NATURALLY OCCURRING ELEMENTS

Key Takeaways

Naturally occurring elements, including radionuclides, chromium, manganese and strontium occur in Wisconsin groundwater, sometimes at concentrations that exceed health guidance levels. Natural earth processes, such as rock weathering, soil erosion and mineral dissolution can cause trace elements to be released into groundwater. In areas where naturally occurring elements may be present in groundwater at levels close to or above health guidelines it is important to regularly test groundwater drinking water supplies to ensure that they are safe.

GCC member agencies continue to work on multiple initiatives related to ensuring that the public is aware of the possibility of high levels of naturally occurring elements including radionuclides, chromium, manganese and strontium in groundwater drinking water supplies (see groundwater management sections – DHS, DNR and UW).

For actions to address naturally occurring elements contamination in groundwater, see the Recommendations Section.

Sections in this document

What are Naturally Occurring Elements and how widespread are they in Wisconsin?

Radionuclides occur naturally in rock formations, and every well in Wisconsin contains some level of dissolved radionuclides. Strontium and hexavalent chromium are metallic elements that may be naturally occurring in rock and soil. Manganese is a common, naturally occurring element found in rocks, soil, water, air and food. Under certain geochemical conditions, such as reducing oxidation-reduction (redox) conditions, these metals may be dissolved from rock or soil and mobilized in groundwater. Human-caused contamination may also be a source of these metals in groundwater.

Radionuclides

Radionuclides are radioactive atoms. It is possible for radionuclides to be created, as is the case with some materials from nuclear power reactors, but they also occur naturally in rock formations and are released to groundwater over millions of years by geochemical reactions. Common naturally occurring radionuclides in groundwater include uranium and thorium, which both decay to different forms of radium, which in turn decays to radon.

Area of Wisconsin where most of the wells that exceed the drinking water MCL for radium are located in the eastern part of the state (red highlight in map above). This band coincides with where the Cambrian-Ordovician sandstone aquifer intersects the Maquoketa shale[1].

There are no NR 140 groundwater quality standards for radionuclides in Wisconsin but drinking water at public water systems is monitored both for specific radionuclides (uranium, radium) and for general indicators of radioactivity (alpha, beta and gamma activity - now included in a broader group called photon emitters). Public water system maximum contaminant levels (MCLs) have been established for the radionuclides uranium and (total) radium, and for alpha and beta (plus photon) particle activity. These MCLs are: 30 micrograms per liter (ug/L) for uranium, 5 picocuries per liter (pCi/L) for total radium (radium-226 plus radium-228), 15 pCi/L for alpha activity and 4 millirems per year (mrem/yr) for beta or gamma activity (WI NR 809.50-809.51).

No public water supply MCL has been established for radon, but the United States Environmental Protection Agency (US EPA) has proposed that radon levels in water should be no higher than 4,000 pCi/L where indoor air radon abatement programs exist, and no higher than 300 pCi/L where indoor air radon abatement programs do not exist.

Radionuclides occur naturally in rock formations, and every well in Wisconsin contains some level of dissolved radionuclides. In most places these levels are not concerning, but some areas of the state tend to have notably high concentrations of radium, radon, and/or gross alpha activity.

In *northern Wisconsin*, there are notably high levels of both radon and gross alpha activity. Here, the geologic source is usually granite bedrock or, in some cases, granitic sand and gravel deposits.

In *eastern Wisconsin*, wells that draw water from the Cambrian-Ordovician deep sandstone aquifer, where it underlies the Maquoketa shale geologic formation, often

have levels of radium above the public drinking water MCL. This band of high radium activity stretches from Brown County in the north to Racine County in the south and primarily affects public wells (high radium levels are present in groundwater drawn from deep bedrock aquifers and drilling wells deep enough to reach these deep aquifers is usually prohibitively expensive for homeowners using private water supply wells). High radium levels in the Cambrian-Ordovician deep sandstone aquifer is due to the fact that the solubility of radium is related to the solubility of sulfate minerals, and sulfate minerals in this part of the aquifer are more soluble than those to the west, where the sandstone aquifer is not "confined" beneath the Maquoketa shale formation.

