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**Arsenic Contamination in Southeast Wisconsin:
Sources of Arsenic and Mechanisms of Arsenic Release**

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PROJECT SUMMARY

Title: Arsenic Contamination in Southeast Wisconsin: Sources of Arsenic and Mechanisms of Arsenic Release

Project ID: WR02R003

Principal Investigators: Dr. Jean Bahr, Professor, Department of Geology and Geophysics, University of Wisconsin - Madison; Madeline Gotkowitz, Associate Professor, Wisconsin Geological and Natural History Survey

Research Assistant: Tara Root, Department of Geology and Geophysics, University of Wisconsin - Madison

Period of Contract: 6/30/2002 – 6/30/2004

Background/Need: Groundwater in about 10 percent of wells open to Quaternary glacial and shallow bedrock aquifers in southeastern Wisconsin has arsenic concentrations greater than the U.S. Environmental Protection Agency's standard of 10 µg/l. Denser clusters of arsenic-impacted wells ($[As]_{aq} \geq 10 \mu\text{g/l}$) occur in localized areas. The lack of anthropogenic sources in these areas indicates that the arsenic is naturally occurring. Improved understanding of the controls on arsenic concentrations in groundwater is needed to inform efforts to prevent or reduce arsenic contamination in drinking water wells in southeastern Wisconsin.

Objectives: The objectives of this study were to characterize the source(s) of arsenic and the controls on arsenic concentrations in groundwater from the Quaternary and Silurian aquifers in southeastern Wisconsin.

Methods: We reviewed existing data to estimate the magnitude and spatial distribution of arsenic concentrations in groundwater from the Quaternary and Silurian aquifers in southeastern Wisconsin. Detailed field investigations were conducted near the city of Lake Geneva in Walworth County.

Using core samples from a borehole at Woods Elementary, geologic sources of arsenic were identified using X-ray diffraction and chemical extractions. We collected groundwater samples from private wells and a monitoring well installed in the borehole at Woods School. We also organized a private well sampling program in the Lake Geneva area. We examined water chemistry data for trends indicative of water-rock interactions that may mobilize arsenic. We conducted a pumping test at the Woods School monitoring well to evaluate the hydrogeology of the study area. Time series sampling during the pumping test provided information about the effect of pumping on arsenic concentrations.

Results and Discussion: The hydrostratigraphy in the Lake Geneva area includes a shallow aquifer consisting of glacially deposited sand and gravel. This aquifer is underlain by a confining unit of low-conductivity clayey till. A deeper discontinuous sand and gravel aquifer occurs beneath this confining unit on top of the Silurian dolomite. Pumping test results indicate that there is little hydraulic connection between the shallow Quaternary aquifer and the deeper Quaternary and shallow Silurian aquifers.

8 % of wells open to the Quaternary and/or Silurian aquifers in the study area have arsenic concentrations greater than 10 µg/l. Near the city of Lake Geneva, more than 20 % of Quaternary and Silurian wells have arsenic concentrations greater than the E.P.A. standard. The highest arsenic concentrations (85 µg/l) occur

in wells open to the Silurian dolomite. The maximum arsenic concentrations in wells open to Quaternary deposits are around 30 µg/l.

Low to moderate solid-phase concentrations of arsenic (2 mg/kg to 20 mg/kg) occur throughout the entire thickness of Quaternary sediments in the study area. From a mass balance perspective, such low to moderate solid-phase arsenic concentrations, under geochemical conditions that release arsenic to groundwater, are sufficient to lead to aqueous arsenic concentrations that exceed the 10 µg/l standard. Arsenic is released from aquifer sediments during laboratory experiments designed to dissolve (hydr)oxide minerals. These results, combined with groundwater chemistry data suggest that arsenic is released to the groundwater via reductive dissolution of (hydr)oxides. In the Lake Geneva area, hydrogeologic, and geochemical factors create reducing conditions that lead to arsenic mobilization in the deep Quaternary and upper Silurian aquifers. Groundwater in shallow Quaternary sediments is not as reducing as in the deeper system and is largely unaffected by arsenic.

Conclusions/Implications/Recommendations:

- Where geochemical conditions are sufficiently reducing, low solid-phase arsenic concentrations associated with (hydr)oxide minerals (on the order of a few parts per million) are sufficient to sustain groundwater arsenic concentrations greater than the 10 µg/l standard.
- All well owners in southeastern Wisconsin should test well water for arsenic because of the potential for even low levels of solid phase arsenic in glacial deposits to impact groundwater in glacial and shallow bedrock aquifers.
- New wells in the Lake Geneva area should not be completed in the deep Quaternary aquifer. The only viable alternative for existing arsenic-impacted wells is treatment to remove arsenic from drinking water.
- A single model of arsenic release is not adequate to account for the occurrence of arsenic in groundwater across the state. Oxidizing conditions cause arsenic release from sulfide minerals in the St. Peter aquifer in the Fox River Valley, but reducing conditions release arsenic to parts of the Quaternary and Silurian aquifers in southeastern Wisconsin. While the findings of this work are limited to the study area, similar geologic and geochemical conditions may be present in the Quaternary aquifer in other areas of Wisconsin.

Related Publications:

Root, T.L., expected spring 2005. Arsenic in Groundwater in Southeastern Wisconsin: Sources of Arsenic and Mechanisms of Arsenic Mobilization. Ph.D. thesis, University of Wisconsin –Madison, Department of Geology and Geophysics.

