Natural Resources policy and other factors, we were not able to find wells on which we could conduct steam disinfection experiments. However, working with staff from the Wisconsin Department of Natural Resources, the Wisconsin Geological and Natural History Survey, the US Geological Survey, and University of Wisconsin Extension, we were able to develop alternative plans to provide useful information. While steam disinfection still is a potentially useful technique to minimize arsenic release while providing adequate disinfection, the limited availability of steam disinfection suggests that, at least at present, techniques such as dosing with acid surfactant followed by low dose chlorination are more attractive.

It is recognized that more data than generated in this study are needed to be able to confidently manage the problem of arsenic release resulting from disinfection. Unfortunately, because of the variables that cannot be fully controlled (e.g., changing groundwater levels or the spatial heterogeneity of mineral deposits), data from only a few sites makes interpretation difficult. Further, the expense of drilling wells and issues concerning access to private land limits experiments. Nevertheless, while the limitations of the current work are acknowledged, it is hoped that the results will contribute to the knowledge base that will eventually lead to enlightened management of our groundwater resources.

MATERIALS AND METHODS

Phase One

The test well was located in the Town of Algoma in northeast Wisconsin and within the Arsenic Advisory Area. The geologic setting may be found in Schreiber et al. (2000). In general, Precambrian rocks are overlain by Cambrian sandstones that are overlain by the Prairie du Chien group. The Prairie du Chien group, consisting of dolomitized limestones, is in turn overlain by the St. Peter Sandstone strata, the Sinnipee Group and finally by Quarternary deposits. The Sinnipee Group consists of dolostone with minor shales (Schreiber et al. 2000). A sulfide mineralization, possibly the result of liquids moving along the sandstone path, forms a layer or zone called the sulfide cement horizon at the base of the Sinnipee Group and at the top of the St. Peter Sandstone layer. The layer is of variable thickness, but is usually a band about 0.5 cm-thick. A rock core obtained from the upper 4.5 m of the sandstone at the field site of the study reported here indicate veins and nodules of sulfide mineralization were scattered throughout. An orange-colored rind, presumed to be an iron oxide coating on some of the mineralization, was present at the time of core recovery. A majority of the sandstone appears oxidized with a white-pink to red color. The well is cased through much of the dolomite, and is open to the top of the St. Peter Sandstone. Hydraulic testing of the well showed that a majority of the groundwater that flows to the well is from the St. Peter sandstone rather than the overlying dolomite. The St. Peter sandstone is under confined conditions at this location. The well itself may be dewatered when pumped at a rate exceeding 15 gpm.

The well was initially tested for arsenic, iron and bacteria to verify that an infestation was present and to determine current background water quality. The well was subsequently purged of three well volumes (about 20 minutes of pumping out the well) and re-sampled. The samples were analyzed for total arsenic, dissolved arsenic, iron, sulfate, and bacteria. Initially, samples were also tested for arsenic III (As^{3+}) to assess the oxidative state of the arsenic before and after

treatment. The well was then subjected sequentially to the three disinfection techniques, each disinfection followed by (1) purging of the disinfectant, (2) a three week period where water was pumped from the well to simulate a normal household water usage of 100 gallons (378 L) every eight hours, and (3) a period where the well was left alone (non-pumping conditions) to allow it to return, to the extent possible, to pre-disinfection and pre-purging conditions Note that it is well-known that, generally, periods of nonuse or occasional use allow biofilms to build-up relatively rapidly. Water samples were taken at various stages, including immediately after disinfection and after the disinfection agent had been purged. Sampling pumped water may not provide a representation of the microbe population, as pumping may not detach or dislodge biofilm particles. Biofilm particles do seem to detach more readily upon pump start-up, particularly after the pump has been off for a period of time (Cullimore, 1993). This was the sampling practice used in this study. Water samples were again analyzed for arsenic, iron and bacteria. Disinfection techniques were (1) a low dose (100 mg/L Cl_2) chlorination, (2) an acid surfactant/low dose (~60 mg/L Cl_2) treatment, and (3) a high dose (1200 mg/L Cl_2) or shock chlorination. These techniques simulate what is being used, or could be used, by well drillers in the field. Field measurements of chlorine concentrations were determined using the "DPD" method (Standard Methods, 1999) with a Hach DR/890 Colorimeter and AccuVac® vials. Each day the field colorimeter calibration was verified with a potassium permanganate standard (Standard Methods, 1999).

The low-dose chlorination treatment of the test well used chlorine bleach (Chlorox®) containing 6% sodium hypochlorite, following the standard practice used by commercial well drillers (Appendix A). A solution calculated to produce a final concentration of ~100 mg/L chlorine in the well was poured into the well and re-circulated for one-half hour. The chlorine

concentration of the recirculation water was tested in the field to be 110 mg/L using the DPD method (Standard Methods, 1999). The well was purged until no chlorine smell was detected. The absence of chlorine was confirmed by field analysis.

Household chlorine bleach, the most common product used to disinfect wells in Wisconsin, is a sodium hypochlorite solution that can contain from 3.0 to 6.0% available chlorine (depending on the brand, density and age). The available chlorine concentration decreases over time, so the percentage stated on the label is only an approximation. In water, bleach very quickly forms hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) according to the following reactions:

$$NaOCl\ (bleach) + H_2O \rightarrow Na^+ + HOCl + OH^- \quad (1)$$

$$HOCl \leftrightarrow H^+ + OCl^- \quad (2).$$

As Equation 2 implies, the dissociation of HOCl is controlled by pH. At pH 7.5, both forms are present in equal concentrations (50:50). Under more acidic conditions HOCl predominates, while under more basic conditions OCl^- predominates.

Both the neutral and ionic forms are considered "free" or "available" chlorine. Both forms kill bacteria given the proper concentration and contact time. However, hypochlorous acid is about 20 times more powerful a germicide than hypochlorite. This means chlorine bleach has the best germicidal properties when the pH is below 7. Unfortunately, this information is not usually accounted for in most disinfection operations. Further, as can be seen from equation 1, the reaction of bleach with water will cause the pH to increase (as will be discussed in more detail later), resulting in a further reduction in biocidal properties.

The acid surfactant treatment of the test well used a commercially available acid surfactant, Aqua-Clear AE®. A solution of 1.8 gallons (6.8 L) of Aqua-Clear AE in 20 gallons

(75.7 L) of well water was poured into the well followed by 80 gallons (308 L) of previously withdrawn well water. The water in the well was mixed by re-circulation (pumping water out of the well and re-injecting the water into the borehole), allowed to sit idle for one hour and re-circulated again for one-half hour. The well was purged until the pH returned to within 0.5 units of original measurement (7.0 units). A solution calculated to produce a final concentration of 60 mg/L chlorine in the well (prepared using Chlorox® bleach) was added to the well and re-circulated for fifteen minutes. The well was purged until no chlorine was detected using the field method for detecting chlorine.

For high dose or shock chlorination treatment of the test well, commercially available chlorine bleach was again used. A solution containing 2 gallons (7.6 L) of bleach in 100 gallons (378.5 L) of well water (final concentration in well estimated to be about 1200 mg/L chlorine in the well) was poured into the well, the well water re-circulated to ensure mixing and then allowed to sit idle for 24 hours (Appendix A). The next day, the well was purged until no chlorine was detected using the field method.

Phase 2

In phase two, ninety-nine private wells in the Arsenic Advisory Area were identified by the WDNR as having arsenic and other data useful to this study. Using the experience of field workers at WDNR, 84 wells were then selected for potential additional data collection. Owners of these 84 wells were sent a brief survey (Appendix B) along with sample bottles and sample collection instructions. They were requested to return the survey to the WSLH along with a sample of their well water for arsenic and bacteria analyses. Follow-up phone calls were made to encourage completion of the survey.

The survey requested information on the disinfection history of their well (e.g., did they have a record of how their well was chlorinated after installation), whether any water treatment devices were installed on their water system, and if the well water was currently used for drinking. This survey information, along with other information collected by the WDNR from the Arsenic Advisory Area (see below), was used to establish use history of the wells and to look for relationships between arsenic releases and well construction and/or disinfection.

Other information collected included the method used to drill the well. Rotary drilling is commonly used to drill wells in this region. The spinning drill bit is cooled by pumping air (air-rotary drilling) or water (wash-rotary drilling) down the outside or inside of the drill bit. The air or water also forces the drilled material to the surface.

There are also different methods of grouting the well, and data was collected on which method was used. The Bradenhead method is where a PVC pipe is placed inside the casing to the bottom of the borehole. With the casing held off the bottom, a seal is placed on the top of the casing and cement is pumped down the PVC pipe. Since the casing is sealed at the top, the cement is pushed up from the bottom. The Bradenhead method tends to clean the hole and provides more control for the well driller in performing the grouting operation. In the Tremie procedure, the injection pipe goes down the outside of the casing. The pipe used must be smaller than in the Bradenhead technique. The result is more mixing of mud with the cement, causing the grout to be more pervious. Finally, a third grouting technique considered is the Cuttings technique. It is only used on shallow wells (not in bedrock). In this case the drill cuttings and drilling mud are poured in the annular space around the casing in place of cement.

Phase 3

To gather information on the effect on biofilms of acid surfactant treatment of wells, three private wells were identified from the Arsenic Advisory Area that had biofilms containing iron and sulfur reducing bacteria. They were treated with acid surfactant and then chlorinated using a low chlorine dose. Acid surfactants were added as explained under Phase 2. The surfactant was allowed to remain in the well for about 24 hours before the well was purged to remove the surfactant. Following this purge, the well was disinfected using a low dose chlorination procedure (Cl_2 concentration in the well about 60 mg/L). Note that the treatments and collection of samples was performed by professional well drillers.

Samples were collected for arsenic and coliform bacteria analysis before the acid surfactant treatment and then shortly after the acid surfactant purging was started (within about 15 minutes after purging commenced). Samples were also collected periodically over the three weeks following the chlorination while the wells were in normal household use. Sampling varied between sites due to the logistics of sampling, which was done by either WDNR field staff or well drillers.

Phase 4

Samples of scale were obtained from the original distribution system pipes that were removed from a private home in the Arsenic Advisory Area. These pipes had been in use since the well was installed in 1995. A cutaway photograph showing scale on the inside of the pipe is presented later (Discussion). A sample of the scale was ground with a mortar and pestle, dried at 103-105° C, and 1 g portions were placed in 250 mL beakers. ASTM Type 1 water (100 mL) was added to the beakers. Household bleach was added, corresponding to 100 and 500 mg/L free chlorine, respectively. The addition of chlorine will raise the pH of most waters. The equations below show that addition of sodium hypochlorite or calcium hypochlorite (granular

calcium hypochlorite is often added to wells by well drillers as it dissolves slowly, providing the release of free chlorine over a longer period of time) results in hydroxide production.

$$NaOCl + H_2O \rightarrow HOCl + NaOH \quad (3)$$

$$Ca(OCl)_2 + 2H_2O \rightarrow 2HOCl + Ca(OH)_2 \quad (4)$$

The addition of chlorine to the 100 and 500 mg/L Cl_2 level raised the pH to approximately 8.0 and 9.3, respectively. A second set of beakers was prepared in the same way, except that after adding the chlorine the pH was lowered to about 5 by addition of dilute nitric acid.. After stirring the beakers with a magnetic stirrer for 30 minutes, the solutions were allowed to sit overnight (a total of about 18 hours chlorine contact time). Aliquots from the beakers were then analyzed for total arsenic. In this way the effect of chlorination on the leaching of arsenic from scale, with and without pH adjustment, were estimated.

Laboratory Analyses

All water samples were collected in polyethylene bottles. Aliquots of samples collected for arsenic and iron analyses by laboratory staff from the test well disinfection experiments (Phase 1) were preserved with 1:1 nitric acid to a pH <2 (0.5% HNO_3) immediately after collection. The remaining samples (phase 2 and 3) that could not be collected by laboratory staff, were preserved with HNO_3 to pH <2 upon receipt in the laboratory. Samples preserved in the laboratory were allowed to sit for a minimum of 16 hours prior to analysis. Sulfate samples were placed on ice immediately after collection and maintained at <4^{o}C in the laboratory prior to analysis. All sulfate analyses were performed within 28 days of collection.

Total arsenic determinations were performed on a Perkin Elmer 4100ZL graphite furnace atomic absorption spectrophotometer (GFAAS) using an electrodeless discharge lamp according to Method 3113B Standard Methods for the Examination of Water and Wastewater (Standard

Methods, 1999). A matrix modifier was used at a rate of 5 µg Pd and 3 µg $Mg(NO_3)_2$ per each 20 µL of sample. The instrument was calibrated each day with five standards in the range of 3.2 µg/L to 100 µg/L with a minimum correlation coefficient (r) of 0.999. Samples containing greater than 100 µg/L were diluted into the calibration range. The method detection limit for arsenic was 1 µg/L. The analytical uncertainty was always less than 5%, with a mean uncertainty of ~2%. The mean spike recovery was 103% (n=39) with a standard deviation of 7.8%.

