# *Manganese*

The aesthetic objective for manganese in drinking water is *≤0.05 mg/L (≤50 µg/L).* The presence of manganese in drinking water supplies may be objectionable for a number of reasons. At concentrations above 0.15 mg/L, manganese stains plumbing fixtures and laundry and produces undesirable tastes in beverages. As with iron, the presence of manganese in water may lead to the accumulation of microbial growths in the distribution system. Even at concentrations below 0.05 mg/L, manganese may form coatings on water distribution pipes that may slough off as black precipitates.

## General

The element manganese is present in over 100 common salts and mineral complexes that are widely distributed in rocks, in soils and on the floors of lakes and oceans. Manganese is most often present as the dioxide, carbonate or silicate. It may exist in oxidation states ranging from –3 to +7; the manganous ($Mn^{2+}$) and manganic ($Mn^{4+}$) oxidation states are the most important for aquatic systems.(1)

In Canada, manganese is primarily employed in the steel industry, where it is used to counteract the effects of sulphur, as a deoxidizing agent and as an ingredient in special alloys. Manganese is also used in the manufacture of dry cell batteries and as an oxidizing agent in the chemical industry. In 1985, about 25 398 t of ferromanganese, 6979 t of silicomanganese, 102 048 t of manganese ore and 3240 t of manganese metal were imported into Canada; 22 408 t of ferromanganese were exported.(2)

## Occurrence

Manganese is the principal constituent of manganese nodules and ferromanganese oxide concretions found in the Great Lakes and in several lakes in eastern Ontario.(3–5) The weathering products of surficial manganese deposits contribute only slightly to the manganese content of river and sea water. Manganese is generally present in natural surface waters as dissolved or suspended matter at concentrations below 0.05 mg/L. A survey of Canadian surface waters undertaken in 1980–1981 showed that the usual range of manganese in freely flowing river water was 0.01–0.40 mg/L. The highest concentrations recorded were in the Carrot River in Saskatchewan; dissolved manganese reached 1.7 mg/L, whereas extractable manganese peaked at 4.0 mg/L.(6) Manganese is more prevalent in groundwater supplies than in surface water supplies owing to the reducing conditions that exist underground. High concentrations of manganese are also found in some lakes and reservoirs as a result of acidic pollution; in 1972–1973, a mean manganese concentration of 0.26 mg/L was recorded in a small acidic lake near Sudbury, Ontario.(7)

During 1974–1976, 67% of 84 national sampling sites for drinking water had manganese concentrations below 0.02 mg/L; concentrations above 0.05 mg/L were recorded at 25% of the stations.(8) A survey of 20 drinking water treatment plants in Ontario during 1985–1986 showed mean manganese concentrations of 0.014 mg/L and 0.008 mg/L in the raw and treated water, respectively. Concentrations of manganese were consistently higher in the distribution system than in the treated water. In Hearst, Ontario, for example, manganese concentrations in raw water, in treated water and in the distribution system (samples taken after a five-minute flush) were 0.023, 0.009 and 0.011 mg/L, respectively.(9)

Industrial emissions containing manganese oxides are the principal source of manganese in the atmosphere. The total atmospheric emission of manganese from anthropogenic sources in Canada was estimated to be 1225 t in 1984; 78.5% of this originated from industrial processes, mainly related to metal alloy production. Emissions stemming from gasoline-powered motor vehicles accounted for a further 17.2%, whereas the remaining 4.3% of atmospheric manganese emissions were due to the burning of coal for power generation, solid waste incineration and pesticide application.(10)

A study of the chemical composition of particulate matter over Edmonton, Alberta, between 1978 and 1979 showed a mean concentration of manganese in air of 0.071 µg/m$^3$. Seasonal variation was considerable: in November 1978, the mean concentration was 0.050 µg/m$^3$; in March/April and July/August 1979, the average concentrations were 0.065 µg/m$^3$ and 0.098 µg/m$^3$, respectively. In a remote, non-urban site (Stony Plain Meteorological Station), the average

concentration was <0.03 µg/m$^3$ during the same sampling periods. At both sites, the manganese is believed to be mainly of crustal origin.[11]

In a 1982 survey across Ontario, the spatial pattern of concentrations of trace metals, including manganese, in precipitation and air was monitored.[12] A general decreasing trend in manganese concentrations from south to north was observed. The mean concentration of manganese in air ranged from 0.007 µg/m$^3$ in the south to 0.0029 µg/m$^3$ in the north. Similarly, the annual dry deposition of manganese ranged from 1.53 µg/m$^2$ in the south to 0.62 µg/m$^2$ in the north. The mean annual concentration of manganese in precipitation ranged from 0.0047 mg/L in the south to 0.0031 mg/L in the north.

