Report for 2003NE36B: Assessing the occurrence of Arsenic in groundwater: Implications for Small Water Supply Systems in Nebraska

- Conference Proceedings:
  - Gosselin, David , Lynne Klawer, F.Edwin Harvey, and Kelli Warren, 2004, Arsenic in Nebraska's Groundwater and Public Water Supplies, "in" Geoscience in a Changing World Annual Meeting and Exposition in Denver, CO, Geological Society of America Abstracts, Denver, CO, p. 356.
- Other Publications:
  - Gosselin, Dave, Lynne Klawer, and Angela Noe, 2004, Arsenic in Nebraska's Groundwater and Public Water Supplies, Earth Science Notes No. 7, Conservation and Survey Division, School of Natural Resources, University of Nebraska-Lincoln, 8 pages.
- Articles in Refereed Scientific Journals:
  - Gosselin, David , Lynne Klawer, R.M. Joeckel, F.Edwin Harvey, Angela Noe, and Kelli Warren, 2004, Arsenic in Rural Nebraska Public Water Supplies, Nebraska, U.S.A., Awwa Journal. (In Review)

Report Follows

COVER PAGE

Grant #: 2003NE36B
Funding Period: April 1, 2003 – September 30, 2004
Title: Assessing the Occurrence of Arsenic in Groundwater: Implications for Small Water Supply Systems in NE
Primary PI(s): David Gosselin
Other PIs: Matt Joeckel and Ed Harvey

SYNOPSIS

Title: Assessing the Occurrence of Arsenic in Groundwater: Implications for Small Water Supply Systems in NE

Project Number: 2003NE36B

Start Date: April 1, 2003

End Date: September 30, 2004

Funding Source: 104(b)

Research Category: Groundwater

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Primary PI: David C. Gosselin, Ph.D.

Other PIs: F. Edwin Harvey, Ph.D. and Robert Matthew Joeckel, Ph.D.

Project Class: Research

Summary

This project is part of an on-going state-wide groundwater resource assessment that is currently focused on arsenic. The **long-term goal** of our research is to reduce the economic impact of arsenic regulations on public water supply systems by evaluating less costly options for achieving compliance with the 10 ug/L MCL. The **specific goal of this project** is to improve our understanding of As in Nebraska's groundwater and apply this knowledge to mitigating the impact of As on public water systems.

Specific Objectives

The specific objectives of this state-wide project are: 1. Determine the chemical form in which the arsenic occurs in groundwater; and 2. Determine the geological and geochemical factors that control the occurrence of arsenic.

Results - Objective 1

As part of our EPA-funded reconnaissance sampling of two wells from 10 public water supplies, we tested 20 wells two to five times for arsenate from April through August 2003. Data indicate that arsenate (As^{5+}) comprises between 70 and 90 percent of the arsenic in the following public water supplies: Anselmo, Broadwater, Cambridge, Elwood, Lodgepole,

McCook, Oshkosh, and Stromsburg. The two wells at Benkelman had less than 40 percent arsenate. In Cambridge, there was about a 20 percent difference in arsenate concentration between the two wells tested. Our conclusions thus far are that Arsenic occurs primarily as As^{+5}. This form of arsenic is preferred for most treatment options. However, wells need to be evaluated on an individual basis.

