

5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Because bromomethane is a gas under ordinary conditions, humans are most likely to be exposed to bromomethane in air. Low levels can be detected in air around the globe, perhaps originating from natural sources in the ocean. Somewhat higher levels occur in urban environments, due to release from industrial point sources and from use of leaded gasoline. Extremely high levels may be encountered in air where bromomethane is being used for fumigation. Trace levels have been detected in some groundwater samples, but levels in surface water and food are usually negligible. Bromomethane may also be generated in drinking water as the result of chlorination, but this has not yet been quantified.

Bromomethane in air is quite stable, undergoing breakdown by reaction with hydroxyl radicals with a half-life of about 11 months. Bromomethane in other media (water, soil) volatilizes sufficiently rapidly that breakdown in these media (via hydrolysis or reaction with organic components) is usually minor.

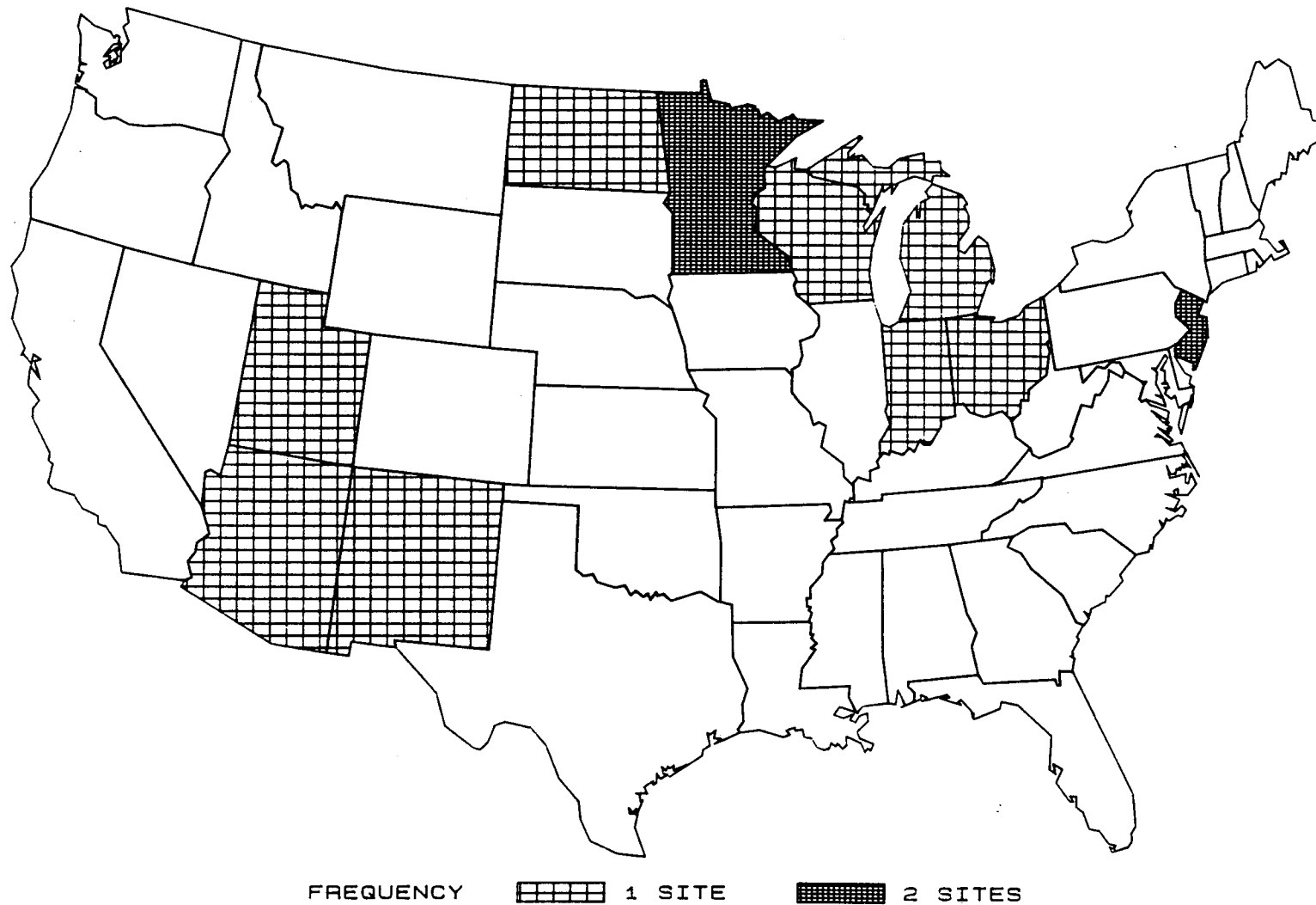
The EPA has identified 1,177 NPL sites. Bromomethane has been found at 12 of the sites evaluated for the presence of this chemical (View 1989). However, we do not know how many of the 1,177 sites have been evaluated for bromomethane. As more sites are evaluated by the EPA, the number may change. The frequency of sites where bromomethane has been found within the United States can be seen in Figure 5-1.

