

## ARSENIC CONCENTRATIONS AND IRON OXYHYDROXIDE FORMATION IN NEW HAMPSHIRE GROUNDWATER

Peters S.C. and J.D. Blum, Department of Geological Sciences, University of Michigan, Ann Arbor, MI. (scpeters@umich.edu)

### **Abstract**

We investigated the sources and chemical transport mechanisms that influence the concentration of arsenic in a naturally contaminated aquifer. Groundwater arsenic concentrations ranged from 0.02  $\mu\text{g/L}$  to 398  $\mu\text{g/L}$ , with a mean value ten times higher than the mean for all of New Hampshire (NH). Arsenopyrite and scorodite were found in aquifer materials, and were the most likely sources of dissolved arsenic. An interesting relationship was observed between pH and dissolved arsenic and iron concentrations. All waters with highly elevated arsenic values ( $>50 \mu\text{g/L}$ ) have very low iron ( $<1 \text{ mg/L}$ ) and high pH ( $>6.5$ ); samples with very low arsenic ( $<25 \mu\text{g/L}$ ) have high iron ( $>1 \text{ mg/L}$ ) and low pH ( $<6.5$ ). pH-dependant iron oxyhydroxide formation may explain our observations, with slow iron oxide formation at pH 5 co-precipitating arsenic from solution, with much faster oxide formation at pH 8 removing iron but not arsenic from solution.

### **Methods**

Samples of groundwater were obtained from 127 domestic bedrock wells within the town of Bow, NH (figure 1). Oxidation-reduction parameters were measured on-site using a flow-through cell. Water was supplied from an unfiltered and untreated outside faucet through a clean polyethylene tube. Before entering the cell, approximately 90% of the water flow was diverted through a T-fitting and discarded. The remaining 10% of the water flow entered the bottom of a 12" long piece of 4" diameter PVC pipe, and out an overflow tube at the top. Temperature, pH, dissolved oxygen, and Eh probes were inserted through a machined acrylic cap that excluded air contact with the water during measurement. Readings were taken at 3 minute intervals until replicate measurements were within 5%. After these measurements were recorded, the flow-through cell was disconnected, and water samples were collected directly from the tap. Samples were syringe filtered to  $< 0.45 \mu\text{m}$  into acid cleaned polyethylene bottles and acidified to pH 2 with ultrapure  $\text{HNO}_3$ .

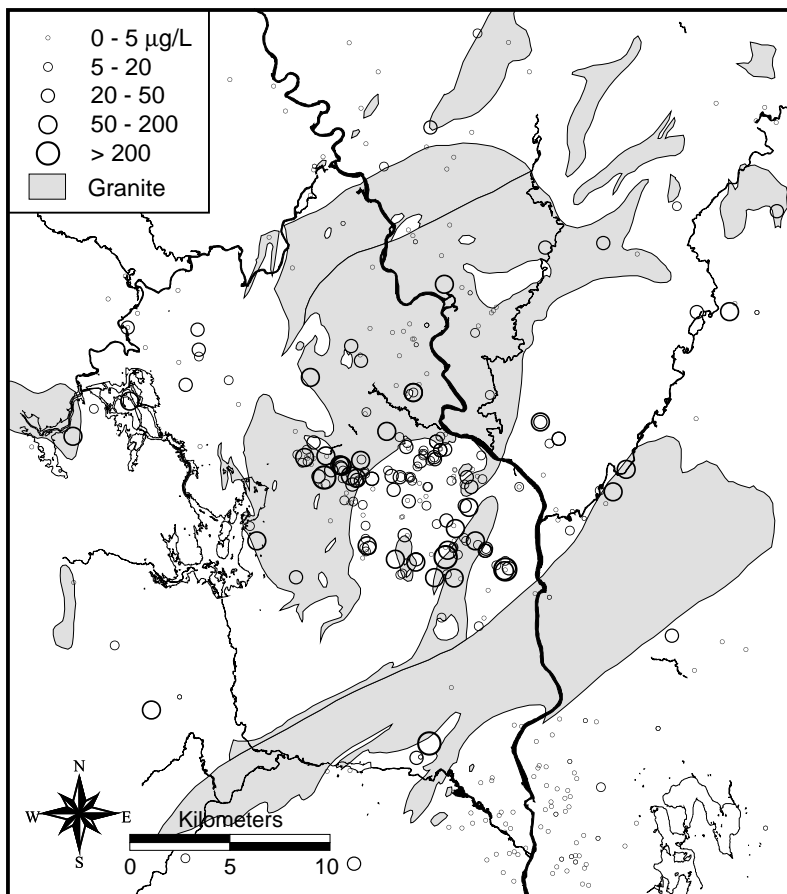
Samples were analyzed for major cations using ICP-OES with pneumatic nebulization and simultaneous CCD detection. Fresh standards were prepared daily, and the calibration was checked against an internal laboratory standard and NIST-1643d. Anions were determined using anion chromatography with suppressed conductivity detection. Arsenic was determined using continuous-flow online hydride generation with magnetic sector ICP-MS detection. The detection limit for arsenic was 0.0003  $\mu\text{g/L}$  [1].

