

IPCS

INTERNATIONAL PROGRAMME ON CHEMICAL SAFETY



Concise International Chemical Assessment Document

63

Manganese and its Compounds:

Environmental Aspects

IOMC

INTER-ORGANIZATION PROGRAMME FOR THE SOUND MANAGEMENT OF CHEMICALS
A cooperative agreement among UNEP, ILO, FAO, WHO, UNIDO, UNITAR and OECD



World Health Organization
Geneva, 2004

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Concise International Chemical Assessment Document 63

MANGANESE AND ITS COMPOUNDS: ENVIRONMENTAL ASPECTS

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World Health Organization
Geneva, 2004

The **International Programme on Chemical Safety (IPCS)**, established in 1980, is a joint venture of the United Nations Environment Programme (UNEP), the International Labour Organization (ILO), and the World Health Organization (WHO). The overall objectives of the IPCS are to establish the scientific basis for assessment of the risk to human health and the environment from exposure to chemicals, through international peer review processes, as a prerequisite for the promotion of chemical safety, and to provide technical assistance in strengthening national capacities for the sound management of chemicals.

The **Inter-Organization Programme for the Sound Management of Chemicals (IOMC)** was established in 1995 by UNEP, ILO, the Food and Agriculture Organization of the United Nations, WHO, the United Nations Industrial Development Organization, the United Nations Institute for Training and Research, and the Organisation for Economic Co-operation and Development (Participating Organizations), following recommendations made by the 1992 UN Conference on Environment and Development to strengthen cooperation and increase coordination in the field of chemical safety. The purpose of the IOMC is to promote coordination of the policies and activities pursued by the Participating Organizations, jointly or separately, to achieve the sound management of chemicals in relation to human health and the environment.

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FOREWORD

Concise International Chemical Assessment Documents (CICADs) are the latest in a family of publications from the International Programme on Chemical Safety (IPCS) — a cooperative programme of the World Health Organization (WHO), the International Labour Organization (ILO), and the United Nations Environment Programme (UNEP). CICADs join the Environmental Health Criteria documents (EHCs) as authoritative documents on the risk assessment of chemicals.

International Chemical Safety Cards on the relevant chemical(s) are attached at the end of the CICAD, to provide the reader with concise information on the protection of human health and on emergency action. They are produced in a separate peer-reviewed procedure at IPCS. They may be complemented by information from IPCS Poison Information Monographs (PIM), similarly produced separately from the CICAD process.

CICADs are concise documents that provide summaries of the relevant scientific information concerning the potential effects of chemicals upon human health and/or the environment. They are usually based on selected national or regional evaluation documents or on existing EHCs. Before acceptance for publication as CICADs by IPCS, these documents undergo extensive peer review by internationally selected experts to ensure their completeness, accuracy in the way in which the original data are represented, and the validity of the conclusions drawn.

The primary objective of CICADs is characterization of hazard and dose–response from exposure to a chemical. CICADs are not a summary of all available data on a particular chemical; rather, they include only that information considered critical for characterization of the risk posed by the chemical. The critical studies are, however, presented in sufficient detail to support the conclusions drawn. For additional information, the reader should consult the identified source documents upon which the CICAD has been based.

Risks to human health and the environment will vary considerably depending upon the type and extent of exposure. Responsible authorities are strongly encouraged to characterize risk on the basis of locally measured or predicted exposure scenarios. To assist the reader, examples of exposure estimation and risk characterization are provided in CICADs, whenever possible. These examples cannot be considered as representing all

possible exposure situations, but are provided as guidance only. The reader is referred to EHC 170.¹

While every effort is made to ensure that CICADs represent the current status of knowledge, new information is being developed constantly. Unless otherwise stated, CICADs are based on a search of the scientific literature to the date shown in the executive summary. In the event that a reader becomes aware of new information that would change the conclusions drawn in a CICAD, the reader is requested to contact IPCS to inform it of the new information.

Procedures

The flow chart on page 2 shows the procedures followed to produce a CICAD. These procedures are designed to take advantage of the expertise that exists around the world — expertise that is required to produce the high-quality evaluations of toxicological, exposure, and other data that are necessary for assessing risks to human health and/or the environment. The IPCS Risk Assessment Steering Group advises the Coordinator, IPCS, on the selection of chemicals for an IPCS risk assessment based on the following criteria:

- there is the probability of exposure; and/or
- there is significant toxicity/ecotoxicity.

Thus, it is typical of a priority chemical that

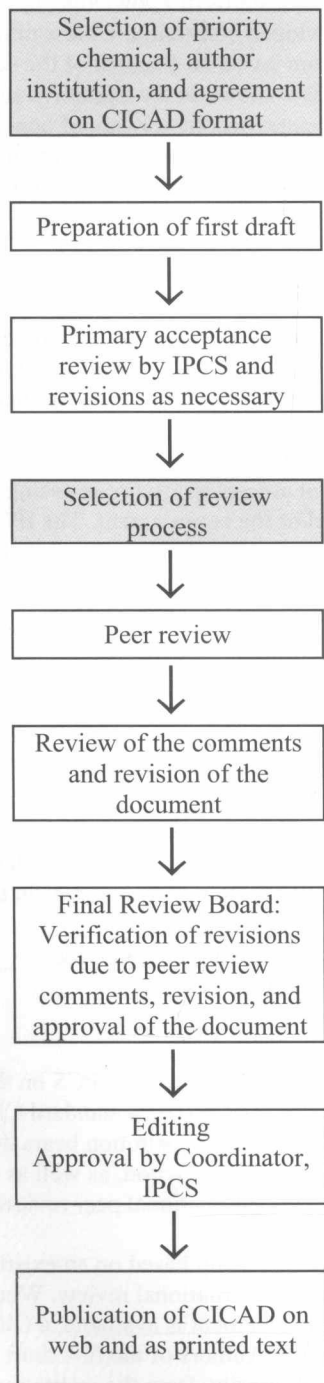
- it is of transboundary concern;
- it is of concern to a range of countries (developed, developing, and those with economies in transition) for possible risk management;
- there is significant international trade;
- it has high production volume;
- it has dispersive use.

The Steering Group will also advise IPCS on the appropriate form of the document (i.e., a standard CICAD or a *de novo* CICAD) and which institution bears the responsibility of the document production, as well as on the type and extent of the international peer review.