Chromium

As water flows underground, metals such as chromium may be dissolved from rock or soil and be mobilized, and therefore present in groundwater. Natural sources of chromium in groundwater include some types of igneous bedrock and soils derived from those bedrock sources. In groundwater, chromium can generally be found in one of two forms, as trivalent chromium (Cr lll, chromium-3), or as hexavalent chromium (Cr VI, chromium-6). The US EPA has established a public water supply MCL for total chromium (trivalent chromium + hexavalent chromium) at 100 µg/L and, in Wisconsin the NR 140 groundwater quality enforcement standard (ES) for total chromium is 100 µg/L.

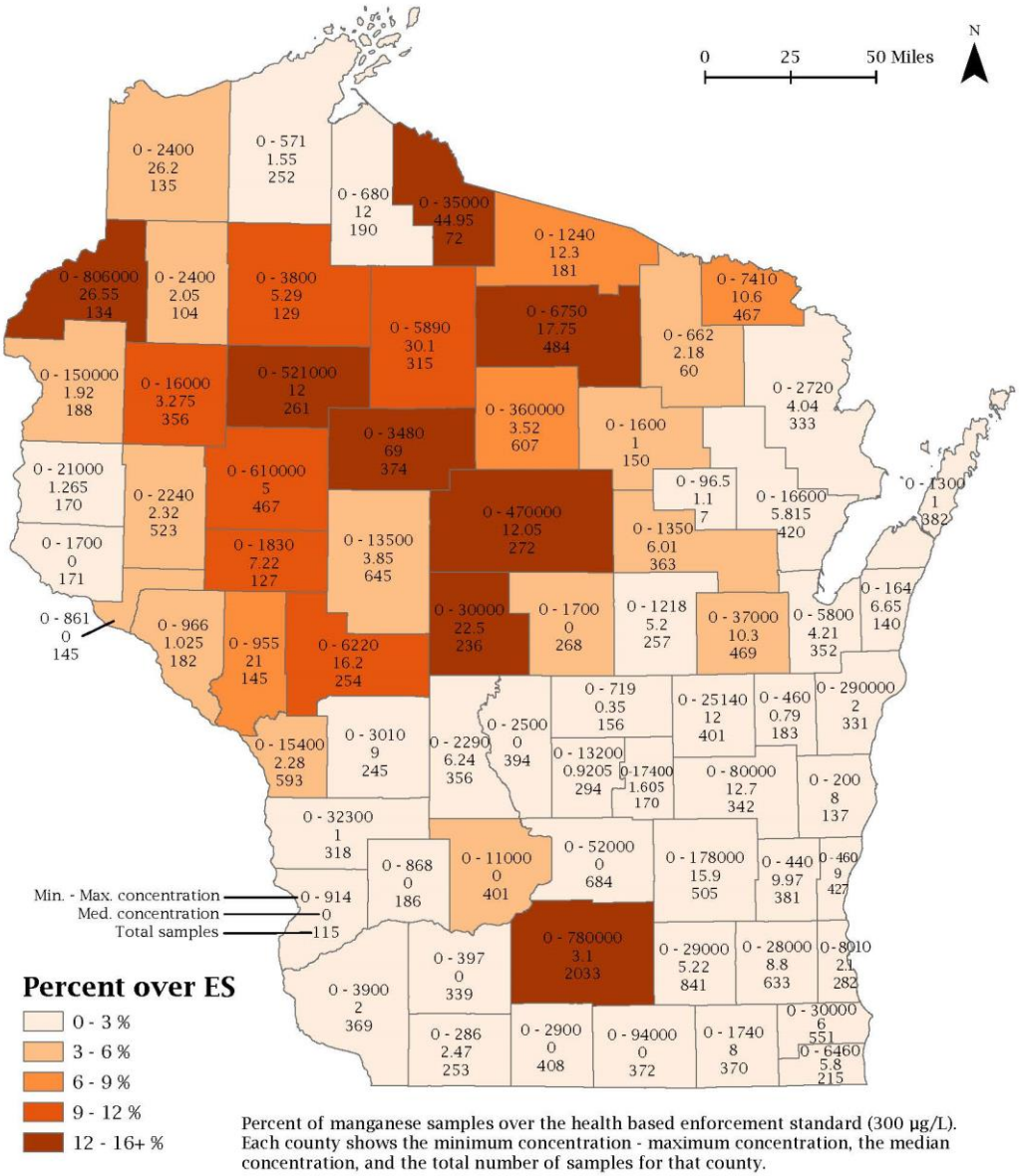
The DHS recently recommended a ch. NR 140 ES for hexavalent chromium of 70 nanograms per liter (ng/L). This standard was proposed by DNR in its "Cycle 10" revisions to ch. NR 140, however, the recommended Cycle 10 groundwater standards, including proposed hexavalent chromium standards, were not approved by the Natural Resources Board at their Feb. 2022 meeting.