### **Results**

To analyze the distribution of arsenic concentrations in water, a cumulative probability distribution function was plotted (figure 2). Curves from a previous survey of arsenic concentrations in randomly selected well water samples statewide in NH are plotted for comparison[2]. For a given concentration, the percentage of households above and below that value can be easily read off the graph. The shape of the curve shows the distribution of concentrations, with steeper slopes indicating a narrower spread of concentrations, while an offset in the x-direction indicates a difference in the median concentration. The concentration of arsenic in water samples from the region near Bow ranges from 0.02  $\mu\text{g/L}$  to 398  $\mu\text{g/L}$  with a median value of 15  $\mu\text{g/L}$ . In the statewide survey, bedrock wells had arsenic concentrations ranging from 0.001  $\mu\text{g/L}$  to 112  $\mu\text{g/L}$ , with a median value of 0.49  $\mu\text{g/L}$ .

The spatial distribution of arsenic concentrations is plotted in figure 1. The highest groundwater arsenic concentrations plot along the borders of Concord age granites (gray) and surrounding metasedimentary rocks. The lowest concentrations occur to the southeast and north, and at a greater distance from the granites. Major rivers (black) are plotted for reference.

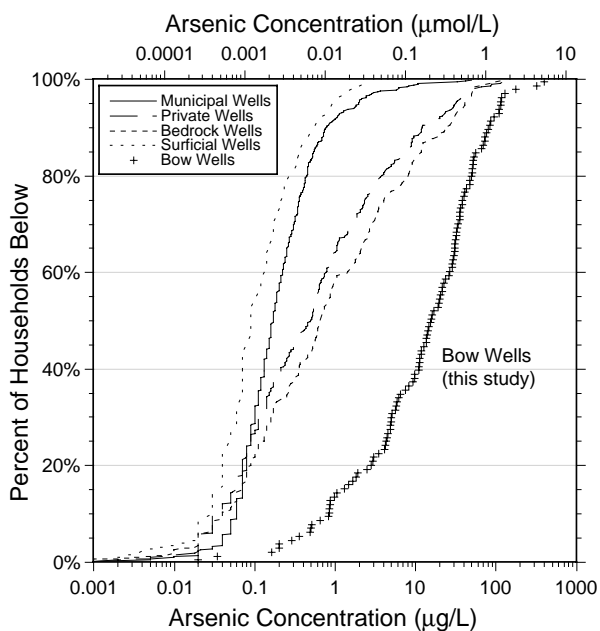
Graphs of iron, arsenic, sulfate, and pH were plotted to help elucidate the geochemical processes resulting in arsenic release and retardation (figures 3 - 7). Iron concentrations range from 0.01  $\mu\text{mol/L}$  up to 112  $\mu\text{mol/L}$ . All waters with high arsenic concentrations ( $>0.5 \mu\text{mol/L}$ ) have very low iron concentrations ( $<15 \mu\text{mol/L}$ ) and high



