

## 5. POTENTIAL FOR HUMAN EXPOSURE

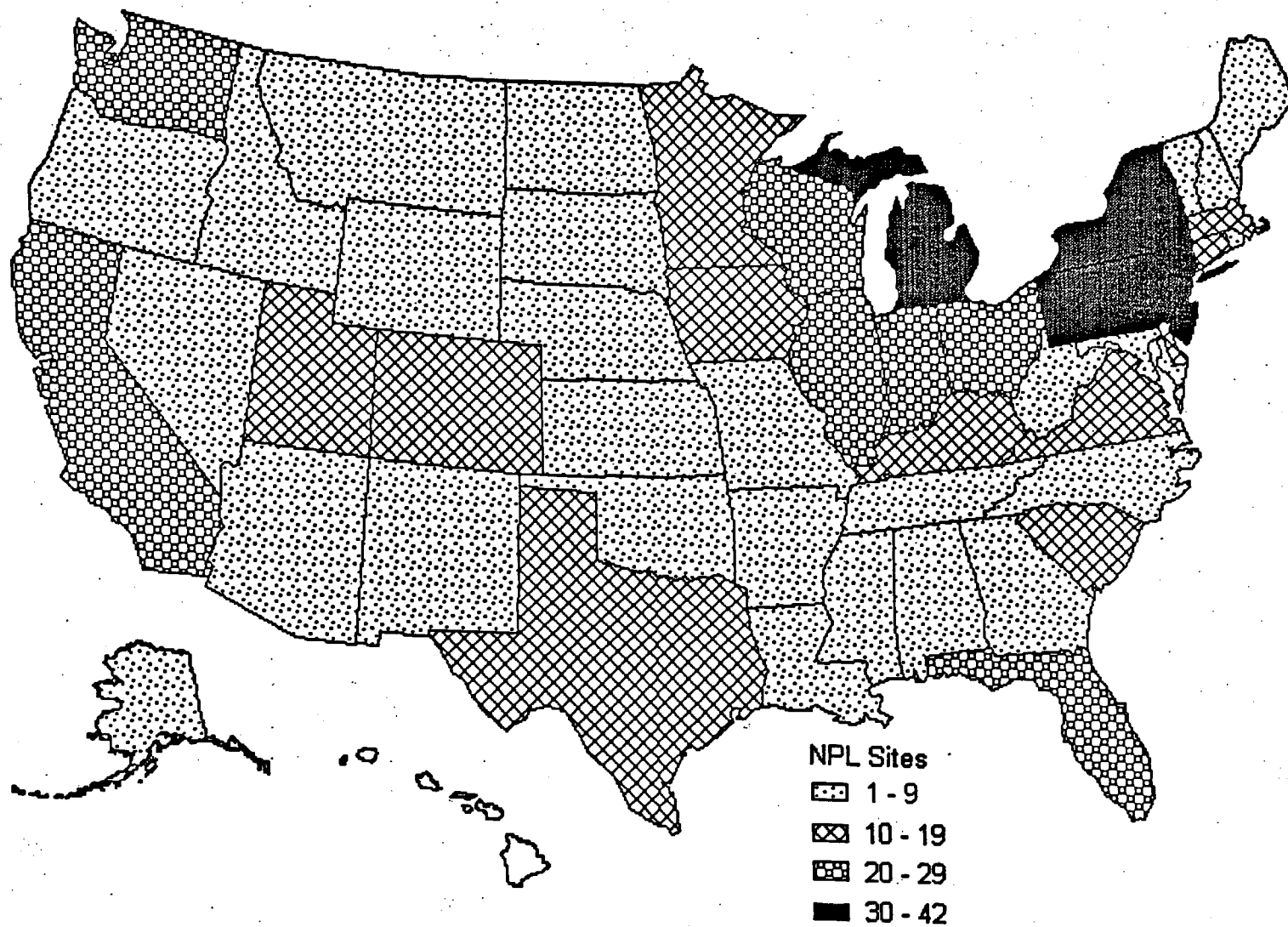
### 5.1 OVERVIEW

Manganese has been identified in at least 603 of the 1,467 current or former EPA National Priorities List (NPL) hazardous wastes sites (HazDat 1998). However, the number of sites evaluated for manganese is not known. The frequency of these sites within the United States can be seen in Figure 5-1. Of these sites, 598 are located in the United States, 3 are located in the Commonwealth of Puerto Rico, 1 is located in Guam, and 1 is located in the Virgin Islands. Available data indicate that manganese is detectable in soil and water at approximately 40–80% of all NPL sites (HazDat 1998) and nearly all other hazardous waste sites. In some cases, this is probably due to natural levels of manganese rather than to disposal of manganese wastes, but at some sites the levels are significantly higher than average. No data were available to indicate the presence of any organomanganese compounds (MMT, maneb, mancozeb, and mangafodipir) at any NPL hazardous waste sites.

Manganese is ubiquitous in the environment. It occurs in soil, air, water, and food. Thus, all humans are exposed to manganese, and manganese is a normal component of the human body. Food is usually the most important route of exposure for humans; typical daily intakes range from 1–5 mg/day.

Above-average exposures to manganese are most likely to occur in or near a factory or a hazardous waste site that releases significant amounts of manganese dust into air. Manganese can be released into air by combustion of unleaded gasoline that contains MMT as an antiknock ingredient. Because these releases are particulate in nature, the fate and transport of the particles are determined mainly by the wind and by the size and density of the particles. Some manganese compounds are readily soluble, so significant exposures can also occur by ingestion of contaminated drinking water. However, manganese in surface water may oxidize or adsorb to sediment particles and settle to the bottom. Manganese in soil can migrate as particulate matter in air or water, or soluble compounds may be dissolved by water and leach from the soil. The extent of leaching is determined mainly by the characteristics of the soil and is highly variable.

FIGURE 5-1. Frequency of NPL Sites with Manganese Contamination



Derived from HazDat 1998

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**5.2 RELEASES TO THE ENVIRONMENT**Inorganic Manganese

According to the Toxics Release Inventory (TRI), in 1996, a total of 58,360,310 pounds (26,527,414 kg) of manganese was released to the environment from 1,978 large processing facilities (TRI96 1998). Table 5-1 lists amounts released from all the facilities that manufacture or process manganese to each medium within each state in 1996 (TRI96 1998). Industrial manufacturers, processors, and users of manganese and manganese compounds are required to report the quantities of these substances released to environmental media annually (EPA 1988a). In addition, an estimated 392,340 pounds (178,336 kg) were released by manufacturing and processing facilities to publicly owned treatment works (POTWs) and an estimated 186,247,598 pounds (84,657,999 kg) were transferred offsite (TRI96 1998). The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list. Also, because these data reflect past releases, they may not be representative of current releases at these facilities.

Manganese has been identified in a variety of environmental media (air, surface water, groundwater, soil, and sediment) collected at 603 of the 1,467 NPL hazardous waste sites (HazDat 1998).

Additional releases of manganese to the environment occur from natural sources and from processes such as combustion of fossil fuel, incineration of wastes, or cement production (EPA 1985c, 1985d). Quantitative data on releases of manganese to specific environmental media are discussed below.

Organic Manganese

*MMT*. No data for releases of MMT to the environment from facilities that manufacture or process MMT were found.

*Maneb or mancozeb*. According to TRI, in 1997, a total of 23,282 pounds (10,583 kg) of maneb were released to the environment from 1 repackaging facility. Table 5-2 lists amounts of maneb released from all the facilities that manufacture or process maneb to each medium in each state in 1997 (TRI97 1998). In addition, an estimated 19,297 pounds (8,772 kg) of maneb were transferred off-site and accounted for

**Table 5-1. Releases to the Environment from Facilities That Manufacture or Process Manganese**

Total of reported amounts released in pounds per year <sup>a</sup>								
STATE <sup>b</sup>	NUMBER OF FACILITIES	AIR <sup>c</sup>	WATER	LAND	UNDERGROUND INJECTION	POTW TRANSFER	OFF-SITE WASTE TRANSFER	TOTAL ENVIRONMENT <sup>d</sup>
AR	28	15,048	255	752	0	874	7,015,580	7,032,509
AZ	8	4,568	1	1	1	51	95,432	100,054
CA	55	41,870	13,005	195,109	0	9,080	1,085,258	1,344,322
CO	14	32,519	29	11,560	0	67	432,425	476,600
CT	16	846	54,000	3,800	0	758	289,429	348,833
DE	1	2,813	4	0	0	0	206,855	209,672
FL	23	7,895	0	374,683	230	878	953,881	1,337,567
GA	42	101,022	31,022	300,977	0	383	792,114	1,225,518
HI	1	0	0	0	7	0	41,616	41,623
IA	48	41,186	997	1,330,109	0	31,515	1,731,683	3,135,490
ID	3	14	0	17,491	0	0	13,478	30,983
IL	120	285,598	14,180	5,809,927	500	22,453	8,594,488	14,727,146
IN	159	297,218	25,588	2,422,228	2,900	45,032	19,377,727	22,170,693
KS	30	33,619	5	697,019	250	1,331	2,271,798	3,004,022
KY	63	155,054	11,686	153,161	0	4,413	5,458,605	5,782,919
LA	17	5,648	31,533	2,805,516	0	5	1,177,652	4,020,354
MA	26	368	19	27	0	16,310	347,007	363,731
MD	17	17,525	68,945	1,458,005	0	1,098	328,746	1,874,319
ME	8	1,189	610	0	0	10	460,914	462,723
MI	128	126,451	5,764	1,205,424	11,000	18,593	10,137,118	11,504,350
MN	27	11,716	342	50	0	56,599	1,280,310	1,349,017