Iron determinations were performed on a Thermo Jarrell Ash 61E simultaneous inductively coupled plasma-optical emission spectrometer (ICP-AES) according to USEPA Method 200.7. The method detection limit for iron was 0.1 mg/L. The instrument was calibrated each day with three standards in the range of 0.3 mg/L to 150 mg/L (a correlation coefficient of 0.999 was required). The method detection limit for iron was 0.1 mg/L. The analytical uncertainty was always less than 3%, with a mean uncertainty of ~0.8%. The mean spike recovery was 96.4% (n=30) with a standard deviation of 3.2%.

All samples for arsenic and iron analysis were tested for turbidity after preservation and prior to analysis. If the turbidity level was >1 NTU, the sample was subjected to a hot acid digestion to solubilize the particulate matter prior to analysis. Samples that were in excess of 1 NTU were digested using a Environment Express hot block according to USEPA SW846 Method 7060A for arsenic and SW846 Method 3005A for iron. Arsenic and iron determinations performed on samples analyzed directly (e.g., turbidity of <1 NTU) or after preliminary digestion (turbidity of >1 NTU) are considered equivalent (EPA 200.7, 3.20). Dissolved arsenic and iron analyses were performed on samples filtered using 0.45µ membrane filters.

Sulfate was measured on a Lachat 8000 automated flow-injection analysis (FIA) system that utilizes methylthymol blue colorimetry according to USEPA Method 375.2. The instrument was calibrated each day with five standards in the range of 4.5 mg/L to 50 mg/L. Since the calibration curve is non-linear, the instrument uses a third order polynomial curve fit yielding a minimum correlation coefficient (r) of 0.995. Samples containing greater than 50 mg/L were diluted into the calibration range. The method detection limit for sulfate was 4.5 mg/L. The analytical uncertainty was always less than 2%, with a mean uncertainty of ~0.6%. The mean spike recovery was 104% (n=12) with a standard deviation of 8.4%.

Microbiological analyses for coliform bacteria, heterotrophic bacteria and iron bacteria were performed using standard techniques described in Standard Methods (1999) as well as in the Wisconsin State Laboratory of Hygiene Environmental Testing Methods Manual (2003). Coliform bacteria were detected with MMO-MUG defined substrate (Colilert™) test. The heterotrophic plate count was performed using R2A agar incubated at 22° C for five days. Iron bacteria were identified and counted microscopically. The presence or absence of sulfate reducing bacteria was performed via selective media culture using the methods of Postgate (1963)

RESULTS

Phase 1

Arsenic and bacteria results for the test well at different stages of treatment are given in Tables 1 and 2. Total arsenic concentrations ranged from 0.5 µg/L to 56.7 µg/L. Relatively low total arsenic concentrations occurred when water was pumped from the well, but the concentrations increased when pumping ceased and the well remained stagnant for several

weeks. Most total dissolved arsenic measurements were about the same as the total arsenic, indicating there was little or no suspended or particulate arsenic in the groundwater samples. Most of the dissolved arsenic was present as As^{3+}, as indicated in Table 1. Total dissolved iron concentrations were about the same as total iron concentrations, again indicating low particulates in the samples. Sulfate concentrations ranged from 13.4 to 18.5 mg/L, typical for groundwater from the St. Peter Sandstone aquifer.

Microbiological results for the test well are given in Table 2. All three species of iron bacteria were detected at one time or another. Highest counts were recorded for *Leptothrix*. Sulfur reducing bacteria were also found in a number of samples. The heterotrophic plate count was quite variable, with the highest count at 3700 colony forming units per milliliter (CFU/mL).

Phase 2

Total arsenic results for the 42 wells whose owners returned surveys and submitted samples are given in Table 3. The Table also includes other arsenic data obtained prior to the survey. Total arsenic concentrations ranged from a high of 202 µg/L to not detectable. Several of the wells exceed 10 µg/L total arsenic even though owners reported that a treatment system of some type was in place. In only a few cases were concentrations from the recent survey appreciably lower than when the well was installed or in previous years. In a few instances the concentration of the sample submitted by the homeowners was appreciably higher than concentrations from previous monitoring. The drilling methods given in Table 3 indicate the wells were drilled using an air-rotary or wash-rotary technique.

Bacteria analysis results from the 42 surveyed sites are given in Table 4. Iron bacteria and sulfur bacteria were present in many of the wells, even when total coliform bacteria were not present. The heterotrophic plate count ranged from <1 to 8700 CFU/ml.

Phase 3

Table 5 presents arsenic and iron levels in the three household wells that were treated with an acid surfactant followed by a low dose of chlorine. As can be seen in Table 5, total arsenic concentrations ranged from not detected to nearly 50 µg/L. In well A the highest level of arsenic was found in the purge water sample collected after the acid surfactant treatment. All total arsenic values exceeded 5 µg/L in this well. Well C had high total arsenic levels, and the levels remained high after treatment. Total iron was low in well A (less than 1 mg/L), except for the purge water following acid surfactant treatment where the iron averaged 5 mg/L. This increase in iron mirrored a similar large increase in total arsenic. No total iron measurements were made on Well B, but Well C had high total iron levels (near 50 mg/L). Like the total arsenic data, the total iron in Well C did not change much from before the acid surfactant treatment.

Table 6 presents bacteria data obtained from the three wells subjected to acid surfactant treatment. The acid surfactant treatments reduced the iron bacteria levels in each well tested and did not cause a subsequent release of arsenic from the well or aquifer. However, the purge water containing the acid surfactant contained significant amounts of arsenic and iron, indicating arsenic release from the rock surface exposed in the well or the pipes. The arsenic and iron levels returned to their initial levels after treatment and remained there for the following three weeks. A portion of the scale removed from the pipes at one of these wells was found to contain 345 µg/g arsenic and 468,000 µg/g iron.

Phase 4

Scale taken from a household distribution system pipe was found to contain 47,000 µg/g total arsenic. The well from which this pipe scale was obtained was previously found to produce

water with about 19 µg/L of total arsenic. The results of a simple leaching test, using chlorine-dosed water unadjusted for pH and adjusted to a pH of 5 are given in Table 7. The table shows that the addition of sodium and calcium hypochlorite caused considerable dissolution of arsenic and that lowering the pH (disinfection is enhanced at lower pH) reduced arsenic dissolution.

DISCUSSION

Phase 1

Figure 1 graphs total arsenic levels in the test well and the effect of low dose chlorination, acid surfactant disinfection and finally high dose (shock) chlorination. At the start of the experiment, simply flushing the system (purging three well volumes; see Fig. 1a) reduced the arsenic concentration. Water drawn from the well after the low dose chlorine treatment (and after the prescribed contact time) had lower total arsenic than the baseline (stagnant) total arsenic concentrations. By the time all the residual chlorine was purged from the well the total arsenic had decreased from over 18 µg/L to 5 µg/L. During pumping simulating normal household water use the total arsenic increased, although at 20 days after disinfection the concentration was recorded to be less than 5 µg/L (Fig. 1a).

After letting the well remain stagnant the total arsenic again increased to 18 µg/L (Fig. 1b), similar to the concentration at the start of the study. As stated earlier, a period of stagnation tends to accelerate the re-growth of biofilms. Therefore, it is suspected that the arsenic increase is related to biofilm growth, suggesting that microbially mediated reduction of arsenic-bearing iron oxides occurs in the stagnant borehole Purging the well again decreased the concentration. However, adding the acid surfactant and then chlorinating to a very low chlorine concentration

(60 mg/L chlorine) caused the arsenic concentration to increase to the highest recorded level (56.7 μg/L). Continued purging casued the total arsenic in the well to drop precipitously. As Figure 1b shows, total arsenic levels remained well under 10 μg/L for the duration of the acid surfactant experiment.

As shown in Figure 1c, the total arsenic concentration did not return to as high a concentration as previously noted under stagnant conditions. However, pumping water out of the well again reduced total arsenic levels. Large dose chlorination did cause an increase in total arsenic immediately after the disinfection was conducted. After the disinfectant was purged, total arsenic was low and remained low under normal pumping conditions until the end of the study. At this well, shock chlorination does not appear to have caused anything other than a temporary increase in arsenic concentrations. Here, where the aquifer is~~n~~ under confined conditions, chemical oxidation resulting from shock chlorination does not appear to be a trigger of arsenic release to well water. The results suggest that acid surfactant treatment and chlorination are followed by an initial release of arsenic. This arsenic increase is probably the result of the destruction, or perhaps erosion, of biofilms. Biofilms likely scavenge dissolved arsenic through a sorption process, or arsenic is released as minerals undergo microbial oxidation. Arsenic readily sorbs onto metal hydroxides or other solid precipitates that can be formed within the biofilm. As will be discussed subsequently, encrustations within the well (scale) system can contain considerable amounts of arsenic.

Figure 2 shows how total iron responded to the treatments. Each of the treatments reduced the total iron concentrations. However, total iron increased once the well remained stagnant for a period of time. Total iron and total arsenic were reasonably well associated.

Figure 3 is a plot of total iron versus total arsenic. The correlation coefficient of 0.74 suggests an association.

Like arsenic, total iron decreased simply due to flushing (unfortunately, no data was available for the total iron level in the purge water-). Iron measurements were made immediately after the treatments. In retrospect, it would be interesting to know if iron levels were high in the purge water, as did the arsenic concentration. However, there is anecdotal evidence, based on field observations, to suggest that iron levels were higher in the purge water. One of the investigators recalled the purge water from the low dose chlorination was cloudy but the purge water from the acid surfactant was brown, indicating it likely had a higher iron concentration. If iron levels did rise, it would add credence to the suggestion that the break up of the biofilm (encrustation) causes release of chemicals trapped in the biofilm (encrustation).

It is interesting that when dissolved arsenic and iron levels were measured, values were close to total arsenic and iron. This indicates that most of the arsenic and iron measured in the water was dissolved. That the arsenic and iron would be in the dissolved state is consistent with turbidity measurements, which found that turbidity was typically low. The dissolved arsenic and iron probably existed as a soluble complex rather than as the free metal ion. Kim et al. (2000) suggest carbonate complexes, such as $As(CO_3)_2^{-1}$ or $AsCO_3^{+1}$, are stable in groundwater (at least in the Midwestern United States). The speciation reported here (Table 1) indicates the dissolved arsenic was mostly As(III). This finding is consistent with the carbonate complexes suggested by Kim et al. (2000). Heterotrophic plate counts during the different treatments are shown in Figure 4. Plate counts were quite variable, but, based on the data, the acid surfactant treatment was least effective at reducing bacteria. However, as mentioned previously, it is well established that heterotrophic plate counts are difficult to interpret. It is not unusual for wells that have no

pathogens to have large heterotrophic plate counts. Counts above about 200 CFU/mL do indicate that a substantial population of bacteria is in the sample (not necessarily the well). Again, heterotrophic counts were high after the acid surfactant treatment.

Iron and sulfur bacteria (Table 2) levels in the well water were quite variable. These levels probably relate to the fact that the bacteria were associated with biofilms (encrustations) that are not homogeneously distributed. Moreover, unless the biofilm is dispersed or broken up, there may be little evidence of the biofilm in the sample. Consequently, as discussed previously, bacteria in wells are difficult to sample. Iron and/or sulfur bacteria were present in some form in every sample. While the treatments did initially reduce the amount of iron and/or sulfur bacteria (at least somewhat), none of the samples were free of them. Highest levels occurred, for the most part, when the well sat idle after the simulated household use. Again, this is consistent with the common observation that biofilms often grow rapidly after a period of pumping followed by a period of stagnation.

To summarize Figures 1, 2 and 4, the initial purge of the well (after treatment) caused a decrease in total arsenic, total iron, and heterotrophic Plate Count. Tests performed on this well before this study also found that pumping the well without treatment with disinfection agents caused the dissolved arsenic to decrease from 18 µg/L to between 2 and 6 µg/L after about 14 days. Therefore, it appears that, for this well at least, simply pumping water from the well can reduce arsenic levels. On the other hand letting the well sit unused caused arsenic levels to increase.

As mentioned, the acid surfactant treatment and the shock chlorination appeared to remove a significant amount of arsenic from the aquifer rock and/or from the well structure (including the distribution pipes). The chlorination and the acid surfactants may have broken up

the structure of the biofilms (encrustations) releasing arsenic from the biofilm in the process. As Phase 3 and 4 data show (to be discussed later), encrustations (scale deposits) can contain high levels of arsenic.

None of the three treatments appeared to have a permanent affect on well water quality. During periods of pumping following each treatment, lower arsenic and iron concentrations reflected the aquifer water quality. After pumping was discontinued, bacteria, arsenic and iron concentrations increased under stagnant conditions. This suggests that the growth of bacterial populations in the borehole or aquifer rock is connected to the release of arsenic and iron to the well water. This observation is significant because if microbiological activity contributes low (but of regulatory significant) levels of arsenic to wells in the Fox River valley area, control of microbiological growth through well disinfection may aid in reducing arsenic concentrations in some settings. These findings suggest that at this test well, chlorination following either of the DNRs recommended procedures did not accelerate release of arsenic from sulfide minerals within the borehole or aquifer rock.

