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

Basic Information

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Publications

There are no publications.

Year 3 Project Report: "Arsenic chemical dynamics in NH groundwater reservoirs: Insights from temporal variability in multi-element signatures of statewide samples."

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Student participants: Ian Carlisle (BS Geology UNH 2015); John Clark (BA Earth Sciences Teaching, UNH 2012; M.Ed. 2013)

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 early part 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 the project

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 was as follows. First we acidified the samples to 5% nitric acid, and then let sit for several days and shook and mixed via ultrasonic mixing. We then took a (quantified) cut for which we measured the arsenic concentration. We subsequently transferred the acidified solution to a cleaned bottle and filled the original bottle with 10% nitric, let sit, and then ran the results for arsenic concentration. We repeated this last bottle-leaching again with 15% nitric. Though we found that the 10% and 15% acidification steps were unnecessary in our pilot studies, since the solutions were stored for some time we have to consider the results we report minimum abundances of arsenic in the groundwater samples.

We have implemented the analysis of arsenic via hydride generator (Klaue and Blum, 1999) plumbed into a high resolution inductively coupled plasma mass spectrometer. Our detection limits were ~ < 0.02 µg/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. In the most recent round robin period the recommended value

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 pH ≤ 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

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 carried 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). We found negligible effects, and that we could correct for effects with standard-sample-standard bracketing techniques.
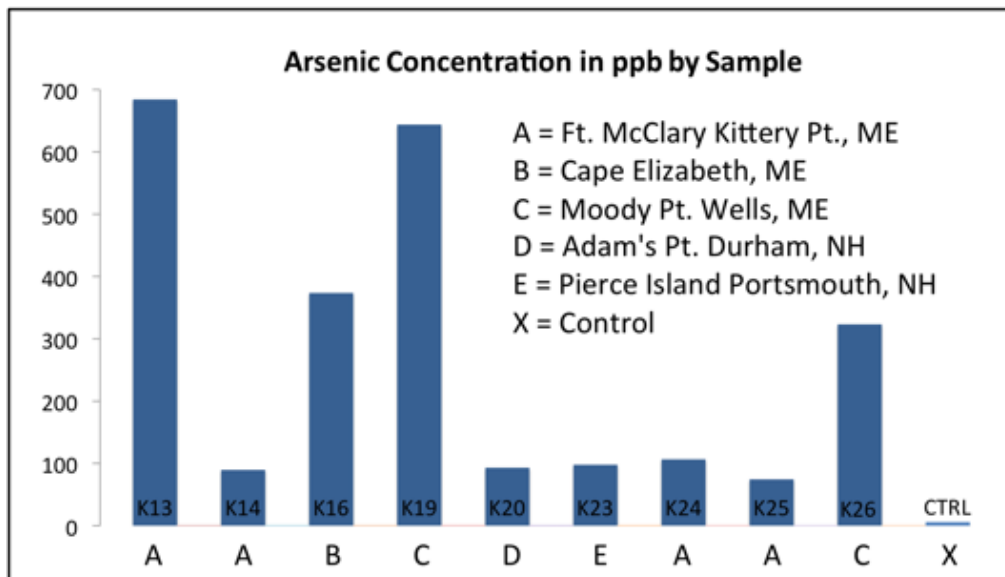
In terms of ensuring that we have no sample biasing issues with the shelf life of our samples, we spent the time on a subset of our samples to ensure we can establish a protocol for future measurements of the remainder of the 900 groundwater samples. Analyses of five samples showed, in cases where the 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 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 (Figure 2). Two samples exceeded 100 ppb in concentration (Figure 2), well above recommended limits. Of the samples studied, 87% fall

below the EPA recommended limit for drinking water (10 ppb), and 79% fall below the 5 ppb mark, which is often suggested as a more appropriate recommended maximum contaminant level for drinking water. Disturbingly there are nearly 70 samples that exceed the EPA recommended drinking water limit, with 11 that bear As concentrations greater than 50 ppb (Figure 2).

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..

