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# 4. PRODUCTION, IMPORT, EXPORT, USE, AND DISPOSAL

#### 4.1 PRODUCTION

## <u>Inorganic Manganese</u>

Table 4-1 lists the facilities in each state that manufacture or process manganese, the intended use, and the range of maximum amounts of manganese that are stored on site. There are currently 2,060 facilities that produce or process manganese in the United States. The data listed in Table 4-1 are derived from the Toxics Release Inventory (TRI96 1998). Only certain types of facilities were required to report. Therefore, this is not an exhaustive list.

Manganese is an abundant element comprising about 0.1% of the earth's crust (Graedel 1978); among the heavy metals only iron is more abundant (Cotton and Wilkinson 1972). It does not occur naturally as a base metal but is a component of over 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), and rhodanate (manganese silicate) (EPA 1984a; HSDB 1993; NAS 1973; Windholz 1983).

Most manganese ore is smelted in electric furnaces to produce ferromanganese, a manganese-iron alloy widely used in the production of steel (EPA 1984a; NAS 1973). Approximately 2 tons of manganese ore are required to make 1 ton of ferromanganese (NAS 1973). Production of 97–98% pure manganese metal is achieved by aluminum reduction of low iron-content manganese ore (HSDB 1998) or from the byproducts of ferromanganese production. Manganese with <0.1% metallic impurities can be produced electrolytically from a manganese sulfate solution (EPA 1984a; HSDB 1998).

Manganese compounds are produced either from manganese ores or from manganese metal. For example, manganese chloride is produced by the reaction of hydrochloric acid with manganese oxide or manganese carbonate (HSDB 1993), manganese sulfate is produced as a by-product of hydroquinone production or by the action of sulfuric acid on manganese compounds (HSDB 1989), and potassium permanganate is produced by the electrolytic oxidation of manganese dioxide in a potassium hydroxide solution (HSDB 1998; Sax and Lewis 1987).

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Table 4-1. Facilities That Manufacture or Process Manganese