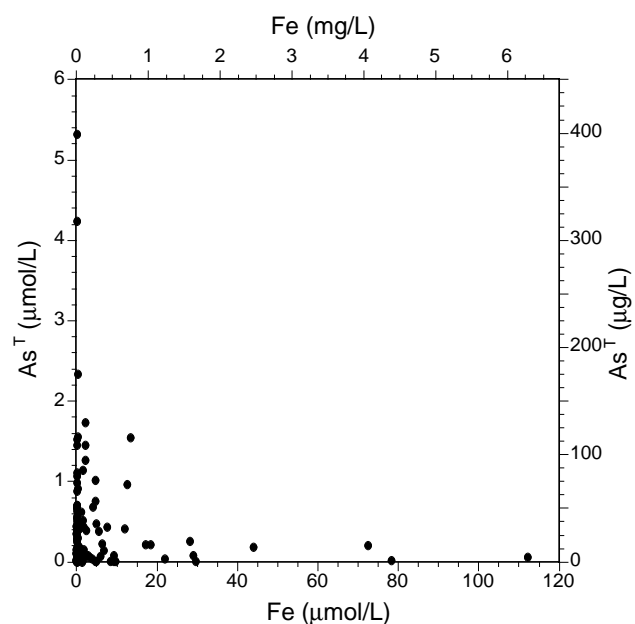
**Figure 1.** Map of the geographic distribution of arsenic concentrations in groundwater. Granites are shaded gray and are the likely source of arsenic rich pegmatites.

pH (>6.5). Conversely, samples with low arsenic (<0.5 µmol/L) have high iron concentrations (>20 µmol/L) and low pH (<6.5). Sulfate concentrations range from 10 µmol/L to 503 µmol/L and are in excess of iron concentrations in all samples (figure 4).

Arsenic concentrations plot well below laboratory measured scorodite saturation, though the two curves have a similar slope (figure 5) [3]. The maximum arsenic concentration at any pH value increases as a function of pH, with the highest concentrations of arsenic occurring in samples with high pH and high dissolved oxygen (figure 6). Iron concentrations vary as a function of pH and dissolved oxygen. Samples at low pH (<6.5) and low DO have high iron concentrations, while at the same pH, samples with high DO have low iron concentrations (figure 7). At higher pH values (>6.5), iron concentrations are low at any value of DO.



**Figure 2.** Cumulative probability distribution of arsenic concentration in New Hampshire groundwater.



**Figure 3.** Plot of arsenic vs. iron concentration in groundwater samples.

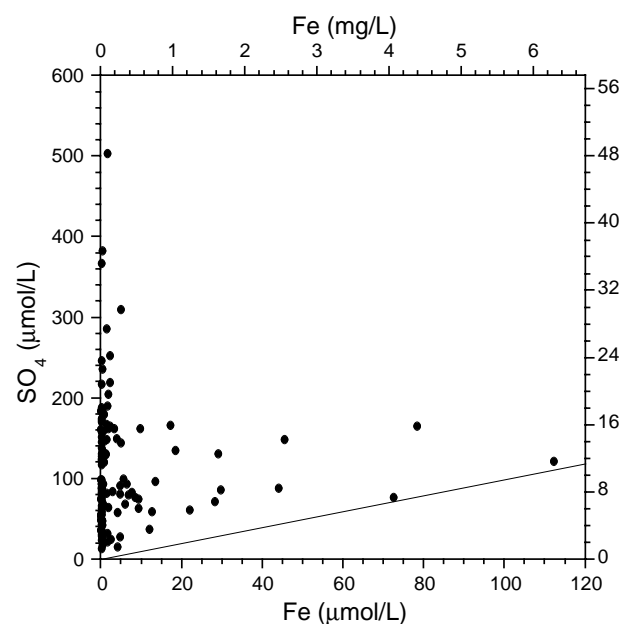
## Discussion

Comparison of the arsenic concentrations in bedrock and surficial well types illustrates that bedrock wells are much more likely to contain high concentrations of arsenic (figure 1). For example, only <1% of the surficial wells contains arsenic in excess of 5  $\mu\text{g/L}$ , compared to 30% of bedrock wells. If anthropogenic contamination were the primary source for observed arsenic concentrations, the highest concentrations would be expected in surficial wells. This observation argues strongly against a primarily anthropogenic source for arsenic contamination in New Hampshire, and instead points to the probability of a natural bedrock source.

