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STATUS AND ROLE OF MANGANESE IN THE ENVIRONMENT

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Abstract

Manganese is the second most abundant heavy metal, and in frequency list of elements it occupies 12th place. The Earth's core contains about 1.5% manganese. According to Indian Standards for Drinking water (IS 10500:2012) manganese concentration in drinking water is 0.1 ppm (acceptable limit) and 0.3 ppm as permissible limit. An attempt has been made to record the presence of manganese in different environmental matrices such as air, water, soil, food, its effects on plants, animals including human beings.

Keywords: Heavy metal, Manganese, Metal, Trace element

Introduction

The Earth and the planetary systems were formed 4.6 billion years ago. The crust of our planet has an average thickness of 40 km and underneath the oceans of 7 km. Its mass of 2×10^{19} t contributes only a proportion of 0.4% of the total earth. The crust covers the earth's mantle which represents 68% of the earth's mass. It consists of magnesium-iron silicates and oxides and reflects the large cosmic abundance of O, Si, Mg and Fe (Wedepohl, 1991).

Ninety chemical elements (those up to ^{92}U excepting ^{43}Tc and ^{61}Pm) have been discovered in the substances that make up the crust and atmosphere of the earth. Fifteen more elements have been synthesised through man's ingenuity or discovered elsewhere in the universe. From these fundamental elements all of the compounds and mixtures that make up the man's environment, and indeed man himself, can be obtained by appropriate combinations (Moore and Moore, 1976).

Manganese is one of the most abundant metals on the earth's surface, making up approximately 0.1% of the earth's crust. Manganese is not found naturally in its pure (elemental) form, but is a component of over 100 minerals (ATSDR, 2000).

An attempt has been made to study the properties of manganese; its presence in different environmental matrices such as air, water, soil, food; its effects on plants, animals, including human beings.

Properties of manganese

Manganese is the first member of Group 7 and Period 4 of the periodic table. Manganese (Mn) has the atomic number 25, an atomic mass of 54.938 g mol^{-1}, a melting point of 1244 ^{o}C, a boiling point of 2060 ^{o}C, and a Mohs hardness of 6. Manganese has a density of 7.20-7.43 g cm^{-3} and belongs to heavy metals. Manganese is a pinkish-gray, chemically active element. It is a hard metal and is very brittle. It is hard to melt, but easily oxidized. Manganese is reactive when pure, and as a powder it will burn in oxygen, it reacts with water (it rusts like iron) and dissolves in dilute acids. Six isotopes of manganese have been produced, of which only ^{55}Mn is stable. The other isotopes, ^{51}Mn, ^{52}Mn, ^{54}Mn, ^{56}Mn and ^{57}Mn, have half-lives ranging from 46 minutes to 310 days. Manganese occurs in four modifications α-, β-, γ- and δ-Mn being resistance up to 720 ^{o}C, 720-1100 ^{o}C, 1100-1136 ^{o}C and 1136-1244 ^{o}C, respectively. Manganese is a base metal; it dissolves in weak acids with formation of Mn (II) salts and liberation of hydrogen, and in hot concentrated solutions of sulfuric acid with the evolution of sulfuric dioxide. Manganese forms several oxides, the most important of which is manganese dioxide (Falbe & Regitz, 1999).

Manganese in the environment

Manganese is one of the most abundant metals in soils, where it occurs as oxides and hydroxides, and it cycles through its various oxidation states. Manganese occurs principally as pyrolusite (MnO_2), and to a lesser extent as rhodochrosite ($MnCO_3$). More than 25 million tonnes of manganese are mined every year, representing 5 million tons of the metal, and reserves are estimated to exceed 3 billion tonnes of the metal. The main mining areas for manganese ores are South Africa, Russia, Ukraine, Georgia, Gabon and Australia. Manganese is widely distributed in soils, sediments, rocks, water, ambient air and biological materials. Within the 16 km Earth's crust, manganese occurs at a concentration of ~950 mg kg^{-1}. Thus, manganese is the second most abundant heavy metal, and in the frequency list of elements it occupies 12^{th} place. The Earth core contains about 1.5% manganese (Falbe & Regitz, 1999), and the manganese content of rocks ranges from 350 to 2000 mg kg^{-1}, with highest concentration in mafic rocks. Manganese is an essential element for all species. Some organisms, such as diatoms, mollusks and sponges, accumulate manganese. Fish can have up to 5 ppm and mammals up to 3 ppm in their tissue, although normally they have around 1 ppm.

