5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

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 non-hazardous 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.

MBOCA has been identified in at least 4 of the 1,350 NPL hazardous waste sites (HAZDAT 1993). However, the number of sites analyzed for MBOCA is not known. The frequency of these sites within the United States can be seen in Figure 5-1.

5.2 RELEASES TO THE ENVIRONMENT

5.2.1 Air

MBOCA may be released to the atmosphere in the exhaust emissions of facilities that manufacture it or use as a curing agent in the manufacture of diisocyanate-based polymers (Keeslar 1986) (Table 5-l).

According to TR191 (1993) a total of 1,362 pounds of MBOCA was released to the atmosphere in 1991, from manufacturing and processing facilities in the United States (see Table 5-l). The TRI data should be used with caution, however, since only certain types of facilities are required to report.

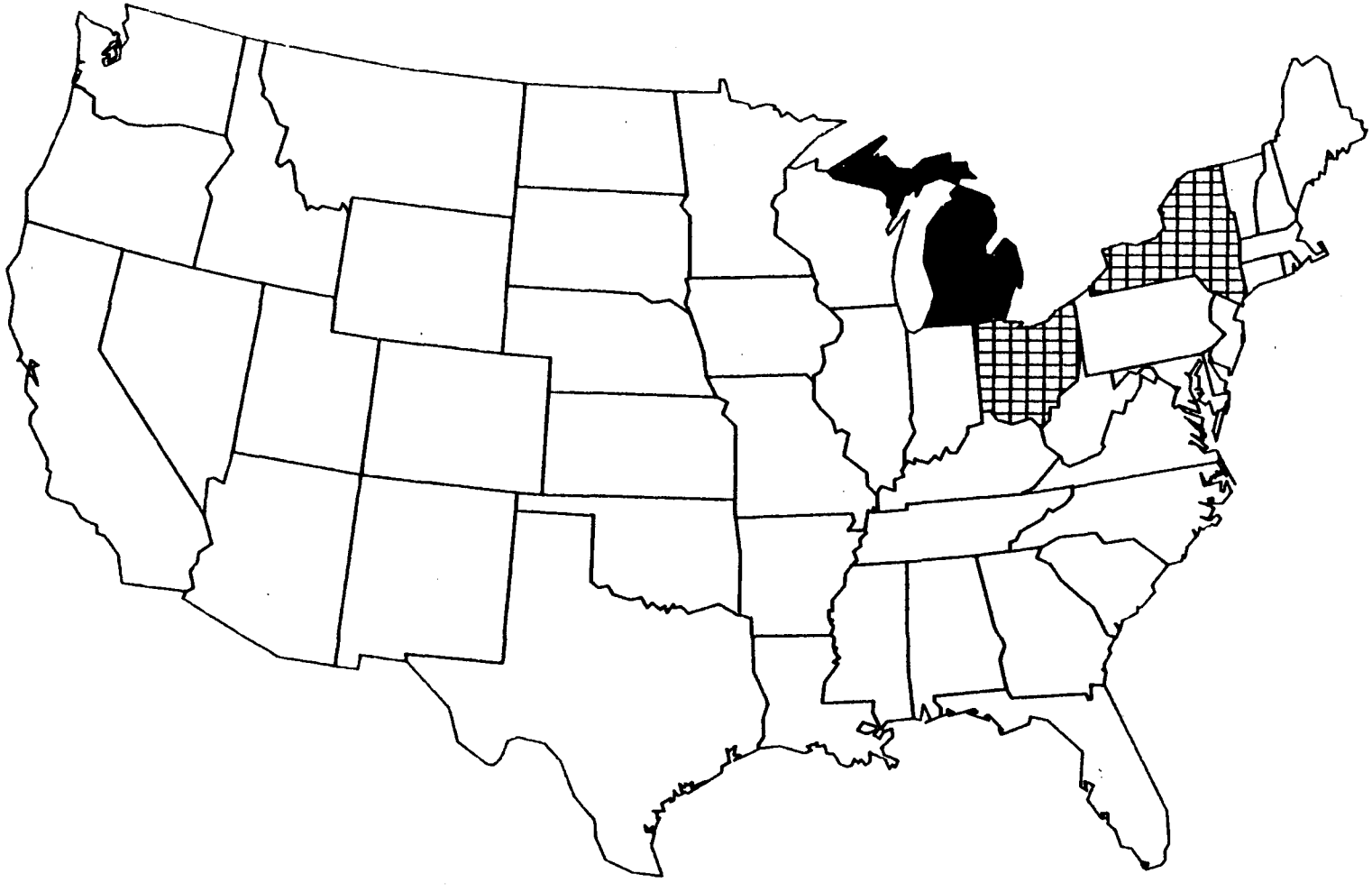
5.2.2 Water

Of the 1,362 pounds of MBOCA released to the ENVIRONMENT from TRI facilities in 1991, no discharges to surface waters were reported. One pound was reported to be transferred to a publicly owned treatment facility works (TR191 1993). The TRI data should be used with caution since only certain types of facilities are required to report.

5.2.3 Soil

Of the 1,362 pounds of MBOCA released to the atmosphere in 1991 from TRI facilities, no releases of MBOCA to land or through underground injection were reported. An additional 5,228 pounds were reported to have been transferred to off-site waste treatment, storage, and

FIGURE 5-1. FREQUENCY OF NPL SITES WITH MBOCA CONTAMINATION *



*Derived from HazDat 1993

