Manganese in Minnesota's Groundwaters

Emphasizing the Health Risks of Manganese in Drinking Water

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Manganese in Minnesota's Groundwaters: Emphasizing the Health Risks of Manganese in Drinking Water

Glossary of Terms

Adsorption: A water treatment method where undesirable constituents in water stick onto the surface of particles. Activated carbon typically is the most effective adsorbent used

Ambient groundwater: Groundwater that is not impacted by any known point sources of pollution, such as a chemical spill, surrounding a well or monitoring location

Anthropogenic: Caused by human activity

Aquifer: any water-bearing bed or stratum of earth or rock capable of yielding groundwater in sufficient quantities that can be extracted (as defined in Minnesota Rules 6115.0630)

Bottled Water: Water that is intended for human consumption and sealed in bottles or other containers with no added ingredients, except that it may contain a safe and suitable antibacterial agent (as defined in Minnesota Rules 1550.3200)

CWI: Minnesota County Well Index, a database that contains information on water wells constructed in Minnesota

DOC: dissolved organic carbon

Greensand: iron potassium phyllosilicate mineral, which usually has a green color

HA: Health Advisory, established by the United States Environmental Protection Agency; non-enforceable guidance for other agencies for unregulated drinking water constituents

HBV: Health Based Value; established by Minnesota Department of Health; the concentration of a chemical below which there is little or no risk to human health; not promulgated

HRL: Health Risk Limit; established by Minnesota Department of Health; the concentration of a chemical that is likely to pose little or no risk to human health; promulgated

Ion exchange: process whereby one or more ions in water, such as calcium and magnesium, are exchanged for other ions, usually sodium,using a media like a resin

MCL: Maximum Contaminant Level. Enforceable water quality standard set by the U.S. Environmental Protection Agency under the Safe Drinking Water Act in 40 CFR 143 for public drinking water supplies.

MDA: Minnesota Department of Agriculture

MDH: Minnesota Department of Health

mg/L: milligrams per liter; 1 mg/L is approximately 1 part per million (ppm) in dilute water

MGS: Minnesota Geological Survey

MGWA: Minnesota Ground Water Association

MN DNR: Minnesota Department of Natural Resources

MPCA: Minnesota Pollution Control Agency

Neurotoxicant: A toxic compound that can cause damage to the central nervous system

SDWA: Safe Drinking Water Act. Federal law originally passed in 1974, it requires EPA to set drinking water quality standards and oversee states, municipalities, and other entities that implement the standards.

SMCL: Secondary Maximum Contaminant Level. Non-enforceable water quality standards set by USEPA under the SDWA in 40 CFR 143.

RAA: Risk Assessment Advice; established by Minnesota Department of Health; technical guidance concerning exposures and risks to human health. RAA may be quantitative (e.g., a concentration of a chemical that is likely to pose little or no health risk to humans) or qualitative (e.g., a written description of how toxic a chemical is in comparison to a similar chemical).

Toxicity: The degree to which a substance can damage an organism

ug/L: Micrograms per liter; 1 ug/L is approximately part per billion (ppb) in dilute water

USEPA: United States Environmental Protection Agency

USGS: United States Geological Survey

UV: Ultraviolet light

Valence: the number of electrons required to create stability in the outer shell of an atom. The valence of an atom is determined by the number of electrons the atom will lose, gain, or share when it forms compounds.

Manganese in Minnesota's Groundwaters: Emphasizing the Health Risks of Manganese in Drinking Water

Manganese is a naturally-occurring element in the groundwater that is well known for causing aesthetic problems with drinking water. Much of Minnesota's soil, bedrock, and groundwater commonly contains manganese. Water professionals recognize that water supplies containing more than ~50 micrograms per liter (ug/L) dissolved manganese can be a household nuisance because atmospheric oxygen causes manganese in these water supplies to precipitate in water mains, leading to stained laundry and fixtures, and distinct aesthetic effects such as discoloration, odor, or taste (Figure 1). More than 60% of ambient groundwater measurements in Minnesota exceed 50 ug/L, suggesting that many water supplies contain excess manganese.

There is increasing recognition of human health effects caused by manganese. Acute neurological effects resulting from inhalation of manganese have long been recognized, and recent studies indicate that ingestion of excess manganese also poses a potential health risk. These studies demonstrate that although manganese is essential for body functions, subtle decreases in memory, attention, and motor skills are positively correlated with drinking water manganese concentrations, especially above 100 ug/L (Figure 2). Infants relying on powdered formula mixed with drinking water containing high levels of manganese are at highest risk; they are unable to excrete excess manganese and they absorb ingested manganese more readily than adults and children.

Non-enforceable guidance was developed to minimize the human health and aesthetic problems associated with excessive levels of manganese in water. Recognizing manganese as a potential public health issue, the Minnesota Department of Health (MDH) developed tiered health-based risk assessment advice (RAA) for manganese in drinking water in 2012: 300 ug/L for adults and children one year of age or older, and 100 ug/L for infants, especially those relying on reconstituted formula. The Environmental Protection Agency (EPA) advises public water suppliers to treat water to less than 50 ug/L manganese to maintain consumer acceptance of the water. However, these are not enforceable health-based drinking water standards. In fact, manganese levels in public and private water supplies are not currently regulated and not required to be monitored. Mitigation of the potential health risk through development of enforceable standards is unlikely, at least within the next five years. Instead, education, risk communication, testing, and treatment are potential approaches to mitigate the potential for health risks associated with manganese in drinking water.

The groundwater community in Minnesota can help educate the water supply industry, water conditioning contractors, public health professionals, educators, and community and political leaders. The distribution of manganese in ambient ground water is not a measure of manganese in tap water, which can change from source to tap. However, these measurements *can* be used to target risk communication, testing, and treatment efforts on regions of the state that have relatively high ambient manganese concentrations in groundwater. Manganese concentrations are variable, commonly exceeding 1,000 ug/L in Southwestern Minnesota while rarely exceeding 50 ug/L in Southeastern Minnesota (Figure 3).

Informing health care providers and consumers about naturally elevated manganese in groundwater can help them make better decisions about the health risk posed by the potential presence of manganese in their drinking-water supply. Awareness of manganese in drinking water is particularly important for families with infants who may reconstitute formula.

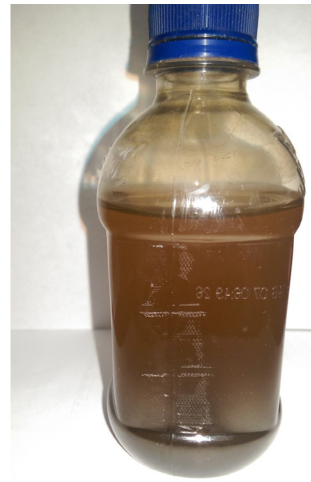

Figure 1. Water containing elevated levels of manganese sampled from a toilet tank in a residence.

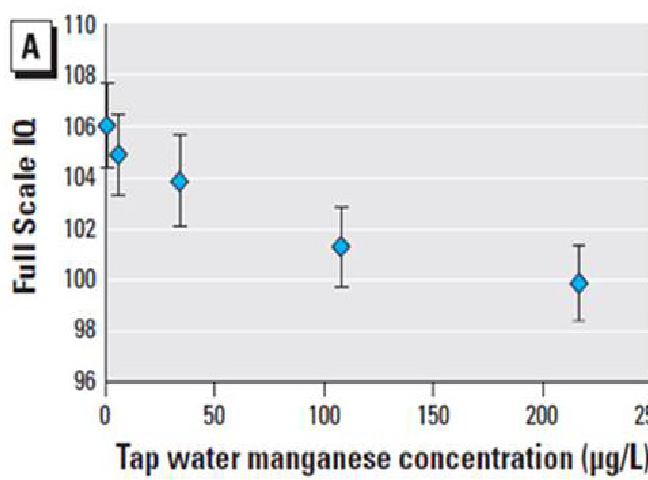

Figure 2. Full Scale IQ as a function of the range of median tap water manganese concentrations. Quintile groups are: 1st = 1, 0-2; 2nd = 6, 3-19; 3rd = 34, 20-66; 4th = 112. 67-153; and 5th = 216, 154-2700. Figure from Bouchard et al., 2011.

Observation of nuisance and aesthetic effects might be used as an indicator of potential health risk: using tap water that stains faucets to mix infant formula may not be protective of health. In addition, using this water as a drinking source also may not be protective of adult and child health. When properly treated to reduce nuisance and aesthetic effects, tap water manganese is likely to be below health guidance values.

Testing for manganese in drinking water provides a definitive method to assess the potential for manganese exposure. Water

Manganese in Minnesota's Groundwaters, cont.

samples can be tested at local labs for approximately $20. The MDH provides information on laboratories and sampling.

For water supplies containing excess manganese, there are many treatment methods. In public supplies, treatment systems are designed to maintain consumer acceptance of the water and meet enforceable standards for some chemicals. Treatment systems used to reduce iron in water through oxidation, a common treatment step in public water supplies, also reduces dissolved manganese concentrations. Information about the efficiency of treatment systems for reducing manganese to specific recommended health standards is sparse. However, common treatment methods such as carbon filtration, reverse osmosis, cation exchange or water softening, adsorption, oxidation and filtration all likely decrease manganese levels. A licensed water conditioning installer or con-tractor can help determine the appropriate water treatment device. Regardless of the treatment option installed, post-treatment testing for manganese and regular maintenance are essential to ensure that manganese levels are protective of health.

