

5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Hydrazine and 1,1-dimethylhydrazine are industrial chemicals that enter the environment primarily by emissions from their use as aerospace fuels and from industrial facilities that manufacture, process, or use these chemicals. Treatment and disposal of wastes containing these chemicals also contribute to environmental concentrations. These chemicals may volatilize to the atmosphere from other media and may sorb to soils. These chemicals degrade rapidly in most environmental media. Oxidation is the dominant fate process, but biodegradation occurs in both water and soil at low contaminant concentrations. The half-lives in air range from less than 10 minutes to several hours, depending on ozone and hydroxyl radical concentrations. Half-lives in other media range up to several weeks, under various environmental conditions. Bioconcentration does occur, but biomagnification through the food chain is unlikely.

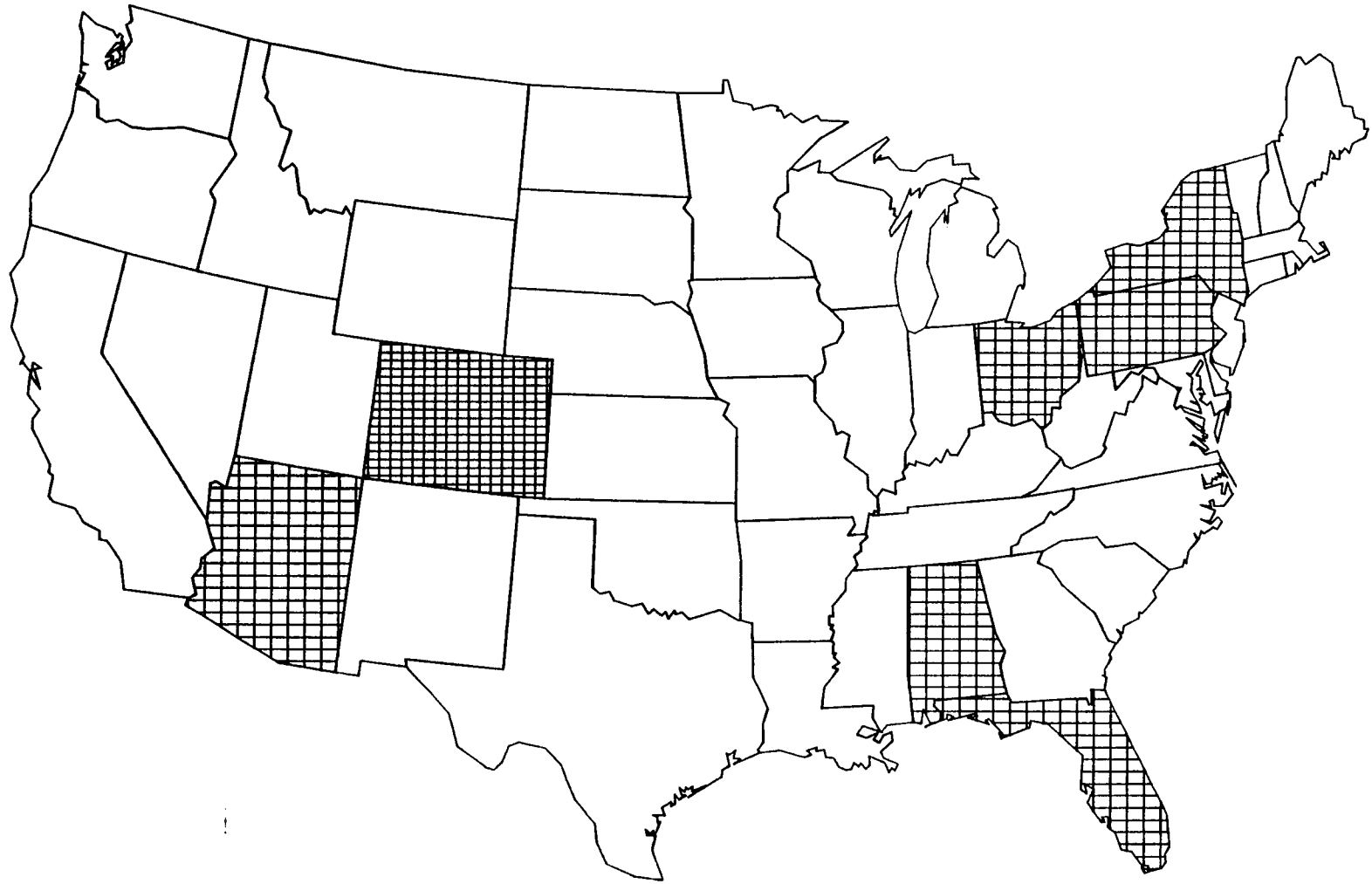
Human exposure to hydrazine and 1,1-dimethylhydrazine is mainly in the workplace or in the vicinity of aerospace or industrial facilities or hazardous waste sites where contamination has been detected. These chemicals have not been detected in ambient air, water, or soil. Humans may also be exposed to small amounts of these chemicals by using tobacco products.