Although the data from Phase 1 do not indicate such, anecdotal observations of well drillers and WDNR field personnel often suggest that the acid surfactant treatment scheme is the most effective biofilm treatment. Again, in this study negative effects of shock chlorination were not demonstrated. While the advantage of one technique over the other may not be obvious, it is clear that biofilms are notoriously difficult, if not impossible, to permanently eradicate from wells. Even if the well is effectively sterilized, bacteria may re-inoculate the well via aerosols drawn into the wellhead (Trest et al. 2000) or perhaps from bacteria carried by water from other parts of the aquifer. Figuring out how to eliminate biofilms in wells, although so far a tough problem may be the key to keeping arsenic levels low.

Phase 2

Figures 5 through 9 describe arsenic levels in relation to the type of aquifer, the type of well drilling technique used, and the chlorination technique used. As discussed, these data were from a survey of well owners (and analyses of samples sent by survey participants) and from other data available in Wisconsin's well database. The attempt was to get as much data as possible, while realizing that not all variables could be controlled.

The effect of drilling technique, either air-rotary drilling or wash-rotary drilling, is shown in Figure 5. In the air rotary technique air is used to cool the drill bit and carry the drilled material to the surface. In the wash-rotary technique, water is used for cooling and to carry the drilled material to the surface. One reason for checking these techniques is the possibility that forcing air into the well might accelerate the oxidation process that is believed the primary cause of high levels of arsenic release. As Figure 5 shows, a higher percentage (about double) of wells drilled using the wash-rotary technique had low (<3 µg/L) total arsenic concentrations reported compared to wells drilled using the air-rotary technique. Air-rotary wells had twice the percentage of wells reporting arsenic concentrations between 10 and 50 µg/L. Also, concentrations reported to be greater than 50 µg/L were only from air-rotary drilled wells. These data must be viewed with caution, as variables such as whether the sample was taken after chlorination or how much pumping occurred before the sample was taken could affect results. The sample size for the air rotary systems was also about 3.5 times larger than the wash-rotary system. Nevertheless, at face value the data suggest wash-rotary is associated with lower arsenic levels in wells.

Grouting methods using Bradenhead, Tremie and Cuttings techniques also have been linked to arsenic in well water. Figure 6 shows the Bradenhead technique, based on the available

data, to be best in terms of yielding low arsenic concentrations (as mentioned in the Introduction, this grouting technique forces the grout from the bottom up using a pipe placed inside the casing). Almost 60% of the Bradenhead wells had arsenic concentrations less than 3 μg/L (Fig. 6a). None of the Bradenhead grouted wells had arsenic in excess of 50 μg/L. The Tremie technique was used the most, but over 50 percent of these wells had total arsenic concentrations greater than 10 μg/L (Figure 6b). Finally, what we are calling the cuttings grouting technique, where shallow wells are sometimes encased by cuttings and mud, was not used often (Fig. 6c). Several of these wells had arsenic concentrations below 3 μg/L, but an equal number had between 10 and 50 μg/ L of arsenic. It is not clear whether factors involved in deciding to use the Bradenhead technique may be confounding the interpretation of the results, but it appears that the Bradenhead technique is preferred from the standpoint of minimizing the amount of arsenic in the well water.

Another variable investigated was whether the source aquifer was classified as unconfined, confined or semiconfined. It has been suggested by some that confined systems, because of their isolation from ambient oxygen, might be less likely to have high arsenic or at least might show observable differences in arsenic buildup tendencies from unconfined wells. However, Figure 7 shows no obvious differences between confined and unconfined wells. Interestingly, semiconfined aquifers (see Fig. 7c) had a much higher percentage of wells with arsenic concentrations less than 3 μg/L. Overall, however, there is no clear indication that confined groundwater aquifers tend to produce water with less arsenic than unconfined aquifers.

Wells for which data were available were also classified according to the chlorination treatment used (Figure 8). These data do suggest that wells that were chlorinated with the lowest chlorine doses had the greatest percentage of wells with low arsenic levels. The sample size for

these wells (Figure 8a) was small (n=13), however. Wells chlorinated at medium or high chlorine doses did yield a large number of wells with total arsenic greater than 10 µg/L. Again, the variables may not be independent. For example, larger chlorine doses may have been used when biofilms were a major problem. The biofilms may be influencing the arsenic levels more than the chlorine.

The wash-rotary drilling effectiveness at producing low arsenic wells did not appear to be diminished when the level of chlorination was increased. Figure 9 shows the effect of chlorine dose on arsenic levels for only those wells constructed by wash-rotary drilling. It appears that the percent of wells with low levels of arsenic is low for all chlorination conditions. Sample size is small, however, so this observation needs to be confirmed. Although not graphed due to the unequal sample size distribution, there was not an obvious difference in arsenic concentrations according to chlorination levels for wells drilled by the air-rotary technique.

Phase 3

Of the three wells treated by acid surfactant followed by low dose chlorination, Well A (Table 5) produced the most useful data. The after treatment purge water contained elevated levels of both arsenic and iron. Concentrations decreased to pre-treatment levels after the well was purged. Figure 10 plots total iron versus total arsenic concentrations. As in the Phase 1 test well, a reasonably strong (r= 0.97) association between arsenic and iron was observed. This suggests that arsenic and iron are being released upon treatment, probably because of the breakup or dissolution of biofilms. Bacteria data (Table 6) , while not showing any pattern, reveal that some type of iron and/or sulfur bacteria were found in most samples. The biofilms (or scale) may have been from the well casing or the pipes of the distribution system. Scale removed from a pipe from Well A was found to contain 345 µg/g of arsenic and 468,000 µg/g of

iron, so this suggest that breakup of the biofilm (encrustation) with an acid surfactant and chlorine could cause the release of arsenic and iron to the well water. As water is pumped out of the well and is replaced by fresh groundwater from the aquifer, concentrations in the well water would be gradually reduced.

The other two wells in Phase 3 provided little useful or comprehensible information. Not much data was obtained on Well B, and arsenic concentrations were always low. Well C was curious in that high arsenic and iron concentrations were found before and after treatment. Concentrations changed little throughout the test period. It may be that well water levels (which will vary under different pumping scenarios) and location of arsenic bearing sulfide minerals play a major role (or they play a different role than they do in, for example, Well A) in the build-up of arsenic in this well. Clearly, there can be great heterogeneity in the water chemistry of closely adjacent wells due to (among other things) the spatial heterogeneity of mineral deposits (Schreiber et al. 2000). Unlike most of the wells studied or reported on, arsenic concentrations were high before treatment and remained high even after treatment and subsequent purging. This well is probably in an over-all more oxygenated environment (perhaps under water table conditions). Here, arsenic release in the well borehole and the surrounding aquifer may be attributed to abiotic oxidation of sulfide minerals. Hence, a decrease in microbial activity would not alter the pattern of arsenic release.

Interpreting results from these three wells would benefit from information on well construction (i.e. casing depth), static and pumping water levels, and geology (that is, is the well open to the top of the St. Peter). Unfortunately, at the time of this writing such information was not available. For example, such information might suggest that the water level in well C was coincident with the top of the St. Peter formation. This could explain the fact that As levels in

this well remained similar after chlorination (when presumably bacteria were not active), indicating that 1) arsenic release is not microbially mediated at this well, and 2) chemical oxidation (chlorination) did not exacerbate arsenic release. Also interesting in Table 6 is that this well has very high levels of Fe-oxidizing bacteria—perhaps this implies that it is naturally under oxidizing, or unconfined, conditions.

Phase 4

A photograph of the inside of a cross-section of pipe obtained from the distribution system sampled for Phase 4 is shown in Figure 11. The scale is an example of what can be found in most household distribution systems in northeastern Wisconsin. Groundwater in this area of the state is generally not as hard as in the southern and southwestern parts of the state. Hardness in northeastern Wisconsin groundwater, while variable, is generally on the order of 100-200 mg/L as $CaCO_3$. A sample of this scale/encrustation was used in the Phase 4 leaching experiments.

As shown in Table 7, the non-pH adjusted solutions removed more than 30 times the amount of arsenic as the pH adjusted solutions. The pH seemed to play a more important role than the chlorine concentration. Given that the scale contained 47,000 μg of arsenic per gram, at the higher pH conditions roughly, 15 per cent of the arsenic was leached from the scale.

Acid surfactants are, as the name implies, acidic. A main component is an organic acid. However, if bleach is used to disinfect after an acid surfactant treatment is flushed, the pH will again increase. This would favor the release of arsenic at this point. In other words, chlorination will increase the pH, and high pH favors the release of arsenic. Kim et al. (2000) also reported increased arsenic leaching as pH increased.

In the field, upon completion of the well drilling operation, the well installer will typically disinfect the well with a gallon of bleach and a couple of handfuls of calcium hypochlorite pellets. In the average well this would lead to concentrations of greater than 700 mg/L of chlorine. It would also lead to a pH increase of around one unit, and will reduce (as explained earlier) the biocidal activity. If a well has iron or sulfur bacteria problems, contractors commonly pour 3 to 4 gallons of bleach into the well. At this application rate well water chlorine concentrations would be about 2000 mg/L, and the pH would increase about 2.5 units. Given these scenarios and the above experiment, chlorination would lead to the release of arsenic associated with scale.

As was discussed earlier, the disinfecting property is greatly enhanced at lower pH levels. Reducing the pH in wells during disinfection would likely provide much better disinfection and could reduce the amount of bleach needed. As these experiments indicate, this could reduce release of arsenic upon chlorination. Having said that, the release of arsenic upon treatment may not be a critical problem if the well is properly flushed.

The practice of throwing some calcium hypochlorite into the well is interesting. These granules dissolve slowly, releasing chlorine over time (as much as several months- commercial versions for toilets provide long-term toilet disinfection). This practice, while providing disinfection, may also be contributing to the continuing release of arsenic. It is also unclear whether adding some solid calcium hypochlorite significantly retards the re-growth of biofilms.

SUMMARY

Although this study was originally designed to test whether steam distillation could reduce arsenic release in wells, the private wells we had intended to use for study became unavailable. Consequently, a number of experiments were done to gain as much insight as

possible on how disinfecting conditions can affect arsenic release. The study utilized four phases. Phase 1 consisted of studies of a test well subjected (sequentially over time) to different disinfection treatments. Phase 2 utilized a larger but imperfect data set, supplemented by results of analyses of samples submitted by surveyed volunteers. In the third phase three wells with biofilms (biological encrustations) were treated with an acid surfactant and then low dose chlorination to test further this often-preferred treatment for biofilms. The fourth phase involved measuring arsenic released from scale treated with chlorine at different pH levels. From each of the phases a common theme arose, namely that the different treatments often caused arsenic levels to temporarily increase in the well water. It is believed that bacterial biofilms or encrustations are being destabilized or solubilized by the chemical treatment. Arsenic contained in or associated with the biofilm or encrustation is then released. Once flushed (several well volumes pumped out), arsenic levels generally decreased.

The role of biofilms or biological encrustations in concentrating or scavenging arsenic is not clear, although it is probably associated with the process by which iron, sulfur and other elements are oxidized by bacteria. The oxidized forms then precipitate. Iron and arsenic correlations observed in this study further suggest the association. Since biofilm growth is a dynamic process involving build-up and decomposition of the mass, arsenic may at times be released to the water. This may explain, at least in some instances, variable concentrations of arsenic in wells.

Extant data from well records suggest that rotary-water drilling is the preferred method to minimize arsenic levels in the water. Whether the aquifer was confined or unconfined did not seem to affect arsenic levels, a result that was somewhat unexpected. Regarding grouting, the

Bradenhead technique was associated with lower arsenic levels, so at this point should be recommended.

Disinfecting at reduced pH levels will greatly increase the biocidal effectiveness of chlorine. This may be important for retarding the re-growth of biofilms (and help to lessen the continued concentration of arsenic in the biofilms). The acidity may also help dissolve mineral components (e.g., hydroxides) in the biofilm so that the disinfectant can better penetrate the encrustation.

Clearly, aquifer hydrologic characteristics are complex, as are the causes of groundwater contamination by arsenic. The hydrology and chemical characteristics of water from a given well can also be very site specific, as indicated by a variety of observations in this study. Continued study, however, offers the hope of gathering information to allow design and construction of wells that will minimize the growth of biofilms and neutralize other factors that might favor arsenic build-up in the well water.

RECOMMENDATIONS FOR FURTHER RESEARCH AND DEVELOPMENT

1. Develop a preventative maintenance regime to minimize biofilm development. The use of techniques like surging (surging water into the well in hopes of dislodging encrustations) or the addition of chelating agents should be evaluated. Chelating agents may solubilize metal hydroxides and other precipitates (carbonates) that provide structure and protection for the biomass.
2. Develop well design and well drilling principles that will minimize or prevent biofilm development.

