

## Manganese

**WHO health-based guideline value (recommended limit): 0.5 mg/l**

**WHO guideline value based on acceptability to consumers: 0.1 mg/l**

**National health-based standard in most countries: 0.5 mg/l**

**Typical range in groundwater: usually <1 µg/l (up to around 1 mg/l)**

This is one of a series of information sheets prepared for a limited number of inorganic constituents of significant health concern that are commonly found in groundwater. The sheets aim to explain the nature of the health risk, the origin and occurrence of the constituent in groundwater, the means of testing and available methods of mitigation. The purpose of the sheets is to provide guidance to WaterAid Country Office staff on targeting efforts for water-quality testing and to encourage further thinking within the organisation on water-quality issues.

### Health and aesthetic effects

Manganese is an essential trace element for human health. The daily nutritional requirement is 30–50 µg/kg of body weight (WHO, 1993). Manganese is readily absorbed in human metabolism but the degree of absorption depends on dose, chemical form and effects of other metals. Manganese dissolved in water is likely to be more bioavailable than solid forms.

At excessive concentrations, manganese can be detrimental to health. Evidence from occupational exposure indicates that manganese can affect neurological function. Miners and welders exposed through airborne contamination for long periods have developed neurological disorders such as Parkinson's disease (Takeda, 2003). Some links have been made between exposure to manganese and a form of motor neuron disease found in the Pacific region, known as Guamian amyotrophic lateral sclerosis (Foster, 1992). Iwami et al. (1994) found correlations between the concentrations of manganese in food and the prevalence of motor neuron disease in the Kii Peninsula of Japan. Cawte et al. (1987) also reported neurological symptoms in manganese ore miners from Australia. Occupational exposure to manganese has also been linked with liver, kidney and lung damage.

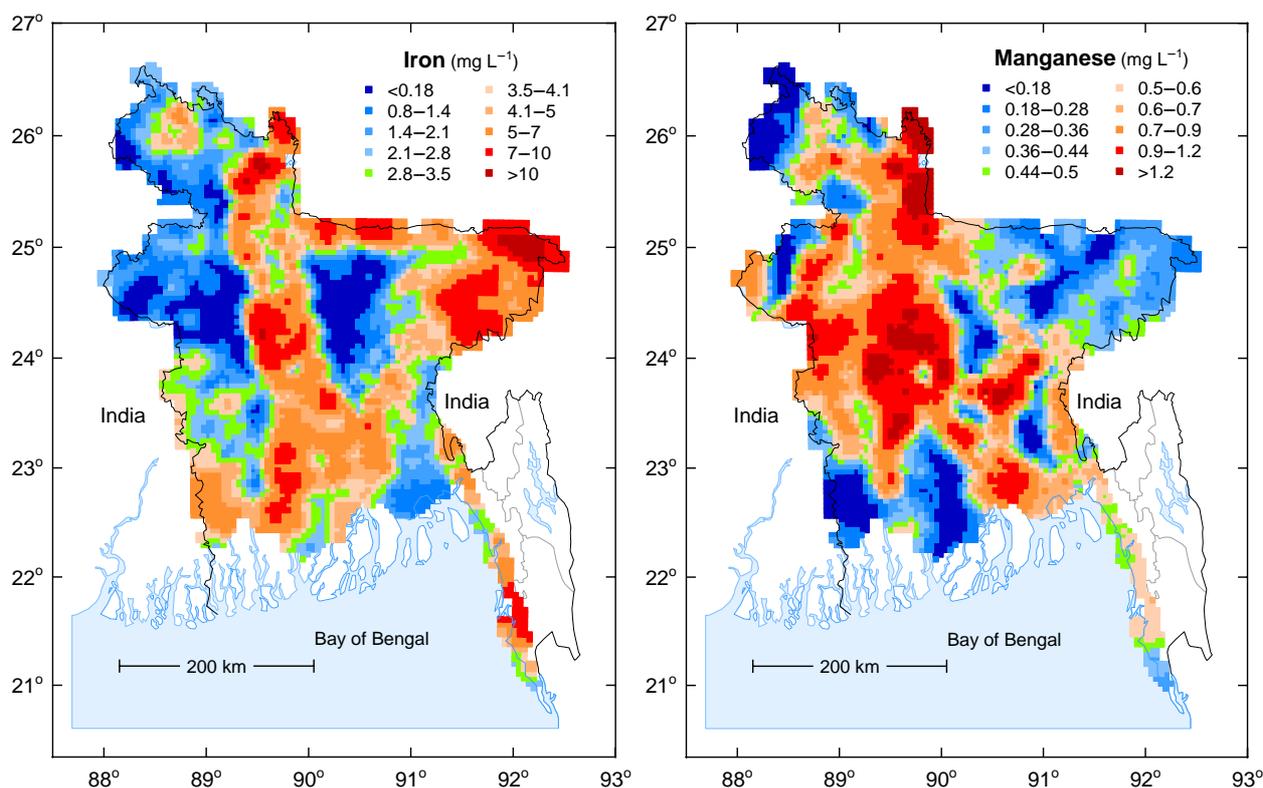
There is little evidence that toxic effects result from manganese ingestion at the concentrations usually found in drinking water, though to date little research has been carried out. As a result of the potential health effects, the WHO has set a provisional health-based guideline value for manganese in drinking water of 0.5 mg/l. However, the presence of manganese can give rise to

