

# Effect of Well Disinfection on Arsenic in Ground Water

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## Abstract

Domestic water wells are routinely subjected to in situ chemical disinfection treatments to control nuisance or pathogenic bacteria. Most treatments are chlorine based and presumably cause strongly oxidizing conditions in the wellbore. Water resource managers in Wisconsin were concerned that such treatments might facilitate release of arsenic from sulfide minerals disseminated within a confined sandstone aquifer. To test this hypothesis, a well was subjected to four disinfection treatments over 9 months time. The first treatment consisted of routine pumping of the well without chemical disinfection; three subsequent treatments included chlorine disinfection and pumping. Pretreatment arsenic concentrations in well water ranged from 7.4 to 18  $\mu\text{g/L}$ . Elevated arsenic concentrations up to 57  $\mu\text{g/L}$  in the chemical treatment solutions purged from the well are attributed to the disintegration or dissolution of biofilms or scale. Following each of the four treatments, arsenic concentrations decreased to less than 10  $\mu\text{g/L}$  during a period of pumping. Arsenic concentrations generally returned to pretreatment levels under stagnant, nonpumping conditions imposed following each treatment. Populations of iron-oxidizing, heterotrophic, and sulfate-reducing bacteria decreased following chemical treatments but were never fully eradicated from the well. Strongly oxidizing conditions were induced by the chlorine-based disinfections, but the treatments did not result in sustained increases in well water arsenic. Results suggest that disruption of biofilm and mineral deposits in the well and the water distribution system in tandem with chlorine disinfection can improve water quality in this setting.

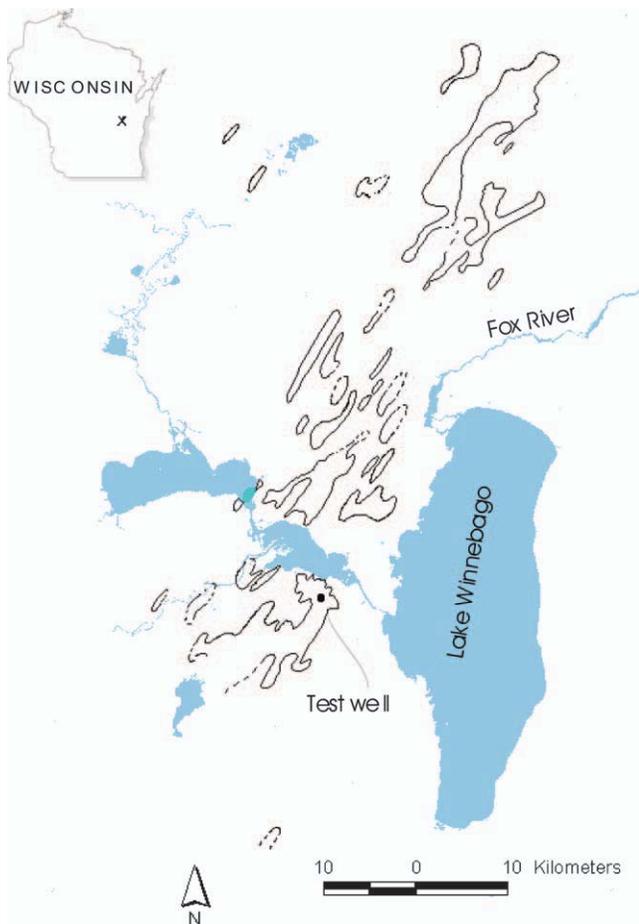
*Some figures in this paper are available in color in the online version of the paper.*

## Introduction

Elevated levels of arsenic in drinking water pose a risk to human health, including increased risks of skin and internal cancers (National Research Council 2001). The U.S. EPA recently lowered the maximum contaminant level for arsenic in drinking water to 10  $\mu\text{g/L}$ . In areas of northeastern Wisconsin, naturally occurring arsenic contamination of ground water results in about 30% of domestic water wells with total arsenic concentrations exceeding 5  $\mu\text{g/L}$  and about 17% of wells exceeding 10  $\mu\text{g/L}$  (Figure 1). Oxidation of sulfide minerals contributes arsenic to well water in this region (Schreiber et al. 2000; Thornburg and Sahai 2004). Where ground water is under confined conditions, mineral oxidation may have occurred at some time in the geologic past or may be due to introduction of air to the aquifer during well drilling or induced by drawdown related to pumping (Schreiber et al. 2003). In this setting, dissolution of arsenic-bearing iron (hydr)oxides also contributes low to moderate levels of arsenic to ground water where conditions are sufficiently reducing (Gotkowitz et al. 2004).

