Arsenic concentrations in domestic well-water in many regions of Minnesota exceed the public drinking-water standard set by the U.S. Environmental Protection Agency.

Arsenic concentrations in domestic well-water throughout large regions of Minnesota exceed the public drinking-water standard set by the U.S. Environmental Protection Agency (Figure 1, p. 4). The scale of the problem is illustrated by the Minnesota Department of Health’s Minnesota Arsenic Research Study, which found that 50% of the 869 domestic wells tested in west-central Minnesota had arsenic concentrations greater than the 10 micrograms of arsenic per liter of water standard. The frequency of arsenic contamination in domestic wells is a serious and widespread public-health concern; long-term exposure to arsenic is toxic to humans, even at extremely low concentrations. In response to this challenge, the Minnesota well code now requires that each new potable water-supply well, estimated at 8,000 to 12,000 wells annually, be tested for arsenic. These tests provide families with important information about drinking-water quality. However, the information can come only after the well has been drilled. Although homeowners can purchase arsenic-removal systems, they are expensive, require maintenance, and do not provide alarms for high arsenic concentrations or system failure. It would be preferable if wells could be placed where the risk of arsenic contamination of groundwater is known to be low.

In Minnesota, the groundwater that provides drinking water to domestic wells commonly comes from glacial deposits, which are composed of discontinuous layers of sand and gravel, called aquifers, as well as very fine-grained sediments such as silt and clay, called aquitards. The layering of these sediment deposits is called stratigraphy. Groundwater (and thus well-water) is stored in the sand and gravel layers. Fine-grained deposits called confining layers form low-permeability boundaries between aquifers (Figure 2, p. 5).
Melinda Erickson and Randal Barnes from the University of Minnesota have demonstrated that the proximity of well screens—a filtering device that screens out sand and gravel from groundwater—to confining layers within glacial deposits is a contributing factor to elevated arsenic concentrations in excess of 10 micrograms of arsenic per liter in Minnesota well-water. However, the exact conditions that lead to unhealthy water in an individual well are not known. In particular, the unexplained variability in arsenic concentrations among domestic wells with similar dissolved chemical composition and geographic proximity currently limits our ability to anticipate where safe drinking water is located in aquifers. Minnesota state agencies have for many years studied groundwater chemistry, geology, and hydrogeology in arsenic-affected areas. To date, the databases from these studies have not been fully integrated, and an understanding of the natural and human-influenced processes that drive arsenic from geological materials into domestic drinking water remains elusive. This knowledge gap limits the efficacy of public policies directed at wise placement and construction of new wells. Progress on this issue requires integrated efforts of public agencies and multiple scientific disciplines.


Arsenic from Rocks: Sources and Release Mechanisms

Evidence suggests that one source of arsenic in groundwater is rocks (solids) within or adjacent to aquifers. Researchers are in the process of identifying the specific types of rocks that release arsenic into groundwater in Minnesota. One suspect is shale, a rock type whose fragments are present in glacial deposits in Minnesota and other Midwest states. However, no one has yet demonstrated a correlation between total solid arsenic concentrations in rocks and total dissolved arsenic concentrations in adjacent groundwater. This is the crux of the arsenic paradox: Arsenic is a rock-derived, naturally occurring groundwater contaminant, but rock concentrations have no apparent correlation to the water-arsenic concentration in adjacent groundwater. The paradox suggests that perhaps the most important factor is not how much arsenic is present in rocks, but rather the types of rocks and minerals that hold the arsenic.

Arsenic can be found in iron-bearing minerals such as pyrite (an iron sulfide) and ferrihydrite (an iron oxyhydroxide). From the perspective of arsenic retention and release to groundwater, these two minerals are arsenic reservoirs that have strong potential to release arsenic to water when chemical conditions in the aquifer change. For example, pyrite is typically a stable arsenic reservoir when oxygen in groundwater is low in concentration. When oxygen is introduced into groundwater via a domestic well, pyrite can dissolve and release arsenic into...
the groundwater. Conversely, ferrihydrite is stable in the presence of oxygen and tends to retain arsenic under such conditions. However, when oxygen concentrations drop, the ferrihydrite can dissolve and release arsenic into groundwater.