Hydrazine has been found in at least 4 of the 1,430 current or former EPA National Priorities List (NPL) hazardous waste sites (HazDat 1996). 1,1-Dimethylhydrazine and 1,2-dimethylhydrazine have been identified in at least 3 and 1 of these sites, respectively. However, the number of sites evaluated for these chemicals 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

Hydrazine occurs naturally as a product of nitrogen fixation by some algae and in tobacco and tobacco smoke (IARC 1974). However, the major environmental sources of hydrazine are anthropogenic. There are no known natural sources of dimethylhydrazines. The estimated total annual environmental release of hydrazine and 1,1-dimethylhydrazine from manufacture and processing reported to the

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



FREQUENCY  1 SITE  2 SITES
*Derived from HazDat 1995

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TRI were about 30,000 and 4,000 pounds, respectively, in 1988 (EPA 1991d). However, more recent data reported to the TRI indicate that environmental releases from manufacture and use of these chemicals total about 17,000 and 200 pounds, respectively (TRI93 1995). 1,1-Dimethylhydrazine may also be released to the environment from the application of daminozide (Alar®), a growth enhancer which contains about 0.005% 1,1-dimethylhydrazine as a contaminant to nonfood plants (EPA 1992c).

5.2.1 Air

The major sources of hydrazine releases to air are expected to be from its use as an aerospace propellant and boiler water treatment agent (HSDB 1995). However, hydrazine released as a boiler water treatment agent is present only briefly since it would oxidize rapidly in water (HSDB 1995). Burning of rocket fuels containing hydrazine and/or 1,1-dimethylhydrazine reportedly produces exhaust gases containing trace amounts of unchanged fuel (IARC 1974). Emissions are also expected from the production and processing of hydrazine (EPA 1991d; WHO 1987). It has been estimated, based on data from Germany, that 0.06-0.08 kg of hydrazine are emitted to the air for every metric ton produced, and an additional 0.02-0.03 kg are emitted for every metric ton subjected to handling and further processing (WHO 1987). On this basis, assuming production volume of about 14,000 metric tons (30 million pounds) (see Section 4.1) and handling or processing of the product, emissions to the air may range from 1,100 to 1,500 kg (500-680 pounds) annually. Atmospheric releases of hydrazine may also occur from tobacco smoking (see Section 5.4.4) and from hazardous waste sites at which this chemical has been detected (HSDB 1995; WHO 1987).

Release of 1,1 dimethylhydrazine to the atmosphere is expected to occur primarily from its use as an aerospace propellant (HSDB 1995). Release of this chemical and 1,2-dimethylhydrazine may also occur from hazardous waste sites at which they have been detected.

As shown in Tables 5-1 and 5-2, an estimated total of 16,452 pounds of hydrazine and 194 pounds of 1,1-dimethylhydrazine, amounting to about 95% and 100% of the total environmental releases, respectively, were discharged to the air from manufacturing and processing facilities in the United States in 1993 (TRI93 1995). The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list.