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MO	49	42,628	755	4,661	0	41,684	1,989,279	2,079,007
MS	23	12,037	24,045	5,141,019	0	38	655,688	5,832,827
MT	1	1,503	3	2,849,437	0	2	2,153	2,853,098
NC	56	28,727	6,716	37,961	0	2,159	2,548,765	2,624,328
ND	5	553	0	0	0	0	294,710	295,263
NE	18	15,192	500	3,776	0	45	3,067,621	3,087,134
NH	4	560	0	0	0	0	36,100	36,660
NJ	27	7,555	51	250	0	2,010	467,550	477,416
NM	1	500	0	5	0	0	255	760
NV	2	13,800	0	2,330,005	0	0	0	2,343,805
NY	63	21,619	72,308	13,172	2,558	32,692	2,450,598	2,592,947
OH	227	696,933	1,055,373	13,749,832	250	56,735	26,531,656	42,090,779
OK	48	12,581	129	8,604	0	646	1,121,380	1,143,340
OR	16	6,219,388	45	281,800	0	7	1,756,325	8,257,565
PA	179	84,012	34,224	187,779	0	995	28,314,230	28,621,240
PR	5	1,000	0	19	0	33	38,222	39,274
RI	5	1,345	28	0	0	0	89,727	91,100
SC	55	31,044	175,594	231,754	0	971	10,879,559	11,318,922
SD	7	5,591	0	0	0	10	96,427	102,028
TN	54	233,442	156,151	3,856,929	0	2,621	7,554,735	11,803,878
TX	84	72,529	4,950	463,257	0	2,016	20,922,520	21,465,272

**Table 5-1. Releases to the Environment from Facilities That Manufacture or Process Manganese**

Total of reported amounts released in pounds per year <sup>a</sup>								
STATE <sup>b</sup>	NUMBER OF FACILITIES	AIR <sup>c</sup>	WATER	LAND	UNDERGROUND INJECTION	POTW TRANSFER	OFF-SITE WASTE TRANSFER	TOTAL ENVIRONMENT <sup>d</sup>
UT	22	85,927	0	1,029,763	0	12,928	570,042	1,698,660
VA	22	26,221	964	267,475	0	570	684,312	979,542
VT	1	2	0	0	0	0	28,504	28,506
WA	27	6,858	52,371	500	0	45	1,193,817	1,253,591
WI	126	49,656	16,662	8,790	0	25,828	10,834,422	10,935,358
WV	15	43,042	58,629	246,842	0	850	2,025,145	2,374,508
WY	2	250	0	29,000	0	5	1,740	30,995

Source: TRI96 1998

<sup>a</sup> Data in TRI are maximum amounts released by each facility

<sup>b</sup> Post office state abbreviations used

<sup>c</sup> The sum of fugitive and stack releases are included in releases to air by a given facility

<sup>d</sup> The sum of all releases of the chemical to air, land, and water, and underground injection wells; and transfers off-site by a given facility

POTW = publicly owned treatment works

Table 5-2. Releases to the Environment from Facilities that Manufacture or Process Maneb

Reported amounts released in pounds per year <sup>a</sup>										
STATE <sup>b</sup>	CITY	FACILITY	AIR <sup>c</sup>	WATER	LAND	UNDERGROUND INJECTION	POTW TRANSFER	OFF-SITE WASTE TRANSFER	TOTAL <sup>d</sup> ENVIRONMENT	
AR	HELENA	BPS INC.	11,641	0	11,641	0	1	11,741	35,024	
GA	VALDOSTA	GRIFFIN LLC	0	0	0	0	0	5,033	5,033	
ND	GRAND FORKS	AGSCO INC.	0	0	0	0	0	990	990	
NJ	PASSAIC	BARTLO PACKAGING INC.	0	0	0	0	0	1,533	1,533	
<b>TOTALS</b>			<b>11,641</b>	<b>0</b>	<b>11,641</b>	<b>1</b>	<b>0</b>	<b>19,297</b>	<b>42,580</b>	

Source: TRIS97 1999

<sup>a</sup> Data in TRI are maximum amounts released by each facility<sup>b</sup> Post office state abbreviations used<sup>c</sup> The sum of fugitive and stack releases are included in releases to air by a given facility<sup>d</sup> The sum of all releases of the chemical to air, land, and water, and underground injection wells; and transfers off-site by a given facility

POTW = publicly-owned treatment works

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approximately 45% of total environmental release (TRI97 1999). No release data were found for mancozeb.

*Mangafodipir*. No data for releases of mangafodipir to the environment were found. Because mangafodipir is a compound used exclusively in a clinical environment, it is not expected to be released to the environment and will not be discussed in subsequent sections concerning fate and transport.

### 5.2.1 Air

#### Inorganic Manganese

According to the Toxics Release Inventory, in 1996, the estimated releases of manganese of 8,896,662 pounds (4,043,937 kg) to air from 1,978 large processing facilities accounted for about 15% of total environmental releases (TRI93 1995). Table 5-1 lists amounts released from these facilities. The TRI data should be used with caution, however, since only certain types of facilities are required to report. This is not an exhaustive list. Also, because these data reflect past releases, they may not be representative of current releases at these facilities.

Manganese has been identified in air samples collected at 18 of the 603 NPL hazardous waste sites where it was detected in some environmental media (HazDat 1998).

The main sources of manganese release to the air are industrial emissions, combustion of fossil fuels, and reentrainment of manganese-containing soils (EPA 1983c, 1984a, 1985c, 1985d, 1987a; Lioy 1983). The principal sources of industrial emissions are ferroalloy production and iron and steel foundries, and the principal sources of combustion emissions are power plants and coke ovens (EPA 1983c, 1985c, 1985d). Total emissions to air from anthropogenic sources in the United States were estimated to be 36 million pounds in 1978, with about 80% (29 million pounds) from industrial facilities and 20% (7 million pounds) from fossil fuel combustion (EPA 1983c). Air emissions reported by industrial sources for 1996 total 8.9 million pounds (TRI96 1998). In 1996, air emissions from 227 facilities in Ohio, the state with the widest range of releases, ranged from 0 to 449,000 pounds/year; only one state (Hawaii) reported no emissions (TRI96 1998).



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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 located (EPA 1984a). Volcanic eruptions may also release manganese to the atmosphere (Schroeder et al. 1987).

### Organic Manganese

*MMT.* MMT was banned as an additive in unleaded gasoline by EPA in 1977 (EPA 1978, 1979, 1981); however, combustion of gasoline containing MMT (before the ban) may have contributed to urban air manganese levels. In 1995 the ban was lifted, and a court decision ordered EPA to register the product for use as a fuel additive, although testing for health effects continues (EPA 1995a). Analysis of manganese levels in the air indicates that vehicular emissions contributed an average of 13 nanograms( $\text{ng}$ ) manganese/ $\text{m}^3$  in southern California, while vehicular emissions were only about 3  $\text{ng}/\text{m}^3$  in central and northern California (Davis et al. 1988). A survey of ambient air concentrations of fine ( $\text{PM}_{2.5}$ ) manganese in rural sites in U.S. national parks and in urban sites in California indicated that from 1988 to 1993, ambient concentrations of manganese ranged from 1  $\text{ng}/\text{m}^3$  in rural sites to 3  $\text{ng}/\text{m}^3$  in urban sites (Wallace and Slonecker 1997). Part of the increase in fine manganese during this period was considered to be the result of the use of MMT in leaded gasoline. It was estimated that automobiles were responsible for 37% of the fine manganese levels in California in 1992. In 1994, the automobile was estimated to contribute to 12% of the fine manganese levels. Wallace and Slonecker (1997) estimated that the background contribution of windblown soil to fine manganese concentration was 1–2  $\text{ng}/\text{m}^3$ . It has been estimated that if MMT were used in all gasoline, urban air manganese levels would be increased by about 50  $\text{ng}/\text{m}^3$  (Cooper 1984; Ter Haar et al. 1975). The U.S. EPA (EPA 1994) estimated that a “substantial number of people” could be exposed to manganese particulate levels above 0.1  $\mu\text{g}/\text{m}^3$  if there were 100% usage of gasoline containing MMT.

Utilizing various environmental modeling approaches, it was estimated in 1994 that air levels of manganese in most USA urban areas would increase less than 0.02  $\mu\text{g}/\text{m}^3$  if MMT were used in all unleaded gasoline (Lynam et al. 1994). Slightly higher levels were predicted for Los Angeles because of extremely high traffic density and unique atmospheric and geographic features. The estimates were based on the assumption that - 30% of the manganese combusted is emitted from the tailpipe. However, emission tunnel experiments revealed that only 10–15% of the manganese in the combusted gasoline was emitted from the tailpipe.

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There is concern in Canada that combustion of MMT may be one of the main sources of manganese contamination in the urban environment, particularly in areas of high traffic density (Loranger and Zayed 1997a; Loranger et al 1994a). In this country, a 10% per year increase in manganese emission rates from MMT in gasoline since 1981 has been estimated (Loranger and Zayed 1994). A positive relationship between atmospheric manganese concentration and traffic density has been reported (Loranger and Zayed 1997a; Loranger et al 1994a). The principal emission product of MMT combustion is a fine particulate matter (0.1–0.4  $\mu\text{m}$  diameter) consisting of manganese oxide (Egyed and Wood 1996; Ter Haar et al. 1975), manganese phosphate, and some manganese sulfate (Lynam et al. 1999). The finding of soluble manganese ( $<0.4 \mu\text{m}$ ) in snow samples obtained close to a highway in Montreal, Canada suggested a possible contamination from mobile sources (Loranger and Zayed 1997; Loranger et al. 1995). However, it has been difficult to assess the exact contribution of mobile sources to overall contamination from natural and industrial sources because of the physico-chemical characteristics of manganese particulate, environmental factors affecting its dispersion, and the difficulties in distinguishing between mobile sources of manganese and background manganese levels (Loranger and Zayed 1997a; Veysseyre et al. 1998).

Based on dispersion modeling estimates using theoretical emission rates, actual traffic volume, and meteorological conditions near a major highway in Canada, the contribution of mobile sources of manganese to atmospheric background manganese was predicted to be approximately 50% at a distance of 25 m (manganese concentration of  $0.026 \mu\text{g}/\text{m}^3$ ) and less than 8% at a distance of 250 m (manganese concentration of  $0.003 \mu\text{g}/\text{m}^3$ ) from the major highway (Loranger et al. 1995b; Loranger and Zayed 1997a). The total uncertainty in the model predictions was estimated to be 50% (Loranger et al. 1995b).

