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Linking As, Se, V, and Mn Behavior to Natural and Biostimulated Uranium Cycling

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There are no limitations on the data

Executive Summary

The project "Linking As, Se, V, and Mn behavior to Natural and Biostimulated Uranium Cycling" successfully investigated Arsenic cycling the Rifle Colorado IFRC. This project trained undergraduate and graduate students at the Colorado School of Mines, Vassar College, and Barnard College. This resulted in both undergraduate theses and a PhD thesis and multiple publications. The science was highly successful and we were able to test the main hypotheses. We have shown that (H1) under reducing conditions that promote uranium immobilization arsenic is readily mobilized, that (H2) thioarsenic species are abundant during this mobilization, and (H3) we have examined arsenic mobilization for site sediment. At the Rifle IFRC Acetate was added during experiments to immobilize Uranium. These experiments successfully immobilized uranium but unfortunately would mobilize arsenic. We developed robust sampling and analysis methods for thioarsenic species. We showed that the mobilization occurred under sulfate reducing conditions and the majority of the arsenic was in the form of thioarsenic species. Previous studies had predicted the presence of thioarsenic species but this study used robust field and laboratory methods to quantitatively determine the presence of thioarsenic species. During stimulation in wells with high arsenic the primary species were trithioarsenate and dithioarsenate. In wells with low levels of arsenic release thioarsenates were absent or minor components. Fortunately after the injection of acetate ended the aquifer would become less reducing and the arsenic concentrations would decrease to pre-injection levels. In aquifers where organic carbon is being added as a remedial method or as a contaminant the transient mobility of arsenic during sulfidogenesis should be considered especially in sulfate rich aquifers as this could impact downgradient water quality.

Hypotheses, Goals, and Objectives

For each of the original goals and objectives we will summarize the progress we made. Dr. Valerie Stucker was a graduate student on the project, has since received her Ph.D. and was a catalyst for the majority of the work. The PI's and co-PI's contributed to make her work and thesis a success. Therefore a significant amount of the work is from her dissertation and publications.

Hypothesis 1) The groundwater flux of redox sensitive elements (e.g. As, Se, V, and Mn) will be increased under natural and stimulated reducing conditions that promote the immobilization of uranium at IFRC.

Task 1.1 is to gather a general characterization of the groundwater including pH, Eh, alkalinity and major ions (including phosphate and carbonate) at the field site focusing on Fe and Mn concentrations to further investigate the proposed As release mechanisms.

Stucker 2013 analyzed site groundwater chemistry to understand arsenic speciation under the ambient conditions before and after stimulation. It was shown that under non-stimulated conditions the arsenic concentrations were significantly lower. Arsenic concentrations only increased under reducing conditions. In addition, monitoring of site wells showed that As, Fe, and Mn fluctuated with flood conditions in the Colorado River. When the Colorado river stage increased the aquifer becomes more oxic and concentrations of redox sensitive elements such as Fe, Mn, and As decrease. See Stucker figure 5.1 for details.

Task 1.2 is to optimize the sorbents for PFMs so they can be utilized for continued uranium as well as arsenic flux measurements.

Task 1.3 is to deploy the PFMs at the Rifle IFRC to determine fluxes during biostimulation and under ambient conditions during changing river stages.

Unfortunately we were not able to get the passive flux meters (PFMs) working for arsenic at the Rifle IFRC site. Development of the PFMs from Uranium took longer than expected. Development of the PFMs and novel sorbents was also part of a senior thesis at Columbia University by Christine Wang. We were not able to get complete capture of the arsenic species. For the same reason that thioarsenic species are highly mobile in the field makes them hard to capture and filter.

Hypothesis 2) Under naturally reducing conditions, mobilization is controlled by the interaction of arsenic oxyanions with Fe and Mn (hydr)oxides. Under biostimulated conditions at the IFRC, aqueous speciation and mobilization is controlled by the formation of thioarsenic species.

Task 2.1 is to optimize and cross calibrate the speciation methods described in the following methods section.

