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

Basic Information

Title:	Arsenic chemical dynamics in NH groundwater reservoirs: Insights from temporal variability in multi-element signatures of statewide samples
Project Number:	2011NH141B
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Descriptors:	None
Principal Investigators:	Julia G Bryce

Publications

There are no publications.

Year 1 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 two-year 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 two-year project, we focused on developing the arsenic method for analysis via hydride generation-high resolution inductively coupled plasma mass spectrometry. We have optimized our analytical protocol for “harvesting” arsenic out of water samples originally collected for a MTBE study, and we have optimized a set of procedures for investigating “leachable” arsenic from samples of local bedrock. Future analyses of other key geochemical parameters (e.g., Fe and Pb) coupled with ongoing laboratory experiments manipulating pH and redox conditions 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 developed the analysis of arsenic on the hydride generator (Klaue and Blum, 1999) that is plumbed into a high resolution inductively coupled plasma mass spectrometry. Generally our detection limits are $\sim < 0.025 \mu\text{g}/\text{kg}$, but during some of our runs our detection limit was as high as $0.09 \mu\text{g}/\text{kg}$ (likely due to a high blank on one of our reagents, which we then replaced). We used standard-sample-standard bracketing to correct for within-run drift, and developed a standard curve using diluted natural water samples.

In a second part of our work, 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); we use 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).

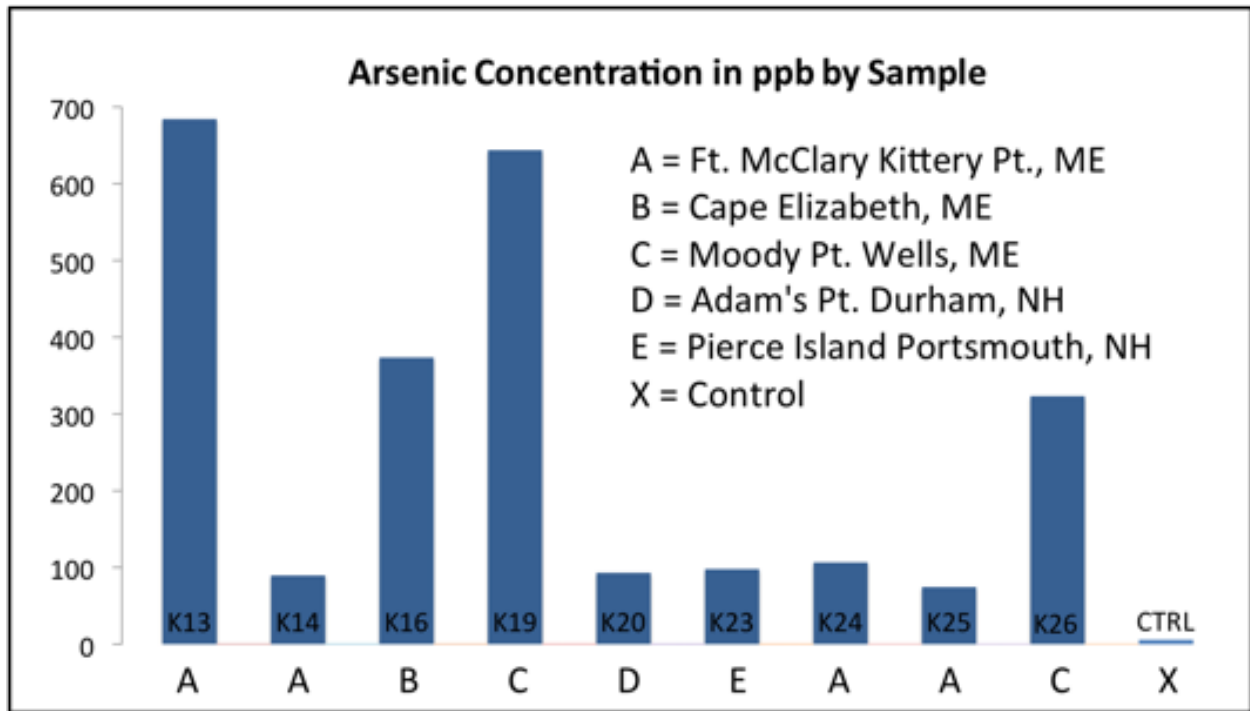
3. Findings and Future work

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 also participated in the USGS Round Robin measurements for standards. 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 our 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.

Figure 1 (following page). 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 metasedimentary 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 academic year. We anticipate that we will submit an abstract to the 2013 Northeastern Regional GSA meeting to be held in NH next spring.

5. *Outreach efforts*

Clark is training to be a teacher, and his involvement in this project has provided him the opportunity to participate in “genuine” scientific research such that he can model it 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 that he involved chemistry, public health and 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. He has committed to continuing to work on the bedrock leaching projects during this upcoming summer and his year working for his M.Ed., the final steps in the process of teacher certification.

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 apply to work on her Ph.D. The arsenic project will constitute part of her Ph.D. thesis. Prado has developed the analytical techniques and worked with Bryce to supervise and develop Clark’s project.