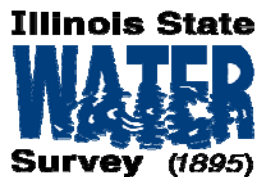SMALL PUBLIC WATER SYSTEMS

Microcosm Study of Arsenic Fate in Mahomet Aquifer Sediment and Groundwater

Robert Sanford
Theodore Flynn
Department of Geology
UIUC

Walton Kelly
Illinois State Water Survey
2204 Griffith Drive
Champaign, Illinois 61820-7495

Disclaimer

This material is based upon work supported by the Midwest Technology Assistance Center for Small Public Water Systems (MTAC). MTAC was established October 1, 1998 to provide assistance to small public water systems throughout the Midwest via funding from the United States Environmental Protection Agency (USEPA) under section 1420(f) of the 1996 amendments to the Safe Drinking Water Act. MTAC is funded by the USEPA under Grant No. X829218-01. Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect the views of the USEPA or MTAC.

Microcosm Study of Arsenic Fate in Mahomet Aquifer Sediment and Groundwater

Robert Sanford
Theodore Flynn
Department of Geology
UIUC

Walton Kelly
Illinois State Water Survey

FINAL Report
March 29, 2006

Introduction

Arsenic (As) occurs naturally in many aquifer systems (WELCH et al., 2000) and when present in drinking water is associated with many health effects (JAIN and ALI, 2000). The USEPA recently lowered the As maximum contaminant level (MCL) from 50 $\mu g\ L^{-1}$ to 10 $\mu g\ L^{-1}$ (0.13 μM). Public water supplies that fail to meet the As MCL by early 2006 must develop a plan for compliance. The Illinois Environmental Protection Agency (IEPA) has sent As rule change letters to 36 communities. Installing new treatment systems or drilling new wells may impose an economic hardship on small water systems (FREY et al., 1998). Although private wells are unregulated, As is of concern to many private well owners because of health concerns.

The concentration and speciation of As in groundwater are controlled by redox conditions and microbial processes. Under oxic conditions the predominant dissolved As species is As(V) and dissolved As concentrations are kept at low levels by adsorption to hydrous ferric oxide (HFO). Under anoxic conditions the predominant As species is As(III). In some aquifer systems As is associated with pyrite and is released by oxidation when the water table is lowered and the pyrite is exposed to oxygen. In some other aquifer systems As is adsorbed to HFO which coats the sand grains. In these systems As is released by reductive dissolution of the HFO coatings (MCARTHUR et al., 2004). Examples of such systems include the Mahomet and Glasford aquifers in central Illinois (KELLY et al., 2005).

The Mahomet-Sankoty Aquifer, an extensive system of buried bedrock valleys in central Illinois, is a major source of potable water (http://www.sws.uiuc.edu/gws/ mahomet.asp). Some wells in the western and central parts of the aquifer have As in excess of the new MCL (KELLY et al., 2005; WARNER, 2001). (Some wells in these areas exceed the former MCL of 50 $\mu g\ L^{-1}$.) Of the 37 communities that have received Arsenic Rule notifications from IEPA, 27 withdraw water from the Mahomet-Sankoty system.

The spatial distribution of As in the Mahomet Aquifer is complex. Wells with high As can be located within 1 km of wells with undetectable As (HOLM, 1995; HOLM et al., 2004). The Mahomet Aquifer is mostly confined and isolated from the surface by thick layers of glacial drift (KEMPTON et al., 1991). As a result, redox conditions are generally anoxic with undetectable O_2 and nitrate (NO_3^-) and high dissolved ferrous iron (Fe(II)). There is evidence of methanogenesis and sulfate (SO_4^{2-}) reduction in some areas, and bacteria in high-As and low-As wells have distinct DNA signatures (KIRK et al.,

2004). Reductive dissolution of HFO appears to be the main process that releases As to solution. High As concentrations are associated with high TOC values, while low As concentrations in nearby wells are associated with low TOC. Undetectable As concentrations are also associated with detectable SO_4^{2-}. The likely explanation is that SO_4^{2-} reduction produces FeS which strongly sorbs As(III). Therefore, the complex spatial distribution of As may be related to the distribution of organic matter and SO_4^{2-} (HOLM, 2005; KIRK et al., 2004).

The data suggest a fundamental relationship between in-situ redox conditions and the presence of soluble As. One benefit of this relationship is that it suggests that if redox condtions are manipulated near wells, it would be possible to lower the As concentration in the water being pumped out. For example the addition of low levels of sulfate and organic carbon would be sufficient to stimulate enough sulfate reduction to sequester the low levels of As present in the groundwater. This may be a very economic approach to lowering concentrations to below the MCL for As for small drinking water systems.