	NUMBER	RANGE OF MAXIMUM		
	OF	AMOUNTS ON SITE		
STATE <sup>a</sup>	FACILITIES	IN POUNDS b	ACTIVITIES AND USES C	
AL	60	100 - 49,999,999	1,2,3,6,7,6,2,1	
AR	29	100 - 49,999,999	1 ,2 ,3 ,5 ,7,8 ,9 ,12 ,13	
AZ	8	1,000 - 999,999	1 ,4 ,5 ,7 ,8 ,9, 10,12	
CA	55	0 - 499,999,999	1, 2, 1, 11, 10, 9, 8, 7, 6, 5, 4, 8, 2, 1	
CO	14	1,000 - 9,999,999	2 ,3 ,4 ,9 ,12	
CT	16	1,000 - 999,999	2 ,3 ,9 ,10	
DE	1	10,000 - 99,999	1 ,5 ,8	
FL	26	100 - 9,999,999	8 ,9 ,10 ,13	
GA	42	0 - 9,999,999	1 ,2 ,3 ,5 ,7 ,8, 9, 10 ,12 ,13	
Н	1	10,000 - 99,999	9	
IA .	51	100 - 9,999,999	1 ,2 ,3 ,5 ,7 ,8 ,9 ,10 ,12	
D	3	1,000 - 999,999	9	
L	121	0 -49,999,999	1, 2, 4, 5, 8, 9, 10, 11, 21, 2, 1	
IN	161	0 - 49,999,999	1 ,2 ,3 ,4 ,5 ,6 ,7 ,8, 9 ,10 ,11 ,12 ,13	
KS	30	1,000 - 499,999,999	1,3 ,4 ,5 ,8 ,9 ,12 ,13	
Υ	63	100 - 499,999,999	1 ,2 ,3 ,4 ,5 ,6 ,7 ,8 ,7 ,10 ,12 ,13	
_A	17	0 - 9,999,999	1 ,2 ,3 ,5 ,7 ,8 ,9 ,10 ,12 ,13	
ИΑ	26	0 - 999,999	1 ,2 ,3 ,4 ,5 ,9 ,10	
MD	17	1,000 - 49,999,999	2 ,4 ,9 ,10 ,13	
ΜE	8	1,000 - 99,999	1 ,3 ,9	
ИΙ	128	0 - 9,999,999	1 ,2 ,3 ,4 ,5 ,6 ,7 ,8, 7, 10 ,12 ,13	
ΛN	28	0 - 9,999,999	8 ,9 ,10 ,12	
MO	49	100 - 9,999,999	1 ,5 ,8 ,9 ,12	
<b>MS</b>	23	100 - 49,999,999	8 ,9 ,13	
ΜT	1	100,000,000 - 499,999,999	7, 6, 5, 4, 5, 2, 1	
1C	57	0 - 9,999,999	1, 2, 3, 5, 8, 9, 10, 11, 12, 2, 1	
ND	5	1,000 - 99,999	2 ,3 ,9	
1E	18	0 - 9,999,999	1 ,2 ,8 ,9 ,12 ,13	
1H	4	1,000 - 999,999	8 ,9	
<b>1</b> J	27	1,000 - 9,999,999	1 ,2 ,3 ,4 ,7 ,8 ,9 ,10	
IM	1	10,000 - 99,999	9	
IV	2	100,000 - 49,999,999	2 ,3 ,7	
ΙΥ	63	0 - 9,999,999	1, 2, 3, 4, 5, 7, 8, 9, 10, 12, 13	
Н	231	0 - 499,999,999	1 ,2 ,3 ,4 ,5 ,6 ,7 ,8 ,7 ,12 ,13	
)K	48	100 - 9,999,999	1 ,2 ,3 ,4 ,5 ,6 ,8 ,9	
)R	17	1,000 - 9,999,999	2 ,3 ,9 ,12 ,13	
Α	179	0 - 99,999,999	1 ,2 ,3 ,4 ,5 ,7 ,8 ,7 ,5 ,4 ,5 ,2 ,1	
rR	5	0 - 999,999	9	
el .	5	1,000 - 999,999	2 ,3 ,9 ,10	
SC .	57	0 - 9,999,999	1, 2, 3, 5, 7, 8, 9, 10, 13	
:D	7	1,000 - 99,999	9 ,13	
N	54	0 - 49,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13	
X	85	0 - 9,999,999	1 ,2 ,3 ,4 ,5 ,6 ,8 ,9 ,10 ,12 ,13	
IT	23	1,000 - 99,999,999	2 ,3 ,7 ,9 ,12 ,13	

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Table 4-1. Facilities That Manufacture or Process Manganese

STATE <sup>a</sup>	NUMBER OF FACILITIES	RANGE OF MAXIMUM AMOUNTS ON SITE IN POUNDS <sup>b</sup>	ACTIVITIES AND USES °	
VA	23	0 - 999,999	1 ,3 ,7 ,7 ,8 ,9	
VT	1	10,000 - 99,999	9	
WA	27	0 - 999,999	1 ,2 ,3 ,6 ,8 ,9	
WI	126	0 - 49,999,999	1, 2, 3, 7, 6, 7, 6, 2, 2, 1	
wv	15	1,000 - 499,999,999	8 ,9 ,10 ,13	
WY	2	0 - 999,999	1 ,5	

Source: TRI96 1998

1. Produce

2. Import

3. Onsite use/processing

4. Sale/Distribution

5. Byproduct

6. Impurity

7. Reactant

8. Formulation Component

9. Article Component

10. Repackaging

11. Chemical Processing Aid

12. Manufacturing Aid

13. Ancillary/Other Uses

<sup>\*</sup> Post office state abbreviations used

<sup>&</sup>lt;sup>b</sup> Range represents maximum amounts on site reported by facilities in each state

<sup>&</sup>lt;sup>c</sup> Activities/Uses:

Most manganese is mined in open pit or shallow underground mines (EPA 1984a; HSDB 1993; NAS 1973). Manganese ores were previously mined in the United States, but no appreciable quantity has been mined in the United States since 1978 (USGS 1998; U.S. Bureau of Mines 1989). The most recent data indicate that a small amount of manganiferous material (having a natural manganese content of 5–15%) was mined in Cherokee County, South Carolina, for use as a brick colorant; mining at this site comprised the only identified mining performed in 1997 (USGS 1998). No other currently operating mines in the United States were identified. Essentially all manganese ore used in manganese production in the United States is now imported (USGS 1998).