The first draft is usually based on an existing national, regional, or international review. When no appropriate source document is available, a CICAD may be produced *de novo*. Authors of the first draft are usually, but not necessarily, from the institution that developed the original review. A standard outline has been developed to encourage consistency in form. The

¹ International Programme on Chemical Safety (1994) *Assessing human health risks of chemicals: derivation of guidance values for health-based exposure limits*. Geneva, World Health Organization (Environmental Health Criteria 170) (also available at <http://www.who.int/pcs/>).

CICAD PREPARATION FLOW CHART



Advice from Risk Assessment Steering Group

Criteria of priority:

- there is the probability of exposure; and/or
- there is significant toxicity/ecotoxicity.

Thus, it is typical of a priority chemical that

- it is of transboundary concern;
- it is of concern to a range of countries (developed, developing, and those with economies in transition) for possible risk management;
- there is significant international trade;
- the production volume is high;
- the use is dispersive.

Special emphasis is placed on avoiding duplication of effort by WHO and other international organizations.

A usual prerequisite of the production of a CICAD is the availability of a recent high-quality national/regional risk assessment document = source document. The source document and the CICAD may be produced in parallel. If the source document does not contain an environmental section, this may be produced *de novo*, provided it is not controversial. If no source document is available, IPCS may produce a *de novo* risk assessment document if the cost is justified.

Depending on the complexity and extent of controversy of the issues involved, the steering group may advise on different levels of peer review:

- standard IPCS Contact Points
- above + specialized experts
- above + consultative group

first draft undergoes primary review by IPCS to ensure that it meets the specified criteria for CICADs.

The second stage involves international peer review by scientists known for their particular expertise and by scientists selected from an international roster compiled by IPCS through recommendations from IPCS national Contact Points and from IPCS Participating Institutions. Adequate time is allowed for the selected experts to undertake a thorough review. Authors are required to take reviewers' comments into account and revise their draft, if necessary. The resulting second draft is submitted to a Final Review Board together with the reviewers' comments. At any stage in the international review process, a consultative group may be necessary to address specific areas of the science. When a CICAD is prepared *de novo*, a consultative group is normally convened.

The CICAD Final Review Board has several important functions:

- to ensure that each CICAD has been subjected to an appropriate and thorough peer review;
- to verify that the peer reviewers' comments have been addressed appropriately;
- to provide guidance to those responsible for the preparation of CICADs on how to resolve any remaining issues if, in the opinion of the Board, the author has not adequately addressed all comments of the reviewers; and
- to approve CICADs as international assessments.

Board members serve in their personal capacity, not as representatives of any organization, government, or industry. They are selected because of their expertise in human and environmental toxicology or because of their experience in the regulation of chemicals. Boards are chosen according to the range of expertise required for a meeting and the need for balanced geographic representation.

Board members, authors, reviewers, consultants, and advisers who participate in the preparation of a CICAD are required to declare any real or potential conflict of interest in relation to the subjects under discussion at any stage of the process. Representatives of nongovernmental organizations may be invited to observe the proceedings of the Final Review Board. Observers may participate in Board discussions only at the invitation of the Chairperson, and they may not participate in the final decision-making process.

1. EXECUTIVE SUMMARY

This CICAD on manganese and its compounds (environmental aspects) was based primarily on the report *Toxicological profile for manganese (update)*, prepared by the Agency for Toxic Substances and Disease Registry of the US Department of Health and Human Services (ATSDR, 2000). Secondary sources of information included CICAD No. 12 on manganese and its compounds (IPCS, 1999a) and data identified following a comprehensive literature search of relevant databases conducted up to December 2002 to identify any relevant references published subsequent to those incorporated in these two reports. For information regarding the assessment of human health effects of manganese, the reader should refer to CICAD No. 12 (IPCS, 1999a). Manganese fungicides have been referred to in the document for source and fate information only, and no attempt has been made to evaluate this group of chemicals for environmental effect. Information on the preparation and peer review of the source document is presented in Appendix 1. Information on the peer review of this CICAD is presented in Appendix 2. This CICAD was considered and approved as an international assessment at a meeting of the Final Review Board, held in Varna, Bulgaria, on 8–11 September 2003. Participants at the Final Review Board meeting are presented in Appendix 3. International Chemical Safety Cards on selected manganese compounds (ICSCs 174, 175, 290, 754, 977, 1169, and 1398), produced by the International Programme on Chemical Safety in a separate, peer-reviewed process (IPCS, 1999b,c, 2001, 2003a,b,c,d), have also been reproduced in this document.

Manganese (Mn) is a naturally occurring element that is found in rock, soil, and water. It is ubiquitous in the environment and comprises about 0.1% of the Earth's crust. Crustal rock is a major source of manganese found in the atmosphere. Ocean spray, forest fires, vegetation, and volcanic activity are other major natural atmospheric sources of manganese. Important sources of dissolved manganese are anaerobic environments where particulate manganese oxides are reduced, the direct reduction of particulate manganese oxides in aerobic environments, the natural weathering of Mn(II)-containing minerals, and acidic environments. The major pool of manganese in soils originates from crustal sources, with other sources including direct atmospheric deposition, wash-off from plant and other surfaces, leaching from plant tissues, and the shedding or excretion of material such as leaves, dead plant and animal material, and animal excrement. The major anthropogenic sources of environmental manganese include municipal wastewater discharges, sewage sludge, mining and mineral processing, emissions from alloy, steel, and iron production, combustion of fossil

fuels, and, to a much lesser extent, emissions from the combustion of fuel additives.

Manganese is released to air mainly as particulate matter, and the fate and transport of the particles depend on their size and density and on wind speed and direction. Some manganese compounds are readily soluble in water. Manganese exists in the aquatic environment in two main forms: Mn(II) and Mn(IV). Movement between these two forms occurs via oxidation and reduction reactions that may be abiotic or microbially mediated. The environmental chemistry of manganese is largely governed by pH and redox conditions; Mn(II) dominates at lower pH and redox potential, with an increasing proportion of colloidal manganese oxyhydroxides above pH 5.5 in non-dystrophic waters. Primary chemical factors controlling sedimentary manganese cycling are the oxygen content of the overlying water, the penetration of oxygen into the sediments, and benthic organic carbon supply. Manganese in soil can migrate as particulate matter to air or water, or soluble manganese compounds can be leached from the soil. In soils, manganese solubility is determined by two major variables: pH and redox potential.

