Iron and Manganese Removal Handbook

Second Edition

American Water Works Association

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Assessing the Problem

This chapter describes the occurrence of iron and manganese in drinking water systems. It presents an overview of applicable regulations and of the potential simultaneous compliance issues that may be impacted by iron and manganese treatment.

SOURCES OF IRON AND MANGANESE

Iron

Iron (Fe) is the second most abundant metal on earth, after aluminum. It accounts for about 5 percent of the earth's crust. Pure iron is rarely found in nature because the iron ions Fe^{2+} and Fe^{3+} readily combine with oxygen- and sulfur-containing compounds to form oxides, hydroxides, carbonates, and sulfides. Iron is most commonly found in nature in the form of its oxides (World Health Organization 2003).

The median iron concentration in rivers has been reported to be 0.7 mg/liter (mg/L). In anaerobic groundwater where iron is in the form of iron(II), concentrations will usually be 0.5 mg/L to 10 mg/L, but concentrations up to 50 mg/L can sometimes be found. Concentrations of iron in drinking water are normally less than 0.3 mg/L. Iron concentrations may be higher in countries where various iron salts are used as coagulating agents in water treatment plants, or where cast-iron, steel, and galvanized iron pipes are used for water distribution (WHO 2003).

Manganese

Manganese (Mn) is found throughout the environment and is needed for normal physiological functions in humans and animals. Exposure to low levels of manganese in the diet is considered essential for human health. The average daily intake from food is 1–5 mg/day (USEPA 2010).

Manganese is detected in approximately 70 percent of groundwater sites in the United States (WHO 2011), but generally below levels of public health concern (USEPA 2002). Average manganese levels in drinking water are approximately 0.004 mg/L (USEPA 2010).

One survey of public water supplies found about 95 percent contained manganese at a concentration of less than 0.1 mg/L (Cooke 2014). The National Inorganic and Radionuclide Survey collected data from 989 community public water systems served by groundwater in 49 US states between 1984 and 1986 and found that manganese was detected in 68 percent of the groundwater systems, with a median concentration of 0.01 mg/L. Supplemental survey data from public water systems supplied by surface water in five states reported occurrence ranges similar to those of groundwater.

GROUNDWATER SOURCES

The iron and manganese found in groundwater are generally in a dissolved state and generally remain stable over time. While most groundwater does not contain microorganisms, in some aquifers the presence of iron and manganese promotes the growth of iron-reducing bacteria called crenoforms. These have scientific names, including *Crenothrix*, *Gallionella, Leptothrix*, and *Sphaerotilus*.

Crenoforms congregate in piping to form heavy, jelly-like, stringy masses that can impair the water-carrying capacity of an entire system. Allowing the formation of these organisms through inadequate removal of iron and manganese and inadequate disinfection of filtered water at the water treatment plant is almost sure to result in a substantial cost in time and money to flush and/or swab distribution lines. Crenoforms are also likely to reform following removal.

According to Cullimore (1993), "It was found during that research phase that 95 percent of the groundwaters tested in Saskatchewan, Canada, were positive for IRB (iron-reducing bacteria). Microscopic examination found that, of the sheathed and stalked IRB, *Crenothrix*, *Leptothrix*, *Sphaerotilus*, and *Gallionella* were frequently dominant types. Given the universal nature of the presence of IRB it becomes more critical to appreciate their relative aggressivity."

Cullimore continues, “The presence of IRB can result in elevated distribution system iron levels even if the raw water iron levels are less than 0.3 mg/L. For systems having problems with red water, consideration should be given to analyzing the water for IRB. The BART (Biological Activity Reaction Test) can be used to identify if a groundwater or distribution system has IRB.” He notes that contaminants can be transported between groundwater and surface water when stream levels are low and aquifers serve as a source of recharge for a surface water.

SURFACE WATER SOURCES

Surface waters include reservoirs, rivers, creeks, and streams, including streams that are fed from upstream reservoirs. In flowing rivers and streams, iron and manganese levels tend to be lower and easier to remove due to the elevated dissolved oxygen (DO) levels. When rivers and streams are impounded, iron and manganese levels will increase.

The amount of iron and manganese that dissolves into the surface water depends on the character of the surrounding soil and the amount of plant life. Decomposition of organic matter (algae, leaves, and other plant material) in the lower sections of a reservoir may result in anaerobic conditions (i.e., near zero oxygen) under which iron and manganese compounds in those zones are converted to soluble compounds.