Alternatively, drinking water supplies containing excess manganese can be replaced with bottled water. Manganese in bottled water, which also can be sourced from groundwater in Minnesota, is enforced to contain less than 50 ug/L by the Federal Food and Drug Administration or the Minnesota Department of Agriculture. Families relying on formula for infant nutrition also may choose to use liquid, ready-to-feed infant formula instead of powdered formula. In some cases, replacing a troublesome water supply with a new permanent water supply may be economical.

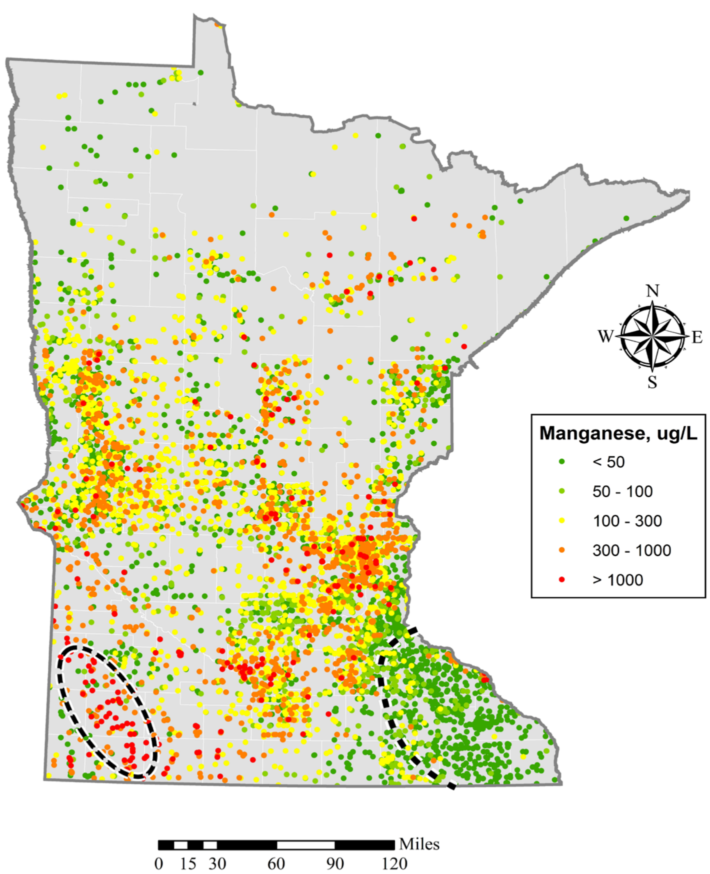

Figure 3. Manganese in groundwater measured at 7,574 wells. Samples collected at various times, for various studies. Data collated and map prepared by MDH, February, 2015. Dashed line encloses area of southeastern Minnesota with low (< 50 ug/L) manganese concentrations. Dashed ellipse encloses area of southwestern Minnesota where manganese concentrations exceed 1,000 ug/L.

Understanding the potential health risk due to manganese in Minnesota's drinking water will take time and careful consideration by the public health, groundwater, and drinking water communities. Potential investigation activities could include:

- Additional health studies, including a study of the neurological effects of exposure in infants and children exposed to low levels of manganese, and a comparison of the effects of drinking water versus dietary exposure.
- Correlation of ambient groundwater manganese concentrations to tap water manganese concentrations to determine typical exposure concentrations.
- Additional assessment of the spatial distribution of manganese in groundwater. This provides an effective way to identify the populations that may be most at risk of exposure to manganese in drinking water. Coordinating between various ambient groundwater quality monitoring programs within state agencies and local governments is necessary. A concerted effort may be needed to increase the density of ambient groundwater measurements in rural areas, and to assess the adequacy of the data to develop geographical correlations based on geology.
- Evaluation of the effectiveness of manganese removal by water softeners and readily-available pitcher or faucet filters, with specific reference to health-based water quality concentrations.

1 Problem Statement and Definition

Manganese is widespread in the groundwater that many Minnesotans use for drinking. Epidemiology and toxicology studies published in the past ten years have shown that dissolved forms of manganese in drinking water pose a greater health risk than previously thought, especially for formula-fed infants, whose exposure may include both manganese from formula fortification and in the water used to mix formula. The widespread presence of manganese above threshold health-based guidance values in Minnesota's groundwater suggests that many people may be exposed to a level that presents a health risk.

Many water supply professionals consider manganese in water as primarily an aesthetic issue, not a health issue because of discoloration and staining associated with manganese-enriched groundwater. Therefore, the message they provide to their customers is that manganese is a "nuisance" contaminant in drinking water, rather than a health concern. The MDH, seeking to alter this misconception, has provided information to professionals and the public regarding the potential health risks associated with manganese in drinking water, and awareness of this public health issue is growing.

The goal of this white paper is to provide information about this issue to facilitate awareness-building and a better understanding among local public health officials, public utility operators, water supply professionals, private well owners, and others. The white paper brings together information about 1) the health effects of manganese in drinking water and the availability of new health-based drinking water guidance, 2) the spatial distribution of manganese in groundwater, including current monitoring programs that test for manganese in Minnesota drinking water, and 3) effective ways to reduce exposure to manganese, especially for those who may be using water with high manganese concentrations to prepare infant formula.

2 Background

Manganese is required for human health; however, several harmful neurotoxic effects of excessive manganese exposure are recognized. Parkinson-like effects are caused by inhalation exposure, especially in occupational settings. Recent work suggests more subtle, harmful effects also are caused by ingestion of low levels of manganese, especially among infants.

Manganese is a ubiquitous component of soils, rocks and water. It can be leached from soil and rock into the underlying groundwater, where mobilization of manganese is favored in chemically-reducing conditions.

In Minnesota, groundwater commonly is used for drinking water supplies. Figure 1 depicts the role pumping wells play within the context of the hydrologic cycle. Approximately 75% of Minnesotans use groundwater for their drinking water supply (MDH, 2015).

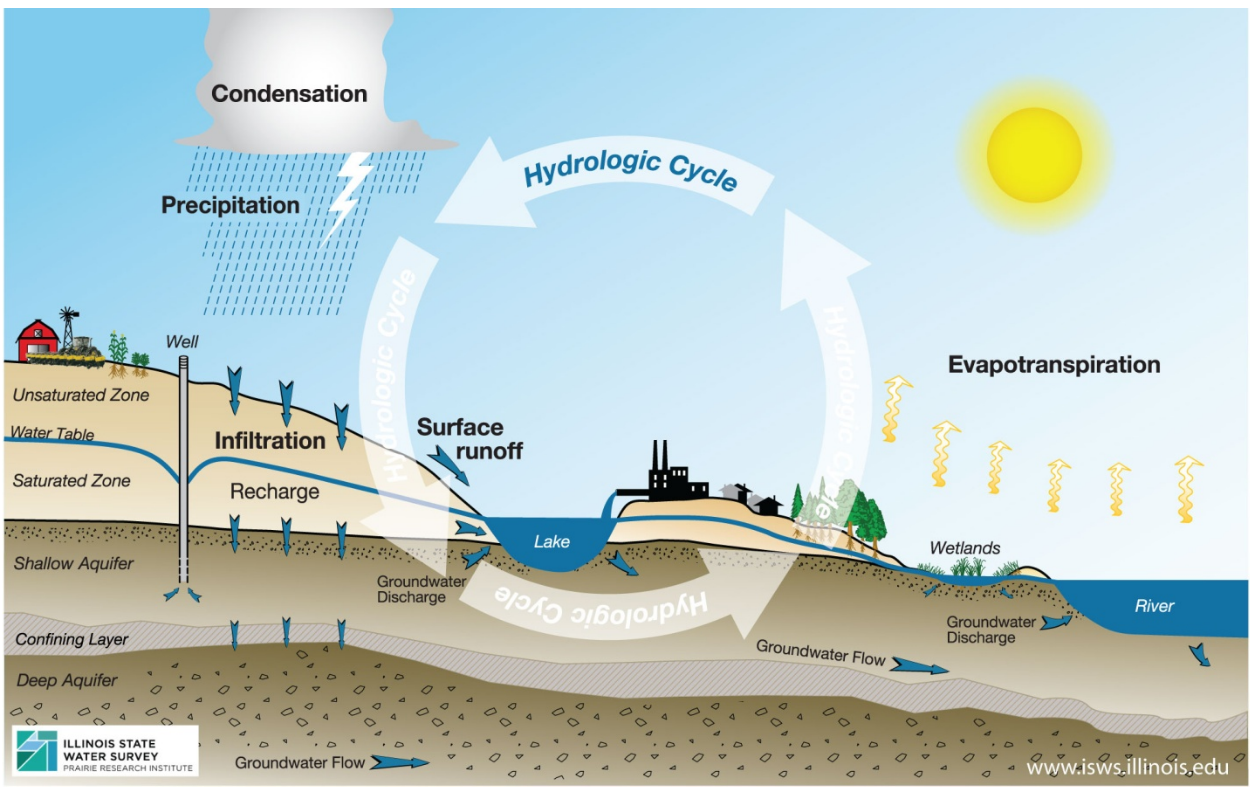

Figure 1. The hydrologic cycle describes the movement of water above, upon, and below the surface of the Earth. Groundwater aquifers supply water to wells, making them important sources of drinking water. (Figure used with permission from the Illinois State Water Survey).