Despite the estimated 10% per year increase in manganese emission rates from the use of MMT in gasoline in Canada, atmospheric manganese concentrations in Montreal have remained fairly constant between 1981 and 1990, and have decreased markedly in 1991 and 1992 (Loranger and Zayed 1994). The decline in manganese concentration after 1990 may have been due to a shutdown in 1991 of a ferromanganese plant located near Montreal. Air concentrations are in general below the U.S.EPA reference concentration (RfC) of  $0.05 \mu\text{g}/\text{m}^3$  for respirable manganese. However, in 1998, it was observed that some atmospheric concentrations in specific microenvironments with important traffic density were higher than the RfC (Zayed et al. 1999).

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*Maneb or mancozeb.* According to TRI, in 1997, the estimated releases of 11,641 pounds (5,291 kg) of maneb to air from 1 repackaging facility accounted for about 27% of total environmental release (TRI97 1999). Table 5-2 lists amounts of maneb released from these facilities.

## 5.2.2 Water

### Inorganic Manganese

According to the Toxics Release Inventory, in 1996, the estimated releases of manganese of 1,917,483 pounds (871,583 kg) to water from 1,978 large processing facilities accounted for about 3% of total environmental releases (TRI96 1998). Table 5-1 lists amounts released from these facilities. The TRI data should be used with caution, however, since only certain types of facilities are required to report. This is not an exhaustive list. Also, because these data reflect past releases, they may not be representative of current releases at these facilities.

Manganese has been identified in surface water and groundwater samples collected at 270 and 486, respectively, of the 603 NPL hazardous waste sites where it was detected in some environmental media (HazDat 1998).

Manganese may be released to water by discharge from industrial facilities or as leachate from landfills and soil (EPA 1979b, 1984a; Francis and White 1987; TRI91 1993). Reported industrial discharges to surface waters, transfers to public sewage, and underground injection (releases to groundwater) for 1996 totaled 1.9 million, 0.4 million, and 0.02 million pounds, respectively (TRI96 1998). In 1991, reported industrial discharges were much less and ranged from 0 to 380 thousand pounds/year for surface water, 0 to 126 thousand pounds/year for transfers to public sewage, and 0 to 250 pounds/year for underground injection per state (TRI91 1993).

Based on comparison to typical background levels of manganese in surface water or groundwater (see Section 5.4.2), it seems likely that some waste sites where manganese is detected contain only natural levels. Although ambient manganese levels are about 200 µg/L in a number of cases, high levels (in excess of 1,000 µg/L) have been detected indicating that manganese wastes may lead to significant contamination of water at some sites. For example, at one site in Ohio where "heavy metals" had been disposed, manganese concentrations up to 1,900 µg/L were found in on-site wells (Cooper and Istok

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1988). Levels in water at two NPL sites in Missouri ranged from 0.009 to 3.7 µg/L (MDNR 1990). No information is available on the method used to determine these values, so it is not clear whether the data refer to total or dissolved manganese.

### Organic Manganese

*Maneb or mancozeb.* According to TRI, in 1997, there was an estimated release of 0 pounds of maneb to water from facilities that manufacture or process maneb (TRI97 1999). In recent investigations of MMT occurrence in rain water and storm runoff collected along highways, MMT was found in most of the samples (Yang and Chau 1999). It is not understood why a readily photodegraded compound still exists in rain and water.

### **5.2.3 Soil**

#### Inorganic Manganese

According to the Toxics Release Inventory, in 1996, the estimated releases of manganese of 47,528,469 pounds (21,603,850 kg) to soil from 1,978 large processing facilities accounted for about 81% of total environmental releases (TRI96 1998). Table 5-1 lists amounts released from these facilities. The TRI data should be used with caution, however, since only certain types of facilities are required to report. This is not an exhaustive list. Also, because these data reflect past releases, they may not be representative of current releases at these facilities.

Manganese has been identified in soil, sediment, and leachate samples collected at 237, 172, and 82, respectively, of the 603 NPL hazardous waste sites where it was detected in some environmental media (HazDat 1998).

Land disposal of manganese-containing wastes is the principal source of manganese releases to soil. Reported industrial releases to land in 1987 totaled 44 million pounds (TRI87 1989). In 1996, reported industrial releases to land ranged from 0 to 13.8 million pounds/year per state (TRI96 1998). An estimated 81% (47,500,000 pounds) of the total environmental release (58,400,000 pounds) of manganese was to land (TRI96 1998). No other data were located on releases of manganese to soils or sediments.

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Organic Manganese

*Maneb or mancozeb.* According to TRI, in 1997, the estimated releases of 11,641 pounds (5,291 kg) of maneb to land from 1 repackaging facility accounted for about 27% of total environmental release (TRI97 1999).

**5.3 ENVIRONMENTAL FATE****5.3.1 Transport and Partitioning**

Elemental manganese and inorganic manganese compounds have negligible vapor pressures (see Table 3-2) but may exist in air as suspended particulate matter derived from industrial emissions or the erosion of soils. Manganese-containing particles are mainly removed from the atmosphere by gravitational settling, with large particles tending to fall out faster than small particles (EPA 1984a). The half-life of airborne particles is usually on the order of days, depending on the size of the particle and atmospheric conditions (Nriagu 1979). Some removal by washout mechanisms such as rain may also occur, although it is of minor significance in comparison to dry deposition (EPA 1984a; Turner et al. 1985).

In a study completed by Evans (1989), there were two mechanisms involved in explaining the retention of manganese and other metals in the environment by soil. First, through cation exchange reactions, manganese ions and the charged surface of soil particles form manganese oxides, hydroxides, and oxyhydroxides which in turn form absorption sites for other metals. Secondly, manganese can be adsorbed to other oxides, hydroxides, and oxyhydroxides through ligand exchange reactions. When the soil solution becomes saturated, these manganese oxides, hydroxides, and oxyhydroxides can precipitate into a new mineral phase and act as a new surface to which other substances can absorb (Evans 1989).

The behavior of heavy metals in the combustion gases of urban waste incinerators was studied by Fernandez et al. (1992). Manganese was detected inside gaseous fly ash particles in the form of oxides and chlorides. When these soluble oxides and chlorides reach environmental media they can leach out and become mobile (Fernandez et al. 1992).

The transport of manganese in air is largely determined by its particle size. About 80% of the manganese in suspended particulate matter is associated with particles having a mass median equivalent of <5  $\mu\text{m}$

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(WHO 1981). The compound's small particle size (approximately 80% with a mass median equivalent diameter (MMAD)  $<5\ \mu\text{m}$  and approximately 50% with an MMAD  $<2\ \mu\text{m}$ ) favors widespread airborne distribution and is within the respirable range (WHO 1981).

The transport and partitioning of manganese in water is controlled by the solubility of the specific chemical form present, which in turn is determined by pH, Eh (oxidation-reduction potential), and the characteristics of the available anions. The metal may exist in water in any of four oxidation states. Manganese(II) predominates in most waters (pH 4–7) but may become oxidized at a pH  $>8$  or 9 (EPA 1984a). The principal anion associated with Mn(II) in water is usually carbonate ( $\text{CO}_3^{-2}$ ), and the concentration of manganese is limited by the relatively low solubility (65 mg/L) of  $\text{MnCO}_3$  (Schaanning et al. 1988). In relatively oxidized water, the solubility of Mn(II) may be controlled by manganese oxide equilibria (Ponnampetuma et al. 1969), with manganese being converted to the Mn(II) or Mn(IV) oxidation states (Rai et al. 1986). In extremely reduced water, the fate of manganese tends to be controlled by formation of a poorly soluble sulfide (EPA 1984a).

Manganese is often transported in rivers as suspended sediments. It has been reported that most of the manganese in a South American river came from industrial sources and was bound to suspended particles in the water (Malm et al. 1988).

In an aquifer studied in France, manganese was shown to originate from within the aquifer itself (Jaudon et al. 1989). In the presence of decreased dissolved oxygen in the groundwater, Mn(IV) has been shown to be reduced both chemically and bacterially into the Mn(II) form (Jaudon et al. 1989). This oxidation state is water soluble and easily released into the groundwater.

Manganese in water may be significantly bioconcentrated at lower trophic levels. A bioconcentration factor (BCF) relates the concentration of a chemical in plant and animal tissues to the concentration of the chemical in the water in which they live. Folsom et al. (1963) estimated that the BCF of manganese was 2,500–6,300 for phytoplankton, 300–5,500 for marine algae, 800–830 for intertidal mussels, and 35–930 for coastal fish. Similarly, Thompson et al. (1972) estimated that the BCF of manganese was 10,000–20,000 for marine and freshwater plants, 10,000–40,000 for invertebrates, and 100–600 for fish. In general, these data indicate that lower organisms such as algae have larger BCFs than higher organisms. In order to protect consumers from the risk of manganese bioaccumulation in marine mollusks, EPA has set a criterion for manganese at 0.1 mg/L for marine waters (EPA 1993).

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The tendency of soluble manganese compounds to adsorb to soils and sediments depends mainly on the cation exchange capacity and the organic composition of the soil (Curtin et al. 1980; Hemstock and Low 1953; Kabata-Pendias and Pendias 1984; McBride 1979; Schnitzer 1969). Baes and Sharp (1983) noted that soil adsorption constants (the ratio of the concentration in soil to the concentration in water) for Mn(II) span five orders of magnitude, ranging from 0.2 to 10,000 mL/g, increasing as a function of the organic content and the ion exchange capacity of the soil; thus, adsorption may be highly variable. In some cases, adsorption of manganese to soils may not be a readily reversible process. At low concentrations, manganese may be "fixed" by clays and will not be released into solution readily (Reddy and Perkins 1976). At higher concentrations, manganese may be desorbed by ion exchange mechanisms with other ions in solution (Rai et al. 1986). For example, the discharge of waste water effluent into estuarine environments resulted in the mobilization of manganese from the bottom sediments (Helz et al. 1975; Paulson et al. 1984). The metals in the effluent may have been preferentially adsorbed resulting in the release of manganese.