Manganese in water can be significantly bioconcentrated by aquatic biota at lower trophic levels. Bioconcentration factors (BCFs) of 2000–20 000 for marine and freshwater plants, 2500–6300 for phytoplankton, 300–5500 for marine macroalgae, 800–830 for intertidal mussels, and 35–930 for fish have been estimated. Uptake of manganese by aquatic invertebrates and fish significantly increases with temperature and decreases with pH, whereas dissolved oxygen has no significant effect. Uptake of manganese has been found to increase with decreasing salinity.

Manganese concentrations in air tend to be lowest in remote locations (about 0.5–14 ng/m³ on average), higher in rural areas (40 ng/m³ on average), and still higher in urban areas (about 65–166 ng/m³ on average). Manganese concentrations in air tend to be highest in source-dominated areas, where values can reach 8000 ng/m³. Annual averages of manganese concentrations may rise to 200–300 ng/m³ in air near foundries and to over 500 ng/m³ in air near ferro- and silico-manganese industries.

Concentrations of dissolved manganese in natural waters that are essentially free of anthropogenic inputs can range from 10 to >10 000 µg/litre. However, dissolved manganese concentrations in natural surface waters rarely exceed 1000 µg/litre and are usually less than 200 µg/litre.

Manganese concentrations in river sediments ranged from 410 to 6700 mg/kg dry weight; sediment from an urban lake receiving inputs from industrial and

residential areas, as well as windborne dust from old mine dumps, contained manganese at concentrations ranging up to 13 400 mg/kg dry weight. Sediment manganese concentrations of 100–1000 mg/kg dry weight have been reported for intertidal mudflats; similar total manganese values were found in the northern Adriatic Sea. Surface sediments in the Baltic Sea contained manganese at mean concentrations of 3550–8960 mg/kg dry weight; the high manganese concentrations were thought to be due to ferro-manganese concretions and riverine loads.

Natural (“background”) levels of total manganese in soil range from <1 to 4000 mg/kg dry weight, with mean values around 300–600 mg/kg dry weight.

Mean manganese concentrations in seaweed range from 130 to 735 mg/kg dry weight, whereas concentrations in shellfish range from 3 to 660 mg/kg dry weight; higher concentrations in shellfish are associated with manganese-rich sediment. Concentrations of manganese found in tissues of marine and freshwater fish tend to range from <0.2 to 19 mg/kg dry weight. Higher manganese concentrations — above 100 mg/kg dry weight — have been reported for fish in polluted surface waters.

Concentrations of manganese in terrestrial plants tend to range from 20 to 500 mg/kg. Members of the Ericaceae family, which includes blueberries, are regarded as manganese accumulators. There are numerous reports of foliar manganese levels in excess of 2000–4000 mg/kg. Mean manganese concentrations in birds’ eggs from a variety of geographical areas range from 1 to 5 mg/kg dry weight, mean liver concentrations range from 3 to 11 mg/kg dry weight, and mean feather concentrations range from 0.3 to 40 mg/kg dry weight. Mean manganese concentrations of up to 17 mg/kg dry weight have been found in tissues (liver, kidney, and whole body) from a variety of reptiles and wild mammals.

Manganese is an essential nutrient for micro-organisms, plants, and animals. Nutritional manganese requirements for terrestrial plants are around 10–50 mg/kg tissue. Critical nutritional levels vary widely between species and among cultivars of a species. Calcareous soils, especially those with poor drainage and high organic matter, are the types of soil that produce manganese-deficient plants.

Most toxicity tests have been carried out using ionic manganese. Little is known about the aquatic toxicity of colloidal, particulate, and complexed manganese; in general, however, toxicities of metals bound into these forms are assumed to be less than those of the aquo-ionic forms. For algae and protozoa, there is a wide range of toxicity values; the most sensitive species appear to be the marine diatom *Ditylum brightwellii*, with a 5-day

EC₅₀, based on growth inhibition, of 1.5 mg/litre, and a freshwater alga *Scenedesmus quadricauda*, with a 12-day EC₅₀, based on total chlorophyll reduction, of 1.9 mg/litre. Tests on aquatic invertebrates reveal 48-h LC₅₀/EC₅₀ values ranging from 0.8 mg/litre (*Daphnia magna*) to 1389 mg/litre (*Crangonyx pseudogracilis*), the lowest LC₅₀ being observed under soft water conditions (25 mg calcium carbonate/litre). A significant reduction in survival and hatching of yellow crab (*Cancer anthonyi*) embryos at ≥ 0.01 mg manganese/litre was found in 7-day tests in seawater. For fish, 96-h LC₅₀s range from 2.4 mg manganese/litre for coho salmon (*Oncorhynchus kisutch*) to 3350 mg/litre for Indian catfish (*Heteropneustes fossilis*), with the lowest LC₅₀ values obtained under soft water conditions (25 mg calcium carbonate/litre). Significant embryonic mortality was observed in rainbow trout (*Oncorhynchus mykiss*) eggs exposed to 1 mg manganese sulfate/litre for 29 days. A single embryo-larval test with a 7-day LC₅₀ of 1.4 mg manganese/litre was identified for amphibians. Acute toxicity in aquatic invertebrates and fish decreased with increasing water hardness; the addition of chelating agents can reduce the toxicity of manganese. There is evidence that manganese can protect organisms against the effects of more toxic metals.

In the field, the high frequency of blue crabs (*Callinectes sapidus*) with shell disease (lesions) in a metal-contaminated estuary was ascribed to manganese toxicity, and the deposition of manganese dioxide on the gills of Norway lobster (*Nephrops norvegicus*) gave rise to a brown or black discoloration of the gills and black corroded areas on the carapace following hypoxic conditions in the south-east Kattegat, Sweden. Increased mortality of rainbow trout (*Oncorhynchus mykiss*) at a hatchery was found to be positively correlated with manganese concentration (<0.5–1 mg/litre). Acid precipitation has caused acid episodes and elevated concentrations of metals. Cage experiments with yearling brown trout (*Salmo trutta*) showed that pH (4.5–5.4) and the concentration of labile inorganic manganese (0.1–0.4 mg/litre) explained all of the observed mortality.

Symptoms of manganese toxicity to terrestrial plants vary widely with species and include marginal chloroses, necrotic lesions, and distorted development of the leaves. Toxic manganese concentrations in crop plant tissues vary widely, with critical values ranging from 100 to 5000 mg/kg. Manganese toxicity is a major factor limiting crop growth on acidic, poorly drained, or steam-sterilized mineral soils. There is a wide range of variation in tolerance to manganese between and within plant species. Factors affecting manganese tolerance include genotype (inter- and intraspecific variation), silicon concentration, temperature, light intensity, physiological leaf age, microbial activity, and the characteristics of the rhizosphere.