The wells used to extract the groundwater for water supplies generally are either managed by municipalities or businesses or privately installed and operated to provide residential supply. Municipalities and businesses generally manage public drinking water supplies, which are broken into various categories:

- Community supplies: these are systems serving a minimum of 25 persons or 15 service connections, year round. There are almost 1,000 community supplies in Minnesota.
- Non-community supplies: these are systems serving at least 25 people for a minimum of 60 days of the year. There are almost 6,000 non-community supplies in Minnesota. Non-community supplies are further subdivided into:
    - transient supplies where consumers use the supplies only temporarily and occasionally; these include gas stations, parks, resorts, campgrounds, restaurants, and motels, and
    - nontransient supplies where 25 or more of the same people consume the well water on a regular basis for at least six months out of a year; these include schools, factories, and hospitals,.

In addition to private wells and public water supply wells, groundwater is used as a source for bottled water distributed in Minnesota.

There is a considerable amount of available information on manganese concentrations in the state's groundwater. Many state and county organizations actively measure manganese concentrations in groundwater to determine ambient water quality. These data can be used to identify regions of the state where the potential for a public health risk related to manganese in drinking water is highest. Education and outreach, testing and water treatment, alternative drinking water supply, public policy, or regulatory changes might be targeted within these regions.

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3 Manganese and Human Health

Living organisms need manganese for their biological processes. Manganese is an essential nutrient that is needed to create carbohydrates, amino acids and cholesterol, plus it is critical for cartilage, collagen, and bone synthesis. Manganese deficiency can result in abnormal skeletal growth and wound healing. In the developed world, people's manganese requirements[1] are easily met by consumption of nuts, legumes, tea, and whole grains.

Ingested manganese within the body can be absorbed by tissues or excreted. Children and adults have fully functioning metabolisms that control the amount of manganese retained in the body, with only 3-5% of ingested manganese absorbed in tissue. In contrast, infants' immature body systems limit their ability to excrete manganese; infants can absorb up to 40% of the manganese they ingest from formula. (Health Canada, 2010, ATSDR, 2012).

While manganese is necessary, excessive ingestion of manganese can be harmful, especially to infants. The neurotoxic effects of inhalation exposure to high doses of manganese have been recognized for more than 100 years. In 1837, John Couper first described effects similar to Parkinsonism among workers grinding manganese at a chemical factory (Guilarte, 2013). Workers affected by manganese inhalation lost strength in their lower extremities, causing them to lean forward when walking, which resulted in short, running steps. They also lost the ability to speak loudly, and had paralyzed facial muscles. More recently, this constellation of health effects, known as "manganism", along with more subtle locomotor effects, has been reported not only in human epidemiology studies, but also in rodent and nonhuman primate studies.

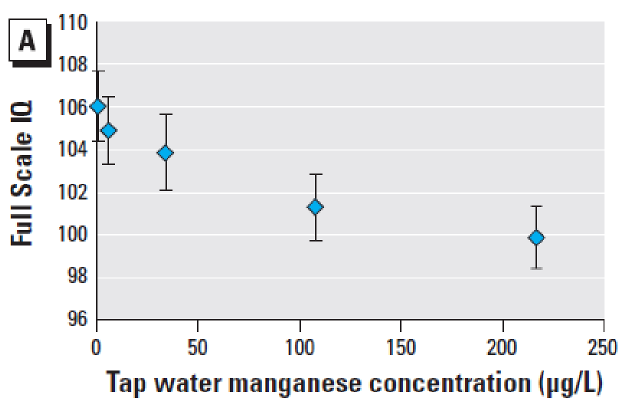

Figure 2. IQ is plotted by median tap water manganese concentration quintiles. The quintiles are as follows: 1st, 1 (0-2); 2nd, 6 (3-19); 3rd, 34 (20-66); 4th, 112 (67-153); and 5th, 216 (154-2700). Figure copied from Bouchard et al. (2011).

The neurotoxic effects of manganese ingested at low levels have only recently been recognized. Since the early 2000s, a handful of epidemiological studies have examined the effects of manganese on children. In 2011, Bouchard and colleagues showed that children whose drinking water source contained more than 200 ug/L manganese had a deficit of more than 6 IQ points compared to children whose drinking water source contained less than 5 ug/L manganese (Figure 2) (Bouchard et al., 2011). In a follow up study, they examined the same group of children and found that decreased memory, attention, and motor skills correlated with increasing manganese water concentration, with the steepest drop in these functions occurring at, or just above, 100 ug/L manganese in drinking water (Oulhote et al., 2014).

[1] The Institute of Medicine recommends a daily intake rate of 0.003 milligrams per day for infants under the age of one, 1.2-1.9 milligrams per day for children, and 1.8-2.3 milligrams per day for adults.

Similar neurological effects were observed in direct experiments on 0-18 month old primates (which is equivalent to children who are 0-6 years old). Golub and coworkers (2005) fed either standard infant formula or manganese-enriched formula to the infant primates, and measured the effects using a variety of sensitive neurobehavioral tests. Those treated with manganese-enriched formula showed differences in consistency and type of play during group interactions (rough vs. chase), changes to their day/night cycle, and impulsivity. The authors proposed that the observed subtle neurological changes in social behavior and regulatory control were due to alterations in brain chemicals sensitive to manganese.

The effects of neonatal (early-life) oral manganese exposure on behavior and cognition also were tested using animal studies. Rats were exposed to manganese via oral ingestion from birth until 23 days of age, and their performance on a series of learning and memory challenges was recorded (Kern et al., 2010). The results of this study are applicable to human manganese exposures: the study focused on low level exposure to manganese in the young animals, which are the most sensitive population. The neurobehavioral endpoints measured in this study included locomotor activity (movement), emotional reactivity (impulsivity), learning ability, and behavioral disinhibition (a lack of restraint), The design of the study allowed for evaluation of subtle effects that are relevant to humans, and the biochemical changes reported in the study are similar to those reported in humans. The exposed young animals had increased locomotor activity, consistent with hyperactivity, and a significant learning deficit. These effects were attributed to manganese targeting pathways in the brain that control higher decision-making functions.

It is clear from the studies in humans and animals that manganese, although a beneficial and essential nutrient at low doses, is a neurotoxicant at high exposure levels for children and adults. In comparison, even a low dose is a neurotoxicant for infants. While high level exposures result in overt manganism, low level exposure effects are subtle, such as IQ loss, in infants and children. At highest risk are infants, who lack the mature systems needed to excrete excess manganese and avoid neurological effects.

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4 Environmental Behavior of Manganese

Manganese is an abundant element that occurs in the environment in both solid and aqueous (dissolved in water) phases, typically with iron. The behavior of manganese and iron is strongly driven by chemical reactions known as oxidation or reduction (“redox” reactions). Redox reactions describe the transfer of electrons between atoms, molecules, or ions, where oxidation is defined as the loss of electrons and reduction is defined as the gain of electrons. Manganese ions change oxidation (valence) state by losing or gaining electrons, which affects its solid properties and solubility in water.

Solid Phase Manganese

Manganese is found in over 100 types of minerals, including sulfides, oxides, carbonates, silicates, phosphates, and borates. The most common manganese-bearing minerals on the Earth’s surface are listed in Table 1 (Nadaska and Michalik, 2010). The amount of manganese dissolved in the groundwater depends on how much of these minerals are present in the aquifer materials as well as their ability to dissolved and their dissolution rate. Manganese’s dissolution rate depends on environmental conditions like temperature, ionic strength, pH and redox state.

Table 1. Common forms of solid-phase manganese [Nadaska and Michalik 2010].

Name, Chem. formula	*Chemical name*	*Hardness/Density*	*Description*
MANGANITE $MnO(OH)$	manganese oxide hydroxide	4/4.3	Grey-black, black, sometimes with large crystals
PYROLUSITE MnO_2	manganese dioxide	2-2.5/4.75	Black and earthy in appearance rather than a hard rock
RHODOCHROSITE $MnCO_3$	manganese carbonate	3.5-4.5/3.45-3.6	A pink mineral with a glasslike shine
RHODONITE $MnSiO_3$	manganese silicate	5.5-6.5/3.4-3.7	A pink, yellow, or brown mineral, often with large crystals
HAUSMANNITE Mn_3O_4	manganese tetroxide	5.5/4.8	A brown-black
PSILOMELANE $BaMn_9O_{16}(OH)_4$	barium manganese oxide hydroxide	5-6/3.7-4.7	Dark steel grey to black
BRAUNITE $3(Mn,Fe)_2O_3.MnSiO_3$		6-6.5/4.8	Brownish-black

Aqueous Manganese

The two most important environmental conditions that control manganese behavior in water are the water’s pH and its reduction or oxidation/reduction potential (ORP).

- pH is a measure of the acidity or alkalinity of a solution. It is presented as a range from 1 to 14, with pH of 7 considered neutral.
- ORP, expressed in voltage, indicates the relative presence of oxidants, such as dissolved oxygen, and describes the oxidizing or reducing tendency of a water. It determines the direction and rate of redox reactions. Its measurement provides a relative indication of water’s redox state, where positive values are more oxidizing, and less positive or more negative values are more reducing.

Groundwater generally has neutral pH; therefore, ORP, also known as redox potential or Eh, generally drives manganese behavior. An Eh-pH diagram, which describes these two variables, is a graphical means of showing the effect of changing redox potential and pH on manganese solubility in aqueous systems.