Based on reports from well owners, staff of the Wisconsin Department of Natural Resources (WDNR) became concerned that sustained and elevated arsenic concentrations in some wells were related to in situ disinfection with NaOCl solution (bleach) (WDNR 2002). In northeast Wisconsin, most domestic wells are drilled in shallow, competent bedrock formations and are constructed with short casings and no screens. In these wells, chlorine-based disinfection solutions, which are strong oxidizers, come into direct contact with aquifer solids and could potentially chemically alter sulfide minerals exposed along uncased portions of the borehole wall. Terashima and Taniguchi (1998) noted that in a laboratory setting, NaOCl readily dissolves most sulfide minerals.

Due to concern about mineral dissolution, WDNR guidance for well disinfection in northeastern Wisconsin specifies use of a chlorine solution at 20% of the strength and 10% of the contact time recommended for wells in nonarsenic-impacted regions of the state (WDNR 2002). This low-dose disinfection treatment presumably reduces the potential for chemical oxidation of aquifer solids. However, an ineffective biocidal treatment might allow microbially facilitated geochemical reactions within the well to persist. Reductive dissolution of metal (hydr)oxides may be



**Figure 1.** Study area in northeast Wisconsin. Contours indicate area where arsenic concentrations in domestic wells typically exceed 10 µg/L. Contours are dashed where inferred.

microbially mediated and is a potential source of trace elements to solution under reducing conditions at circum-neutral pH (Lovley 2000; Smedley and Kinniburgh 2002).

The field-based experiment discussed in this publication was designed to evaluate effects of several common disinfection treatments on arsenic concentrations in domestic wells. Previous work at this field site (Figure 1) demonstrated that reducing conditions develop in well water during periods of non- and low-ground water pumping, and the onset of reducing conditions correlates to increasing arsenic and iron in well water (Gotkowitz et al. 2004). This suggests that reduction of arsenic-bearing iron (hydr)oxides is a likely mechanism of arsenic release to water having a long residence time in the well borehole. Positive results for sulfate-reducing, heterotrophic, and iron-oxidizing bacteria, along with detectable levels of organic carbon, indicated that borehole conditions at this site are conducive to microbiological growth.

### Well Disinfection Practices

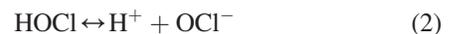
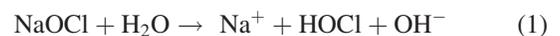
Well disinfection is used to control pathogenic and nonpathogenic “nuisance” bacteria that cause odor, color, and clogging problems in water and remediation wells. Well drillers and homeowners often repeatedly shock chlorinate wells in an attempt to control biological growth.

However, this method of disinfection, in which the well and the distribution system are treated with a strong chlorine solution, provides only temporary treatment of coliform contamination in wells affected by a continuing source of fecal bacteria (Oliphant et al. 2002).

Iron-oxidizing and sulfate-reducing bacteria and aerobic and anaerobic heterotrophic bacteria can contribute to the biofouling of wells (Taylor et al. 1997). These microbes produce biofilm, a slimy substance comprised of microbes growing in association with a solid surface. Biofilm may include an encrustation of biologically mediated precipitation of iron, manganese, sulfur, and other elements (Smith and Tuovinen 1985). The encrustation may form a physical barrier between a disinfection solution and a microbial population, resulting in an ineffective disinfection procedure. Biofilms are notoriously resistant to most disinfection practices (Momba et al. 1998; Oliphant et al. 2002).

Biofilms provide sorption and ion exchange sites, and they may host a variety of contaminants. Therefore, disinfection practices that mobilize or dissolve biofilm and mineral deposits may release constituents of concern associated with them. Seiler (2006) found that chlorine disinfection of wells screened in unconsolidated Quaternary sediments caused temporary increases in trace element concentrations of the well water. He attributed changes in water quality to a combination of mechanical and chemical processes, including mobilization of trace elements from oxidation of organic matter. In this setting, postdisinfection purging of well water returned trace element concentrations to pretreatment levels, and chemical disinfection did not cause a sustained decline in water quality.

Household chlorine bleach, the most common product used to disinfect wells in Wisconsin, is a sodium hypochlorite (NaOCl) solution containing 3.0%–6.0% available chlorine. The available chlorine varies with the particular manufacturer and the density and age of the product. Because the available chlorine concentration decreases over time, the percentage stated on the product label is an approximation. In water, bleach quickly forms hypochlorous acid (HOCl) and hypochlorite ion (OCl<sup>-</sup>) according to the following reactions:



As Equation 2 implies, pH controls the dissociation of hypochlorous acid. Hypochlorous acid and hypochlorite are present in equal concentrations at pH 7.5. Under more acidic conditions, hypochlorous acid predominates, whereas hypochlorite is favored under basic conditions.