Currently, there are 1,847 facilities in the United States that indicate that they produce manganese or its compounds (TRI96 1998). These 1,847 facilities are scattered across the United States, with the largest numbers in Ohio (231), Pennsylvania (179), and Indiana (161). Over 1,894 facilities are involved in the distribution or use of manganese or manganese compounds (TRI96 1998). Table 4-1 lists the number of facilities in each state, the ranges of the maximum amounts stored at each facility, and the uses of the material (TRI96 1998).

### Organic Manganese

*MMT*. The organomanganese compound methylcyclopentadienyl manganese tricarbonyl (MMT)is produced in either of the following ways: via the reaction of manganous chloride, cyclopentadiene, and carbon monoxide in the presence of manganese carbonyl and an element of group II or IIIA, or, via the reaction of methylcyclopentadiene with manganese carbonyl (EPA 1984a; HSDB 1999; Sax and Lewis 1987).

No production data from facilities that manufacture or process MMT were found. However, it is reported (HSDB 2000) that production in the U.S. in 1976 probably exceeded 4,966 pounds.

*Maneb or mancozeb*. Table 4-2 lists the facilities in the United States that manufacture or process the fungicide maneb, the intended use, and the range of maximum amounts that are stored on site. The data in Table 4-2 are derived from the Toxics Release Inventory (TRI97 1999). Only certain types of facilities were required to report. Therefore, as with the list of manganese manufacturers or processors, this is not an exhaustive list. In 1997, 3 facilities (in Arizona, New Jersey, and North Dakota) reported repackaging maneb and storing between 10,000 and 99,999 pounds of it on site. One facility in Georgia

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Table 4-2. Facilities that Manufacture or Process Maneb

	RANGE OF MAXIMUM						
FACILITY	LOCATION	AMOUNTS ON SITE IN POUNDS	ACTIVITIES AND USES				
BPS INC.	HELENA, AR	10,000 - 99,999	REPACKAGING				
GRIFFIN LLC	VALDOSTA, GA	1,000,000 - 9,999,999	IMPORT, ON-SITE USE/PROCESSING, FORMULATION COMPONENT				
AGSCO INC.	GRAND FORKS, ND	10,000 - 99,999	REPACKAGING				
BARTLO PACKAGING INC.	PASSAIC , NJ	10,000 - 99,999	REPACKAGING				

Source: TRI97 1999

<sup>&</sup>lt;sup>a</sup> Post Office state abbreviations used

reported importing, using maneb as a formulation component, and storing between 1,000,000 and 9,999,999 pounds of maneb on site (Table 4-2).

No production data from facilities that manufacture or process mancozeb were found.

Maneb may be manufactured by any of the following methods: heating sodium ethylenebis(dithiocarbamate) with an aqueous solution of manganese(II) sulfate, reacting a water-soluble ethylenebisdithiocarbamate with manganous sulfate or chloride, neutralizing an aqueous nabam solution with acetic acid and adding manganese chloride solution, or reacting ehtylenediamine with carbon disulfide in the presence of sodium hydroxide in order to produce sodium salt, which is then treated with manganese salt to precipitate maneb (HSDB 1999). In the United States, maneb is available as a white powder that contains 80% of active ingredient.

Mancozeb is a polymeric mixture of a zinc salt and maneb containing 20% of manganese and 2.55% of zinc (HSDB 1999). Its chemical name is manganese ethylenebis(dithiocarbamate) (polymeric) complex with zinc salt. It may be in the form of a wettable or dustable powder, a suspension concentrate, or dry seed treatment.

*Mangafodipir*. Manganese(II) dipyridoxyl diphosphate (MnDPDP), or mangafodipir trisodium, is classified as a drug or therapeutic agent, and no production data were found for it.