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

State ^a	City	Facility	Reported amounts released in pounds per year						
			Air	Water	Land	Underground injection	Total environment ^b	POTW transfer	Off-site waste transfer
AL	MUSCLE SHOALS	OCCIDENTAL CHEMICAL CORP.	75	33			108		
AL	ARAB	HALL CHEMICAL CO.	250				250		
AL	MCINTOSH	OLIN CORP.	6				6		
AR	EL DORADO	GREAT LAKES CHEMICAL CORP.	24				24		
AR	EL DORADO	GREAT LAKES CHEMICAL CORP.	18				18		
AZ	NA	NA							
CA	CARSON	DEEPWATER IODIDES INC.	5				5		
CA	SACRAMENTO	AEROJET SACRAMENTO OPS.	9				9		2,874
GA	BRUNSWICK	HERCULES INC.	30				30		
IL	WOOD RIVER	AMOCO	19				19	1,400	
IL	NA	3M							
IL	ROCKFORD	SUNDSTRAND AEROSPACE	500				500		
KS	PITTSBURG	ALLIED-SIGNAL INC.	15				15		
KY	MURRAY	VANDERBILT CHEMICAL CORP.	1				1		
LA	GEISMAR	UNIROYAL CHEMICAL CO. INC.	222				222		
LA	WESTLAKE	OLIN CORP.	690				690		2,802
LA	NORCO	SHELL OIL PRODS.	933				933		4,500
MA	NA	NA							
MA	WILMINGTON	ZENECA RESINS	1				1		491

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Table 5-1. Releases to the Environment from Facilities That Manufacture or Process Hydrazine (continued)

State ^a	City	Facility	Reported amounts released in pounds per year							
			Air	Water	Land	Underground injection	Total environment ^b	POTW transfer	Off-site waste transfer	
MA	LEOMINSTER	BF GOODRICH	332					332		
MO	KANSAS CITY	BAYER CORP.	439	1				440		
NJ	NEWARK	FAIRMOUNT CHEMICAL CO. INC.	2,500					2,500		
NJ	WEST DEPTFORD	JOHNSON MATTHEY INC.	5					5		
NJ	SOUTH PLAINFIELD	DEGUSSA CORP.	1,360					1,360		
NJ	NA	E. I. DU PONT DE NEMOURS & CO.								
NY	NORWICH	PROCTER & GAMBLE	130					130		
NY	ROCHESTER	OLIN CORP.	161					161	3	
OH	WICKLIFFE	HALL CHEMICAL CO.	5					5		
OH	PAINESVILLE	LUBRIZOL CORP.	50					50		
OH	AVON LAKE	BF GOODRICH	3					3		
OK	TULSA	DOWELL	5					5		
		SCHLUMBERGER INC.								
PR	PONCE	BILCHEM LTD.	255					255		
TN	NEWPORT	GREAT LAKES CHEMICAL CORP.	1					1		
TN	NA	NA								
TN	MEMPHIS	DREXEL CHEMICAL CO.	10		5			15	5	
TX	BAYTOWN	MILES INC.	500	750				1,250		92,000
TX	NA	PHELPS DODGE CORP.								
TX	PASADENA	LUBRIZOL CORP.	6,131					6,131		3,617
TX	NA	HOECHST-CELANESE CHEMICAL GROUP								
TX	DEER PARK	SHELL OIL CO.	914					914		

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Table 5-1. Releases to the Environment from Facilities That Manufacture or Process Hydrazine (continued)

State ^a	City	Facility	Reported amounts released in pounds per year						
			Air	Water	Land	Underground injection	Total environment ^b	POTW transfer	Off-site waste transfer
TX	HOUSTON	ASHLAND CHEMICAL CO.	31				31		27
TX	BEAUMONT	MOBIL OIL BEAUMONT REFINERY	14				14		
VA	ELKTON	MERCK & CO. INC.	50				50		
WI	MARINETTE	SPECIALTYCHEM PRODS. CORP.	1				1		
WV	NEW MARTINSVILLE	BAYER CORP.	757				757		
Totals			16,452	784	5		17,241	1,408	106,311

Source: TRI93 1995

^a Post office state abbreviations used

^b The sum of all releases of the chemical to air, land, water, and underground injection wells by a given facility

NA = not available; POTW = publicly owned treatment works

Table 5-2. Releases to the Environment from Facilities That Manufacture or Process 1,1-Dimethylhydrazine