Both the neutral and the ionic forms are considered “free” or “available” chlorine and both are effective biocides, given the proper concentration and contact time. However, hypochlorous acid is a much more powerful germicide than hypochlorite, and chlorine bleach solutions have the best biocidal properties at a pH less than 7 (Snoeyink and Jenkins 1980). Control of pH during well disinfection is typically not accounted for in most guidance

provided to homeowners. Further, as can be seen from Equation 1, the reaction of sodium hypochlorite with water causes an increase in pH, resulting in further reduction in biocidal properties.

Acids such as sulfamic acid ( $\text{NH}_2\text{SO}_3\text{H}$ ) are sometimes used in conjunction with in situ chlorine disinfection treatments to dissolve encrustations in the wellbore (Smith 1995). The acid increases the effectiveness of the disinfectant by increasing its penetration into scale, biofilm, and aquifer solids that harbor microbes, in part due to dispersal of clay minerals.

## Site Description

### Hydrogeologic Setting and Well Construction

The hydrogeologic and geochemical conditions of arsenic contamination are well characterized at the site selected for this study (Figure 1) (Schreiber et al. 2003). The hydrostratigraphy includes glacial and glaciolacustrine deposits underlain by a thick sequence of Paleozoic rocks. Most domestic water wells are completed in the upper 45 m of bedrock, within the Sinnipee Group dolomite and underlying sandstone of the St. Peter Formation. The St. Peter constitutes a regionally extensive aquifer of variable thickness that is generally confined in the area of the test well but may be locally unconfined due to variation in topography or dewatering from pumping. The hydraulic conductivity of the aquifer is on the order of 1 m/d (Gotkowitz et al. 2004). Where the St. Peter is absent, domestic water wells are typically completed in dolomite of the Sinnipee and underlying Prairie du Chein Groups.

The test well is constructed similarly to domestic wells in the area. The base of the Sinnipee dolomite and the upper portion of the St Peter sandstone are exposed in the uncased portion of the well, which extends from the base of casing at 18.9 m to a total depth of 26.0 m below ground surface. The aquifer is confined at this location, with a static water level at 8.6 m below ground surface. Borehole flowmeter measurements indicate that natural gradients are insufficient to induce measurable flow into and out of the borehole under nonpumping conditions (Gotkowitz et al. 2004).

### Site Geochemistry

In the area surrounding the field site, solid-phase arsenic is associated with iron-sulfide minerals, including pyrite and marcasite, and iron (hydr)oxides. Solid-phase concentrations of arsenic range from tens to hundreds of parts per million (ppm) in minerals that form sulfide cement at the Sinnipee-St. Peter contact and in sulfide-rich nodules and veins disseminated within the St. Peter sandstone. Where sulfide minerals are not present in the sandstone, arsenic concentrations average less than 5 ppm. In some samples collected at this site, iron oxide-weathering products of the sulfide minerals have higher associated arsenic concentrations than the iron-sulfide minerals (Gotkowitz et al. 2004).

Results of residential water well testing provided by the WDNR indicate that ground water arsenic concentrations vary from nondetectable levels to hundreds of micrograms per liter within a 4-km<sup>2</sup> area of the test well. Ground water in the St. Peter aquifer is Ca-Mg-HCO<sub>3</sub> type, with a pH of 7.1 and low dissolved oxygen (D.O.) concentrations (about 0.35 mg/L). Ground water is under reducing conditions with an oxidation-reduction potential (ORP) of -50 mV (Gotkowitz et al. 2004).

Based on several pumping tests at the field site, Gotkowitz et al. (2004) attributed variability in ground water arsenic concentrations to the residence time of ground water in the wellbore. Arsenic ranged from 1.8 to 22 µg/L at the site, with higher concentrations related to longer residence times. Samples collected during a pumping regime intended to simulate domestic use (380 L, or about 1.3 well volumes, pumped every 8 h at a rate of 38 L/min) ranged from about 3 to 6 µg/L. The well water became more reducing during this domestic pumping schedule than under fully purged conditions, with D.O. decreasing to 0.25 mg/L and ORP to -100 mV. These findings indicate that pumping at a rate and volume similar to domestic use does not fully purge the well of water with a long residence time in the borehole.

## Methods

### Well Treatments

The experiment consisted of four treatments applied sequentially over 9 months at the test well. This experimental design is not ideal because long-lasting effects of one treatment can impact or mask the effects of subsequent treatments. An alternative approach such as subjecting each of a series of wells to a single disinfection treatment would presumably suffer from differing initial conditions related to the small-scale variability in mineral assemblages and solid-phase arsenic concentrations at the site documented by Schreiber et al. (2003). The single-well approach was also preferred to a multiwell experimental design because of the differences in water quality in wells of similar design as noted by Schreiber et al. (2000).