**A Strategy for Understanding Arsenic in Minnesota Groundwater**

The overall goal of our research effort is to help Minnesotans to place their wells where the probability of safe water is highest. Our research strategy has involved gathering and integrating existing geographical information systems (GIS) databases that have information relevant to arsenic in groundwater, conducting research in regions of the state where aquifers are well understood, inviting experts from multiple disciplines to work collaboratively, and building novel geochemical databases from state-of-the-science measurements. To unravel the arsenic paradox, we have also attempted to bring new research perspectives to existing databases by working to identify the chemical form of the arsenic in aquifer and confining-layer rocks (called arsenic speciation), to determine the depth and geographic location of arsenic-bearing aquifer and confining-layer rocks (distribution), and to describe the conditions leading to arsenic release from aquifer and confining-layer rocks to groundwater (biogeochemical processes).

**Synthesis of Existing GIS Databases.** We have completed the integration of existing GIS databases for our research (Table 1, p. 7). The specific databases we used were strong candidates for providing arsenic-relevant information— for example, well placement and construction, surface water bodies and water quality (lakes and rivers), groundwater location (aquifers and confining layers), underground geology, land-surface geology and land use, arsenic concentration in groundwater, and other chemicals in groundwater.

**Focus on Regions with Elevated Arsenic and Documented Aquifers and Confining Layers.** The Traverse-Grant region of west-central Minnesota has an abundance of wells with elevated levels of arsenic (Figure 1). In addition, multiple databases exist with information for the Traverse-Grant region relevant to our study of arsenic release to groundwater. These datasets were generated by the Minnesota Department of Health, the Minnesota Department of Natural Resources–Division of Water, and the Minnesota Geological Survey. The availability of this much complementary information for a region in Minnesota is uncommon, and was the primary motivation for beginning our research efforts in the Traverse-Grant region.

In addition to databases, the original rotary-sonic drill cores used to generate the maps of underground geology in the Traverse-Grant region are still available from the Minnesota Department of Natural Resources–Division of Lands and Minerals. Rotary-sonic drilling extracts intact cylinders of sediment about 10 centimeters (approximately 4 inches) in diameter. An average length of core brought up by the drill crew for each drill run is about 6 meters (roughly 20 feet) in length, and drilling operations can access depths of 120 meters (400 feet) below the ground surface. These cores were drilled in numerous locations (Figure 3, p. 8), and are stored in four-foot boxes in the archive facility in Hibbing, Minnesota.

In May 2009, we sampled 10 archived rotary-sonic drill cores from the Traverse-Grant region of Minnesota from among 250 archived samples that
were available. In particular, we sampled the interfaces between layers of sediments deposited by glaciers (glacial tills) that have low-water permeability (confining layers) and sand and gravel deposits with higher water permeability (aquifers) (Figure 2). We chose these samples because Erickson and Barnes previously observed a correlation between elevated arsenic concentrations in well-water and the proximity of the well screen to glacial-till, or confining-layer, deposits.

**Measuring Arsenic Speciation and Distribution in Glacial Deposits in Minnesota.** Our analysis of the archived Traverse-Grant core samples is ongoing. We are subjecting the glacial tills (confining layer) and sand and gravel (aquifer) deposits from the Traverse-Grant region to a laboratory procedure called *sequential extraction*. Sequential extractions allow us to identify different forms of arsenic, and are especially useful in identifying arsenic that is easily released from aquifer or confining-layer rocks. The results of the sequential extractions will be added to our now completed GIS database for future analysis. The sequential-extraction data will also be interpreted in the context of biogeochemical conditions in the subsurface aquifer. Our hypothesis is that the most important information is not how much arsenic is present in aquifer solids, but the specific forms of arsenic that are present. Our sequential extractions are the first step in identifying the chemical form(s) of arsenic in the geological materials holding groundwater in west-central Minnesota.

The best method for measuring arsenic speciation in aquifer and confining-layer solids is X-ray absorption spectroscopy. This technique measures the exact form of arsenic without any chemical preprocessing of the sample and avoids the assumptions required for the sequential extractions. We have used two of the Department of Energy’s synchrotron facilities to conduct these analyses: the Advanced Light Source in Berkeley, California and the Advanced Photon Source in Argonne, Illinois.

Our data tell us that arsenic speciation in glacial tills (confining layers) can be complex. We have observed three different forms of arsenic in approximately equal proportions (Figure 4, left, p. 9): arsenic $1^-$, $3^+$, and $5^+$. The Arabic numerals refer to the charge of the arsenic atoms, and this information helps us to understand how arsenic-bearing rocks and minerals will respond to changing conditions in the aquifer. For example, an aquifer that has arsenic with lower valence states is more likely to release arsenic if dissolved oxygen increases.