Arsenic Concentration in ppb by Sample

A = Ft. McClary Kittery Pt., ME
B = Cape Elizabeth, ME
C = Moody Pt. Wells, ME
D = Adam's Pt. Durham, NH
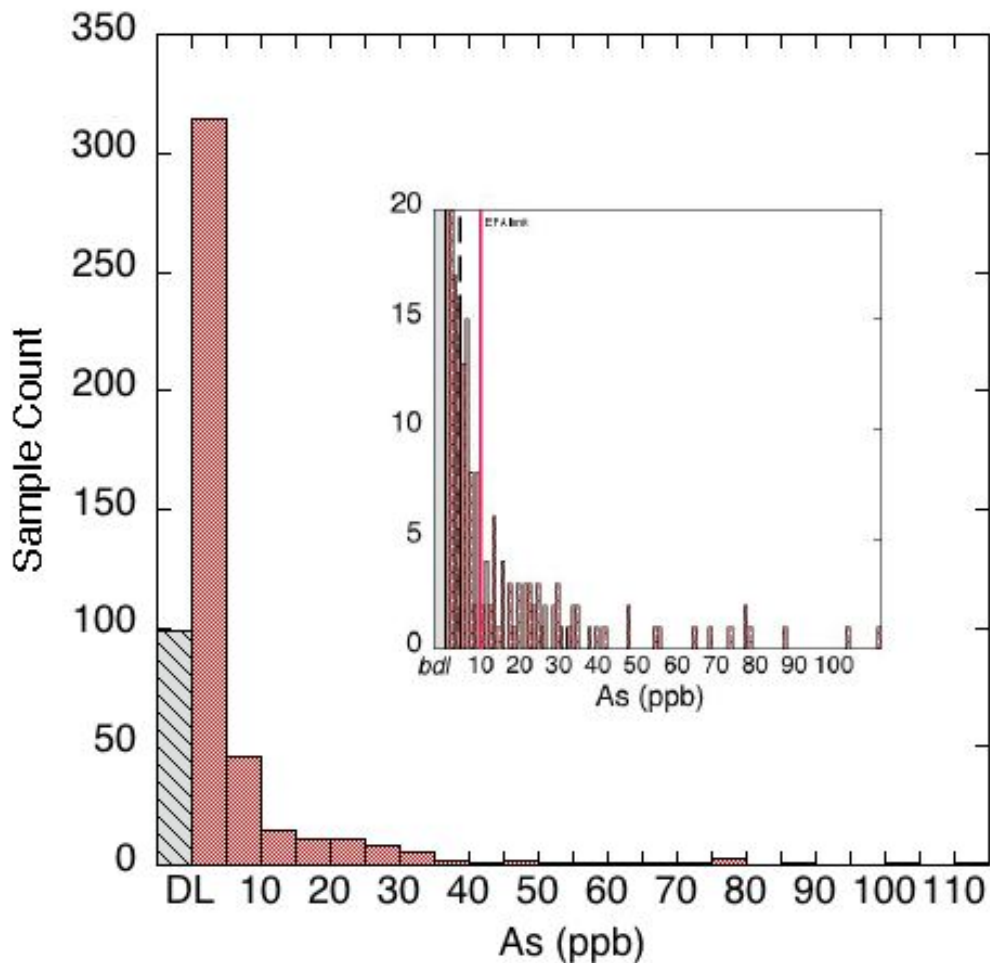E = Pierce Island Portsmouth, NH
X = Control

Figure 2. As concentrations in NH groundwaters. DL refers to the 0.2 ppb detection limit we have established in our lab. Inset allows for the discernment of the relative abundance of samples exceeding recommended drinking water limits.

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.

Results of a time-series project carried out by Mr. Ian Carlisle (UNH BS Geology, 2014) for his capstone research project found ~10% variations in As content in a well over a short sampling time that may link with groundwater recharge associated with storm events. Given the low number of such targeted studies, we recommend future studies should target temporal changes in As abundance.

We are working together with our USGS colleagues to analyze the data in a geospatial framework and plan 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 2013, 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 and Mr. Carlisle, whose analytical and student research 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 the student projects.