State ^a	City	Facility	Reported amounts released in pounds per year							
			Air	Water	Land	Underground injection	Total environment ^b	POTW transfer	Off-site waste transfer	
AL	NA	OLIN CORP.								
CA	SACRAMENTO	AEROJET SACRAMENTO OPS.	65					65		2,851
LA	GEISMAR	UNIROYAL CHEMICAL CO. INC.	104					104		
LA	WESTLAKE	OLIN CORP.	25					25		74
Totals			194					194		2,925

Source: TRI93 1995

^a Post office state abbreviations used

^b The sum of all releases of the chemical to air, land, water, and underground injection wells by a given facility

NA = not available; POTW = publicly owned treatment works

5.2.2 Water

Releases of hydrazine and 1,1-dimethylhydrazine to water may occur during production, processing, use, or disposal of the chemical. Hydrazine was detected at a concentration of 0.01 µg/L in effluent from one industrial facility (EPA 1984b). However, since these chemicals are rapidly oxidized in water (see Section 5.3.2.2), the unreacted compounds are not likely to persist in detectable concentrations.

As shown in Tables 5-1 and 5-2, an estimated total of 784 pounds of hydrazine amounting to about 4.5% of the total environmental releases and no 1,1-dimethylhydrazine were discharged to surface water from manufacturing and processing facilities in the United States in 1993 (TRI93 1995). An additional 423 pounds of hydrazine (1% of the total) were discharged by underground injection. The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list.

5.2.3 Soil

No data were located documenting release of hydrazine or dimethylhydrazines to soil. However, releases to soil may occur from spills and leakage of underground storage tanks during the use of hydrazine and 1,1-dimethylhydrazine as rocket propellants (Street and Moliner 1988). Deposition from air is not expected to be significant (see Section 5.3.1). Hydrazine and dimethylhydrazines may be released to soil from hazardous waste sites at which these chemicals have been detected.

1,1-Dimethylhydrazine may also be released to soil from the application of daminozide (Alar®) as a growth enhancer on nonfood plants. The use of this chemical on food products was voluntarily cancelled in 1989 by the manufacturer (Uniroyal Chemical Company) (EPA 1992c). Daminozide contains about 0.005% 1,1-dimethylhydrazine as an impurity and about 0.012% of a daminozide solution that hydrolyzes to 1,1-dimethylhydrazine after 24 hours (EPA 1992c). No data were located on the amount of daminozide used annually, but it is estimated that, in 1989, 90% of potted chrysanthemums and 40-50% of 65 million square feet of bedding plants were treated with this chemical.

As shown in Tables 5-1 and 5-2, 5 pounds of hydrazine (<0.1% of the total environmental release) and no 1,1-dimethylhydrazine were reported discharged to land from manufacturing and processing facilities in the United States in 1993 (TRI93 1995). The data listed in the TRI should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list.

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

Hydrazine or dimethylhydrazines released to water or soil may volatilize into air or sorb onto soil. These chemicals have low vapor pressures and are miscible in water (see Table 3-2). Therefore, volatilization is not expected to be an important removal process. Reported evaporation rates from aqueous solutions under laboratory conditions were 0.49 mg/cm² minute for hydrazine and 13 mg/cm² minute for 1,1-dimethylhydrazine (EPA 1984a). The significance of these values to environmental conditions is unknown. Data from other studies indicate that volatilization of these chemicals from water increases with higher concentrations of the chemical and in the presence of sunlight (due to increased temperature of the hydrazine pool). Based on air dispersion modeling, volatilization of hydrazine from surface soil following a spill is expected to be sufficient (16-100 mg/cm² hour) to generate a short-term ambient air concentration of 4 mg/m³ up to 2 km downwind of the spill under worst-case meteorological conditions (MacNaughton et al. 1981). Degradation of hydrazine would likely reduce the concentration within several hours (see Section 5.3.2.1).

Atmospheric transport of hydrazine or dimethylhydrazines may occur, but transport will be limited by the high reactivity of the chemicals in the atmosphere (see Section 5.3.2.1). No data were located on deposition of hydrazine or dimethylhydrazines from air to water or soil, but deposition would also be limited by their high reactivity.