#### 4.2 IMPORT/EXPORT

### Inorganic Manganese

The United States currently relies on imports to fill its need for manganese (USGS 1998). The latest data show that the United States imported a gross weight of manganese ore and concentrate (containing 20% or more manganese) of 1.05 billion pounds (478,000 metric tons) in 1996; similar imports decreased to 790 million pounds (357,000 metric tons) in 1997 (USGS 1998). Domestic steel output is the main determinant of manganese demand and is projected to be relatively stable for the remainder of the 1990s. However, steel production has grown at an annual rate of about 1.4% from 1985–96, and U.S. steel demand reached a record high in 1997 (USGS 1998). Therefore, manganese consumption could increase

by the year 2000, but the majority of the demand for manganese will continue to be met by imports (USGS 1998). In 1996 and 1997, countries from which the United States imported manganese ore and concentrates included Australia, Brazil, Gabon, Mexico, Morocco, and South Africa, with Gabon, the dominant ore source, providing approximately 60% of ore imports (USGS 1998).

The United States also exports manganese ore and concentrates, having exported 70 million pounds (31,600 metric tons) in 1996 and 186 million pounds (84,300 metric tons) in 1997. The 1997 export level of manganese ore represents the highest level since 1984 (USGS 1998). Because only one mining activity of manganiferous material was identified in 1997 (see 4.1 Production), and since this material contained a low natural manganese content, mining cannot account for the manganese ore and concentrate exports of 1996–97. Therefore, the United States' stockpile disposal program accounts for these exports; the government's inventory of manganese was lowered by about 4% due to its exports to countries including Belgium, Canada, Colombia, Israel, Italy, the Netherlands, Norway, and the United Kingdom (USGS 1998).

Ferromanganese is also imported, with import quantities of 824 million pounds (374,000 metric tons) in 1996 and 670 million pounds (304,000 metric tons) in 1997 (USGS 1998). All grades of ferromanganese exports totaled 22 million pounds (9,8000 metric tons) and 26 million pounds (11,800 metric tons) in 1996 and 1997, respectively (USGS 1998).

## Organic Manganese

MMT. Import and export data were not located for MMT.

*Maneb or mancozeb*. No import data were located for maneb or mancozeb. Export data show that 250,000 pounds of maneb and 840,000 pounds of mancozeb were exported from the U.S. during 3 months of 1990 (Bason and Colburn 1998).

Mangafodipir. Import and export data were not located for mangafodipir.

## 4.3 USE

## Inorganic Manganese

Metallic manganese (ferromanganese) is used principally in steel production to improve hardness, stiffness, and strength. It is used in carbon steel, stainless steel, high-temperature steel, and tool steel, along with cast iron and superalloys (EPA 1984a; HSDB 1998; NAS 1973). Currently, 85-90% of the total manganese demand is attributable to its use in steel making (USGS 1998). Manganese compounds have a variety of uses. Manganese dioxide is commonly used in production of dry-cell batteries, matches, fireworks, porcelain and glass-bonding materials, amethyst glass, and as the starting material for production of other manganese compounds (EPA 1984a; HSDB 1998; NAS 1973; Venugopal and Luckey 1978). 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 (EPA 1984a; HSDB 1997). Manganese sulfate is used primarily as a fertilizer (60% of total consumption) and as a livestock supplement (30% of total consumption); it is also used in some glazes, varnishes, ceramics, and fungicides (EPA 1984a; HSDB 1997; Windholz 1983). Potassium permanganate's oxidizing power allows it to be used as a disinfectant; an antialgal agent; for metal cleaning, tanning, and bleaching; and as a preservative for fresh flowers and fruits. Approximately 80% of the potassium permanganate consumed in this country is used in water and waste-treatment plants for water purification purposes (HSDB 1997). Another common source of manganese is found in the street drug "Bazooka". It is a cocaine-based drug contaminated with manganese-carbonate from free-base preparation methods (Ensing, 1985).

#### Organic Manganese

MMT. MMT is a fuel additive developed in the 1950s to increase the octane level of gasoline and thus improve the antiknock properties of the fuel (Davis 1998; EPA 1984a; HSDB 1993; Lynam et al. 1990; NAS 1973). It can also be used as a fuel oil additive and a smoke inhibitor (HSDB 1999). MMT was introduced into Canada in 1976 and its use has increased so substantially that it completely replaced tetraethyl lead in gasoline in that country in 1990 (Zayed et al. 1999). Ethyl Corporation, the manufacturer of MMT, has been marketing its product to U.S. refineries since late 1995 (Davis 1998). There are no data concerning the extent of its use in the U.S.