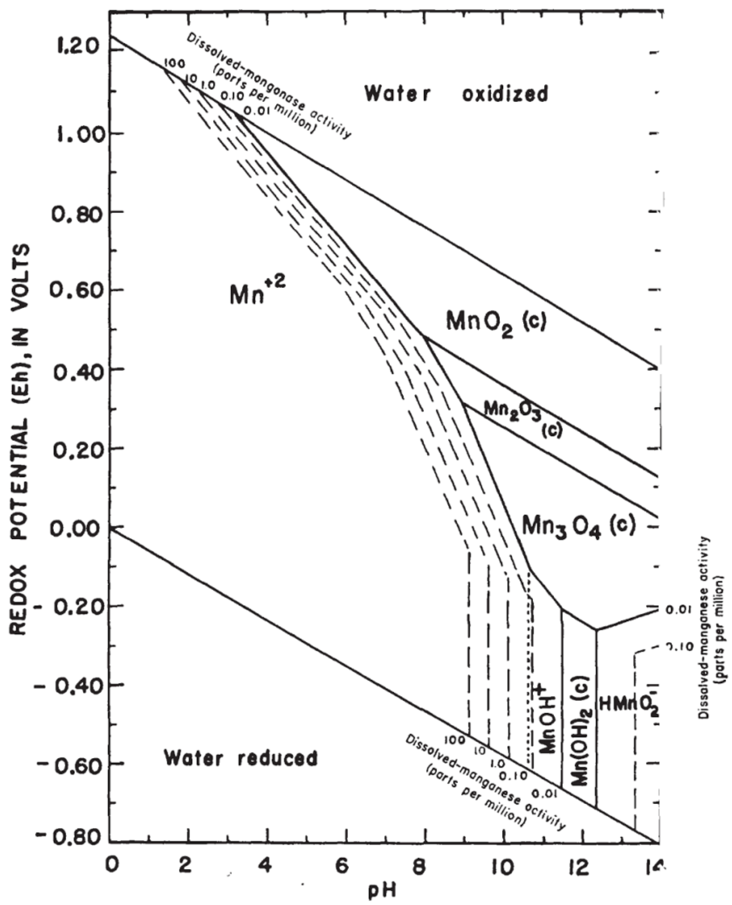

Figure 3. Eh-pH diagram describing the stability of solid "(c)" and aqueous phases of manganese as a function of redox potential and pH, at standard temperature (25 °C) and pressure (1 atmosphere). In the solid stability fields, manganese precipitates and forms the insoluble compound. The stability fields of the solids (solid lines) represent the boundaries at a concentrations of 0.01 ppm (parts per million) dissolved manganese (~10 ug/L). Dashed lines represent the stability-field boundaries when dissolved Mn+2 concentrations are 0.10, 1.0, 10, and 100 ppm.

Figure 3 illustrates that the concentration of dissolved manganese increases at low pH and at low redox potential. The Eh-pH diagram also indicates that solid-form manganese can occur in several oxidation states (+2, +3, +4, or +6), but the dominant dissolved species in natural waters is Mn^{+2} (Hem, 1985).

Manganese concentrations in surface waters generally are low. Surface water is more oxidized than groundwater, which is isolated from atmospheric oxygen. Therefore, manganese concentrations are generally low in surface waters because oxidation of Mn^{+2} to relatively insoluble Mn^{+3}/Mn^{+4} leads to spontaneous formation of particulate manganese oxides and hydroxides. These particles drop out of suspension in surface waters, leaving the water relatively depleted in manganese. Thus, in surface water and relatively oxygenated aquifer systems, dissolved manganese does not accumulate.

In groundwater, manganese concentrations can be high when the aquifer has reducing conditions. As surface water infiltrates downward into groundwater and becomes increasingly isolated from the atmosphere, oxygen is depleted resulting in more reducing conditions (a "downward" shift on the Y axis on Figure 3). Under these reducing conditions, manganese converts to its more soluble form, Mn^{+2}. Therefore, much higher dissolved manganese concentrations commonly are found in groundwater that has low amounts of oxygen such as deep, isolated aquifers (Nadaska and Michalik, 2010; Mitsch and Gosselink, 2007). The

Minnesota Pollution Control Agency (MPCA) performed ambient monitoring as part of the Baseline Study in the early to mid-1990s to assess the hydrogeochemistry of the state's principal aquifers. The MPCA confirmed that manganese concentrations in groundwater increased as ORP decreased.

It is really easy to see how redox conditions affect the various manganese forms in the water just by pumping water from a deep well. The manganese oxidizes and precipitates once this water is brought to the surface and placed into contact with air (and it associated oxygen), resulting in the dark, cloudy water shown in Figure 4. This cloudy, black-tinted water contains suspended particles of manganese oxides/hydroxides. These are the stains and coatings that can affect plumbing fixtures and laundry. This generally is referred to as the "aesthetic" or "nuisance" effects of excessive manganese in water supplies.

Figure 4. Water containing elevated levels of manganese sampled from a residence.

Manganese also can dissolve into groundwater. This opposite reaction is referred to as reductive dissolution. When an aquifer which is regularly supplied with oxygenated recharge water suddenly becomes starved of this water, the aquifer can become enriched in manganese. Oxygen depletion in aquifers can happen because of land-use changes at the surface or the release of organic substances (i.e., oil or other contamination) into groundwater, which drives oxygen consumption by microbial communities. In either case, oxygen depletion leads to a change in the overall redox state of groundwater, which can dissolve solid-form manganese through reduction reactions.

Bacteria also can make some of the manganese coatings that develop on plumbing fixtures and water treatment equipment. Certain bacteria derive their energy by reacting with soluble forms of iron and manganese. These organisms thrive in waters that have high levels of iron and manganese. The bacteria change the iron and manganese from a soluble form into thick mats of black or reddish brown slimes. These slimes can clog plumbing and water treatment equipment and can slough off in globs to create iron or manganese stains on laundry. Precipitation caused by bacteria occurs fast and tends to concentrate staining. The elimination of these bacteria from wells often is a difficult and expensive undertaking. (University of Minnesota website see links)

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5 Regulation of Manganese in Water Supplies and Groundwater

Manganese levels in drinking water supplies are not currently regulated or enforced in Minnesota, with the exception of bottled water. The existing regulatory framework has resulted in several federal and state threshold water quality concentrations which are used in various ways to address the potential public health risks associated with prevalent manganese in groundwater.

Federal Regulations and Guidance

The US Environmental Protection Agency (USEPA) is responsible for establishing drinking water quality standards under Title XIV of the Public Health Safety Act, more commonly known as the Safe Drinking Water Act (SDWA). Under the SDWA, the USEPA developed the National Primary Drinking Water Regulations ("primary standards"), which are the legally-enforceable water quality standards that apply to public water supplies. Primary standards are the basis for Maximum Contaminant Levels (MCLs) that represent the highest contaminant levels allowable in drinking water. There is no primary standard (and no enforceable MCL) for manganese.

The SDWA also sets *non*-enforceable standards. These are the National Secondary Drinking Water Regulations ("secondary standards"), and are the basis for Secondary Maximum Contaminant Levels (SMCLs). The SMCLs provide technical guidance for regulating constituents that can cause unwanted cosmetic or aesthetic effects. A secondary standard (SMCL) of 50 ug/L was established for manganese because concentrations above this level typically cause laundry staining, scaling on fixtures, and deleterious appearance, odor, and/or taste (USEPA, 2004). These aesthetic issues affect consumer acceptance of the water.

The USEPA also provides Health Advisory (HA) values for unregulated contaminants that may cause non-cancerous health effects. HA values are set for a range of exposure times and include a 1-day, a 10-day and a Lifetime Health Advisory value. For manganese, the Lifetime HA value has been set to 300 ug/L to protect against neurological effects. The 1- and 10-day HA value for acute, or short term, exposures is 1,000 ug/L (or 300 ug/L for infants under 6 months old; USEPA, 2004). The January 2004 US EPA Drinking Water HA concluded that the recommendation to reduce manganese concentrations in water supplies to below 50 ug/L (the SMCL), to avoid aesthetic effects, also is more than adequate to protect human health.

The SMCL and the HA values serve as technical guidance for local, state, and federal agencies, who are responsible for implementing (enforcing) USEPA primary standards. The enforcement agencies may establish higher or lower levels depending on the local conditions and goals, such as unavailability of alternate water sources, provided that public health and welfare are not adversely affected.

Minnesota Regulations and Guidance

The Minnesota Department of Health (MDH) enforces the primary drinking water quality standards in the nearly 7,000 public water suppliers in the state. Public water suppliers, however, are not required to treat drinking water for manganese because there is no primary standard for this chemical.

The MDH does provide health-based guidance so water suppliers can understand the potential health risks of unregulated chemicals, like manganese. Three types of health-based guidance values have been established for manganese in drinking water by the MDH. Each type varies based on the extent of information available, the methodologies used to establish guidance and whether the guidance has been formally adopted by rulemaking (MDH, 2012), as outlined in Table 2. Guidance values include Risk Assessment Advice (RAA), Health-Based Values (HBVs) and Health Risk Limits (HRLs).

Table 2. Minnesota manganese guidance values.

Type	**Basis**	**Manganese Values**
Health Risk Limits (HRL)	Formally adopted through the rulemaking process, outlined in Minnesota's Health Risk Limit Rules	HRL_{93} = 100 ug/L
Health-Based Values (HBV)	Have the same data requirements as HRLs, but have not been formally adopted through the rulemaking process	HBV_{08} = 300 ug/L
Risk Assessment Advice (RAA)	Based on more limited data or newer methodologies and can be either numeric or qualitative (9)	RAA_{12} = 100 ug/L for infants under one year; 300 ug/L for adults and children one year of age or older

In 2012, the MDH re-evaluated health-based values for manganese and developed tiered[2] (meaning multiple values) health-based guidance. This approach was used to develop RAAs (RAA_{12}) of 100 ug/L for infants under one year of age, especially those that drink formula reconstituted with tap water, and 300 ug/L for adults and children one year of age or older (or infants who are breastfed). The value corresponding to the RAA_{12} of 300 ug/L was originally adopted as a HBV in 2008 (HBV_{08}=300 ug/L) while the more restrictive RAA_{12} is the same as the manganese HRL issued by the MDH in 1993 (HRL_{93}=100 ug/L). These health-based guidance values can be used by public water suppliers, private well owners, and agencies that regulate groundwater use protection.