#### Organic Manganese

*MMT.* MMT is generally unstable in light and is expected to degrade quickly in air. Although recent information indicates that MMT levels in the environment can increase from automobile emissions (Zayed et al. 1999), no information on the transport and partitioning of MMT in the environment was located. Transport and partitioning of inorganic manganese compounds derived from the combustion of gasoline containing MMT are discussed above.

*Maneb or Mancozeb.* Few data on the transport and partitioning of these maneb and mancozeb were located. Calumpang et al. (1993) reported a half-life of 2.9 days for mancozeb determined in a silty clay loam soil placed in experimental columns and maintained under field conditions. In other studies, the half-life for maneb in soil was estimated to be 3 weeks and 4-8 weeks (Nash and Beall 1980; Rhodes 1977). Using chemical and physical properties, Beach et al. (1995) estimated that the half-life in soils for maneb and mancozeb to 70 days. The high  $K_{oc}$  value estimated for these compounds (>2000) suggested to these authors that the potential for leaching into ground water would be low. However, the potential for solubility in surface water was considered to be moderate, despite the relatively low solubility of maneb and reportedly insolubility of mancozeb.

### **5.3.2 Transformation and Degradation**

#### **5.3.2.1 Air**

#### Inorganic Manganese

Very little information is available on atmospheric reactions of manganese (EPA 1984a). Manganese can react with sulfur dioxide and nitrogen dioxide, but the occurrence of such reactions in the atmosphere has not been demonstrated.

## 5. POTENTIAL FOR HUMAN EXPOSURE

Organic Manganese

*MMT*. MMT photolyses rapidly by sunlight in the atmosphere with a very short half-life, i.e., less than 2 minutes (Ter Haar et al. 1975; Garrison et al. 1995). MMT is converted to a mixture of solid manganese oxides and carbonates. The organic portion of the solid consists of a complex mixture of acids, esters, and hydrocarbon polymers that results from the partial oxidation of the cyclopentadienyl ring, carbon monoxide insertion reactions and polymerization of multifunctional compounds (Ter Haar et al. 1975).

*Maneb or mancozeb*. Maneb, once released to the atmosphere, will exist primarily in the particulate-phase in the ambient atmosphere, where it can be removed by wet and dry deposition (Eisenreich et al. 1981; HSDB 1999). Maneb may undergo some photodegradation in sunlit air (Freitag et al. 1985; HSDB 1999). Mancozeb will also exist as particulate matter in the atmosphere (HSDB 1999).

**5.3.2.2 Water**Inorganic Manganese

Manganese in water may undergo oxidation at high pH or Eh (see Section 5.3.1.2) and is also subject to microbial activity. For example, Mn(II) in a lake was oxidized during the summer months, but this was inhibited by a microbial poison, indicating that the oxidation was mediated by bacteria (Johnston and Kipphut 1988). The microbial metabolism of manganese is presumed to be a function of pH, temperature, and other factors, but no data were located on this.

Organic Manganese

*MMT*. The rate of MMT degradation in natural aquifer and sediment systems was determined to be very slow under anaerobic conditions (Garrison et al. 1995). Calculated half-lives ranged from approximately 0.2 to 1.5 years at 25°C. However, MMT photolyzed rapidly in purified, distilled water exposed to sunlight. The disappearance of MMT followed first-order kinetics, with a calculated half-life of



## 5. POTENTIAL FOR HUMAN EXPOSURE

0.93 min. Reaction products included methylcyclopentadiene, cyclopentadiene, carbon monoxide, and a manganese carbonyl that readily oxidized to trimanganese tetroxide.

*Maneb or mancozeb.* Maneb released to water may be subject to abiotic degradation to ethylene thiuram disulfide, ethylene thiourea (ETU), ethylenediamine (EDA), and ethylene thiuram monosulfide (ETM) (Hylin 1973; HSDB 1999). The rate of degradation is influenced by the aeration of water and pH. In addition, maneb may undergo some photodegradation in sunlit water (Freitag et al. 1985; HSDB 1999). Maneb is not expected to undergo significant volatilization from water. Mancozeb hydrolyzes, with a half-life less than 1–2 days at pH 5–9, in water rapidly (HSDB 1999).

### 5.3.2.3 Sediment and Soil

#### Inorganic Manganese

The oxidation state of manganese in soils and sediments may be altered by microbial activity. Geering et al. (1969) observed that Mn(II) in suspensions of silt or clay loams from several areas of the United States was oxidized by microorganisms, leading to the precipitation of manganese minerals. Other studies (Francis 1985) have shown that bacteria and microflora can increase the mobility of manganese in coal-waste solids by increasing dissolution of manganese in subsurface environments.

#### Organic Manganese

*MMT.* The hydrophobicity of MMT ( $\log K_{ow} = 3.7$ ) suggests that it can sorb to soil or sediment particles (Garrison et al. 1995). MMT was found to be stable in a stream bottom sediment under anaerobic conditions. Photodegradation of MMT is not likely to occur in sediments, and it may equilibrate between the sediment, sediment porewater, and water column manganese (Garrison et al. 1995).

*Maneb or mancozeb.* In a laboratory experiment, maneb was shown to degrade readily (within 2 days) to ETU in soil (Nash and Beall 1980). A half-life of maneb in soil was determined to be 36 days. Maneb was found not to move below 1 cm depth of soil. However, soluble  $^{14}\text{C}$ -degradation products ( $<40 \mu\text{g/L}$ ) of maneb (not measurable as EDA or ETU) did move through the soil with leachate water. The mobility of maneb in soil is influenced by the level of organic matter in the soil, such that mobility decreases with

## 5. POTENTIAL FOR HUMAN EXPOSURE

increasing organic matter (Helling et al. 1974). A half-life of maneb in soil was reported to be 4–8 weeks in fine sand with 2.4% organic matter content (Rhodes 1977). <sup>14</sup>C-residues did not leach much below a 5-inch soil depth.

Mancozeb degrades rapidly in soil (Calumpang et al. 1993). Under field conditions, the half-lives of mancozeb, ethylenethiourea (ETU), and ethyleneurea (EU) in soil were 2.9, 2.5, and 4.8 days, respectively. Mancozeb is immobile in soil. Ethylene leached to a maximum of 8 cm of soil 14 days after application of mancozeb.

#### 5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to manganese depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. In reviewing data on manganese levels monitored or estimated in the environment, it should also be noted that the amount of chemical identified analytically is not necessarily equivalent to the amount that is bioavailable.

##### 5.4.1 Air

###### Inorganic Manganese

Table 5-3 summarizes data collected over a period of nearly 30 years from numerous urban, nonurban, and source-dominated areas of the United States. Direct comparisons of data from different time periods are complicated because of changes in sample collection and analytical methodology. However, it is clear that manganese levels tend to be higher in source-dominated and urban areas than in nonurban areas. These data also indicate that concentrations in all areas have tended to decrease over the past three decades (EPA 1984a; Kleinman et al. 1980). This is probably due primarily to the installation of emission controls in the metals industry (EPA 1984a, 1985d). A concurrent decrease in total suspended particulates (TSP) was observed in most areas. Annual averages of manganese in urban and rural areas without significant manganese pollution are in the range of 0.01–0.07  $\mu\text{g}/\text{m}^3$  (WHO 1997). The daily intake of manganese in the air by the general population in areas without manganese emitting industries was estimated to be below 2  $\mu\text{g}/\text{day}$  (WHO 1981). In areas with major foundry facilities, intake may rise to 4–6  $\mu\text{g}/\text{day}$ , and in areas associated with ferro- or silicomanganese industries, it may be as high as 10  $\mu\text{g}$ , with 24-hour peak values exceeding 200  $\mu\text{g}/\text{day}$  (WHO 1981).

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**Table 5-3. Average Levels of Manganese in Ambient Air<sup>a</sup>**

Sampling location	Concentration (ng/m <sup>3</sup> )		
	1953–1957	1965–1967	1982
Nonurban	60	12	5
Urban	110	73	33
Source dominated	No data	250–8,300	130–140

<sup>a</sup>Adapted from EPA 1984a

## 5. POTENTIAL FOR HUMAN EXPOSURE

During 1988–1993, ambient concentration of fine ( $PM_{2.5}$ ) manganese ranged from  $1 \text{ ng/m}^3$  in rural sites in U.S. National Parks to  $3 \text{ ng/m}^3$  in urban sites in California (Wallace and Slonecker 1997). There is concern in Canada regarding the combustion of MMT as an important source of manganese contamination in the urban environment, especially in areas of high traffic density. For instance, Loranger and Zayed (1997a) reported significantly higher levels of both respirable and total manganese levels at a high traffic density site ( $0.024 \text{ }\mu\text{g/m}^3$  and  $0.050 \text{ }\mu\text{g/m}^3$ , respectively) in Montreal in contrast to a low traffic density site ( $0.015 \text{ }\mu\text{g/m}^3$  and  $0.027 \text{ }\mu\text{g/m}^3$ , respectively). Temporal variation of respirable and total manganese was similar for both sites, and atmospheric manganese concentrations reflected a positive relationship with the traffic density. However, as discussed in Section 5.2.1, it has been difficult to assess the exact contribution of the combustion of MMT by vehicles to manganese levels in the environment.

### Organic Manganese

*MMT.* In Montreal, Canada, atmospheric concentrations of MMT, and respirable and total manganese, were measured in 5 microenvironments including a gas station, an underground car park, downtown Montreal, near an expressway, and near an oil refinery (Zayed et al. 1999). The overall mean concentrations of respirable manganese, total manganese, and MMT measured for all the microenvironments were  $0.036 \text{ }\mu\text{g/m}^3$ ,  $0.103 \text{ }\mu\text{g/m}^3$ , and  $0.005 \text{ }\mu\text{g/m}^3$ , respectively. It was noted by the authors that respirable manganese ( $0.053 \text{ }\mu\text{g/m}^3$ ) measured near the expressway was equal to the U.S. EPA Reference Concentration (RfC) of  $0.05 \text{ }\mu\text{g/m}^3$ . Moreover, by comparing the RfC to the 95th percentile of atmospheric manganese in Montreal, it appears that possibly 5% of a “theoretical population” generated by Monte-Carlo simulations would be exposed to a higher concentration and could be at risk (Loranger and Zayed 1997b).