Manganese

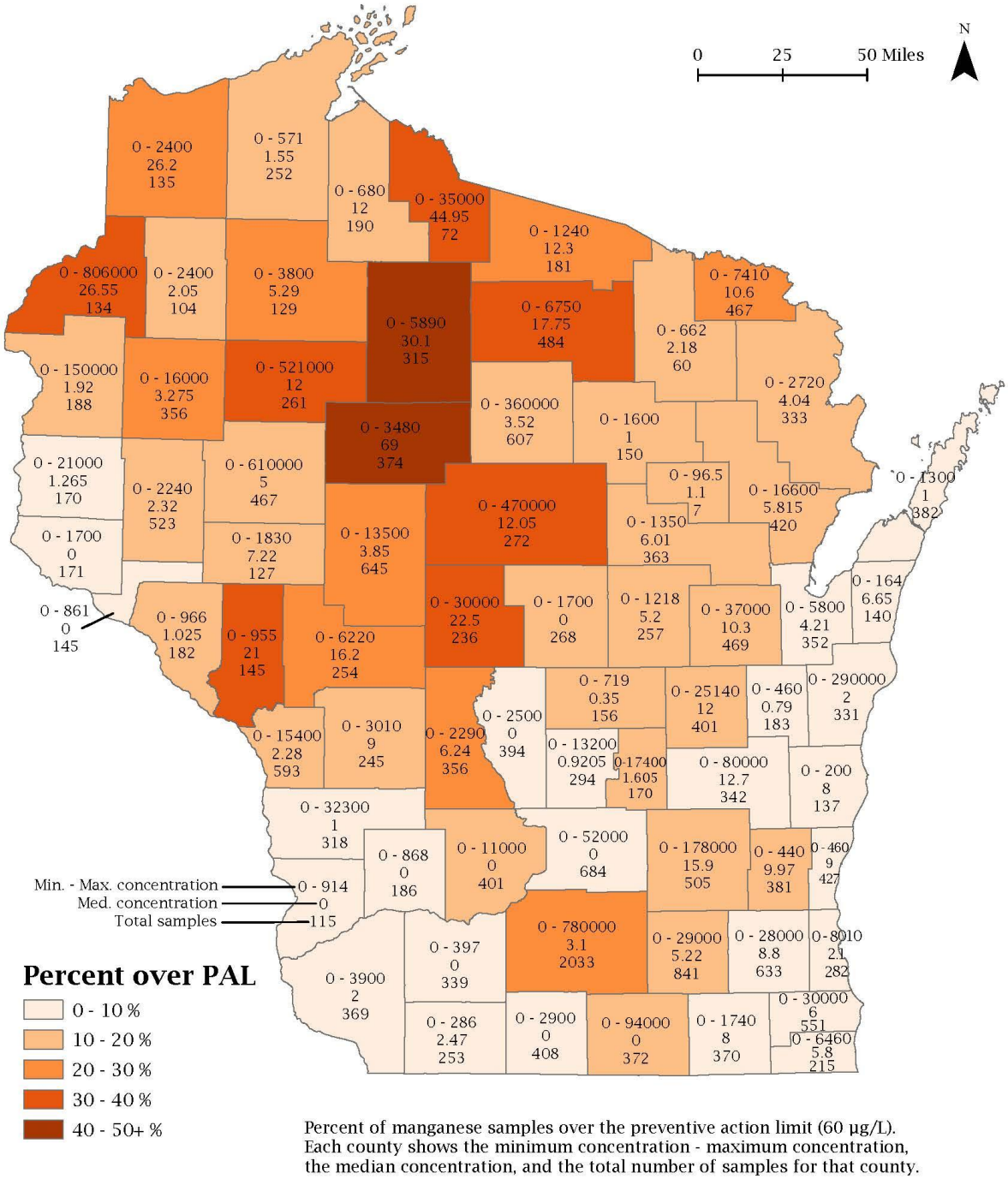
Manganese is a common, naturally occurring element found in rocks, soil, water, air and food. Manganese is an essential element and is needed to form healthy bones, produce glucose and heal wounds. Small amounts of manganese are part of a healthy diet. Manganese is naturally found in breastmilk and included in infant formula to ensure proper development. Although the primary source of exposure to manganese is food, drinking water can increase the overall dietary intake of manganese. High levels of manganese can affect our health.