3. Develop a protocol for regular monitoring of wells for biofilm problems, so that they can be diagnosed as early as possible. The biofilm literature suggests biofilms are most easily treated when discovered early.
4. Study Well C from Phase 3 in more detail. Examine why arsenic levels are so high.
5. Steam disinfection, or at least hot water shocking, is still worthy of study. The difficulty lies in finding appropriate sites to apply the technique in a way that allows the generation of useful data. However, research on the efficacy of steam distillation on arsenic release is still desirable should circumstances permit.
6. More research is needed on how biofilms become re-established. Are microbes entering from the surrounding aquifers? It has been established (at the Wisconsin State Laboratory of Hygiene; Trest et al. 2000) that air drawn into wells during pumping likely carries microorganisms into wells, so the effect of filtering that air on biofilm growth and re-growth would be useful information.
7. Because the pH of the water is so important to the efficacy of chlorine treatment as well as the release of arsenic from encrustations, more study on optimizing pH during chlorination should be done. The study should take into account safety concerns with handling acids (especially in the presence of chlorine) and the overall complexity of the treatment scheme for use by well drillers and homeowners. Developing practical techniques of application should be part of the effort.
8. The role of biological encrustations in scavenging arsenic and how these encrustations release arsenic needs more attention. A better understanding of the chemical and biological mechanisms would be helpful.

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Table 1. Arsenic, iron and sulfate data from test well subjected to different treatment procedures.

Date Collected	Time	Comment	Dissolved As^{3+} (μg/L)	Total Dissolved As (μg/L)	Total As (μg/L)	Total Dissolved Iron (mg/L)	Total Iron (mg/L)	Sulfate (mg/L)
6/6/2002	10:42	Sample of stagnant water prior to purging well	10.2	16.6	18.5	1.9	4.1	17.9
6/6/2002	11:21	Well purged for about 30 minutes prior to sampling	9.4	8.8	10.1	1.0	1.1	18.2
6/6/2002	13:35	Sample of "low dose" chlorine laced water			7.9			
6/6/2002	14:06	Sampled following purge of Cl_2 from well	ND (LOD 1)	3.1	4.9	ND (LOD 0.1)	1.1	16.5
6/7/2002	8:30	Sampled about 19 hrs following low chlorination	8.4	9.3	9.8	0.4	0.4	16.6
6/13/2002	8:30	Sampled 7 days following low chlorination	6.3	5.9	6.8	0.6	0.9	15.4
6/26/2002	9:30	Sampled 20 days following low chlorination	2.1	4.0	3.8	0.5	0.6	13.4
6/26/2002	16:30	Sampled 20 days following low chlorination and after daily use		1.4	1.8	0.2	0.2	13.9
7/16/2002	9:15	Sampled 40 days following low chlorination		3.2		ND (LOD 0.1)		
9/5/2002	10:00	Sample of stagnant water prior to purging well		13.6	17.9	3.4	8.3	15.8
9/10/2002	10:10	Well purged for about 30 minutes prior to sampling			13.6			
9/10/2002	12:17	Sample of acid surfactant laced water			56.7			
9/10/2002	14:16	Sampled following purge of acid surfactant from well and light chlorination		3.2	3.4	ND (LOD 0.1)	0.2	16.0
9/11/2002	8:15	Sampled about 18 hrs following low chlorination		5.9	6.5	0.5	0.7	15.8

Table 1. (continued) Arsenic, iron and sulfate data from test well subjected to different treatment procedures.

Date Collected	Time	Comment	Dissolved As^{3+} (μg/L)	Total Dissolved As (μg/L)	Total As (μg/L)	Total Dissolved Iron (mg/L)	Total Iron (mg/L)	Sulfate (mg/L)
9/16/2002	8:15	Sampled 6 days following acid surfactant		2.8	3.2	0.5	0.9	15
9/23/2002	8:30	Sampled 13 days following acid surfactant		2.8	2.8	0.5	0.6	14.3
9/30/2002	8:30	Sampled 20 days following acid surfactant		1.5	1.7	0.5	0.5	15.9
11/6/2002	9:34	Sample of stagnant water prior to purging well	3.1	7.4	7.9	2.9	3.1	16.6
11/6/2002	11:40	Well purged for about 30 minutes prior to sampling	3.1	3.9	3.9	0.7	0.7	17.1
11/7/2002	12:10	Sample of "high dose" chlorine laced water after 25 hrs of disinfection			10.3			
11/7/2002	13:20	Sampled following purge of Cl_2 from well	ND (LOD1)	ND (LOD =1)	0.5	ND (LOD 0.1)	ND (LOD 0.1)	15.7
11/8/2002	11:00	Sampled about 22 hrs following high chlorination	1.7	1.6	3.4	0.3	2.0	16.6
11/15/2002	13:30	Sampled 8 days following high chlorination	ND (LOD 1)	1.2	1.5	0.3	0.4	15.7
11/22/2002	15:45	Sampled 15 days following high chlorination	1.3	1.4	1.8	0.5	0.5	14.6
12/2/2002	12:00	Sampled 25 days following high chlorination	ND (LOD 1)	ND (LOD 1)	1.2		0.3	14.9
12/26/2002	10:30	Stagnant water after 3 weeks of no pumping	12.7	15.1	13.7	0.3	1	18.5

Table 2. Iron bacteria (*Leptothrix, Gallionella, and Crenothrix*), heterotrophic plate count and sulfate reducing bacteria data from test well subjected to different treatment procedures.

Date Collected	Time	Comment	*Leptothrix* (orgs/mL)	*Gallionella* (orgs/mL)	*Crenothrix* (orgs/mL)	Heterotrophic Plate Count (CFU/mL)	Sulfur Reducing Bacteria
6/6/2002	10:42	Sample of stagnant water prior to purging well	0	14	0	300	Present
6/6/2002	11:21	Well purged for about 30 minutes prior to sampling	0	7	0	1	Absent
6/6/2002	13:35	Sample of "low dose" chlorine laced water					
6/6/2002	14:06	Sampled following purge of Cl_2 from well					
6/7/2002	8:30	Sampled about 19 hrs following low chlorination					
6/13/2002	8:30	Sampled 7 days following low chlorination	0	0	28	190	Absent
6/26/2002	9:30	Sampled 20 days following low chlorination					
6/26/2002	16:30	Sampled 20 days following low chlorination and after daily use	0	0	9		Absent
7/16/2002	9:15	Sampled 40 days following low chlorination					
9/5/2002	10:00	Sample of stagnant water prior to purging well	14	0	28	1500	Absent
9/5/2002	10:00	Duplicate	21	11	21	2000	Absent
9/10/2002	10:10	Well purged for about 30 minutes prior to sampling	14	0	0	610	Present
9/10/2002	12:17	Sample of acid surfactant laced water					
9/10/2002	14:16	Sampled following purge of acid surfactant from well and light chlorination					

Table 2. (continued)Iron bacteria (*Leptothrix, Gallionella, and Crenothrix*), heterotrophic plate count and sulfate reducing bacteria data from test well subjected to different treatment procedures.

Date Collected	Time	Comment	*Leptothrix (orgs/mL)*	*Gallionella (orgs/mL)*	*Crenothrix (orgs/mL)*	Heterotrophic Plate Count (CFU/mL)	Sulfur Reducing Bacteria
9/11/2002	8:15	Sampled about 18 hrs following low chlorination					
9/16/2002	8:15	Sampled 6 days following acid surfactant	0	0	0	0	Present
9/16/2002	8:15	Duplicate	0	0	5	48	Present
9/23/2002	8:30	Sampled 13 days following acid surfactant	0	0	0	280	Absent
9/23/2002	8:30	Duplicate	8	0	0	1600	Present
9/30/2002	8:30	Sampled 20 days following acid surfactant	0	0	0	280	Absent
9/30/2002	8:30	Duplicate	0	0	7	2500	Absent
11/6/2002	9:34	Sample of stagnant water prior to purging well	110	0	0	3700	Absent
11/6/2002	11:40	Well purged for about 30 minutes prior to sampling	14	0	14	29	Absent
11/7/2002	12:10	Sample of "high dose" chlorine laced water after 25 hrs of disinfection					
11/7/2002	13:20	Sampled following purge of Cl_2 from well					
11/8/2002	11:00	Sampled about 22 hrs following high chlorination					
11/15/2002	13:30	Sampled 8 days following high chlorination	14	0	14	6	Absent
11/22/2002	15:45	Sampled 15 days following high chlorination	42	0	0	1	Absent
12/2/2002	12:00	Sampled 25 days following high chlorination	14	0	14	28	Absent
12/26/2002	10:30	Stagnant water after 3 weeks of no pumping					

Table 3. Arsenic (As) data from 42 Wells whose Owners Submitted Samples for Analysis in Connection with a Survey Concerning Their Well. Results of the Survey as Well as Historical Data are Included

Well Construction Date	Drilling Method	Total As from this Survey (μg/L)	Total As After Well Installed (μg/L)	Total As in 2001 (μg/L)	Total As in 2002 (μg/L)	Comment
Feb-97	air short	N.D.				Shock chlorinated every 6 mo.
Jun-97	air long	11.6				
Sep-98	air long	N.D.	2.0	1.2	N.D.	As treatment system in place
Aug-98	air long	N.D.	0.7	0.9	1.2	
May-00	air long	30.3				Reverse osmosis system in place
Nov-98	long	27.1	33.0			
Oct-98	long	5.6				
Jan-99	long	202				Distillation system in place
Dec-98	air long	N.D.				
Nov-99	long	9.4				
Aug-99	long	N.D.				
Nov-99	air long	15.9	14.0	18.7	15.1	Reverse osmosis system in place; untreated water has iron and smells
Dec-99	air long	10.2	9.1			
Jan-00	air long	1.4	21.2	23.5	22.1	
Dec-99	air long	9.1	10.0			Distillation system in place
Apr-00	wash	1.8	4.0	1.1		
Apr-00	air long	6.0	12.0			
May-00	air long	10.4	0.0			Reverse osmosis system in place
Jun-00	air short	33.2	9.0	5.8		
Jan-00	air long	4.2	5.6	4.8	3.3	Taste, odor and color problems
Jan-00	air long	11.2				Iron filter in place
Aug-01	wash	1.2				Sediment filter in place
Mar-01	long	N.D.				
Jul-00	air long	19.6	27.0	21.0		Reverse osmosis system in place
Jul-00	air long	N.D.	0.0	N.D.		
Sep-00	wash	N.D.	3.0	1.9		Unknown treatment system in place
Aug-00	air short	2.9	72.0	4.3		Reverse osmosis system in place

Table 3. Arsenic (As) data from 42 Wells whose Owners Submitted Samples for Analysis in Connection with a Survey Concerning Their Well. Results of the Survey as Well as Historical Data are Included

Well Construction Date	Drilling Method	Total As from this Survey (μg/L)	Total As After Well Installed (μg/L)	Total As in 2001 (μg/L)	Total As in 2002 (μg/L)	Comment
Aug-00	air short	13.8	41.0	7.4		
Feb-01	air long	1.4				
Sep-00	wash	22.9	71.0	25.1	23.8	
Oct-00	wash	2.5	4.4	2.7	2.2	Water has odor and iron; bottled water in use
Dec-00	wash	N.D.				
Jan-01	wash	3.7				Iron filter in place
May-01	wash	2.5				bottled water in use
May-01	wash	N.D.				
Aug-01	wash	N.D.				Water has slight sulfur odor
Nov-01	wash	N.D.				
Oct-01	long	2.9				
Dec-01	wash	N.D.		3.4		
Jan-02	wash	6.7				
Jan-02	wash	N.D.				
Jan-02	wash	N.D.				

N.D. = not detected (limit of detection changed after 2001 from 0.6 μg/L to 1.μg/L)
Air = air rotary drilled in both the upper and lower hole, 1 gallon bleach per 100 gallons of water
Short = shallow cased (<100 feet)
Long = additional casing used (>100 feet)
Wash = air and mud rotary drilled in the upper hole and water in the lower hole, additional casing (>100 feet), 0.375 gallons of bleach per 100 gallons of water

Table 4. Bacteria data from 42 Wells whose Owners Submitted Samples for Analysis in Connection with a Survey Concerning Their Well.

Construction Date	Drilling Method	Total Coliforms	Crenothrix	Gallionella	Leptothrix	HPC	Sulfate Reducing Bacteria
Feb-97	air short	Absent	540	0	690	11	Absent
Jun-97	air long	Absent					
Sep-98	air long	Present (MUG=Absent)	0	0	2	0	Absent
Aug-98	air long	Absent					
May-00	air long	Absent					
Nov-98	long	Absent					
Oct-98	long	Absent	1	0	55	3	Absent
Jan-99	long		0	140	0	<1	Absent
Dec-98	air long	Absent					
Nov-99	long	Absent	70	0	0	1	Present
Aug-99	long	Absent	0	0	0	<1	Absent
Nov-99	air long	Absent	70	0	0	1	Absent
Dec-99	air long	Absent					
Jan-00	air long	Absent					
Dec-99	air long	Absent	0	0	210	18	Absent
Apr-00	wash	Present (MUG=Absent)					
Apr-00	air long	Absent					
May-00	air long	Absent	35	0	0	39	Absent
Jun-00	air short	Present (MUG=Absent)	0	0	11	8700	Absent
Jan-00	air long	Absent				<1	Absent
Jan-00	air long	Absent	70	0	140	9	Absent
Aug-01	wash	Absent	0	2	0	4	Absent
Mar-01	long	Absent					
Jul-00	air long	Absent					
Jul-00	air long	Absent					
Sep-00	wash	Absent					
Aug-00	air short	Absent	0	0	1	43	Absent
Aug-00	air short	Present					

		(MUG=Absent)					
Feb-01	air long		0	26	26	120	Present
Sep-00	wash	Absent					
Oct-00	wash	Absent	0	0	0	150	Present
Dec-00	wash	Absent					
Jan-01	wash	Absent	0	0	0	86	Absent
May-01	wash	*OS					
May-01	wash		0	0	2	18	Absent
Aug-01	wash	Absent	4	0	0	92	Absent
Nov-01	wash	Absent					
Oct-01	long	Absent	1	0	0	200	Present
Dec-01	wash	*OS					
Jan-02	wash	Absent					
Jan-02	wash	Absent					
Jan-02	wash	Absent					

*OS = sample received 48 hours after collection
Air = air rotary drilled in both the upper and lower hole, 1 gallon bleach per 100 gallons of water
Short = shallow cased (<100 feet)
Long = additional casing used (>100 feet)
Wash = air and mud rotary drilled in the upper hole and water in the lower hole, additional casing (>100 feet), 0.375 gallons of bleach per 100 gallons of water

Table 5. Arsenic and iron levels in three household wells treated with Acid Surfactant followed by low dose (60 mg/L) chlorination. Wells were purged after the acid surfactant treatment and again after chlorine disinfection.

