Title: **Geologic and Geochemical Controls on Arsenic in Groundwater in Northeastern Wisconsin**

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Background/Need:

Wells in the Fox River Valley (FRV) of northeastern Wisconsin contain high concentrations of arsenic. The geologic source is thought to be the contact of the Ordovician St Peter Sandstone (Ancell Group) and Platteville Formation (Sinnipee Group), where pyrite and marcasite are the major minerals in a sulfide-bearing secondary cement horizon (SCH). The arsenic is also found as a sorbed phase to colloidal-size, iron oxyhydroxide surfaces, suggesting that pyrite/marcasite in the SCH is altering to a nanocrystalline iron oxyhydroxide and that arsenic is sorbing or precipitating onto the hydroxide surfaces. In this area, sulfide oxidation is the likely dominant process controlling arsenic release to highly impacted wells (arsenic >100 μg/L). The introduction of oxygen through the well borehole is a likely cause of oxidation of the sulfide-bearing aquifer material in confined portions of the aquifer. However, this is not obviously the cause of low (1 to 10 μg/L) to moderate (10 to 100 μg/L) arsenic contamination.

There are many reports of low to moderate levels of arsenic contamination in aquifers in the mid-western United States. These concentrations are significant because the U.S. EPA has recently announced a lowering of the drinking water standard for arsenic from 50 to 10 μg/L. This lower standard in turn demands a greater understanding of factors controlling low levels of arsenic release to groundwater supplies. Recent sampling from over 3,300 domestic wells in Outagamie and Winnebago Counties in northeastern Wisconsin showed that 3% of these wells exceed 50 μg/L arsenic, while a full 17% are impacted at levels between 10 and 50 μg/L.

Objectives:

Investigate geologic controls on the occurrence and magnitude of arsenic in groundwater in the FRV, including characterizing arsenic-rich mineralization below the top of the St. Peter sandstone, the spatial variability of arsenic within these mineralized deposits, and the effect of variability in local and regional stratigraphy on the occurrence of arsenic in groundwater in the study area. Characterize geochemical and hydraulic conditions that contribute to low- and high-level arsenic impacts in wells.

Methods:

Sample the SCH and other mineralized zones for metals and mineralogical characteristics, map the geographic distribution of the St. Peter, and relate this information to the distribution of arsenic in groundwater; evaluate regional groundwater geochemistry data for patterns indicative of geochemical mechanisms of release; conduct a field study to compare and contrast water quality and hydrogeologic conditions at wells with high and low arsenic levels.

Results and Discussion:

There is a high degree of variability in the distribution of iron-sulfide mineralization at the Sinnipee-St. Peter contact and a high degree of variability of arsenic within the mineralization. Overall, regional trends of increasing arsenic concentration and morphotypes of mineralization occur in outcrops in the St. Peter sandstone from north to south along the FRV. At a smaller scale, there are trends of increasing arsenic concentration in the St. Peter sandstone where the sandstone pinches out. Arsenic concentrations in non-mineralized areas of the sandstone average less than 5 parts per million (ppm), while concentrations in mineralized zones vary from 10s to 100s ppm. In many cases, iron oxide weathering products of the sulfide mineralization have higher associated arsenic concentrations than the iron-sulfide mineralization. The St. Peter is also an arsenic-rich formation in other areas, such as the Pine Bluff area west of Madison, suggesting that this sandstone may be a source of arsenic to groundwater in other areas. In the far western portions of Outagamie and Winnebago Counties, to the west of the subcrop of the St. Peter sandstone, arsenic entrained in glacial sediments may be a source of arsenic to groundwater.

Study results support the hypothesis that high levels of arsenic in groundwater occur where mineralization is oxidized in well boreholes. Within the Town of Algoma, two factors affect water levels and the potential for this oxidation: variations in topography and stratigraphy that result in lower water levels in the St. Peter, and groundwater withdrawal from increasing numbers of domestic water wells completed in the St. Peter.

Two distinct geochemical mechanisms appear to contribute low to moderate arsenic concentrations to well water in this aquifer. Oxidation of sulfide minerals may release arsenic to groundwater in confined portions of the aquifer; oxidation may have occurred at some time in the geologic past, or current levels of oxygen dissolved in the groundwater may be sufficient to permit slow oxidation to occur.

Reductive dissolution of arsenic-bearing iron oxides also seems to contribute low to moderate levels of arsenic to groundwater when the geochemical environment becomes sufficiently reducing. This occurs under typical domestic water use patterns, because increasing groundwater residence time in wells correlates to the on-set of strongly reducing conditions and higher arsenic concentrations. The well borehole is a microbiologically active environment, and biogeochemical reactions likely contribute to the observed increase in arsenic concentrations.

Conclusions/Implications/Recommendations:

Because the introduction of oxygen through the borehole and dewatering of the aquifer are not the sole causes of arsenic contamination in wells, preventing further declines in the potentiometric surface will not prevent low to moderate levels of arsenic contamination in this aquifer. Although the reduction of arsenic-bearing iron oxides may release relatively low concentrations of arsenic to well water, this mechanism of release is significant with regard to meeting a drinking water standard of 10 µg/L. While well disinfection (chlorination) has the potential to oxidize aquifer sediments, disinfection may be critical at limiting arsenic contamination in settings similar to the field site, where microbes facilitate iron cycling and associated arsenic sorption and release. Because arsenic concentrations in the aquifer are heterogeneous, and much of the sandstone hosts very low arsenic concentrations, mixing of water in a fully purged well constructed with a long open interval results in low well water concentrations. Reducing the volume of well bore storage relative to water use may also limit arsenic concentrations in well water.

Related Publications:

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: A.H. Welch, and K.G. Stollenwerk (Editor), Arsenic in Ground Water: Geochemistry and Occurrence. Kluwer Academic Publishers, Norwell, Massachusetts, pp. 259-280.

Gotkowitz, M.B., M.E. Schreiber, J.A. Simo. Effects of water use on arsenic release to well water in a confined aquifer. In Review.

Key Words: *arsenic, sulfide oxidation, iron oxide reduction*

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Final Report: A final report containing more detailed information on this project is available for loan from Wisconsin's Water Library, University of Wisconsin - Madison, 1975 Willow Drive, Madison, Wisconsin 53706 (608) 262-3069.