Experimental Approach and Methods

The purpose of this study was to measure the effects of the addition of SO_4^{2-}, NO_3^-, hydrogen (H_2), and acetate on Mahomet Aquifer groundwater chemistry. The goal was to characterize how these processes affect As solubility in the Mahomet Aquifer. We hypothesized:

1. Nitrate addition will stimulate Fe(II) oxidation and lead to the sorptive removal of As from solution.
2. Sulfate addition with an appropriate electron donor (H_2) will stimulate SO_4^{2-} reducing bacteria leading to the formation of sulfide which will promote the lowering of the As concentration.
3. The absence of sufficient electron donor (reductant) or acceptor (oxidant) will lead to conditions that favor elevated Fe(II) and As concentrations.

We collected sediments from the Mahomet Aquifer during the drilling of a private well in McLean County on 28 July, 2005. The sediment used for these experiments, a fine quartz sand, was collected from a depth below the land surface of 208-218 ft. The sediment was stored completely saturated with anoxic groundwater in HDPE bottles at 4°C until the experimental preparation began. Between 20 and 40 g of sediment were removed directly from the HDPE bottles and placed in 160 mL serum bottles, which were then sealed with a butyl stopper. In an anaerobic chamber, we then added 80 mL of Mahomet Aquifer groundwater from well SWS 2s in Tazewell County (Table 1).

Table 1. Groundwater chemistry of well SWS-2s.

pH	[Fe(II)]	[As$_{(tot)}$]	[SO$_4^{2-}$]	[NO$_3^-$]	[NO$_2^-$]
7.6	3 mg/L	34 µg/L	8 mg/L	-	-

After removal from the anaerobic chamber, we added the reagents to the bottles via syringe and purged the headspace with either an N_2/CO_2 (90:10) or $N_2/CO_2/H_2$ (80:10:10) gas mixture. All amendments had an initial concentration of 500 µM. The following treatments were used for a total of 39 microcosms, including 3 autoclaved controls with no amendments:

	$+SO_4^{2-}$	$-SO_4^{2-}$	$+NO_3^-$
Acetate	3	3	3
No donor	3	3	3
H₂ + Acetate	3	3	3
H₂	3	3	3

The experiment was started on 13 September, 2005, and the microcosm bottles were placed in a covered, opaque container at ~18-22° C for incubation. After one month of incubation, there were signs of SO_4^{2-} reduction and biofilm formation in the bottles. They were sampled twice over a four month period for changes in the amount of SO_4^{2-}, S^{2-}, NO_3^-, nitrite (NO_2^-), As, and Fe(II) present in the groundwater.

During the course of the experiment, certain amendments resulted in changes to the As concentrations. To determine if these changes were due to predicted mechanisms, separate amendments were made at the end of the experiment designed to reverse the results obtained initially. After amendments were made bottles were incubated for two weeks and then sampled for As. To bottles that received NO_3^- alone, H_2 and acetate were added. This would result in the reduction of ferric oxides and the release of dissolved As. To bottles that received SO_4^{2-} alone (no electron donor), H_2 (10% of headspace) was added. This would result in stimulating the SO_4^{2-} reducing bacteria, releasing sulfide and lowering the dissolved As concentration. Finally to bottles that initially received NO_3^- and acetate, additional NO_3^- was added. This was done to exhaust any residual acetate and stimulate Fe(II) oxidation which would lead to the lowering of the As concentration due to sorption.

Figure 1. Microcosm set-up.

Analytical Methods

All anion measurements except for arsenate were made using a Dionex ICS-1000 ion chromatograph (Sunnyvale, CA). The detection limits for SO_4^{2-}, NO_3^-, and NO_2^- on

this system are all ~1 µg/L. Fe(II) measurements were made using the ferrozine method (VIOLLIER et al., 2000), a colorimetric method that also has a detection limit of 1 µg/L. Total As concentrations were determined using hydride generation (QUINAIA 2001) on a Nu Plasma HR ICP-MS. This method has a detection limit of ~0.1 µg/L.

Results and Discussion

Results of sample analyses are discussed below based on the specific analytes. Triplicate microcosms were used to obtain samples for which an average concentration is reported. Since these are biological incubations, considerable variability in the measured concentrations of certain chemicals was expected (See Appendix). This is due to the fact that rates of biological reactions will not always be consistent from microcosm to microcosm. Therefore when samples are taken at specific time points, the specific biogeochemical conditions in replicate samples may vary considerably. This does not impact the interpretation of the results, as clear and consistent trends in data are still apparent even with this variability.