The four treatments included a control phase, consisting of pumping with no chemical disinfection, and three types of chemical disinfection combined with pumping. Each of the four treatments began with a 1- to 2-month stagnant phase, during which the well was not pumped. This was followed by purging three to four well volumes from the well immediately before treatment, purging of the treatment solution until the chlorine odor dissipated (a qualitative measure suggested in WDNR treatment guidance), and several weeks of pumping at a rate and schedule simulating domestic water use. The domestic pumping schedule consisted of pumping 378 L of water three times per day at a rate of 38 L/min. This results in a total daily withdrawal typical of a four-person residence, assuming a per capita residential water use rate of 284 L/d (Vickers 2001).

Samples of well water were collected periodically throughout the disinfection treatments. Samples meant to characterize water quality under stagnant conditions were

collected after purging about 0.2 of a well volume (42–75 L). About five well volumes were purged before collecting samples representative of conditions before and after chemical treatments. Samples from periods of the domestic pumping routine were collected 3–7 min into a 10-min pumping cycle at purge volumes ranging from 0.3 to 0.9 of a well volume.

Before the first treatment, which consisted of pumping only, the well remained under stagnant, nonpumping conditions for 51 d. Fifty well volumes were purged from the well before pumping the well at the domestic schedule for 2 weeks.

The second treatment was a low-dose chlorine disinfection following WDNR (2002) recommendations for this arsenic-impacted area in Wisconsin. After a 32-d stagnation period, approximately four well volumes were purged from the well. Chlorox bleach (Chlorox Company, Oakland, California) containing 6% sodium hypochlorite was mixed with 378 L of well water to produce a solution of about 100 mg/L chlorine. The solution was poured into the well and recirculated through the well, pump, and associated pipe for one-half hour. About 5.8 well volumes were then purged to the sanitary sewer until the water was free of chlorine odor. The well was pumped at the domestic schedule for 3 weeks, after which pumping was discontinued for 51 d.

The third treatment involved the addition of an acid-surfactant to the well followed by low-dose chlorination. A 9% solution of commercially available sulfamic acid (Aqua-Clear AE, Baroid Industrial Drilling Products, Houston, Texas) was mixed in 378 L of water, poured into the well, mixed by recirculation for one-half hour, left in the well for 1 h, and recirculated again for one-half hour. About 3800 L of ground water (13 well volumes) were purged from the well, at which point the purge water returned to within 0.5 pH units of original measurement (pH 7.0). The acid treatment was followed immediately with a low-dose chlorination of 60 mg/L  $\text{Cl}^-$  (prepared using Chlorox bleach in 378 L of well water), which was poured in the well and recirculated for 15 min. About 1700 L (5.5 well volumes) were purged to waste until the water was free of chlorine odor. The well was pumped at the domestic schedule for 3 weeks, followed by 37 d of non-pumping conditions before the final disinfection treatment.

The high-dose disinfection of the test well followed DNR guidance for nonarsenic-impacted regions in Wisconsin. Chlorox bleach was mixed with 378 L of well water to obtain a solution of 1200 mg/L  $\text{Cl}^-$ . The solution was recirculated for about one-half hour and then allowed to sit idle for 24 h. About 11 well volumes (3380 L) were purged from the well until the chlorine odor had dissipated. The domestic pumping schedule was maintained for 3 weeks and was followed by stagnant, nonpumping conditions for 24 d before collecting a final sample of well water.

#### Field and Laboratory Procedures

Field parameters, including temperature, pH, D.O., and ORP, were measured with a submersible water quality sensor and data logger installed above the pump near the base

of the test well. Sensors were calibrated before deployment and were checked for drift following recovery of the unit from the well. Field measurements of chlorine concentrations were determined using the DPD (N,N-diethyl - p - phenyldiamine) method (American Public Health Association [APHA] 1999) with a Hach DR1/890 Colorimeter and AccuVac vials (Hach Company, Loveland, Colorado). The field colorimeter calibration was verified with a potassium permanganate standard (APHA 1999).

Aliquots of samples collected for total arsenic and iron analyses were preserved with nitric acid to a pH less than 2 (0.5%  $\text{HNO}_3$ ). Those collected for dissolved fractions were filtered (0.45  $\mu\text{m}$ ) prior to acid preservation. Samples analyzed for arsenite ( $\text{As}^{3+}$ ) were speciated on-site using anion exchange cartridges (Le et al. 2000). Samples collected for sulfate analysis were unfiltered and unpreserved. All samples were placed on ice following collection and transported to the Wisconsin State Laboratory of Hygiene for analysis. Total arsenic (detection limit < 1  $\mu\text{g/L}$ ) was determined by graphite furnace atomic absorption spectrophotometer according to Method 3113B (APHA 1999). Iron was measured by inductively coupled plasma-optical emission spectrometer according to U.S. EPA Method 200.7 (detection limit < 0.1 mg/L). Sulfate was measured by methylthymol blue colorimetry according to U.S. EPA Method 375.2 (detection limit < 4.5 mg/L).