Earth crust

Manganese is widely distributed in soils, sediments, rocks, water, ambient air and biological material. World-wide, the average manganese content of soil units varies from 270 (podozols) to 525 mg/kg dry weight (DW) (cambisols); the grand mean calculated for world soils is 437 mg/kg DW (Kabata-Pendias & Pendias, 2001). Manganese in the continental and oceanic earth's crust in abundance rock species is presented in Table 1, whereas Table 3 represents manganese concentration in different fuels. Manganese constitutes approximately 0.1% of the earth's crust, and is a naturally occurring component of nearly all soils (ATSDR, 2000). Natural levels of manganese range from less than 2 to 7,000 ppm, with a geometric mean concentration of 330 ppm (Shacklette & Boerngen, 1984). The estimated arithmetic concentration is 550 ppm. Accumulation of manganese occurs in the subsoil rather than on soil surface (ASTDR, 2000). An estimated 60-90% of soil manganese is associated with the sand fraction (WHO, 1981). Table 2 depicts principle chemical species of manganese in acidic and alkaline soil solutions under oxic conditions.

Table 1. Manganese in the continental and oceanic earth's crust in abundant rock species (in ppm)

	Mn concentration
Shales	850
Greywackes	750
Limestones	700
Granitic rocks	325
Gneisses, mica schists	600
Basaltic and gabbroic rocks	1390
Granulites	895
Continental crust	800
Oceanic crust (Ocean ridge basalt)	1200

Table 2. Principal chemical species of manganese in acidic and alkaline soil solutions under oxic conditions (Florence, 1977; Sposito, 1983)

Mn(II)	Acid:	Mn^{2+}, $MnSO^0_4$, Org
	Alkaline:	Mn^{2+}, $MnSO^0_4$, $MnCO^0_3$, $MnHCO^+_3$, $MnB(OH)^+_4$

Org = Organic complexes, e.g. with fulvic acid

Table 3. Manganese in fuels

Fuel source	Mn concentration
Brown coal	92 mg kg^{-1}
Hard coal	156 mg kg^{-1}
Crude oil	0.5 mg L^{-1}

Air matrix

Air concentration of manganese compounds vary widely depending on the proximity of point sources such as ferroalloy production facilities, coke ovens, or power plants. Average ambient concentration near industrial sources have been reported to range from 220 to 300 ng/m^3, while levels in urban and rural areas without point sources have been reported to range from 10 to 70 ng/m^3 (Barceloux, 1999). Existing data indicate that little differences were found between ambient manganese levels in areas where methylcyclopentadienyl manganese tricarbonyl (MMT) is used in the gasoline and areas where MMT is not used (Lynam *et al*., 1999). The US EPA estimated 40 ng/m^3 as an average annual background concentration of manganese in urban areas based on measurements in 102 US cities (US EPA, 1990). According to US EPA (1984) the concentrations of manganese average 5 ng/m^3 in the ambient air of non-industrialized areas and up to 33 ng/m^3 in industrialized areas. Source dominated air levels may reach 0.13 µg/m^3 or above.

Based on annual mean air concentrations and a respiratory rate of 20 m^3 per day, the daily intake of manganese from air by populations living in areas without manganese-emitting industries is clearly below 2 µg, in areas with major foundries it was about 4-6 µg, and in areas with manganese industries it may rise to 10 µg, with 24-h peak values exceeding 200 µg. Normally, the daily intake via inhalation constitutes less than 0.1% of total daily intake and rarely exceeds 1%, even in heavily polluted areas. Since approximately 80% of manganese particles in air are within the respirable range of less than 5 µm and the lungs serve as a depot from where manganese is slowly and continuously absorbed, in the case of high exposure a considerable amount of inhaled manganese can enter the blood (Schroeder *et al*., 1966; WHO, 1981).

