

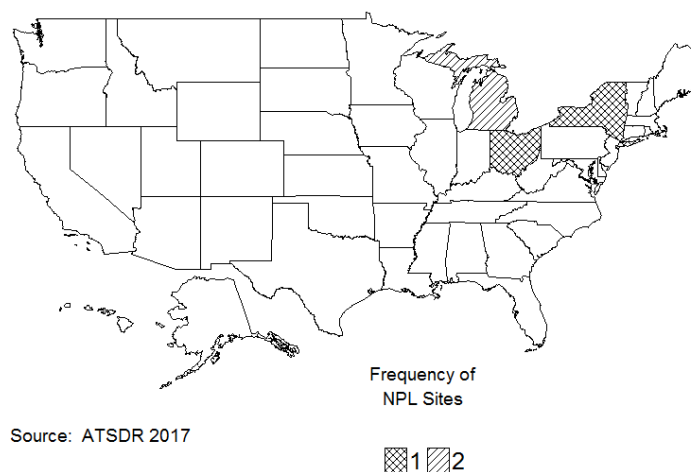
## CHAPTER 5. POTENTIAL FOR HUMAN EXPOSURE

### 5.1 OVERVIEW

MBOCA has been identified in at least 4 of the 1,854 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (ATSDR 2017). However, the number of sites in which MBOCA has been evaluated is not known. The number of sites in each state is shown in Figure 5-1. All four these sites are located within the United States.

MBOCA may be discharged to the environment as a result of an uncontained, open cycle, manufacturing process. Such a discharge could constitute a release to the atmosphere as a fugitive dust or as a spill of MBOCA pellets or heated liquid MBOCA. Otherwise nonhazardous solid wastes may become contaminated by MBOCA in the manufacturing process, thus making such wastes hazardous. The dust can settle to soil or surface waters where it will be strongly adsorbed to the organic matter in the soil or water column; therefore, it is unlikely to contaminate groundwater. Microbial degradation is a potentially significant degradation process and may be quite rapid if appropriate organisms are present in the soil or water. In air or surface waters, MBOCA may undergo photooxidation by alkoxyradicals. Members of the general population are unlikely to be exposed to MBOCA unless they live in an area that has been contaminated. Workers in plants that manufacture or use MBOCA have the potential to be highly exposed by inhalation or dermal contact.

**Figure 5-1. Number of NPL Sites with 4,4'-Methylenebis(2-chloroaniline) (MBOCA) Contamination**



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- The general population is not expected to be exposed to MBOCA. However, ingestion of plants grown in contaminated soil could lead to oral exposure.
- MBOCA is primarily used as a curing agent for polymers. Occupational exposure is expected to be primarily via inhalation and/or dermal contact during use or production of MBOCA.
- MBOCA is not expected to volatilize from water or soil. It is not expected to transport through soil due to rapid and tight adsorption to organic matter. MBOCA is bioaccumulated by food plants grown in contaminated soil.

**5.2 PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL****5.2.1 Production**

MBOCA is a man-made chemical and has not been found in nature (IARC 1974). It is produced commercially by reacting formaldehyde with *o*-chloroaniline (HSDB 1991; IARC 1974). Pure MBOCA is a colorless crystalline solid (Smith and Woodward 1983). The technical grade of MBOCA that is available in the United States comes mainly from Japan in the form of tan/yellow fused prills or pastilles. The diamine purity is 99.8%, typically with 0.2% free *o*-chloroaniline (monomer). Isomers are produced as side reactions such as trimers and tetramers-diamines with three- and four-ring structures joined by methylene groups. Isomers constitute up to 8–10% of MBOCA. The dimer makes up to 90–92% of the MBOCA produced today for coatings and cast polyurethanes. There is no commercial use for pure dimer MBOCA other than for laboratory work.

MBOCA has been produced commercially in the United States for some time. The first reported production was in 1956 (IARC 1974). U.S. production of MBOCA was estimated to be 3.3–5.5 million pounds in 1970 and 7.7 million pounds in 1972 (IARC 1974). In 1982, production of MBOCA in the United States was reported to have ceased (HSDB 1991).