5.2 RELEASES TO THE ENVIRONMENT

5.2.1 Air

Since bromomethane is highly volatile, nearly all environmental releases of bromomethane are into the-air. The most important anthropogenic releases are from fumigation activities, since bromomethane is simply dispersed into the air after fumigation is completed. Based on current estimates that about 80% of bromomethane production is used for fumigation (65% for soil fumigation and 15% for space fumigation), and assuming that nearly all of this is ultimately released to air, approximately 34 million pounds/year may be released to air by this practice (HSDB 1989; IARC 1986). Air releases may also occur in association with industrial production and processing of bromomethane, as shown in Table 5-1 (TRI 1989). Based on the data reported, total releases to air from industrial activities in the United States were 1.3 million pounds in 1987. However, the quality of the TRI data must be viewed with caution since the 1987 data represent first-time, incomplete reporting of estimated releases by these facilities. Not all sources of chemical wastes are included, and not all facilities that should have reported have done so.

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



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* Derived from View 1989

TABLE 5-1. Releases to the Environment from Facilities
That Manufacture or Process Bromomethane^a

Facility	Location	Total (lbs)						
		Air	Underground injection	Water	Land	Environment	POTW ^b transfer	Off-site transfer
Amoco Chemical Company	Decatur, AL	131,000	0	0	0	131,000	0	0
Great Lakes Chemical Co. El Dorado-Main Plant	El Dorado, AR	621,000	2,200	0	0	623,200	0	3,080
Gerber Products Company Ethyl Corporation	Fort Smith, AR Magnolia, AR Hollister, CA	20,000 83,000 250	No Data 0 0	No Data 0 0	0 0 0	20,000 83,000 250	0 0 0	0 0 0
Asgrow Florida Company	Belle Glade, FL	1,850	0	0	0	1,850	0	0
Hms Chemicals Inc	Palmetto, FL	250	0	0	0	250	0	0
Florida Fertilizer Co. Inc.	Wauchula, FL	357	0	0	0	357	0	0
Hercules-Brunswick Plant	Brunswick, GA	72,900	0	0	0	72,900	0	0
Borden, Inc. Grocery & Specialty Products	Lowell, MA	18,200	No Data	0	0	18,200	No Data	No Data
Borden, Inc. Grocery & Specialty Prds.	Warren, MI	14,200	No Data	0	0	14,200	No Data	0
Mobay Corporation - Agricultural Chemicals Div.	Kansas City, MO	11,500	0	0	0	11,500	0	0
Comet Delta, Inc.	Greenville, MS	21,300	0	0	0	21,300	0	0
Coastal Chemical Corporation	Greenville, NC	29	0	0	0	29	0	0
The Pillsbury Company	Buffalo, NY	12,000	No Data	0	0	12,000	0	No Data
Hershey Chocolate U.s.a. Hershey Plant	Hershey, PA	40,879	0	0	0	40,879	0	No Data
Consolidated Cigar Corp.	Cayey, PR	7,140	0	0	0	7,140	0	0
Amoco Chemical Company Cooper River	Wando, SC	220,000	0	0	0	220,000	0	0
Cargill Flour Milling	Saginaw, TX	30,000	0	0	0	30,000	0	0
Totals		1,305,855	2,200	0	0	1,308,055	0	3,080

^aDerived from TRI 1989.

^bPOTW -- publicly-owned treatment works.