Water samples for microbiological analyses were collected in sterilized containers from a sterilized sample port and were transported on ice to the Wisconsin State Laboratory of Hygiene. Methods are documented in APHA (1999) and the Wisconsin State Laboratory of Hygiene (2003) Environmental Testing Methods Manual. Iron bacteria, including *Leptothrix*, *Gallionella*, and *Crenothrix*, were identified and counted microscopically. Plate counts for heterotrophic bacteria were performed using R2A agar incubated at 22 °C for 5 d. The presence or absence of sulfate-reducing bacteria was detected via selective media culture using the methods of Postgate (1963). Two samples were collected for five of the bacteria sampling events in order to evaluate the sensitivity of testing results to obtain the first flush of water from the well and piping. The samples were collected by filling two bottles sequentially. In each case, samples for microbiological analyses were collected before water collected for other analyses.

## Results and Discussion

During the experiment, total arsenic in well water ranged from less than 1 to 18.5  $\mu\text{g/L}$  (Table 1). Arsenic was lowest in water collected immediately after purging the high-dose disinfection solution. Samples collected at the conclusion of three of the four nonpumping phases contained the highest dissolved arsenic concentrations, from 15.1 to 18.5  $\mu\text{g/L}$ . Most dissolved arsenic concentrations were only slightly lower than total arsenic, indicating that there was little or no suspended or particulate arsenic in the ground water samples. Dissolved arsenic was primarily  $\text{As}^{3+}$ .

Samples of the three chemical treatment solutions purged from the well were analyzed for total arsenic (Table 1). The acid-surfactant treatment solution contained

**Table 1**  
**Analytical Results for Well Water during Treatments**

Treatment	Days Since Experiment Began	Sample Description	Dissolved As <sup>3+</sup> (µg/L)	Dissolved As (µg/L)	Total As (µg/L)	Dissolved Fe (mg/L)	Total Fe (mg/L)	SO <sub>4</sub> <sup>2-</sup> (mg/L)	Leptothrix (per mL)	Gallionella (per mL)	Crenothrix (per mL)	Heterotrophic Bacteria (per mL)	Sulfate-Reducing Bacteria
Pumping only	0	First flush after 51 d of not pumping	—	18	—	2.8	—	16	—	—	—	—	—
	0	Sample after purge <sup>1</sup>	—	1.8	—	0.1	—	14	—	—	—	—	—
	2	Domestic pumping <sup>1</sup>	5.6	6.3	—	—	—	—	—	—	—	—	—
	14	Domestic pumping <sup>1</sup>	5.6	6.4	—	0.5	—	18	—	—	—	—	—
Low-dose chlorination	0	First flush after 32 d of not pumping <sup>1</sup>	10.2	16.6	18.5	1.9	4.1	18	0	14	0	300	Present
	0	Sample after pretreatment	9.37	8.8	10.1	1.0	1.1	18	0	7	0	1	Absent
	0	Treatment water <sup>2</sup> (0.5)	—	—	7.9	—	—	—	—	—	—	—	—
	0	Posttreatment purge	<1.0	3.1	4.9	<0.1	1.1	16	—	—	—	—	—
	1	Domestic pumping	8.44	9.3	9.8	0.4	0.4	17	—	—	—	—	—
	7	Domestic pumping	6.33	5.9	6.8	0.6	0.9	15	0	0	28	190	Absent
	20	Domestic pumping	2.1	1.4	1.8	0.2	0.2	14	—	—	—	—	—
Acid-surfactant + low-dose chlorination	0	First flush after 51 d of not pumping	—	13.6	17.9	3.4	8.3	16	21	11	21	2000	Absent
	0	Pretreatment purge	—	—	—	—	—	—	14	0	0	610	Present
	0	Treatment water <sup>2</sup> (1.0)	—	—	56.7	—	—	—	—	—	—	—	—
	0	Posttreatment purge	—	3.2	3.4	<0.1	0.2	16	—	—	—	—	—
	1	Domestic pumping	—	5.9	6.5	0.5	0.7	16	—	—	—	—	—
	6	Domestic pumping	—	2.8	3.2	0.5	0.9	15	0	0	0	370	Present
	13	Domestic pumping	—	2.8	2.8	0.5	0.6	14	8	0	0	1600	Present
	20	Domestic pumping	—	1.5	1.7	0.5	0.5	16	0	0	7	2500	Absent
High-dose chlorination	0	First flush after 37 d of not pumping	3.1	7.4	7.9	2.9	3.1	17	110	0	0	3700	Absent
	0	Pretreatment purge	3.1	3.9	3.9	0.7	0.7	17	14	0	14	29	Absent
	0	Treatment water <sup>2</sup> (24)	—	—	10.3	—	—	—	—	—	—	—	—
	0	Posttreatment purge	<1.0	<1.0	<1.0	<0.1	<0.1	16	—	—	—	—	—
	1	Domestic pumping	1.7	1.6	3.4	0.3	2.0	17	—	—	—	—	—
	8	Domestic pumping	<1.0	1.2	1.5	0.3	0.4	16	14	0	14	6	Absent
	5	Domestic pumping	1.3	1.4	1.8	0.5	0.5	15	42	0	0	<1	Absent
	25	Domestic pumping	<1.0	<1.0	1.2	—	0.3	15	—	—	—	—	—
Nonpumping period	0	First flush after 24 d of not pumping	12.7	15.1	13.7	0.3	1.0	19	47	0	9	49	Absent

<sup>1</sup>Results published previously in Gotkowitz et al. (2004).

