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Julia G. Bryce

University of New Hampshire, julie.bryce@unh.edu

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Arsenic chemical dynamics in NH groundwater reservoirs: Insights from temporal variability in multi-element signatures of statewide samples

Basic Information

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|---------------------------------|---|
| Title: | Arsenic chemical dynamics in NH groundwater reservoirs: Insights from temporal variability in multi-element signatures of statewide samples |
| Project Number: | 2011NH141B |
| Start Date: | 3/1/2011 |
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| Principal Investigators: | Julia G Bryce |

Publications

There are no publications.

Year 2 Project Report: “Arsenic chemical dynamics in NH groundwater reservoirs: Insights from temporal variability in multi-element signatures of statewide samples.”

PI Julia G. Bryce, USGS Collaborator Joe Ayotte, UNH Staff Florencia Prado

1. *Problem and Objectives*

The purpose of this project is to measure the concentrations of arsenic, a key regulated contaminant, in public and private groundwater wells distributed across the state of New Hampshire. In the first year of this project, we focused on developing the arsenic method for analysis via hydride generation-high resolution inductively coupled plasma mass spectrometry. We optimized our analytical protocol for “harvesting” arsenic out of water samples originally collected for a MTBE study, and we optimized a set of procedures for investigating “leachable” arsenic from samples of local bedrock. By the end of year two we have prepped nearly 500 samples and run approximately 380. Ongoing analyses of other key geochemical parameters (e.g., Fe and Pb) coupled with additional leaching laboratory experiments manipulating pH provide the opportunity to investigate geochemical controls on arsenic mobility in geochemical environments such as those found in the bedrock-hosted aquifers of southern NH.

2. *Methods and Project Activities*

Our work is focused on developing analytical protocols to measure arsenic contents in existing samples. Nearly 900 samples exist from sampling campaigns led by J. Ayotte originally designed to study MTBE occurrences in groundwaters sampled from public and private drinking water supplies. Since some of the existing samples are older than recommended “hold” times for water samples, we first needed to ensure no arsenic has been lost from the system, via selective adsorption onto the bottle sides and/or via co-precipitation with other elements. Our approach to ensuring all arsenic is in solution is as follows. First we acidified the samples to 5% nitric acid, and then let sit for several days and shoot and mixed via ultrasonic mixing. We then took a (quantified) cut for which we measured the arsenic concentration. We subsequently transferred the sample to a cleaned bottle and acidified to 10% nitric, let sit, and then ran the results for arsenic concentration. We repeated this last bottle-leaching with 15% nitric.

We have implemented the analysis of arsenic via hydride generator (Klaue and Blum, 1999) plumbed into a high resolution inductively coupled plasma mass spectrometry. Our detection limits are generally $\sim < 0.025 \mu\text{g}/\text{kg}$. We ran two blind standards provided by Joe Ayotte to run every 15-30 samples throughout each run day. We also used standard-sample-standard bracketing with NIST certified reference standard 1643e to correct for within-run drift and also ran standard curves using diluted natural water samples to assess matrix effects. Our lab has participated in the biannual USGS round robin since Fall 2012. We will continue to participate until all 900 water sample analyses have been completed.

In another component of the study, we carried out leaching experiments with chipped bedrock samples to elucidate the geochemical controls on the contributions of

arsenic from metasedimentary bedrock units. Our first analyses in support of these investigations include the analysis of environmentally mobile arsenic in the Kittery formation. Our approach is adapted from that described in Peters and Blum (2003), wherein we used partial leaching in dilute acid to identify the readily mobilized As fractions. In addition to the acid leaching (carried out at $\text{pH} \leq 1$), we carried out a subsequent study exposing the samples to solutions of elevated pH to test for the role of pH-selective absorption onto minerals on As mobilization (e.g., Peters and Blum, 2003 and references therein).

3. *Findings and Future work*

In our assessments of accuracy and precision we ran a standard (NIST SRM 1643e, Trace elements in water) and found excellent accuracy and reproducibility. We have also participated in the USGS Round Robin measurements for standards every six months during this study. Following procedures we have developed, we reported our assessment of the standard, which came in below the median value reported for the unknown standard we were assigned. Though it is difficult to address the meaningfulness of the “median” value as it includes several different types of analytical approaches (some of which would not be used validly for samples with As of low abundance), we are continuing to run the standard using other techniques (e.g., standard addition) to ensure that we are accurately measuring sample values. Any offset in our values likely comes from a mismatch between the matrix of the standard we are using and the matrix of unknowns. Accordingly we will be carrying out investigations of the influence of several different “matrix”-modifiers to ensure that our analytical protocols are not impacted by the high abundance of certain elements (e.g., Fe).