complaints from consumers at concentrations lower than this. Manganese oxides precipitating from domestic water supplies can cause black staining of food, laundry and sanitary ware and can impart a metallic taste. Build-up of oxide deposits can also cause problems in water-distribution systems. The WHO guideline value set on the basis of acceptability from consumers is 0.1 mg/l.

### Occurrence in groundwater

Manganese is an abundant element in the earth's crust. Upper crustal abundance is around 0.05–0.1% MnO (Taylor and McLennan, 1985). The element is distributed mainly in manganese oxides of which pyrolusite (MnO<sub>2</sub>) is the most common. Manganese also occurs as an impurity in iron oxides, some silicates and carbonates. It occurs more rarely as a major constituent of rhodocrosite (MnCO<sub>3</sub>). The structure and compositions of manganese oxides are complex due to variable oxidation states and to their ion-exchange properties. These properties are important in soils and aquifers as they can play a significant role in trace-metal adsorption. In sediments, manganese oxides also typically occur as fine-grained and poorly-crystalline forms which are easily dissolved under favourable conditions. Manganese occurs in several oxidation states, from –III to VII, but usually in the forms II or IV in the environment.

Concentration ranges of manganese in groundwater span several orders of magnitude, from <0.001 mg/l to values occasionally in excess of 1 mg/l. Manganese commonly coexists with iron in water. However, where this occurs, the concentrations of iron are generally greater because iron has a greater crustal abundance. Problems with



**Figure 1. Smoothed maps of the distribution of dissolved iron and manganese in groundwater in Bangladesh (smoothed to a 5 km grid, from BGS and DPHE, 2001).**

manganese in groundwater are widespread, and many countries throughout the world have areas with unacceptably high concentrations.

The principal controls on manganese concentration in groundwater are pH (acidity) and redox (oxidation-reduction) condition. Manganese is mobilised under acidic conditions. Hence concentrations can be relatively high in acidic waters such as some industrial waters and those issuing from mines rich in weathered sulphide minerals (coal, gold or base-metal mines). In this situation, high manganese concentrations are often accompanied by high concentrations of other metals such as iron, copper, zinc and arsenic, as well as sulphate, which are all derived by oxidation of the sulphide minerals. Under such conditions, dispersion of dissolved manganese away from the site of oxidation is greater than that of iron (Hem, 1992).

In pH-neutral conditions, the mobility of manganese is determined by ambient redox conditions. Under aerobic conditions typical of many shallow aquifers and surface waters, manganese is stable in its oxidised form,  $Mn(IV)O_2$  which is highly insoluble. Hence, concentrations of manganese in aerobic water are usually low and commonly below analytical detection limits. Under anaerobic conditions, manganese is reduced to the more soluble form,  $Mn(II)$ , which is released from

minerals.  $Mn^{2+}$  is the soluble form in most waters. As a result, much higher manganese concentrations can be found in anaerobic groundwaters. As dissolved oxygen concentrations in groundwater tend to decrease with well depth, anaerobic conditions and hence high manganese concentrations tend to occur more commonly in deep wells. Under strongly reducing conditions in the presence of dissolved sulphide, manganese can be immobilised by the formation of insoluble manganese sulphide ( $MnS$ ), although this is usually only important at high pH ( $>8$ ). As anaerobic conditions occur commonly in aquifers, problems with iron and manganese in groundwater are relatively widespread, though the concentrations attained vary widely.