<sup>2</sup>Number in parentheses is number of hours treatment solution remained in wellbores prior to purging.

a fivefold increase in total arsenic concentration, which we attribute to the dissolution of biofilm and mineral deposits in the well and pipe; the purpose of the acid-surfactant application in tandem with low-dose chlorination is to disrupt these deposits. This suggests that effective removal of mineral and biosolids removes contaminant mass from the water supply system, and it underscores the necessity of thorough purging of the well following treatment.

Lower arsenic concentrations prevailed during each of the four periods of domestic pumping following treatments (Table 1). During this phase of the experiment, the pumping-only treatment attained similarly low arsenic as the low-dose chlorination treatment. Concentrations generally increased during periods of nonuse (stagnant conditions), although arsenic concentration never exceeded levels previously noted at the field site (Gotkowitz et al. 2004). The results of this work are consistent with those previously noted for this site—that arsenic concentration in well water increases with residence time in the well. None of the treatments, including the high-dose chlorination that is no longer recommended for wells in this setting, appear to have increased arsenic solubility or mobility in the ground water system.

The arsenic measured during the nonpumping phase that followed the acid-surfactant and low-dose chlorination, 7.4 µg/L, was the lowest observed under stagnant conditions. This may result from eliminating a large amount of biofilm, mineral deposits, and associated trace elements from the well and pump. The limitations inherent in this experimental design preclude evaluating the long-lasting effects of this treatment from the high-dose treatment that followed it.

Concentrations of iron followed similar patterns to that of arsenic. Dissolved and total iron ranged from less than detection (0.1 mg/L) to about 1.0 mg/L in samples collected after well treatment, but concentrations following periods of nonpumping ranged from 1.9 to 3.4 mg/L of dissolved iron and up to 8.3 mg/L of total iron. Sulfate concentrations ranged from 13.4 to 18.5 mg/L, typical for

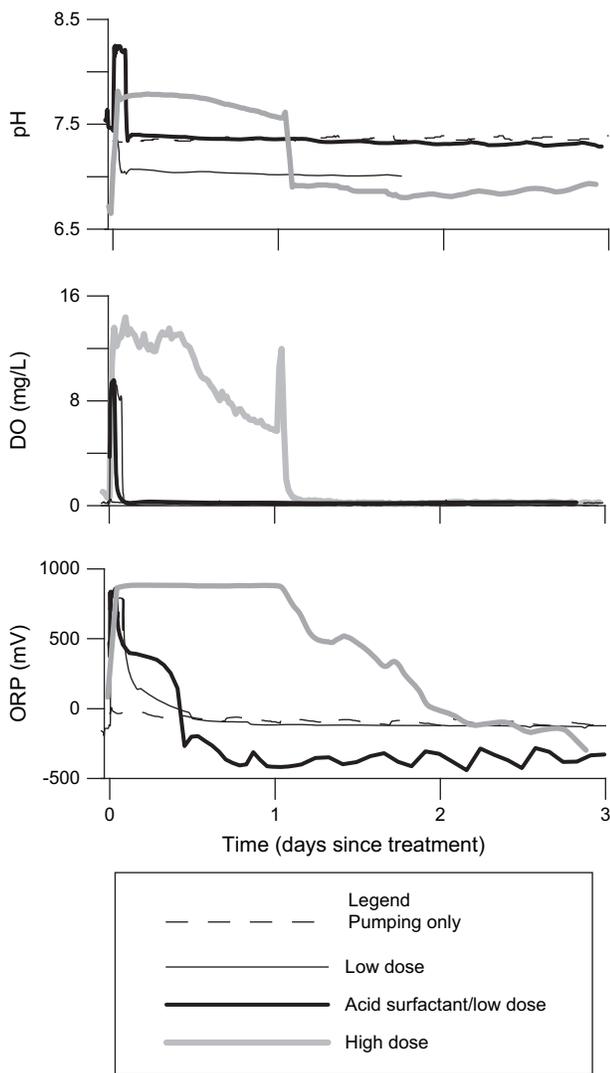
ground water from the St. Peter Sandstone Aquifer. Dissolved arsenic and iron concentrations showed a regular decrease with all four periods of domestic pumping, and sulfate concentrations did not vary significantly throughout the experiment.