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The ocean is another important source of bromomethane release to air. It seems likely that this is the result of bromomethane production by marine organisms, but the exact source is not known (IARC 1986). Singh et al. (1983b) calculated that the amount released from the ocean was large enough to account for most bromomethane in the atmosphere, but Penkett et al. (1985) showed that anthropogenic releases were the most important source. This is supported by the observation that atmospheric levels are about 40% higher in the northern hemisphere (0.015-0.026 ppb) than the southern hemisphere (0.011-0.019 ppb) (Penkett et al. 1985; Singh et al. 1983b).

Use of bromine-containing additives (ethylene dibromide) in leaded gasoline results in the release of bromomethane in exhaust fumes (about 70-220 $\mu\text{g}/\text{m}^3$ of exhaust) (Harsch and Rasmussen 1977), and this may have been a significant source of bromomethane release in the past. Combustion of unleaded gasoline releases much less bromomethane (about 4-5 $\mu\text{g}/\text{m}^3$), so current emissions from this source are presumably much lower than previously, and are likely to decrease further as leaded gasoline continues to be phased out.

5.2.2 Water

Because of its volatility, very little bromomethane is released to water. As shown in Table 5-1, no surface water releases were reported in the United States from industrial producers or processors of bromomethane (TRI 1989), although in one case about 2,000 pounds of bromomethane was released to groundwater through underground injection. Some bromomethane may leach from fumigated soil into surface water (EPA 1986b; IARC 1986). Most of this would be expected to quickly volatilize into air (see Section 5.3.1.), although some could migrate downward into groundwater where evaporation is not significant.

Bromomethane has not been detected in surface waters near any of 405 waste sites (including 99 NPL sites) where it was investigated, but it was detected in six groundwater samples from two locations (both NPL sites) (CLPSD 1989). The geometric mean of six samples from these two sites was 17 $\mu\text{g}/\text{L}$.

5.2.3 Soil

Soil fumigation is the primary use of bromomethane in the United States, accounting for approximately 65% of total consumption (EPA 1989c; IARC 1986). Based on reported production for 1984 (43 million pounds), this would be about 28 million pounds/year. However, as discussed in Section 5.3.1, most bromomethane will tend to evaporate from the soil within 1-2 days, so soil contamination is normally not persistent. No industrial releases of bromomethane to soil were reported for 1987 (TRI 1989; see Table 5-1), and bromomethane has not been detected in soils or sediments at 455 hazardous waste sites, including 99 NPL sites (CLPSD 1989).

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5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

Bromomethane is a readily volatile compound, with a boiling point of 3.6°C (Windholz 1983) and a vapor pressure at 20°C of 1,420 mmHg (Mabey et al. 1982). Consequently, bromomethane has a strong tendency to volatilize into air from other media (soil, water).

Because bromomethane is quite soluble in water (approximately 13-18 g/L) (EPA 1986b), some bromomethane in air may partition into clouds, rain, or surface waters. This tendency is described by the Henry's law constant (H), which for bromomethane has a value of 0.2 atm·m³/mole (Mabey et al. 1982). This value is sufficiently large to indicate that partitioning of bromomethane from air into water will be quite small. Conversely, the rate of bromomethane volatilization from water into air will be quite high, depending on mixing, temperature, and depth. The measured rate constant for volatilization is 22.5 cm/hr, which corresponds to a volatilization half-life of 3.1 hours for water 1 meter deep (Lyman et al. 1982). Half-lives of volatilization for lakes and deeper rivers range from 1 to 5 days (EPA 1986b). Rapid volatilization into indoor air would also be expected if contaminated water were used for showering, bathing, or cooking, but this has not been studied.

Bromomethane, either as a gas or dissolved in water, has relatively low affinity for soils. This has been established by direct observation (Brown and Rolston 1980; Chisholm and Koblitsky 1943; Fuhr et al. 1948), and is also expected on the basis of the relatively small K_{oc} (measured values range from 1 to 10) for this chemical (EPA 1986b; Roy and Griffin 1985). Volatilization of bromomethane from soil is also relatively rapid, with half-lives ranging from 0.2 to 0.5 days, depending on depth (Jury et al. 1984). Bromomethane is not expected to bioconcentrate in aquatic organisms because of its low octanol/water partition coefficient (K_{ow}) (estimated to be about 13) (Callahan et al. 1979). The bioconcentration factor (BCF) for bromomethane has not been measured experimentally. However, based on an empirical relation between the BCF and the K_{ow} (Neely et al. 1974), the estimated BCF for bromomethane is about 3. This low estimated BCF indicates that bromomethane should not significantly bioconcentrate (EPA 1986b).