MBOCA has been manufactured in the United States by two companies: E.I. Du Pont de Nemours and Company (Deepwater, New Jersey) and Anderson Development Company (Adrian, Michigan). However, E.I. Du Pont de Nemours and Company ceased MBOCA production in 1978, and Anderson Development Company ceased production in 1979. Presently, all MBOCA used in the United States is imported. As of 1985, there were at least four production sites in the United States that use imported MBOCA: Polyester Corporation (Southampton, New York), American Cyanamid Company (Bound Brook, New Jersey), E.I. Du Pont de Nemours and Company (Deepwater, New Jersey), and Anderson Development Company (Adrian, Michigan) (OHM/TADS 1985). However, in 1992, Allchem Industries,

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Inc. (Gainesville, Florida), Maypro Industries, Inc. (Harrison, New York), and Miki Sangyo (USA), Inc. (New York, New York), were also reported to produce MBOCA for commercial sale (Van et al. 1992).

Twenty-four industrial sites (Table 5-1) were listed in the 2016 Toxics Release Inventory (TRI) as producers and/or users of MBOCA (TRI16 2017). However, since not all producers of MBOCA are required to report to TRI, the companies listed on the inventory cannot be considered the exclusive producers of MBOCA in the United States. This is not an exhaustive list.

**Table 5-1. Facilities that Produce, Process, or Use MBOCA**

State <sup>a</sup>	Number of facilities	Minimum amount on site in pounds <sup>b</sup>	Maximum amount on site in pounds <sup>b</sup>	Activities and uses <sup>c</sup>
DE	2	1,000	9,999	6
FL	1	100,000	999,999	7
IA	1	1,000	9,999	6
IL	3	1,000	9,999	12
IN	1	1,000	9,999	6
MI	1	No data	No data	No data
NE	1	10,000	99,999	12
NJ	1	No data	No data	No data
NY	1	10,000	99,999	6
OH	3	100	99,999	6, 12
PA	1	No data	No data	No data
TN	1	1,000	9,999	10, 11
TX	4	1,000	99,999	6, 7
WI	3	1,000	99,999	6
WV	1	No data	No data	No data

<sup>a</sup>Post office state abbreviations used.

<sup>b</sup>Amounts on site reported by facilities in each state.

<sup>c</sup>Activities/Uses:

- |                      |                             |                          |
|----------------------|-----------------------------|--------------------------|
| 1. Produce           | 6. Reactant                 | 11. Manufacture Aid      |
| 2. Import            | 7. Formulation Component    | 12. Ancillary            |
| 3. Used Processing   | 8. Article Component        | 13. Manufacture Impurity |
| 4. Sale/Distribution | 9. Repackaging              | 14. Process Impurity     |
| 5. Byproduct         | 10. Chemical Processing Aid |                          |

Source: TRI16 2017 (Data are from 2016)

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**5.2.2 Import/Export**

In 1978, approximately 0.4 million pounds of MBOCA were imported into the United States (HSDB 1991). The amount of MBOCA imported into the United States increased in 1983 to 1.51 million pounds. In 1991, approximately 2.0 million pounds of MBOCA were imported into the United States. The MBOCA was manufactured by two Japanese producers and a Taiwanese producer.

**5.2.3 Use**

The majority of MBOCA consumed in the United States has been used as a curing agent for isocyanate-containing polymers, and only about 1% is used in epoxy/epoxy-urethane resin blends (IARC 1974). These cured polymers have many commercial and military uses. MBOCA was reported to be the most widely used agent for curing castable liquid polyurethane elastomers (HSDB 1991; IARC 1974; Sax and Lewis 1987). Commercially, these MBOCA-cured polyurethanes have been used to produce shoe soles, rolls for postage stamp machines, cutting bars in plywood manufacturing, rolls and belt drives in cameras, computers, and reproducing equipment, and wheels and pulleys for escalators and elevators (NRC 1981). MBOCA has also been reported to be formulated with other aromatic diamines and sold under trade names as a curing agent (IARC 1974). MBOCA has also been used in the manufacture of gun mounts, jet engine turbine blades, radar systems, and components in home appliances (HSDB 1991), and as a wiring patting and curing agent (Cowles 1978). Military applications of MBOCA-cured polyurethanes include ball seals on nuclear submarines, positioning strips in Poseidon missiles, and encapsulation of electric components (NRC 1981).

**5.2.4 Disposal**

Because MBOCA is defined as a "hazardous waste," companies that generate wastes containing  $\geq 100$  kg MBOCA are required to conform with EPA regulations (EPA 1989; HSDB 1991). For more information on the regulations and guidelines that apply to MBOCA, see Chapter 7.