Aqueous matrices

Manganese is naturally occurring in many surface and groundwater sources and in soils that may leached into these waters. Human activities are also responsible for much of the manganese contamination in water in some areas. Ambient manganese concentrations in sea water have been reported to range from 0.4 to 10 µg/L (ATSDR, 2000), with an average of about 2 µg/L. Manganese concentration in freshwater typically range from 1 to 200 µg/L (Barceloux, 1999). Table 4 depicts manganese concentration in aqueous matrices. ATSDR (2000) reported that a US river water survey found dissolved manganese levels of less than 11 to more than 51 µg/L. The United States Geological Survey's National Ambient Water Quality Assessment (NAWQA) had gathered limited data since 1991 on representative study basins around the US. The report indicates a median manganese level of 16 µg/L in surface water with 99th percentile concentrations of 400 to 800 µg/L (Leahy & Thompson, 1994; USGS, 2001). Higher levels in aerobic waters are usually associated with industrial pollution.

The detection frequency of manganese in US groundwater was high (approximately 70% of sites assayed had measurable manganese levels) due to the ubiquity of manganese in soil and rock, but the levels detected in groundwater are generally below levels of public health concern (US EPA, 2003). Manganese was detected in about 97% of surface water sites (at levels far below those likely to cause health effects) and universally in sediments and aquatic biota tissues (at levels which suggest that it does not bioaccumulate) (US EPA, 2003).

Table 4. Manganese in aqueous matrices (µg kg^{-1})

Water matrices	Mn concentration
River water	4
Sea water (Deep water)	0.01

Manganese concentrations in lakes and rivers around the world range from 0.001 to about 0.6 ppm (WHO, 1981). Higher concentrations in aerobic waters are usually associated with industrial pollution. Reducing conditions in groundwater and some lakes and reservoirs are conducive to high levels up to 1.3 ppm in neutral waters and 9.6 ppm in acidic water (US EPA, 1984). In the USA, in a number of public drinking water surveys mean manganese levels ranging from 0.004 to 0.03 ppm were reported (ATSDR, 1992; US EPA, 1984). In Germany, the drinking water supplied to 90% of all households contained less than 0.02 ppm of manganese (Umwelt-Survey, 1991). In some regions of the Greece, drinking water was shown to contain between 1.8 and 2.3 ppm (Kondakis *et al.*, 1989).

Manganese concentrations in the vast majority water supplies range from 5 to 25 µg/L; hence, assuming a daily water intake of 500-2200 mL, the average daily intake of manganese via drinking water is about 2.5-55 µg (range 2-200 µg), which corresponds to not more than 1-2% of total daily manganese intake (WHO, 1981). In consideration of potential health risk of manganese and its compounds, several recommended and statutory limits have been made by various institutions. Standards and Guidelines of manganese in drinking water from various institutes are presented in Table 5.

Table 5. **Standards and Guidelines for manganese in drinking water (ppm)**

Metal	India[a]	WHO[b,*]	CEC[c]		CH[d]	USA[e]	YU[f]
			GL	MAC			
Manganese	0.1	0.1	0.02	0.05	0.05	0.05	0.05

[a] Indian Standards for drinking water (IS 10500 : 2012)
[b] WHO (1984), Guidelines for Drinking Water Quality, Vol. 1, Recommendations
[*] In WHO Guidelines for Drinking Water Quality (2011) the guideline for Mn was discontinue (WHO, 2011)
[c] Council of the European Communities, Council Directive Relating to the Quality of Water Intended for Human Consumption (80/778/EEC). GL= guide level, MAC = maximum admissible concentration
[d] Switzerland: Ordinance on Food Additives and Food Contaminants (1986)
[e] National Research Council (NRC) (1977), Drinking Water and Health. National Academy of Sciences, Washington D.C.
[f] Yugoslavia: Ordinance on Microbiology and Physiological Standards of Drinking Water (1979)