TABLE 5-1. Releases to the Environment from Facilities That Manufacture or Process 4,4'-Methylenebis(2-Chloroaniline) (MBOCA)[a]

Facility	Location[b]	Reported amounts released in pounds						
		Air	Underground injection	Water	Land	Total environment[c]	POTW transfer	Off-site waste transfer
PERMA-FLEX ROLLERS INC.	NEWARK, DE	0	0	0	0	0	0	0
TOWNLEY MFG. CO. INC.	CANDLER, FL	750	0	0	0	750	0	0
GALLAGHER CORP.	GURNEE, IL	0	0	0	0	0	0	0
MARTIN ENGINEERING CO.	NEPONSET, IL	0	0	0	0	0	0	0
ANDERSON DEVELOPMENT CO.	GARY, IN	0	0	0	0	0	0	0
GATES RUBBER CO. POLYFLEX PLANT	ELIZABETHTOWN, KY	0	0	0	0	0	0	255
PERMATHANE CUSTOM MOLDED URETHANES	WESTBROOK, ME	5	0	0	0	5	0	3,606
VAIL RUBBER WORKS INC.	SAINT JOSEPH, MI	10	0	0	0	10	1	250
POLYURETHANE SPECIALTIES CO. INC.	LYNDHURST, NJ	0	0	0	0	0	0	0
DICAR INC.	PINE BROOK, NJ	0	0	0	0	0	0	0
CONAP INC.	OLEAN, NY	92	0	0	0	92	0	367[d]
MONARCH INDUSTRIAL TIRE CORP.	AKRON, OH	500	0	0	0	500	0	0
D. S. BROWN CO.	NORTH BALTIMOR, OH	0	0	0	0	0	0	0
GRIFFITH POLYMERS INC.	HILLSBORO, OR	0	0	0	0	0	0	750
BELOIT CORP. MANHATTAN DIV.	AIKEN, SC	0	0	0	0	0	0	0
BAILEY-PARKS URETHANE	MEMPHIS, TN	5	0	0	0	5	0	0
TRCW INDUSTRIAL WHEELS INC.	NASHVILLE, TN	0	0	0	0	0	0	0
DICAR INC.	TOMBALL, TX	0	0	0	0	0	0	0
TROSTEL POLYURETHANE	LAKE GENEVA, WI	0	0	0	0	0	0	0
Totals		1,362	0	0	0	1,362	1	5,228

[a]Derived from TRI91 (1993); MBOCA used in these facilities is imported from Japan because MBOCA has not been produced in the United States since 1979.
[b]Post office state abbreviations used
[c]The sum of all releases of the chemical to air, land, water, and underground injection wells by a given facility
[d]Corrections regarding the amounts of released MBOCA have been filed with EPA (Form R).