Microbiological testing indicates that the borehole contains iron-oxidizing, heterotrophic, and sulfate-reducing bacteria (Table 1). All three species of iron bacteria were detected at one time or another, but the iron-oxidizing populations are not remarkably high at any time tested. The greatest numbers of bacteria were present in samples of stagnant water collected following low-dose and acid-surfactant/low-dose treatments. The acid-surfactant/low-dose treatment appears to have been ineffective in ridding the borehole of each type of bacterial community. The high-dose treatment was most effective in ridding the well of heterotrophic and sulfate-reducing bacteria, although counts of iron-oxidizing strains remained elevated throughout this treatment. Results for the five sets of duplicate samples (Table 2) show that the microbiological results were not fully repeatable. Heterotrophic plate counts in duplicate samples vary over an order of magnitude. Results of the present/absent test for sulfate-reducing bacteria were not repeatable for two of the five pairs of samples.

In situ monitoring of pH, D.O., and ORP demonstrates rapid change in well water chemistry induced by each chemical treatment (Figure 2). All three treatments raised pH, D.O., and ORP. Oxidizing conditions prevailed longer in association with high-dose chlorination because of its longer application time in the well (24 h) prior to purging. Exposure of the D.O. membrane and the redox platinum reference electrode to the NaOCl solutions may have affected instrument performance and response time, although both instruments gave reliable results when checked to calibration standards after measurements were collected. In general, these in situ measurements demonstrate the sudden shift to more oxidizing conditions under all three treatments and the relatively short duration of these conditions under the low-dose and acid-surfactant/low-dose treatments.

**Table 2**  
**Comparison of Duplicate Samples Collected for Microbiological Analyses**

Treatment	Day	Sample Description	<i>Leptothrix</i> (per mL)	<i>Gallionella</i> (per mL)	<i>Crenothrix</i> (per mL)	Heterotrophic Bacteria (CFU/mL)	Sulfate- Reducing Bacteria
Pumping only	0	First flush after 51 d of not pumping	14	0	28	1500	Absent
		Duplicate	21	11	21	2000	Absent
Acid-surfactant + low-dose chlorination	6	Domestic pumping	0	0	0	370	Present
		Duplicate	0	0	5	48	Absent
Acid-surfactant + low-dose chlorination	13	Domestic pumping	8	0	0	1600	Present
		Duplicate	0	0	0	280	Absent
Acid-surfactant + low-dose chlorination	20	Domestic pumping	0	0	7	2500	Absent
		Duplicate	0	0	0	280	Absent
Nonpumping period	24	First flush after 24 d of not pumping	47	0	9	49	Absent
		Duplicate	19	0	9	65	Absent



**Figure 2. In situ measurements of pH, D.O., and ORP during four treatments. The high-dose treatment solution is purged from the well on day 1.**

Following each chemical treatment, the borehole environment returned to circumneutral pH, low D.O., and reducing conditions prevalent during the pumping-only treatment.

## Conclusions

This set of experiments was motivated by concern about the potential for well disinfection with NaOCl solutions to exacerbate the release of naturally occurring arsenic to well water. The results demonstrate that in this setting, common disinfection procedures do not increase concentrations of arsenic in well water. Although each chemical treatment induced strongly oxidizing conditions in the wellbore, there is no evidence of lasting negative changes to water quality. Throughout the four experimental treatments, arsenic remained within the range of concentrations previously observed at this site.

Acid-surfactant treatment of the water supply system removed arsenic mass from the system. Overall, lower arsenic concentrations following this treatment indicate

that physical or chemical cleaning of water supply systems can potentially reduce arsenic concentrations in domestic well water in this setting. Although these results underscore the need to fully purge the system following treatment, the findings are consistent with Seiler's (2006) observation of only short-term increases in trace elements following in situ chlorination.

Interpretation of these results is limited by the experimental design. The test well was treated multiple times, and long-lasting effects of one treatment cannot be isolated from effects of subsequent treatments. However, arsenic and iron concentrations remained low during the initial phase of domestic pumping without chemical treatment and throughout each period of domestic pumping following the chemical treatments. When pumping was discontinued for several weeks, numbers of bacteria and iron and arsenic concentrations increased. This is consistent with previous results from this site suggesting that microbially facilitated reduction of arsenic-bearing iron(hydroxides) may contribute arsenic to water with a long residence time in the well (Gotkowitz et al. 2004).

There is no conclusive evidence from these experiments that effective biocidal action alone results in lower arsenic concentrations. Microbiological growth did not appear limited by the acid-surfactant/low-dose chlorination; however, this treatment resulted in arsenic concentrations as low as those observed following high-dose chlorination. The increase in one or more types of bacteria following each of the stagnant phases at the well demonstrates the failure of all treatments to permanently eradicate microbes, or the biofilm that harbors them, from the well. Overall, these results suggest that disruption of biofilm and mineral deposits in the well and water distribution system in tandem with chlorine disinfection and routine pumping is useful to improve water quality in this setting.

