5. POTENTIAL FOR HUMAN EXPOSURE

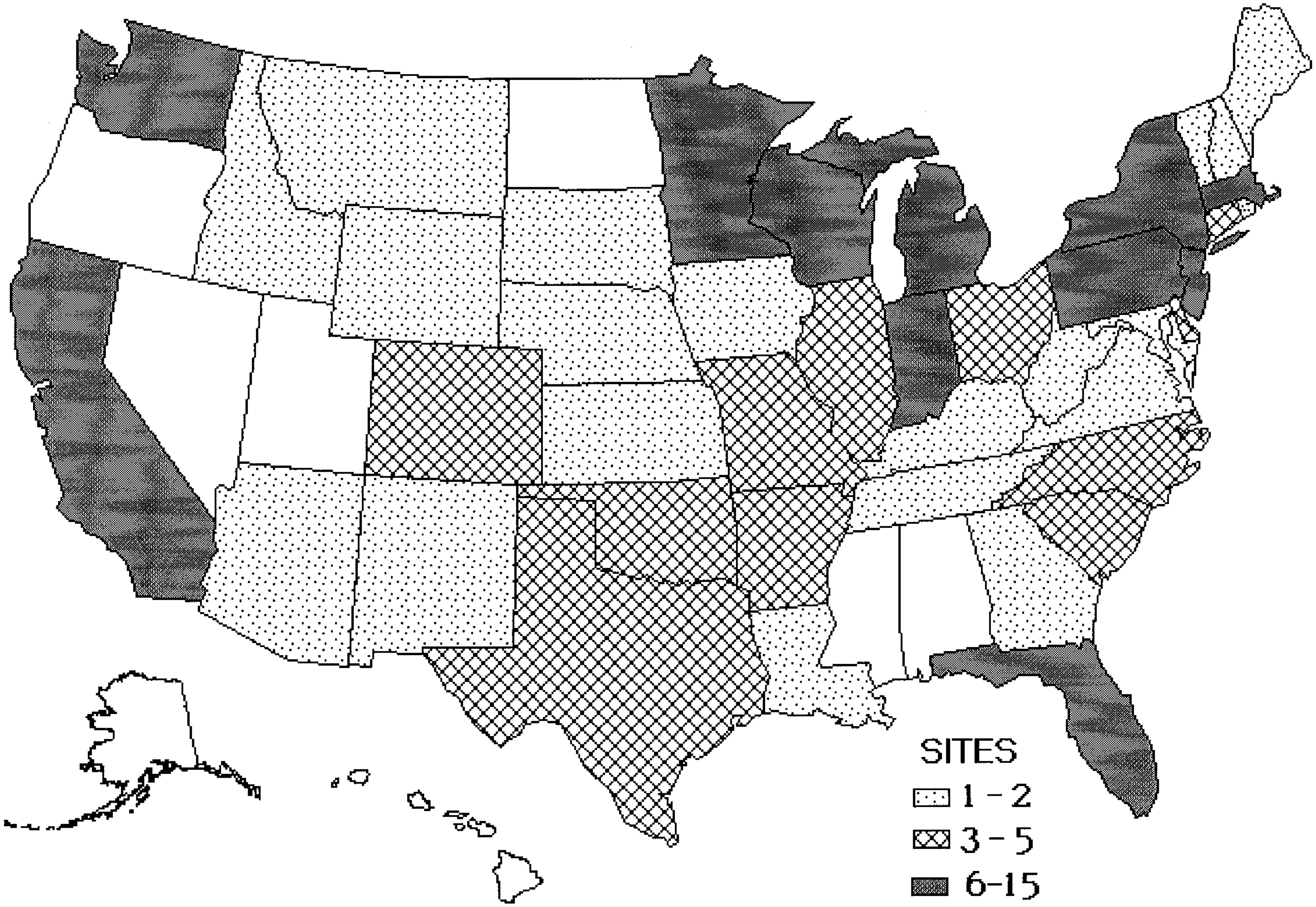
5.1 OVERVIEW

Chloromethane has been identified in at least 172 of the 1,467 current or former EPA National Priorities List (NPL) hazardous waste sites (HazDat 1998). However, the number of sites evaluated for chloromethane is not known. The frequency of these sites within the United States can be seen in Figure 5-1. Of these sites, 171 are located in the United States and 1 is located in the Commonwealth of Puerto Rico (not shown).

