

# Health Hazards of Manganese Oxide in Agriculture and Industrial Application: Policies to Prevent Exposure

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**Abstract**—In agriculture the presence of manganese in the soil upto a certain level is required, however if the levels becomes high the crops and livestock become hazardous for human consumption. In industries, Manganese dioxide is commonly used in the production of dry-cell batteries, matches, fireworks, porcelain and glass-bonding materials, and amethyst glass; it is also used as the starting material for the production of other manganese compounds. In this paper a study has been carried out on the various hazards of Manganese Dioxide on humans both in agriculture and Industry.

**Keywords:** Manganese Dioxide, Hazard, Metal fume Fever

## 1. INTRODUCTION

Manganese (Mn) is the eleventh abundant element forming the Earth's crust. In terms of abundance, manganese-containing compounds are after iron (Fe) in the earth's crust. Manganese alloy is an essential ingredient for the fabrication of steel, and thus has a very high economic viability. Metallic manganese (ferromanganese) is used principally in steel production along with cast iron and superalloys to improve hardness, stiffness, and strength (NAS, 1973; US EPA, 1984; HSDB, 1998). The predominant portion (approximately 90%) of manganese is processed into ferromanganese in blast furnaces (4). Manganese compounds have a variety of uses. Manganese dioxide is commonly used in the production of dry-cell batteries, matches, fireworks, porcelain and glass-bonding materials, and amethyst glass; it is also used as the starting material for the production of other manganese compounds (NAS, 1973; Venugopal & Luckey, 1978; US EPA, 1984). Total amount of manganese in soil is between 20 to 3000 ppm and 600 ppm on average. Divalent manganese is absorbed by clay minerals and organic material, and In terms of nutrition plant, divalent manganese ions (Mn<sup>2+</sup>) is most important (Malakouti and Tehrani, 1999). In soil manganese occurs as exchangeable manganese, manganese oxide, organic manganese and component of Ferro-manganese silicate minerals, the manganese ion (Mn<sup>2+</sup>) is similar in size to magnesium (Mg<sup>2+</sup>) and ferrous iron (Fe<sup>2+</sup>) and can substitute for these elements in silicate minerals and iron oxides. Manganese reactions in soils are quite complex. The amount of available manganese is influenced by soil pH, organic

matter, moisture, and soil aeration (Schulte and Kelling, 1999).

## 2. SOURCES OF MANGANESE OXIDES

Crustal rock is a major source of manganese found in the atmosphere. Ocean spray, forest fires, vegetation, and volcanic activity are other major natural sources of manganese in the atmosphere (Schroeder et al., 1987; Stokes et al., 1988). Stokes et al. (1988) estimated that two-thirds of manganese air emissions were from natural sources. Air erosion of dusts and soils is also an important atmospheric source of manganese, but no quantitative estimates of manganese release to air from this source were identified (US EPA, 1984). An important source of dissolved manganese is anaerobic environments where particulate manganese oxides are reduced, such as some soils and sediments, wetlands, and the anaerobic hypolimnia of lakes and fjords. Manganese ores of major commercial importance are (i) pyrolusite (MnO<sub>2</sub>, Mn 63.2%); (ii) psilomelane (manganese oxide, containing water and varying amounts of oxides of Ba, K and Na as impurities; Mn commonly 45-60%); (iii) manganite (Mn<sub>2</sub>O<sub>3</sub> · H<sub>2</sub>O, Mn 62.4%); and (iv) braunite (3Mn<sub>2</sub>O<sub>3</sub>, MnSiO<sub>3</sub>, Mn about 62% and SiO<sub>2</sub> about 10% (1).

## 3. HAZARDOUS SOURCE

Land disposal of manganese-containing wastes is the principal source of manganese releases to soil. Nriagu & Pacyna (1988) estimated that total worldwide anthropogenic releases of manganese to soils during 1983 ranged from 706 000 to 2 633 000 tonnes, with the predominant source being coal fly ash. In 1991, reported industrial releases to land in the USA ranged from 0 to 1000 tonnes. More than 50% of the total environmental release of manganese (3753 tonnes) was to land (TRI91, 1993). Estimated releases of manganese to soil in 1996 were 21 600 tonnes, representing 80% of total environmental releases (TRI96, 1998).

#### 4. IMPORTANCE OF MANGANESE IN AGRICULTURE

Manganese is one of the main micronutrients, which has an important role in plant as a component of enzymes involved in photosynthesis and other processes. Manganese is part of an important antioxidant (superoxide dismutase) structure that protects plant cells by deactivating free radicals which can destroy plant tissue. Manganese plays vital roles in photosynthesis, as a structural component of the Photosystem II watersplitting protein. It also serves as electron storage and delivery to the chlorophyll reaction centers (3). Manganese is uptake by plant roots as the divalent ion  $Mn^{2+}$ . Also is needed in small amount and uptake usually is less than 1kg Mn/ha in cereals and around 2kg Mn/ha in sugar beet (7). Manganese fertilizer increases the crop yield and quality, due to improved plant nutrition and increasing photosynthesis in plants, so crop yield and quality increases by increasing photosynthetic efficiency (6).