Nitrate Reduction: Nitrate reduction occurred in less than one month for most treatments (Data not shown). This is not surprising, since NO_3^- is a very favorable electron acceptor and is even known to catalyze the oxidation of Fe(II) (see Fe(II) section below). Residual NO_3^- and NO_2^-, an intermediate in NO_3^- reduction to ammonium or to N_2, was observed after one month in bottles that did not receive acetate or H_2. This would be expected if carbon is limiting in the system, which is often the case in groundwater.

Sulfate Reduction: Results indicate that SO_4^{2-} reduction was much quicker with H_2 present in the headspace than with acetate alone (Figure 2). 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. The combination of acetate and H_2 would theoretically produce the fastest rates of SO_4^{2-} reduction. This, however, cannot be assessed with the data collected from this experiment. In the absence of electron donors, SO_4^{2-} concentrations remained high as was expected.
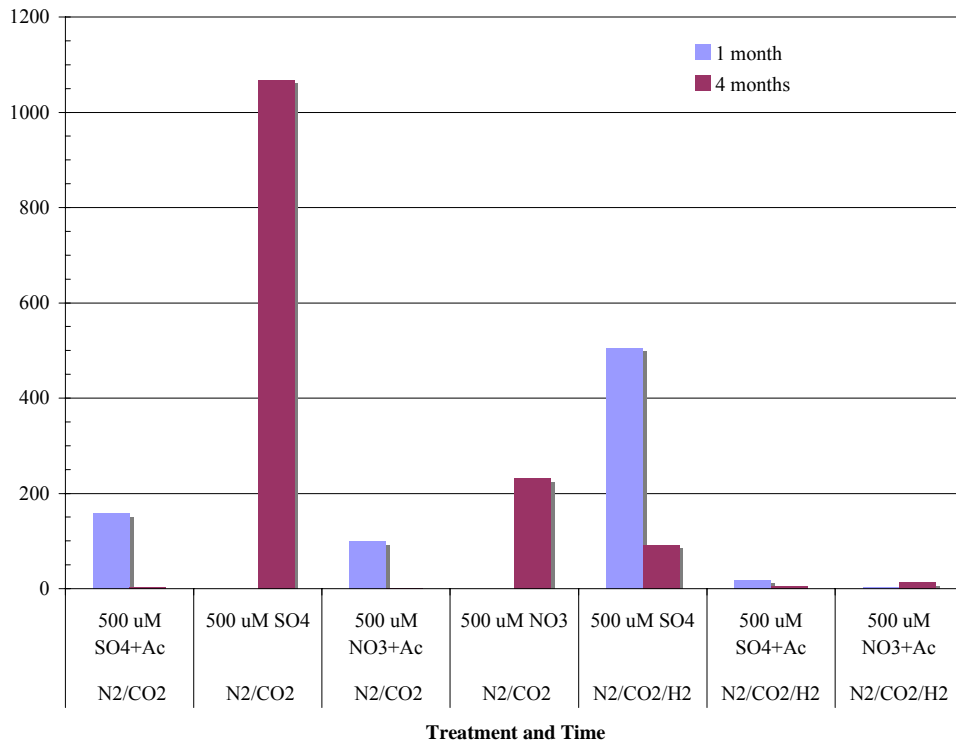
Figure 2. Sulfate concentrations after 1 and 4 months of incubation in Mahomet aquifer microcosms receiving different treatments. Note that the SO_4^{2-}-only and NO_3^--only microcosms were only monitored for SO_4^{2-} at 4 months.