Public Water Supplies

Many public water suppliers treat their water to mitigate the nuisance and aesthetic effects that generally occur in water containing more than 50 ug/L of manganese, despite this lack of specific regulation. There are currently 918 community suppliers in Minnesota that provide drinking water from groundwater supplies. Not all of these supplies contains elevated manganese; however, a total of 107 community suppliers report some type of "manganese removal" and an additional 115 community suppliers report "manganese/iron removal" (personal communication, Rindal, 2015). Based on populations served, approximately 25% of

[2] The tiered based approach is unique to manganese. This unique methodology requires classification of these guidance values as Risk Assessment Advice (RAA).

Minnesotans have access to drinking water that undergoes some sort of treatment to reduce manganese levels.

Private Drinking Water Supplies

Approximately 1,350,000 Minnesotans obtain drinking water from private water wells. The quality of water from these wells is not regulated, and sampling and monitoring is the responsibility of well owners. It is common for private well owners to use treatment systems to mitigate nuisance or aesthetic effects in their water.

Bottled Water

Bottled water, unlike public or private water supplies, is regulated by the Food and Drug Administration (FDA) as a food product under the Federal Food, Drug and Cosmetic Act (FFDCA). Bottled water is sourced from various types of water supplies - artesian waters, mineral water, spring water, municipal water and groundwater. The FDA enforces a 50 ug/L limit among those sources. Sources for bottled water production in Minnesota must be approved by the Minnesota Department of Agriculture (MDA). The MDA enforces the federal government's allowable level of 50 ug/L for bottled water in Minnesota. Mineral water[3], containing naturally elevated levels of total dissolved solids, is exempt from these standards both at the federal and state level.

Groundwater Use Protection

The MPCA is charged with protecting the overall quality of Minnesota's groundwater. In Minnesota's rules for Water Quality Standards (chapter 7050) all groundwater in Minnesota is protected as a Class 1 (Domestic Consumption) resource. The applicable standards include the MCLs and SMCLs. The SMCL for manganese, 50 ug/L, is considered by agencies in developing groundwater quality monitoring requirements, intervention limits, and clean-up goals for the remediation of groundwater contaminated by anthropogenic sources. Various state agency programs also consider the direct use of the groundwater for drinking and may apply the health-based guidance values administered by the MDH in setting site- and facility- specific groundwater requirements.

Potential for Regulatory Action

The SDWA requires the USEPA to develop a Candidate Contaminant List (CCL) that identifies unregulated contaminants that are known, or are likely to be found, in drinking water supplies. This list is updated every five years and prioritizes the review and investigation efforts for unregulated contaminants. The USEPA must evaluate at least five contaminants on the CCL and make a regulatory determination on whether or not to issue primary standards for those contaminants. Regulatory determinations are based on whether or not the contaminant has adverse human health effects, widespread occurrence that could impact public health, and the potential to reduce public health risks (USEPA, 2012a). If an affirmative regulatory determination is made, the new primary standards must be adopted by rule (USEPA, 2012b).

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[3] "Mineral water" means water from one or more boreholes or springs, that contains not less than 250 parts per million total dissolved solids, and originating from a geologically and physically protected underground water source. It is distinguished from other types of water by its constant level of minerals and trace elements at the point of emergence from the source. (as defined in Minn. R. 1550.3200).

Since 1998, there have been three CCLs. Manganese was one of 60 contaminants included on the first list, but a review of the data available at that time resulted in a negative regulatory determination and no new standard. In February 2015, the USEPA published the draft of the 4th CCL for public comment. Manganese was included on this list based on new information regarding its occurrence and potential health effects. Although primary standards for manganese may be developed in the future, changes to the manganese standard are unlikely within the next five years.

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6 Manganese Distribution in Groundwater

The distribution of manganese can be described by analyzing the data collected by a variety of ambient groundwater monitoring programs. Several county, state and federal programs with available data are listed in Table 3. Collation and reduction of the data resulted in 8,222 individual manganese records representing untreated groundwater. Data reduction steps included, for example, calculation of median values for wells sampled on more than one date. The spatial distribution, sampling techniques, analytical methods, and laboratory reporting limits for these programs vary, reflecting the research emphases of the various sponsoring agencies and counties. Despite these variations, these data provide a very good statewide ambient groundwater characterization. However, the actual human exposure to manganese may be less in many cases. For example, many private well owners may have treatment devices installed on their inside taps to remove excess manganese and prevent staining.

Table 3. Manganese Data Sets

Data Source	Number of records	Date Acquired	Note
MDH	1809	January 2015	Safe Drinking Water Act compliance data
MDH	1120	January 2015	Source Water Protection investigative data
MDH	861		Minnesota Arsenic Research Study (MARS)
Anoka County	190	1997	Marsh, 1997
MGS	59	1992	Lively, et. al, 1992
MDNR	2337	January 2015	County Geologic Atlas, LCCMR studies, Regional Hydrologic Atlas, etc.
MPCA	42	1994	Wall and Regan, 1994
MPCA	1664	January 2015	Ambient Groundwater Monitoring Program/Baseline Study
USGS	140	1995, 1998	Smith and Nemetz, 1995; Fong et al., 1998
Dakota County	788	February 2015	Ambient Groundwater Monitoring Program

Statistical Observations

Manganese concentrations in the state’s groundwater ranged from below reporting limits to more than 5,000 ug/L, with a median value of 101 ug/L (Figure 5). Approximately 66% of the samples were above the secondary MCL of 50 ug/L, 50% were above 100 ug/L, and 22% were above 300 ug/L.

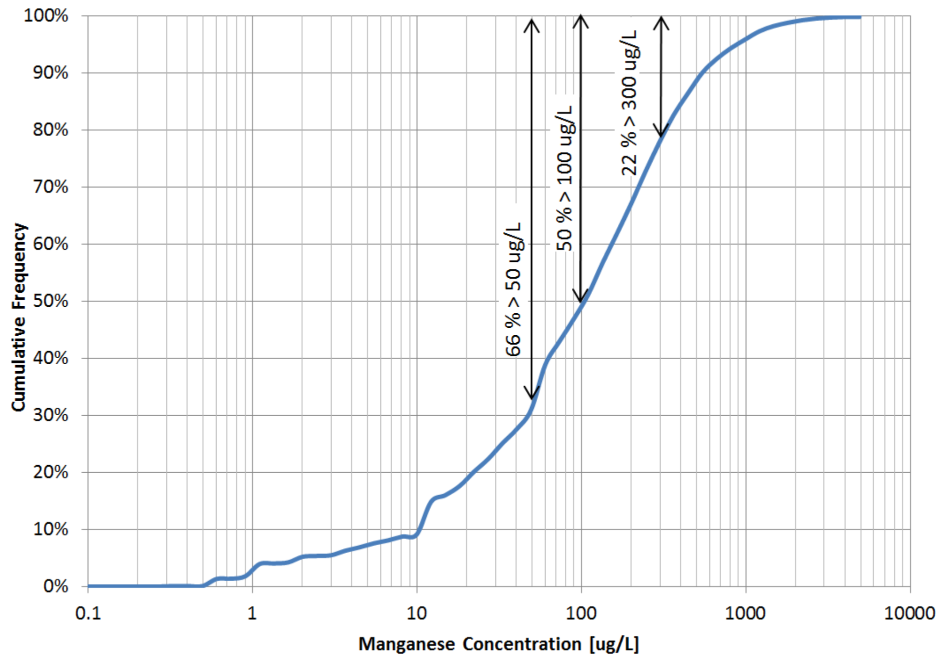

Figure 5. Frequency distribution of manganese concentrations in Minnesota's groundwater.

Spatial Distribution

Figure 6 shows the spatial distribution of the ambient groundwater data, classified based on the water quality standards and health-based guidance (50 ug/L, 100 ug/L, 300 ug/L). The data density indicate a general emphasis on monitoring in more densely-populated regions of the state.

In general, manganese concentrations in the groundwater are spatially quite variable, sometimes over relatively short distances. The data show a few noticeable spatial patterns. In Southeastern Minnesota, manganese concentrations rarely exceed 50 ug/L. In contrast, concentrations commonly exceed 1,000 ug/L in portions of Southwestern Minnesota. In addition, geostatistical analysis indicates there is some spatial correlation between manganese concentrations in the dataset. The spatial correlation was used to develop a predictive model of the distribution of manganese in groundwater, based on probability (Figure 7). For this dataset, the probability of manganese concentration exceeding 100 ug/L is spatially correlated, consistent with an exponential model[4]. Other variables, such as the well depth or aquifer, also impact the probability estimated by ordinary kriging as a lumped parameter[5].