5.3.2 Transformation and Degradation

5.3.2.1 Air

The main degradation pathway for bromomethane in air is reaction with photochemically-generated hydroxyl radicals. The rate constant for this reaction has been measured to be 4.14×10^{-14} cm³·molecule⁻¹·sec⁻¹ at 25°C, and 2.7×10^{-14} cm³·molecule⁻¹·sec⁻¹ at -8°C (the average temperature of the troposphere) (Davis et al. 1976). Assuming a concentration of atmospheric hydroxyl radicals of 9×10^5 molecules/cm³, this corresponds to a tropospheric half-life of about 11 months. Thus, breakdown is relatively slow, and

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bromomethane will tend to become widely dispersed in the atmosphere. Molecules that diffuse upward and reach the stratosphere may undergo direct photolytic degradation by ultraviolet radiation (Robbins 1976), but this degradation pathway accounts for only a small fraction (about 3%) of atmospheric bromomethane degradation (EPA 1986b).

5.3.2.2 Water

Bromomethane tends to undergo slow hydrolysis in water, yielding methanol, bromide ion, and hydrogen ion. The rate constant of this reaction has been measured to be about 3×10^{-7} /second at 25°C (Castro and Belser 1981), and hydrolytic half-lives may range between 20 and 38 days, depending on temperature and pH (Castro and Belser 1981; Ehrenberg et al. 1974; Mabey and Mill 1978). It should be noted that these hydrolysis half-lives are considerably longer than typical volatilization half-lives (see Section 5.3.1). Thus, most bromomethane will volatilize from water before extensive hydrolysis occurs.

5.3.2.3 Soil

The principal fate of bromomethane in soil is volatilization, but some may react with organic soil constituents to yield nonvolatile end products, including bromide ion (Brown and Rolston 1980; Goring et al. 1975; Shiroishi et al. 1964). There is little evidence that bromomethane in soil is degraded by microorganisms (EPA 1986b).

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1 Air

As shown in Table 5-2, bromomethane has been detected in air samples from regions all around the globe. Concentrations over the oceans and in rural areas are typically less than 0.025 ppb ($0.1 \mu\text{g}/\text{m}^3$), while concentrations in suburban and urban areas may range up to 1.2 ppb ($5 \mu\text{g}/\text{m}^3$). These values are all much lower than may be encountered near places where bromomethane is being used for fumigation (25 ppm or $100,000 \mu\text{g}/\text{m}^3$) (Bond and Durnas 1987).

5.4.2 Water

Bromomethane occurs in ocean waters at a concentration of about 1-2 ng/L (Lovelock 1975; Singh et al. 1983b), but is not a common contaminant in fresh waters in the United States. It was not detected in storm water runoff from 15 U.S. cities (Cole et al. 1984) or in influents to sewage treatment plants in four cities (Levins et al. 1979), and was detected in only 1.4% of over 900 surface water samples recorded in the STORET database (Staples et al. 1985). The median concentration in these positive samples was less than 10 $\mu\text{g}/\text{L}$.

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TABLE 5-2. Summary of Bromomethane Levels in Air

Location	Concentration ($\mu\text{g}/\text{m}^3$) ^a		References
	Maximum	Mean	
Northern Hemisphere	No data	0.02-0.08	Penkett et al. 1985; Singh et al. 1979b
Arctic	0.09	0.043	Berg et al. 1984
Oceanic	No data	0.09	Singh et al. 1983b
Rural/Suburban United States	No data	0.002-0.32 ^b	Brodzinsky and Singh 1983; Harsch and Rasmussen 1977; Shah and Heyerdahl 1988
Urban United States	0.25-5.1	0.16-2.2	Brodzinsky and Singh 1983; Harsch and Rasmussen 1977; Shah and Heyerdahl 1988; Shikiya et al. 1984; Singh et al. 1981b, 1982
Source dominated ^c	1.1x10 ⁵	No data	Bond and Dumas 1987
Hazardous waste sites	No data	- ^d	La Regina et al. 1986

^a1 $\mu\text{g}/\text{m}^3$ = 0.25 ppb (0.00025 ppm).