Chloromethane (also commonly known as methyl chloride) is a natural and ubiquitous constituent of the oceans and atmosphere (both the troposphere and the stratosphere). It is a product of biomass combustion and is also created from biogenic emissions by wood-rotting fungi. Chloromethane has been detected in surface waters, drinking water, groundwater, and soil. Chloromethane is a constituent of municipal and industrial solid waste leachate; it is a component of industrial waste discharges, and is also present in the effluents of publicly owned treatment works (POTWs). It is an impurity in vinyl chloride (Zaidman et al. 199 l), so chloromethane could be released to the environment during the manufacture of vinyl chloride or introduced into NPL sites from vinyl chloride wastes. Chloromethane in air has a half-life of about 1 year (see Table 3-2) with various estimates in the range of 0.6-3 years (see Section 5.3.2.1 below). Chloromethane is the dominant organochlorine species in the atmosphere. In the upper atmosphere, chloromethane, through its sheer abundance, plays a role in chemical reactions that remove ozone from the upper troposphere and stratosphere (Crutzen and Gidel 1983; Gidel et al. 1983; Singh et al. 1983). Since these processes are believed to be largely part of natural background cycles, chloromethane has not been the focus of ozone depletion control efforts under the Clean Air Act (CAA) and the Montreal Protocol, which are targeted at such anthropogenic halogenated compounds as chlorofluorocarbons (EPA 1996b; Finlayson-Pitts and Pitts 1986; IPCC 1995).

In water, chloromethane is expected to volatilize rapidly (Mabey and Mill 1978). It is not expected to sorb to sediments or to bioconcentrate. Chemical hydrolysis and biodegradation are not expected to be significant processes. In soil, chloromethane is expected to volatilize from the surface, but when present in a landfill, it will probably leach into groundwater. In groundwater, hydrolysis may be the only removal mechanism available to chloromethane, with an estimated half-life of ~4 years based on available data

Figure 5-1. Frequency of NPL Sites with Chloromethane Contamination



Derived from HazDat 1998

(Elliott and Rowland 1995; Mabey and Mill 1978). Air concentrations of chloromethane are generally in the low per billion range, but urban locations appear to have elevated concentrations compared to background concentrations. Although detailed information is lacking, water concentrations are likely to vary considerably depending on the season and the geographic location. Very little information is available concerning chloromethane concentrations in soil. The general population is not expected to be exposed to concentrations of chloromethane much above 3 ppb in urban locations. In rural locations, the exposure concentration is expected to be ≈0.7-0.9 ppb. Occupational exposure to chloromethane may result in exposures of ≈ 10 parts per million (ppm); however, the database for occupational exposure is outdated (late 1980s or earlier) and not sufficiently comprehensive to allow reliable predictions of average or probable occupational exposure levels. The population with the highest potential exposures probably would include those people who work in chloromethane manufacturing or use industries.

5.2 RELEASES TO THE ENVIRONMENT

According to the Toxics Release Inventory (TRI), in 1996, a total of 4,827,803 pounds (2,189,855 kg) of chloromethane was released to the environment from 96 processing facilities (TRI96 1998). This total consists of chloromethane released to air (4,457,775 pounds), water (803 pounds), soil (80 pounds), and via underground injection (99,705 pounds). Table 5-l lists the amounts released to the environment by each site. In addition, an estimated 9,758 pounds (4,426 kg) were released by manufacturing and processing facilities to POTWs and an estimated 259,682 pounds (117,790 kg) were transferred off-site (TRI96 1998). The TRI data should be used with caution because only certain types of facilities are required to report this information. This is not an exhaustive list.

Chloromethane has been identified in a variety of environmental media (air, surface water, groundwater, soil, and sediment) collected at 172 of the 1,467 current and former NPL hazardous waste sites (HazDat 1998).

5.2.1 Air

According to the TRI, in 1996, the estimated release of chloromethane of 4,457,775 pounds (2,022,013 kg) into the air from at least 95 processing facilities accounted for about 92.3% of total anthropogenic environmental releases (TRI96 1998). Table 5-l lists the amounts released from these facilities. The TRI

Table 5-1. Releases to the Environment from Facilities that Manufacture or Process Chloromethane