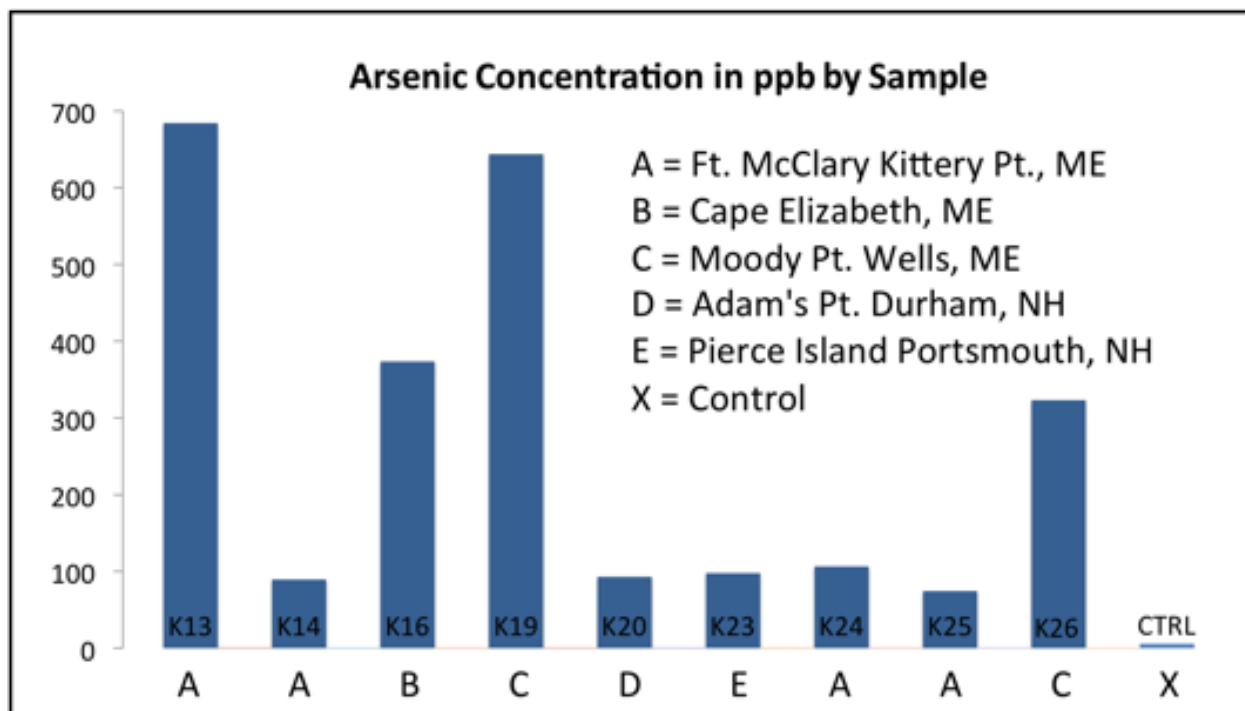
In terms of ensuring that we have no sample biasing issues with the shelf life of our samples, we spent the time on a subset of our samples to ensure we can establish a protocol for future measurements of the remainder of the 900 groundwater samples. Analyses of five samples showed, in cases where the original sample is above the detection limit, that we have a > 99% yield for the total arsenic in the system during the acidification to 5% nitric. Accordingly we will adopt these protocols with the rest of the unknown samples.

Our initial investigations of the environmentally mobile arsenic confirm the extreme range in arsenic that we can find over relatively short spatial scales in metasedimentary bedrock (Figure 1), as well as the strong sensitivity of subsequent arsenic remobilization due to changing pH in oxidizing conditions. We will complement our existing results on the Kittery with leaching studies of additional sub-samples from two existing ~100-foot six-inch drill cores through the Kittery and Elliot formations around the Great Bay in Southeastern NH and potentially from other bedrock units that host samples we have collected in the southern NH region.

The concentrations of arsenic in groundwater from the private and public water supplies measured thus far have been highly variable, with many samples exceeding the EPA-recommended drinking water limit. Two samples exceeded 100 ppb in concentration, well above recommended limits. Later this summer, once we have the majority of the 900

samples, we plan to work together with Joe Ayotte (USGS) to link our geochemical data to geospatial data for presenting the data in a coherent fashion and inform any additional sampling measures.

Figure 1. Arsenic concentrations in bedrock-leaching solutions from the Kittery formation. Note the extreme variability in the arsenic that is potentially environmentally mobile from different localities in the Kittery formation medasedimentary bedrock as well as the variability within individual localities. Forthcoming elemental analyses will help to identify the geochemical processes responsible for these wide variations.



4. Presentation

Results of the bedrock-leaching were presented at the 2012 UNH Undergraduate research project by Mr. John Clark (UNH BA-Earth Sciences Teaching, 2012). Clark started his activities on the project in summer 2011 and continued during the 2011-2012 and 2012-2013 academic years. We are working together to complete the analyses by the end of CY 2013 and hope to work together with USGS to prepare a publication of the results shortly thereafter.

5. Outreach efforts

Clark has finished his professional degree to be a secondary school science teacher, and his involvement in this project has provided him the opportunity to participate in “genuine” scientific research he can model with his future middle school students. He originally participated in this project as part of a summer research internship provided by a National Science Foundation grant for which Bryce is a co-PI. His attraction to the project came

because of his belief that this was a project involving chemistry, public health and the environmental sciences, in such a way that he could engage his future students. His continued involvement during the academic year is a testimony to his long-standing interest.

In the spring, we featured the results of this project in a hands-on lab day for a cadre of high school chemistry and Earth Science teachers separately supported by a Dreyfus Foundation Grant. The teachers were involved in sample collection, ICP analyses, and discussion of USGS studies of As in NH groundwaters, and are working with PI Bryce and Ms. Prado to establish As in groundwater as a unit in their chemistry and Earth Science classrooms.

6. *Personnel development- students, faculty and staff*

In addition to Mr. Clark, whose analytical efforts were supported by this project, this project is responsible for convincing Ms. Florencia Prado, a talented staff member to enter the Ph.D. program. Prado has developed the analytical techniques and worked with Bryce to supervise and develop Clark's project.