Maneb or mancozeb. Maneb is used as a foliar fungicide for fruits and vegetables, in the seed treatment of vegetables and field crops (esp., small grains such as wheat), and as a fungicide for deciduous fruits and nuts. As a foliar spray, it displays a wide spectra activity, able to control blights, leafspots, blotches, and mildews on fruits, vegetables, and ornamentals. The principal diseases that it controls include early and late blight of potato and tomato, downy mildew and anthracnose on vegetables, and "rot" diseases of apricots, peaches, and grapes. In the most recent available data, 68% of maneb's use was for vegetables, 28% for seed treatment of field crops and vegetables, and 4% for deciduous fruits and nuts in 1978 (HSDB 1999).

Mancozeb is a fungicide used to control many fungal diseases such as blight, leaf spot, rust, downy mildew, and scab in field crops, fruits, nuts, vegetables, ornamentals, etc. In particular, it is used to control the following: early and late blights of potatoes and tomatoes; leaf spot diseases on celery, cucurbits, beets, berries, and currants; rusts on cereals, vegetables, roses, carnations, asparagus, beans, and plums; downy mildews on hops, vines, onions, leeks, lettuce, cucurbits, ornamentals, and tobacco; scab on apples and pears; sigatoka disease in bananas; shot-hole of stone fruit; anthracnose of beans and cucurbits; damping-off disease of vegetables; black leg of beet; needle cast in forestry; and many seed-borne diseases of cereals (HSDB 1999). Mancozeb can also be used for foliar application or as a seed treatment (HSDB 1999). Mancozeb may be applied as a foliar spray, using aerial or ground equipment, or by chemigation. Major crops treated are apples, potatoes, and tomatoes. In the United States, mancozeb is applied to approximately 80% of onion crops (HSDB 1999).

Most recent available data show, in 1989, that the combined annual use of maneb and mancozeb in the United States was 8,000–12,000 thousand pounds active ingredient (8–12 million pounds) (Bason and Colburn 1998), making maneb and mancozeb, collectively, the 16th most used pesticides. However, information regarding the quantity of specific pesticides produced or used is difficult to access because it is proprietary (Bason and Colburn 1998), and therefore, this is only an estimate. In 1989, forestry use of maneb and mancozeb, collectively, was less than 1,000 pounds active ingredient, and 1981 urban application was 32,000 pounds active ingredient.

*Mangafodipir*. Mangafodipir trisodium (MnDPDP) is used as both a liver- and pancreas-specific contrast agent for magnetic resonance imaging (MRI); it improves lesion detection in MRI of these

organs by selectively enhancing the normal parenchyma, but not lesions, so that the contrast between tumorous and normal tissue is increased (Wang 1998).

#### 4.4 DISPOSAL

Manganese is listed as a toxic substance under Section 313 of the Emergency Planning and Community Right to Know Act (EPCRA) under Title III of the Superfund Amendments and Reauthorization Act (SARA) (EPA 1998). Disposal of wastes containing manganese is controlled by a number of federal regulations (see Chapter 7).

Disposal of waste manganese into water requires a discharge permit from the EPA (see Chapter 7), but disposal of solid wastes such as manganese metal or manganese compounds is not regulated under current federal law. There are incomplete federal records of this disposal because most, but not all, solid manganese wastes are disposed of by being deposited on land or by being trucked to off-site disposal facilities (TRI96 1998). The total amount of waste manganese disposed of in this way in 1996 was in excess of 230 million pounds (TRI96 1998) (See Table 5-1). No information was located regarding predicted future trends in manganese disposal.

### Organic Manganese

*Maneb or mancozeb*. Disposal of maneb and mancozeb must comply with state and federal regulations for the management of hazardous waste. Generators of small quantities of this waste may apply for partial exemption from the hazardous waste regulations (HSDB 1999).

No information on disposal of MMT was located.