Surface freshwater data suggest that higher manganese concentrations occur during periods of higher stream flow, such as spring runoff, and lower concentrations tend to occur downstream of lakes that act as settling areas for sediment. Soft water streams, rivers, and lakes appear to be the most sensitive freshwater environments, with laboratory tests and field observations showing that dissolved manganese concentrations of around 1 mg/litre can cause toxic effects in aquatic organisms. An overall guidance value for the protection of 95% of species with 50% confidence was derived at 0.2 mg manganese/litre for soft waters for the freshwater environment. Other factors, such as acid precipitation, acid mine drainage, land use, and municipal wastewater discharges, can increase dissolved manganese levels and thus increase the risk to sensitive species, especially in soft water areas. Evaluation of the likely toxicity of manganese to organisms in the field has to take account of speciation conditions in both the test and the specific field area. In the marine environment, manganese can be taken up and accumulated by organisms during hypoxic releases of dissolved manganese from manganese-rich sediments. Even taking into account the possible mitigating effects of suspended sediment, salinity, and oxygen levels in natural environments, adverse effects in the field have been observed. An overall guidance value for the protection of 95% of species with 50% confidence was derived at 0.3 mg manganese/litre for the marine environment.

When evaluating the risk to the terrestrial environment from anthropogenic releases of manganese, account must be taken of local natural ("background") levels, which are in turn controlled by a variety of physical and chemical parameters. Different communities and ecosystems would also respond differently, depending on their "normal" exposure to manganese. For these reasons, deriving a single guidance value for the terrestrial environment is inappropriate.

2. IDENTITY AND PHYSICAL/CHEMICAL PROPERTIES

Table 1 lists common synonyms and other relevant information on the chemical identity and properties of manganese and several of its most important compounds. Manganese is a naturally occurring element that is found in rock, soil, water, and food. It can exist in 11 oxidation states ranging from -3 to +7, but the most common ones are +2 (e.g., manganese chloride $[\text{MnCl}_2]$), +4 (e.g., manganese dioxide $[\text{MnO}_2]$), and +7 (e.g., potassium permanganate $[\text{KMnO}_4]$). Manganese and its compounds can exist as solids in the soil and as solutes or small particles in water. Most manganese salts are readily soluble in water, with only the phosphate and

the carbonate having low solubilities. The manganese oxides (manganese dioxide and manganese tetroxide) are poorly soluble in water. Manganese can also be present in small dust-like particles in the air.

Additional physical/chemical properties for manganese and select manganese compounds are presented in the International Chemical Safety Cards reproduced in this document.

3. ANALYTICAL METHODS

Atomic absorption spectrophotometric analysis is the most widely used method for determining manganese in biological materials and environmental samples. Fluorimetric, colorimetric, neutron activation analysis, and plasma atomic emission techniques are also recommended for measuring manganese in such samples. Inductively coupled plasma (ICP) atomic emission analysis is frequently employed for multianalyte analyses that include manganese. In most cases, distinguishing between different oxidation states of manganese is impossible, so total manganese is measured. The detection limits of these methods range from <0.01 to 0.2 mg/kg for biological tissues and fluids, from 5 to 10 $\mu\text{g}/\text{m}^3$ for air, and from 0.01 to 50 $\mu\text{g}/\text{litre}$ for water (Kucera et al., 1986; Abbasi, 1988; Lavi et al., 1989; Mori et al., 1989; Chin et al., 1992; ATSDR, 2000).

Determination of manganese requires an acid extraction/digestion step before analysis. The details vary with the specific characteristics of the sample, but treatment usually involves heating in nitric acid, oxidation with hydrogen peroxide, and filtration and/or centrifugation to remove insoluble matter (ATSDR, 2000).

Meneses et al. (1999) and Llobet et al. (2002) used ICP mass spectrometry with a detection limit of 0.02 mg/kg for soil and herbage. Pandey et al. (1998) used a sequential ICP optical emission spectrometer with an ultrasonic nebulizer for atmospheric particulates at a detection limit of 0.001 $\mu\text{g}/\text{litre}$, whereas ICP with atomic emission spectrophotometry was used for atmospheric particulates (Brewer & Belzer, 2001; Espinosa et al., 2001), sediment (Leivuori, 1998; Leivuori & Vallius, 1998), shellfish (Blackmore et al., 1998; Blackmore, 1999; Rainbow & Blackmore, 2001), feathers (Connell et al., 2002), and liver tissue (Mason & Stephenson, 2001).

Beklemishev et al. (1997) used the catalytic kinetic method for analysis of manganese in water. The method relies on an indicator reaction that is catalysed by Mn(II) (the oxidation of 3,3',5,5'-tetramethylbenzidine by

Table 1: Chemical identity of manganese and its compounds.^a

Synonyms	Manganese	Manganese chloride ^b	Manganese sulfate	Manganese tetroxide	Manganese dioxide	Potassium permanganate	MMT ^c	Maneb ^d	Mancozeb
Elemental manganese		Manganese chloride	Manganous sulfate	Trimanganese tetroxide	Manganese peroxide	Permanganic acid, potassium salt ^e	Methylcyclopentadienyl manganese tricarbonyl ^f	Manganese ethylene-bis(dithiocarbamate)	Manganese ethylene-bis(dithiocarbamate)
Colloidal manganese		Manganese dichloride	Sulfuric acid manganese	Mango-manganic oxide ^g	Manganese binoxide	Chameleon mineral	Methyl-cymantrene	Trimangol 80	(polymeric) complex with zinc salt
Cutaval ^b				Manganese oxide	Manganese black		Antiknock-33	Ethylene-bis(dithiocarbamic acid), manganous salt	Dithane M-45
				Hausmannite	Battery manganese		Manganese tricarbonyl methylcyclopentadienyl	Manzate	Manzaeb
					Pyrolusite			Dithane	Zimaneb
Chemical formula	Mn	MnCl ₂	MnSO ₄	Mn ₃ O ₄	MnO ₂	KMnO ₄	C ₉ H ₇ MnO ₃	C ₄ H ₆ MnN ₂ S ₄	C ₄ H ₆ MnN ₂ S ₄ ·C ₄ H ₆ N ₂ S ₄ Zn
CAS No.	7439-96-5	7773-01-5	7785-87-7	1317-35-7	1313-13-9	7722-64-7	12108-13-3	12427-38-2	8018-01-7
Relative molecular mass	54.94 ^g	125.85 ^g	151.00 ^g	228.81 ^g	86.94 ^g	158.04 ^g	218.10	265.31	541.03
Colour	Grey-white ^g	Pink ^g	Pale rose-red	Black ^g	Black	Purple	Dark orange-red ^h	Yellow-brown	Greyish-yellow
Physical state	Solid	Solid	Solid	Solid	Solid	Solid	Liquid ^h	Powder	Powder
Melting point	1244 °C ^g	650 °C	700 °C	1564 °C	535 °C	<240 °C (decomposes)	1.5 °C	Decomposes on heating	Decomposes without heating
Boiling point	1962 °C ^g	1190 °C ^g	Decomposes at 850 °C	No data	No data	No data	232.8 °C	No data	No data
Solubility	Dissolves in dilute mineral acids ^g	Very soluble in water (723 g/litre at 25 °C) ^b ; soluble in alcohol	Soluble in water (520 g/litre at 5 °C) ^b and alcohol	Insoluble in water; soluble in hydrochloric acid	Soluble in hydrochloric acid; insoluble in water	Soluble in water (64 g/litre at 20 °C) ^g , acetone, and sulfuric acid	Practically insoluble in water (0.029 g/litre at 25 °C) ^b ; completely soluble in hydrocarbons	Slightly soluble in water; soluble in chloroform	Practically insoluble in water (0.006 g/litre at 25 °C) ^b as well as most organic solvents
Log K _{ow} ⁱ	N/A	N/A	N/A	N/A	N/A	N/A	3.7 ⁱ		1.33 ^b
HLC ^j	N/A	N/A	N/A	N/A	N/A	N/A	0.019 ^j		