Root, T.L., Bahr, J.M., and Gotkowitz, M.B., 2005. Controls on Arsenic in Groundwater in Southeastern Wisconsin, in Vlassopoulos, D., Benning, L., Meng, X., and O'Day, P., *Advances in Arsenic Research*, American Chemical Society Symposium Series. (*In press*)

Tara Root received a student research award from the Hydrogeology Division of the Geological Society of America for work on this project (2002).

Key Words: Arsenic, groundwater, Quaternary and Silurian aquifers, southeastern Wisconsin

Funding: University of Wisconsin System and the Wisconsin Department of Natural Resources with additional support from the United States Geological Survey, the Geological Society of America, the Wisconsin Geological and Natural History Survey, and the United States Department of Energy Office of Civilian Radioactive Waste Management.

INTRODUCTION

Toxicological studies have shown that long-term consumption of arsenic-contaminated water may cause serious health problems including a variety of cancers, cardiovascular diseases, and nervous system disorders (Jain and Ali, 2000). Based on a review of epidemiological data, the National Research Council determined “the lifetime excess cancer risks in the United States for bladder and lung cancers combined at arsenic concentrations in drinking water between 3 and 20 $\mu\text{g/l}$...[are] between 9 and 72 per 10,000 people” (NRC, 2001, p. 223). Due to concern about the health risks associated with arsenic consumption, the U.S. Environmental Protection Agency (E.P.A.) lowered the maximum contaminant level for arsenic in drinking water from 50 $\mu\text{g/l}$ to 10 $\mu\text{g/l}$ in October 2001.

Arsenic in groundwater commonly comes from naturally occurring minerals in aquifer sediments (Smedley and Kinniburgh, 2002). Arsenic-rich pyrite is one of the most common arsenic-bearing minerals (Nordstrom, 2001). Oxidation of arsenic-rich sulfide minerals is one possible mechanism for releasing arsenic to groundwater (Smedley and Kinniburgh, 2002). Arsenic is also found in association with (hydr)oxide minerals, both as sorbed species and incorporated into the mineral structure. Reductive dissolution of (hydr)oxides is another possible mechanism of arsenic mobilization (Smedley and Kinniburgh, 2002). Desorption of arsenic may occur via reductive mechanisms or competition with other species for sites on mineral surfaces (Smedley and Kinniburgh, 2002).

Arsenic concentrations exceed the 10 $\mu\text{g/l}$ standard in approximately 10 percent of wells open to Quaternary glacial and shallow bedrock aquifers in southeastern Wisconsin. Denser clusters of arsenic-impacted wells ($[\text{As}]_{\text{aq}} \geq 10 \mu\text{g/l}$) occur in localized areas. Maximum groundwater arsenic concentrations are on the order of 100 $\mu\text{g/l}$. The lack of anthropogenic sources in these areas indicates that the arsenic is naturally occurring.

In 1998, Wisconsin Department of Natural Resources personnel first noted the occurrence of moderate levels of arsenic contamination in southeastern Wisconsin groundwaters in wells open to the Silurian Dolomite near the town of Lake Geneva (Figure 1). The Wisconsin Geological and Natural History Survey then conducted a preliminary study to evaluate the extent of arsenic contamination and determine if geochemical conditions in the Lake Geneva area are similar to those in the Fox River Valley, where oxidation of arsenic bearing sulfide minerals has been identified as the cause of high arsenic concentrations ($>100\mu\text{g/l}$) in groundwater (Schreiber et al., 2003). The results of the preliminary study indicated that geochemical conditions in the Lake Geneva area are significantly different from those in the Fox River Valley. However, no arsenic sources or mechanisms of arsenic release to groundwater were identified during the preliminary study (Gotkowitz, 2000).

The study described in this report was designed to build on the work completed for the preliminary study with the goals of characterizing the source(s) of arsenic and the controls on arsenic mobility in the Quaternary and shallow Silurian aquifers in southeastern Wisconsin. The following work was completed in order to meet these objectives:

1. review of existing geochemical and geological data,
2. core collection and solid-phase characterization of aquifer materials,
3. groundwater chemistry monitoring, and
4. aquifer testing.

PROCEDURES AND METHODS

Preliminary Data Review: Information about the geology, hydrogeology, and geochemistry of the study area (Figure 1) was obtained from previously published reports (Mickelson et al., 1984; Clayton et al., 1991; Gotkowitz, 2000; SEWRPC/WGNHS, 2002). The magnitude and spatial extent of the arsenic contamination were determined from data in the Wisconsin Department of Natural Resources' Ground Water Retrieval Network, Gotkowitz (2000).