However, valence state does not tell us everything we need to know about arsenic speciation. Our X-ray absorption spectroscopy measurements also help us to identify the form of arsenic present. The arsenic species we observed can be divided into three basic categories (Figure 4, right, p. 9): arsenate and arsenite salts, arsenic stuck (adsorbed) to minerals or dissolved, and arsenic in sulfur-bearing minerals. We can interpret each of the categories in terms of potential arsenic release to groundwater.
For example, the arsenate and arsenite salts may indicate the amount of arsenic in groundwater at the time of drilling. This arsenic-speciation category is easily released to groundwater. The adsorbed portion of the total arsenic may be stable arsenic, meaning that the arsenic will remain associated with the mineral unless the chemistry of the groundwater changes. Changes in an aquifer that could lead to arsenic release to groundwater include phosphorus contamination of the groundwater (which can replace adsorbed arsenate and arsenite at mineral surfaces and release arsenic into groundwater), and low-oxygen conditions—brought on, for example, by biological activity (which can result in the dissolution of iron oxyhydroxide minerals, such as ferricydrate, releasing adsorbed arsenic into groundwater). For the glacial-till sample for which data are presented in Figure 4, more than half of the total arsenic was present in sulfur-bearing minerals. This portion of the arsenic should remain in the solid phase under low-oxygen conditions. When these rocks and minerals are exposed to

Table 1. Summary of GIS Database Integration for Arsenic Geochemistry

<table>
<thead>
<tr>
<th>Database</th>
<th>Source</th>
<th>Description</th>
<th>Relevancy to Arsenic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minnesota Arsenic Research Study</td>
<td>Minnesota Department of Health</td>
<td>Focused arsenic water study of west-central Minnesota domestic wells</td>
<td>Focused geochemical database of domestic wells that can then be correlated with sediment cores</td>
</tr>
<tr>
<td>County Well Index</td>
<td>Minnesota Geological Survey (MGS) and Minnesota Department of Health</td>
<td>Extensive well data containing location, depth, and static water level for wells drilled in Minnesota, as well as stratigraphy</td>
<td>Locations of all domestic wells in state that include “cuttings” record with general water and sediment data</td>
</tr>
<tr>
<td>Rotosonic</td>
<td>Department of Natural Resources (DNR)</td>
<td>Drilled, stratigraphically intact cores cataloged and stored in Hibbing</td>
<td>The intact, stratigraphic layers allow us to interpolate out and model the subsurface layer and hydrology</td>
</tr>
<tr>
<td>Groundwater Monitoring Assessment Program</td>
<td>Minnesota Pollution Control Agency</td>
<td>A sampling of nearly 1,000 private Minnesota wells throughout the state for geochemistry</td>
<td>Geochemical database of domestic wells that can then be correlated with sediment cores</td>
</tr>
<tr>
<td>Digital Elevation Model</td>
<td>Minnesota Land Management Information Center</td>
<td>Digital elevation model for the entire state of Minnesota</td>
<td>Allows us to digitally align data layers with elevation to get topography and visual information for modeling and figure purposes</td>
</tr>
<tr>
<td>Geomorphology</td>
<td>University of Minnesota at Duluth-MGS-DNR</td>
<td>Surface map of the various geomorphology types and boundaries in Minnesota</td>
<td>Provides surface layer that can inform us of what material and how groundwater recharge is coming through and how that might affect the arsenic cycle</td>
</tr>
<tr>
<td>Traverse-Grant Hydrogeology</td>
<td>MGS-DNR</td>
<td>Highly detailed surface and subsurface hydrogeology of the Traverse-Grant region of west-central Minnesota</td>
<td>Critical, extensive database that has already interpolated and analyzed water-sediment interactions and integrated several databases</td>
</tr>
</tbody>
</table>

Photo courtesy of Brandy M. Toner.

Research-team members Alan Knaebel, Sarah Nicholas, and Gary Meyer examine new drill-core materials obtained from a rotary-sonic drill core operation.
Using Arsenic Speciation to Improve Drinking-Water Quality

For the glacial-till (or confining-layer) sample discussed in the previous section (which has 4.25 milligrams of arsenic per kilogram of solid sediment), we estimate that if all of the arsenic in a one-liter volume of aquifer material is released, then a concentration of 22 milligrams of arsenic per liter of water would result. This value is approximately 2,000 times the maximum contaminant level of 10 micrograms of arsenic per liter of water permitted by law. Thankfully, in the existing groundwater surveys, arsenic concentrations this high have not been encountered.

However, the calculation provides some perspective on why large regions of Minnesota have elevated groundwater arsenic: Only a little arsenic must be released from the solid phase to cause health concerns. The possibility of households with groundwater wells having very high levels of arsenic is a genuine risk given what we know about the heterogeneity of arsenic speciation in groundwater.