POTW = publicly owned treatment works

disposal facilities (TRI91 1993). The TRI data should be used with caution since only certain types of facilities are required to report.

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

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 ($1x10^{-5}$ mmHg at 25°C) (Keeslar 1986; NIOSH 1978b) and its strong adsorption to organic matter.

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).

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 mg/kg, 2,000 mg/kg, 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 uptake in the roots of cucumbers and beans (up to 17 mg/kg MBOCA); the shoots of these plants contained less than 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.

5.3.2 Transformation and Degradation

5.3.2.1 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.

5.3.2.2 Water

Studies examining the biodegradation of MBOCA, using activated sludge microorganisms, suggested that MBOCA was readily degraded (from 2.02 mg/L 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).

5. POTENTIAL FOR HUMAN EXPOSURE

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 more than 800 years (EPA 1988c).

Studies of microbial degradation of MBOCA showed several biodegradation products, including nmonoacetyl MBOCA and *N,N'*-diacetyl MBOCA (Yoneyama and Matsumura 1984). 4,4'-Diamino-3,3'-dichlorobenzophenone was produced from metabolic conversion of MBOCA by soil microorganisms (Voorman and Penner 1986a).

5.3.2.3 Sediment and Soil

Carbon dioxide production from soil samples treated with MBOCA was less than 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 megatetium* and n*ocardiopsis 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 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).

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1 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 mg/m^3 and 0.25 mg/m^3, 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 $\mu g/m^3$. 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 $\mu g/m^3$. Wipe samples of 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 $\mu g/100\ cm^2$ near the trimmers work table to 19.1 $\mu g/100\ cm^2$ 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 $\mu g/100\ cm^2$ (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 μg/m^3 (Ichikawa et al. 1990). MBOCA levels were measured at 0.001-0.042 mg/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).

5.4.2 Water

A specialty chemical manufacturing plant in Adrian, Michigan, that produced more than 1 million pounds per 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):

Industrial lagoon sediment	>1,600 ppm
Industrial lagoon effluent water	250 ppb
Industrial site deep well water	1.5 ppb
Surface runoff water from site	1 ppb
Sewage treatment plant, influent water	<0.5 ppb
Sewage treatment plant, effluent water	<0.5 ppb
Sewage treatment plant, activated sludge	18 ppm (estimated)
Raisin River water	≤0.1 ppb

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).

5.4.3 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 kilometer radius) typically had 1.74 mg/kg MBOCA in the top 2 inches of soil and 0.02 mg/kg in the next 4 inches.

5.4.4 Other Environmental Media

No studies were located on the levels of MBOCA found in other Enviromental 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).

5.5 GENERAL POPULATION AND OCCUPATIONAL 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 have detectable levels of MBOCA in their urine. Concentrations for the mixers ranged from 5 to greater than 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 preceeding week (Clapp et al. 1991). Another investigation of workers in a polyurethane elastomer factory reported that preshift 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 less than 0.5 μg/L 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).

Results of a voluntary biological monitoring program implemented by the PMA 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 less than 25 μg MBOCA/L increased from 77% to 86% of the total amount collected. Over this same time period, urine samples containing greater than 50 μg 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).

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).

5.6 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 to 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).

5.7 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 MBOCA 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 MBOCA.

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 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.

5.7.1 Identification of Data needs

Physical and Chemical Properties. The physical and chemical properties of MBOCA are sufficiently defined to allow assessments of the Environmental fate of the compound to be made (see Chapter 3 and Tables 3-1 and 3-2). no further information is needed.

Production, Import/Export, Use, Release, and Disposal. Presently, conflicting information exists on the number of people that have been or are being exposed to MBOCA in the workplace; the numbers range from 114 (NOES 1992) to 2,094 (Schulte et al. 1988). The general population is not likely to be exposed to MBOCA.

Information is unavailable on current or historical MBOCA production in the United States. MBOCA is only used in the workplace in 18 facilities in the United States (TR190 1992). Information on potential food contamination with MBOCA would also be useful in reducing risks associated with general population exposures. MBOCA may be released to the environment in waste waters or fugitive emissions from plants. Additional information is needed on atmospheric releases

of MBOCA from manufacturing facilities to assess the potential for general population exposure.