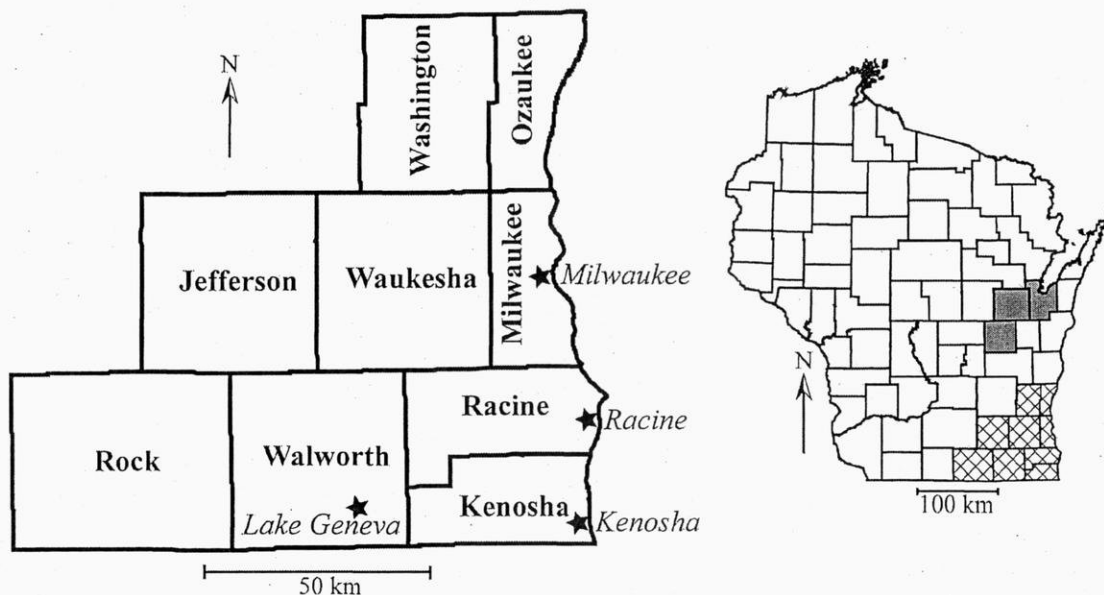


Figure 1. - Map of study area. Study area is hatched on state map and enlarged on the left side of the figure. The shaded area on the state map shows the location of the Fox River valley.

Collection and Analysis of Geologic Samples: 100 m of continuous core were collected by roto sonic drilling from a borehole approximately 10 m away from an existing arsenic-impacted well near the town of Lake Geneva. Core samples were sent to ALS Chemex for analysis to determine the chemical composition of the bulk sediment. The mineralogy of core samples was determined using X-ray diffraction. Loss-on-ignition (Ben-Dor and Banin, 1989), done by the University of Wisconsin Soil and Plant Analysis Laboratory (SPAL), was used to estimate the percent organic matter in core samples. Selective sequential extractions were conducted to gather information about the solid-phase associations of arsenic in aquifer sediments. During these extractions, a series of reagents was used to dissolve specific mineral phases from bulk core samples. The relative amount of arsenic released during each extraction provided information about the distribution of arsenic in the solid-phase. (See Appendix B for a summary of the extraction scheme. Details of the extraction scheme are in Root (expected 2005)). The reagents used in the extractions were chosen because they have been shown to be effective at dissolving specific minerals. However, the efficiency of the extractions depends on the affinity and specificity of the selected reagent for the targeted mineral. Because it is not possible to quantify the affinity or specificity of the reagent for the targeted minerals, sequential extractions are operationally defined and provide qualitative rather than quantitative information (LaForce et al, 2002).

Groundwater Sampling and Analysis: We worked with the Geneva Lakes Environmental Protection Agency to sponsor a private well sampling program in the Lake Geneva Area. During this program, arsenic analyses were obtained from 75 wells. 29 Additional groundwater samples were obtained from 18

residential supply wells and a monitoring well installed in the borehole from which the core was collected. Temperature, pH, redox potential, conductivity, and dissolved oxygen measurements were made in the field. Samples for determination of major cations, dissolved metals, and dissolved arsenic were filtered to 0.45 μm and preserved with OPTIMA nitric acid. Filtered (0.45 μm), non-preserved samples were collected for determination of major anions. The inflection point titration method was used to determine alkalinity (Wilde and Radtke, 2003). Other major anions were determined by ion chromatography at SPAL. Major cations, metals, and arsenic were determined by inductively coupled plasma-optical emission spectrometry.

RESULTS AND DISCUSSION

Magnitude and extent of arsenic contamination: 8 % of wells open to the Quaternary and/or Silurian aquifers in the nine-county study area have arsenic concentrations greater than 10 $\mu\text{g/l}$ (Table 1). 77 % of those same wells have detectable concentrations of arsenic. There are clusters of arsenic-impacted wells within this region. For example, near the Woods School and the city of Lake Geneva (Figure 1) more than 20 % of Quaternary and Silurian wells have arsenic concentrations greater than the E.P.A. standard. The highest arsenic concentrations (85 $\mu\text{g/l}$) occur in wells open to the Silurian dolomite. The maximum arsenic concentrations in wells open to Quaternary deposits are around 30 $\mu\text{g/l}$.

No spatial trends are obvious in the data (Figure 2). Arsenic concentrations exceeding 10 $\mu\text{g/l}$ appear to be prevalent in wells open to the Silurian aquifer near the town of Lake Geneva and in southern Ozaukee County (Figure 2a). However, sample density is high near the most populous areas and sparse in rural areas; it is not clear whether the clusters of arsenic-impacted wells are the result of geological and/or hydrogeological variability or are an artifact of the non-random sample distribution. The highest arsenic concentrations in wells open to the Quaternary aquifer occur in the central and eastern portions of the study area (Figure 2b).

Arsenic Sources: Typical background concentrations of arsenic in geologic materials are on the order of 2 to 5 ppm. Solid-phase arsenic concentrations in core samples from the study area ranged from less than detection (2 ppm) to 21 ppm (Figure 3). However, based on mass balance calculations (Appendix C), these moderate solid-phase concentrations are sufficient to sustain groundwater arsenic concentrations greater than 10 $\mu\text{g/l}$.

An organic horizon in the sand and gravel unit contained the highest concentration of arsenic (21 ppm) in the core samples (Figure 3). Relatively high arsenic concentrations (15 ppm) were also found in samples of clay in a dissolution opening in the top of the Silurian Dolomite. The sand and gravel units and upper till units contain relatively little arsenic (<2 ppm to 4 ppm). The lower till units have low to moderate arsenic concentrations (<2 ppm to 7 ppm). The large number of arsenic analyses that were below the detection limit makes it difficult to quantify relationships between arsenic and other elements. However, the overall shapes of the iron, manganese, and organic matter profiles roughly parallel that of arsenic. Sulfur concentrations, in contrast to those of other constituents, generally decrease with depth (Figure 3).