Hydrazine undergoes complex interactions with soils, including both reversible physical-sorption and irreversible chemisorption to colloids (Mansell et al. 1988). In a study on the adsorption and leaching characteristics of hydrazine fuels, no adsorption of 1,1-dimethylhydrazine was observed on sand, with almost 100% of the chemical leaching with water (Braun and Zirrolli 1983). In three other soils, adsorption ranged from 26% to 80%. No correlation between adsorption and soil organic content or pH was observed. The mechanisms of attenuation in soil materials were not reported. However,

reported results of additional hydrazine adsorption studies with clays and soils indicate that adsorption may be correlated with soil organic matter and clay content and is highly dependent on pH; hydrazine appears to be adsorbed by different mechanisms under acidic and alkaline conditions (Moliner and Street 1989b).

In a study of hydrazine in aqueous systems, the chemical was reported to be absorbed by guppies from a 0.5 µg/L solution (Slonim and Gisclard 1976). After 96 hours, the hydrazine concentration in fish was 144 µg/g, indicating a moderate tendency to bioconcentrate. However, the bioconcentration of hydrazine and dimethylhydrazines is not expected to be important in aquatic systems because of the rapid degradation of these chemicals in water (see Section 5.3.2.2) as well as their low octanol-water partition coefficients.

5.3.2 Transformation and Degradation

5.3.2.1 Air

Hydrazine and dimethylhydrazines degrade rapidly in air through reactions with ozone, hydroxyl (OH) radicals, and nitrogen dioxide (WHO 1987). The reaction of hydrazine and 1,1-dimethylhydrazine with ozone is probably the major fate of these chemicals in the atmosphere. The reaction rate constant for hydrazine, derived from its decay rate in the presence of excess ozone, was about $3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and for 1,1-dimethylhydrazine the rate was greater than $1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Carter 1984). Major reaction products were hydrogen peroxide for the hydrazine reaction and dimethylnitrosamine (about 60%) for the 1,1-dimethylhydrazine reaction. Estimated atmospheric half-lives ranged from less than 10 minutes for hydrazine during an ozone pollution episode to less than 2 hours under usual conditions, with a half-life about one-tenth that time for 1,1-dimethylhydrazine (Tuazon et al. 1981). Reported results of additional studies indicate a reaction rate constant for hydrazine of $2.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, resulting in an estimated half-life of less than 1 minute (Stone 1989). -.

The reported measured rate constant for reaction of hydrazine with atmospheric hydroxyl (OH) radicals producing ammonia and nitrogen gas was $6.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Harris et al. 1979). The rate constant for 1,1-dimethylhydrazine was not measured since the chemical decomposed rapidly in the test system, but the value was estimated at $5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Assuming an average OH radical

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concentration of about 10^6 molecule/cm³, the tropospheric half-lives of both chemicals due to reaction with OH were estimated to be about 3 hours. The half-lives are expected to range from less than 1 hour in polluted urban air to 3-6 hours in less polluted atmospheres (Tuazon et al. 1981).

Hydrazine and 1,1-dimethylhydrazine react rapidly with nitrogen oxides in both the light and dark, with a half-life of about 2 hours for hydrazine and less than 10 minutes for 1,1-dimethylhydrazine (Pitts et al. 1980).

Hydrazine and 1,1-dimethylhydrazine may also be removed from the atmosphere by autoxidation. In a dark reaction chamber, the approximate half-lives of hydrazine ranged from 1.8 to 5 hours, with the lower value measured at higher humidity. Reported values for 1,1 dimethylhydrazine under similar conditions were 5.9-9 hours. Surface interactions are important in controlling the rates of these reactions (Stone 1989).

Although data were not located for 1,2-dimethylhydrazine, this chemical is expected to be degraded in the atmosphere by undergoing the same reactions as hydrazine and 1,1-dimethylhydrazine, although the rate and extent of degradation may be different.