Manganese and food

Manganese is found in variety of food including nuts, grains, fruits, legumes, tea, leafy vegetables, infant formulas, and some meat and fish. Food is the most frequent source of manganese exposure in the general population (ATSDR, 2000; IOM, 2002; US EPA, 2003). Heavy tea drinkers may have a higher manganese intake than the general population. An average cup of tea may contain 0.4 to 1.3 mg manganese (ATSDR, 2000). Investigations of plant foodstuff in Germany revealed that black tea (400 mg/kg DM) as well as cocoa (39 mg/kg DM) and coffee (31 mg/kg) contribute high amounts to the human dietary manganese intake, whilst sugar (0.24 mg/kg DM) as well as cornflakes (0.2-2.0 mg/kg DM) and starch-rich food-stuff contribute to low amounts. Whole grains, cereal products and spices are also rich dietary sources of manganese. For example, rye and wheat grain contain 25 mg/kg DM, while rolled oats contain about double that amount due to fact that oats prefer an acidic soil pH. Coarse wholemeal bread made from rye as well as crispbread contain about 30 mg/kg DM, whereas white bread and bread made more than one kind of flour contain only half that manganese contain. In general, fruits contain < 10 mg/kg DM, except for pineapples, strawberries and bananas, all of which are richer in manganese. The manganese contain of vegetables was shown to range between 5 and 34 mg/kg DM, with the tendency that leaf vegetables have high contents; root vegetables, stem bulges and bulbs have medium contents; and tubers as well as mushrooms have low contents. Despite their partly high manganese concentrations, spices have less influence on the manganese supply on humans because of small amounts that are ingested. Table salt is extremely manganese-poor (Anke *et al.*, 1999).

In general, the manganese content of animal-derived foods is lower than that of plant-derived foods. The liver and kidney of cattle contain high levels of manganese (2.7-6.4 mg/kg DM), while meat from lamb, cow, broiler and pig have low contents (0.5-0.6 mg/kg DM). Fish has similar manganese content to meat, though some types of sausages and canned fishes contain higher manganese levels due to presence of manganese rich additives (Anke *et al.*, 1999). Marine molluscs can bioaccumulate high concentration of manganese (Saric, 1986). By contrast, milk and dairy products are poor manganese source; for example, cow's milk, human breast milk and butter contain 0.62, 0.12 and 0.14 mg/kg DM, respectively (Anke *et al.*, 1999). Manganese concentration in foodstuff/vegetable is presented in Table 6.

Table 6. Manganese concentration in foodstuff/vegetable in mg kg^{-1} dry matter (Anke, *et al*., 2003)

Foodstuff/vegetable	Mn concentration
Sugar	0.24
Wheat floor	9.9
Wheat and rye bread	16
Roll	6.9
Lentil	13
Apple	4.3
Potato	6.2
Asparagus	24
Lettuce	34
Mushroom	5.1

Manganese and plants

Plant species vary considerably in their manganese requirement, sensitivity and tolerance. Levels of 20 mg/kg DM are often sufficient for normal growth, but a variety of vegetable plants develop signs of deficiency if manganese level falls below 50 mg/kg DM (Bergmann, 1992; Rengel, 2000). The critical manganese deficiency level for most plants ranges from 15 to 25 mg/kg DM (Kabata-Pendias & Pendias, 2001). Of all cell components, chloroplasts are the most sensitive to manganese deficiency.

In plants, a characteristic feature of manganese deficiency is an initial appearance of interveinal chloroplast spots, followed by necrotic spots or brown crock-like lesions and cavities on young leaves. A severe lack of manganese leads to rapid death of the leaves, inhibition of plant growth, depression of inflorescence and fructification, and stunted leaf and root development due to an insufficient synthesis of chloroplasts, chlorophyll and proteins that leads in turn to lack of cellular energy (Bergmann, 1992).

Plants which show particular sensitivity to manganese deficiency include oats, peas, sugar beet, tomatoes, cucumbers, and some fruit trees and bushes. Maize, peanuts, sorghum, cotton and potatoes also respond sensitively to manganese deficiency. In conifers, the young needles show an initial yellowish-green discolouration, but they later turn yellow and finally die (Bergmann, 1992).