Based on the apparent negative correlation between arsenic and sulfur in our samples, solid-phase arsenic is not associated with sulfide minerals. The similarities in the profiles of arsenic, iron, and manganese (Figure 3) suggest that solid-phase arsenic is associated with iron and/or manganese-(hydr)oxide minerals. X-ray diffraction (XRD) did not reveal the presence of (hydr)oxides; however, poorly crystalline (hydr)oxides present at a few weight percent are not detectable using XRD.

The results of the selective sequential extractions (Figure 4) also indicate that arsenic is associated with (hydr)oxide minerals in many of the sediment samples. In all samples except those from the brown till, the majority of arsenic was released during extractions targeting arsenic sorbed on surfaces of hydroxide or clay minerals or co-precipitated with oxides (Appendix B).

Relatively high arsenic concentrations are found in the organic-rich horizon in the core (Figure 3), but this horizon is not likely a significant regional source of arsenic. The organic material was likely deposited in small wetlands situated in topographic lows that are not laterally extensive (John Attig, Wisconsin Geological and Natural History Survey personal communication).

Table 1. - Summary of arsenic concentrations in wells open to the Silurian and/or Quaternary aquifers in southeastern Wisconsin.

	Number of wells open to specified unit(s)	Maximum As (µg/L)	Minimum As (µg/l)	As ≥ 10 µg/l	5 µg/l ≤ As < 10 µg/l	2 µg/l ≤ As < 5 µg/l	D.L. < As < 2 µg/l**	As < D.L.**
Summary data for all wells	235	85	< D.L.	Number of wells*				
				18	28	50	62	77
				% of wells*				
				8	12	21	26	33
Wells open to:								
Quaternary	136	32	< D.L.	Number of wells*				
				8	7	19	44	58
				% of wells*				
				6	5	14	32	43
Silurian	96	85	< D.L.	Number of wells*				
				10	21	29	18	18
				% of wells*				
				10	22	30	19	19
Quaternary through Silurian	3	3	< D.L.	Number of wells*				
				0	0	2	0	1
				% of wells*				
				0	0	67	0	33

*For wells with multiple arsenic analyses, only the maximum arsenic concentration was considered.

**Detection limit ranges from 0.3 mg/L to 5 mg/l.

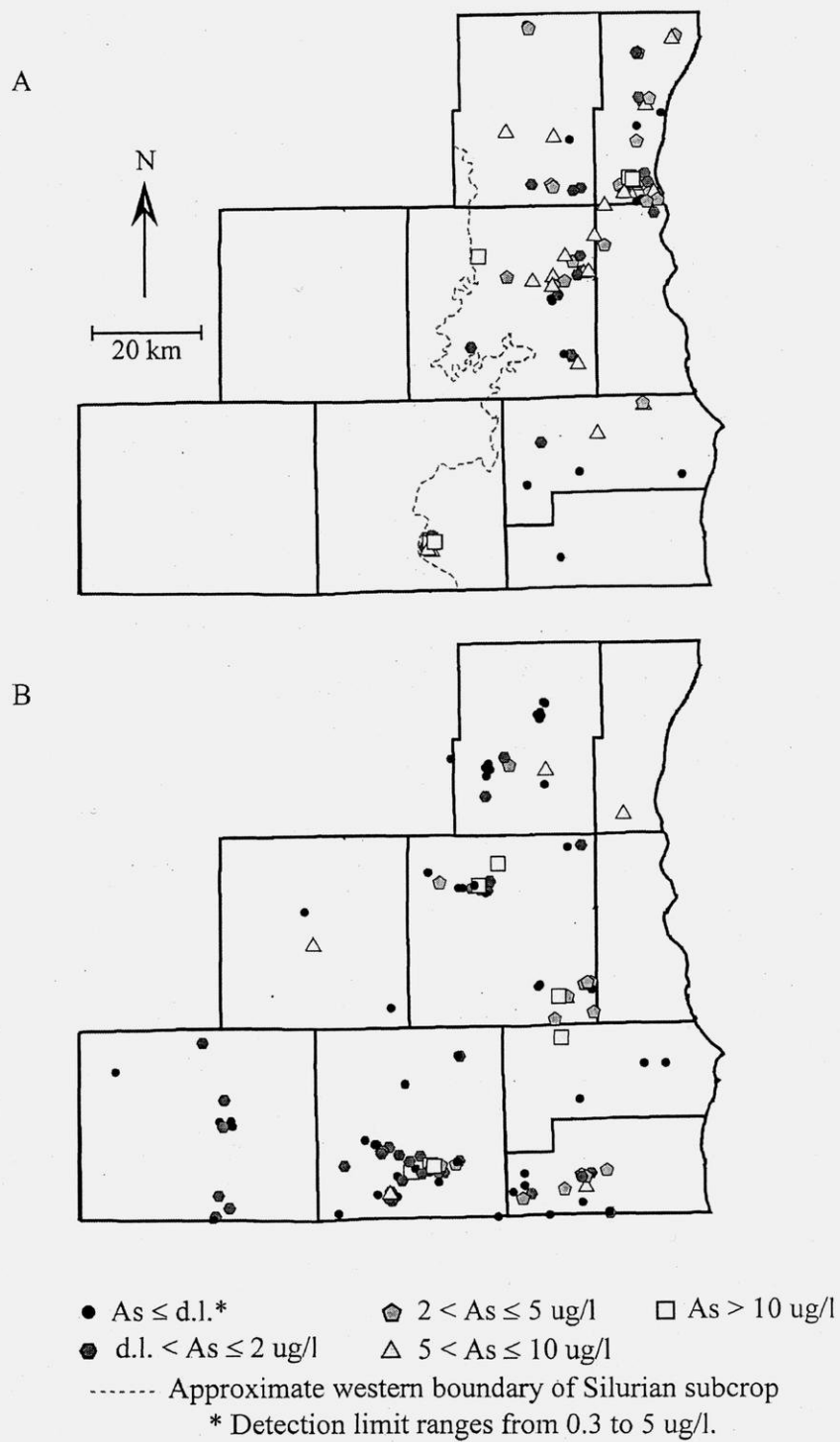


Figure 2. - Maps showing distribution of arsenic concentrations in wells open to A) the Silurian aquifer and B) the Quaternary aquifer.