5.3.2.2 Water

Hydrazine and 1,1-dimethylhydrazine degrade in aqueous systems, but the rate of degradation is dependent on specific aquatic environmental factors, including pH, hardness, temperature, oxygen concentration, and the presence of organic matter and metal ions (Moliner and Street 1989a; Slonim and Gisclard 1976; WHO 1987). Oxidation and biodegradation are the primary removal mechanisms. Reaction of hydrazine with dissolved oxygen is catalyzed by metal ions, particularly copper (EPA 1984a). The reaction rate is strongly influenced by pH; degradation proceeds more rapidly in alkaline solutions. Hydrazine is rapidly removed from polluted waters, with less than one-third of the original concentration remaining in dirty river water after 2 hours (Slonim and Gisclard 1976). More than 90% of the hydrazine added to pond or chlorinated, filtered county water disappeared after 1 day. However, chlorinated, filtered, and softened city water contained almost the original amount of hydrazine after 4 days. Organic matter in the water and hardness were reported to be the major factors in the differing rates of degradation.

The primary reaction pathway for hydrazine degradation in water produces nitrogen gas and water (Moliner and Street 1989a). In oxygen-deficient waters or in the presence of metal ions which serve as catalysts, ammonia may also be produced.

The reaction of 1,1-dimethylhydrazine with dissolved oxygen in water may proceed by a process catalyzed by copper ions or by an uncatalyzed reaction (Banerjee et al. 1984). The products include dimethylnitrosamine, formaldehyde, dimethylamine, and other related chemicals. Dimethylnitrosamine did not form in dilute solutions, which might be encountered in ambient waters, but was reported in concentrated solutions, which could be present in the vicinity of spills (EPA 1984a). The reported half-life of 1,1-dimethylhydrazine in ponds and seawaters ranged from 10 to 14 days, presumably because of reaction with oxygen and other free radicals (EPA 1984a).

Biodegradation may be a significant removal process at low hydrazine concentrations in ambient waters, but at higher concentrations the chemical is toxic to microorganisms. In the presence of bacterial cells, more than 90% of the hydrazine was degraded in six water samples containing 11 µg/mL of the chemical within 2 hours (Ou and Street 1987b). Lower degradation rates were reported with increasing hydrazine concentrations. No degradation was reported for incubation of these waters without bacteria. Additional studies indicate that hydrazine and 1,1-dimethylhydrazine are toxic to bacterial populations. Concentrations of hydrazine and 1,1-dimethylhydrazine that reduced bacterial metabolism by 50% ranged from 14.6 to 145 mg/L and from 19.2 to 9,060 mg/L, respectively (Kane and Williamson 1983). Thus, biological treatment would not be useful for spills of these chemicals into the aquatic environment.

5.3.2.3 Sediment and Soil

Hydrazine appears to degrade more rapidly in soil than in water, with oxidation and biodegradation as the main removal processes. Hydrazine applied to nonsterile Arredondo soil (fine sand) at concentrations of 10, 100, and 500 µg/g was completely degraded in 1.5 hours, 1 day, and 8 days, respectively (Ou and Street 1987a). In this study, comparison to degradation rates in sterile soils indicated that autoxidation appeared to be the major factor contributing to disappearance of the chemical, but the study authors attributed about 20% of removal to biodegradation. Several heterotrophic soil bacteria were reported to degrade hydrazine, indicating that microbial degradation may contribute to removal of the chemical from soil (Ou 1987).

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1 Air

No monitoring data were located for hydrazine or dimethylhydrazines in ambient air. Since these chemicals are readily degraded in the atmosphere (see Section 5.3.2.1), they are not expected to be present measurable levels, except in the vicinity of production or processing facilities or spills.

5.4.2 Water

No monitoring data were located for hydrazine or dimethylhydrazines in ambient water. Since these chemicals are readily degraded in aquatic systems (see Section 5.3.2.2), they are not expected to be present at measurable levels, except in the vicinity of production or processing facilities, spills, or possibly, hazardous waste sites.

5.4.3 Sediment and Soil

No data were located documenting hydrazine or dimethylhydrazine concentrations in ambient soil or sediments. Since these chemicals are readily degraded in soil (see Section 5.3.2.3), they are not expected to be present at measurable levels, except in the vicinity of production or processing facilities, spills, or hazardous waste sites.

