Understanding Natural Geochemistry

What's the issue?

As groundwater flows through rock formations and past mineral deposits, it dissolves metals and other elements into the water. Even groundwater that looks clear typically has many substances in it. Often, these chemicals are dissolved at non-toxic concentrations and do not affect how safe the water is to drink. Some of them – such as iron and sulfate – we remove for aesthetic reasons. Occasionally, natural elements do dissolve at high enough concentrations that they can affect the safety of humans and the environment.

Natural geologic formations are sources of trace elements that can be released to groundwater under certain circumstances. *Photo: WGNHS*

A complex combination of geochemical factors affects whether or not an element will leach into groundwater at dangerous levels. For any element that exists in a rock formation, the stability of the mineral in which it is incorporated as well as the temperature, pH, and oxygen dissolved in the groundwater strongly control the degree to which it mobilizes. Identifying where and why naturally occurring substances are released to groundwater requires detailed local information about all of these factors as well as extensive understanding of when small changes in one property might cause large changes in another. Developing this basic scientific knowledge is the critical first step toward developing recommendations for public water systems, homeowners, and well drillers that effectively protect the health and safety of the people of Wisconsin.

GCC in Action: *Discovery of Naturally-Occurring Arsenic in Wisconsin Groundwater*

An early example of advances in geochemical understanding in Wisconsin leading to protection of public health is the story of arsenic. Naturally-occurring arsenic was unexpectedly discovered in 1987 during a feasibility study for a proposed landfill in Winnebago County. Follow up sampling by the Department of Natural Resources (DNR) and reports from nearby homeowners indicated the problem appeared to be widespread in the region, more likely due to natural sources than industrial contamination. As a result, in 1992 the DNR, the Department of Health Services (DHS), and local health officials teamed with researchers funded by the Wisconsin Groundwater Research and Monitoring Program (WGRMP) to sample thousands of private wells in the Winnebago and Outagamie counties and later surrounding counties to analyze where and why arsenic levels were elevated (Burkel, 1993; Burkel and Stoll, 1995). These initial studies confirmed that the arsenic was naturally occurring and isolated the geologic formations acting as sources. Further geochemical studies linked arsenic mobilization to oxidation of pyrite and associated it with low pH and fluctuating groundwater levels. This information helped the DNR outline a Special Well Casing Depth Area (SWCDA) and develop well construction guidelines to protect drinking water wells in this area from exposure. Simultaneously, DHS worked with local health officials to inform residents of health risks, provide low-cost testing of private wells, and gather information about people with long-term exposure to arsenic in one of the largest epidemiological studies ever conducted in Wisconsin (Knobeloch, 2002; Zierold et al., 2004).

In the early 2000s, the Environmental Protection Agency (EPA) lowered the maximum contaminant level for arsenic from 50 ppb to 10 ppb (the current standard), which raised concerns for schools and residents in southeastern Wisconsin that had been observing arsenic levels in the 10-50 ppb range. Initial testing by the DNR and WGNHS revealed that the geochemical explanations for arsenic contamination in northeastern Wisconsin could not explain the problem in southeastern Wisconsin (Gotkowitz, 2002), so the WGRMP funded further research to analyze the sources and mechanisms of arsenic release in the region and develop more appropriate guidelines (Sonzogni et al., 2003; Bahr et al., 2004; West et al., 2012). One of the important outcomes of more recent studies has been improved understanding of how chlorine disinfection, which is often used to treat microbial biofilms (slime) in wells, can affect the release of arsenic (Gotkowitz et al, 2008). While chlorination must be limited in much of northeastern Wisconsin since it has a similar effect as oxygen on sulfide-bound arsenic, it does not affect arsenic bound to iron compounds in southeastern Wisconsin and may in fact help reduce arsenic levels in those areas by controlling microbes that contribute to iron dissolution.

DHS and DNR staff presenting on health implications of arsenic at an Ozaukee County well water informational event attended by over 150 residents. *Photo: Ozaukee County Public Health Department*.

Understanding the occurrence of arsenic in Wisconsin's groundwater is a classic example of interagency cooperation. Initial work with DHS and local health departments and town boards in the early 1990s effectively defined the problem and raised awareness. Research supported by the joint solicitation helped define the extent and mechanisms of release in northeastern Wisconsin. With assistance from well drillers, the DNR used this scientific information to identify drilling methods that reduce arsenic in the SWCDA. Importantly, when evidence emerged that southeastern Wisconsin is also vulnerable to high arsenic, the solutions that were effective in northeastern Wisconsin were not simply applied to the area. Rather, careful study informed more appropriate and effective solutions for the new region of concern, leading to better protection of drinking water and public health.

Other Projects in Other Places

Radium in Southeastern Wisconsin

Another well-known example of natural contamination in Wisconsin is radium in southeastern Wisconsin. By the late 1990s, drawdown in this region due to decades of large-scale pumping was causing concerning increases in radium levels in drinking water. Initial links between radium and geologic formations in eastern Wisconsin had been drawn by GCC researchers in 1990 (Taylor and

Mursky, 1990), but the source of radium was poorly understood, making it difficult to know how to manage drinking water sources. Research funded by the WGRMP in the late 1990s more clearly demonstrated that high radium is most common near the edge of the Maquoketa shale, which runs from Brown County in the north to Racine County in the south (Grundl, 2000). A remaining puzzle was why radium levels were elevated to the east of the Maquoketa shale boundary but not to the west – conventional understanding of the sources of radium did not seem sufficient to explain observations. In the early 2000s, researchers at the University of Wisconsin and the Wisconsin Geological and Natural History Survey (WGNHS) leveraged new models and knowledge about groundwater flow patterns in the Waukesha area to elucidate the relationship between radium and sulfate minerals in the area, collecting much needed information on the geochemical backdrop of the region in the process (Grundl et al., 2003). Today, there are still unanswered questions about the precise geochemical processes that control radium activity, but our improved understanding of radium sources helps water managers in eastern Wisconsin define their options: treat water from deep aquifers, blend with water from shallow aquifers, or find alternate surface sources for drinking water.

Chromium in Dane County

More recently in Dane County, residents were surprised to learn in 2011 that hexavalent chromium (Cr [VI]) is present in Madison drinking water in very low concentrations. While trivalent chromium (Cr [III]) is an essential trace nutrient in low concentrations, Cr (VI) is a suspected carcinogen. As DHS responded to questions about the health effects of Cr (VI), WGNHS quickly embarked on a sampling study to determine whether there was a naturally occurring source of chromium in the local bedrock formations (Gotkowitz et al., 2012). Findings indicate that chromium naturally occurs in all formations, but only the upper aquifers seem to have the geochemical conditions to promote mobility of aqueous Cr (VI). WGRMP-funded researchers at UW-Madison and the Wisconsin State Laboratory of Hygiene followed up with a project to explore what geochemical environments create ideal conditions for Cr (VI) mobility in key geologic formations across the state (Gorski et al., 2015). Work like this helps Wisconsin communities prepare for a federal drinking water standard for Cr (VI), which does not currently exist but is expected to in the future.

Sampling irrigation wells for Cr(VI). *Photo: Patrick Gorski*

Discovery triggers geochemical questions, science improves understanding and helps GCC agencies better protect human health – this pattern is repeated by GCC agencies and researchers whenever natural contaminants are identified in groundwater in unexpected amounts in a new location. This continues today with ongoing investigations that are exploring the occurrence of strontium near Green Bay and the presence of heavy metals in geologic formations near LaCrosse, among others.

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