Although the well code now requires all new wells to be tested for arsenic, the next step must be to better understand which aquifers present elevated risk for arsenic contamination. Can the below-ground geologic information currently available help us identify aquifers that have higher risk for elevated arsenic in groundwater? Or, to put it another way, do glacial deposits have a uniform or predictable arsenic speciation? The research effort required to satisfactorily answer this question is beyond the scope of one research group or a single state or federal agency. To gather expertise and resources together to address this question, we have formed a new group, the Minnesota Arsenic Geochemistry Consortium.

Leveraging Resources: The Minnesota Arsenic Geochemistry Consortium

The consortium is a multidisciplinary group composed of scientists and professionals from five institutions and agencies: the University of Minnesota, the U.S. Geological Survey, the Minnesota Department of Natural Resources—Division of Waters, the Minnesota Department of Health, and the Minnesota Geological Survey. The strength of this group comes from the diversity of disciplinary perspectives represented by individual members, as well as the complementary missions of the agencies and institutions they serve.

The primary goal of the consortium is locating and preserving safe drinking water for communities in Minnesota. Achieving this goal requires good communication among members to leverage expertise and resources through joint field research, laboratory analyses, database building and integration, and policy-relevant data interpretation. To facilitate a discussion of the current state of knowledge around issues related to arsenic in Minnesota groundwater, we hosted a day-long symposium at the University of Minnesota in 2009. A consensus emerged among participants that new scientific approaches are needed to address the sources of arsenic in groundwater, and that one key area for collaboration is a shift in focus from total arsenic concentrations to solid-phase arsenic speciation and the origin of glacial deposits. In addition, participants agreed that coordinated research efforts could yield substantial progress in understanding arsenic contamination of groundwater; that collaboration adds value to mission-oriented agency activities; and that opportunities exist to share funds, expertise, personnel, and equipment.

After the symposium, consortium members identified joint projects where field, laboratory, and computational research could be coordinated to share information and maximize efficiency, and some collaborative work has begun. For example, fresh aquifer and confining-layer sediment samples are important for the next phase of
arsenic-speciation research, but the rotary-sonic drilling operations needed to obtain the samples are resource intensive. In response to this challenge, the Minnesota Geological Survey invited members of our research team to participate in two rotary-sonic drill core operations during 2010. These operations resulted in 426 arsenic samples from 10 new rotary-sonic drill cores from south-central Minnesota (Sibley, Nicollet, and Blue Earth Counties) (Figure 3). These samples were collected in the field during drilling operations, then preserved in argon gas and frozen. To the best of our knowledge, this is the most robust preservation to date for arsenic-speciation samples. The U.S. Geological Survey also collected 120 sediment samples from these rotary-sonic drill cores to augment our current research. The collaborative efforts of the Minnesota Arsenic Geochemistry Consortium will continue to yield valuable results as the Minnesota Geological Survey and U.S. Geological Survey complete their below-ground geological and geochemical analyses. These research outcomes will ensure that the arsenic-speciation data generated by the University of Minnesota will have maximum utility for understanding where arsenic will be a problem in groundwater. In addition, these new studies will allow us to apply the methods developed with the archived cores for the Traverse-Grant region to new areas of the state.

Looking ahead, we recognize that the path toward safer drinking water will not be easy. The work will continue to require a high level of coordination in research activities, integration and interpretation of complex databases, and innovation in data analysis by experienced professionals from multiple disciplines. Currently, we are working hard to understand the relevant (and feasible) spatial scale(s) for subsurface arsenic-speciation mapping in Minnesota, with the goal of building a useful subsurface map for guiding domestic well-drilling.

Brandy M. Toner is an assistant professor at the University of Minnesota in the Department of Soil, Water, and Climate, and a graduate faculty member in the earth sciences, water resources science, land and atmospheric sciences, and environmental engineering graduate programs. She is a low-temperature geochemist and spectroscopist, and her research focuses on how metals move through natural systems. Sarah L. Nicholas is a Ph.D. student in the land and atmospheric sciences graduate program in the Department of Soil, Water, and Climate at the University of Minnesota. Her dissertation research examines the solid-phase sources of arsenic in Minnesota groundwater. Lindsey J. Briscoe is a researcher in the field of environmental geochemistry at the University of Minnesota in the Department of Soil, Water, and Climate. In the fall of 2011, she began a Ph.D. program in earth sciences at the University of Minnesota. Alan R. Knaeble is a senior scientist at the University of Minnesota in the Department of Geology and Geophysics. He has worked for 20 years as a glacial geologist, mapping glacial deposits throughout Minnesota. His work has focused primarily on mapping surface and subsurface deposits to understand the glacial history and stratigraphy across central Minnesota. He also supervises the sediment and core laboratories at the Minnesota Geological Survey. James A. Berg is a hydrogeologist with the Minnesota Department of Natural Resources. He works in the county atlas program which, along with the Minnesota Geological Survey, produces county-scale maps showing the distribution of aquifers, groundwater-flow directions, distribution of natural geochemical characteristics, and aquifer pollution sensitivity. He has produced atlases and regional assessments of the elevated arsenic regions of western Minnesota. Melinda L. Erickson is the groundwater