5.4.4 Other Environmental Media

Hydrazine and 1,1-dimethylhydrazine have been detected in tobacco. 1,1-Dimethylhydrazine was reported at concentrations ranging from not detected to 147 ng/g in various types of tobacco in the United States (Schmeltz et al. 1977). Mainstream smoke from blended U.S. cigarettes contained an average of 31.5 ng of hydrazine per cigarette (Liu et al. 1974). Sidestream smoke may have higher hydrazine concentrations. The authors reported 94.2 ng of hydrazine in sidestream smoke from one cigarette. Although hydrazine may be an impurity in maleic hydrazide, a pesticide formerly used on tobacco plants, reports on studies of tobacco from both treated and untreated plants indicate that the application of maleic hydrazide is not the major source of hydrazine in tobacco. It has been suggested

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that these chemicals may be produced in tobacco by bacterial or enzymatic processes which occur during curing (Schmeltz et al. 1977).

1,1-Dimethylhydrazine has been detected in several food products because of its presence as an impurity (about 0.005%) in daminozide (Alar)[®], a plant growth enhancer. 1,1-Dimethylhydrazine was detected in several processed fruits at maximum levels ranging from 0.007 to 0.60 ppm (Saxton et al. 1989). The fruits had been treated with, and contained residues of, daminozide. It appears that during thermal processing, some of the daminozide degrades to 1,1-dimethylhydrazine, adding to the quantity of 1,1-dimethylhydrazine already present. However, daminozide is no longer used on food plants in the United States since its registered uses for food products were voluntarily cancelled in 1989 (EPA 1992c). Therefore, 1,1-dimethylhydrazine is no longer expected to be present in foods prepared from food plants grown in the United States.

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Exposure of the general population to hydrazine and dimethylhydrazines is expected to be extremely low (WHO 1987). Because of the high reactivity of these chemicals, they are unlikely to remain in environmental media for extended periods. These chemicals have not been detected in ambient air, water, or soil.

Occupational exposures to hydrazine and 1,1-dimethylhydrazine may occur in facilities that manufacture, process, transport, or use these chemicals. The National Institute for Occupational Safety and Health (NIOSH) conducted a National Occupational Exposure Survey (NOES) during 1981-1983 and estimated that 59,675 and 2,197 workers were potentially exposed to hydrazine and 1,1-dimethylhydrazine, respectively, at that time (EPA 1991d). Since most hydrazine production processes involve closed systems, the potential for exposure is generally low (Fajen and McCammon 1988). The greatest potential for exposure probably occurs during process stream sampling, with measured time-weighted average (TWA) concentrations ranging from 0.04 to 0.27 ppm and excursions up to 0.91 ppm. Workplace breathing zone air levels of hydrazine and 1,1-dimethylhydrazine ranged from 0.22 to 1.98 ppm and from 0.23 to 4.61 ppm, respectively, in a rocket propellant plant (Cook et al. 1979). Workers in facilities where exposure to these chemicals is possible are required to wear protective respirators. Analysis of samples from within the respirators indicated that these chemicals

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are not usually present at detectable levels. Thus, routine exposure to these levels is not expected, but respirator failures and other accidental exposures may occur.

Occupational exposures may also occur to military and civilian personnel during the use of these chemicals as aerospace propellants. Exposure to workers may occur during loading or unloading of propellants, transfer operations, or testing of spacecraft components that use hydrazine fuels (Fajen and McCammon 1988). Although full-body supplied-air suits are usually worn during these operations, spills and other accidents may lead to short-term, high-level exposures, rather than longer-term, lowlevel exposures.

Exposure may also result from the use of hydrazine as an oxygen scavenger in boiler systems (Fajen and McCammon 1988). Long-term concentrations in areas where hydrazine was added to the boiler systems were generally below 0.1 ppm, but short-term concentrations ranged up to 0.23 ppm. In addition, those individuals who work as daminozide applicators in greenhouses may be exposed to 1,1-dimethylhydrazine (EPA 1992c).