At the present time, there is no information on the amounts of MBOCA disposed by different methods except for TRI data on the amounts released into different media (see Tables 5-1 and 5-2). Additional information on currently used disposal methods would allow the determination of their efficiency. Also needed is information on the availability of MBOCA residues from polyurethanes and other plastics.

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 1990, became available in May of 1992. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

Environmental Fate. The fate of MBOCA in soil has been described (EPA 1979; Voorman and Penner 1986a; Yoneyama and Matsumura 1984), and some information is available on the spread and transport of MBOCA in surface waters (Parris et al. 1980). Additional data on the aquatic fate of MBOCA, its residence time in the water column, and its absorption to sediment or organic matter in the water would assist in assessing drinking water contamination. Information on the fate of MBOCA adsorbed to sediment would be useful in assessing uptake by aquatic organisms and reentry of MBOCA into the water column. Information on the half-life of MBOCA in the environment would also be useful for assessing the risk for human exposure.

Bioavailability from Environmental Media. Available pharmacokinetic data suggest that MBOCA is absorbed by humans following dermal and inhalation exposures (Chin et al. 1983; Cocker et al. 1988, 1990; Ichikawa et al. 1990; NIOSH 1986b). MBOCA has been measured in the urine of workers following dermal and/or inhalation exposures, suggesting rapid absorption and excretion. Information on the absorption of MBOCA by humans as a result of ingestion of contaminated water or food has not been found and would be useful in assessing the uptake of MBOCA from contaminated foods. Further information on the uptake of MBOCA by all three exposure routes, particularly the differentiation of dermal and inhalation exposure in workers, would be helpful in determining potential uptake of MBOCA as a result of exposure to contaminated air, water, or foods, or contact with contaminated surfaces.

Food Chain Bioaccumulation. The bioconcentration factor of MBOCA has been estimated to be 5.75 in aquatic organisms (HSDB 1991). In addition, it has been shown that MBOCA binds to and penetrates the roots of plants grown in contaminated soil and is not easily removed by rinsing. However, MBOCA stays very close to the root surface and is not distributed throughout the plant, and the roots bioaccumulate the chemical (Voorman and Penner 1986b). This information suggests that there is a potential for food chain bioaccumulation both from aquatic organisms and the root systems of terrestrial plants. Actual data on the potential for aquatic organisms to bioaccumulate MBOCA would be useful in determining potential food chain concentrations.

Exposure Levels in Environmental Media. Some information exists on levels of MBOCA found in the workplace and the ENVIRONMENT around facilities that manufacture or use MBOCA (Keeslar 1986; Parris et al. 1980). Further information on atmospheric levels of MBOCA in areas other than the workplace would be helpful for estimating general population exposure.

Reliable monitoring data for the levels of MBOCA at hazardous waste sites are also needed. The

information collected on levels of MBOCA in the ENVIRONMENT could be combined with the information on body burden to assess the potential risk of adverse health effects in populations living near hazardous waste sites.

Exposure Levels in Humans. Certain population groups are known to have a higher risk of exposure to MBOCA than others. The highest exposures are found in workers at manufacturing facilities that use MBOCA in the production of polyurethane plastics (Clapp et al. 1991; Ichikawa et al. 1990; Schulte et al. 1988; Ward et al. 1987). The next highest levels are found in populations that live near facilities where uncontrolled MBOCA releases occur (Keeslar 1986). Specific information on where such releases occur, on the populations living near such facilities, and on the levels to which they may be exposed was not found. This information is needed to assess whether health studies on these populations need to be conducted.

Exposure Registries. No exposure registries for MBOCA 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 subregistries to be established. 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.

5.7.2 On-going Studies

The NIOSH is conducting a long-term study of former MBOCA workers in Adrian, Michigan. The health of the workers will be followed for 10-15 years to help assess the risk of MBOCA as a potential human carcinogen (FEDRIP 1991; Keeslar 1986).