

Microcosm Study of Arsenic Fate in Mahomet Aquifer Sediment and Groundwater

*Robert Sanford, Theodore Flynn, Department of Geology, UIUC
and Walton Kelly, Illinois State Water Survey*

A recent study of the Mahomet Aquifer in central Illinois has suggested a fundamental relationship between in-situ redox conditions and the presence of soluble arsenic. One benefit of this relationship is that it suggests that if redox conditions are manipulated near wells, it would be possible to lower the arsenic concentration in the groundwater in situ. For example, the addition of low levels of sulfate (SO_4^{2-}) and organic carbon may be sufficient to stimulate enough sulfate reduction to sequester the low levels of arsenic present. This may be an economic approach for small drinking water systems to lower concentrations to below arsenic's maximum contaminant level (MCL) of 10 $\mu\text{g/L}$.

This was a laboratory study designed to measure the effects of the addition of SO_4^{2-} , nitrate (NO_3^-), hydrogen (H_2), and acetate on Mahomet Aquifer groundwater chemistry. Hypotheses tested included: (1) nitrate addition would stimulate ferrous iron (Fe(II)) oxidation and lead to the sorptive removal of arsenic from solution; (2) sulfate addition with an appropriate electron donor (H_2) would stimulate SO_4^{2-} -reducing bacteria leading to the formation of sulfide which would promote the lowering of the arsenic concentration by precipitation of sulfide phases; and (3) the absence of sufficient electron donor (reductant) or acceptor (oxidant) would lead to conditions that favor elevated Fe(II) and arsenic concentrations.

Fine grained quartz sand for the laboratory experiments was collected from the Mahomet Aquifer during the drilling of a private well in McLean County. Between 20-40 g of sand and 80 mL of Mahomet Aquifer groundwater were placed in 160 mL serum bottles, which were then sealed with a butyl stopper. Reagents were added to the bottles via syringe and the headspace was purged to remove oxygen and keep the bottles anaerobic. Bottles were incubated at ~18-22°C for approximately four months.

Nitrate reduction occurred in less than one month for most treatments, which is not surprising, since NO_3^- is a very favorable electron acceptor. Sulfate reduction also occurred, and was much quicker with H_2 present in the headspace than with acetate alone. This was expected because acetate oxidation coupled to SO_4^{2-} reduction is mediated by a small subset of all SO_4^{2-} -reducing bacteria and yields less energy than H_2 as an electron donor. In the absence of electron donors, SO_4^{2-} reduction was not observed, as expected.

Ferrous iron varied considerably depending on both the electron donor and the electron acceptor amendments. In the absence of H_2 , the Fe(II) concentrations were fairly consistent for all treatments with the exception of the NO_3^- -only amended microcosms. The data suggest that the Fe(II) was oxidized by NO_3^- and nitrite (NO_2^-) reducing bacteria to ferric oxide. These microcosms had a reddish hue, supportive of the presence of ferric oxides. At four months, Fe(II) was not detected in the NO_3^- -amended samples. In samples that received NO_3^- and an electron donor, either acetate or acetate plus H_2 , the Fe(II) concentrations remained high. Sulfate-fed samples had suppressed Fe(II) concentrations when H_2 was present, although the lowest concentrations were clearly obtained when both acetate and H_2 were present. This would be expected since sulfide generated during SO_4^{2-} reduction would readily react with the Fe(II) in solution and precipitate out as FeS. Arsenic would also be expected to precipitate out with the

generated iron sulfide. Acetate alone did not stimulate sufficient sulfide generation to drop the Fe(II) concentration.

Arsenic concentrations ranged from about 1-10 $\mu\text{g/l}$ depending on the treatment applied. The original groundwater used in the microcosm experiments contained 34 $\mu\text{g/L}$. Results indicate that arsenic concentrations dropped under two different redox conditions as predicted. When an oxidizing environment was present (adding NO_3^-), all the Fe(II) was oxidized and the arsenic concentration dropped to the lowest level observed. Sulfate reducing conditions in the presence of H_2 provided the next best conditions for lowering the As concentration.

There was an interesting relationship between Fe(II) and arsenic. They were positively correlated for all the microcosms that received an amendment (minus controls); i.e., when the Fe(II) concentration was lowest the arsenic concentration was most suppressed. This is not surprising geochemically speaking, and suggests a simple metric for evaluating groundwater for the potential to have high arsenic concentrations whether the water is oxic or anoxic. Ferrous iron is depressed in oxidized waters due to the formation of insoluble ferric oxides which serve as a sorption site for soluble arsenic species. Ferrous iron is depressed under anaerobic SO_4^{2-} reducing conditions due to the formation of insoluble iron sulfide, which also can precipitate out arsenic. However, this relationship between dissolved Fe(II) and arsenic is not typically observed in groundwater samples, including those collected from the Mahomet aquifer, suggesting other mechanisms are affecting Fe(II) and/or arsenic concentrations in situ.

To evaluate whether the mechanism of arsenic loss was as predicted, specific microcosms were selected for secondary amendments. The NO_3^- -only microcosm with the lowest arsenic concentration was amended with H_2 and acetate, which we predicted would stimulate ferric-iron reduction and lead to the release of sorbed arsenic. A second amendment of H_2 was added to the SO_4^{2-} -only microcosm, which showed no loss of arsenic relative to the control, to stimulate SO_4^{2-} reduction, potentially leading to the generation of sulfide and the precipitation of Fe and arsenic. These second amendments were incubated for two weeks. As predicted, the NO_3^- -only and SO_4^{2-} -only microcosms showed increased and decreased arsenic concentrations, respectively. The arsenic concentration increased to levels observed in the original groundwater in the amended NO_3^- -only microcosm, indicating that the release of sorbed arsenic under iron-reducing conditions can be rapid.

Arsenic concentrations in the microcosms behaved for the most part as predicted. Under both oxidizing (NO_3^-) and SO_4^{2-} -reducing conditions, arsenic levels dropped. Somewhat unexpected was the decrease in arsenic concentrations when any electron donor was added. It remains to be established if this was associated with sorption to biomass as suggested. The fact that arsenic concentrations increased rapidly from oxidized sediments when ferric-iron reducing conditions were stimulated, suggests that it may be best to maintain either oxidizing or reducing conditions in an aquifer. Any oscillation between oxidizing and reducing conditions may lead to oscillation in arsenic concentrations. Finally, although the observed relationship between Fe(II) and arsenic suggests that it may be possible to use Fe(II) as a predictor for possible arsenic hot spots in aquifers known to retain arsenic, this relationship not always observed in aquifers, including the Mahomet Aquifer.