No universal method exists for the disposal of carcinogenic compounds such as MBOCA (HSDB 1991). Product residues and sorbent media containing MBOCA have been packaged in epoxy-lined drums and disposed of at EPA-approved sites (OHM/TADS 1985). Destruction via chemical reaction is another method that has been used to dispose of small amounts of MBOCA (HSDB 1991). This method, in which MBOCA is oxidized with potassium permanganate, is generally used for laboratory wastes containing small amounts of MBOCA.

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Incineration technologies have been investigated for the disposal of MBOCA. MBOCA has been considered a good candidate for rotary kiln incineration at a temperature range of 820–1,600°C, with residence times of seconds for liquids and gases and hours for solids (EPA 1981b; HSDB 1991). MBOCA is also listed as a good candidate for fluidized bed incineration at temperatures ranging from 450 to 980°C and residence times similar to those for rotary kiln incineration (EPA 1981). Disposal of MBOCA contained in waste waters using activated carbon adsorption has been studied (HSDB 1991). Saturated filters used to remove MBOCA from waste water via carbon absorption can subsequently be destroyed by rotary kiln or fluidized bed incineration (EPA 1979). Biodegradation treatment of MBOCA using continuous flow reactors that are designed to remove potential hazardous chemicals from water and waste water may be also useful in clean-up operations. Similarly, activated carbon processes and ozone oxidation provide effective disposal treatment (EPA 1979). There is, however, no information on the availability of MBOCA residues from polyurethanes and other plastics.

**5.3 RELEASES TO THE ENVIRONMENT**

The Toxics Release Inventory (TRI) data should be used with caution because only certain types of facilities are required to report (EPA 2005). This is not an exhaustive list. Manufacturing and processing facilities are required to report information to the TRI only if they employ  $\geq 10$  full-time employees; if their facility is included in Standard Industrial Classification (SIC) Codes 10 (except 1011, 1081, and 1094), 12 (except 1241), 20–39, 4911 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4931 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4939 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4953 (limited to facilities regulated under RCRA Subtitle C, 42 U.S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited to facilities primarily engaged in solvents recovery services on a contract or fee basis); and if their facility produces, imports, or processes  $\geq 25,000$  pounds of any TRI chemical or otherwise uses  $>10,000$  pounds of a TRI chemical in a calendar year (EPA 2005).

**5.3.1 Air**

Estimated releases of 1,500 pounds (~0.68 metric tons) of MBOCA to the atmosphere from 25 domestic manufacturing and processing facilities in 2016, accounted for about 54% of the estimated total

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environmental releases from facilities required to report to the TRI (TRI16 2017). These releases are summarized in Table 5-2.

**Table 5-2. Releases to the Environment from Facilities that Produce, Process, or Use MBOCA<sup>a</sup>**

State <sup>c</sup>	RF <sup>d</sup>	Reported amounts released in pounds per year <sup>b</sup>							
		Air <sup>e</sup>	Water <sup>f</sup>	UI <sup>g</sup>	Land <sup>h</sup>	Other <sup>i</sup>	Total release		
							On-site <sup>j</sup>	Off-site <sup>k</sup>	On- and off-site
DE	2	0	0	0	0	1,213	0	1,213	1,213
FL	1	No data	No data	No data	No data	No data	No data	No data	No data
IA	1	No data	No data	No data	No data	No data	No data	No data	No data
IL	3	1	0	0	3	0	1	3	4
IN	1	No data	No data	No data	No data	No data	No data	No data	No data
MI	1	No data	No data	No data	No data	No data	No data	No data	No data
NE	1	4	0	0	0	0	4	0	4
NJ	1	No data	No data	No data	No data	No data	No data	No data	No data
NY	1	1	0	0	0	0	1	0	1
OH	3	6	0	0	65	0	6	65	71
PA	1	No data	No data	No data	No data	No data	No data	No data	No data
TN	1	1,487	0	0	0	0	1487	0	1,487
TX	4	No data	No data	No data	No data	No data	No data	No data	No data
WI	3	1	0	0	0	0	1	0	1
WV	1	No data	No data	No data	No data	No data	No data	No data	No data
Total	25	1,500	0	0	68	1,213	1,500	1,281	2,781

<sup>a</sup>The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.