	Date Collected	Time	Comment	Total Arsenic (μg/L)	Total Iron, (mg/L)
Well A					
	1/7/2003	9:45	Before treatment	6.5	0.2
	1/8/2003	9:30	Treatment purge water	36.6	5.5
	1/8/2003	9:45	Treatment purge water	43.3	4.5
	1/9/2003	13:21	1 Day after treatment	5.4	N.D.
	1/14/2003	13:11	6 Days after treatment	7.7	0.1
	1/21/2003	13:01	13 Days after treatment	6.3	0.2
	1/28/2003	13:09	20 Days after treatment	5.1	0.2
	4/23/2003	8:00	3 Months after	8.1	0.5
Well B					
	2/25/2003	9:00	1 week after treatment	1	
	3/4/2003	9:00	2 weeks after treatment	ND (LOD 1).	
	3/12/2003	9:00	3 weeks after treatment	ND (LOD 1).	
Well C					
	6/16/2003	10:00	Before treatment	49.3	47.3
	6/18/2003	10:00	1 day after treatment	46.3	46.7
	6/25/2003	8:22	1 week after treatment	48.8	47.6
	7/3/2003	10:45	2 weeks after treatment	48.1	47.6
	7/8/2003	10:30	3 weeks after treatment	49.8	48.4

Table 6. Bacteria levels in three household wells treated with acid surfactant (A.S.) followed by low dose (60 mg/L) chlorination. Wells were purged after the acid surfactant treatment and again after chlorine disinfection.

	Date Collected	Time	Comment	Total Coliforms	*Leptothrix*	*Gallionella*	*Crenothrix*	Sulfate Reducing Bacteria	heterotrophic Plate Count
Well A									
	1/7/2003	9:44	Before treatment	Absent	0	0	5	Absent	4
	1/9/2003	13:20	1 day after A.S. treatment	Absent	2	0	0	Present	<1
	1/14/2003	13:10	~6 days after A.S. treatment and 5 days after Cl_2 treatment	Absent	0	0	0	Present	8
	1/21/2003	13:00	~13 days after treatment	Absent	0	0	4	Absent	170
	1/21/2003	13:00	Duplicate	Absent	0	0	9	Absent	94
	1/28/2003	13:08	~20 days after treatment	Absent	0	0	9	Absent	44
	1/28/2003	13:08	duplicate	Absent	0	0	0	Absent	30
	4/23/2003	8:00	~3 months after treatment	No Test Done[1]	0	0	4	No Test Done[1]	
Well B									
	2/25/2003	12:00	~1 week after A.S. and Cl_2 treatment	Present	34	51	190	Present	290
	3/4/2003	9:00	~2 weeks after treatment	Present	21	0	0	Absent	7
	3/12/2003	9:00	~3 weeks after treatment	No Test Done[1]	3	0	8	Present	42
Well C									
	6/16/2003	10:00	Before treatment	Absent	0	0	0	No Test Done[1]	
	6/25/2003	8:24	1 week after A.S. and Cl_2 treatment	Absent	0	1100	0	0	0
	7/3/2003 8:22	10:45	2 weeks after treatment	Old Sample[2]					
	7/8/2003 10:30	10:30	3 weeks after treatment	No Test Done[1]	0	84000	0	0	0

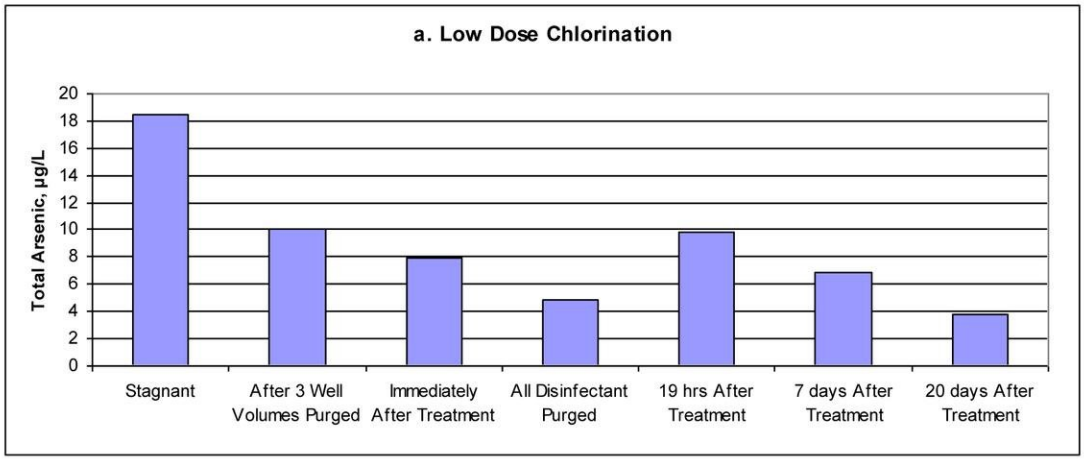
[1]Laboratory accident
[2]Sample was delayed in mail and was too old to be tested.

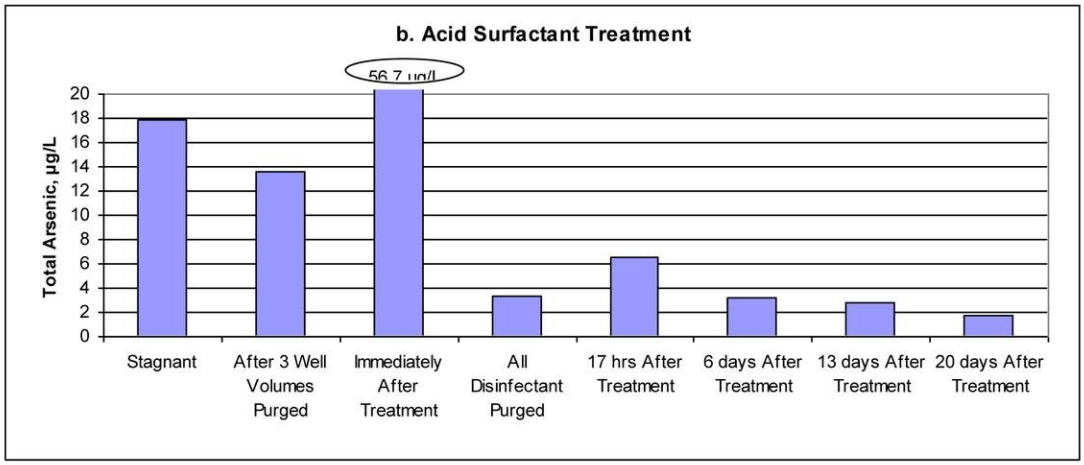
Table 7. Arsenic released from scale upon exposure to a chlorine solution prepared from household bleach. One gram of scale was added to a beaker along with 100 mL of reagent grade water. The scale contained approximately 47,000 µg/g total arsenic.

Chlorine (mg/L as Cl_2)	pH Adjustment	Total Arsenic (µg/L)
100	no adjustment	69000
100	adjusted to 5.0	2200
500	no adjustment	70000
500	adjusted to 5.0	1500

LIST OF FIGURES

Figure 1: Total Arsenic Found in Phase 1 Well After Three Different Treatments





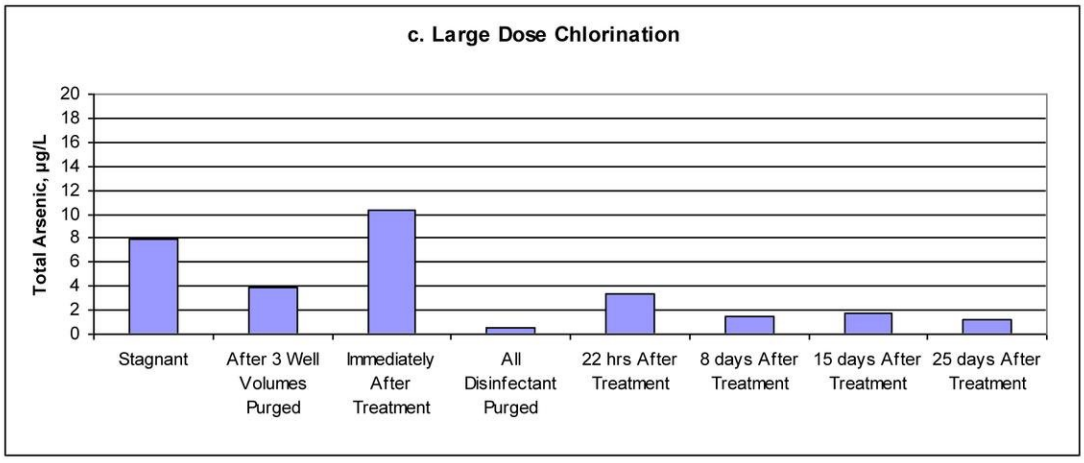
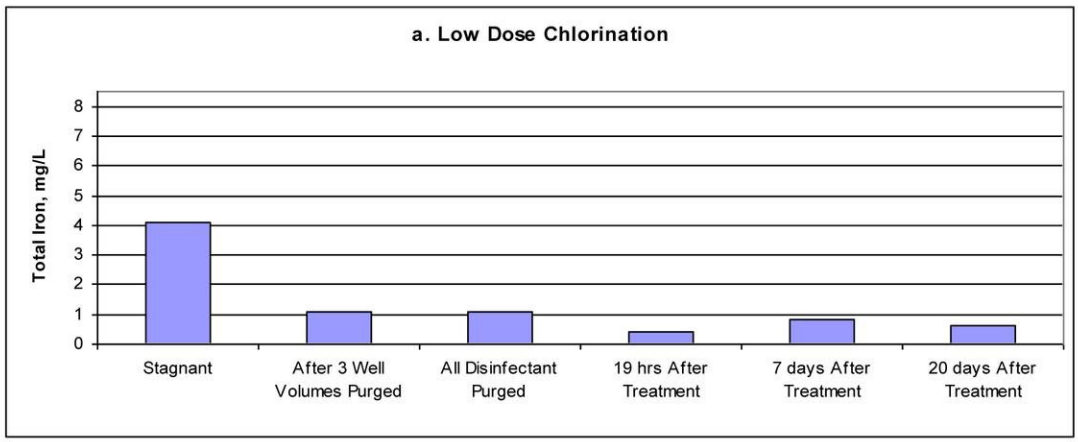
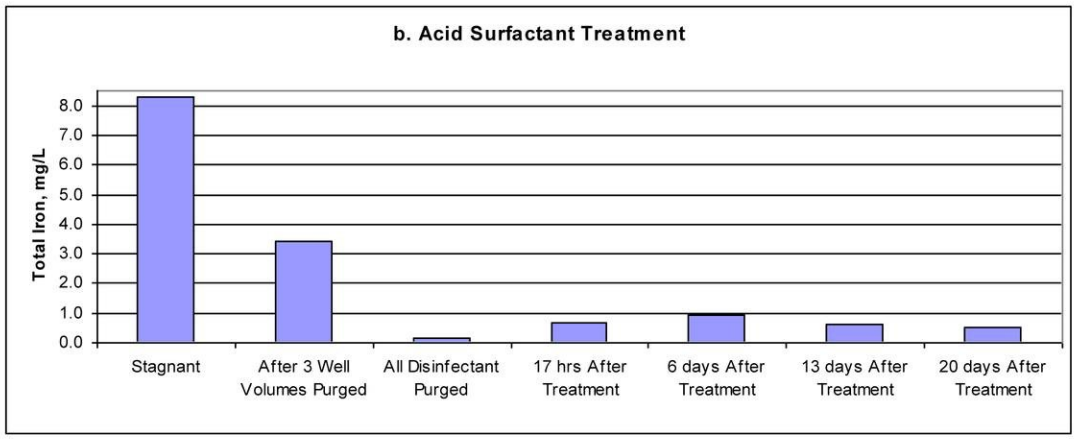