A considerable amount of time was spent developing and calibrating methods. Field samples were immediately flash frozen on liquid nitrogen at the well. Stucker used an Ion chromatograph coupled to an ICP MS (IC ICP MS) for analysis with minimal exposur of the sample to the atmosphere. We tried to develop a simpler method at Vassar that used hydride generation. The hydride generation is a simpler analysis but the method was able to work for inorganic arsenic species but not the thioarsenic species. Therefore field measurements are only reported for the IC ICP MS.

Task 2.2 is to determine arsenic speciation during changes in river stage to determine the mobile species under ambient conditions; this will involve collecting new samples in 2012.

Samples were collected and analyzed. These results became part of talks and presentations to DOE by Dr. Williams but have not been included in publications.

Task 2.3 is to analyze the arsenic speciation under biostimulated conditions.

This was a major portion of the work and is presented in Stucker et al., 2014.

Hypothesis 3) Mineralogical associations control the aqueous concentrations of As, Se, V, and Mn under reducing conditions. Laboratory experiments and mineralogical characterizations can be used to predict field scale observations and therefore used to parameterize reactive transport models.

Task 3.1 is to characterize the mineralogy, particularly identifying oxide and sulfide minerals. If sufficient arsenic is present, solid phase surface speciation will be determined using Synchrotron methods. For this task we will jointly write a proposal for beam time with John Bargar.

Beamtime was obtained on SSRL beamline 4-1 in 2012. The knowledge gained from the analyses was used in Stucker et al., 2014.

Task 3.2 is to perform laboratory microcosm experiments under simulated field conditions and monitor changes in the aqueous and solid phases.

Laboratory experiments were performed to better understand arsenic speciation and transport. This was included in Stucker et al., 2014.

Task 3.3 is to perform in situ column experiments at the IFRC site in collaboration with Dr. John Bargar, that will provide data that will inform reactive transport models in development for the site.

Alessi et al., (2014) performed in situ column experiments. We collaborated with Dr. Bargar on other aspects of the experiment but we were not able to further expand the arsenic part of the work.

PRODUCTS

Publications

Alessi, D.S., Lezama-Pacheco, J.S., Janot, N., Suvorova, E.I., Cerrato, J.M., Giammar, D.E., Davis, J.A., Fox, P.M., Williams, K.H., Long, P.E., Handley, K.M., Bernier-Latmani, R. and Bargar, J.R. (2014) Speciation and Reactivity of Uranium Products Formed during in Situ Bioremediation in a Shallow Alluvial Aquifer. Environmental Science & Technology 48(21), 12842-12850.

Hobson, C., Williams, K.H., Stucker, V. and Ranville, J. (2014) Arsenic Chronospeciation in a Biostimulated Aquifer. Goldschmidt.

Stucker, V.K., Silverman, D.R., Williams, K.H., Sharp, J.O. and Ranville, J.F. (2014) Thioarsenic Species Associated with Increased Arsenic Release during Biostimulated Subsurface Sulfate Reduction. Environmental Science & Technology 48(22), 13367-13375.

Stucker, V.K., Williams, K.H., Robbins, M.J. and Ranville, J.F. (2013) Arsenic geochemistry in a biostimulated aquifer: An aqueous speciation study. Environmental Toxicology and Chemistry 32(6), 1216-1223.

Stucker, V., Ranville, J.F., Giloteaux, L. and Williams, K.H. (2011) Impacts of acetate biostimulation for uranium bioreduction on aqueous arsenic geochemistry. AGU Fall Meeting Abstracts 1, 1065.

Stucker, V. (2013) Effects of Bioremediation on Uranium and Arsenic Geochemistry at a Former Uranium Mill Site. PhD Thesis.

Collaborations:

The development of new collaborations was one of the main successes of the proposal. The transfer of knowledge has greatly increased sampling capacity both at the IFRC Rifle and also at the home institutes. The PIs spent many days working at Rifle sharing their novel techniques and learning new techniques that were brought back to their home institutes and used in subsequent work. In addition, shared knowledge about filter and sampling for arsenic and microbial populations will greatly enhance the science. Key collaborators include John Bargar, Michael Wilkins, Kelly Wrighton, Scott Fendorf, Eric Roden, and Rick Colwell.