^a Adapted from ATSDR (2000). All information obtained from Sax & Lewis (1987), except where noted.^b HSDB (1998).^c Zayed et al. (1994).^d Ferraz et al. (1988).^e Windholz (1983).^f NTP (1999).^g Lide (1993).^h Verschuere (1983).ⁱ K_{ow} = octanol-water partition coefficient; HLC = Henry's law constant.^j Garrison et al. (1995).

potassium periodate [KIO_4]) and is carried out on the surface of a paper-based sorbent. The method has a detection limit ($0.005 \mu\text{g/litre}$) that is much lower than those of other, more established methods.

A nuclear magnetic resonance method (Kellar & Foster, 1991) and a method using on-line concentration analysis (Resing & Mottl, 1992) were used to determine both free and complexed manganese ions in aqueous media. The latter method was highly sensitive, with a detection limit of 36 pmol/litre (1.98 ng/litre when concentrating 15 ml of seawater). A similar detection limit was achieved by Sarzanini et al. (2001) for seawater using flow-injection preconcentration coupled with electrothermal atomic absorption spectrometry.

The technique of diffusive gradients in thin films (DGT) has been used for *in situ* trace manganese speciation measurements. A concentration–depth profile of labile manganese was obtained in a stratified estuary by deployment of a string of DGT devices across the redoxcline (Denney et al., 1999). Gauthreaux et al. (2001) used a modified sequential extraction procedure to speciate the chemical forms of manganese in sediment using flame atomic absorption spectrophotometry. Concentrations were determined in five different fractions for each sample: manganese in the exchangeable form, manganese bound to carbonates, manganese bound to manganese/iron oxides, manganese bound to organic matter, and manganese in the residual form. Techniques such as X-ray absorption near-edge structure spectroscopy enable *in situ* quantification of the oxidation state of manganese (Bargar et al., 2000).

4. SOURCES OF ENVIRONMENTAL EXPOSURE

4.1 Natural sources

Manganese is ubiquitous in the environment. It comprises about 0.1% of the Earth's crust (NAS, 1973; Graedel, 1978). Manganese does not occur naturally as a base metal but is a component of more than 100 minerals, including various sulfides, oxides, carbonates, silicates, phosphates, and borates (NAS, 1973). The most commonly occurring manganese-bearing minerals include pyrolusite (manganese dioxide), rhodocrosite (manganese carbonate [MnCO_3]), rhodonite (manganese silicate), and hausmannite (manganese tetroxide [Mn_3O_4]) (NAS, 1973; Windholz, 1983; US EPA, 1984; HSDB, 1998).

Ferromanganese minerals such as biotite mica and amphiboles contain large amounts of manganese, and manganese-rich nodules (especially found in the North-

east Pacific; Schiele, 1991) have been identified on the seafloor in conjunction with cobalt, nickel, and copper (Reimer, 1999; Ahnert & Borowski, 2000). Similarly, manganese crusts occur as pavement-like encrustations of ferromanganese oxides on exposed abyssal hard substrates related to all types of submarine elevations (Ahnert & Borowski, 2000). Black smokers (hydrothermal vents on the seafloor releasing predominantly iron and sulfide) are an additional source releasing manganese into the (oceanic) hydrosphere (Gamo et al., 2001). Important sources of manganese include soils, sediments, and metamorphic and sedimentary rocks (Reimer, 1999).

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. Atmospheric particulate matter collected in the Antarctic indicated that manganese was derived from either crustal weathering or the ocean (Zoller et al., 1974). 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. Other possible sources include the direct reduction of particulate manganese oxides in aerobic environments by organics, with or without ultraviolet light, the natural weathering of Mn(II)-containing minerals, and acid drainage and other acidic environments. The major pool of manganese in soils originates from crustal sources. Addition of manganese to soils can also result from direct atmospheric deposition, wash-off from plant and other surfaces, leaching from plant tissues, and the shedding or excretion of material such as leaves, dead plant and animal material, and animal excrement (Stokes et al., 1988).

4.2 Anthropogenic sources

The major anthropogenic sources of environmental manganese include municipal wastewater discharges, sewage sludge, mining and mineral processing (particularly nickel), emissions from alloy, steel, and iron production, combustion of fossil fuels, and, to a much lesser extent, emissions from the combustion of fuel additives.

The manganese content in ore produced worldwide was estimated to be $8.8 \text{ million tonnes}$ in 1986. Production levels of manganese ore and its total manganese metal content remained nearly the same through 1990 (US Department of the Interior, 1993). Levels of ore produced worldwide in 1995, 1996, and 1997 declined

slightly, with total manganese metal content declining proportionately to 8.0, 8.1, and 7.7 million tonnes, respectively (US Department of the Interior, 1996, 1998). Sites of substantial workable manganese-iron deposits include the former USSR, South and North Africa, South America, India, and China (Schiele, 1991). Most manganese is mined in open-pit or shallow mines (NAS, 1973). Although modern steelmaking technologies call for lower unit consumption of manganese, worldwide demand for steel is projected to increase moderately in the future, particularly in developing countries (US Department of the Interior, 1995, 1998). The demand for manganese in other industries (e.g., dry-cell battery manufacturing) might also increase, but the overall effect of these other uses on global trends in manganese production and use is minor (EM, 1993; US Department of the Interior, 1995, 1998).