Manganese deficiency occurs most commonly in calcareous, humours sandy and lower moor soils with a high pH value (6.5-8.0) owing to the low manganese availability and high bacterial activity in this pH range and, simultaneously, to the intensive oxidation of Mn^{2+} to the less accessible Mn (IV) oxides. Plants deficient in manganese accumulate elevated amount of nitrate and nitrite, which disrupt protein production. On the other hand, manganese excess disrupts carbohydrate metabolism (Bergmann, 1992).

Manganese toxicity in plants may be expected when soils Mn levels exceed 1000 mg/kg DW (WHO, 1981). In leaves, this concentration is mostly sufficient to induce symptoms of toxicity. As with manganese deficiency, the ability of plants to tolerate an excess of manganese varies greatly from species to species, and also from variety to variety. Rice is able to tolerate very high manganese levels of up to 2500 mg/kg DM in the shoots, and between 4000 and 8000 mg/kg DM in the leaves, whereas sensitive plants such as lettuce, beans and roses show signs of toxicity at levels of only 200-400 mg/kg DM (Bergmann, 1992).

In contrast to manganese deficiency, toxic concentrations of manganese in plants usually affect the old leaves first, initially appearing as brown spots (deposits of MnO_2) mainly on the leaf underside or as chlorotic and necrotic lesions which spread from the tips and margins to the leaf surface, often accompanied by rolling of the leaf edges. The precipitation of MnO_2 is indicative of the detoxification of Mn by the plant. In case of severe toxicity, younger parts of plants are also affected such that the chlorophyll content is reduced and plant growth in inhibited (Bergmann, 1992).

Human health

The neurological effects of inhaled manganese have been well documented in humans chronically exposed to elevated levels in workplace. The syndrome known as "manganism" is characterised by weakness anorexia, muscle pain, apathy, slow speech, monotonous tone of voice, emotionless "mask-like" facial expression, and slow clumsy movement of the limbs. These effects are irreversible. The minimal exposure level producing neurological effects is not certain but is probably in the range 0.1-1 mg/m^3 (ATSDR, 1992). An epidemiological study was conducted in Greece to investigate the possible correlation between manganese exposure from water and neurological effects in elderly people (Kondakis *et al.,* 1989). The levels of manganese were 3.6-14.6 µg/L in the control area and 81-282 µg/L and 1800-2300 µg/L in the test areas. The authors concluded that progressive increase in the manganese concentration in drinking water are associated with progressively higher prevalence of neurological signs of chronic manganese poisoning and higher manganese concentrations in the hairs of the older persons.

Harmful excessive manganese exposure in the workplace was recognised during the nineteenth century (Couper, 1837). The inhalation of manganese rich dust by workers in manganese mines, steel mills and chemical industry can increase susceptibility of the respiratory tract to infection (manganese pneumonia) and can also induce multiple damage to the central nervous system (mangasism) due to an accumulation of manganese in the brain (as the critical target organ for manganese toxicity). Acute toxic symptoms of excessively inhaled manganese appear initially partly as nonspecific and partly as severe (but reversible) psychiatric disorders clinically termed locura manganica, manganic madness, manganese mania or manganese psychosis (symptoms of fatigue, loss of appetite, headache, emotional liability, hallucinations, apathy, speech disorders, ataxia) that resemble schizophrenia. These conditions may be followed by chronic, irreversible neurological disorders of the extra pyramidal system (symptoms include severe muscular rigidity of the limbs, mask-like face, fine tremor, bradykinesia, dystonia, excessive salvation and perspiration) that resemble Parkinson's disease. An important significance of chronic manganism is its progressive development, even when exposure has cessed (Barbeau 1984; Hurley & Keen, 1987; Keen *et al.*, 1999, 2000; Mergler & Baldwin 1997; Reidies 2003; Verity 1999).

Conclusion

Owing to the availability of manganese in different environmental matrices such as air, water, soil and food and its constant exposure to human beings above permissible limits at some locations leads to the adverse health effects. There is an urgent need from local authorities to monitor the manganese concentration in different matrices and further to ensure that the manganese concentration should not cause any adverse health effects on individuals and further to enhance consumer acceptance of water resources. Removal of manganese from groundwater by using appropriate technologies should be attempted where the exposure limits are more so as to bring its concentration within permissible limits of statutory norms.

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