#### 5. HAZARDOUS EFFECT ON AGRICULTURAL PRODUCTS

Symptoms of manganese toxicity to terrestrial plants vary widely with species and include marginal chloroses, necrotic lesions, and distorted development of the leaves. Manganese is the cause of recognizable disorders in some crops, such as crinkle leaf in cotton and stem streak necrosis in potato (8). In such instances, induced deficiencies of other mineral nutrients, such as iron, magnesium, and calcium, are involved to various degrees. Toxic manganese concentrations in crop plant tissues vary widely, with critical values ranging from 100 to 5000 mg/kg (2).

Manganese toxicity is a major factor limiting crop growth on acidic, poorly drained, or steam-sterilized mineral soils. Acidic (pH 4.4) oxisol soils in Hawaii, USA, containing 15 g total manganese/kg need to be limed to raise the pH to 5.7 or above, resulting in soluble manganese concentrations of less than 2 mg/litre, for normal watermelon (*Citrullus lanatus*) growth (Hue & Mai, 2002). Soil acidification enhances the solubility of metals such as aluminium and manganese. Soil acidification can be caused by acidic deposition, acid soils brought to the surface by construction projects, and industrial acid deposition. The pH of soils containing toxic levels of manganese is generally higher (<5.5) than the pH of soils containing toxic levels of aluminium (<4) (Foy et al., 1978, 1988).

Manganese tends to accumulate in shoots rather than roots, leading to visible symptoms in leaves (Loneragan, 1988), whereas aluminium toxicity predominantly causes damage to roots without definitive foliar symptoms. Foliar symptoms of manganese toxicity have been noted in hydroponic studies at 50 mg manganese/litre for chlorosis of entire young leaves

(white birch *Betula platyphylla japonica*) and at >1 mg manganese/litre for brown speckle at the leaf marginal and interveinal area in older leaves (Kitao et al., 2001). Kaus & Wild (1998) found that Douglas-fir (*Pseudotsuga menziesii viridis*) showing symptoms similar to iron deficiency chlorosis had accumulated significantly more manganese than trees without chlorosis. Excess manganese in soil has been found to accumulate in leaves of broad-leaved deciduous plants of northern Japan. This resulted in declines in light-stimulated net photosynthetic rate (Kitao et al., 1997).

Significant adverse effects on growth and behaviour of herring gull (*Larus argentatus*) chicks were observed following a single intraperitoneal injection of manganese acetate (25 mg/kg body weight) (Burger & Gochfeld, 1995). Sierra et al. (1998) reported no significant toxic effects on feral pigeons (*Columba livia*) exposed to manganese tetroxide dust at concentrations of 239  $\mu\text{g}$  manganese/ $\text{m}^3$  (7 h/day, 5 days/week) for 13 weeks.

#### 6. HAZARDOUS EFFECT IN INDUSTRIAL APPLICATIONS

Consumption of manganese dioxide ore in industry is basically in dry batteries of about 14,600 tonnes in 2010-11, (excluding EMD). Dry battery industry also consumes EMD along with natural manganese dioxide ore.

The inorganic compounds do not penetrate the body via skin like some organic compounds, such as certain tricarbonyls. Inhalation of dust or fume is the major route of entry in occupational manganese poisoning. Also inhaled large particles are ingested after mucociliary clearance from the lungs. Gastrointestinal absorption is generally low (5%). Very few poisonings have occurred after ingestion.

##### Manganese Exposure Symptoms and Results

- **Metal fume fever**

Inhalation of manganese oxide fumes may cause a flu-like syndrome similar to "metal fume fever", treatment is symptomatic.

- **Chemical pneumonia**

In the case of severe exposure to fumes or dust of various manganese salts, a severe chemical pneumonia may occur.

- **Acute intoxication by ingestion**

Acute intoxication by ingestion rarely occurs and is caused by accidental or voluntary ingestion of a manganese salt (as the ingestion of tablets of potassium permanganate), this chemical causes massive burns of the digestive tract, oedema of the upper respiratory tract and circulatory collapse.

- **Chronic intoxication**

The primary target organ of manganese toxicity is the central nervous system, particularly the extra-pyramidal system; the lungs may also be injured in the case of chronic exposure to manganese [1].

## 7. EVALUATION OF HEALTH HAZARDS OF MANGANESE OXIDE BY INTERNATIONAL BODIES

WHO (1981, 1986, 1987, 1999) has previously evaluated manganese, concluding that chronic manganese poisoning is a hazard in occupational settings. However, little information was available to assess the potential health risks in community exposure scenarios.

WHO has established a provisional guideline value of 0.5 mg/litre for manganese in drinking-water based on health (WHO, 1993), an annual air quality guideline of 0.15 µg/m<sup>3</sup> (WHO, 1999), and a workplace exposure limit in air of 0.3 mg/m<sup>3</sup> for respirable particles containing manganese (WHO, 1984, 1986, 1987, 1999).

Manganese Compounds are not more toxic than those of other widespread metals, such as copper and nickel. Exposure to manganese dusts and fumes should not exceed the ceiling value of 5 mg/m<sup>3</sup> even for short periods because of its toxicity level. Only a limited amount is absorbed by the intestines, but this small amount shows severe effects on the kidneys and on the liver. In 2005, a study suggested a possible link between manganese inhalation and central nervous system toxicity in rats. Manganese exposure in United States is regulated by Occupational Safety and Health Administration [9].

India is working on formulating some strong policies to limit the use of manganese dioxide.

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