Fate of Fe(II). 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 (Figure 3). The data suggest that the Fe(II) was oxidized by NO_3^- and NO_2^- reducing bacteria to ferric oxide. Visually these microcosms showed a reddish hue (See Appendix 1), supportive of the presence of iron-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 (Figure 4). Sulfate-fed samples had suppressed Fe(II) concentrations when H_2 was
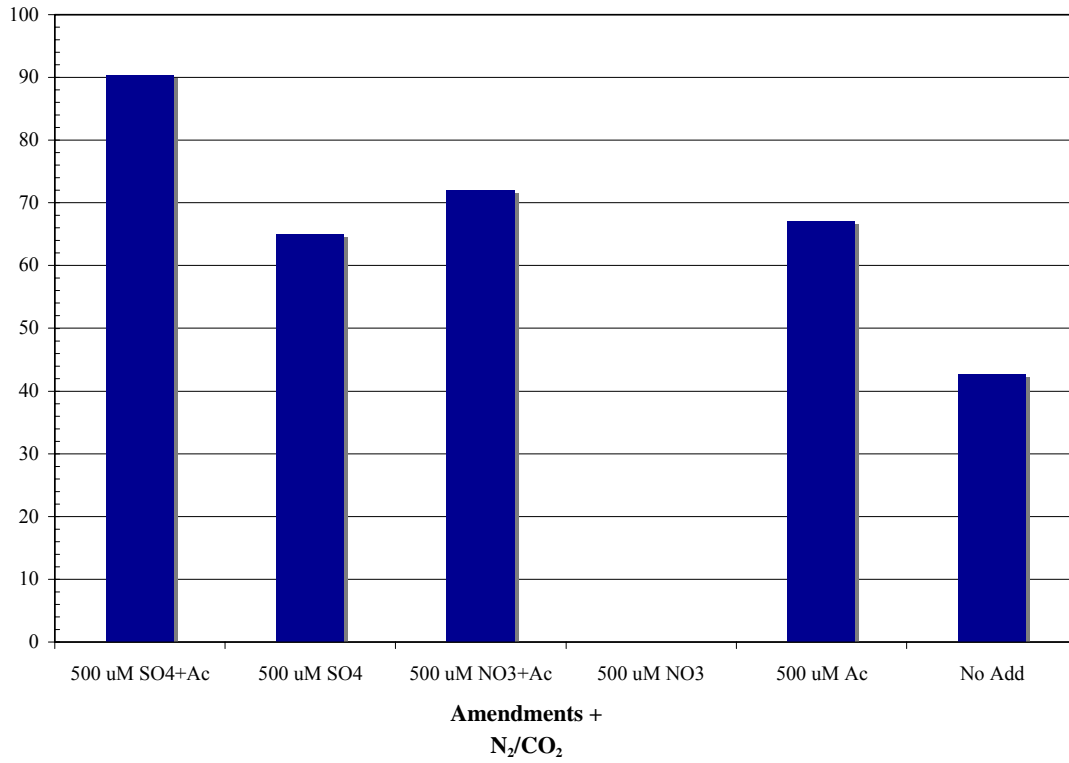
Figure 3. Ferrous iron concentration in Mahomet aquifer microcosms receiving various amendments in the absence of H_2.
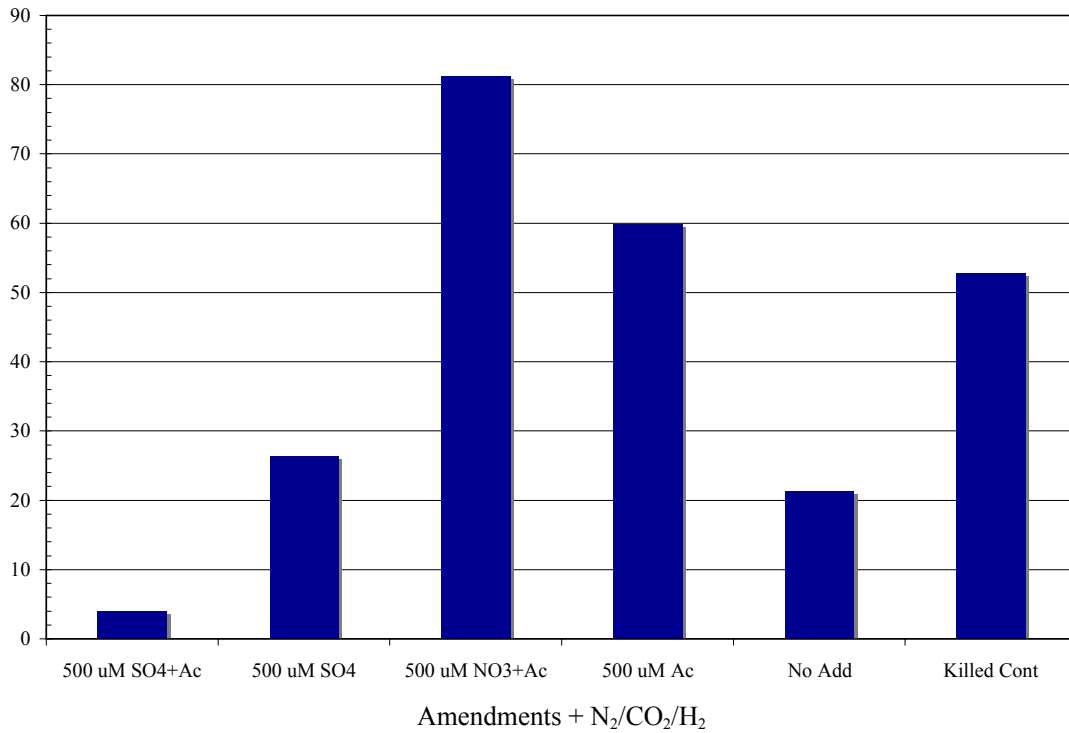

Figure 4. Ferrous iron concentration in Mahomet aquifer microcosms receiving various amendments in the presence of H_2 (100,000 ppmv).