[4] https://en.wikipedia.org/wiki/Variogram
[5] https://en.wikipedia.org/wiki/Kriging

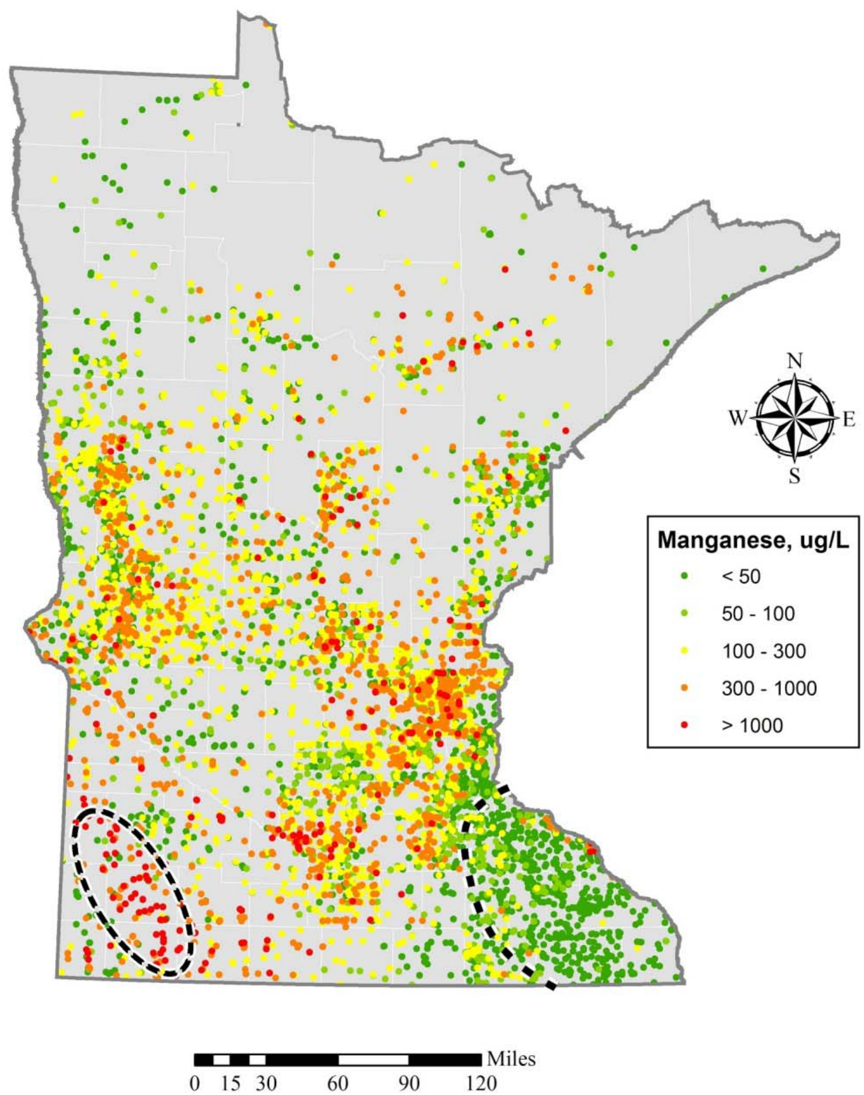

Figure 6. Manganese in groundwater measured at 7,574 wells. Samples collected at various times, for various studies. Data collated and map prepared by the Minnesota Department of Health, February, 2015. Dashed line encloses area of southeastern Minnesota with low (< 50 ug/L) manganese concentrations. Dashed ellipse encloses area of southwestern Minnesota where manganese concentrations exceed 1,000 ug/L.

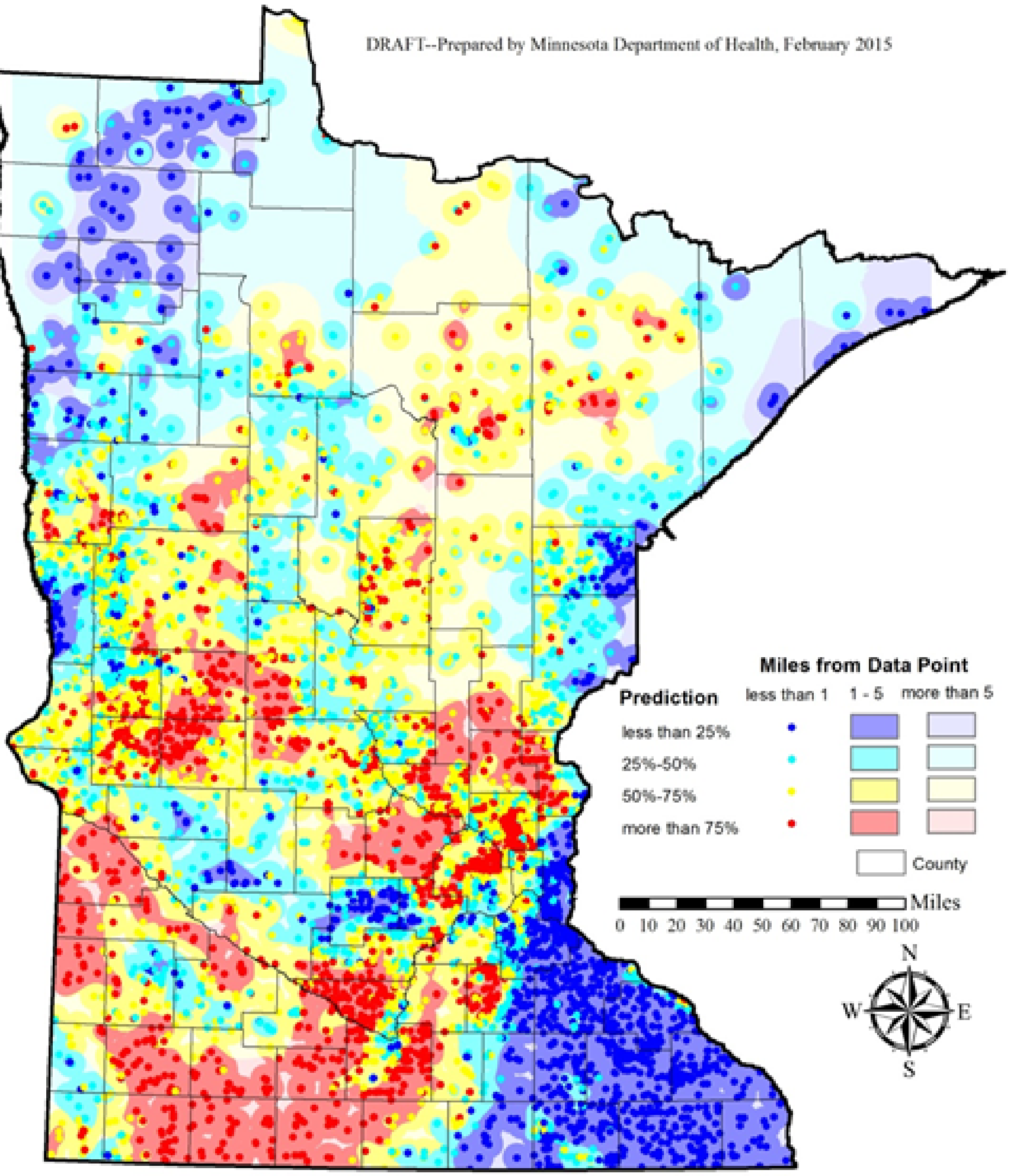

Figure 7. Probability map indicating areas where manganese concentrations in the groundwater will exceed 100 ug/L <25% of the time, 25%-50% of the time, 50%-75% of the time, and > 75% of the time. The map was derived using a general model of spatial variation based on the variability of manganese concentrations and the number of data points. Areas within 1 mile of a sampled well are shown as dots with the most intense color, and shading decreases with distance from each well.

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7 Impact Mitigation

Education and Outreach to Impacted Communities

The groundwater community in Minnesota can play a role by educating others about the potential for health risks associated with manganese in drinking water. Awareness can be improved especially among the water supply industry, physicians and public health professionals, well owners, water conditioning installers or contractors, political and community leaders and educators. Outreach efforts may be targeted in Southwestern Minnesota and other regions of the state that have elevated ambient manganese concentrations in the groundwater.

Identifying and Mitigating Impacted Water Supplies

A water supply with manganese above the HRL of 100 ug/L also exceeds the SMCL of 50 ug/L; therefore, water that poses a potential health risk likely will also have aesthetic issues such as the tendency to stain fixtures or laundry. Many public water supplies containing high manganese concentrations likely are treated to mitigate these aesthetic issues. However, water testing is the only reliable method to provide assurance that water supplies contain levels of manganese below health risk criteria. The results of testing provide a quantitative assessment of whether a municipality is successfully reducing manganese to protective levels, or whether additional treatment should be considered.

Testing

Testing for manganese in all water supplies currently is voluntary: there are no specific requirements for testing for either public or private water supplies.[6] The MDH has begun to sample all new community public water supplies for manganese and only samples non-community wells for manganese if they are investigating a water quality problem such as lead or copper concerns.[7] Water quality can change in transport from the wellhead to the household tap, so sampling for individual supplies should take place at the individual drinking water tap. New private residential wells are not required to be tested for manganese, and samples are typically taken from wellhead, not the tap. Note that sampling ambient groundwater monitoring, as discussed in Section 6, is also limited to samples taken from the wellhead, rather than from the tap.

Local labs can test tap water samples relatively inexpensively (approximately $20). The MDH provides information on qualified laboratories and detailed sampling information. There are no regulatory penalties associated with voluntary testing: the MDH cannot enforce water quality standards in private drinking water supplies or require treatment or replacement of the water source (i.e., drilling a new well). However, if testing of tap water reveals that concentrations exceed health-based guidance values, public water supply consumers or well owners,

[6] per phone conversation with Basam Banat, Principal Engineer with MDH Community Public Water Supply Unit on July 16, 2015

[7] per phone conversation with Brenda Eschenbacher, Sanitarian with MDH Non-Community Public Water Supply Unit on July 16, 2015

especially those who intend to use the water source to mix infant formula, could consider treatment, or temporary alternative water supplies, such as bottled water.