Manganese is invariably present in arable soil.[13] The average manganese content of Canadian soil is 0.08 mg/g[14]; concentrations range from non-detectable to 7 mg/g.[15]

Manganese is associated, in trace amounts, with every kind of plant and animal tissue.[13] The manganese content of foodstuffs varies considerably. Generally, low concentrations are found in dairy products (mean 0.12 mg/kg) and meats (mean 0.33 mg/kg).[16] Manganese is relatively evenly distributed throughout all of the food groups derived from plant sources (mean 2.66 mg/kg).[16] California wines analysed in Canada contained manganese at concentrations ranging from 0.18 to 1.64 mg/kg,[17] whereas manganese concentrations in carbonated beverages and fruit juices ranged from <0.01 to 0.03 mg/L and from 0.18 to 1.3 mg/L, respectively.[18]

## Canadian Exposure

In Canadian studies, daily dietary intake of manganese has been estimated to be 4.1 mg[19] and 3.3 mg.[16] A more recent estimate of average daily intake, calculated using data from Canadian per capita food consumption for 1981 and 1982[20] and literature values of the manganese content of the various dietary components,[16,19,21–26] was 4.7 mg (females 3.9 mg; males 5.6 mg).[27]

If a daily water consumption of 1.5 L and a manganese concentration of 0.02 mg/L in the drinking water are assumed, the daily intake of manganese from Canadian drinking water would be approximately 0.03 mg. Actual daily intake of manganese from drinking water varies considerably, depending on the sampling area in Canada.

If an average concentration of manganese in air of 0.0001 mg/m$^3$ and a daily respiratory volume of 20 m$^3$ are assumed, the total daily intake of manganese through the respiratory tract would be 0.002 mg.

Based on the above figures, the total daily exposure of a Canadian to manganese from all environmental sources would be just over 4.7 mg. The greatest source of this exposure is from food. Intake from food is substantially higher than intake from drinking water, even in areas where the manganese content of water is high. In a 1975 study, the U.S. Environmental Protection Agency estimated total daily intake of manganese to be approximately 3 mg.[28]

## Analytical Methods and Treatment Technology

Manganese in water can be determined by atomic absorption spectrometry by direct aspiration into an air–acetylene flame (detection limit 0.01 mg/L). Alternatively, low concentrations can be determined by chelation with ammonium pyrrolidine dithiocarbamate, extraction into methyl isobutyl ketone and aspiration into an air–acetylene flame.[29]

The removal of manganese from water supplies is often done in conjunction with iron removal. Manganese can be removed by the conventional treatment process of chlorination–filtration, at a pH of 8.4 or above.[30] It is difficult to remove manganese to achieve concentrations below 0.05 mg/L.

## Health Considerations

### Essentiality

Manganese is an essential element in humans and animals, functioning both as an enzyme co-factor and as a constituent of metalloenzymes. It has been implicated in carbohydrate metabolism, lipid and sterol metabolism and oxidative phosphorylation. Furthermore, experimental studies in animals suffering from manganese deficiency have suggested a role for manganese in the prevention of tissue damage following lipid peroxidation and in the normal functioning of the central nervous system.[31]

Gross deficiencies of manganese have never been observed in the general population, but a recent experimental study involving human subjects fed a manganese-deficient diet (0.11 mg/d) resulted in the development of dermatitis and hypocholesterolaemia and elevated concentrations of serum calcium and phosphorus.[32]

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.[31] A statistical analysis of the metabolic studies showed that a daily manganese intake of approximately 5 mg is required to consistently maintain a positive balance.

**Absorption, Distribution and Excretion**

The main routes of absorption for manganese are the respiratory and gastrointestinal tracts; cutaneous absorption of inorganic manganese is negligible.[13] Organically bound manganese may be absorbed through the skin.[33]

Manganese is absorbed in the small intestine by a high-affinity, low-capacity active transport mechanism.[34] In the young infant, absorption of manganese is very high, approaching 99% at birth[35]; absorption gradually decreases with age to around 5.5% in the adult.[36,37] Absorption of manganese in humans is affected by a large number of dietary factors. At low manganese intake levels, manganese bioavailability is enhanced by ascorbic acid and by meat-containing diets but is inhibited by some dietary fibre sources.[31] Several metal ions — in particular iron, magnesium and calcium — are known to decrease the absorption and retention of manganese.[31] There is evidence that manganese uptake is higher from soft drinking water than from hard drinking water.[38]

The total body burden of manganese in an adult human is between 10 and 20 mg.[39] Bones contain the highest amount, about 25% of the body burden[40]; most of this seems to be deposited in the inorganic portion of the bone, which acts as a buffer. Manganese also accumulates in tissues that are rich in mitochondria and endoplasmic reticulum; the principal sites of accumulation after the skeleton are the liver, skeletal muscle, connective tissue and intestine. On a concentration basis (µg Mn/g tissue), the testes, liver, pancreas and kidneys are the tissues that accumulate the most manganese.[25]

The regulation of manganese excretion seems to be the main homeostatic mechanism for manganese,[41] although there is some evidence that regulation of absorption can also occur.[42,43] Endogenous manganese is excreted via the liver in bile[44] for eventual elimination in the faeces, with pancreatic and other intestinal secretions increasing when the biliary system is overloaded.[45] It is difficult to quantify biliary excretion routes, as reabsorption can occur; however, reabsorption appears to be low[46] and may depend on the amount of calcium in the faeces.[47] Variations in dietary manganese have little effect on the small amount of manganese excreted in the urine.[48]

There are relatively few data describing the rate of elimination of manganese from humans. In a recent study involving 14 subjects, it was shown that orally administered manganese was eliminated by two sequential processes with biological half-lives of 13 (range 6–30) and 34 (range 26–54) days, respectively.[49] Both the rate of excretion and the amount of manganese eliminated are influenced by a number of factors, including manganese intake, the iron status in the body, the influence of other dietary components and innate differences in the genetic make-up of the individual.