*Maneb or mancozeb.* Ambient levels of maneb (calculated from manganese) were  $<0.02$ ,  $0.03$ , and  $0.77 \text{ mg/m}^3$  in a tractor cabin, breathing zone, and during weighing of the pesticide, respectively (Savolainen et al. 1989).

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**5.4.2 Water**Inorganic Manganese

Many factors, both environmental (e.g., the presence of high or low levels of other inorganics in drinking water) and biological or host-related (e.g., age, nutritional status, and alcohol consumption) can significantly influence the uptake of manganese by an individual (EPA 1993b). The determination of a single concentration of manganese in drinking water, then, must be recognized as a process that is limited in its ability to reflect the variable nature of manganese toxicity (EPA 1993b).

Concentrations of manganese in surface water are usually reported as dissolved manganese. Although total manganese may be a better indicator, since manganese adsorbed to suspended solids may exceed dissolved manganese in many systems, the bioavailability of manganese in this form has not been established (EPA 1984a; NAS 1977). In a 1962–1967 survey of U.S. surface waters, dissolved manganese was detected in 51% of 1,577 samples, at a mean concentration of 59 µg/L. Individual values ranged from 0.3 to 3,230 µg/L. Mean concentrations for 15 different drainage basins in the United States ranged from 2.3 µg/L in the western Great Lakes to 232 µg/L in the Ohio River drainage basin (Kopp and Kroner 1967). A later (1974–1981) survey of United States river waters reported a median dissolved manganese concentration of 24 µg/L in samples from 286 locations, with values ranging from <11 µg/L (25th percentile) to >51 µg/L (75th percentile) (Smith et al. 1987). Natural concentrations of manganese in seawater reportedly range from 0.4 to 10 µg/L (EPA 1984a).

Mean manganese concentrations in groundwater are similar to those in surface water, although some individual samples may be considerably higher. Reported mean groundwater concentrations were 20 and 90 µg/L in an analysis of California shallow groundwater from two geologic zones (Deverel and Millard 1988). Values up to 1,300 µg/L and 9,600 µg/L have been reported in neutral and acidic groundwater, respectively (EPA 1984a). Concentrations of 9,500–18,600 µg/L have been reported in four private wells in Connecticut (CDHS 1990). It is not known whether these measurements were total or dissolved manganese.

A 1962 survey of public drinking water supplies in 100 large United States cities reported 97% contained <100 µg/L of manganese (Durfor and Becker 1964). Similarly, a 1969 survey of 969 systems reported 91% contained <50 µg/L, with a mean concentration of 22 µg/L (U.S. DHEW 1970). Several other

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studies reported similar manganese concentrations, with mean values ranging from 4 to 32 µg/L (EPA 1984a; NAS 1980a; WHO 1981).

### Organic Manganese

*MMT*. No studies were located reporting surface or ground water concentrations of MMT.

*Maneb or mancozeb*. No studies were located regarding environmental concentrations of maneb or mancozeb in groundwater, surface water, or public water supplies. Beach et al. (1995) estimated the likelihood of ground water and surface water contamination of maneb and mancozeb in different agricultural environments and for different crops. They reported that maneb and mancozeb are not susceptible to leaching, but would be highly susceptible to sediment runoff in Arizona (lettuce production), soil adsorbed runoff in Florida (tomato production) and Michigan (asparagus production). In addition, mancozeb would be highly susceptible to soil-adsorbed runoff in Texas (watermelon production). No studies to date have investigated potential increases in manganese concentrations of surface or ground water bodies as a result of maneb or mancozeb use.

### **5.4.3 Sediment and Soil**

#### Inorganic Manganese

Manganese comprises about 0.1% of the earth's crust (Graedel 1978; NAS 1973), and manganese occurs naturally in virtually all soils. Average natural ("background") levels of manganese in soils range from around 40 to 900 mg/kg, with an estimated mean background concentration of 330 mg/kg (Cooper 1984; Eckel and Langley 1988; EPA 1985c; Rope et al. 1988; Schroeder et al. 1987). The maximum value reported was 7,000 mg/kg (Eckel and Langley 1988).

Accumulation of manganese in soil usually occurs in the subsoil and not on the soil surface; 60–90% of manganese is found in the sand fraction of the soil (WHO 1981). A preliminary survey was conducted in Utah to provide an initial field measurement of the contamination by manganese oxides from exhaust in roadside soil and plant species due to the addition of MMT to motor vehicle fuels. Soil (0–5 cm) manganese concentrations were strongly correlated with distance from roadways with moderate and moderately high traffic volumes (Lytle et al. 1994). In addition, exchangeable manganese was found to

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be significantly higher in an organic soil located at stations with a high traffic density comparing to another one with a low traffic density (Brault et al. 1994). The average soil manganese concentration measured at 1 meter from a moderate to moderately-high traffic volume roadside was 3,046  $\mu\text{g/g}$  dry weight. At 15m, the average soil manganese concentration decreased to 254  $\mu\text{g/g}$  dry weight.

#### Organic Manganese

*MMT*. No studies were located which measured the concentration of MMT in sediment or soil; all studies have focused on increased concentrations of manganese in these media as a result of combustion of the fuel additive.

*Maneb or mancozeb*. No studies were located that measured the concentration of these compounds after application of the compounds in the field on existing crops. All studies to date have involved localized application or laboratory measurements intended to report half-lives of the compounds in particular environments (Helling et al. 1974; Nash and Beall 1980; Rhodes 1977). None of the studies has reported increased manganese concentrations in either soil or sediment as a result of application of these fungicides.

#### **5.4.4 Other Environmental Media**

##### Inorganic Manganese

Manganese is a natural component of most foods. A summary of mean manganese concentrations in 234 foods analyzed by the FDA is included in Table 5-4. The highest concentrations (up to 50 ppm) are found in nuts, tea, legumes, pineapples, and whole grains, with lower levels (up to 5 ppm) found in milk products, meats, fish, and eggs (Davis et al. 1992a; Pennington et al. 1986). Tea and leafy green vegetables were the major dietary sources of manganese for young women taking part in a dietary study in Wisconsin (Davis et al. 1992a). Bioaccumulation of manganese by plants was examined using oats (*Avena nova*) and beans (*Phaseolus vulgaris*) (Brault et al. 1994). These plants were grown in sandy and organic soil at a control site (greenhouse) and at two outdoor sites weakly near <20,000 vehicles/day, and 132,000 vehicles/day respectively. The highest manganese accumulation was found in the fruits and stems of oats grown in the organic and sandy soils at the station with the highest traffic density. Lönnerdal (1997) reported that infant formulas currently contain 30–75 ppb (0.03–0.075 ppm) manganese, as

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**Table 5-4. Manganese Concentrations in Selected Foods<sup>a</sup>**

Type of food	Range of mean concentrations (ppm)
Nuts and nut products	18.21–46.83
Grains and grain products	0.42–40.70
Legumes	2.24–6.73
Fruits	0.20–10.38
Fruit juices and drinks	0.05–11.47
Vegetables and vegetable products	0.42–6.64
Desserts	0.04–7.98
Infant foods	0.17–4.83
Infant formulae (soy) and enteral products	0.31–2.87
Infant formulae (cow-milk based)	0.03–0.075
Meat, poultry, fish, and eggs	0.10–3.99
Mixed dishes	0.69–2.98
Condiments, fats, and sweeteners	0.04–1.45
Beverages (including tea)	0.00–2.09
Soups	0.19–0.65
Milk and milk products	0.02–0.49

<sup>a</sup>Adapted from Cook 1997, Lönnerdal 1997, Pennington et al. 1986



## 5. POTENTIAL FOR HUMAN EXPOSURE

compared to concentrations of 3–10 ppb (0.003–0.01 ppm) in breast milk and 30 ppb (0.03 ppm) in cow's milk.

During a 1992 survey conducted by Canada's Department of Fisheries and Oceans, concentrations of manganese were detected in the muscle samples of bluefin tuna (*Thunnus thynnus*) (Hellou et al. 1992). Concentrations of manganese in 14 samples of fish muscle ranged from 0.16 to 0.31 µg manganese/g dry weight, with a mean of 0.22 µg/g. Although the analysis was administered with a high accuracy of 94% using inductively coupled plasma mass spectrometry (ICP-MS), the sample population was small.

In the field survey conducted by Lytle et al. (1994), terrestrial and aquatic plant samples were collected along motorways and local urban roadways throughout Utah during 1992 and 1993. Manganese was detected in the plant samples, with manganese concentrations ranging from 30.2 to 13,680 µg/g dry weight. Manganese was detected in plants found nearest to the motorway. Loranger et al. (1994b) evaluated the use of the pigeon as a monitor for manganese contamination from motor vehicles in urban and rural areas of Canada, a country in which MMT has been used to replace lead in gasoline. Manganese concentrations were similar in the 2 groups of pigeons for all tissues except the liver and feces; urban pigeons had about 35% more manganese than rural ones. Loranger et al. (1994b) suggested that although pigeon feces and liver may be good biomarkers of manganese contamination, it is premature to associate the excess manganese with the combustion of MMT.

#### Organic Manganese

*MMT.* No studies were located concerning concentrations of MMT on food stuffs.

*Maneb or mancozeb.* Maneb and mancozeb residues in various food and crop samples have been evaluated. According to the FOODCAM database, a national database of information generated by state agencies involved in the regulation of agricultural, public health, and the environment, maneb residues were detected (concentrations not reported) in only 2 of 13,085 food samples analyzed during 1989 (Minyard and Roberts 1991). No maneb residues were found in 39 fruit and vegetable samples in California during 1989 (Okumara et al. 1991). Residues of maneb (<0.1–4.0 ppm) and ETU (<0.05 ppm) were detected in various crop samples obtained from an area where maneb was used as a fungicide (Pease and Holt 1977).