Manganese compounds are produced from manganese ores or from manganese metal. 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 (Schiele, 1991). 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). Manganese chloride is used as a precursor for other manganese compounds, as a catalyst in the chlorination of organic compounds, in animal feed to supply essential trace minerals, and in dry-cell batteries (US EPA, 1984; HSDB, 1998). Manganese sulfate (MnSO_4) is used primarily as a fertilizer and as a livestock supplement; it is also used in some glazes, varnishes, ceramics, and fungicides (Windholz, 1983; US EPA, 1984; HSDB, 1998). Maneb (manganese ethylene-bis-dithiocarbamate) is used as a broad-spectrum contact fungicide and is also used for seed treatment of small grains such as wheat. Maneb is therefore a potential source of manganese in soil and plants (Ferraz et al., 1988; Ruijten et al., 1994). Potassium permanganate is used as an oxidizing agent, disinfectant, and antialgal agent; for metal cleaning, tanning, and bleaching; as a purifier in water and waste treatment plants; and as a preservative for fresh flowers and fruits (HSDB, 1998). The organomanganese compound MMT (methylcyclopentadienyl manganese tricarbonyl), an antiknock additive in unleaded gasoline, is produced by the addition of molten sodium metal to methylcyclopentadiene to give methylcyclopentadienyl-sodium. Anhydrous manganese dichloride is then added to afford methylcyclopentadienylmanganese, which is subsequently reacted with carbon monoxide to give MMT (NAS, 1973; US EPA, 1984; Sax & Lewis, 1987;

HSDB, 1998; Kirk & Othmer, 2001). MMT has been approved for use in Argentina, Australia, Bulgaria, the USA, France, and the Russian Federation and has been conditionally approved for use in New Zealand (Zayed et al., 1999; Zayed, 2001); more recently, Ethyl Corp. (a major producer of MMT) noted that MMT is now sold in 25 countries (Kaiser, 2003).

The main anthropogenic sources of manganese release to air are industrial emissions (such as ferroalloy production and iron and steel foundries, power plants, and coke ovens), combustion of fossil fuels, and re-entrainment of manganese-containing soils (Liroy, 1983; US EPA, 1983, 1984, 1985a,b; Ruijten et al., 1994; ATSDR, 2000). Problems with air pollution — especially dust and smoke containing manganese dioxide and manganese tetroxide — arise during the mining, crushing, and smelting of ores as well as during steel production (Schiele, 1991). Approximately 2 tonnes of manganese ore are required to make 1 tonne of ferro-manganese alloy (NAS, 1973). Steel emissions were found to be the predominant source of manganese in urban particulate matter (Sweet et al., 1993). Manganese can also be released to the air during other anthropogenic processes, such as welding and fungicide application (Ferraz et al., 1988; MAK, 1994; Ruijten et al., 1994). Nriagu & Pacyna (1988) estimated that total worldwide emissions of manganese in 1983 ranged from 10 560 to 65 970 tonnes, with the predominant sources being coal combustion, secondary non-ferrous metal production, and sewage sludge incineration. Total emissions to air from anthropogenic sources in the USA were estimated to be 16 400 tonnes in 1978, with about 80% (13 200 tonnes) from industrial facilities and 20% (3200 tonnes) from fossil fuel combustion (US EPA, 1983). Air emissions by US industrial sources reportable to the Toxics Release Inventory (TRI) for 1987 totalled 1200 tonnes (TRI87, 1989). In 1991, air emissions from TRI facilities in the USA ranged from 0 to 74 tonnes, with several US states reporting no emissions (TRI91, 1993). Estimated releases of manganese to air in 1996 were 4000 tonnes, representing 15% of total environmental releases (TRI96, 1998). Figures in Table 2 (see section 6) show decreasing emissions of manganese to air in the USA as a result of air pollution control.

Combustion of MMT leads to the emission of manganese phosphates and manganese sulfate, with manganese oxides such as manganese tetroxide a minor component (NICNAS, 2003). The size of particles emitted to the atmosphere varies from 0.1 to 0.45 μm (Waldron, 1980). Combustion products of MMT also include manganese phosphate and manganese sulfide (Zayed et al., 1999; Zayed, 2001). One of the principal sources of inorganic manganese as a pollutant in the urban atmosphere is the combustion of MMT, particularly in areas of high traffic density (Sierra et al., 1998). MMT was used as a gasoline additive in the USA for a

number of years, resulting in manganese emissions. Davis et al. (1988) found that motor vehicles made a significant contribution to levels of airborne manganese in areas such as southern California (around 40% of total airborne manganese) compared with, for example, central and northern California, where the addition of manganese to gasoline was much lower. According to a statistical model of source apportionment, the calculated average vehicular contribution of manganese in southern California was about 13 ng/m³, around 4 times the value calculated for both central and northern California.

In Canada, MMT use as a fuel additive has gradually increased since 1977. Manganese emissions from gasoline combustion rose sharply from 1977 through the early 1980s, reaching an estimated 220 tonnes by 1985 (Jaques, 1984). In 1990, lead was completely replaced by MMT in gasoline in Canada (Loranger & Zayed, 1994). MMT use peaked in 1989 at over 400 tonnes, which was more than twice the usage in 1983 and 1.5 times the usage in 1986. MMT use declined to about 300 tonnes by 1992, owing to reductions in its concentration in gasoline. However, ambient monitoring data for manganese in Canadian cities without industrial sources for the 1989–1992 period did not reflect this peak in MMT use. Air manganese levels (PM_{2.5}, or particulate matter with an aerodynamic diameter less than or equal to 2.5 µm) remained constant at 11–13 ng/m³ for small cities and 20–25 ng/m³ for large cities (Health Canada, 1994; Egyed & Wood, 1996). Manganese emission levels can vary depending on the concentration of MMT in gasoline and gasoline usage patterns. One study reported a correlation between atmospheric manganese concentrations in 1990 air samples and traffic density in Montreal, Canada (Loranger & Zayed, 1994). However, a later study by these investigators reported that atmospheric manganese concentrations in Montreal decreased in 1991 and 1992, despite an estimated 100% increase in manganese emission rates from MMT in gasoline (Loranger & Zayed, 1994). Another study suggested that the high manganese levels in Montreal were, in part, due to the presence of a silico- and ferromanganese facility that ceased operation in 1991 (Egyed & Wood, 1996).