Figure 2: Total Iron Found in Phase 1 Well After Three Different Treatments





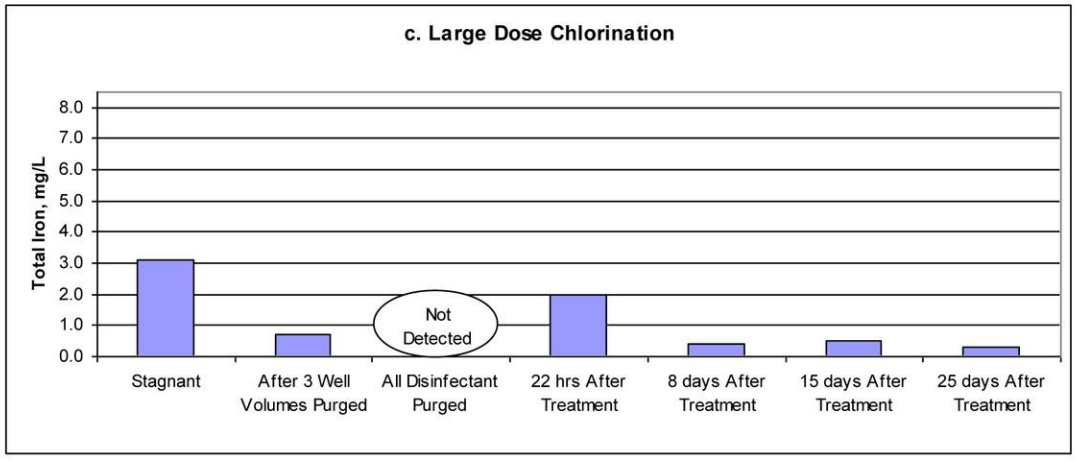


Figure 3: Total Iron Versus Total Arsenic in Phase 1 Well

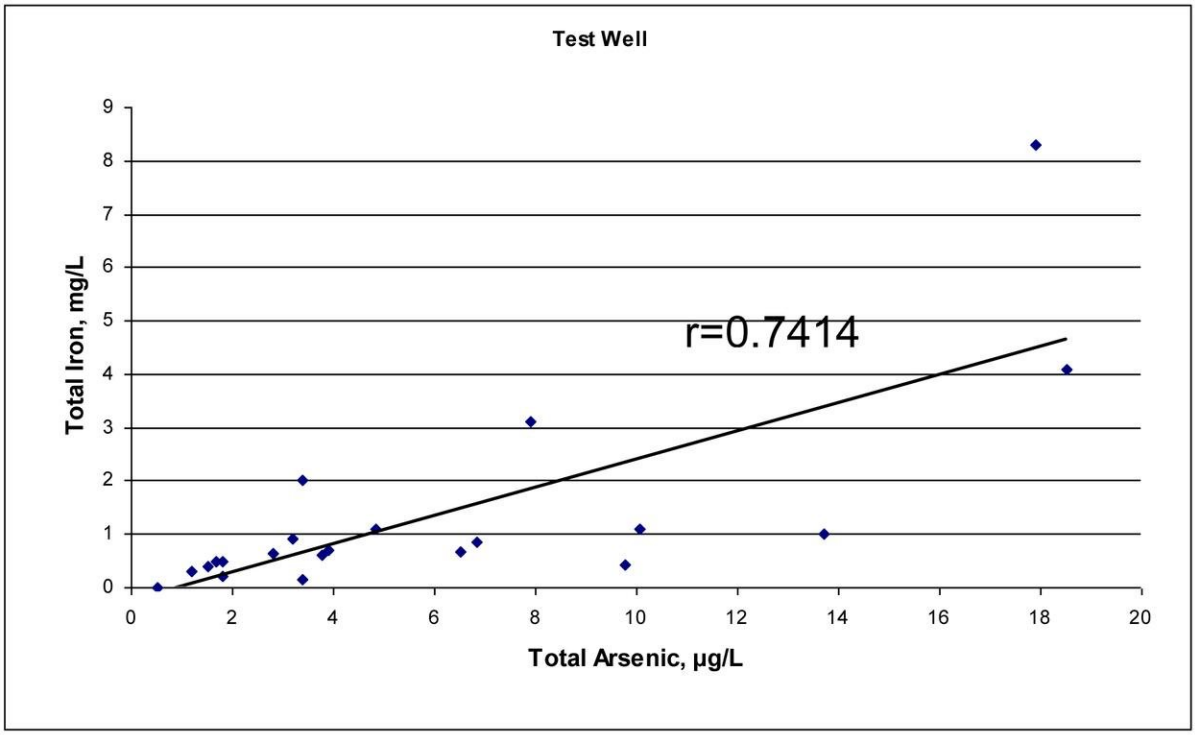
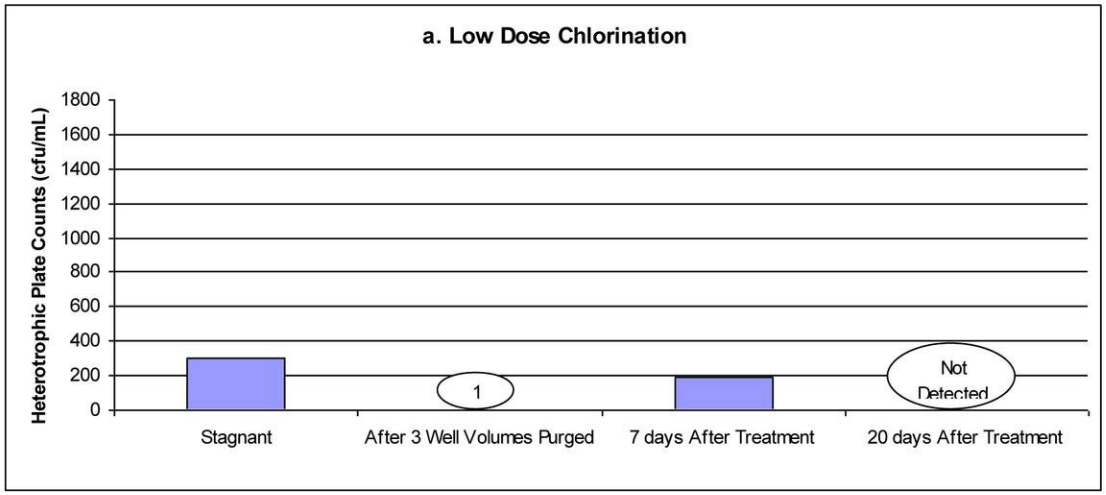
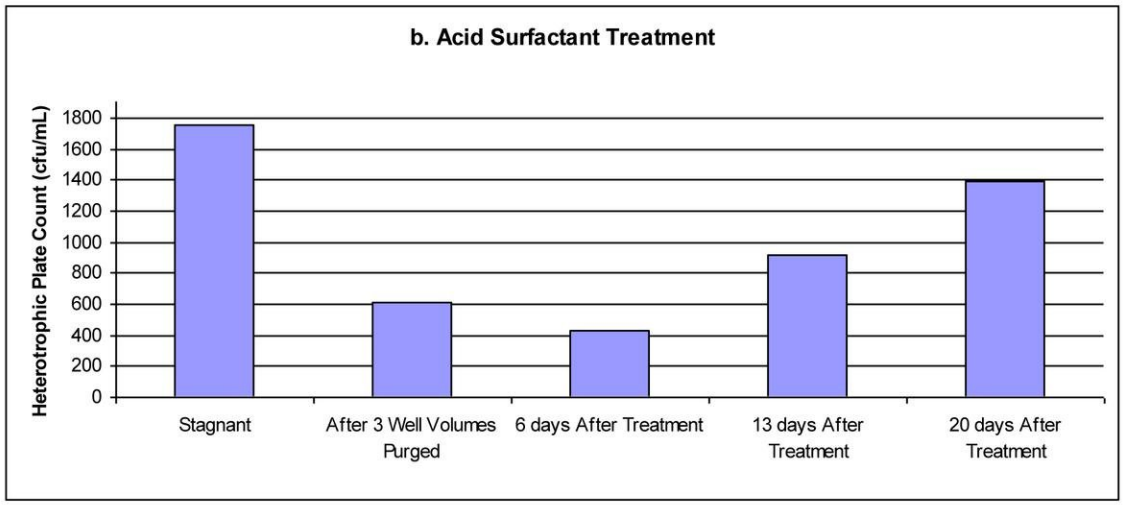


Figure 4: Heterotrophic Plate Counts (cfu/mL) Found in Phase 1 Well After Three Different Treatments





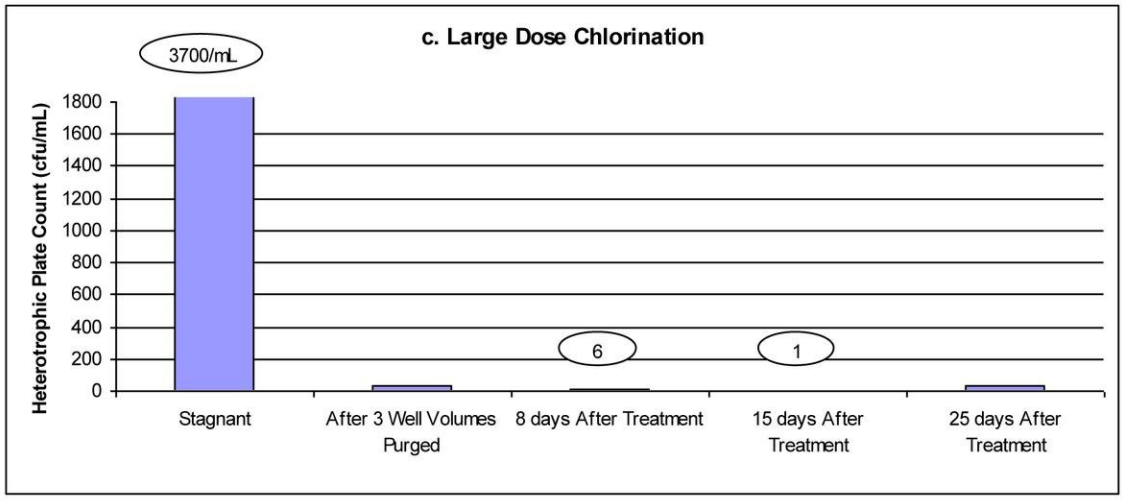
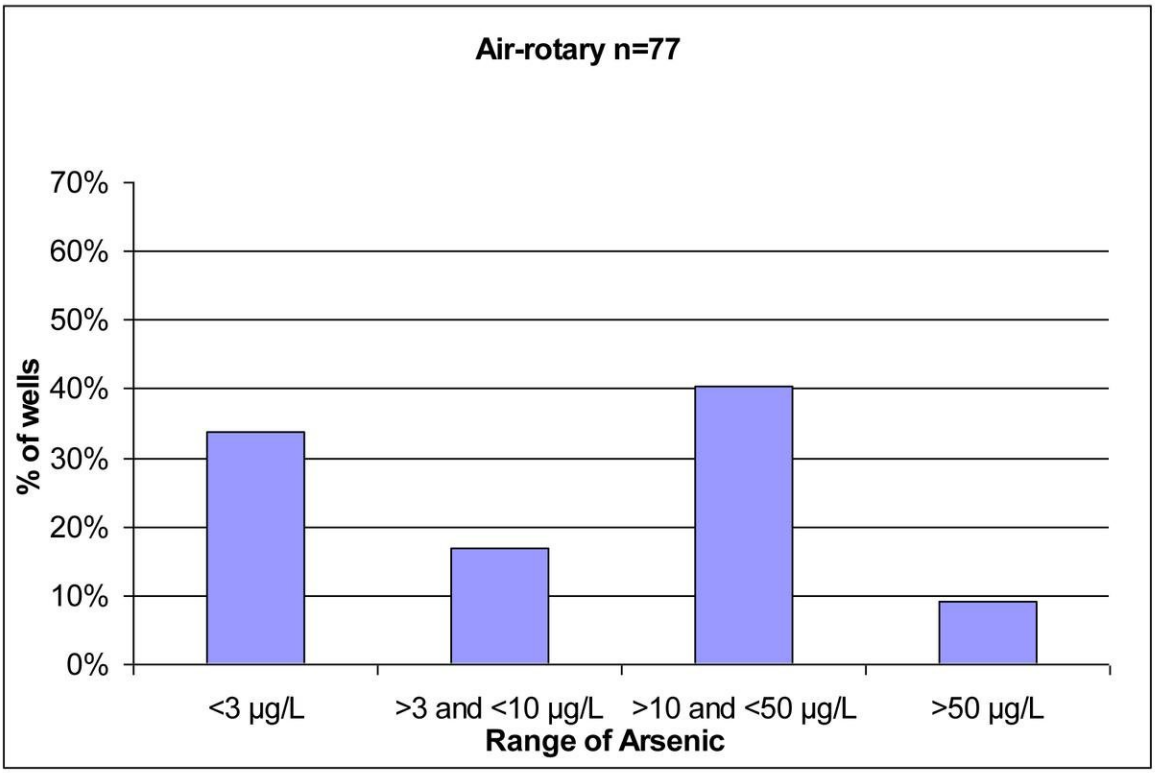