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 (Figure 3). Visual evidence of a black precipitate in the H_2-fed microcosms supports this assessment of the activity (See Appendix 1).

Fate of Arsenic. Arsenic concentrations ranged from about 1-10 µg/l depending on the treatment applied (Figures 5 and 6). The original groundwater used in the microcosm experiments contained 34 µg/L and was chosen because it is greater than the new MCL for drinking water. It is possible that some of the As adsorbed to ferric oxides on the sediments obtained for the study, since the sediments were obtained from a different location. Results indicate that the As concentration dropped under two different redox conditions as predicted. When an oxidizing environment was present by adding NO_3^-, all the Fe(II) was oxidized and the As 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 (Figure 6). It is also interesting that the As concentration was lowered by about 50% in all microcosms receiving an electron donor. Perhaps it is possible that bacterial growth provided an organic sorbent for the added As and thus accounts for the lower concentrations in these microcosms. This type of result may be an artifact of the type of incubation done and may not occur in the dynamic flow environment in groundwater because biomass concentrations stay relatively low in the aquifer.

An interesting relationship appeared in the data between Fe(II) and As concentrations (Figure 7). These two were positively correlated for all the microcosms that actually received an amendment (minus controls); when the Fe(II) concentration was lowest the As concentration was most suppressed. This is not surprising geochemically speaking, and suggests a simple metric for evaluating groundwater for the potential to have high As concentrations whether the water is oxic or anaerobic. Ferrous iron is depressed in oxidized waters due to the formation of insoluble ferric oxides which serve as a sorption site for soluble As 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 As. Since Fe(II) is relatively easy to measure, this relationship could possibly be exploited in future projects. However, this relationship between Fe(II) and As is not typically observed in groundwater samples, including those collected from the Mahomet aquifer (KELLY et al., 2005), suggesting other mechanisms are affecting Fe(II) and/or As concentrations in situ.

To evaluate whether the mechanism of As loss was as predicted, specific microcosms were selected for alternative secondary amendments. We hypothesize that the NO_3^- + acetate microcosm received additional NO_3^- only because the excess oxidant (NO_3^-) would lead to the generation of more ferric oxide and drop the As concentration. The NO_3^--only microcosm with the lowest As concentration was amended with H_2 and acetate. We predicted these electron donor amendments would stimulate ferric-iron reduction and lead to the release of soluble As. To the SO_4^{2-}-only microcosm, which showed no loss of As relative to the control, a second amendment of H_2 (100,000 ppmv)

was made to stimulate SO_4^{2-} reduction. The generation of sulfide should lead to the precipitation of Fe and As. These second amendments were incubated for two weeks, and results are shown in Figure 8. As predicted, the NO_3^--only and SO_4^{2-}-only microcosms showed increased and decreased As concentrations, respectively. The NO_3^- + acetate microcosm did not show any change, however this may be due to the slow kinetics of Fe(II) oxidation coupled to NO_3^- reduction. A longer incubation time may yield the predicted result. Of interest is the fact that the As concentration increased to levels observed in the original groundwater in the NO_3^--only microcosm amended with H_2 and acetate. This shows that when iron-reducing conditions occur in groundwater, the release of sorbed As can be rapid. This is consistent with field observations made by other investigators (MCARTHUR et al., 2004; KELLY et al., 2005).