5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Populations with potential exposures to hydrazines above ambient levels include those exposed occupationally (see Section 5.5), such as during the manufacture or agricultural application of hydrazines, people living or working near military or aerospace installations using these chemicals as fuels, or people living near hazardous waste sites where these chemicals have been detected. Others who may be exposed to these chemicals at above ambient levels include individuals who chew or smoke tobacco and those exposed to sidestream smoke (see Section 5.4.4). Furthermore, hydrazine is a metabolite of several drugs (e.g., hydralazine, isoniazid), and it has been suggested that individuals taking these drugs may be exposed to hydrazine, based on the detection of hydrazine in the urine of patients taking hydralazine (Timbrell and Harland 1979) and the blood plasma of patients taking isoniazid (Blair et al. 1985).

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

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adequate information on the health effects of hydrazines 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 hydrazines.

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 hydrazine and dimethylhydrazines are sufficiently well characterized to allow estimation of their environmental fate (see Table 3-2) (HSDB 1993; IARC 1975; Verschueren 1983). On this basis, it does not appear that further research in this area is required.

Production, Import/Export, Use, Release, and Disposal. Hydrazine is produced at one facility and 1,1-dimethylhydrazine is produced at two locations (SRI 1992). However, production volume and import and export information are not available. This information would be useful in assessing potential exposure to workers and the general population. Since 1,2-dimethylhydrazine is produced only in gram quantities for research, additional information is not required.

According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit substance release and off-site transfer information to the EPA. The Toxics Release Inventory (TRI), which contains this information for 1993, became available in May of 1995. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

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Environmental Fate. The environmental fate of hydrazine and 1,1-dimethylhydrazine has been well defined (Atkinson and Carter 1984; EPA 1984a; Moliner and Street 1989a, 1989b; Ou and Street 1987a, 1987b; Stone 1989; WHO 1987). These chemicals are highly reactive and degrade readily in environmental media. Thus, they are not likely to be present in air or water and it is not likely that exposure to the general population is of concern. Nevertheless, because these chemicals may migrate to groundwater, additional studies might be useful to assess the potential for transport of these chemicals from hazardous waste sites and their fate in closed water systems such as groundwater.

Bioavailability from Environmental Media. Hydrazine is known to be absorbed following inhalation (Llewellyn et al. 1986), oral (dissolved in water) (Preece et al. 1992a), and dermal (Smith and Clark 1971, 1972) exposures. Little is known about the absorption of 1,1-dimethylhydrazine and 1,2-dimethylhydrazine, but based on their chemical properties, the absorption is most likely similar to that of hydrazine. No information was located on the bioavailability of hydrazine or dimethylhydrazines from environmental media. This information would be helpful in evaluating the impact of environmental exposures on human health.

Food Chain Bioaccumulation. Hydrazine in water may bioconcentrate in aquatic organisms to a moderate degree (Slonim and Gisclard 1976), but because of its high reactivity, the chemical is rapidly degraded in aquatic systems. This property, as well as the low octanol-water partition coefficient of hydrazine, makes food chain bioaccumulation unlikely.

Exposure Levels in Environmental Media. Hydrazine and dimethylhydrazines have not been detected in ambient air, water, or soil, since they are highly reactive and degrade readily in environmental media. Hydrazine and 1,1-dimethylhydrazine have been detected in workplace air and in tobacco (Cook et al. 1979; Schmeltz et al. 1977). Since these chemicals are highly reactive and exposure of the general population is not expected to be of concern, monitoring of ambient environmental media does not appear to be required. However, monitoring of workplace air would help to determine potential sources and magnitude of exposure.

Exposure Levels in Humans. Hydrazine and dimethylhydrazines have not been detected in human tissues as a result of exposure to these chemicals from environmental media. Hydrazine has been detected in the urine of individuals taking medication (hydralazine) which may metabolize to hydrazine (Timbrell and Harland 1979). Since hydrazine and dimethylhydrazines are rapidly

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metabolized *in vivo*, it is unlikely that any free chemical would be present in biological tissues within a few days after environmental exposure. Studies that investigate the levels of hydrazines in humans within the first few days after exposure, along with their relationship to exposure levels, would be useful. This information is necessary for assessing the need to conduct health studies on these populations.

Exposure Registries. No exposure registries for hydrazines were located. These substances are not currently in a subregistry of the National Exposure Registry. These substances 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 these substances.

5.7.2 On-going Studies

No information was located regarding on-going studies on the environmental fate or exposure levels of hydrazine or dimethylhydrazines.