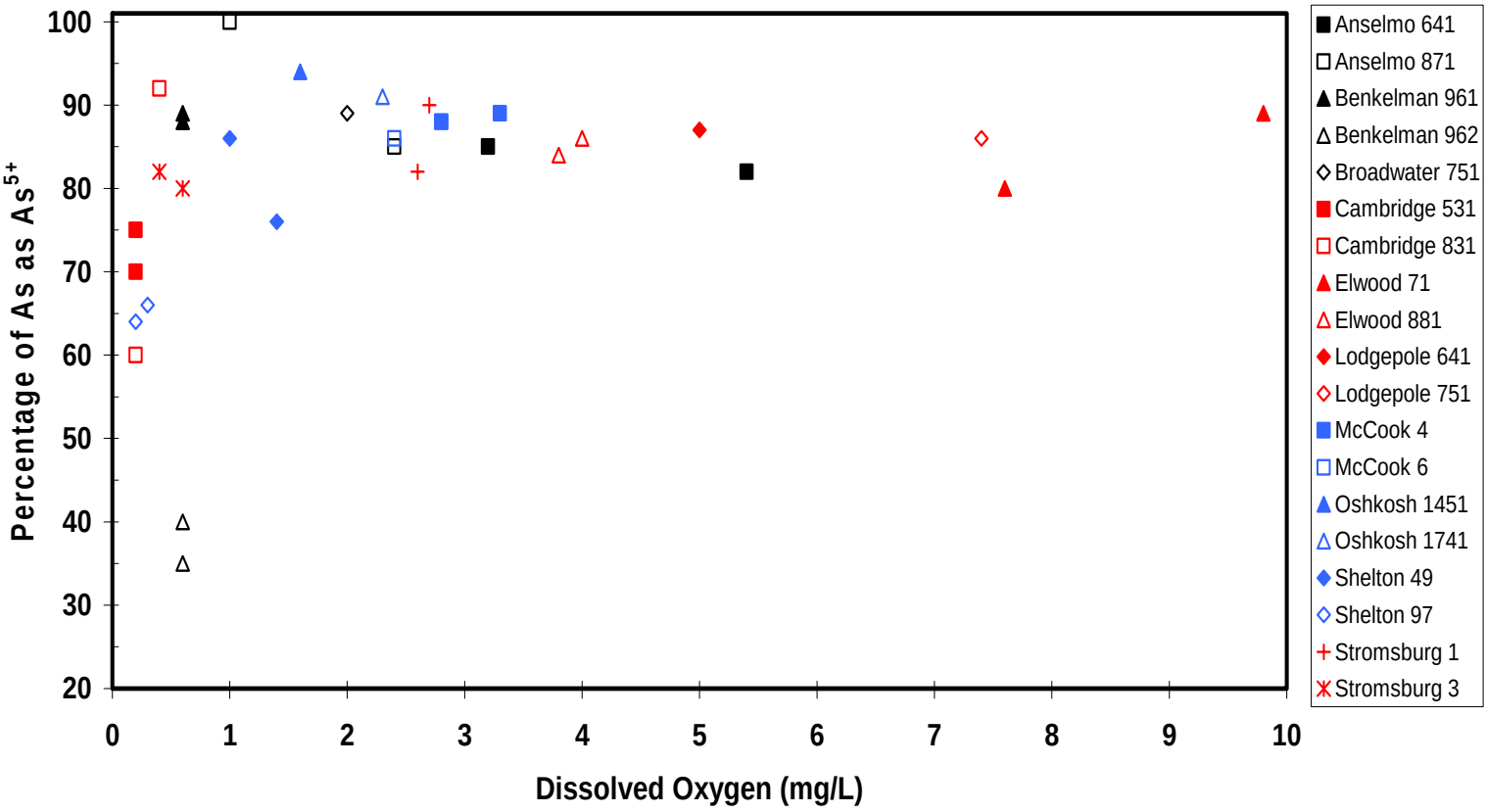

Fig 1. Public water supplies Arsenic5+ concentrations versus dissolved oxygen expressed as percentages.

Results - Objective 2

In Nebraska, arsenic in the groundwater is derived from the interaction between the water and geologic material through which it flows. Therefore, it is crucial to assess the availability of arsenic from the various geologic materials that comprise Nebraska's aquifers. We obtained two cores (~90 feet total) of unsaturated and saturated alluvial sand and gravel from Cambridge in the Republican River valley and from Oshkosh in the North Platte valley. Both of these valleys are recognized for their high arsenic levels. We have also acquired samples from the Conservation and Survey Division archive that includes: Quaternary sand and gravels, loess and glacial till, Cretaceous bedrock, and Tertiary Bedrock. To determine arsenic availability, sequential extraction procedures will be used on approximately 22 samples.

We conducted leaching experiments to assess the source of As in a variety of geologic units including cores specifically extracted for this project. Unfortunately, the results of the experiments were not definitive. The extraction method we used was developed by Keon et al. (2001). Based on data from our initial trial runs with this methodology that provided positive results on our Quality Assurance/Quality Control (QA/QC) samples and selected unknown study samples, we made the decision to use this method and go forward with the extraction process. Archived samples from the Conservation and Survey Division's geologic sample storage facility were obtained from known groups (White River) and formations (Carlile Shale) that should have high arsenic concentrations. These controls as well as a process blank and standard were placed in each extraction group for QA/QC. The results with this second submission did not repeat the trial run's success. The following are examples of the problems we had with the second group: several of the process blanks indicated arsenic contamination while the known standard (15.0 to 40.0 μg/L) indicated no detection or less than 50% recovery; or the standard would have 94% recovery while the blank and samples would test between 6.8 to 10.7 μg/L. In most cases the blank and samples were nearly identical. The laboratory performed an internal audit as our trial run or first submission was tested by a different analyst with very good results. The audit was able to determine that the samples had been diluted far too much by the second analyst especially in comparison to the first analysts work. They also discovered they mistakenly destroyed our samples and therefore were unable to do any retesting. The analyst who performed the second run is no longer with the lab so they will not be able to review with them if there may have been an error in factor multiplication and/or other problems. This investigation took several months and just concluded late winter 2005.

The laboratory has acknowledged their errors and has offered to run new samples at their expense. We plan to perform new extractions sometime this summer –early fall and then submit these samples to the laboratory's first analyst to ascertain if As is present in these samples. We anticipate a successful outcome as in the trial run and would like to add an addendum to this report at that time.