**Toxic Effects**

Manganese is regarded as one of the least toxic elements. Chronic ingestion experiments in rabbits, pigs and cattle at 1–2 mg/g dose levels showed no immediate effects other than a change in appetite and a reduction in the incorporation of iron into haemoglobin.[33] However, more recent experimental and epidemiological studies have shown that exposure to manganese can indeed lead to deleterious changes, some of which are referred to below.

In general, cations are more toxic than anions, and $Mn^{2+}$ is more toxic than $Mn^{3+}$.[50] The associated anion may affect the toxicity of manganese; the citrate ion, for example, is more toxic than the chloride ion. Toxicity varies not only with the valence state, but also with the route of administration and, when manganese is inhaled, with particle size.

Apart from acute “metal fume fever” caused by inhaled or swallowed manganese dioxide, toxicity in humans is usually the result of chronic inhalation of high concentrations of manganese in dusts from industrial sources.[51–56] The principal effects of long-term occupational exposure to inorganic manganese compounds are “manganese pneumonia” or pneumonitis[13] and, more commonly, manganism. The neurological manifestations and biochemical alterations due to manganism have been detailed by Donaldson and Barbeau.[57]

Except for one isolated incident, manganese intoxication due to drinking water has not been documented. In 1941, the cause of an encephalitis-like disease in Japan was attributed to contaminated well water that had a manganese concentration of 14 mg/L; however, concentrations of other metals, especially zinc, were also excessive, and it was never unequivocally established whether the high concentration of manganese was solely responsible for the disease.[58] In another area of Japan, a manganese concentration of 0.75 mg/L in a drinking water supply had no apparent adverse effect on the health of its consumers.[52]

A number of experimental studies have shown that exposure to manganese can cause deleterious effects on the male reproductive system. In rabbits, chronic parenteral administration of manganese resulted in degenerative changes to the seminiferous tubules, eventually leading to infertility.[59] Administration of $Mn_3O_4$ (hausmannite) at a concentration of 1050 ppm in the diet of mice resulted in retarded growth and weight gain of the testes, seminal vesicles and preputial glands.[60]

In a recent epidemiological fertility study of Belgian workers exposed to manganese dust in a factory

producing manganese oxide, sulphate and carbonate, it was found that the number of children born to exposed male workers (aged 16–35) was half that in a control group.[61]

Questions have been raised in the literature regarding a possible link between manganese and human birth defects.[41,62,63] Manganese dust is reported to affect the behaviour of the offspring of mice exposed during gestation.[64]

Manganese has been shown to be mutagenic in several microbial studies[65,66] as well as in human cell line studies.[67,68]

Manganese produces lymphosarcomas[69] and adenomas[70] in mice. However, there is no evidence that manganese exposure causes cancer in humans,[71] despite the often large occupational exposures.

### Acceptable Daily Intake

No adverse health effects were noted in humans with the following daily manganese intakes[39]:

| | Average (mg) | Range (mg) |
|---|---|---|
| Food | 3.0 | 2.0–7.0 |
| Water | 0.005 | 0.0–1.0 |
| Air | 0.002 | 0.0–0.029 |

## Other Considerations

The presence of manganese in drinking water supplies may be objectionable for a number of reasons unrelated to health. At concentrations exceeding 0.15 mg/L, manganese stains plumbing fixtures and laundry and causes undesirable tastes in beverages.[72] Oxidation of manganese ions in solution results in precipitation of manganese oxides and incrustation problems. Even at concentrations of approximately 0.02 mg/L, manganese may form coatings on water distribution pipes that may slough off as black precipitates.[73] The growth of certain nuisance organisms is also supported by manganese.[72,74] The presence of “manganese” bacteria, which concentrate manganese, may give rise to taste, odour and turbidity problems in the distributed water.

## Rationale

1. Manganese is among the elements least toxic to mammals; only exposure to extremely high concentrations from human-made sources has resulted in adverse human health effects.

2. At levels exceeding 0.15 mg/L, manganese stains plumbing fixtures and laundry and causes undesirable tastes in beverages. Even at concentrations as low as 0.02 mg/L, problems may be encountered; however, it is difficult to remove manganese to achieve concentrations below 0.05 mg/L.

3. The aesthetic objective for manganese in drinking water is therefore ≤0.05 mg/L. Manganese at this recommended limit is not considered to represent a threat to health, and drinking water with much higher concentrations has been safely consumed. A maximum acceptable concentration has, therefore, not been set.

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