^bMedian value.

^cData measured 25 m from a flour mill being fumigated with bromomethane.

^dDetected, but not quantified; detection limit $\approx 0.4 \mu\text{g}/\text{m}^3$.

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Bromomethane has been detected (but not quantified) in drinking water supplies of several U.S. cities (Coleman et al. 1976; EPA 1975; Kool et al. 1982; Kopfler et al. 1977; Shackelford and Keith 1976). Bromomethane in drinking water is presumably generated as an inadvertent byproduct following chlorination.

Occurrence of bromomethane in groundwater is somewhat more likely than in surface water, since evaporation is restricted. Bromomethane has been detected in groundwater in New Jersey (Greenberg et al. 1982) but not in Wisconsin (Krill and Sonzogni 1986).

5.4.3 Soil

No data were found on bromomethane levels in soil. Bromomethane is not expected to be a stable constituent of soil, since it either evaporates or reacts with organic soil components (see Section 5.3.2.3). However, bromide ion may be retained in fumigated soil (IARC 1986). Bromomethane was not detected in 353 sediment samples from STORET stations in the United States (Staples et al. 1985).

5.4.4 Other Environmental Media

Although bromomethane is used extensively as a fumigant for grains and other food products, it is rarely detected unchanged as a residue in foods. Most of the fumigant is rapidly lost to the atmosphere, and the remaining portion reacts with the food components, producing residues of inorganic bromide (IARC 1986; NAS 1978). Daft (1987, 1988, 1989) and Cova et al. (1986) reported that bromomethane was not detected in hundreds of food products, and Duggan et al. (1983) found bromomethane in only 3 of 5,631 samples of vegetables. The tolerances for residues on agricultural commodities and processed foods that have been set by EPA and FDA are for bromide ion, not bromomethane (21 CFR 193; 40 CFR 180).

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Inhalation of bromomethane in ambient air is the predominant exposure route for most people in the United States. Singh et al. (1981b) calculated that average daily doses of bromomethane from air in 3 U.S. cities ranged from 4.5 to 24.5 $\mu\text{g}/\text{person}$, based on total air intake of 23 m^3/day by an adult. These estimates were based on 1979 monitoring data in urban areas. It is likely that urban bromomethane levels are currently lower than in the past, due to decreased emissions from automobiles using leaded gasoline (see Section 5.2.1). Based on the very low levels of bromomethane in water and the negligible levels in food, it appears that exposure of the general population to bromomethane from sources other than air is likely to be insignificant under normal circumstances.

Exposure of workers to bromomethane is highly variable, depending on conditions. Exposure levels inside factories are regulated by OSHA, and the 8-hour average concentration is not permitted to exceed 5 ppm (OSHA 1989).

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Highest exposures are most likely to occur during fumigation activities, especially when bromomethane is first released to the environment after fumigation ends. Exposure levels under these conditions could reach from 25 to 2,500 ppm (IARC 1986; NIOSH 1984a; Van Den Oever et al. 1982), which would correspond to a dose of 100-10,000 mg/hour for an exposed worker. NIOSH estimated that about 105,000 workers in the United States were potentially exposed to bromomethane in the workplace in 1980 (NIOSH 1984a).

5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Members of the general population are not likely to be exposed to high levels of bromomethane except in the immediate vicinity of industrial facilities that release the gas into air, or near locations where bromomethane is being used as a soil or a space fumigant. This includes individuals returning to work or live in locations that have recently been fumigated, especially if insufficient time has been allowed for the chemical to disperse. Individuals living near waste sites that contain bromomethane might also be exposed, although the level of exposure is not known. Individuals involved in the production of bromomethane and those licensed to use it as a fumigant may be exposed to high levels if proper safety precautions are not followed.

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 bromomethane 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 bromomethane.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that, if met, would reduce or eliminate the uncertainties of human health assessment. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

5.7.1 Data Needs

Physical and Chemical Properties. The physical and chemical properties of bromomethane are sufficiently well known to allow estimation of environmental fate. Although there is some disparity in reported values for the solubility in water and Henry's law constant for bromomethane (see Table 3-1), further studies to define these parameters more precisely do not appear essential, since volatilization from water is so rapid.