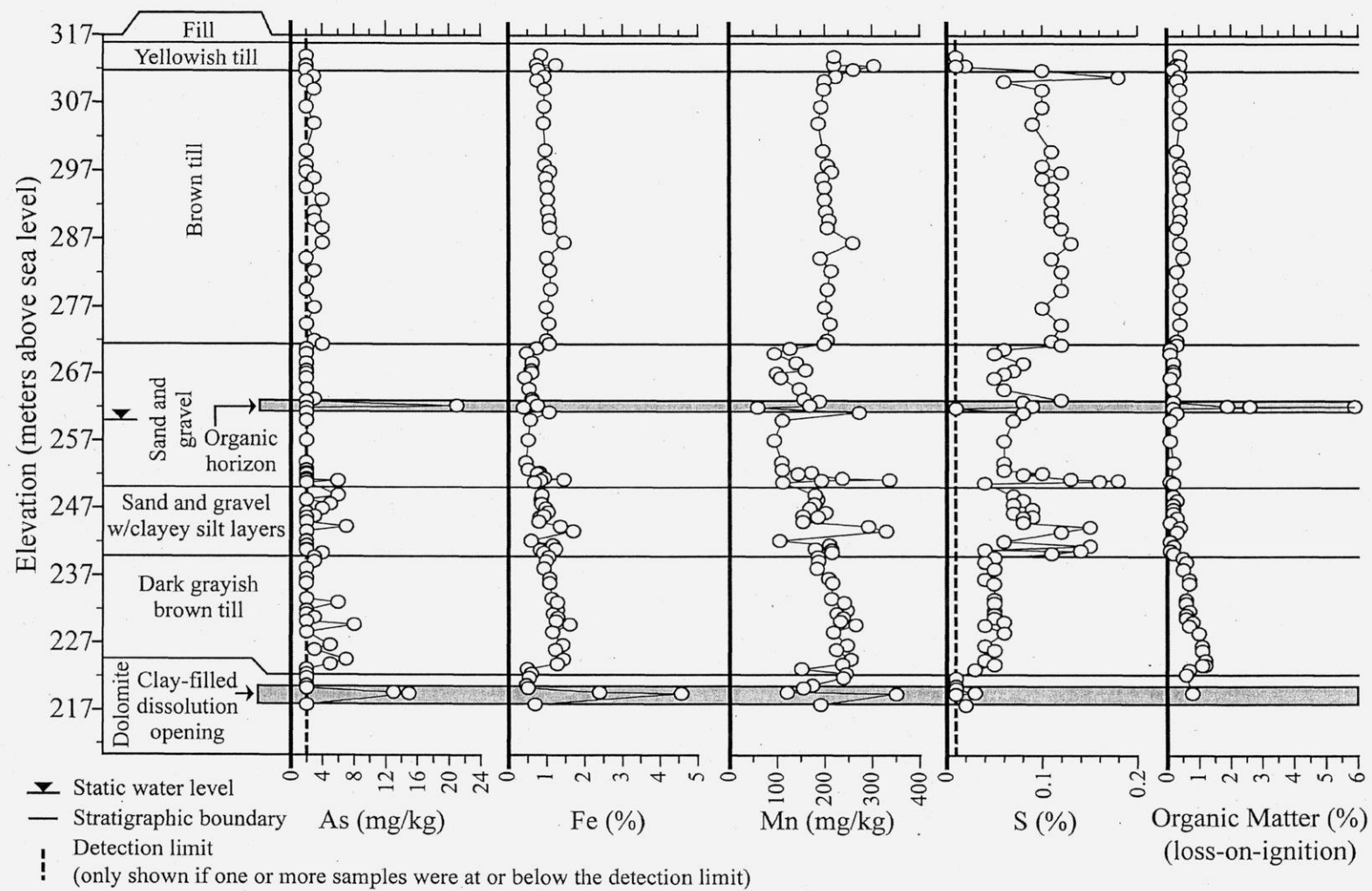
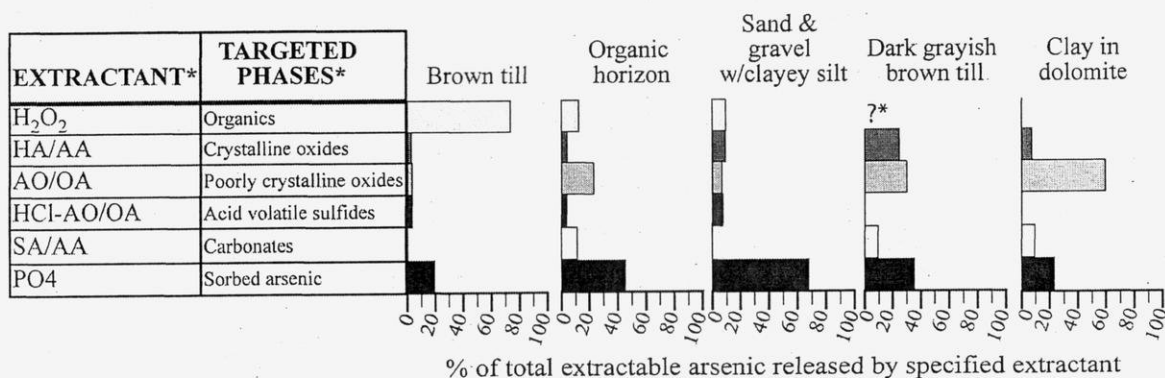


Figure 3. – Lithology and chemical composition of core samples.