It is clear that the contribution of MMT to overall manganese levels in the environment is complex. The contribution of MMT to atmospheric manganese concentrations is difficult to establish, since it may be masked by more substantial variation associated with other industrial activities as well as road dust and windblown dust (Bankovitch et al., 2003). However, even though manganese may be a small percentage of total suspended particulate matter measured in cities, such as Montreal, the contribution of MMT to air manganese levels could be significant, in that it may account for stable manganese levels in the face of declining total suspended particulate concentrations.

Factors such as unfavourable meteorological conditions and high traffic density could lead to an increase in manganese levels (PM_{2.5}) attributable to MMT (Wallace & Slonecker, 1997; Davis et al., 1998).

Manganese can be released to water by discharge from industrial facilities or as leachate from landfills and soil (US EPA, 1979, 1984; Francis & White, 1987; TRI91, 1993). Sea disposal of mine tailings and liquor is another source of manganese to the marine environment, particularly in tropical areas (Florence et al., 1994). Nriagu & Pacyna (1988) estimated that total worldwide anthropogenic inputs of manganese to aquatic ecosystems during 1983 ranged from 109 000 to 414 000 tonnes, with the predominant sources being domestic wastewater and sewage sludge disposal. In the USA, reported industrial discharges of manganese in 1991 ranged from 0 to 17.2 tonnes for surface water, from 0 to 57.3 tonnes for transfers to public sewage, and from 0 to 0.114 tonnes for underground injection (TRI91, 1993). An estimated total of 58.6 tonnes, or 1% of the total environmental release of manganese in the USA, was discharged to water in 1991 (TRI91, 1993). In 1996, the estimated release of manganese to water was 870 tonnes (TRI96, 1998).

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).

5. ENVIRONMENTAL TRANSPORT, DISTRIBUTION, TRANSFORMATION, AND ACCUMULATION

5.1 Transport and distribution between media

Elemental manganese and inorganic manganese compounds have negligible vapour pressures but can exist in air as suspended particulate matter derived from industrial emissions or the erosion of soils (US EPA, 1984). In the troposphere, manganese is likely to be found in oxide, sulfate, or nitrate forms or as mineral complexes related to its natural origin in soil or rock (Stokes et al., 1988). Manganese-containing particles are

was one mechanism by which colloidal manganese could dominate speciation.

There is evidence that afforestation of upland areas has increased manganese concentrations in surface waters. Analysis of sites in the United Kingdom between 1988 and 1996 shows a significant positive correlation between mean manganese concentrations and the percentage of conifer cover in the catchment (Heal, 2001). Enhanced manganese concentrations arise from foliar leaching and wash-off of manganese in fine mist and dry particles that are captured from the atmosphere by the trees (Shanley, 1986; Heal, 2001). Litter from conifer plantations may also enhance manganese leaching from soil into runoff. Soil and water acidification in catchments planted with conifers has been widely documented and is associated with enhanced manganese concentrations in surface waters (Heal, 2001). The extent to which land use influences manganese concentrations in upland catchments is modified by catchment hydrology and soil type (Heal, 2001; Heal et al., 2002). Heal et al. (2002) identified summer baseflow and the summer–autumn hydrological transition as critical periods for increased manganese concentrations in runoff. It is only when manganese enters lakes, estuaries, and the ocean, where residence times are considerably longer, that chemical processes will become dominant and the system will approach an equilibrium speciation (Laxen et al., 1984).

Manganese is often transported in rivers adsorbed to suspended sediments. Most of the manganese from industrial sources (metallurgical and chemical plants) found in the Paraíba do Sul-Guandu River, Rio de Janeiro, Brazil, was bound to suspended particles (Malm et al., 1988). A positive correlation between manganese concentrations and suspended sediment levels has been reported for a wide variety of rivers in the United Kingdom (Laxen et al., 1984; Neal et al., 1998, 2000). The tendency of soluble manganese compounds to adsorb to soils and sediments can be highly variable, depending mainly on the cation exchange capacity and the organic composition of the soil (Hemstock & Low, 1953; Schnitzer, 1969; McBride, 1979; Curtin et al., 1980; Baes & Sharp, 1983; Kabata-Pendias & Pendias, 1984). Laxen et al. (1984) proposed that the “particulate” and “dissolved” phases for rivers and streams can be decoupled with weathering processes, leading to suspended sediment and influxes of Mn(II) species leaching from anoxic soil and groundwaters. The speciation in any particular river or stream will depend principally on the hydrogeological conditions of the catchment at time of sampling. Suspended sediment, with a manganese content dependent upon the catchment geology, will be mixed with Mn(II) species in varying proportions.

Primary chemical factors controlling sedimentary manganese cycling are the oxygen content of the overlying water, the penetration of oxygen into the sediments, and benthic organic carbon supply (Lynn & Bonatti, 1965; Grill, 1978; Balzer, 1982; Sundby et al., 1986; Hunt & Kelly, 1988). Manganese exchange between water and sediment is an interdependent process. A cycle between sediment and water is maintained, since dissolved Mn(II) is particle-reactive (Hunt, 1983). Once incorporated into sediments, solid-phase manganese oxides (manganese dioxide) undergo reduction to soluble Mn(II) during anaerobic decomposition of organic matter (Pohl et al., 1998). Release from sediment to water occurs by diffusion processes as a result of a steep Mn(II) concentration gradient across the sediment pore water and bottom water interface (Balzer, 1982; Kremling, 1983; Jung et al., 1996). Recycling at a redox boundary is involved in the formation of enriched manganese horizons. Manganese precipitating on the oxic side of a redox boundary consists of a Mn(IV) oxide. If the boundary is displaced towards the sediment surface or into the water column, the oxide undergoes rapid reduction and dissolution. Removal of Mn(II) by diffusion in the pore water is a slow process, and so supersaturation and precipitation of carbonate are likely to occur, transforming labilized oxide to stable carbonate. Under intermittently anoxic conditions, fixation of an enriched horizon may occur by precipitation of manganese dioxide from the water column during oxic periods, burial in sediment, and transformation to carbonate (Schaanning et al., 1988). A clear enrichment of dissolved manganese was observed at low salinities (<7.5‰) during estuarine mixing (L'Her Roux et al., 1998).