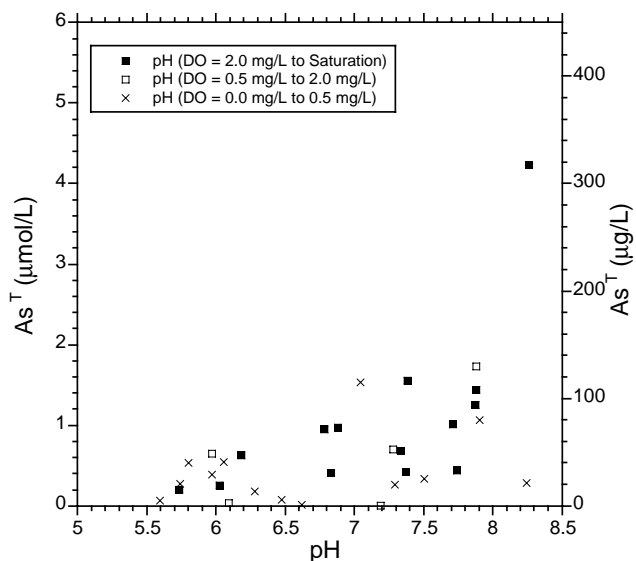
Bedrock wells drilled within the town of Bow have median arsenic concentrations approximately 10 times the comparable value of bedrock wells statewide. This suggests a significant source of arsenic in the local bedrock. Samples of the bedrock aquifer materials have been shown to contain the weatherable arsenic minerals arsenopyrite and scorodite [2]. These minerals occur in pegmatites that border and radiate outwards from granitic plutons into surrounding rocks (figure 2). Several samples of elevated arsenic concentration do not plot near any known pluton boundary. Because this map is based on only ~1-5% outcrop exposure, it is likely that a number of smaller plutons and pegmatites were either missed due to soil and till cover, or lie at shallow depths beneath the land surface.

Congruent arsenopyrite and/or scorodite dissolution followed by conservative transport would typically show a positive correlation between iron and arsenic concentrations in groundwater. Similarly, pyrite dissolution should result in a positive correlation between iron and sulfate. Since this is not what is observed in water samples (figures 3,4), significant adsorption/precipitation of iron oxides is probably taking place after initial mineral dissolution. Samples with high concentrations of iron and no arsenic can result from dissolution of non-arseniferous pyrite. However, explanation of why high arsenic samples always have low iron requires an additional mechanism.

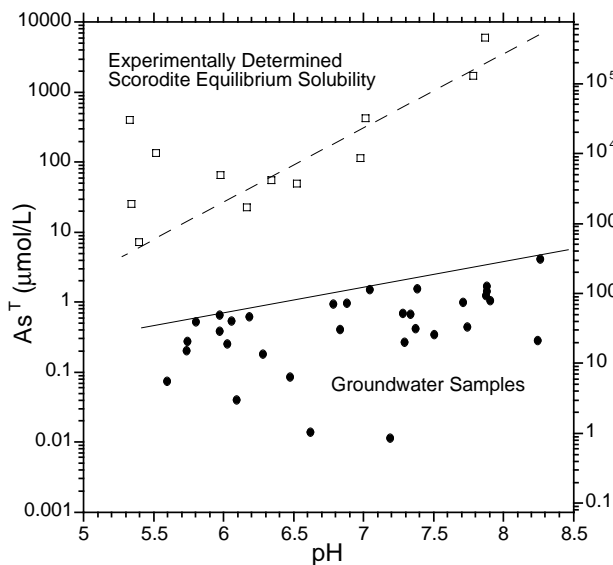
All of the groundwater samples plot below the scorodite solubility curve (figure 5), suggesting that saturation with this mineral phase is not reached [3]. However, given the similarity between the slopes of the maximum groundwater concentration and the scorodite solubility curve leaves open the possibility that the laboratory measurement conditions did not match the natural conditions found in this aquifer and that scorodite may, in some way, control the maximum arsenic concentration in this system.