A ch. NR 140 health based groundwater quality enforcement standard (ES) has been established in Wisconsin for manganese at 300 µg/L. The US EPA has also set a lifetime health advisory level (HAL) of 300 µg/L for manganese in drinking water. In addition to the health based groundwater and health advisory standards, a welfare based ch. NR 140 groundwater quality ES for manganese has been set at 50 µg/L, and the US EPA has an aesthetic based public drinking water Secondary Standard for manganese established also at 50 µg/L.

The maps below show Wisconsin counties with manganese over the ch. NR 140 health based ES of 300 µg/L (Map 1) and over the health based preventive action limit (PAL) of 60 µg/L (Map 2). The purpose of the maps is to provide a high level overview of Manganese contamination in Wisconsin. The data used is from 1975 to May 2024. For sample locations with multiple samples taken over time, the sample with the highest result was used. Samples that would knowingly skew the data (such as samples from mines and monitoring wells) were omitted.



Map 1. Percent of manganese samples over the ch. NR 140 health based ES (300 µg/L).



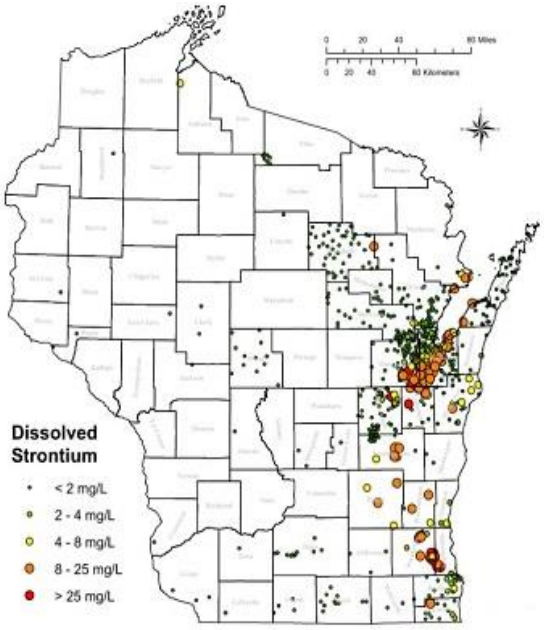
Map 2. Percent of manganese samples over the ch. NR 140 health based PAL (60 ug/L).

Strontium

Naturally occurring, non-radioactive strontium is present in Wisconsin groundwater and has been found at very high concentrations in some parts of the state. Non-radioactive, or "stable strontium", naturally occurs in rock and soil and, under certain geochemical conditions, is dissolved from rock and soil sources and mobilized in groundwater. Very high levels of naturally occurring strontium have been documented in municipal water supply wells in eastern Wisconsin[2].

Strontium's chemical behavior is similar to calcium and strontium minerals have been found in carbonate bedrock deposits in Wisconsin. The weathering and dissolution of carbonate bedrock containing strontium minerals may be a source of elevated strontium in groundwater. Highly mineralized brines have also been shown to contain very high levels of dissolved strontium.

No public water supply MCL has been established for strontium, but the US EPA has established a lifetime health advisory level for strontium in drinking water at 4,000 µg/L. The DHS recently recommended a ch. NR 140 ES for strontium of 1,500 µg/L. This standard was proposed by DNR in its "Cycle 10" revisions to ch. NR 140, however, the recommended Cycle 10 groundwater standards, including proposed strontium standards, were not approved by the Natural Resources Board at their Feb. 2022 meeting.



Statewide distribution of dissolved strontium in Wisconsin's aquifers[3].

What are the human health concerns?

Radionuclides

People who drink water containing alpha, beta or gamma radiation, or radium or uranium in excess of established MCLs, over many years, may have an increased risk of getting cancer. In the case of uranium, an increased risk of kidney toxicity is possible as well.