Conclusions

Arsenic concentrations in the microcosms behaved for the most part as predicted. Under both oxidizing (NO_3^-) and SO_4^{2-} reducing conditions, As levels dropped. Somewhat unexpected was the decrease in As concentrations when any electron donor was added. It remains to be established if this was associated with sorption to biomass as suggested. We also show that the As concentration rapidly increased from oxidized sediments when ferric-iron reducing conditions were stimulated. This 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 the As concentration. Finally, a relationship between Fe(II) and As emerged from our small study. Although this suggests that it may be possible to use Fe(II) as a predictor for possible As hot spots in aquifers known to retain As, this relationship between Fe(II) and As is not always observed in groundwater samples, including those collected from the Mahomet aquifer.
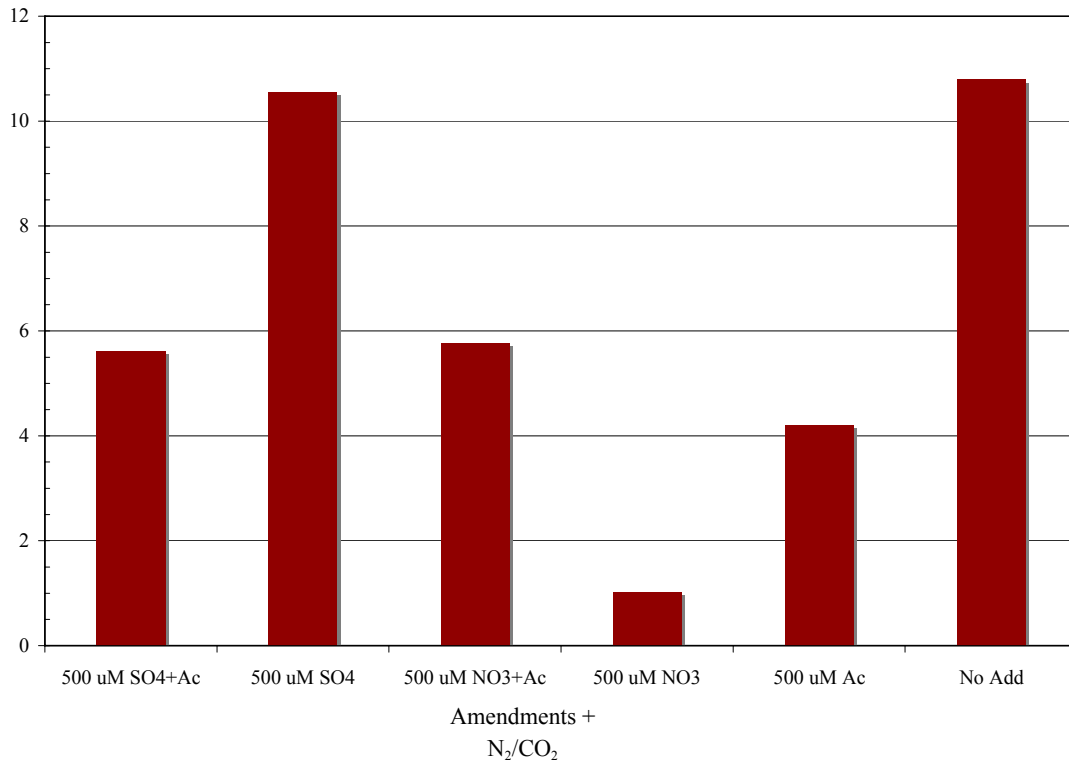
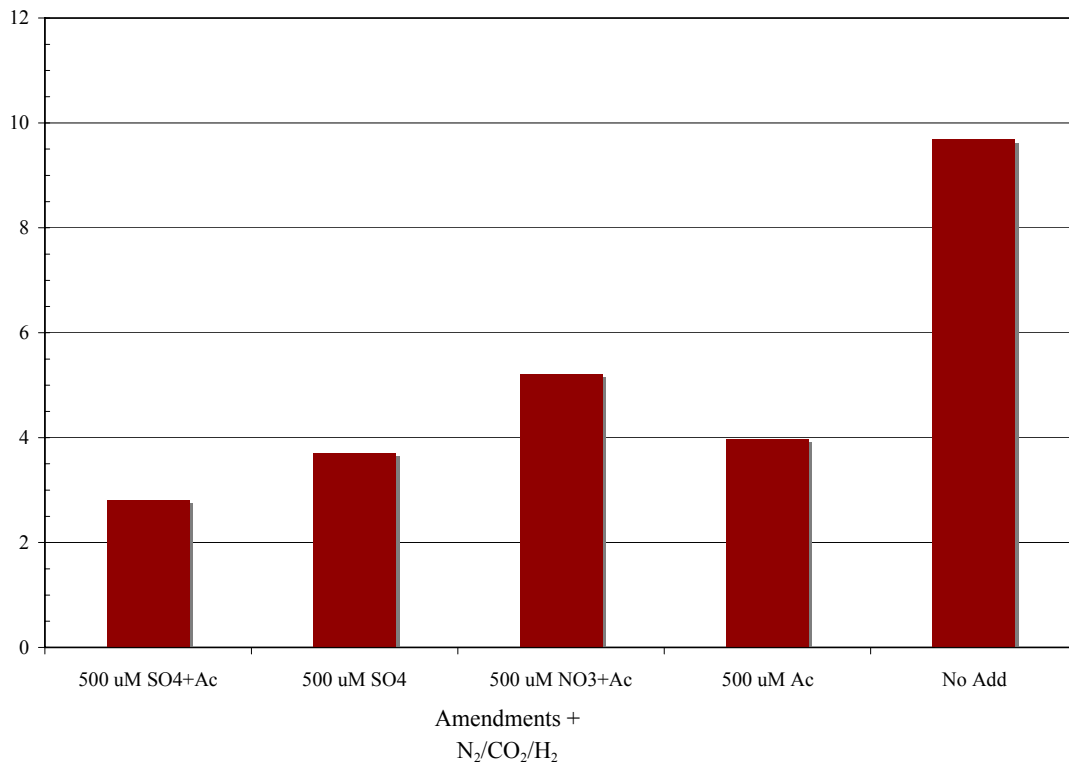Figure 5. Arsenic concentrations after 4 months of incubation with different treatments in the absence of H_2.