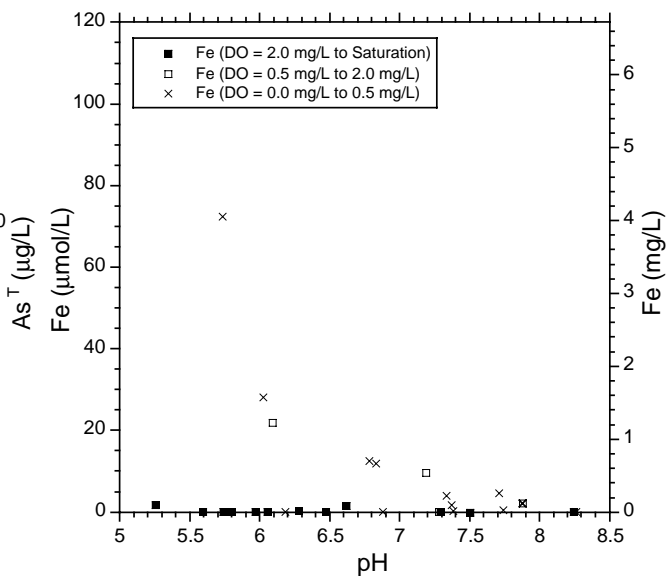
**Figure 4.** Plot of iron vs. sulfate concentration in groundwater samples. Line represents 1:1 relationship.



**Figure 5.** Plot of total arsenic concentration vs. pH at different dissolved oxygen concentrations in groundwater samples.



**Figure 6.** Plot of total arsenic concentration vs. pH in groundwater samples. Experimentally determined scorodite solubility is represented by the open symbols [3].



**Figure 7.** Plot of iron concentration vs. pH at different dissolved oxygen concentrations.

The samples with highest concentrations of arsenic have little or no iron, and are at significantly higher pH values than the remainder of the samples (figure 6). At higher pH, iron oxyhydroxide formation is kinetically faster by a factor of  $10^5$  to  $10^8$  over the rate found at the lower pH values observed in this groundwater system [4]. In the highest concentration arsenic samples, there is excess dissolved oxygen to oxidize and precipitate iron oxyhydroxides (figure 7). We hypothesize that the rapid formation of these iron oxyhydroxides at high pH proceeds without adsorption of arsenic to the newly forming surface. The resulting solution then becomes depleted in iron, while retaining the original high arsenic concentration. Conversely, at low pH, iron precipitation is slower, allowing for the adsorption and coprecipitation of arsenic. The kinetics of iron oxyhydroxide formation and arsenic coprecipitation are the most likely controlling factors in this aquifer system.

### **Conclusion**

Groundwaters in a crystalline bedrock aquifer in central New Hampshire have been contaminated through the weathering of arsenopyrite and scorodite in the aquifer materials. While the transport mechanisms are still not clearly understood, we hypothesize that pH dependent iron oxyhydroxide precipitation kinetics exert primary control over the dissolved arsenic concentration.

### **References**

1. Klaue, B. and Blum, J.D., (1999), *Analytical Chemistry*, 71(7): p. 1408-1414.
2. Peters, S.C., Blum, J.D., Klaue, B., and Karagas, M.R., (1999), *Environmental Science and Technology*, 33(9): p. 1328-1333.
3. Krause, E. and Ettl, V.A., (1988), *American Mineralogist*, 73: p. 850-854.
4. Stumm, W. and Morgan, J.J., *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*. 3rd ed. Environmental Science and Technology, New York: Wiley-Interscience. 1022pps.