Chromium

Trivalent chromium is an essential nutrient, but hexavalent chromium is acutely toxic and has been classified as "likely to be carcinogenic to humans" by the US EPA. Water quality analysis for chromium is generally done for "total chromium" (trivalent chromium + hexavalent chromium). Information on how chromium affects the human body through oral exposure is limited. Animals studies have shown that oral exposed to large amounts of hexavalent chromium can have

significant adverse effects on the stomach and small intestines, and also may cause damage to the sperm of male animals. Studies have shown that exposure to large amounts of hexavalent chromium can cause cancer in research animals and past studies have shown that hexavalent chromium can cause teratogenic and possibly mutagenic effects. Newer studies have shown that hexavalent chromium may have interactive effects with other substances such as benzo(a)pyrene and arsenic.

Manganese

High levels of manganese can affect our health. According to the DHS, studies indicate that exposure to high levels of manganese can affect the nervous system. Studies on research animals suggest that high levels of manganese may also affect reproduction and impact the kidneys. People over the age of 50 and infants less than six months old are the most sensitive to these effects. In older adults, high levels of manganese may cause a disorder similar to Parkinson's disease. In infants, exposure to high levels of manganese may affect brain development and impact learning and behavior. Some studies among people indicate that people with certain medical conditions (iron-deficiency anemia, liver disease) may also be more sensitive to the effects of manganese.

The state public health based groundwater enforcement standard and US EPA health advisory level for manganese of 300 µg/L are intended to protect against these effects. According to DHS, manganese above this level may pose an immediate health risk for sensitive groups. When manganese levels are above 300 µg/L, people over the age of 50 and infants less than six months old should stop using the water for drinking and preparing foods and beverages that use a lot of water. Manganese at these levels also pose a long-term health risk for everyone. There are also rare occasions when manganese concentrations in groundwater exceeds 1,000 µg/L. The US EPA has determined that concentrations above this level pose an immediate health risk to all consumers.

In addition to the groundwater and health advisory standards, the US EPA has established a secondary water quality standard of 50 µg/L for manganese in a water supply, and a state public welfare groundwater quality ES has been established for manganese at this level in ch. NR 140. Manganese concentrations greater than 50 µg/L in groundwater and drinking water supplies causes esthetic issues related to taste and color.

Strontium

Strontium mimics calcium and is absorbed by growing bones. High levels of strontium have been linked to bone calcification effects and may cause bones to grow shorter and thicker than normal. Small amounts of strontium are not known to be harmful. People with calcium deficiencies, kidney conditions, and Paget's disease, a disease that causes your body to generate new bone faster than normal, may be more sensitive to the effects of high levels of strontium.

How is naturally occurring elements contamination trending over time?

Historically, about 80 public water systems exceeded a radionuclide drinking water standard, causing these communities to search for alternative water supplies or treatment options. The vast majority of these systems are now serving water that meets radionuclide drinking water standards. The DNR continues to work with the remaining water systems to ensure that they develop a compliance strategy and take corrective actions.

Further Reading

- DHS resources for contaminants in drinking water
- DNR overview of radium in drinking water wells
- DNR overview of radon in drinking water wells
- WGNHS report on distribution of radionuclides in groundwater
- DNR Manganese and drinking water
- Origin and Distribution of Dissolved Strontium in the Cambrian-Ordovician Aquifer of Northeastern Wisconsin Grundl, T.J. 2000.
- Maquoketa shale as radium source for the Cambro-Ordovician aquifer in eastern Wisconsin. Wisconsin groundwater management practice monitoring project, DNR-141. Available at http://digital.library.wisc.edu/1711.dl/EcoNatRes.GrundlMakoqueta
- Hexavalent Chromium (Cr(VI)) in WI Groundwater: Identifying Factors Controlling the Natural Concentration and Geochemical Cycling in a Diverse Set of Aquifers

References

1. Luczaj, J., Masarik, K. 2015. Groundwater Quantity and Quality Issues in a Water-Rich Region: Examples from Wisconsin. Available at *https://www.mdpi.com/2079-9276/4/2/323*.
2. United States Geological Survey (USGS). 1963. Occurrence and Distribution of Strontium in Natural Water. Geological Survey Water-Supply Paper 1496-D. Available at *https://pubs.usgs.gov/wsp/1496d/report.pdf*
3. Luczaj, J., M. Zorn, J. Baeten. 2013. An Evaluation of the Distribution and Sources of Dissolved Strontium in the Groundwater of Eastern Wisconsin, with a Focus on Brown and Outagamie Counties. University of Wisconsin System Groundwater Research Report WR12R004. Available at *https://www.wri.wisc.edu/wp-content/uploads/FinalWR12R004.pdf*.