Results - Related EPA-funded Studies

The average concentrations for the 20 public water supplies range from 4.2 to 22.1 μg/L. Twelve of those wells have average As concentrations greater than the MCL. Only four of these (Stromsburg 1 and 3, Anselmo 871, Broadwater 551) have average As concentrations greater than 13 μg/L. An additional four wells (Benkelman 962, Cambridge 831, Lodgepole 751, Oshkosh 1741) have average concentrations between 9.3 and 9.8 μg/L, but they have values that, at times, exceed 10 μg/L. The two wells at Elwood and Shelton 49 have the lowest average As concentrations at 6.3, 5.5, and 4.2 μg/L, respectively. Wells from the same PWS which derive their water from similar geologic units can have comparable As concentrations (for example, McCook); or one well can have concentrations up to 60 percent higher than another (for example, Anselmo). Arsenics concentrations varied by as little as 1.5 μg/L to as much as 7.0 μg/L in individual wells over the one-year study. In some cases, the apparent variation in As concentrations brings the well into compliance with the MCL. Analytical variability may be responsible for up to at least +/- 10% of the observed variation among the samples.

Our conclusions thus far are as follows: 1. Arsenic concentrations are variable in individual wells on different time scales. 2. In some cases, monthly variability is large enough to bring the As concentrations into compliance with the MCL. However, this variability is not predictable. 3.

A well should be pumped for at least 30 minutes prior to sampling. Mitigating arsenic by well field management does not appear to be an adequate solution for PWS.

Recommendations for Water Quality Management

1. USGS and NURE data document a complex spatial and geologic distribution of As in ground water throughout Nebraska. The non-uniform occurrence of As reflects differences in the geology, ground-water flow systems, and associated geochemical environments throughout the state. The geologic, hydrogeological and geochemical factors make the prediction of As concentrations very difficult. It is recommended that assessing historical, quality controlled data and information can improve the likelihood of finding a new source of water that has lower arsenic concentrations.

2. Although our data were relatively constant, in some parts of the U.S. individual PWS wells show significant variability. We recommend four quarterly samples to assess the extent to which the drinking water public is exposed to As.

3. Short-term pumping tests indicate As concentrations can be variable during the first 30 to 60 minutes of pumping. It is recommended that a well be allowed to pump for at least 30 minutes prior to sampling. *(Current NHHSS protocol states "Allow the cold water tap to run approximately 3 minutes." NHHSS is now revising the sample protocol because of the 24-hour pump test results and this studies recommendation.*) An alternative sampling protocol that could be used is that the well should be sampled at the midpoint or average time that the pump typically runs if the primary purpose of the sampling is to assess the As concentrations to which the drinking water public is exposed.

4. Annual and short-term pumping test data indicate that mitigating As by pumping management is not an adequate solution for public water supplies.

5. Arsenic occurs primarily as arsenate, As^{+5}, in the public water supplies assessed in this study. This form of arsenic is preferred for most treatment options. Although our data indicates that arsenate predominates, it is recommended that wells need to be evaluated on an individual basis.

6. To address the arsenic issue, partnerships between local communities and the University of Nebraska's Public Policy Center, UNL Water Research Initiative, the UNL Rural Initiative and state regulatory agencies should be used to assist communities in their decision-making process regarding the various options to lower arsenic concentrations.

7. Continue outreach and information dissemination through the Arsenic Information Website: http://nesen.unl.edu/nearsenic.

Additionally, we have been funded from Region 7 of the U.S. Environmental Protection Agency (Federal Assistance Identifier MM-98749401-0) to continue our work with 13 additional Nebraska PWS. This study will run through October 31, 2005 and will include the appropriate recommendations discussed previously.

We are also working with the Nebraska Health and Human Services System on the following project: “Evaluation of Geologic Rehabilitation of Public Water Supply Wells Having High Arsenic and Uranium: A Collaborative project between NHHSS and UNL”. Characterizing As concentrations at distinct intervals within a well will be important to determine the factors that influence the availability of As. This study will focus on the vertical distribution of As in Nebraska’s alluvial sediments and document the extent to which it occurs in association with clay-bearing units. The project is scheduled to run through the summer (2005) with anticipated results by late summer early fall.

Information Dissemination

Project information has been disseminated through a variety of avenues including 18 newspaper articles, 14 arsenic study presentations, 11 Nebraska Public Policy Center Community Water and Development Project presentations, eight poster presentations, three educational outreach activities, two radio interviews, and one University of Nebraska-Lincoln Conservation and Survey Division Publication . The Arsenic Information System website (http://nesen.unl.edu/nearsenic/) was developed to inform not only the PWSs involved in the project, but also a wider audience such as educators, researchers, government agencies and the public in general.

Additional Funding

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Sources of Information

Keon, N.E.; Swartz, C.H.; Brabander, D.J.; Harvey, C.; & Hemond, H.F., 2001. Validation of an arsenic sequential extraction method for evaluating mobility in sediments. *Environmental science & Technology* 35(13):2778.

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