STATE[b]	CITY	FACILITY	AIR[c]	WATER	LAND	UNDERGROUND INJECTION	POTW TRANSFER	OFF-SITE WASTE TRANSFER	TOTAL ENVIRONMENT[d]
AL	MOBILE	INTERNATIONAL PAPER	38,005	0	0	0	0	0	38,005
AL	THEODORE	HULS AMERICA INC.	8,924	0	0	0	0	250	9,174
AR	PINE BLUFF	INTERNATIONAL PAPER	43,005	5	0	0	0	0	43,010
AR	WEST MEMPHIS	CPS CHEMICAL CO.	4,250	0	0	0	0	0	4,250
CA	LOS ANGELES	AMVAC CHEMICAL CORP.	0	0	0	0	0	26	26
CO	BOULDER	SYNTEX CHEMICALS INC.	5,070	0	0	0	0	3,000	8,070
CO	MEAD	BOULDER SCIENTIFIC CO.	740	0	0	0	0	0	740
CT	GROTON	PFIZER INC-GROTON SITE	71,300	250	0	0	0	0	71,550
CT	SHELTON	SPONGES INTL.	253,791	0	0	0	0	0	253,791
DE	NEW CASTLE	ZENECA INC.	18	0	0	0	61	0	79
FL	PERRY	BUCKEYE FLORIDA L.P.	36,013	1	0	0	0	0	36,014
GA	AUGUSTA	BLACKMAN UHLER CHEMICAL DIV.	730	0	0	0	0	0	730
GA	AUGUSTA	NUTRASWEET KELCO CO.	45,002	0	0	0	0	0	45,002
GA	CLYATTVILLE	TENNECO PACKAGING	27,000	0	0	0	0	0	27,000
GA	SAINT MARYS	GILMAN PAPER CO.	35,005	5	0	0	0	5	35,015
IA	MUSCATINE	MONSANTO CO.	9,300	0	0	0	0	0	9,300
IL	KANKAKEE	HENKEL CORP.	5,560	0	0	0	0	0	5,560
IL	MAPLETON	LONZA INC.	1,393	0	0	0	0	0	1,393
IL	MAPLETON	SHEREX CHEMICAL CO. INC.	75,000	0	0	0	5	0	75,005
IL	MC COOK	AKZO NOBEL CHEMICALS INC.	214,600	0	0	0	0	0	214,600
IL	MORRIS	AKZO NOBEL CHEMICALS INC.	157,000	0	0	0	0	5	157,005
IL	RINGWOOD	MORTON INTL. INC.	331	0	0	0	0	0	331
IL	TUSCOLA	CABOT CORP.	7,079	0	0	0	0	0	7,079
IN	HUNTINGTON	ECOLAB INC.	10,320	0	0	0	0	0	10,320
KS	GALENA	ALLCO CHEMICAL CORP.	34,600	0	0	0	0	0	34,600
KS	GARDEN CITY	PALMER MFG. & TANK INC.	1	0	0	0	0	1,850	1,851
KS	WICHITA	VULCAN CHEMICALS	138,033	0	0	73,441	0	0	211,474
KY	CARROLLTON	DOW CORNING CORP.	33,948	150	0	0	0	144,108	178,206
KY	WICKLIFFE	WESTVACO CORP.	27,405	0	0	0	0	0	27,405
LA	BASTROP	INTERNATIONAL PAPER CO.	31,027	0	0	0	0	0	31,027
LA	BATON ROUGE	EXXON CHEMICAL	92,000	14	0	0	0	1,632	93,646
LA	BATON ROUGE	RHONE-POULENC INC.	4,261	0	0	0	0	0	4,261
LA	GEISMAR	VULCAN MATERIALS CO.	259,500	0	0	0	0	5	259,505
LA	KILLONA	WITCO CORP.	4,175	0	0	0	0	0	4,175
LA	LULING	MONSANTO CO.	12,900	0	0	20,000	0	0	32,900
LA	PLAQUEMINE	DOW CHEMICAL CO.	26,400	0	60	0	0	0	26,460
LA	ZACHARY	FERRO CORP.	288	2	0	0	0	0	290
LA	ZACHARY	GEORGIA-PACIFIC CORP.	54,007	0	0	0	0	0	54,007
MD	BALTIMORE	FMC CORP.	162	0	0	0	71	4,090	4,323
MD	LUKE	WESTVACO CORP.	32,000	0	0	0	5,800	0	37,800
MI	KALAMAZOO	CYTEC IND. INC.	4,696	0	0	0	250	748	5,694
MI	MIDLAND	DOW CHEMICAL USA	9,963	0	0	0	0	0	9,963
MI	MIDLAND	DOW CORNING CORP.	13,041	0	0	0	0	71,788	84,829
MI	MUSKEGON	ESCO CO.	1,500	0	0	0	1	0	1,501