In soils, manganese solubility is determined by two major variables: pH and redox potential. Water-soluble manganese in soils is directly proportional to pH, with oxidation state being another major determinant of manganese solubility. The lower oxidation state, Mn(II), predominates in reducing conditions, resulting in higher concentrations of dissolved manganese in flooded soils or other reducing situations (Stokes et al., 1988). This is normally reflected in higher manganese bioavailability in flooded soils; in some situations, however, there is competition by iron, and plant absorption of manganese is decreased or unaffected by flooding (Adriano, 1986). The oxidation state of manganese in soils and sediments can be altered by microbial activity (Geering et al., 1969; Francis, 1985). Geering et al. (1969) observed that Mn(II) in suspensions of silt or clay loams was oxidized by microorganisms, leading to precipitation of manganese minerals. Fungi are known to enhance the bioavailability of micronutrients. Accordingly, the solubilization of the sparingly soluble manganese dioxide by the fungus *Trichoderma harzianum* was reported by Altomare et al. (1999). Herzl & Roevros (1998) found that microbial uptake represented around

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60% of the transfer of dissolved manganese to the particulate phase in the Scheldt estuary, Belgium. While microorganisms are believed to play an important role in the cycling of manganese in aquatic environments, specific microbial groups indigenous to these systems have not been well characterized (Thamdrup et al., 2000; Stein et al., 2001). There are two main mechanisms involved in the retention of manganese by soil. Firstly, through cation exchange reactions, manganese ions and the charged surface of soil particles form manganese oxides, hydroxides, and oxyhydroxides, which in turn form adsorption sites for other metals. Secondly, manganese can be adsorbed to other oxides, hydroxides, and oxyhydroxides through ligand exchange reactions (Evans, 1989).

5.2 Transformation

MMT degradation in natural aquifers and sediment systems was determined to be very slow under anaerobic conditions. MMT has been found to be persistent in natural aquatic and soil environments in the absence of sunlight, with a tendency to sorb to soil and sediment particles. Calculated half-lives of MMT in aquatic and soil environments range from approximately 0.2 to 1.5 years at 25 °C (Garrison et al., 1995). In the presence of light, photodegradation of MMT is rapid, with identified products including a manganese carbonyl that readily oxidizes to manganese tetroxide (Garrison et al., 1995). MMT is photolysed rapidly by sunlight in the atmosphere, with a very short half-life of less than 2 min (Ter Haar et al., 1975; Garrison et al., 1995). MMT is photolysed rapidly in purified, distilled water exposed to sunlight, with degradation following first-order kinetics and a calculated half-life of less than 1 min (Garrison et al., 1995). Maneb released to water may be subject to abiotic degradation, with the rate of degradation dependent on the aeration of the water and the pH. In addition, manebe may undergo some photodegradation in sunlit water. Manebe is not expected to undergo significant volatilization from water. Mancozeb hydrolyses rapidly in water, with a half-life of less than 1–2 days at pH 5–9 (ATSDR, 2000).

The hydrophobicity of MMT (octanol–water partition coefficient [$\log K_{ow}$] = 3.7) suggests that it can sorb to soil or sediment particles (Garrison et al., 1995). MMT was found to be stable in stream bottom sediments under anaerobic conditions. Photodegradation of MMT is not likely to occur in sediments, and MMT may equilibrate between the sediment, sediment pore water, and water column manganese (Garrison et al., 1995). Calumpang et al. (1993) reported a half-life of 2.9 days for mancozeb determined in a silty clay loam soil. In other studies, the half-life of manebe in soil was estimated to be between 20 and 60 days (Rhodes, 1977; Nash & Beall, 1980). Using chemical and physical properties,

Beach et al. (1995) estimated the half-life of manebe and mancozeb in soils to be 70 days.

In the laboratory, microorganisms have been shown to transform both soluble and solid manganese; thus, they potentially have substantial effects on local manganese cycles. Physiological, biochemical, and structural studies of manganese oxidizers and reducers in the laboratory form the basis on which models of the participation of microorganisms in the cycling of manganese have been proposed. Field analyses of the distribution of manganese oxidizers and reducers, structural properties of manganese precipitates, and *in situ* activity measurements support the hypothesis that microorganisms play an integral role in the cycling of manganese in some environments (Nealson, 1983). Microbial oxidation of Mn(II) occurs at rates up to 5 orders of magnitude greater than those of abiotic Mn(II) oxidation (Tebo, 1991). Johnson et al. (1995) found that microbial catalysis was overwhelmingly responsible for manganese oxidation in the lower epilimnion of a freshwater dam during the summer months. Microbial oxidation of Mn(II) to Mn(IV) by spores of the marine *Bacillus* sp. was observed by Bargar et al. (2000), whereas Stein et al. (2001) found three freshwater bacterial isolates capable of manganese oxidation. Elevated manganese levels on the carapace of crayfish (*Cherax destructor*) are thought to be the result of manganese-oxidizing bacteria forming biofilms (King et al., 1999). Nealson et al. (1991) isolated and identified manganese-reducing bacteria in the Black Sea. The major group of organisms isolated from the 80- to 90-m (manganese reduction) zone were in the genus *Shewanella*. Microbially mediated reduction of complexed Mn(III) has also been observed in the laboratory (Kostka et al., 1995). Further studies have isolated manganese-reducing bacteria in marine sediments, oxic regions of lake water columns, and the rhizosphere of non-mycorrhizal plants (Posta et al., 1994; Bratina et al., 1998; Thamdrup et al., 2000).

5.3 Accumulation

Manganese is an essential element (see section 7.1) and is, therefore, actively assimilated and utilized by both plants and animals; however, it can be significantly bioconcentrated by aquatic biota at lower trophic levels. Bioconcentration factors (BCFs) of 2000–20 000 for marine and freshwater plants, 2500–6300 for phytoplankton, 300–5500 for marine macroalgae, 800–830 for intertidal mussels, and 35–930 for fish have been estimated (Folsom et al., 1963; Thompson et al., 1972; Bryan & Hummerstone, 1973; Pentreath, 1973; Rai & Chandra, 1992). Ichikawa (1961) reported that marine fish did not accumulate manganese to the same extent as organisms at lower trophic levels, with typical BCFs of about 100. Uptake of manganese by aquatic invertebrates and fish significantly increases with temperature (Miller et al., 1980) and decreases with pH (Rouleau et