These field-based experiments demonstrate that chemical disinfection did not increase concentrations of arsenic and iron in well water. This may be related to the site-specific mineralogic and hydrogeologic conditions at the test site. Future work should include controlled laboratory studies of biotic and abiotic mechanisms of trace metal behavior in chlorinated well water.

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## References

American Public Health Association (APHA). 1999. *Standard Methods for the Examination of Water and Wastewater*, 20th ed. Washington, D.C.: American Public Health Association.

- Gotkowitz, M.B., M.S. Schreiber, and J.A. Simo. 2004. Effects of water use on arsenic release to well water in a confined aquifer. *Ground Water* 42, no. 4: 568–575.
- Le, X.C., S. Yalcin, and M. Ma. 2000. Speciation of submicrogram per liter levels of arsenic in water: On-site species separation integrated with sample collection. *Environmental Science & Technology* 34, no. 11: 2342–2347.
- Lovley, D.R. 2000. Fe(III) and Mn(IV) reduction. In *Environmental Microbe-Metal Interactions*, ed. D.R. Lovley, 320–435. Washington, D.C.: ASM Press.
- Momba, M.N.B., T.E. Cloete, S.N. Venter, and R. Kfir. 1998. Evaluation of the impact of disinfection processes on the formation of biofilms in potable surface water distribution systems. *Water Science and Technology* 38, no. 8–9, 283–289.
- National Research Council. 2001. *Arsenic in Drinking Water: 2001 Update*. Washington D.C.: National Academy Press.
- Oliphant, J.A., M.C. Ryan, A. Chu, and T. Lambert. 2002. Efficacy of coliform bacteria monitoring and shock chlorination in wells finished in a floodplain aquifer. *Groundwater Monitoring and Remediation* 22, no. 4: 66–72.
- Postgate, J.R. 1963. Versatile medium for the enumeration of sulfate reducing bacteria. *Applied Microbiology* 11, no. 3: 265–267.
- Schreiber, M.E., M.B. Gotkowitz, J.A. Simo, and P.G. Freiberg. 2003. Mechanisms of arsenic release to ground water from naturally occurring sources, eastern Wisconsin. In *Arsenic in Ground Water: Geochemistry and Occurrence*, ed. A.H. Welch and K.G. Stollenwerk, 259–280. Norwell, Massachusetts: Kluwer Academic Publishers.
- Schreiber, M.E., J.A. Simo, and P.G. Freiberg. 2000. Stratigraphic and geochemical controls on naturally occurring arsenic in groundwater, eastern Wisconsin, USA. *Hydrogeology Journal* 8, no. 2: 161–176.
- Seiler, R.L. 2006. Mobilization of lead and other trace elements following shock chlorination of wells. *Science of the Total Environment* 367, no. 2–3: 757–768.
- Smedley, P.L., and D.G. Kinniburgh. 2002. A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry* 17, no. 5: 517–568.
- Smith, S.A. 1995. *Monitoring and Remediation Wells: Problem Prevention, Maintenance, and Rehabilitation*. Boca Raton, Florida: Lewis Publishers.
- Smith, S.A., and O.H. Tuovinen. 1985. Environmental analysis of iron-precipitating bacteria in ground water and wells. *Ground-water Monitoring Review* 5, no. 4: 45–52.
- Snoeyink, V.L., and D. Jenkins. 1980. *Water Chemistry*. New York: John Wiley and Sons.
- Taylor, S.W., C.R. Lange, and E.A.L. Lesold. 1997. Biofouling of contaminated ground-water recovery wells: Characterization of microorganisms. *Ground Water* 35, no. 6: 973–980.
- Terashima, S., and M. Taniguchi. 1998. Mineralogical associations of arsenic and antimony in thirty five geochemical reference materials by sequential extraction with hydride generation and atomic absorption spectrometry. *Journal of Geostandards and Geoanalysis* 22, no. 1: 103–112.
- Thornburg, K., and N. Sahai. 2004. Arsenic occurrence, mobility, and retardation in sandstone and dolomite formations of the Fox River Valley, eastern Wisconsin. *Environmental Science & Technology* 38, no. 19: 5087–5094.
- Vickers, A. 2001. *Handbook of Water Use and Conservation*. Amherst, Massachusetts: Waterplow Press.
- Wisconsin Department of Natural Resources. 2002. *Well Chlorination in Arsenic Sensitive Areas*. Bureau of Drinking Water and Groundwater. Pub DG-069 2002 Madison, Wisconsin: Wisconsin Department of Natural Resources.
- Wisconsin State Laboratory of Hygiene. 2003. *Methods and Quality Assurance Manual*. Madison, Wisconsin: University of Wisconsin-Madison.

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