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Production, Import/Export, Use, and Disposal. Large quantities of bromomethane are produced and used in this country (TRI 1989), and there is significant opportunity for humans to be exposed to both during production and use (IARC 1986). Information is available on current volumes, and available data suggest production is increasing (IARC 1986). The main use of bromomethane is as a fumigant for soil, agricultural produce, and structures (IARC 1986), but data on the amount of bromomethane used for each type of fumigation were not located. Due to its volatility, nearly all releases from fumigation are to air (TRI 1989), and this is the medium most likely to be contaminated. Currently there are no regulations which restrict this release.

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 1987, became available in May of 1989. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

Environmental Fate. The fate of bromomethane in the environment is dominated by rapid evaporation into air, where it is quite stable (EPA 1986b). The rates of volatilization from soil and water have been studied and are known with reasonable precision (although such rates are typically sitespecific) (Jury et al. 1984; Lyman et al. 1982). The rates of breakdown by hydrolysis, reaction with hydroxyl radical, and direct photolysis in the stratosphere have also been estimated (Castro and Belser 1981; Davis et al. 1976; Robbins 1976). Further studies to improve the accuracy of available rate constants for these processes would be helpful, but do not appear to be essential in understanding the basic behavior of bromomethane in the environment.

Bioavailability from Environmental Media. Bromomethane is known to be well absorbed following inhalation and oral contact (Gargas and Andersen 1982; Medinsky et al. 1984). Small amounts may also be absorbed across the skin, but this has not been quantified. No information was located regarding the relative bioavailability of bromomethane from media such as food or soil. However, since bromomethane has a low K_{oc} value (Mabey et al. 1982), it is not likely that bioavailability would be much reduced by these matrices. Moreover, since bromomethane is rarely found in these media, research on this subject does not appear essential.

Food Chain Bioaccumulation. Although the bioconcentration, bioaccumulation, and biomagnification of bromomethane have not been formally investigated, it seems clear that these are not of significant concern. This is the result of several factors, including the high volatility and high water solubility of the compound, its low K_{ow} , and its relatively rapid metabolism by reaction with organic materials (Mabey et al. 1982; Medinsky et al. 1985). On this basis, it does not appear that research in this area is essential.

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Exposure Levels in Environmental Media. Several studies are available documenting bromomethane concentrations in ambient air (Brodzinsky and Singh 1983; Harsch and Rasmussen 1977), but data for bromomethane in water are rare. Bromomethane has been analyzed for, but rarely detected, in foods (Daft 1987, 1988, 1989). Human exposure levels of bromomethane by inhalation of urban air have been calculated (Singh et al. 1981b). However, these levels are based on monitoring data more than 10 years old. Since urban air concentrations of bromomethane may have decreased due to reduced emissions from automobiles, exposure levels calculated from past data should be taken as an upper limit, and new levels calculated from current monitoring data would be useful. Additional monitoring data on levels in air near sites where bromomethane is being made or used would also be valuable in defining environmental levels.

Exposure Levels in Humans. Bromomethane is not normally measured in human tissues such as blood or urine, even in people exposed to high levels. This is because bromomethane is removed from the body very quickly after exposure ceases. Consequently, this is not likely to be a useful means of monitoring exposure of humans to low levels of bromomethane. Increased levels of bromide have been detected in blood of persons exposed to bromomethane in accidents or in the workplace, but no studies were located regarding bromide levels in persons potentially exposed to bromomethane near waste sites. Since bromide is a normal component of serum, and since the serum bromide level is quite variable, it does not seem that broad surveys of blood bromide levels in persons living near waste sites would be useful. However, site-specific studies at locations where bromomethane exposure is likely might prove helpful.

Exposure Registries. No exposure registries for bromomethane were located. This compound is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. The compound 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 the exposure to this compound.

5.7.2 On-going Studies

No information was located on any on-going studies on the fate and transport of bromomethane. However, two studies related to human exposure to bromomethane are being supported by the U.S. Department of Agriculture and conducted at the University of California, Davis. One project will analyze bromomethane residues on foods, and the second will quantitate exposure levels of field workers to bromomethane and develop appropriate procedures to minimize exposure from this source. Remedial investigations and feasibility studies at NPL sites that contain bromomethane will provide further information on environmental concentrations and human exposure levels near waste sites.