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

<sup>c</sup>Post office state abbreviations are used.

<sup>d</sup>Number of reporting facilities.

<sup>e</sup>The sum of fugitive and point source releases are included in releases to air by a given facility.

<sup>f</sup>Surface water discharges, waste water treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).

<sup>g</sup>Class I wells, Class II-V wells, and underground injection.

<sup>h</sup>Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other onsite landfills, land treatment, surface impoundments, other land disposal, other landfills.

<sup>i</sup>Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown.

<sup>j</sup>The sum of all releases of the chemical to air, land, water, and underground injection wells.

<sup>k</sup>Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI16 2017 (Data are from 2016)

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**5.3.2 Water**

No MBOCA was released to surface water or publically owned treatment works from 25 domestic manufacturing and processing facilities in 2016 (TRI16 2017). These releases are summarized in Table 5-2.

**5.3.3 Soil**

Estimated releases of 68 pounds (~0.03 metric tons) of MBOCA to soils 25 domestic manufacturing and processing facilities in 2016, accounted for about 2.4% of the estimated total environmental releases from facilities required to report to the TRI (TRI16 2017). No MBOCA was released via underground injection (TRI16 2017). These releases are summarized in Table 5-2.

**5.4 ENVIRONMENTAL FATE****5.4.1 Transport and Partitioning**

**Air.** Volatilization of MBOCA from soil or surface waters is unlikely to be a major factor for Environmental fate because of its very low vapor pressure ( $1 \times 10^{-5}$  mmHg at 25°C) (Keeslar 1986; NIOSH 1978b) and its strong adsorption to organic matter.

**Water.** MBOCA partitions to soil rather than water as a result of its relatively low solubility in water (13.9 mg/L) and its amine groups, which have an affinity for soil organic matter. This binding is rapid and very tight and results in virtually no movement of MBOCA through soil (Voorman and Penner 1986a).

**Sediment and Soil.** The partitioning of MBOCA in the soil affects the uptake of the compound by plants grown in contaminated soil and its subsequent ingestion by humans. MBOCA is bioaccumulated by food plants (e.g., carrots, orchard grass, beans, cabbage, beet, sorghum, cucumber), but movement of the compound within the plant is extremely limited. MBOCA applied to leaf surfaces resulted in adsorption to the leaf cuticle but no movement beyond the application site. Exposure of roots of bean, sorghum, and carrots to aqueous solutions of 5 mg/L of MBOCA for 8 days resulted in relatively high concentrations on the root surfaces of these plants (37, 2,000, and 20 mg/kg, respectively), demonstrating bioconcentration at that site but limited translocation to plant shoots (1.7 mg/kg, 2–5 mg/kg, and virtually undetectable, respectively). MBOCA applied to soils at a concentration of 5 mg/kg again showed an

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uptake in the roots of cucumbers and beans (up to 17 mg/kg MBOCA); the shoots of these plants contained <0.2 mg/kg. This limited translocation may be due to the low water solubility of MBOCA (Voorman and Penner 1986b). This may be of concern in cases of accidents (or even during routine operations) in which MBOCA is released to the air.

#### 5.4.2 Transformation and Degradation

**Air.** The photooxidation half-life of MBOCA in air is estimated to be between 0.290 and 2.90 hours based on reactions with hydroxyl radicals (Howard et al. 1991), suggesting that this may be a significant fate process.

**Water.** Studies examining the biodegradation of MBOCA, using activated sludge microorganisms, suggested that MBOCA was readily degraded (from 2.02 to 0.09 mg/L) in a continuous biological reactor within 24 hours, but not during a 7-day static incubation test (EPA 1979; Tabak et al. 1981). Other degradation processes were also effective in reducing the concentrations of MBOCA present in simulated waste water. Ozone oxidation reduced an initial concentration of 1.52 mg/L MBOCA to nondetectable levels within 5 minutes. Between 21 and 35 mg of carbon per liter, depending on the type of carbon, were required to reduce 1.0 mg/L MBOCA to 0.1 mg/L (EPA 1979). MBOCA was not susceptible to oxygen stripping (EPA 1979).