Note: As = arsenic, S = sulfur

Figure 4. Arsenic Valence States and Major Arsenic Species for a Minnesota Glacial Till (73-foot depth)

<table>
<thead>
<tr>
<th>Arsenic Valence States</th>
<th>Major Arsenic Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(3+)</td>
<td>Arsenate + arsenite salts</td>
</tr>
<tr>
<td>As(1-)</td>
<td>As adsorbed to minerals or dissolved</td>
</tr>
<tr>
<td>As(5+)</td>
<td>As in S-bearing minerals</td>
</tr>
</tbody>
</table>

As in S-bearing minerals

[Diagram of Arsenic Valence States and Major Arsenic Species]
specialist in the Minnesota Water Science Center of the U.S. Geological Survey, and a faculty member at the University of Minnesota. Her primary research interests are the geochemistry, fate, and transport of organic chemicals and metals in groundwater. She has been involved in research related to better understanding naturally occurring elevated arsenic in upper Midwest groundwater since 1998. The research on which this article is based was supported in part by a grant from CURA’s Faculty Interactive Research Program. The program was created to encourage University faculty to conduct research with community organizations and collaborators on issues of public policy importance for the state and community. These grants are available to regular faculty at the University of Minnesota and are awarded annually on a competitive basis. Additional funding was provided by the College of Food, Agricultural and Natural Resource Sciences at the University of Minnesota, which provided research start-up funds to Brandy Toner.

**2012–2013 Faculty Interactive Research Program Competition**

The Center for Urban and Regional Affairs invites proposals for our Faculty Interactive Research Program. The purpose of the program is to encourage University faculty members to carry out research projects that involve a significant urban-related public policy issue for the state or its communities, and that include active engagement with groups, agencies, or organizations in Minnesota involved with the issue. Each award will provide support for one month of the faculty member’s time in the summer of 2012 and a half-time graduate research assistant for the 2012–2013 academic year. Where appropriate, we can provide limited support for miscellaneous research expenses. Supplemental funding for a half-time graduate research assistant in the summer of 2013 is available to successful proposals that contribute to the planning and development of the University’s vision to create a new, sustainable community on the 5,000-acre UMore Park property in Dakota County. For those interested in learning more about eligible research opportunities with UMore Park, an informational forum and networking opportunity will be held on January 26, 2012 from 1 to 3 PM. Contact Brianna Chatters at chatt033@umn.edu for details.

Faculty members who are selected will be expected as part of their project to: interact or engage with appropriate community organizations or agencies, prepare a report for the organization or agency where appropriate, and prepare a 3,500-word manuscript for publication in the CURA Reporter.

Research projects should focus on issues and concerns important to Minnesota, such as communities of color, the criminal-justice system, demography, state or local economic development, education, employment, energy, the environment, health, housing, state and local government, welfare and poverty, human and social services, transportation, or land use and development. A list of recently funded projects can be found on the CURA website at www.cura.umn.edu/FIRP/projects.

Applications are invited from all University faculty members who, in conformity with the tenure regulations, are classified as “regular” (tenure code = P,N,C) members of the faculty. The program is designed particularly for faculty who hold 9-month appointments (appointment term not equal to “A”), although we have frequently supported projects of regular faculty on 12-month appointments. In special cases, we can support joint projects.

During the period of support for the faculty member, the recipient of the project award is expected to be devoted to the project full-time; accordingly, those receiving awards may not accept other employment. This provision does not preclude acceptance of additional supplementary support for the same project, except for that portion allocated to the faculty member’s salary.

More information, including application instructions and forms, can be found at www.cura.umn.edu/FIRP/announcement. Applications must be received in the CURA office by 4:30 PM, Friday, March 30, 2012. Grant recipients will be notified in April. Please contact Ed Goetz at 612-624-8737 or egoetz@umn.edu if you have questions.