In much of North America, attempts to remove iron and manganese from impounded surface waters encounter a further challenge at least twice a year: just after the breakup of ice in the spring and just before water freezes in the fall or winter. Colder, denser water at the top of a reservoir sinks to the bottom, while warmer water at the bottom rises to the top, a phenomenon called a *water inversion* or *turnover*. The water that rises to the top brings with it soluble compounds of iron and manganese. As wind and wave action mixes oxygen from the air with the water, iron and manganese are gradually oxidized. The oxidized elements precipitate, or separate out of solution. These elements sink to the bottom again as solids and are brought back into solution where oxygen is absent and carbon dioxide has been formed. While some of the Mn^{2+} is very slowly oxidized in this way, the action of certain bacteria causes a much faster rate of oxidation. The scientific name for this process is microbially mediated oxidation. Microbially mediated Mn^{2+} oxidation can contribute significantly to manganese cycling in a reservoir.

Preparing for Inversion

An operator faces the challenge of learning how to read the signs of an inversion and how to adjust the treatment process to adapt to the increased levels of iron and manganese in the raw water coming into the treatment plant, usually through a combination of actions such as adding chemicals, shortening filter runs by backwashing more often, or other measures. If time and technology permit, measurements of DO should be taken, and a temperature profile should be developed to assist in identifying stratification. Records of operating data help operators know just when to prepare for increased levels of iron and manganese in the raw water. Because these occurrences do not necessarily happen at the same time every year, a strong case can be made for historical record keeping, which can illustrate patterns over time. Guided by records showing DO levels, stratification data, weather data, time lapses between events, and dates of events, the operator can respond proactively when levels of iron and manganese elevate.

It should be noted that gases are usually released as a part of the total water inversion occurrence, but by the time odors can be detected, iron and manganese have long since been released into the raw water.

Reducing Iron and Manganese in Feedwater

Because changes in the operation of the reservoir may reduce iron and manganese levels in the raw water supply, utilities should consider adjusting their reservoir management strategies or coordinating with the agency that operates the reservoir to determine the best actions to control these metals. During much of the year in temperate climates, the water nearest the reservoir surface is least likely to contain iron and manganese, but may contain other contaminants, such as algae. The inlet to the water treatment plant feedline should ideally move up and down, so water can always be taken from a level below surface plant growth but above the zone that lacks oxygen. Other iron and manganese reduction methods include installing an aeration system in the reservoir to increase oxygen levels or adding a mixing system to minimize stratification.

Some water treatment plants have intakes on streams or rivers located downstream of a reservoir. Unlike reservoirs, which generally have relatively low turbidity, streams and rivers can experience moderate to high turbidities during rain events (50 to 100 ntu) along with elevated iron and manganese associated with reservoir turnover. In some instances, high algae levels and taste-and-odor events occur simultaneously, adding to treatment challenges. Treatment and chemical feed systems that are flexible enough to address a wide range of water quality conditions should be considered.

HEALTH EFFECTS

Iron

Iron is an essential element in human nutrition. Estimates of the minimum daily requirement for iron depend on age, sex, physiological status, and iron bioavailability, and requirements range from about 10 to 50 mg/day. As a precaution against storage of excessive iron in the body, the Joint FAO[1]/WHO Expert Committee on Food Additives (JECFA 1983) established a provisional maximum tolerable daily intake (PMTDI) of 0.8 mg/kg of body weight. This applies to iron from all sources except iron oxides used as coloring agents, and iron supplements taken during pregnancy and lactation, or taken for specific clinical requirements. Allocation of 10 percent of this PMTDI to drinking water gives a value of about 2 mg/L, which does not present a hazard to health.

The taste and appearance of drinking water will usually be affected below this level, although iron concentrations of 1 to 3 mg/L can be acceptable for people drinking anaerobic well water. Iron (as Fe^{2+}) concentrations of 40 µg/liter can be detected by taste in distilled water. In a mineralized spring water with a total dissolved solids content of 500 mg/L, the taste threshold value was 0.12 mg/L. In well water, iron concentrations below 0.3 mg/L were characterized as unnoticeable, whereas levels of 0.3 to 3 mg/L were found acceptable (WHO 2003; Dahi[2] 1991).

Manganese

According to the USEPA, "Chronic (long-term) exposure to high levels of manganese by inhalation in humans may result in central nervous system (CNS) effects. Visual reaction time, hand steadiness, and eye-hand coordination were affected in chronically-exposed workers. A syndrome named *manganism* may result from chronic exposure to higher levels; manganism is characterized by feelings of weakness and lethargy, tremors,

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1 Food and Agriculture Organization of the United Nations

2 Dahi, E., 1991. Personal communication.

a mask-like face, and psychological disturbances. Respiratory effects have also been noted in workers chronically exposed by inhalation. Impotence and loss of libido have been noted in male workers afflicted with manganism" (USEPA 2010).