The estimated photooxidation half-life of MBOCA in surface water is between 1.3 and 72 days, while in groundwaters, MBOCA may have a half-life of 8 weeks to 1 year (Howard et al. 1991). The estimated hydrolysis half-life of MBOCA in water at 25°C and pH 7 is >800 years (EPA 1988c). Studies of microbial degradation of MBOCA showed several biodegradation products, including N-monoacetyl MBOCA and N,N'-diacetyl MBOCA (Yoneyama and Matsumura 1984). 4,4'-Diamino-3,3'-dichloro-benzophenone was produced from metabolic conversion of MBOCA by soil microorganisms (Voorman and Penner 1986a).

**Sediment and Soil.** Carbon dioxide production from soil samples treated with MBOCA was <1% of the total applied, suggesting that aromatic rings are resistant to microbial degradation and oxidation (Voorman and Penner 1986a). These investigators did detect a metabolite with the methylene carbon oxidized to a carbonyl. Microbial degradation of MBOCA has been shown to occur using *Bacillus megaterium* and *nocardiopsis* sp. isolated from soil. These microorganisms readily metabolize MBOCA, with 39 and 24%, respectively, of the original concentration remaining after 3 hours of incubation. The



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major degradation pathways were: (1) acetylation of MBOCA to N-monoacetyl MBOCA and then to N,N'-diacetyl MBOCA and (2) hydroxylation of N-monoacetyl MBOCA to N-hydroxy-N-acetyl MBOCA with the final metabolite being N-hydroxy-N,N'-diacetyl MBOCA (Yoneyama and Matsumura 1984). Also present was a metabolite with the methylene carbon oxidized to a carbonyl (Voorman and Penner 1986a).

The estimated half-life of MBOCA in soil based on aerobic biodegradation may range between 1 and 6 months (Howard et al. 1991).

### 5.5 LEVELS IN THE ENVIRONMENT

**Reliable evaluation of the potential for human exposure to MBOCA depends, in part, on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of MBOCA in unpolluted atmospheres and in pristine surface waters are often so low as to be near the limits of current analytical methods. In reviewing data on MBOCA 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.**

Table 5-3 shows the lowest limit of detections that are achieved by analytical analysis in environmental media. An overview summary of the range of concentrations detected in environmental media is presented in Table 5-4.

**Table 5-3. Lowest Limit of Detection Based on Standards<sup>a</sup>**

Media	Detection limit	Reference
Air	1 ng/m <sup>3</sup>	Skarping et al. 1985
Water	25 ng/L	Rice and Kissinger 1981, 1982
Soil/sediment	25 ng/L	Rice and Kissinger 1981, 1982
Whole blood	25 pg	Sabbion and Neumann 1990

<sup>a</sup>Detection limits based on using appropriate preparation and analytics. These limits may not be possible in all situations.

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**Table 5-4. Summary of Environmental Levels of MBOCA**

Media	Low	High	For more information
Outdoor air (ppbv)	No monitoring data were identified.		
Indoor air (ppbv)	No monitoring data were identified.		
Surface water (ppb)	1	1	Section 5.5.2
Ground water (ppb)	No monitoring data were identified.		
Drinking water (ppb)	No monitoring data were identified.		
Food (ppb)	No monitoring data were identified.		
Soil (ppm)	4.6	1146	Section 5.5.2

Detections of MBOCA in air, water, and soil at NPL sites are summarized in Table 5-5.

**Table 5-5. MBOCA Levels in Water, Soil, and Air of National Priorities List (NPL) Sites**

Medium	Median <sup>a</sup>	Geometric mean <sup>a</sup>	Geometric standard deviation <sup>a</sup>	Number of quantitative measurements	NPL sites
Water (ppb)	1.84	1.56	2.29	2	1
Soil (ppb)	28	41.6	124	4	1

<sup>a</sup>Concentrations found in ATSDR site documents from 1981 to 2017 for 1,854 NPL sites (ATSDR 2017). Maximum concentrations were abstracted for types of environmental media for which exposure is likely. Pathways do not necessarily involve exposure or levels of concern.

**5.5.1 Air**

Monitoring of MBOCA dust and vapor in the ambient air of a production facility in 1969 showed that the maximum 8-hour average concentrations were 0.32 and 0.25 mg/m<sup>3</sup>, respectively. Significant levels were detected only in areas adjacent to the pelletizing unit, although even these levels were only intermittently high. Skin absorption was the major source of exposure and could be effectively controlled with appropriate protective clothing and engineering controls (Linch et al. 1971).