Figure 5: Effect of Drilling Techniques (Air-rotary or Wash-rotary) on Arsenic Concentrations



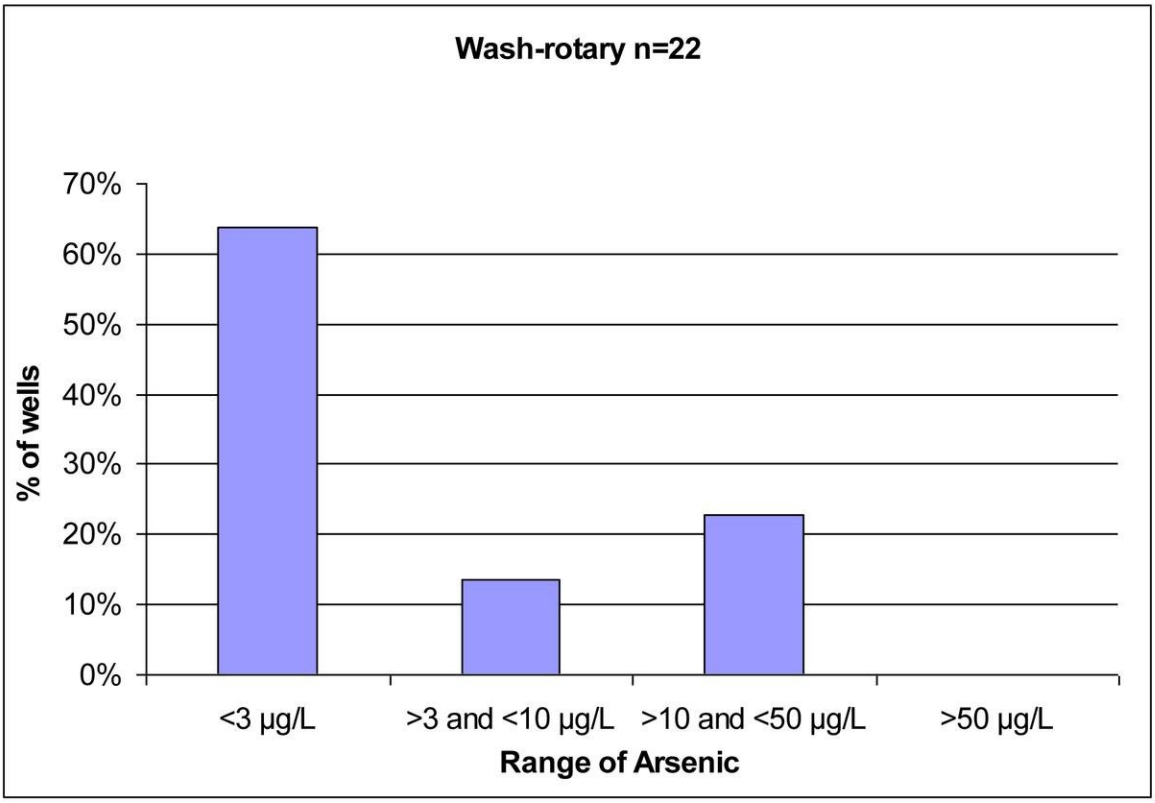
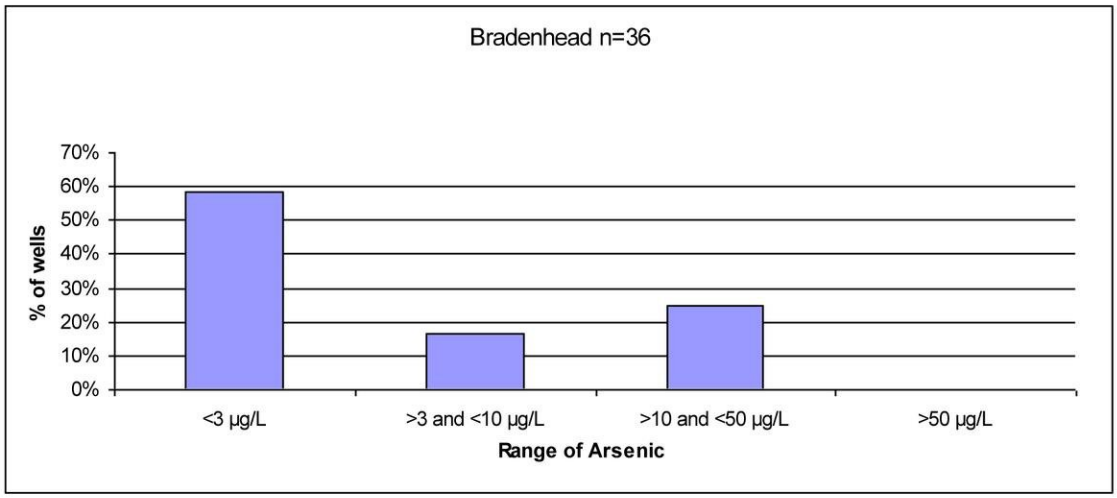


Figure 6: Effect of Three Different Types of Grouting Techniques on Arsenic Concentrations



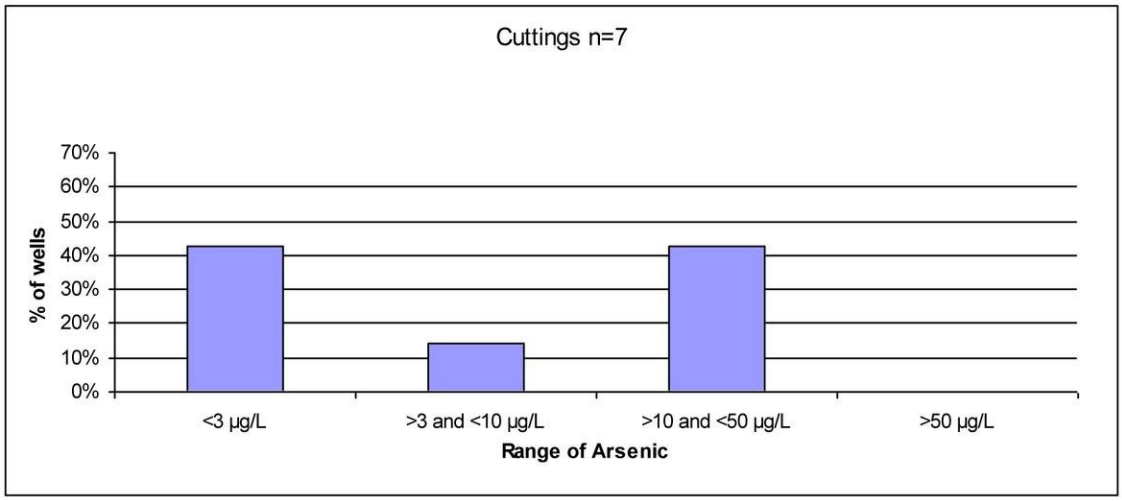
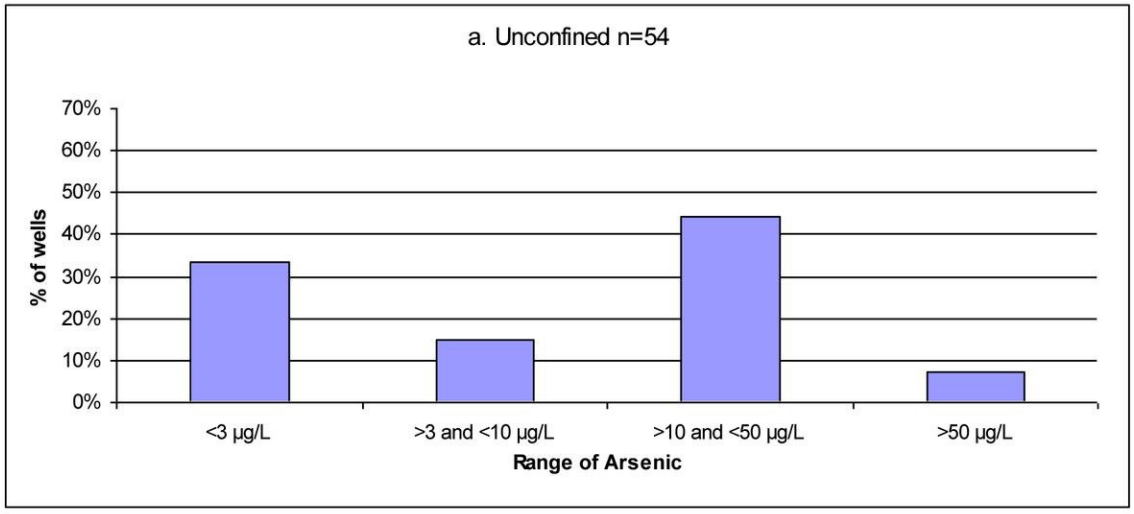
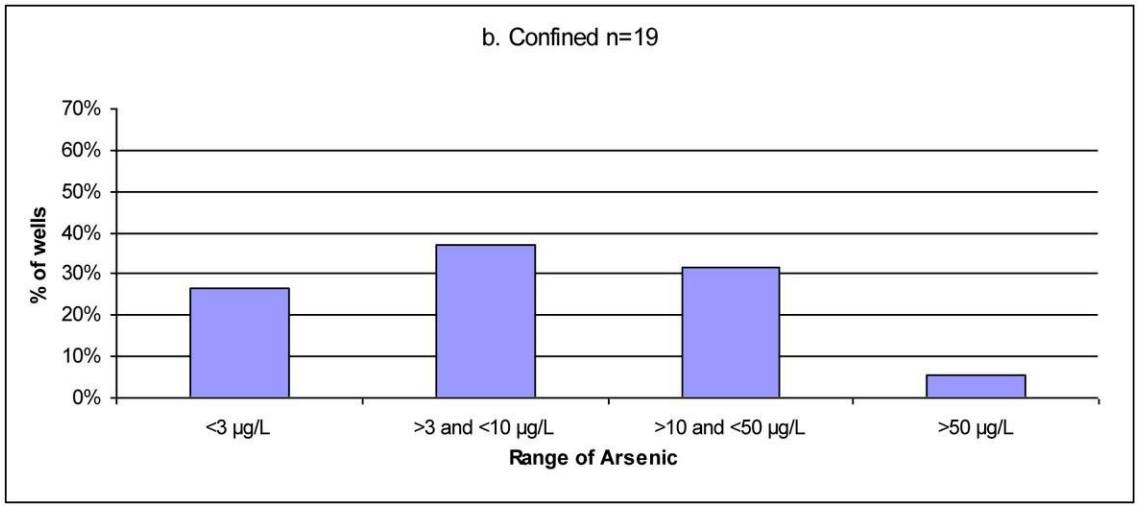