**Data not available for this sample. Results are presented as % of arsenic released by the extractants for which data are available.

Figure 4. - Summary of results of selective sequential extractions.

Hydrogeology: Review of the stratigraphy in the Woods School core and existing geologic logs from the Lake Geneva region revealed that there are two water-bearing sand and gravel horizons in the Quaternary deposits in the study area (Figure 5). These two aquifers are separated by a clayey till that acts as a confining unit. The lower Quaternary aquifer is discontinuous; it was not encountered in the Woods School borehole but is evident in some geologic logs. The lower Quaternary aquifer lies directly above the Silurian dolomite.

During the pumping test, 5.2 m of drawdown occurred in a deep Quaternary well (i.e. well 2 in Figure 5) in response to pumping in a shallow Silurian well (i.e. well 3 in Figure 5). No measurable drawdown occurred in a monitoring well open to the shallow Quaternary aquifer (i.e. well 1 in Figure 5). This lack of response in water level in the shallow Quaternary well indicates that there is little hydraulic connection between the shallow Quaternary aquifer and the deeper Quaternary and shallow Silurian aquifers.

Controls on Arsenic Mobility: Comparison of groundwater arsenic concentrations with well construction records revealed a correlation between arsenic and well completion depth. All low-arsenic ($[As]_{aq} < 4 \mu\text{g/l}$) wells are completed in the shallow sand and gravel above the dark grayish brown till (well 1 in Figure 5 and Figure 6). The moderate ($4 \mu\text{g/l} \leq [As]_{aq} < 20 \mu\text{g/l}$) and high-arsenic ($[As]_{aq} \geq 20 \mu\text{g/l}$) wells are all open beneath the dark grayish brown till in the deep Quaternary and shallow Silurian aquifers (wells 2 and 4 in Figure 5 and Figure 6). Low-arsenic groundwater samples tend to have higher sulfate than moderate and high-arsenic samples (Figure 6b). The Eh of the groundwater samples is variable (Figure 6c), but in general, moderate and high-arsenic samples tend to be more reducing than low-arsenic samples.

If arsenic were being mobilized via oxidative dissolution of sulfide minerals, one would expect to see a positive correlation between arsenic and sulfate in the groundwater. The negative correlation between arsenic and sulfate in groundwater samples from the study area (Figure 6b) indicates that sulfide oxidation is not occurring in these aquifers and that arsenic is being mobilized by some other mechanism. Arsenic concentrations are higher in more strongly reducing waters (Figure 6c) supporting the hypothesis that arsenic is mobilized via reductive dissolution of (hydr)oxides. Reduction of (hydr)oxides is often coupled to microbial oxidation of organic matter (Nickson et al., 2000). Thus, the positive correlation between arsenic and organic matter in the core (Figure 3) further supports the reductive dissolution hypothesis.