Figure 6. Arsenic concentrations after 4 months of incubation with different treatments in the presence of H_2.
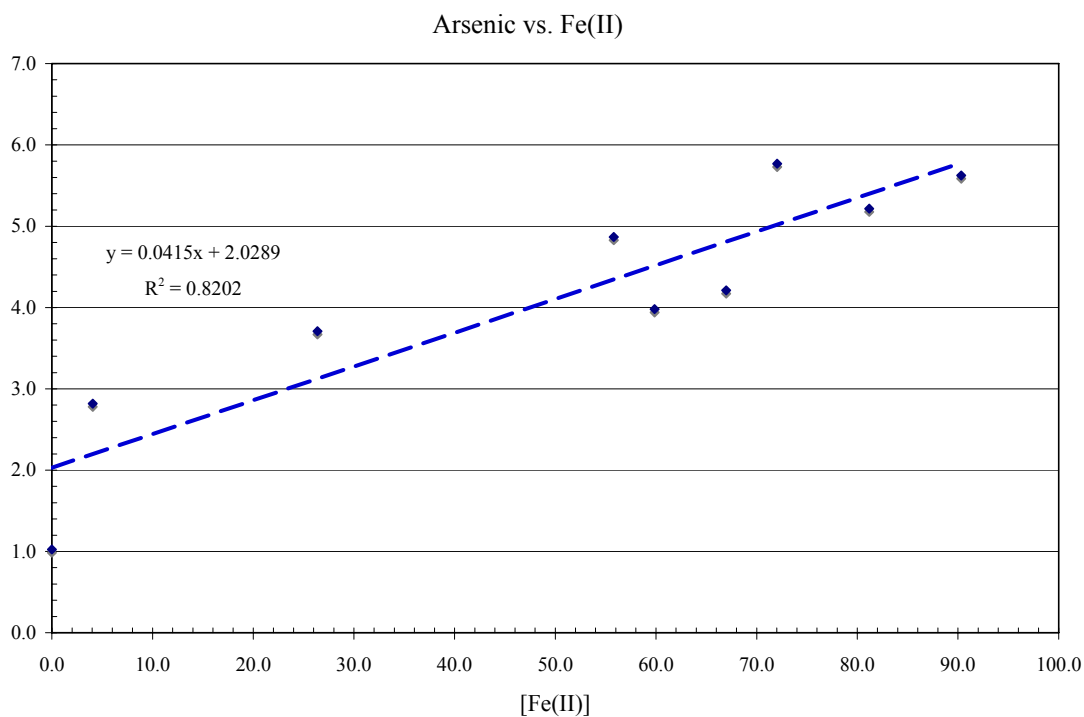
9

Figure 7. Plot shows the ferrous iron concentration verses the As concentration for all of the microcosms used in the experiment. Data points represent average of three microcosms. Data from the controls is not included. The dotted lines represent the regression line best fit for the plotted data. This suggested a positive correlation between the As and Fe(II) concentration.
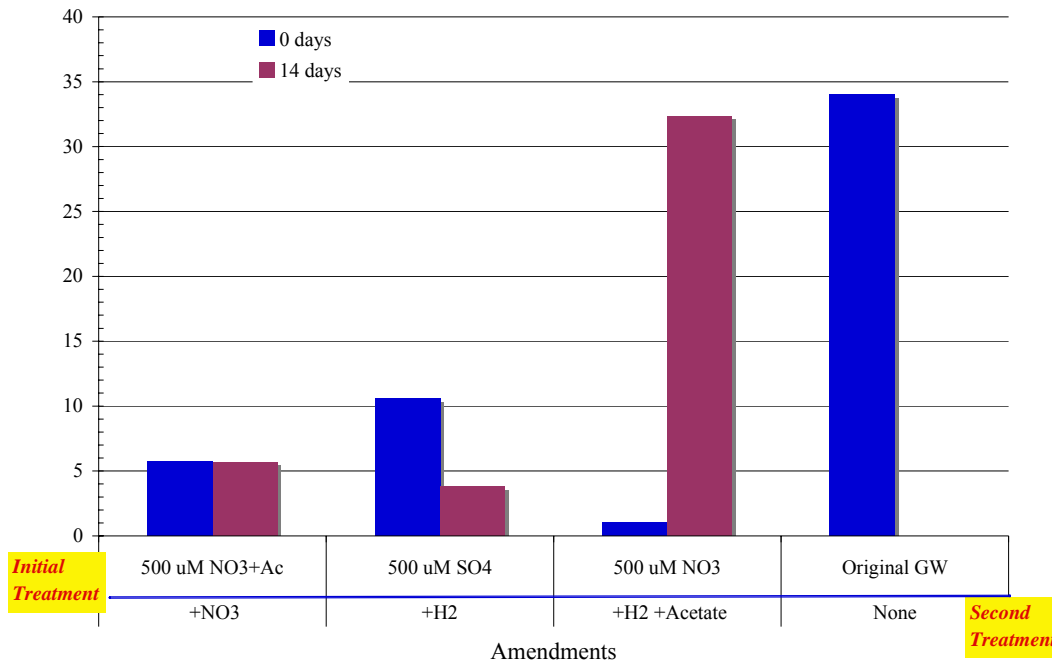
Impact of Second Amendments on Arsenic