As groundwaters infiltrate through soils and aquifers, their compositions typically evolve from aerobic to anaerobic, the rates of change depending on the rates of diffusion of oxygen and other oxidants in the system. Reduction reactions in aquifers and soils follow a sequence as the conditions become progressively more reducing. Typically the first compound to be removed from the system is oxygen, followed by nitrate and thereafter manganese. Progressively more reducing conditions lead to reduction of iron followed by sulphate. Hence, although anaerobic conditions in aquifers are typically demonstrated by the presence

of iron and manganese in the groundwater, regional distributions of these dissolved constituents are not necessarily coincident as a consequence of redox zonation. An example is given by the groundwaters in alluvial aquifers of Bangladesh. These are predominantly anaerobic, with regionally high concentrations of iron and manganese (up to 61 mg/l and 10 mg/l respectively; BGS and DPHE, 2001). Despite this, the regional distributions of the two elements differ significantly (Figure 1). These also differ significantly from the distributions of arsenic, which is also released to groundwater under anaerobic conditions (BGS and DPHE, 2001). Decoupling of correlations between iron and manganese can also occur through differing kinetics of oxidation as Mn(II) is oxidised much more slowly than Fe(II) by oxygen.

The mobilisation of manganese is increased in organic-rich waters through complexation with organic acids (humic or fulvic acids). Such conditions occur for example in peaty soil waters and upland lakes associated with them. They also occur in some strongly reducing aquifers. Waters with high concentrations of organic acids typically have a brown coloration (not caused by particulate matter) and may develop a surface froth.

Some forms of bacteria gain energy by oxidation of soluble Mn in water and can produce notable surface slimes where concentrations of manganese are high. Bacteria can accelerate the oxidation process and may also exacerbate staining problems.

### Testing for manganese

The occurrence of black staining of laundry, food and domestic water-distribution pipes and occasional development of slimes means that manganese in water can often be detected qualitatively. This may be a first indicator of potential manganese problems.

Simple, semi-quantitative analysis of manganese can be carried out using field-test kits, a number of which are available on the market. These usually work on the principle of oxidation of manganese to permanganate using either periodate or persulphate, followed by colorimetric analysis of the resulting pink-coloured solution. An alternative is the 1-(2-pyridylazo)-2-naphthol (PAN) method which forms an orange complex with manganese. In this method, metal interferences can be eliminated using a cyanide inhibitor. Field measurement can be carried out using a comparator or portable colorimeter.

Although precision is generally compromised with these methods, they can be useful for measurement of manganese in conditions where laboratory facilities are scarce or inadequate and are useful for

initial reconnaissance testing with subsequent analysis carried out by laboratory techniques.

Laboratory analysis of manganese can be carried out precisely using inductively-coupled plasma atomic-emission spectrometry (ICP-AES). This has the advantage of being a rapid, multi-element technique. However, the technique is not commonly available in developing countries because of high capital and consumables costs and a relatively high degree of skill required for operation. Alternatively, atomic absorption spectrometry (AAS) or colorimetry are suitable and precise methods which have been well tried and tested in many developing countries.

### Water treatment

Removal of manganese from water can be achieved most simply in the same way as for removal of iron, i.e. by aeration, settling and filtration. Concentrations of manganese in groundwater are usually less than those of iron and so in principle, the removal process should not be technically difficult. Oxidation can be facilitated by addition of oxidants such as chlorine, hypochlorite (bleach) or permanganate.

Removal can also be achieved by ion exchange using exchange resins or zeolite. Domestic water softeners can remove manganese (and iron), although they are less efficient for waters with very high concentrations (several milligrams per litre). Bacterial slimes and particulate manganese can cause additional efficiency problems. Removal can also be achieved by adsorption using suitable materials such as clay (e.g. glauconite).

Polyphosphates are often used in water-distribution systems to prevent the build-up of manganese oxide deposits. Polyphosphates complex the manganese and prevent oxidation and precipitation, although the complexes can break down at high temperatures (e.g. in boilers). The technique is useful at moderate concentrations of dissolved iron and manganese but is less effective where concentrations of the two reach in excess of 1 mg/l.

### Data sources

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