Ambient air and personal air monitoring was conducted at a plastics factory where MBOCA was used in the production of urethane. The results obtained from 10 ambient air samples (6 in the general work area, 4 in the area where MBOCA was melted) indicated that MBOCA was not present in the general area above the level of detection (0.015 µg/filter), and was present in the air near the MBOCA melting pot at levels up to 92 µg/m<sup>3</sup>. Personal air monitoring indicated that only those employed as mixers and molders were exposed to detectable levels of MBOCA, ranging from 0.06 to 0.70 µg/m<sup>3</sup>. Wipe samples of

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surfaces that workers were most likely to be exposed to contained low levels of MBOCA throughout. Surface wipe samples showed MBOCA contamination ranging from 0.1  $\mu\text{g}/100\text{ cm}^2$  near the trimmers work table to 19.1  $\mu\text{g}/100\text{ cm}^2$  adjacent to the MBOCA melting pot. Surfaces that were rarely wiped clean, but were not near the melting pot (such as the tops of storage cabinets), contained an average of 4.7  $\mu\text{g}/100\text{ cm}^2$  (Clapp et al. 1991). MBOCA air levels were also evaluated in a polyurethane elastomer factory, and the air exposure levels ranged from 0.2 to 8.9  $\mu\text{g}/\text{m}^3$  (Ichikawa et al. 1990). MBOCA levels were measured at 0.001–0.042  $\text{mg}/\text{m}^3$  in the air of a factory producing rubber ski boots (Smith and Woodward 1983).

MBOCA was present at only trace concentrations in air samples of dust taken 1.5 feet above ground level in a residential area known to be contaminated with MBOCA (Keeslar 1986).

### 5.5.2 Water

A specialty chemical manufacturing plant in Adrian, Michigan, that produced >1 million pounds/year of MBOCA during the late 1970s was found to have released significant quantities of it in its waste water discharges. Water sampling surveys found the following concentrations of MBOCA associated with the facility (Parris et al. 1980): >1,600 ppm in industrial lagoon sediment; 250 ppb in industrial lagoon effluent water; 1.5 ppb in industrial site deep well water; 1 ppb in surface runoff water from site; <0.5 ppb in sewage treatment plant, influent water; <0.5 ppb in sewage treatment plant, effluent water <0.5 ppb; 18 ppm (estimated) in sewage treatment plant, activated sludge; and  $\leq 0.1$  ppb in Raisin River water.

Samples of well water from a residential area adjacent to the manufacturing plant, however, did not contain detectable levels of MBOCA, suggesting that groundwater contamination had not occurred (Keeslar 1986).

### 5.5.3 Sediment and Soil

Soil samples taken on the site of a manufacturing plant using MBOCA contained levels as high as 1,146 ppm, while concentrations along public roads near the site ranged from 4.6 to 590 ppm (Keeslar 1986). Soil from the yards of residences adjacent to the site (within a 1-km radius) typically had 1.74  $\text{mg}/\text{kg}$  MBOCA in the top 2 inches of soil and 0.02  $\text{mg}/\text{kg}$  in the next 4 inches.

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### 5.5.4 Other Media

No studies were located on the levels of MBOCA found in other environmental media. However, it has been shown that MBOCA binds to, and penetrates, the roots of plants grown in contaminated soil. Once in the plant, MBOCA stays very close to the root surface and is not distributed throughout the plant (Voorman and Penner 1986b).

### 5.6 GENERAL POPULATION EXPOSURE

The general population is not likely to be exposed to MBOCA. However, members of the general population may be exposed to MBOCA if they consume certain types of plants (e.g., root crops) grown in MBOCA-contaminated soil. MBOCA has been found to adhere to the leaves and roots of plants, and the compound is not removed by rinsing with water (Voorman and Penner 1986b).

### 5.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Populations living near areas known to be contaminated with MBOCA can be considered to have high potentials for exposure. Although adults living in a contaminated area of Adrian, Michigan did not have detectable levels of MBOCA in their urine, young children (all under the age of 6 years) from the area had urine concentrations of 0.3–1.0 ppb. The levels in children were believed to be a direct consequence of their frequent contact with contaminated soils. MBOCA was detected in the residences of this area, primarily on floors, carpeting, and vacuum cleaner bags; however, other household surfaces did not have significant concentrations of MBOCA (Keeslar 1986).