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

STATE[b]	CITY	FACILITY	AIR[c]	WATER	LAND	UNDERGROUND INJECTION	POTW TRANSFER	OFF-SITE WASTE TRANSFER	TOTAL ENVIRONMENT[d]
MI	WYANDOTTE	BASF CORP.	14,060	0	0	0	499	852	15,411
MN	ROCKFORD	DIVERSIFOAM PRODS.	81,018	0	0	0	0	0	81,018
MO	KANSAS CITY	BAYER CORP.	6,595	0	9	0	0	0	6,604
MO	SPRINGFIELD	SYNTEX AGRIBUSINESS INC.	26,640	0	0	0	0	0	26,640
MO	VERONA	DUCOA L.P.	342	0	0	0	0	0	342
MS	NATCHEZ	INTERNATIONAL PAPER	38,009	1	0	0	0	0	38,010
MS	REDWOOD	INTERNATIONAL PAPER	31,000	0	0	0	0	0	31,000
NC	CANTON	CHAMPION INTL. CORP.	33,000	0	0	0	0	0	33,000
NC	RIEGELWOOD	FEDERAL PAPER BOARD CO. INC.	32,010	1	0	0	0	0	32,011
NJ	DEEPWATER	DUPONT CHAMBERS WORKS	44,070	119	0	0	0	0	44,189
NJ	OLD BRIDGE	CPS CHEMICAL CO. INC.	1,902	0	0	0	0	0	1,902
NY	WATERFORD	GE CO.	74,000	45	0	0	0	0	74,045
OH	CINCINNATI	MORTON INTL. INC.	126,200	0	0	0	51	0	126,251
OH	EUCLID	LINDERME TUBE CO.	165,000	0	0	0	0	30,900	195,900
OH	HAVERHILL	ARISTECH CHEMICAL CORP.	31,000	0	0	0	0	0	31,000
OH	MARIETTA	AMOCO PERFORMANCE PRODS. INC.	220,750	0	0	0	0	0	220,750
PA	FOLCROFT	PPG IND. INC.	5	0	0	0	0	0	5
PA	PHILADELPHIA	ROHM & HAAS CO.	5,747	0	0	0	0	0	5,747
PA	PITTSBURGH	PRESSURE CHEMICAL CO.	10,006	0	0	0	0	0	10,006
PA	TAMAQUA	AIR PRODS. & CHEMICALS INC.	2,700	0	0	0	0	0	2,700
PR	BARCELONETA	MERCK SHARP & DOHME QUIMICA	38	0	0	0	0	0	38
SC	CHARLESTON	ALBRIGHT & WILSON AMERICAS	219,074	0	0	0	0	0	219,074
SC	ELGIN	NIPA HARDWICKE INC.	66	0	0	0	0	30	96
SC	GOOSE CREEK	BAYER CORP. BUSHY PARK	2,445	3	5	0	0	0	2,453
SC	GREEN POND	BALCHEM CORP.	204	0	0	0	0	0	204
TN	COUNCE	TENNECO PACKAGING	26,005	0	0	0	0	0	26,005
TN	MEMPHIS	ENENCO INC.	106,000	0	6	0	820	6	106,832
TN	MOUNT PLEASANT	ZENECA SPECIALTIES	200	0	0	0	0	0	200
TN	NEWPORT	GREAT LAKES CHEMICAL CORP.	337	0	0	0	27	0	364
TX	BAYTOWN	CHEMICALS INC.	250	0	0	0	0	0	250
TX	BAYTOWN	EXXON CHEMICAL AMERICAS	430,000	150	0	0	0	0	430,150
TX	BEAUMONT	BASF CORP.	5,080	0	0	0	0	0	5,080
TX	CLEBURNE	SACHEM INC.	421	0	0	0	0	13	434
TX	CORSICANA	CORSICANA TECHS. INC.	1,665	0	0	0	0	0	1,665
TX	DEER PARK	AKZO NOBEL CHEMICALS INC.	12	0	0	0	0	0	12
TX	FREEPORT	DOW CHEMICAL CO.	10,100	0	0	0	0	0	10,100
TX	FREEPORT	RHONE-POULENC INC.	14,930	0	0	0	0	0	14,930
TX	HOUSTON	ISK BIOSCIENCES CORP.	6,847	0	0	0	0	334	7,181
TX	HOUSTON	WITCO CORP.	21	0	0	0	0	0	21
TX	LONGVIEW	EASTMAN CHEMICAL CO.	200,150	0	0	0	0	0	200,150
TX	ORANGE	INLAND PAPERBOARD & PACKAGING	30,000	0	0	0	0	0	30,000
TX	PASADENA	PETROLITE CORP.	2,011	0	0	0	1,900	40	3,951
TX	PASADENA	ZENECA INC.	77,924	0	0	0	0	0	77,924
TX	TEXAS CITY	STERLING CHEMICALS INC.	174,007	0	0	6,264	0	0	180,271

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

STATE[b]	CITY	FACILITY	AIR[c]	WATER	LAND	UNDERGROUND INJECTION	POTW TRANSFER	OFF-SITE WASTE TRANSFER	TOTAL ENVIRONMENT[d]
VA	DANVILLE	HICKSON DANCHEM CORP.	6,494	0	0	0	4	0	6,498
VA	ELKTON	MERCK & CO. INC.	8,970	0	0	0	0	0	8,970
VA	FRANKLIN	UNION CAMP CORP.	26,000	0	0	0	0	0	26,000
WI	JANESVILLE	SHEREX CHEMICAL WHOLLY OWNED	23,164	0	0	0	250	0	23,414
WI	MILTON	TOMAH PRODS. INC.	6,514	1	0	0	1	0	6,516
WI	MILWAUKEE	BELL AROMATICS	8,184	0	0	0	18	0	8,202
WV	BELLE	DU PONT	108,000	0	0	0	0	0	108,000
WV	FRIENDLY	OSI SPECIALTIES INC.	189,265	56	0	0	0	0	189,321
		TOTALS	4,457,775	803	80	99,705	9,758	259,682	4,827,803

Source: TRI96 1998

[a] Data in TRI are maximum amounts released by each facility

[b] Post office state abbreviations used

[c] The sum of fugitive and stack releases are included in releases to air by a given facility

[d] The sum of all releases of the chemical to air, land, and water, and underground injection wells; and transfers off-site by a given facility

POTW = publicly owned treatment works

data should be used with caution, however, since only certain types of facilities are required to report this information. This is not an exhaustive list.