Figure 7: Arsenic Concentrations in Wells From Different Aquifer Types





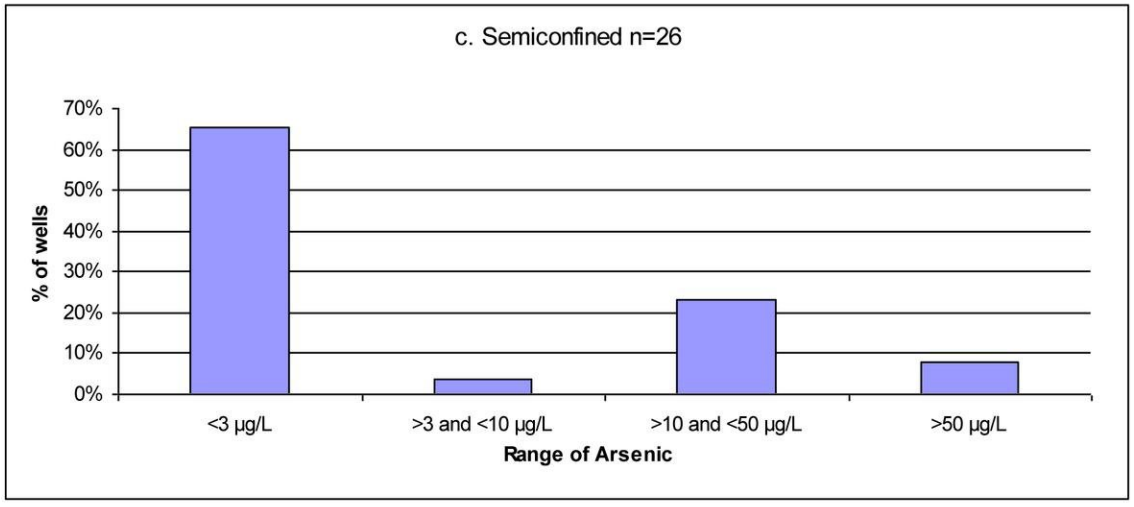
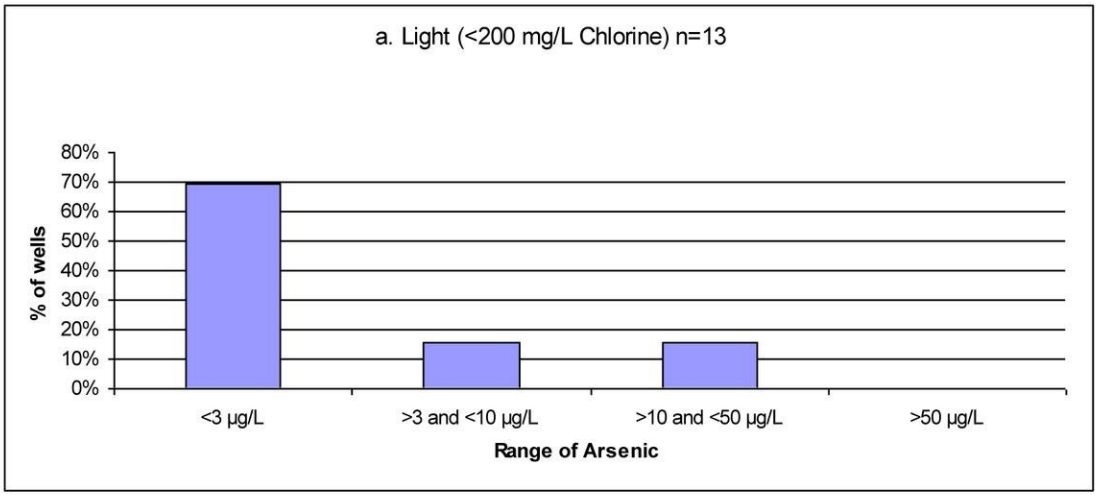
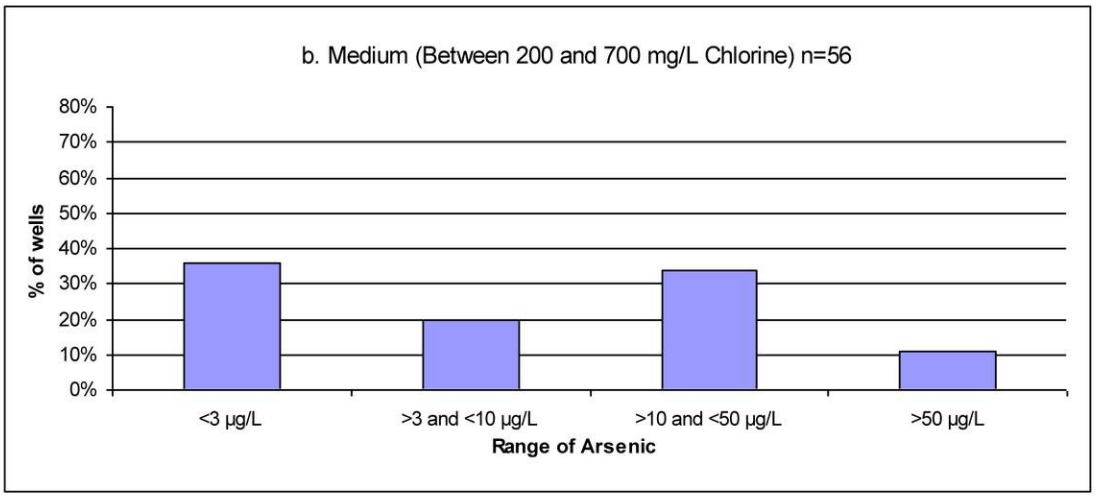


Figure 8: Effect of Reported Chlorination Levels on Arsenic Concentrations in Wells





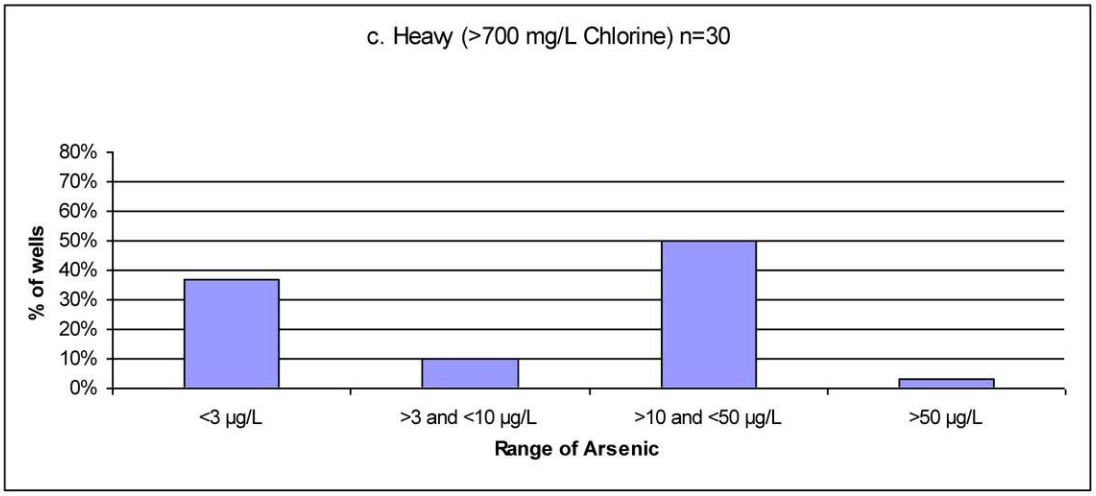
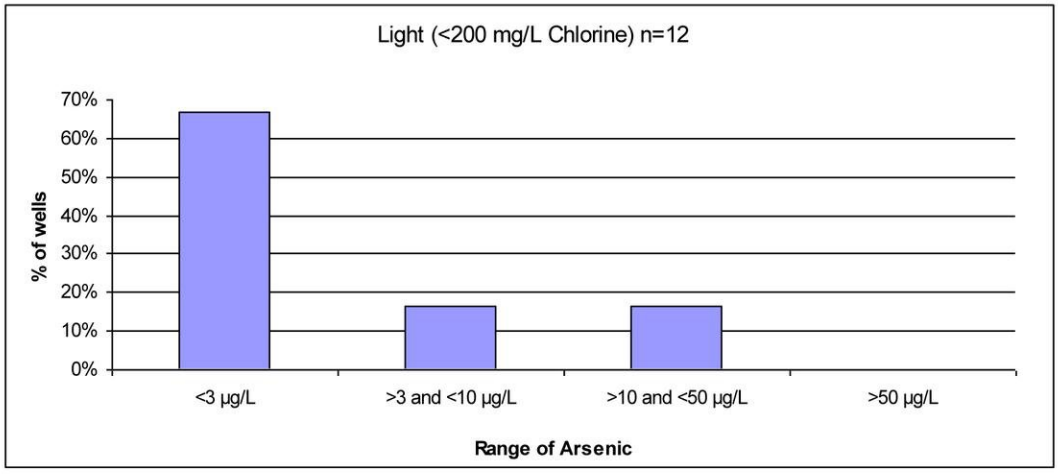
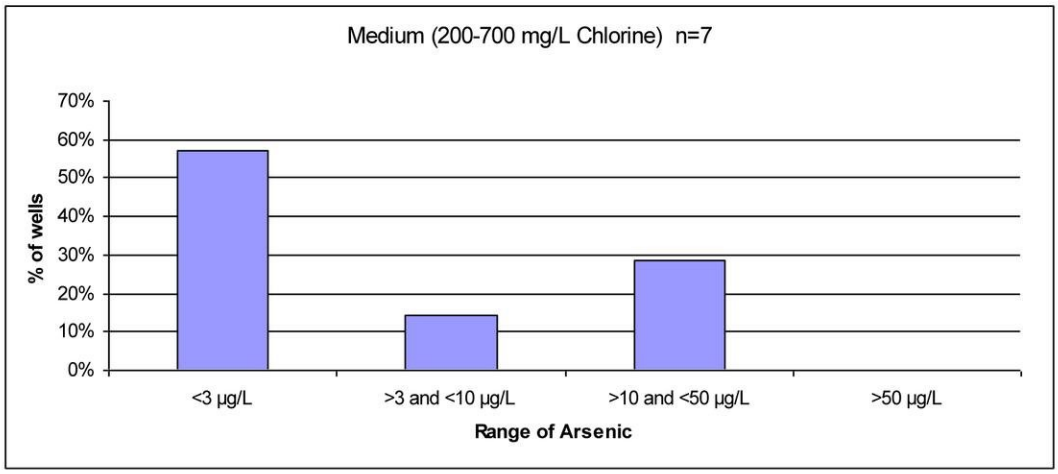


Figure 9: Effect of Chlorine Dose on Arsenic Levels in Wells Constructed by the Wash-Rotary Drilling Method





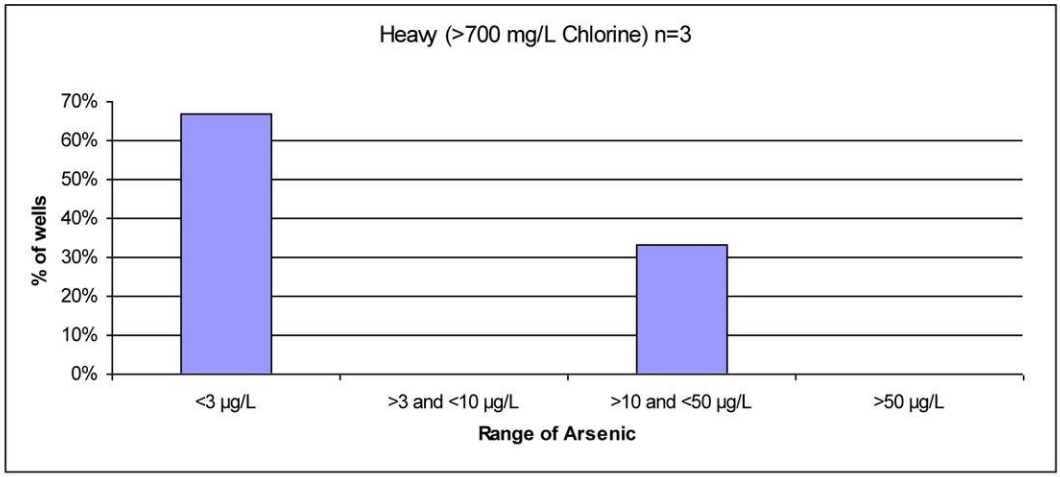


Figure 10: Total Iron Versus Total Arsenic in Phase 3, Well A

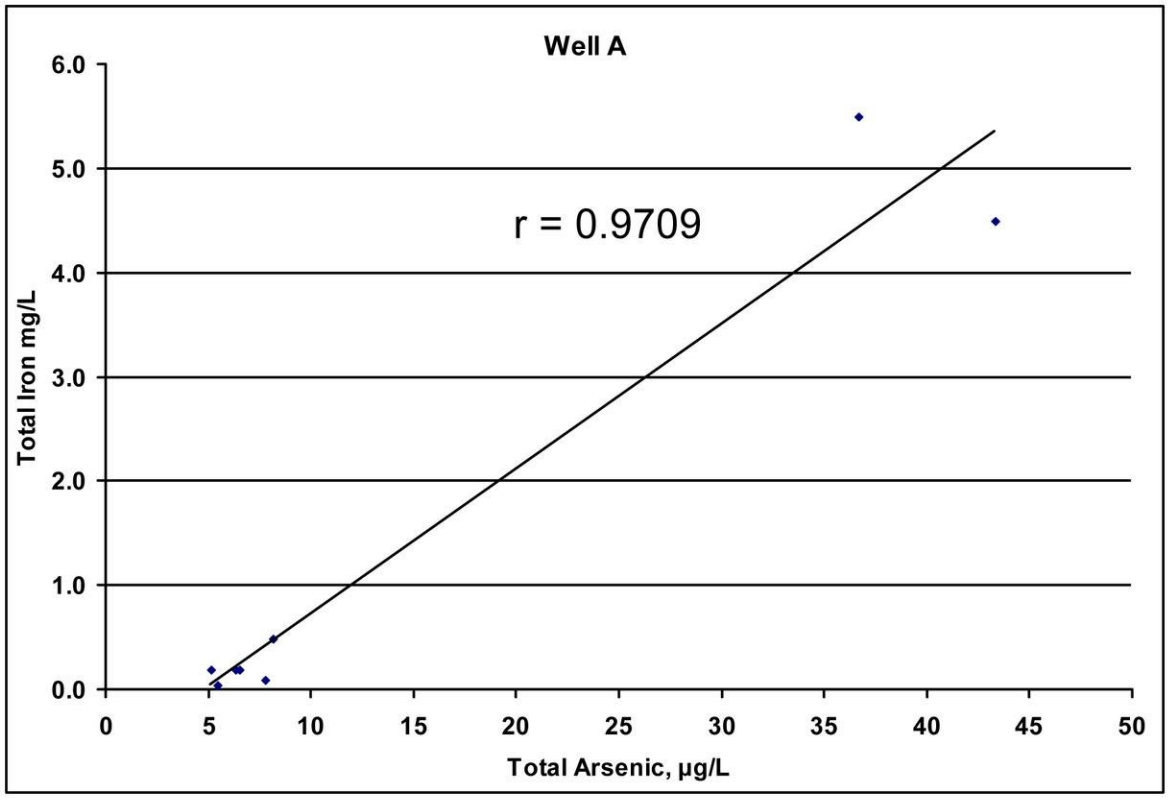


Figure 11. Photograph of cutout of pipe from a private residence in northeastern Wisconsin showing scale/encrustations (a sample of the scale was used for arsenic leaching tests).