## 5. POTENTIAL FOR HUMAN EXPOSURE

Mancozeb residues were not detected in treated crop samples (apples, dried onion, and grapes) that were analyzed as a part of the comprehensive California Priority Pesticide Program for 1989 (Okumura et al. 1991). Other samples of grapes had residues that were within tolerance limits for mancozeb. Tomato fruits sprayed with mancozeb up to four times in 45 days had residue levels below detection limits except for green fruits harvested 30 days after the first spray and green or ripe fruits harvested 30-45 days after the fourth spray (residue levels ranged from 0.96 mg/kg to 3.27 mg/kg) (Patil et al. 1995). Residue levels decreased to below detection limits in green or ripe tomatoes when the fruit were harvested 10 days after spraying or later. These data indicate that mancozeb residue levels on tomatoes are dependent on the number of mancozeb applications and time of harvest. Following an accidental aerial spray of a grain field, residues of mancozeb (expressed as maneb) and ETU were detected in barley, oats, and wheat (Rosenberg and Siltanen 1979). The highest concentrations of residues were detected 1 meter from a potato field, the intended target area for aerial spraying. At this distance, samples of barley, oats, and wheat contained 21, 5.5, and 15 ppm maneb, and 0.08, 0.01, and 0.09 ppm ETU, respectively.

**5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE**

The EPA has reported that 7,550 cases of manganism have been recorded in the literature since the first report in 1937 (EPA 1993b). Typical daily human exposure levels to manganese from water, air, and food are summarized in Table 5-4 (EPA 1984a). As the table illustrates, the most significant exposure for the general population is from food, with an average ingestion rate of 3,800 µg/day (EPA 1984a). Other estimates of daily intake for adults range from 2,000 to 8,800 µg (EPA 1984a; NAS 1977; Patterson et al. 1984; Pennington et al. 1986; WHO 1984a). Even though gastrointestinal absorption of manganese is low (3–5%), oral exposure is the primary source of absorbed manganese (Table 5-5).

Manganese intake among individuals varies greatly, depending upon dietary habits. For example, an average cup of tea may contain 0.4–1.3 mg of manganese (Pennington et al. 1986; Schroeder et al. 1966). Thus, an individual consuming three cups of tea per day might receive up to 4 mg/day from this source alone, increasing the average intake from all dietary sources.

The EPA Reference Dose (RfD)/Reference Concentration (RfC) workgroup in June 1990 set an RfD for manganese in food of 0.14 mg manganese/kg/day, equivalent to 10 mg/day for a 70-kg man based on chronic manganese uptake (EPA 1993b). The Food and Nutrition Board of the NRC estimated the adequate and safe intake of manganese for adults at 2–5 mg/day (NAS 1980b). This level was chosen

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**Table 5-5. Summary of Typical Human Exposure to Manganese<sup>a</sup>**

Parameter	Exposure medium		
	Water	Air	Food
Typical concentration in medium	4 µg/L	0.023 µg/m <sup>3</sup>	1.28 µg/calorie
Assumed daily intake of medium by 70-kg adult	2 L	20 m <sup>3</sup>	3,000 calories
Estimated average daily intake by 70-kg adult	8 µg	0.46 µg <sup>b</sup>	3,800 µg
Assumed absorption fraction	0.03 <sup>c</sup>	1 <sup>c</sup>	0.03 <sup>d</sup>
Approximate absorbed dose	0.24 µg	0.46 µg	114 µg

<sup>a</sup>Adapted from EPA 1984a

<sup>b</sup>Assumes 100% deposition in the lungs

<sup>c</sup>No data; assumed value

<sup>d</sup>See Section 2.3.1.2

## 5. POTENTIAL FOR HUMAN EXPOSURE

because it includes an "extra margin of safety" of 5 mg/day below the level of 10 mg/day, which the NRC considered to be safe for occasional intake (IRIS 1993). It is possible that a significant proportion of Americans, especially females, are not consuming sufficient manganese (Davis and Greger 1992; NAS 1980a; Pennington et al. 1986). However, infants may be ingesting more than the estimated safe and adequate dose of 0.3–1.0 mg/day for their age group (Pennington et al. 1986) because of the relatively high manganese levels in prepared infant foods (Table 5-3) and formulas (Lönnerdal 1997).

In the workplace, exposure to manganese is most likely to occur by inhalation of manganese fumes or manganese-containing dusts. This is a concern mainly in the ferromanganese, iron and steel, dry-cell battery, and welding industries (WHO 1986). Exposure may also occur during manganese mining and ore processing. Ordinarily, manganese is mined in an open pit or shallow underground mine; however, manganese carbonate used to be mined from deep mines in Butte, Montana (HSDB 1993). The most recent data indicate that only a very small amount of manganese is still mined in the United States; in 1997, manganiferous material having a natural manganese content between 5 and 15% for use in coloring brick was mined in Cherokee County, South Carolina (USGS 1998). Excluding insignificant quantities of similar low-grade manganiferous ore, the United States has not mined significant amounts of manganese since 1978 and now relies on imports to fill its needs (U.S. Bureau of Mines 1989). Therefore, mining is no longer a source of manganese exposure for many workers in the United States. In 1980, it was estimated that in the United States about 300 workers were exposed to pure manganese and about 630,000 workers were exposed to other forms of manganese (NOES 1989). Concentrations of 1.5–450 mg manganese/m<sup>3</sup> have been reported in U.S. manganese mines (EPA 1984a), 0.30–20 mg manganese/m<sup>3</sup> in ferroalloy production facilities (Saric et al. 1977), and 3–18 mg manganese/m<sup>3</sup> in a dry-cell battery facility (Emara et al. 1971). Steel-manufacturing facilities are significant employers in the U.S. There is a potential for manganese exposure to workers in these facilities. Current occupational exposures in a metal-producing plant in the United States were reported as a mean of 0.066 mg/m<sup>3</sup>, median of 0.051 mg/m<sup>3</sup> as respirable dust, and 0.18 mg/m<sup>3</sup> in total dust (Gibbs et al. 1999). Exposure levels should not exceed the OSHA time-weighted average Permissible Exposure Limit (PEL) of 1 mg total manganese/m<sup>3</sup> (see Table 7-1). Assuming inhalation of 10 m<sup>3</sup> of air during an average workday, maximum occupational exposure would be 10 mg manganese/day. This exceeds the average exposure from ambient air by a factor of more than 10<sup>4</sup> and is about 2.5 times the average exposure from the diet. Thus, for workers in industries using manganese, the major route of exposure may be inhalation from workplace air rather than from ingestion of food.

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Occupational exposure to manganese resulting from the combustion of MMT in Montreal, Canada has been studied. Sierra et al. (1995) conducted a study of Montreal automotive workers (garage mechanics) and nonautomotive workers (control group). Exposure to manganese was measured for 5 consecutive working days. In addition, their environmental exposure (at home) was measured on 2 days of the same week. Air sampling was performed by portable pumps; for sampling at homes, workers were asked to wear the pumps as much as possible. At the workplace, the mechanics were exposed to manganese concentrations ranging from 0.010–6.673  $\mu\text{g}/\text{m}^3$  (mean of 0.45  $\mu\text{g}/\text{m}^3$ ), while nonautomotive workers were exposed to concentrations manganese ranging from 0.011–1.862  $\mu\text{g}/\text{m}^3$  (mean of 0.04  $\mu\text{g}/\text{m}^3$ ). The average environmental concentrations for the mechanics (0.012  $\mu\text{g}/\text{m}^3$ ) and for the nonautomotive workers (0.008  $\mu\text{g}/\text{m}^3$ ) were similar to manganese concentrations measured in Montreal in 1992. Based on measurements of manganese particle size distributions, Sierra et al. (1995) estimated that less than 10% of the manganese exposure of the garage mechanics was due to MMT; however, the exact contribution of MMT could not be determined.

A similar study conducted in Montreal by these investigators, but involving taxi drivers and garage mechanics, revealed that garage mechanics at work were exposed to an average of 0.250  $\mu\text{g}/\text{m}^3$  and taxi drivers to 0.024  $\mu\text{g}/\text{m}^3$  (Zayed et al. 1994). In another study, exposure of office workers and taxi drivers to both respirable and total manganese was evaluated (Zayed et al. 1996). Manganese concentrations measured for the office workers ranged from 0.001–0.034  $\mu\text{g}/\text{m}^3$  (respirable manganese) and from 0.002–0.044  $\mu\text{g}/\text{m}^3$  (total manganese). For the taxi drivers, the manganese concentrations ranged from 0.007–0.032  $\mu\text{g}/\text{m}^3$  (respirable manganese) and from 0.008–0.073  $\mu\text{g}/\text{m}^3$  (total manganese). Zayed et al. (1996) concluded that the higher exposure to atmospheric manganese in the outdoor urban environment may be at least partly due to the use of MMT in cars. Nevertheless, these investigators indicated that the exposures of taxi drivers to manganese were well below existing exposure and health guidelines.

In order to assess the potential health risks from MMT combustion, Loranger and Zayed (1995) conducted a multi-media assessment (i.e., food, water, and ambient air) of manganese exposure in two groups of workers (garage mechanics and blue-collar workers) potentially exposed to different levels of manganese from MMT. Garage mechanics were exposed to higher air manganese concentrations (0.42  $\mu\text{g}/\text{m}^3$ ) than blue-collar workers (0.04  $\mu\text{g}/\text{m}^3$ ). However, for the garage workers, exposure to atmospheric manganese represented only approximately 4% of the total absorbed dose, while ingestion of food represented 95.7% of the total multi-media dose. For the blue collar workers, atmospheric

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manganese contributed only 0.3% to the total absorbed dose, whereas ingestion of food represented 99.2% of the total multi-media dose. These results were consistent with values of multi-media doses predicted by GADUS, an environmental fate/exposure model (Loranger and Zayed 1997b). Based on governmental standards or criteria for occupational and environmental exposures, Loranger and Zayed (1995) concluded that the manganese levels in food and air may not cause any problems for these workers.

Based on an analysis of data obtained from a large, continuous personal exposure study in Toronto, Canada, a city with widespread use of MMT, it was determined that the general population was exposed to low concentrations (median concentration was  $0.008 \mu\text{g}/\text{m}^3$ ) of airborne  $\text{PM}_{2.5}$  manganese (Lynam et al. 1999). Ambient levels of manganese in Toronto were approximately the same as cities where MMT is not used. Traffic densities were not taken into consideration. Also, high levels of airborne manganese were measured in the Toronto subway.