Chloromethane has been identified in air samples collected at 16 of the 172 NPL hazardous waste sites where it was detected in some environmental media (HazDat 1998).

Most releases of chloromethane will be to air, since it is a gas at ambient temperatures, and manufacturing practices suggest that little will be discharged by any other route. Chloromethane discharged to water will volatilize rapidly, based on the Henry's law constant; however, the amount volatilized will vary depending on a number of factors, including the temperature, turbulence, and depth of the receiving water.

Chloromethane will be released from manufacturing and use (fugitive emissions) as well as from production resulting from human and natural activities. Chloromethane present in waste waters also may be released to air during aeration (Pincince 1988). Release from all sources amounts to 7-18 billion pounds (3.2-8.2x10^9 kg) annually on a worldwide basis. Sources include the oceans, forest fires, burning wood, burning coal, volcanoes, burning plastic (Chopra 1972; Crutzen et al. 1979; Edgerton et al. 1984, 1986; Edwards et al. 1982a, 1982b; Khalil et al. 1985; Kleindienst et al. 1986; Palmer 1976; Rasmussen et al. 1980; Singh et al. 1979, 1981a, 1981b, 1982, 1983; Tassios and Packham 1985; Yung et al. 1975), fungal activity (Fabian 1986; Harper 1985; Harper and Hamilton 1988; Harper et al. 1988), and release from some trees (Isidorov et al. 1985). It is estimated that biomass burning in grasslands and forested areas accounts for about 20% (range, 10-40%) of the total global budget of chloromethane, with emissions from the oceans making another significant contribution (Rudolph et al. 1995). Various estimates of average global annual production rates, and significantly different estimates of the contributions from different natural production, sources have been made. Estimates from terrestrial ecologists tend to emphasize the role of such sources as biomass burning, while oceanographers may emphasize the role of biogenic emissions from marine phytoplankton. The global budget figures presented below are based on a study by Edwards et al. (1982b) and are used primarily to emphasize the overwhelming contributions from nonindustrial production.

In comparison with an estimated total global budget of 7-18 billion pounds (3.2-8.2x10^9 kg) annually, 1980 worldwide production of chloromethane was ≈ 794 million pounds (3.6x10^8 kg) (Edwards et al. 1982b), of which ≈6% was released into the environment from production, storage, transport, and use emissions (Edwards et al. 1982a; Singh et al. 1981a, 1981b). This amounts to worldwide releases of 47.6 million pounds (2.1x10^7 kg) from manufacturing and use activities in 1980. U.S. production capacity of chloromethane in 1995 was around 920 million pounds (417.3 million kg), with total releases to environmental media estimated from the 1996 TRI at around 4.8 million pounds (2.2 million kg) (CMR 1995; TRI96 1998). Thus, well over 90% (perhaps up to 99%) of ambient air concentrations of chloromethane on a global scale appear to come from releases from natural sources rather than from manufacturing or other emissions from anthropogenic processes or uses. Releases associated with manufacturing and production processes in the United States would constitute less than 1% of the global budget.

Typical estimates for the natural background concentrations of chloromethane in ambient air are ≈1 ppb (Harper et al. 1990). Chloromethane concentrations are often in excess of rural background concentrations in the ambient air of cities in the United States (Singh et al. 1982, 1983) (see Section 5.1). The authors suggested that this elevation may be the result of manufacturing or other anthropogenic emission sources in the urban areas, over and beyond releases from combustion or other background sources that would determine the levels in more rural areas. Other than data from the TRI or rough estimates based on global budgets, no studies were identified that attempt to make quantitative estimates for natural or anthropogenic releases of chloromethane to the air in the United States.

5.2.2 Water

According to the TRI, in 1996, there were estimated releases of chloromethane of 803 pounds (364 kg) to water from 15 documented processing facilities. These releases accounted for less than 0.1% of total anthropogenic environmental releases (TRI96 1998). Table 5-l lists the amounts released from these facilities. The TRI data should be used with caution, however, since only certain types of facilities are required to report this information. This is not an exhaustive list.

Chloromethane is released into the water from a number of sources, including industrial discharges and effluents from municipal waste treatment plants, but insufficient information is available to quantify the releases. During the manufacture of chloromethane, process water contacts the reaction mixtures (see Section 4.1) (Edwards et al. 1982a; Key et al. 1980). This water is stripped during manufacture and treatment to remove most of the dissolved chloromethane and then discharged (some chloromethane manufacturing plants use the process water on-site as a source of dilute hydrochloric acid [HCl] rather than discharging it). Data regarding the use and fate of process water in use applications were not found in the available literature; however, spent process water is probably treated (including aeration) prior to discharge.