Workers using or producing MBOCA have the highest potential for exposure. MBOCA is commercially used as a curing agent for isocyanate polymers by specialty manufacturers of industrial and commercial polyurethane products (e.g., as gears, gaskets, sport boots, and roller skate wheels). The form of MBOCA to which workers could be exposed is likely to be either a liquid emulsion, dust, or solid pellets (NIOSH 1986b; Schulte et al. 1988). Occupational exposures may occur at several stages of polymer production, especially where prepolymers are mixed with molten curing agent before molding (Edwards and Priestly 1992). In most cases, dermal absorption is the most important occupational exposure pathway (Edwards and Priestly 1992; Lowry and Clapp 1992). The National Occupational Health Survey estimated that 2,094 workers were potentially exposed to MBOCA in the workplace in 1980 (Schulte et al. 1988). A urinary monitoring program can determine aggregate worker exposure to MBOCA (Ward et al. 1986). Workers in a plastics plant that mixed or molded urethane products containing MBOCA were found to

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have detectable levels of MBOCA in their urine. Concentrations for the mixers ranged from 5 to >100 µg/L urine (average concentration, 61.9 µg/L), whereas concentrations for the molders were considerably lower, nondetectable to 50 µg/L urine (average concentration, 14.8 µg/L). The greatest exposure route was inferred to be direct skin contact with MBOCA, despite the fact that the mixers wore gloves while transferring dry MBOCA, melting it, or dispensing the molten fluid (Clapp et al. 1991).

After 2 days away from work, only 1 of 13 workers in the plastics plant had detectable levels of MBOCA in his urine. This worker also had the highest peak urinary MBOCA levels during the preceding week (Clapp et al. 1991). Another investigation of workers in a polyurethane elastomer factory reported that pre- and postshift urinary levels were not significantly different in all exposed workers and that levels measured 48 hours after cessation of work were not always the lowest (Ichikawa et al. 1990). The difference may partially be explained by the actual levels of MBOCA in the workplace; workers that had MBOCA in the urine after 2 days away from work had the highest levels of the compound when last measured, suggesting that they were exposed to higher MBOCA levels than workers without any MBOCA in urine after the weekend. The reported findings may also reflect differences in metabolic rates between workers, or that different depots of MBOCA are excreted over different time frames from the body.

Workers in a manufacturing plant using MBOCA had urine concentrations of MBOCA ranging from 13 to 458 ppb (mean 145 ppb). Their immediate families were found to have had exposures to MBOCA also; urine levels of MBOCA ranged from 0 to 15 ppb (Keeslar 1986). These findings suggest that direct exposure to MBOCA itself in an occupational setting or at a hazardous waste site may not be necessary for exposure, and that people can also be exposed to MBOCA by contact with an MBOCA-exposed individual. Monitoring of workers at seven facilities in Australia that used MBOCA in the manufacture of polyurethane polymers showed that average MBOCA levels in the urine of the workers dropped from 29.6 to 10.4 mg/L within 8–9 months after the implementation of an exposure prevention program (Wan et al. 1989). Another study of 150 workers in 19 factories with industrial exposure to MBOCA showed that, at the end of the workshift, excretion levels ranged from <0.5 to 1,600 µg/L of MBOCA, with the highest average urine concentrations (600 µg/L) in workers directly involved in MBOCA manufacture or use; urine MBOCA levels dropped after exposure controls were implemented in the plant (Ducos et al. 1985). Similar decreases in urine MBOCA concentrations were observed following improvements in ventilation and with the use of protective clothing by workers exposed to MBOCA (Thomas and Wilson 1984).

## 5. POTENTIAL FOR HUMAN EXPOSURE

Results of a voluntary biological monitoring program implemented by the Polyurethane Manufacturers Association suggest that exposure to MBOCA among users of the compound decreased between 1985 to 1990. Following implementation of a number of engineering controls to limit exposure, including the use of closed transfer systems and the use of a fused, hardened MBOCA pellet, worker urine specimens containing  $<25 \mu\text{g MBOCA/L}$  increased from 77 to 86% of the total amount collected. Over this same time period, urine samples containing  $>50 \mu\text{g MBOCA/L}$  decreased from 12 to 8% of the total number of samples collected (Lowry and Clapp 1992). Workers in shipyards where MBOCA is used as a potting and molding agent for wiring may also have potentially high exposures to MBOCA (Cowles 1978).