Occupational exposure to maneb and mancozeb can occur by the inhalation or dermal routes during the formulation and spray application of these pesticides (HSDB 1999). The general population is unlikely to be exposed to excess levels of pesticide residues on food, since crops analyzed for these compounds were found to have either non-detectable levels of the compounds or levels within allowable limits (Okumura et al. 1991) (see Section 5.4.4).

## 5.6 EXPOSURES OF CHILDREN

This section focuses on exposures from conception to maturity at 18 years in humans and briefly considers potential pre-conception exposure to germ cells. Differences from adults in susceptibility to hazardous substances are discussed in 2.6 Children's Susceptibility.

Children are not small adults. A child's exposure may differ from an adult's exposure in many ways. Children drink more fluids, eat more food, and breathe more air per kilogram of body weight, and have a larger skin surface in proportion to their body volume. A child's diet often differs from that of adults. The developing human's source of nutrition changes with age: from placental nourishment to breast milk or formula to the diet of older children who eat more of certain types of foods than adults. A child's behavior and lifestyle also influence exposure. Children crawl on the floor, they put things in their

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mouths, they may ingest inappropriate things such as dirt or paint chips, they spend more time outdoors. Children also are closer to the ground, and they do not have the judgement of adults in avoiding hazards (NRC 1993). Children and children in strollers may also have increased exposure to exhaust fumes due to their height above ground.

Children would be exposed to manganese in the same manner as adults. The main source of exposure of children to manganese is through food. Infants and young toddlers may be exposed to concentrations higher than the estimated safe and adequate dose for their age group because of the increased levels of the element in infant formulas as compared to breast milk (Collipp et al. 1983; Cook 1997; Dorner et al. 1989; Keen et al. 1986; Lönnerdal et al. 1983, 1994). Manganese concentrations in blood serum of children of different ages are provided in Table 2-7. The data indicate that manganese concentrations decrease slightly from the time the infant is 5 days of age until he or she is 12 months of age (Alarcón et al. 1996; Rukgauer et al. 1997). Manganese concentrations increase after this time, and they have been measured as an average of  $1.4 \pm 1.25$   $\mu\text{g/L}$  in children aged 1 month to 18 years (Rukgauer et al. 1997).

Children are exposed *in utero* because manganese in maternal blood crosses the placenta to satisfy the fetus's need for manganese. The compound has been measured in cord blood plasma of premature and full-term infants and their mothers (Wilson et al. 1991). Full-term babies have higher (but not statistically significantly different) blood concentrations of manganese than premature babies, and pregnant women have higher blood concentrations than nonpregnant women. However, no correlations were observed between maternal and infant concentrations of manganese. Manganese in breast milk has been found to range from 3.4 to 10  $\mu\text{g/L}$  (Arnaud and Favier 1995; Collipp et al. 1983) depending on the maturity of the milk. The Food and Nutrition Board of the NRC based the recommended manganese intake of infants on the analyses of pooled human milk samples. Accordingly, manganese intakes of infants fed some formulas appear high, but no signs of toxicity have been observed (Lönnerdal et al. 1983). It is unknown whether nursing mothers exposed to higher-than-average concentrations of manganese would excrete increased concentrations of the metal in their breast milk.

Young children often eat dirt (exhibiting what is called soil pica, the ingestion of a material unfit for food) and exhibit frequent hand-to-mouth activity; they can be exposed to manganese through this unique pathway if the soils contain the metal. Current estimates indicate that soil pica may be more prevalent in the general population than previously thought and that most children periodically ingest soil to varying degrees; this may be a potential health concern (EPA 1986d; Stanek and Calabrese 1995). However, no

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information was found concerning the bioavailability of manganese from soil and, therefore, determining the actual risk posed to children from this exposure pathway is difficult. This behavior should not pose an increased risk of exposure to manganese in most residential situations where the manganese levels are in the normal or background range. If the soils are from a hazardous waste site that contains high concentrations of manganese, then increased exposure to the compound may occur. However, until bioavailability of manganese from soil is determined, a child's ingestion of a given amount of soil containing manganese cannot be translated into actual levels of exposure.

Children who suffer from cholestatic liver disease or who have gastrointestinal disorders that mandate they be given parenteral nutrition may be at increased risk from overexposure to manganese. Increased manganese concentrations in blood and brain, and symptoms of neuromotor dysfunction were observed in an 8-year-old girl with cholestatic liver failure (Devenyi et al. 1994). Children with or without chronic liver disease and a 5-year-old boy who had gastrointestinal disorders, all of whom were administered parenteral nutrition, had abnormal MRI scans indicative of manganese accumulation (Fell et al. 1996; Ono et al. 1995) accompanied by motor disorders (Fell et al. 1994).

Because manganese is a trace element that is essential for normal human health and is predominantly obtained from food, it is unlikely that toxic amounts of manganese will be absorbed from food. However, diets vary and some are higher in manganese than others (diets high in grains and tea, for instance). One case study suggested that a 59-year-old man developed manganism-like symptoms from abusing vitamins and minerals. This man had very high manganese concentrations in blood, urine, feces, hair, and brain (Banta and Markesbery 1977). Both manganese and iron are bound by transferrin and these elements compete for the binding protein in the body. Therefore, diets that are low in iron allow transferrin to bind more manganese. For this reason, it is important to provide children with a balanced diet to maintain optimal iron and manganese stores in the body. Studies show that adults absorb only 3–5% of manganese ingested from the diet (Davidsson et al. 1988, 1989; Mena et al. 1969); infants have increased absorption relative to adults (Dorner et al. 1989). Neonatal animals also exhibit increased absorption relative to older animals (Ballatori et al. 1987; Miller et al. 1975; Rehnberg et al. 1981).

Children may be exposed to organic manganese compounds through a variety of routes. They may be exposed to MMT combustion products via inhalation of these products in air, or ingestion of them after deposition on the soil. Children may be exposed to maneb and mancozeb by eating fruits and vegetables that have residues of these pesticides on them



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**5.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES**

As discussed in Section 5.5, workers in industries using or producing manganese are mostly likely to have high exposure to manganese, primarily by inhalation of manganese dusts in workplace air. Populations living in the vicinity of ferromanganese or iron and steel manufacturing facilities, coal-fired power plants, or hazardous waste sites may also be exposed to elevated manganese particulate matter in air or water, although this exposure is likely to be much lower than in the workplace. Populations living in regions of natural manganese ore deposits may be exposed to above-average levels in soil, water, or air. Children are especially likely to receive above-average doses from manganese-containing soils since they have a higher intake of soil (mainly through hand-to-mouth contact) than adults (Calabrese et al. 1989).

People ingesting large amounts of foods high in manganese also have a potential for higher-than-usual exposure. Included in this group would be vegetarians, who ingest a larger proportion of grains, legumes, and nuts in their diets than the average U. S. population, and heavy tea drinkers. While the intake of manganese from vegetarians may exceed the estimates of daily dietary intake, the bioavailability of manganese from vegetable sources is substantially decreased by dietary components such as fiber and phytates (EPA 1993b). In addition to the population with these dietary habits, individuals with iron deficiency show increased rates of manganese absorption (Mena et al. 1969, 1974); iron deficiency leads to increased brain manganese concentrations in experimental animals (Aschner and Aschner 1990).

Manganese is eliminated from the body primarily through the bile. Interruption of the manufacture or flow of bile can impair the body's ability to clear manganese. Several studies have shown that adults and children (Devenyi et al. 1994; Fell et al. 1996; Hauser et al. 1994, 1996; Pomier-Layrargues et al. 1998; Rose et al. 1999; Spahr et al. 1996), as well as experimental animals (Rose et al. 1999), with cholestatic liver disorders have increased manganese levels in their blood and brain and are at risk from potentially increased exposure to manganese due to their decreased homeostatic control of the compound.

In addition to oral diets, people on partial and total parenteral nutrition may be exposed to increased amounts of manganese. Forbes and Forbes (1997) found that of 32 patients receiving home parenteral nutrition due to digestive problems, 31 had elevated serum manganese levels (0.5–2.4 mg/L compared to normal range of 0.275–0.825 mg/L). It is unclear whether these levels reflected steady-state conditions due to the time the samples were taken. However, these levels are much higher than other studies involving patients on TPN; thus, it is unlikely that these levels represent steady-state conditions. Further,

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the normal range reported by authors is elevated compared to other studies, suggesting the possibility that the blood samples were contaminated with exogenous manganese. The authors observed no clinical evidence of toxicity in the patients. Fourteen of the patients suffered iron deficiency anemia; because low iron concentrations are associated with increased manganese uptake, the anemia may have exacerbated the increased blood manganese concentrations. Increased blood manganese levels and MRI scans indicative of increased manganese in brains have been reported in children fed entirely on parenteral nutrition (Fell et al. 1996; Kofritsa et al. 1998; Ono et al. 1995). Interestingly, only in the Fell et al. (1996) study were neurotoxic effects reported. Whole-blood manganese in the children from this study ranged from 9.9–110 µg/L. Devenyi et al. (1994) found hyperintense signals in the brain of an 8-year-old child who had cholestatic liver disease and exhibited dystonia and other motor dysfunctions. Nagatomo et al. (1999) reported that two elderly patients who had been administered TPN for 3–4 months exhibited clinical signs of manganism (including masked facies, marked rigidity, hypokinesia) with associated elevated blood manganese levels and hyperintense signals on MRI, localized to the basal ganglia, especially the globus pallidus. Signs of manganism abated upon levodopa treatment and the administration of Ca-EDTA; the high intensity signals on MRI abated when manganese supplementation ceased. In addition to patients on parenteral nutrition, uremic patients on hemodialysis have been found to have increased manganese levels due to increased concentrations of manganese in the dialysis solution (Lin et al. 1996). These studies indicate that while increased levels of manganese in blood and brain are often associated with TPN administration, adverse neurological effects are not always reported. Nagatoma et al. (1999) found increased serum concentrations of manganese and brain abnormalities in two patients who showed parkinsonism with psychiatric symptoms after 3–4 months of total parenteral nutrition. Discontinuation of manganese supplementation in the parenteral diet, coupled with levodopa treatment gradually improved both the symptoms and brain abnormalities in the patients.