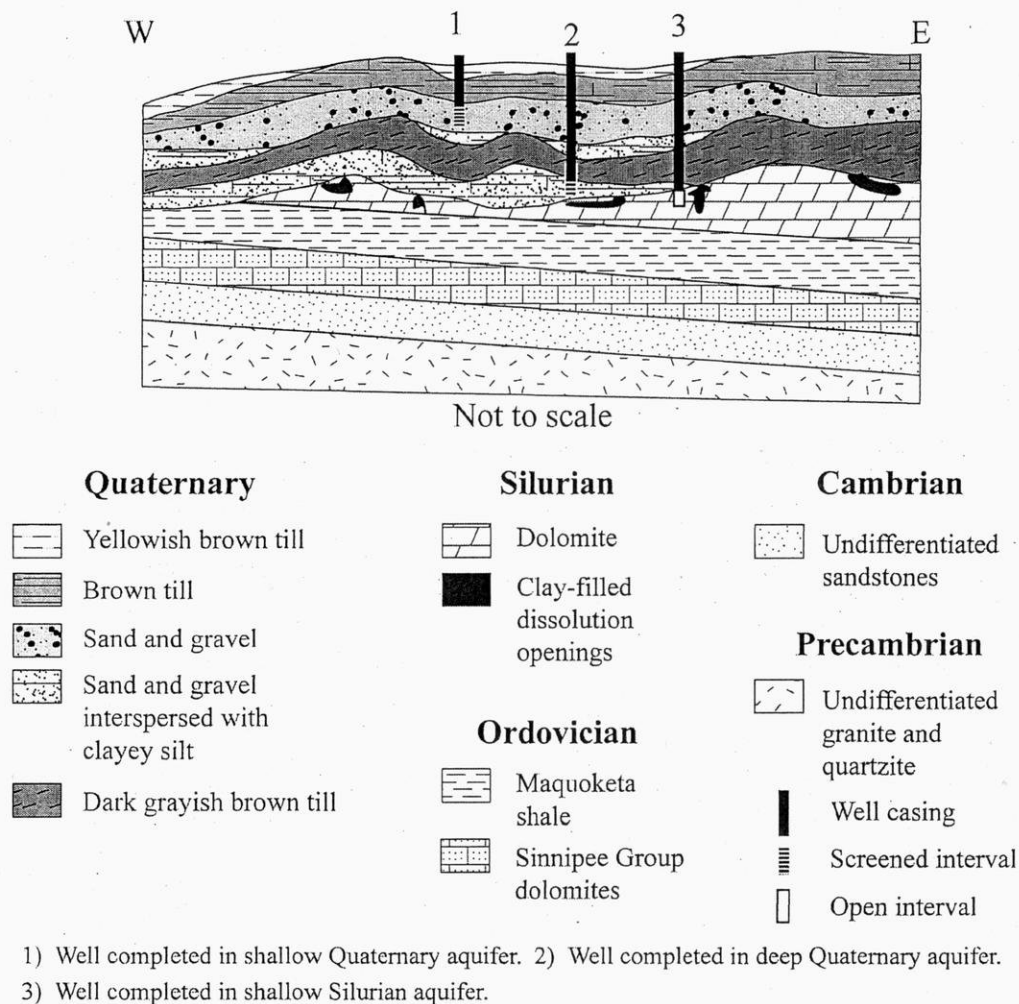


Figure 5. - Generalized cross-section showing stratigraphy and typical well construction in the study area.

During the pumping test, arsenic concentrations in the pumped well (i.e. well 3 in Figure 5) fluctuated early in the test (48 $\mu\text{g/l}$ to 60 $\mu\text{g/l}$), but overall there was little change in water chemistry with time. This indicates that groundwater arsenic concentrations are being controlled by processes occurring in the aquifer rather than processes local to the well bore.

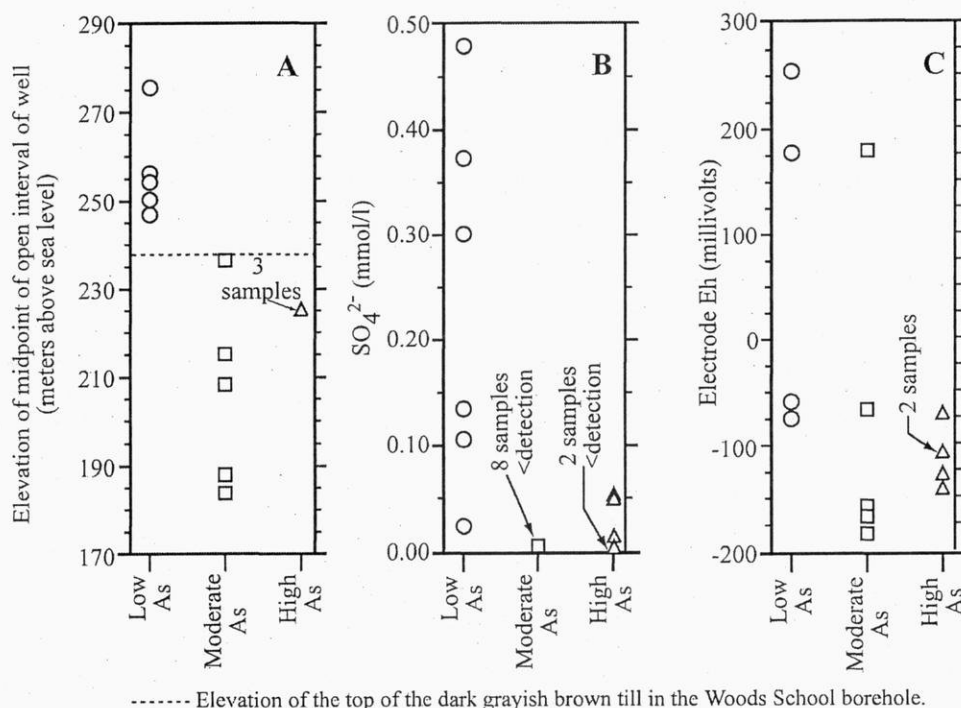


Figure 6. - Chemical and physical characteristics of low-As ($<4 \mu\text{g/l}$), moderate-As ($4 \mu\text{g/l}$ to $20 \mu\text{g/l}$), and high-As ($>20 \mu\text{g/l}$) samples. (For samples with As $<7 \mu\text{g/l}$, detection limit = $0.3 \mu\text{g/l}$.)

CONCLUSIONS AND RECOMMENDATIONS

Low to moderate (2 mg/kg to 20 mg/kg) solid-phase arsenic concentrations are found throughout the entire thickness of the Quaternary and upper Silurian units near Lake Geneva. From a mass balance perspective, these solid-phase concentrations are sufficient to sustain groundwater arsenic concentrations greater than the $10 \mu\text{g/l}$ standard under geochemical conditions that release arsenic to groundwater. While moderate ($4 \mu\text{g/l} \leq [\text{As}]_{\text{aq}} < 20 \mu\text{g/l}$) to high ($[\text{As}]_{\text{aq}} \geq 20 \mu\text{g/l}$) arsenic concentrations are found in groundwater from the deep Quaternary and shallow Silurian aquifers, groundwater in shallow Quaternary sediments is largely unaffected by arsenic. The results of this study indicate that geologic, hydrogeologic, and geochemical factors create reducing conditions that lead to arsenic mobilization via reductive dissolution of (hydr)oxide minerals in the deep Quaternary and shallow Silurian aquifers.

Given our present understanding of the problem, the only viable mitigation measure for existing arsenic-impacted wells is treatment to remove arsenic from the water. In the study area, new wells should not be completed in the deep Quaternary or shallow Silurian aquifers.