Figure 8. Effect of secondary treatment on As concentration after two weeks of incubation. Original concentration of As in groundwater shown on the right of figure.

References

Frey M. M., Owen D. M., Chowdhury Z. K., Raucher R. S., and Edwards M. A. (1998) Cost to Utilities of a Lower MCL for Arsenic. *Journal American Water Works Association* 90(3), 89-102.

Holm T. R. (1995) Ground-water quality in the Mahomet aquifer, McLean, Logan, and Tazewell Counties, pp. 42. Illinois State Water Survey.

Holm T. R., Kelly, W. R., Wilson, S. D., Roadcap, G. R., Talbott, J. L., Scott, J. S. (2004) Arsenic Geochemistry and Distribution in the Mahomet Aquifer, Illinois, pp. 102. Waste Management and Research Center.

Holm T. R., Kelly, W. R., Wilson, S. D., Roadcap, G. R., Talbott, J. L., Scott, J. S. (2005) Arsenic Distribution and Speciation in the Mahomet and Glasford Aquifers, Illinois. In *Advances in Arsenic Research. Integration of Experimental and Observational Studies and Implications for Mitigation*, Vol. ACS Symposium Series 915 (ed. P. A. O'Day, D. Vlassopoulos, X. G. Meng, and L. G. Benning), pp. 148-160. American Chemical Society.

Jain C. K. and Ali I. (2000) Arsenic: Occurrence, toxicity and speciation techniques. *Water Research* 34(17), 4304-4312.

Kelly W. R., Holm T. R., Wilson S. D., and Roadcap G. S. (2005) Arsenic in glacial aquifers: Sources and geochemical controls. *Ground Water* 43(4), 500-510.

Kempton J. P., Johnson W. H., Cartwright K., and Heigold P. C. (1991) Mahomet Bedrock Valley in East-Central Illinois: Topography, Glacial Drift Stratigraphy, and Hydrogeology. In *Geology and Hydrogeology of the Teays-Mahomet Bedrock Valley System*, Vol. Special Paper 258 (ed. J. P. K. W.N. Melhorn), pp. 91-124. Geological Society of America.

Kirk M. F. (2004) Bacterial sulfate reduction limits arsenic concentration in groundwater from a glacial aquifer system. M.S., University of Illinois.

Kirk M. F., Holm T. R., Park J. H., Jin Q. S., Sanford R. A., Fouke B. W., and Bethke C. M. (2004) Bacterial Sulfate Reduction Controls Natural Arsenic Contamination of Groundwater. *Geology* 32(11), 953-956.

McArthur J. M., Banerjee D. M., Hudson-Edwards K. A., Mishra R., Purohit R., Ravenscroft P., Cronin A., Howarth R. J., Chatterjee A., Talukder T., Lowry D., Houghton S., and Chadha D. K. (2004) Natural organic matter in sedimentary basins and its relation to arsenic in anoxic ground water: the example of West Bengal and its worldwide implications. *Applied Geochemistry* 19(8), 1255-1293.

Quinaia, S. and Rollemberg, M. (2001) Selective Reduction of Arsenic Species by Hydride Generation - Atomic Absorption Spectrometry. Part 2 - Sample Storage and Arsenic Determination in Natural Waters. *Journal of the Brazilian Chemical Society* 12(1), 37-41.

Viollier, E., Inglett, P.W., Hunter, K., Roychoudhury, A.N., and Van Cappellen, P. (2000) The ferrozine method revisited: Fe(II)/Fe(III) determination in natural waters. *Applied Geochemistry* 15(6), 785-790.

Warner K. L. (2001) Arsenic in glacial drift aquifers and the Implication for drinking water - lower Illinois River basin. *Ground Water* 39(3), 433-442.

Welch A. H., Westjohn D. B., Helsel D. R., and Wanty R. B. (2000) Arsenic in ground water of the United States: Occurrence and geochemistry [Review]. *Ground Water* 38(4), 589-604.