Nonetheless, chloromethane has been found in waste water effluents, possibly as a result of its formation (Coleman et al. 1976; Gould et al. 1983) or incomplete removal during industrial waste water treatment (Snider and Manning 1982). Chloromethane has been detected in the leachate of both municipal (Gould et al. 1983; Sabel and Clark 1984) and hazardous waste landfills (Brown and Donnelly 1988; Kosson et al. 1985; Venkataramani et al. 1984). Chloromethane has been identified in 21 surface water and 100 groundwater samples collected at the 172 NPL hazardous waste sites where it was detected in some environmental media (HazDat 1998).

5.2.3 Soil

According to the TRI, in 1996, the estimated release of chloromethane of 80 pounds (36.3 kg) to soil from four processing facilities accounted for less than 0.1% of total anthropogenic environmental releases (TRI96 1998). Table 5-l lists the amounts released from these facilities. The TRI data should be used with caution, however, since only certain types of facilities are required to report this information. This is not an exhaustive list.

Chloromethane is probably released into the soil during the landfilling of sludges and other wastes (e.g., still bottoms) generated from industrial processes and municipal sewage treatment; however, no specific information concerning chloromethane-containing wastes was located in the literature. Chloromethane has been detected in the leachate of both municipal (Sabel and Clark 1984) and hazardous waste landfills (Brown and Donnelly 1988; Kosson et al. 1985; Venkataramani et al. 1984), indicating that disposal of these materials apparently results in contamination of soils. Chloromethane has been identified in 34 soil and 13 sediment samples collected at the 172 NPL hazardous waste sites where it was detected in some environmental media (HazDat 1998).

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

Most chloromethane discharged into the environment will be released into the air, where it will be subjected to transport and diffusion into the stratosphere (Singh et al. 1979, 1982, 1983). The relatively uniform concentration of chloromethane in the northern and southern hemispheres (Singh et al. 1979, 1982, 1983) indicates its widespread distribution and the importance of transport processes in its distribution. The water solubility of chloromethane is high enough that small amounts may be removed from the atmosphere by precipitation; however, no information confirming this environmental pathway was located in the literature.

The dominant transport process from water will be volatilization. The results of two EXAMS model runs and the value of the Henry’s law constant (calculated from the solubility and the vapor pressure) suggest that volatilization will be significant in surface waters. EXAMS is an environmental model that predicts the behavior of a chemical in surface waters. Using the code test data for a pond developed by the Athens Environmental Research Laboratory of the EPA, the half-life for volatilization was calculated to be 2.5 hours. For a lake, the half-life was calculated to be 18 days. Input data included the molecular weight, the vapor pressure, Henry’s law constant, the octanol/water partition coefficient, the sediment sorption coefficient, and the water solubility. The volatilization rates predicted by the EXAMS model appear to be in agreement with the observation of Lurker et al. (1983) who reported chloromethane concentrations in waste water and in the air above the waste water at the Memphis North Wastewater Treatment Plant in Memphis, Tennessee. Based on the log octanol/water partition coefficient (Hansch and Leo 1985) and the sorption coefficient and BCF calculated from it (see Table 3-2), chloromethane is not expected to concentrate in sediments or in biota.

In soil, the dominant transport mechanism for chloromethane present near the surface probably will be volatilization (based on its Henry’s law constant, water solubility, and vapor pressure), but no experimental information was located in the literature to confirm this. The actual volatilization rate for a chemical in soil is influenced by a number of factors, including surface roughness, soil type, rainfall, leaching, depth of incorporation, temperature, and ground cover (Jury et al. 1987). Since chloromethane is not expected to sorb to soils, any chloromethane present in lower layers of the soil will be expected to leach to lower horizons as well as to diffuse to the surface and volatilize. The presence of chloromethane in groundwater confirms the importance of leaching as a transport route (Greenberg et al. 1982c; Jury et al. 1987; Page 1981).

5.3.2 Transformation and Degradation

5.3.2.1 Air

The dominant tropospheric removal mechanism for chloromethane is generally thought to be hydrogen abstraction by hydroxyl radical (Dilling 1982; Fabian 1986; Gusten et al. 1984; Lovelock 1975; Rasmussen et al. 1980; Robbins 1976; Singh et al. 1979). The hydroxyl radical reaction with chloromethane has been experimentally determined in a number of studies (Butler et al. 1978; Cox et al. 1976; Davis et al. 1976a; Howard and Evenson 1976; Jeong and Kaufman 1980, 1982; Jeong et al. 1984; Paraskevopoulos et al. 1981; Perry et al. 1976). The data of Howard and Evenson (1976) (discharge flow-laser magnetic resonance), Perry et al. (1976) (flash photolysis-resonance fluorescence), Davis et al. (1976a) (flash photolysis-resonance fluorescence), Paraskevopoulos et al. (1981) (flash photolysis-resonance adsorption), and Jeong and Kaufman (1980, 1982) (discharge flow-resonance fluorescence) are in agreement (Atkinson 1985; NASA 1981).