Water Treatment

Specific information about the effectiveness of common treatment methods in removing manganese from water is sparse. However, treatment used to remove iron in water through oxidation, a common treatment step in public water supplies, also removes manganese concentrations. The oxidation of iron tends to occur faster than the oxidation of manganese, so treatment systems can be overwhelmed by iron and be less effective for decreasing manganese.

Complex water quality problems require designing a sophisticated treatment system. An example of a complex problem would be a non-community water-supply well producing a large volume of water that contains both fecal coliform bacteria and manganese. Treatment would begin with chlorination to eliminate the bacteria. The chlorination would also oxidize manganese which would necessitate filtration of the manganese particles. The factors to consider in selecting the appropriate treatment system include: concentration of manganese, volume to be treated, other constituents present in the water, and cost. Sophisticated water treatment systems, although commonly used to treat public water supplies, are rarely used to treat the water obtained from private wells. Common water treatment options are listed in Table 4. Regardless of the treatment used, post-treatment testing for manganese at the primary drinking water tap is essential to ensure that manganese levels are protective of health.

Table 4. Typical water treatment options

Summary of Water Treatment Options to reduce Manganese

Whole House Treatment Point of Entry (POE)	Brief description of process	Advantages	Disadvantages	Relative Cost
Ion exchange (water softening)- includes softening with either sodium chloride or potassium chloride	The water is passed through a resin bed that exchanges the sodium or potassium with the ions; manganese, calcium, magnesium and iron. The ions are removed from the softener resin bed through backwashing and regeneration. Not all softeners reduce manganese; need to check the manufacturers specifications.	Relatively easy to use. Calcium and Magnesium, the minerals that contribute to hard water will be removed. Chloride is safe for a well owner to handle. Softening with potassium chloride regeneration may be more effective than sodium chloride to reduce managanese.[3]	May not be as effective on water with iron and manganese greater than 500 ug/L.[5] Particulates or oxidized manganese may plug the system. Owner has to purchase chloride and fill the supply storage tank. The regenerate discharges a brine that is concentrated with chloride to a septic system or a wastewater treatment plant.	Capital – Moderate O&M – Moderate
Oxidizing Filters	The most common oxidizing filter is Greensand which is glauconite coated with manganese dioxide that oxidizes the dissolved manganese and then filters it out of the water. Other filter media utilized may be birm, anthracite, silica, pyrolusite or specialty media. Birm filters do not require regeneration, however, the raw water must contain a certain amount of dissolved oxygen and the pH should be 7.5 for manganese removal. [2] Synthetic zeolite softens the water and requires less backwash.[5]	When properly maintained greensand filters are extremely efficient for moderate levels of iron and manganese, recommended when combined iron and manganese is between 300 and 1000 ug/L.[2]	Greensand filters require periodic regeneration of the coated gluconate with permanganate which is messy and a strong oxidizer. It must be handled and stored carefully using specific safety measures.[2] Requires regular backwashing to remove precipitate.	Capital – High O&M – High
Oxidation by Ozonation and filtration	Ozone is generated using electricity then injected in the water where is oxidizes dissolved metals such as manganese into particles that can be filtered out.[2]	Reduces bacteria and metals such as manganese. May be useful when there are multiple water quality problems such as metals and bacteria.[2]	Significant maintenance is required. May be more expensive than conventional treatment options	Capital – High O&M – High

Summary of Water Treatment Options to reduce Manganese

Whole House Treatment Point of Entry (POE)	Brief description of process	Advantages	Disadvantages	Relative Cost
Oxidation by Aeration (mixing with air) & Filtration	An aerator is used to introduce oxygen to the water. Manganese and other impurities may become oxidized into a solid which can then be filtered out of the water. Multiple tanks or a large tank containing a filter may be required because the water may require a long detention time for the manganese to settle on top of the filter bed. The filtered manganese should not be discharged into the septic system and may be discharged on the lawn.	Reduction of manganese, iron, hydrogen sulfide, volatile organic chemicals and dissolved gases may occur. Aeration does not add chemicals to the water. Recommended when combined iron and manganese is exceed 10,000 ug/L [2]	Water that contains too much oxygen can become very corrosive. The filter needs to be backwashed and regenerated. A large tank or multiple tanks may be required for filtering.	Capital – High O&M – Low[2]
Oxidation by Continuous Chlorination & Filtration (most commonly used on public water supplies)	Utilization of a feed pump to feed chlorine (chlorine is the most common used, potassium permanganeate and hydrogen peroxide can also be used) as the oxidant into the water and then filtering out the manganese particles is effective.[2] Chlorination is usually driven by need to treat biologicals. Multiple tanks or a large tank containing a filter may be required because the water may require a long detention time for the manganese to settle on top of the filter bed. The filtered manganese should not be discharged into the septic system and may be discharged on the lawn.		Significant maintenance is required. A carbon filter may be needed to remove the chlorine taste. Not recommend for very high manganese levels because a very high pH is required to oxidize the manganese.[2] A large tank or multiple tanks may be required for filtering.	Capital – High O&M – High
Polyphosphate sequestration (most commonly used on public water supplies)	The phosphate is fed into the water using a chemical feed pump that often requires trial and error dose adjustments.	Is effective in the pH range of 5.0 to 8.0 where most other treatment techniques are effective in water with a pH of 7.0.	Manganese is not removed, and the sequestration may fail once ingested. Water treated with these chemicals may have a metallic taste.[5]	Capital – High O&M – High

Summary of Water Treatment Options to reduce Manganese

Point of Use (POU)	Brief description of process	Advantages	Disadvantages	Relative Cost
Carbon filter in a pour through pitcher, faucet mounted or inline to a refrigerator water dispenser and ice cube maker	The carbon filter may be either granular activated carbon (GAC) or a carbon block which is typically more effective that GAC because it has more surface area. The effectiveness of both can depend on how quickly water pours through them[4]. A carbon filter that also contains an ion exchange resin may remove up to 50% of the manganese in the water but the efficiency may decrease with use. To find a filter with the ion exchange resin, find language on the package stating that the filter reduces iron. If the tap water sits in a pour-through pitcher long enough for the manganese to oxidize and form dark colored particles that settle to the bottom of the pitcher	Relatively inexpensive, widely available and easy to use. May reduce a large number of chemicals besides manganese, including: chlorine, voc's and pesticides.	A lot of iron and manganese in the water can fill up the filter and shorten its useful life. A carbon filter should not be used if manganese level is greater than 200 ug/L if trying to achieve a level of 100 ug/L or less. There is no clear indication that filter is no longer reducing manganese	Capital – Low O&M – Low
Reverse osmosis (RO)	RO is similar to other membrane processes, such as ultrafiltration and nanofiltration, since water passes through a semi-permeable membrane. However, in the case of RO, the principle involved is not filtration. Instead, it involves the use of applied hydraulic pressure to oppose the osmotic pressure across a non-porous membrane, forcing the water from the concentrated solution side to the dilute solution side. The water does not travel through pores, but rather dissolves into the membrane, diffuses across, then dissolves out into the permeate. Most inorganic and many organic contaminants are rejected by the membrane and will be retained in the concentrate.[1]	Effective for many chemicals. Many units contain a sediment and a carbon filter. When both a reverse osmosis membrane and carbon filter are used in the system a large number of chemicals may be reduced, besides manganese, including nitrate nitrogen, chlorine arsenic, voc's and pesticides.	Waste three to 20 times more water than produced.[4]	Capital – High O&M – High
Distillation	Distillers use heat to boil the water to produce steam which rises to a cooling section where the steam cools and condenses back to a liquid. The collected water may have up to 99.5 percent of impurities removed [6]. The impurities remain in the boiling chamber and are discarded.	Effective for reducing nearly all impurities: naturally occurring, and microroganisms.[6]	High operational cost to heat the water to generate steam. Requires maintenance to deal with precipitates. The water may taste "flat" because the oxygen and minerals are reduced.	Capital – Moderate O&M – High

Summary of Water Treatment Options to reduce Manganese

Point of Use (POU)	Brief description of process	Advantages	Disadvantages	Relative Cost
Oxidation and settling	Oxidation by aeration can be as simple as leaving a pitcher of water standing overnight. Shaking or stirring can enhance aeration. Successful removal of iron and manganese is evidenced by accumulated sediment.	No chemicals used.	Uncertain how effective this would be in reducing below HRL.	Capital – $0 O&M – $0

[1] US EPA 2004 - US EPA Drinking Water Health Advisory for Manganese January 2004
http://water.epa.gov/action/advisories/drinking/upload/2004_02_03_support_cc1_magnese_dwreport.pdf
[2] Penn State - Penn State Extension http://extension.psu.edu/natural-resources/water/drinking-water/water-testing/pollutants/iron-and-manganese-in-private-water-systems
[3] MDH Well Management Newsletter Spring /Summer 2014 http://www.health.state.mn.us/divs/eh/wells/newsletter/springsummer14.pdf
[4] EWG website http://www.ewg.org/research/ewgs-water-filter-buying-guide/filter-technology
[5] NebGuide University of Nebraska-Lincoln Extension http://extensionpublications.unl.edu/assets/pdf/g1491.pdf
[6] NebGuide University of Nebraska-Lincoln Extension http://extensionpublications.unl.edu/assets/pdf/g1493.pdf

Methods Typically Used by Water Suppliers

Water treatment methods commonly used by water suppliers, such as ultra-violet radiation, air-stripping, and carbon filtration have some capacity to remove manganese. The most common methods for removing manganese include:

- Adsorption – manganese ions are sorbed onto a solid substrate;
- Ion exchange (water softening) – regular home water softeners are generally used to remove calcium and magnesium because these contribute to hardness. Since calcium and magnesium are both divalent ions, home water softeners also will generally remove manganese;
- Suspension/sequestration – can be accomplished by adding polyphospates to the water supply. This does not remove the manganese, but it isolates the ion to temporarily prevent its oxidation. The effects upon human consumption are unknown.
- Oxidation, precipitation, and filtration or settling – Oxidation converts aqueous divalent manganese to relatively insoluble manganese oxides/hydroxides. Common oxidizers, like those listed in Table 5, have different reaction rates and optimal conditions for effectiveness (Knocke et al, 1990).