In comparison to other groups within the general population, persons living close to high density traffic areas, automotive workers, and taxi drivers may be exposed to higher concentrations of manganese arising from the combustion of MMT. Farmers, people employed as pesticide sprayers, home gardeners, and those involved in the manufacture and distribution of maneb and mancozeb may be exposed to higher concentrations of these pesticides than the general public. People who ingest fruits and vegetables that have been treated with these pesticides and that contain higher-than-usual residues of the compounds (due to incomplete washing or over-application) may be exposed to increased concentrations of the pesticides. It is possible that medical workers may be exposed to higher concentrations of mangafodipir than the general population, although exposure routes other than i.v. are not expected to pose a significant risk.

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**5.8 ADEQUACY OF THE DATABASE**

Section 104(I)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of manganese is available. Where adequate information is not available, ATSDR, in conjunction with the NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of manganese.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce or eliminate the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

**5.8.1 Identification of Data Needs**

**Physical and Chemical Properties.** The fundamental physical and chemical properties of manganese and manganese compounds are known (see Table 3-2), and additional research does not appear necessary.

**Production, Import/Export, Use, Release and Disposal.** Information is available on U.S. import of manganese ore and production of ferromanganese (HSDB 1989; TRI87 1989; TRI91 1993; U.S. Bureau of Mines 1989), but more recent data would be valuable. It is clear that most manganese is used in steel production, but detailed information on the amount and type of manganese compounds used in various other products was not located and would be helpful in evaluating possible consumer exposures. Information on the import, export, and use of MMT in U.S. fuels would be very helpful in targeting potentially exposed populations for the identification of adverse health effects.

According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit chemical release and off-site transfer information to the EPA. The Toxics Release Inventory (TRI), which contains this information for 1991, became available in May of

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1993. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

Data from the TRI database provide valuable information on the amounts of manganese released to different environmental media (e.g., air, soil, and water) each year, although details on the chemical form and physical state of the waste materials are not included. These disposal practices are not regulated under current federal law. TRI data may not be complete estimates of total release. Also, because these data reflect past releases, they may not be representative of current releases at these facilities.

**Environmental Fate.** The partitioning of manganese between water and soil can be fairly well predicted using thermodynamic equilibrium concepts, if soil-specific information is available (Baes and Sharp 1983; Rai et al. 1986). However, the kinetics of these reactions have not been studied in detail. Kinetic studies could help determine the residence time of manganese released into water or soil. Information on the conversion of manganese to different forms, especially the combustion products of MMT, in the air, water, and soil is also needed. The fate of manganese particles released into the air is determined by the particle size, and the direction and distance of particle transport at a site can be predicted from meteorological data and particle size data (EPA 1984a; Nriagu 1979). Transport of manganese in water is determined mainly by the solubility of the manganese compounds present, although suspended particles may also be transported in flowing waters (EPA 1984a; Schaanning et al. 1988).

The primary transformations which manganese undergoes in the environment are oxidation/reduction reactions (EPA 1984a; Rai et al. 1986). Reactions of manganese with airborne oxidants have not been studied. Information on the rate and extent of such reactions would be helpful in understanding the fate of atmospheric releases. The transformation of manganese in water or soil is dependent mainly on Eh, pH, and available counter ions (EPA 1984a). In some soils, manganese may also be oxidized by bacteria (Geering et al. 1969; Johnston and Kipphut 1988). More work is needed on the environmental factors, such as soil composition and pH, that may determine the form in which manganese will appear and thus impact manganese availability and absorption.

Modeling has also provided interesting insight into the contribution of the combustion of MMT to atmospheric manganese (Loranger et al. 1995b). According to the model estimations, the contribution of

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direct emissions from motor vehicles to the atmospheric background manganese (as measured from sampling stations) would be about 50% at <25m and less than 8% at 250m. These results are confirmed with an *in situ* study using snow as the environmental indicator where the average deposition rates of manganese for the top and bottom layers ranged from 0.01 to 0.21 mg/m<sup>2</sup>day (Loranger et al. 1996). The average concentrations of manganese decreased with distance from the road. However, it was impossible to distinguish between directly-emitted manganese from automobiles, manganese enriched road dust, and the naturally-occurring manganese in crustal materials. No study to date has provided the complete answer to this question and this constitutes one of the major remaining data needs regarding the environmental significance of manganese from MMT and the resulting potential for exposure.

**Bioavailability from Environmental Media.** Manganese is known to be absorbed following inhalation or oral exposure (Mena et al. 1969; Pollack et al. 1965), but dermal exposure is not considered to be significant. The uptake of manganese from air, food, milk, and water has been studied (Davidsson et al. 1988, 1989a). However, absorption from soil has not been investigated. In view of the potential for tight binding of manganese to some soil types, studies on this subject would be valuable in evaluating risk to humans, especially children who may ingest contaminated soils near hazardous waste sites. Additional information would also be valuable on the relative bioavailability of different manganese compounds across various environmental media.

**Food Chain Bioaccumulation.** It has been established that while lower organisms (e.g., plankton, aquatic plants, and some fish) can significantly bioconcentrate manganese, higher organisms (including humans) tend to maintain manganese homeostasis (EPA 1984a; Folsom et al. 1963; Thompson et al. 1972). This indicates that the potential for biomagnification of manganese from lower trophic levels to higher ones is low, and it does not appear that additional research in this area is essential at this time.

**Exposure Levels in Environmental Media.** Reliable monitoring data for the levels of manganese in contaminated media at hazardous waste sites are needed so that the information obtained on levels of manganese in the environment can be used in combination with the known body burden of manganese to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites.

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Manganese levels have been monitored in all environmental media, including air, water, soil, and food (EPA 1984a; NAS 1980a; Pennington et al. 1986). The EPA has estimated average human intake levels of manganese from water, air, and food (EPA 1984a). These estimates were based mainly on monitoring data from the 1960s and 1970s. More recent data on airborne MMT and manganese would be valuable in identifying any trends in environmental contamination and potential populations that may suffer higher manganese body burdens following increased use of MMT (Davis 1999; Weiss 1999).

More specific data on levels in the environment around those particular sites where manganese is believed to have been dumped would be helpful in determining the extent of exposure levels around such waste sites. In particular, data on the concentration of manganese in the air around hazardous waste sites would be valuable in assessing the potential significance of this exposure pathway.

**Exposure Levels in Humans.** This information is necessary for assessing the need to conduct health studies on these populations. Manganese is a normal component of human tissues and fluids (Sumino et al. 1975; Tipton and Cook 1963). Increased average levels of manganese have been detected in blood and urine of populations exposed to high concentrations of manganese in the workplace (Roels et al. 1987b), but no similar data are available for populations surrounding hazardous waste sites. Surveys of manganese levels in the blood or urine of populations living near waste sites could be useful in identifying groups with above-average levels of manganese exposure. However, because of the variability in these values, it is not likely that such data would be helpful in identifying individuals with above-average exposures. More information is also needed to determine whether iron-deficient populations have a higher manganese body burden. Manganese and iron have many physico/chemical similarities and there is a possibility of competition between these elements. Increased manganese concentrations have been shown to inhibit the metabolic function of the iron-dependent enzyme, aconitase (Zheng et al. 1998). Iron deficiency is the single most prevalent nutritional deficiency in the world, and so the potential health risk associated with iron deficiencies exacerbating the brain manganese burden may represent a crucial issue of exposure and susceptibility, and has yet to be evaluated. Air concentrations in areas with high traffic density are sometimes higher than the guide level (Zayed et al. 1999), therefore, some individuals could be at risk. Research focusing on the environmental level of exposure of certain groups of the population, such as those living near a major highway, is needed.

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**Exposures of Children.** Children are exposed daily to manganese. The compound is an essential trace element vital for the body to function properly. However, exposure and body burden studies are lacking for children, especially infants and toddlers. These data are needed because studies in infants indicate that absorption of manganese is high. Studies in animals indicate that neonates do not excrete manganese as readily as more mature animals. Two studies link ingestion exposure of excess manganese to neurological deficits (poorer performance in school and on neurobehavioral tests; He et al 1994; Zhang et al. 1995.). Intake values for the subjects in these studies were not reported. It would be useful to know if effects such as these are associated with accumulation of manganese in the brain. Although the primary pathway for exposure is the diet, studies involving exposures to airborne manganese (e.g., in dust that may be present at a nearby hazardous waste site or manganese-processing plant) would aid in understanding other pathways that may contribute significantly to children's total body burden of manganese. In addition, since most manganese is provided from plant foods, which are often limited in children's diets, dietary exposure/body burden studies would aid in understanding manganese requirements for maintaining good health.

Soil ingestion is likely the only unique exposure pathway for children. Additional studies concerning bioavailability of manganese from soil would provide important information concerning the proportion of the total daily manganese intake that could originate from ingested soils.

Although infants differ in their weight-adjusted intake of manganese, it is unknown whether older children differ in this parameter. Studies concerning this endpoint would be very valuable.

Studies involving inhalation or ingestion exposure to MMT in the young are very few (Komura and Sakamoto 1992b, 1994). Although these studies indicate that MMT had very little measurable effect on development, only one dose level was used. Although analytical data indicate that environmental MMT is unlikely to persist (Lynam et al. 1999), it is unknown what typical body burdens of manganese might be in children following long-term exposure to MMT combustion products. Additional studies measuring these endpoints in the young would be helpful.

Aside from limited developmental studies involving gestational exposure, there are no data on the effects of exposure of the young to maneb and mancozeb. Studies evaluating acute, intermediate, and chronic exposures to these pesticides via inhalation and oral exposures are needed.

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Child health data needs relating to susceptibility are discussed in 2.12.2 Identification of Data Needs.

**Exposures Registries.** No exposure registries for inorganic or organic manganese were located. This substance is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. The substance will be considered in the future when chemical selection is made for the establishment of subregistries. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to exposure to this substance.

### 5.8.2 Ongoing Studies

On-going remedial investigations and feasibility studies at NPL sites contaminated with manganese will add to the available database on exposure levels in the environment and exposure levels in humans.