The geochemical conditions that cause groundwater arsenic contamination in the Lake Geneva area are different from those responsible for the high groundwater arsenic concentrations in the Fox River Valley. This indicates that a single model is not adequate to account for the occurrence of arsenic contamination at a regional scale. The results of our detailed field and laboratory studies pertain to the Lake Geneva area. However, these results demonstrate that sediments in the Quaternary aquifer may contain sufficient solid-phase arsenic to impact the quality of groundwater in the aquifer under certain geochemical conditions, and because arsenic can be mobile under a variety of geochemical conditions, it is very difficult to predict whether a well will be impacted by arsenic. Therefore, drillers and well owners should be encouraged to test their wells for arsenic.

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APPENDIX A: AWARDS AND PUBLICATIONS

Related Publications:

Root, T.L., expected spring 2005. Arsenic In Groundwater In Southeastern Wisconsin: Sources Of Arsenic And Mechanisms Of Arsenic Mobilization. Ph.D. thesis, University of Wisconsin –Madison, Department of Geology and Geophysics.

Root, T.L., Bahr, J.M., and Gotkowitz, M.B., 2005. Controls On Arsenic In Groundwater In Southeastern Wisconsin, *in* Vlassopoulos, D., Benning, L., Meng, X., and O'Day, P., Advances In Arsenic Research, American Chemical Society Symposium Series. (*In Press.*)

Conference Abstracts:

Root, T.L., Bahr, J.M., and Gotkowitz, M.B., 2003. Arsenic In Ground Water In Southeastern Wisconsin: Sources Of Arsenic And Mechanisms Of Arsenic Mobilization, *in* AWRA-Wisconsin Section 27th Annual Meeting Program And Abstracts.

Root, T.L., Bahr, J.M., and Gotkowitz, M.B., 2002. Arsenic Contamination In Southeast Wisconsin: Sources Of Arsenic And Mechanisms Of Arsenic Mobilization, *in* GSA Abstracts With Programs, Vol. 34, No. 6.

Root, T.L., Bahr, J.M., and Gotkowitz, M.B., 2002. Arsenic Contamination In Southeast Wisconsin: Identifying Sources Of Arsenic And Mechanisms Controlling Arsenic Release, *in* NGWA Midwest FOCUS Ground Water Conference Abstract Book.

Root, T.L., Bahr, J.M., and Gotkowitz, M.B., 2002. Arsenic Contamination In Southeast Wisconsin: Sources Of Arsenic And Mechanisms Of Arsenic Mobilization, *in* AWRA-Wisconsin Section 26th Annual Meeting Program And Abstracts.

Awards: Tara Root received a student research award from the Hydrogeology Division of the Geological Society of America for work on this project (2002).

APPENDIX B: SUMMARY OF EXTRACTION PROCEDURE

Extraction Step	Extractant	Targeted Phases	References
1	PO ₄ (mixture of 0.5M NaH ₂ PO ₄ & 0.5M Na ₂ HPO ₄)	Sorbed arsenic	(Keon et al. (2001); Jackson and Miller (2000))
2	SA/AA (1M sodium acetate adjusted to pH of 5 using acetic acid)	Carbonate minerals	(LaForce et al. (2002); Tessier et al. (1979))
3	HCl (1N HCl)	Acid volatile sulfides and very poorly crystalline oxides	(LaForce et al. (2002); Keon et al. (2001))
3a	HCl-AO/OA (Results of step 4 subtracted from step 3)	Acid volatile sulfides	
4	AO/OA (mixture of 0.175M ammonium oxalate & 0.1M oxalic acid)	Poorly crystalline oxides	(LaForce et al. (2002); Keon et al. (2001); Fey and LeRoux (1997))
5	HA/AA (1M hydroxylamine hydrochloride in 25% acetic acid)	Crystalline oxides	(LaForce et al. (2002); Chao and Zhu (1983); Tessier (1979))
6	H ₂ O ₂ (30% H ₂ O ₂ adjusted to pH of 2 using HNO ₃)	Organic matter	(Yong et al. (2001); Shuman (1983); Tessier (1979); Gupta and Chen (1975))

APPENDIX C: MASS BALANCE CALCULATIONS

Definitions

n = porosity

V_s = volume of solids

V_t = total volume

ρ_s = density of solid

$[As]_s$ = solid-phase arsenic concentration

$[As]_{aq}$ = aqueous arsenic concentration

Assumptions

$\rho_s = 2600 \text{ kg/m}^3$

$[As]_s = 5 \text{ mg/kg}$

$[As]_{aq} = 10 \mu\text{g/l}$

1. What is the total solid-phase mass of arsenic in a 1 m^3 volume of aquifer?

$$V_s \times \rho_s \times [As]_s$$

2. What volume of water is in a 1 m^3 volume of aquifer?

$$n \times V_t$$

3. What is the total aqueous-phase mass of arsenic in a 1 m^3 volume of aquifer?

$$\text{volume of water} \times [As]_{aq}$$

4. How long can an arsenic concentration of $10 \mu\text{g/l}$ be sustained?

mass of arsenic in sediment / mass of arsenic in water = pore volumes that can be impacted by arsenic in sediment

pore volumes \times residence time = length of time arsenic concentrations of 10 mg/l can be sustained.

Results of mass balance calculations for various porosities and residence times are shown in the table on the following page.

Results of Mass Balance Calculations

n	residence time (years)	years arsenic concentration of 10 µg/l can be sustained
0.10	25	292500
0.20	25	130000
0.30	25	75833
0.10	50	585000
0.20	50	260000
0.30	50	151667
0.10	100	1170000
0.20	100	520000
0.30	100	303333