Absorption. Limited data indicate that gastrointestinal absorption of manganese is low, averaging approximately 3 percent. The body has mechanisms that can usually control the total amount of manganese by increasing its elimination if excess levels are consumed. Because manganese and iron compete for gastrointestinal absorption, manganese uptake from the gut is likely to be increased in iron-deficient persons. Inhaled manganese may be absorbed in the lungs if the particles are small enough. Absorption through the skin is expected to be very low, less than 1 percent (Cooke 2014).

Short-term (acute) toxicity. Studies in animals and humans indicate that inorganic manganese has a very low acute toxicity by any route of exposure. However, acute inhalation exposure to high levels of manganese dust can cause an inflammatory response in the lung. In a human study, women took daily manganese supplements of 15 mg for 90 days. No toxic effects to the blood were seen (Cooke 2014).

Long-term (chronic) toxicity. Conclusive evidence that overexposure to manganese can result in adverse health effects has been observed in miners and steelworkers exposed by inhalation to manganese dusts. The range of effects seen is called manganism or referred to as *manganese-induced Parkinsonism*, because some of the symptoms are similar to those seen in cases of Parkinson's disease. Symptoms include muscle tremor, reduced motor skills, difficulty and slowing of walking, slurred speech, and sometimes psychiatric disturbances (Cooke 2014).

A few reports in the literature examine the effects of excess oral exposure of humans to manganese. One report describes symptoms of lethargy; increased muscle tone, spasm, and tremors; and mental abnormalities in persons drinking water contaminated by manganese from dry-cell batteries buried nearby. The actual length of time that people were drinking the water was not clear. The exposure time spanned a period of two to three weeks for some individuals and potentially much longer for others who developed symptoms. When the water was tested, it contained manganese at a concentration of 14.3 mg/L, which is well above the secondary standard set by USEPA. Those who studied this event believe it likely that other factors, possibly chemicals in the water besides manganese, contributed to the health effects (Cooke 2014).

The greatest exposure to manganese is usually from food. Adults consume between 0.7 and 10.9 mg/day in the diet, with even higher intakes being associated with vegetarian diets (Freeland-Graves et al. 1987; Greger 1999; Schroeder et al. 1966). Manganese intake from drinking water is normally substantially lower than intake from food. At the median drinking water level of 10 μg/L determined in the National Inorganic and Radionuclide Survey (NIRS), the intake of manganese from drinking water would be 20 μg/day for an adult, assuming a daily water intake of 2 liters. Exposure to manganese from air is generally several orders of magnitude less than that from the diet, depending on proximity to a manganese source (USEPA 2003). USEPA has also included manganese on its Contaminant Candidate List 4.

REGULATORY STANDARDS

According to the USEPA and WHO, iron and manganese in drinking water do not have adverse health consequences at the concentrations typically encountered in source waters. The USEPA and WHO have established a secondary MCL of 0.3 mg/L for iron and 0.05 mg/L for manganese. According to the USEPA, these secondary standards are established only as guidelines to assist public water systems in managing their drinking water for aesthetic considerations such as taste, color, and odor. An AWWA task group suggested limits of 0.05 mg/L for iron and 0.01 mg/L for manganese for an "ideal" water for public use (Bean 1962).

The Canadian drinking water quality guideline for iron is an aesthetic objective (AO) of less than or equal to 0.3 mg/L. The Canadian drinking water guideline for manganese is an AO of less than or equal to 0.05 mg/L.

It should be noted that the presence of manganese in drinking water will be objectionable to consumers if the manganese is deposited in water mains and causes water discoloration. Concentrations below 0.05 mg/L are usually acceptable to consumers, although this may vary with local circumstances.

According to Health Canada (1987), "The Recommended Daily Intake (RDI) of manganese for Canadians has yet to be established. In a recent comprehensive literature survey of studies of manganese metabolism in humans, it was concluded that previous estimates for a safe and adequate daily dietary allowance for manganese (2.5–5.0 mg/d) were too low, and a new range of 3.5–7.0 mg/d was recommended for adults."

Design Standards

In addition to the water quality regulations, several design standards describe needed treatment requirements. Several of these design standards are detailed in this handbook in the specific treatment sections.

Simultaneous Compliance

When addressing treatment for iron and manganese, the Safe Drinking Water Act should be considered in its entirety. Simultaneous compliance issues may include the following:

- Filter-top chlorination for manganese reduction, which can increase disinfection by-products
- Accumulation of radium in greensand filters
- The use of membranes to provide greater pathogen removal, which behaves differently from conventional filter sand with respect to manganese removal

To avoid simultaneous compliance issues, it is essential that all of the potential regulatory consequences be identified and that they be evaluated through studies, including jar and pilot testing.