Using the measured rate constants for the chloromethane reaction with hydroxyl radicals, several researchers have made estimates of tropospheric total lifetimes or half-lives (Crutzen and Gidel 1983; Dilling 1982; Fabian 1986; Khalil and Rasmussen 1981; Singh et al. 1979). The various half-life estimates are in the neighborhood of 1 year (see Table 3-2), with values ranging from 0.6 to 3 years. The differences in the estimated half-lives are associated mainly with differences in assumptions on the levels of hydroxyl free radical concentrations in the upper troposphere.

5.3.2.2 Water

In water, chloromethane can degrade by hydrolysis or by biodegradation. Although few data are available on the biodegradation of chloromethane in water, neither hydrolysis nor biodegradation in surface waters appears to be rapid when compared with volatilization. Chloromethane hydrolysis proceeds via an S_N2 mechanism (bi-molecular) in which no intermediate ions are formed, and methanol and HCl are the only products. The kinetics of chloromethane hydrolysis have been measured by Heppolette and Robertson (1959) and Laughton and Robertson (1956) by bubbling chloromethane into water and following the reaction by measuring the conductance of the water. The rate constant for hydrolysis of chloromethane at 50 °C was reported to be 7.6×10^{-7} sec^{-1}, with a half-life of 10.6 days. When extrapolated to 20 °C and neutral conditions using the thermodynamic constants calculated by Heppolette and Robertson (1959), a rate constant was calculated of 1.04×10^{-8} sec^{-1} with a half-life of ≈ 2.1 years. More recent hydrolysis data from Elliot and Rowland (1995) are in good agreement with the estimates of Mabey and Mill (1978) and the measurements of Zafiriou (1975). Actual measurements conducted at 22 and 9 °C in pure water, sea water, and salt solution yield the same values of k (not listed), from which the Arrhenius relation was derived: $k(\text{in } s^{-1})=9.5\times10^{10}e^{-12,800/T}$. This relation was used to estimate the values at 25 and 15 °C given in Table 3-2. These rates are expected to be unaffected by pH ranges normally encountered in the environment (Mabey and Mill 1978). The hydrolysis half-lives are too long to be of environmental significance in surface waters, considering the rapid volatilization of chloromethane from surface water (Mabey and Mill 1978). In groundwater, however, hydrolysis may be the only degradation mechanism available and, hence, may be a more significant factor. Biodegradation may also occur in groundwater, but rates are thought to be highly variable.

Very little information is available concerning the biodegradation of chloromethane in water. In studies involving such bacteria as *Methylococcus capsulatus,* formaldehyde was a product of chloromethane biodegradation (Stirling and Dalton 1979). In pure culture conditions, some microbial strains can degrade chloromethane. Hartmans et al. (1986) reported that pure cultures of a *Hyphomicrobium sp.* were obtained with a chloromethane-minima1 medium. Abiotic hydrolytic dehalogenation was not significant, so that the observed cell growth and chloride formation confirmed biodegradation as the predominant transformation process (Hartmans et al. 1986). Since these laboratory conditions do not commonly occur in the environment, these same species may not degrade chloromethane in the environment to any significant degree. Biodegradation of chloromethane, however, cannot be ruled out based on the available information. As with reactions of other chloroalkanes, chloromethane may degrade anaerobically via reductive dechlorination to form methane (Vogel et al. 1987).

5.3.2.3 Sediment and Soil

Very limited information concerning soil transformation and degradation of chloromethane was located in the literature. In lower soil horizons, hydrolysis may be the only relevant abiotic process since no other non-biological removal mechanisms have been identified. Biological processes, especially from some fungi, can release chloromethane (Fabian 1986; Harper 1985; Harper and Hamilton 1988; Harper et al. 1988). Research also suggests that members of the so-called white rot fungus family may degrade (mineralize) chloromethane (Harper et al. 1990). These same fungi (especially *Phanerochaete chrysosporium)* can also dehalogenate aliphatic halocarbons such as chloroform, dichloromethane, and carbon tetrachloride

(Khindaria et al. 1995) possibly forming chloromethane as an intermediate product that, in turn, could be further dehalogenated.

Doronina et al. (1996) isolated eight strains of non-methane-utilizing bacteria that are able to grow on chloromethane as the carbon and energy source. The new isolates were classified as *Hyphomicrobium* spp. (strains CMl, CM2, CM9, CM29,CM35) and *Methylbacterium* spp. (strains CM4, CM30, CM34). All strains possessed an inducible but unknown enzyme that catalyzed the conversion of chloromethane to HCI and formaldehyde. The formaldehyde was oxidized via formate to CO_2 or assimilated through icl^+ or icl^- variants of the serine pathway. Vanelli et al. (1998) found that *Methylobacterium* sp. (strain CM4) metabolized chloromethane quantitatively with a molar yield of 2.8 g of whole-cell protein/mol of C. Based on the protein yield data and the properties of the transposon mutants, they proposed a pathway for chloromethane metabolism that depends on methyltransferase and dehydrogenase activities.