Table 5. Common oxidants used in water treatment.

Oxidant	Reaction	Comments
Air (O2)	2Mn2+ + 2SO4-2+ 2Ca(HCO3)2 + O2 <=> 2MnO2(s) +2CaSO4 + 2H2O + 4CO2	Very slow
Chlorine (HOCl)	Mn2+ + HOCl + H2O <=> MnO2(s) + Cl - + 3H+	Slow. Concerns regarding trihalomethanes, residual chlorine.
Potassium Permanganate (KMnO4)	3Mn2+ + 2MnO4- + 2H2O <=> 5MnO 2(s) + 4H+	Fast
Chlorine dioxide (ClO2)	Mn2+ + 2ClO2 + 2H2O <=> MnO2(s) + 2ClO2- + 4H+	Fast but temperature dependent. DOC will interfere.
Ozone (O3)	Mn2+ + O3 + H2O <=> MnO2(s) + 2O2 + 2H+	Fast. DOC will interfere.

Residential Treatment Considerations

Household water treatment to decrease staining caused by manganese and iron typically is designed to treat all of the water in the home ("whole house" treatment). Treatment options include devices[8] purchased from a retailer or from a professional. A licensed water conditioning

[8] Three independent water treatment certification agencies websites were consulted: Underwriter's Laboratories (UL), NSF International and the Water Quality Association. No devices are specifically certified for reducing manganese; however, there are many water treatment devices that may reduce manganese concentrations. As more states establish a drinking water standard for manganese, the manufacturers of treatment systems may begin to have their treatment devices certified for manganese removal.

installer or contractor[9] can help determine the appropriate water treatment device by considering the water quality and the consumer's desired results. Regular maintenance is a critical factor in maintaining effectiveness of any selected water treatment device. A low cost alternative is to let water stand in a container until manganese particulates settle to the bottom, making sure not to consume the accumulated sediment.

Alternative Water Supply

Drinking water containing elevated manganese concentrations can be replaced temporarily or permanently with bottled water supplied from another source. Alternatively, a new well could be installed in a different aquifer. In some locations, connection to a public water supply system may be possible. For families relying on formula for infant nutrition, bottled water could be used to reconstitute formula, or they may choose to use pre-mixed, "ready-to-feed" infant formula. Table 6 provides additional consideration of these alternative water supplies.

Table 6. Costs and considerations related to alternative water supply options.

Alternative water supply	Estimated Costs	Notes
Supplied/bottled water	Approximately $365 a year per person ($1/gal x 1 gal/day x 365 day/year)	Levels of manganese < 50ug/L, as regulated by MDA or FDA
Connection to PWS	Varies widely	May be unavailable
Replacement well	On the order of $5,000 to $15,000	No guarantee manganese concentration will be lower in new well

[9] The Minnesota Department of Labor and Industry licenses water conditioning installers and contractors. Only licensed water conditioning persons can install and service water conditioning equipment in single-family dwellings. There is guidance available for hiring a water treatment contractor.

8 Opportunities to Improve Understanding of the Issue

Understanding the potential health risk due to manganese in drinking water will likely take time and careful consideration by the public health, groundwater, and drinking water communities.

The toxicity and health effects research outcomes related to manganese exposure through ingestion is relatively new. Further study of the neurological effects of exposure in infants and children exposed to low levels of manganese is warranted, along with comparison of the effects of drinking water versus dietary exposure.

Understanding the spatial distribution of manganese in ambient groundwater provides an effective way to identify the populations that may be most at risk of exposure to manganese in drinking water. This effort could be refined to the degree that, perhaps with adequate data distribution at the county-scale, predictions could be made about the occurrence of manganese in groundwater. To improve this approach, coordination should take place between various ambient groundwater quality monitoring programs (i.e., MDH, MPCA, MDA, MN DNR, local governments, etc.). Additional considerations to this approach include:

- Correlation between groundwater and drinking water exposure: What is the correlation between manganese concentrations in wells and the manganese concentrations in tap water supplied from them?
- Data density: Spatial analysis is dependent on an abundance of accurately-located and verified location data. The analysis could be refined by locating and sampling water wells which have not yet been accurately located and verified. Additional sampling and analysis for manganese from wells in sparsely-sampled areas will improve the data distribution.
- Incomplete records: Inadequate well construction (e.g., dug-wells, multi-aquifer wells) can cause problems with data interpretation. How does missing information on well construction or geology for some wells affect the assessment?
- Understanding the correlation between geology and manganese-enriched groundwater: Studies of how different geologic environments affect manganese concentrations in groundwater. This may provide an aerial screening tool for elevated manganese occurrences. Improved information about geochemical controls on manganese release to groundwater. Improved information on the spatial and vertical distribution of manganese-bearing minerals within Minnesota.

Further evaluation of the effectiveness of manganese removal by common treatment technologies is warranted, especially with specific reference to health-based water quality concentrations. Specific evaluations of common, and readily-available point-of-use treatment methods, such as pitcher and/or faucet filtration units may provide information about relatively simple treatment strategies.

9 Review of Major Findings and Issues

Health studies indicate neurological sensitivity to manganese exposure levels over 100 ug/L in infants under the age of 1. These findings led the MDH to issue a tiered RAA for manganese: 100 ug/L for infants, and 300 ug/L for children and adults. The RAA takes into account the high potential risk of exposure to infants: they may be relying on reconstituted formula as their primary source of nutrition and exposed to manganese in both the drinking water and powdered formula. The risk of neurological problems also is increased in infants because they readily absorb ingested manganese and retain it, primarily in the tissues of the brain, longer than adults and children.

Groundwater containing manganese above the RAA values is routinely used as a drinking water source in Minnesota. Manganese in groundwater is largely controlled by the distribution of solid-phase manganese in aquifers and local redox conditions. Ambient water quality monitoring and other monitoring programs related to public water supplies form the basis for a statewide assessment of manganese concentrations in groundwater. Ambient groundwater measurements do not represent exposure conditions for people using groundwater as a drinking water source because manganese concentrations may change from the groundwater source (i.e., the supply well) to the drinking water source (i.e., the tap) in water distribution systems. However, they can be used to identify potentially susceptible populations. The distribution of manganese in ambient groundwater indicates that manganese concentrations in Southeastern Minnesota typically are less than 50 ug/L, and commonly exceeds 1,000 ug/L in Southwestern Minnesota.

Groundwater and water supply professionals are generally aware of the widespread occurrence of manganese in groundwater because the manganese oxides/hydroxides precipitate from water supplies containing more than about 50 ug/L. These precipitates cause staining and other aesthetic effects. However, people may not be aware of the health implications related to manganese in drinking water, especially for infants who rely on reconstituted formula for nutrition. Although some public water suppliers may monitor levels of manganese for aesthetic purposes, manganese levels are not regulated in drinking water supplies, with the exception of bottled water supplies.

Healthcare providers and consumers, especially new parents, should be aware of the health risk posed by manganese in their drinking water supply. When water supplies are treated to below about 50 ug/L manganese to reduce aesthetic effects, these water supplies are adequately protective of health. However, because manganese levels are not typically measured, observation of stained fixtures or clothing should be used an indicator of potential health risk, especially within areas of the state with high natural manganese concentrations in groundwater. Using a tap water source that stains faucets to mix formula for infants is likely not protective of health. Using this water as a drinking water source also may not be protective of adult and child health.

Many effective technologies are available for treating water supplies. Carbon filtration, reverse osmosis, cation exchange (water softening), adsorption, oxidation and filtering all likely remove manganese, although data regarding the efficiency of manganese removal of those systems is not available. Post-treatment testing would be required in most situations to ensure protective levels. Alternative water supplies such as bottled water or “ready-to-feed” infant formula are also practical solutions to mitigate or prevent exposure in formula-fed infants.

Helpful Links

Home Water Treatment Units: Point-of-Use Devices
http://www.health.state.mn.us/divs/eh/water/factsheet/com/pou.html

Deceptive Sales of Water Treatment Systems
http://www.health.state.mn.us/divs/eh/water/factsheet/com/pousales.html

Treatment systems for household water supplies: Iron and manganese removal
http://www.extension.umn.edu/environment/water/treatment-systems-for-household-water-supplies-iron-and-manganese-removal/

MDH Information: information sheet on manganese in groundwater, and in fall of 2012 MDH published a short article in their Waterline newsletter.

More recently MDH included an article on manganese in groundwater in their spring/summer 2014 Minnesota Well Management News publication.

Also see: http://www.health.state.mn.us/divs/eh/water/swp/manganese/index.html