

PROJECT SUMMARY

Title: Mineral transformation and release of arsenic to solution under the oxidizing conditions of well disinfection

Project ID:

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Background/Need: Guidance for disinfection of domestic wells in arsenic-sensitive areas of Wisconsin calls for a treatment at 20 percent of the chlorine strength and 10 percent of the contact time recommended for non-arsenic impacted wells. This guidance is based upon an assumption that the oxidizing strength of chlorine causes chemical oxidation of arsenic-rich sulfide minerals. However, microbially-mediated reductive dissolution of arsenic-bearing iron (hydr)oxides also contributes arsenic to groundwater in some areas of Wisconsin. Therefore, a low-dose chlorination treatment may not be a preferred method of disinfection in all settings where groundwater and wells are arsenic-impacted.

Objectives: Investigate geochemical and biogeochemical mechanisms of arsenic release to well water from arsenic-rich sulfide minerals and iron (hydr)oxides during *in situ* disinfection with chlorine

Methods: In laboratory batch experiments, arsenic-rich aquifer sediments were subjected to deionized water with 8 mg/L O₂ or chlorine disinfection solution at 1200 mg/L Cl⁻. Solution chemistry was monitored during 24 hours of reaction. The second portion of this project utilized a field setting to monitor microbial populations and water chemistry in a test well completed in the St. Peter sandstone. The well was subjected to periods of routine pumping, periods of non-use, and treatment with a low-dose chlorine disinfection.

Results and Discussion: In laboratory experiments, lower As concentrations occurred under strongly oxidizing compared to moderately oxidizing conditions, probably due to formation of differing types of Fe oxides, or differing rates of Fe oxide formation. Sulfide oxidation was enhanced in a sample subjected to a 1200 mg/L chlorine solution compared to a sample subjected to 8 mg/L O₂ in nanopure water. Under high chlorine, initial release of dissolved As (30 µg/L) and Fe (250 µg/L) was followed by rapid precipitation of Fe oxides and a reduction in arsenic concentration. The Fe oxides presumably adsorbed arsenic from solution. Increases in Fe and As concentrations in solution later in the 24-hour experiment suggest deflocculation of the Fe oxides resulted in release of As-Fe nanoparticles. Under the moderately oxidizing control treatment of 8

mg/L O₂, aqueous arsenic concentrations increased steadily over the 24-hour period to 58 µg/L, exceeding those measured under high-chlorine treatment.

Results from field experiments indicate that microbially facilitated reduction of arsenic-bearing iron (hydr)oxides contribute regulatory significant concentrations of arsenic to well water in areas of northeast Wisconsin. Water with a longer residence time in the well had higher concentrations of arsenic and iron, which correlated to increases in numbers of Fe(III), As(V)- and sulfate-reducing microorganisms in the well. *In situ* well disinfection with low-dose chlorine caused strongly oxidizing conditions in the well bore for less than one day, but with no apparent detrimental effect on water quality. Arsenic concentrations were lower during both phases of routine pumping than during non-pumping phases. Populations of microorganisms in well water returned to pre-treatment levels within three weeks of low-dose disinfection, suggesting that either fresh formation water re-inoculated the well or that biofilm and scale in the well harbored microbes from the disinfectant.

Conclusions/Implications: These experiments do not support recommendation of low-dose chlorination in all arsenic-impacted areas of Wisconsin. In areas where the primary source of aqueous arsenic is reductive dissolution of Fe (hydr)oxides, such as glacial aquifers in southeast Wisconsin, imposing strongly oxidizing conditions over short time periods is unlikely to promote arsenic release from aquifer solids because arsenic is not found in association with sulfide minerals. In these settings, high-dose chlorination may be more effective in ridding the well of pathogenic and nuisance bacteria.

In northeast Wisconsin, the St. Peter sandstone aquifer contains arsenic-bearing sulfide minerals and arsenic-bearing iron oxides. The complexity and variability in arsenic geochemistry and aquifer mineralogy in this region preclude a single preferred method for well disinfection. Where the source of arsenic is more likely attributable to reduction of iron hydr(oxides), effectively ridding the well of Fe-reducing bacteria through routine pumping or *in situ* chlorination may improve well water quality. Effective well disinfection may reduce arsenic in well water in settings where the arsenic is a result of biogeochemical reactions that occur within the well.

Low-dose chlorination may be preferred to high-dose treatment where oxidation of arsenic-bearing sulfide minerals is the primary source of aqueous arsenic. Strongly oxidizing conditions imposed under high-dose chlorine treatment increased the rate of sulfide oxidation in a laboratory setting. However, strongly oxidizing conditions lead to complex cycling of iron and arsenic. These experiments were limited in nature and do not provide evidence of long-term geochemical impacts to water quality from high-dose chlorination.

Related Publications: West, N., M. Schreiber and M. Gotkowitz, 2006. Effect of chlorination on arsenic release from sulfide minerals. GSA Program with Abstracts Annual Meeting.

Key Words: arsenic, well disinfection, microbes, sulfide minerals

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