Under anaerobic conditions as encountered in deeper soil profiles or in many sediments, a bacterial strain called MC isolated from municipal anaerobic digester sludge flora seems capable of metabolizing chloromethane into acetate (Messmer et al. 1993; Zitomer and Speece 1995). It is not clear, however, that such anaerobic biodegradation processes are common around waste sites with chloromethane site contamination. The biochemistry of chloroaliphatics degradation in the newer aerobic isolates is largely unexplored, but progress has been made in understanding some of the anaerobic dehalogenation reactions (Leisinger 1996).

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to chloromethane depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. In reviewing data on chloromethane 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.

5.4.1 Air

Chloromethane has been the subject of numerous studies conducted to determine the atmospheric chloride balance. In the development of a database for ambient air monitoring, more than 242 sites in the United States were monitored for chloromethane during a 5-year period (Eichler and Mackey 1986).

Table 5-2 presents monitoring data for chloromethane for urban/suburban and rural/remote air masses. The ranges and averages presented in Table 5-2 cannot be compared directly since the measurements taken at urban/suburban locations were all taken at ground level, while many of the rural/remote analyses were made at higher altitudes.

A volatile organic carbon (VOC) database reported by Shah and Singh (1988) contained 706 data points (300 cities from 42 states), with the following results for chloromethane concentration:

	Concentration of chloromethane
Average	740 ppt
Upper quartile	721 ppt
Median	652 ppt
Lower quartile	607 ppt

The average value is higher than the upper quartile (75% value) and may be skewed because of a few high values. Thus, the median may be a better representation of chloromethane concentration. The data were also grouped by types of air mass so that the influence of urban centers could be estimated (Shah and Singh 1988):

Air mass	Median concentration	Data points
Remote	713 ppt	5
Rural	923 ppt	2
Suburban	641 ppt	599
Urban	810 ppt	100

From these data, it appears that source contributions from industrial processes do not have a significant impact on the ambient concentration of chloromethane, although some elevation may occur. There are fewer data points, however, for rural/remote data than for urban/suburban data, so a direct comparison is difficult.

Average urban levels reported by Singh et al. (1982, 1983) were 660–960 ppt, while background levels were 600–700 ppt. For these results, the ambient air levels of chloromethane in cities in the United States may be slightly elevated from background levels, due to the higher numbers of combustion sources.

Table 5-2. Detection of Chloromethane in Air[a]

Media type/location	Sampling dates	No. of samples	Sample type	Analytical method	Concentration (ppt) Range	Concentration (ppt) Mean	Percent occurrence	Reference
Urban/suburban air								
Los Angeles, CA	4/9–21/79	NS	Continuous	GC/ECD	1,037–7,761	3,001	100	Singh et al. 1981b
Phoenix, AZ	4/23/79–5/6/79	NS	Continuous	GC/ECD	1,231–5,685	2,391	100	Singh et al. 1981b
Oakland, CA	6/28/79–7/10/79	NS	Continuous	GC/ECD	483–5,000	1,066	100	Singh et al. 1981b
Houston, TX	5/15–24/80	NS	Continuous	GC/ECD	531–2,284	955	100	Singh et al. 1982
St. Louis, MO	5/30/80–6/8/80	NS	Continuous	GC/ECD	531–1,015	732	100	Singh et al. 1982
Denver, CO	6/16–26/80	NS	Continuous	GC/ECD	519–1,157	763	100	Singh et al. 1982
Riverside, CA	7/2–12/80	NS	Continuous	GC/ECD	437–1,593	703	100	Singh et al. 1982
Staten Island, NY	3/27/80–4/5/80	NS	Continuous	GC/ECD	466–1,280	701	100	Singh et al. 1982
Pittsburgh, PA	4/8–16/80	NS	Continuous	GC/ECD	450–852	665	100	Singh et al. 1982
Chicago, IL	4/21–30/80	NS	Continuous	GC/ECD	575–1,311	856	100	Singh et al. 1982
Los Angeles, CA	4/29/76–5/4/76	NS	Grab	GC/ECD	708–944	834	100	Singh et al. 1977a
Stanford Hills, CA	11/24–30/75	NS	Grab	GC/ECD	700–1,700[a]	1,022	100	Singh et al. 1977a
Rural/remote air								
Pullman, WA	12/74–2/75	7[b]	Grab	GC/MS	503–566	530	100	Grimsrud and Rasmussen 1975
Alaska	5/24–30/75	45[c]	Grab	GC/MS	505–970[d]	NS	100	Robinson et al. 1977
Point Barrow, AK	5/7 & 13/82	51[e]	Grab	GC/ECD	634–660	647	100	Rasmussen and Khalil 1983
Pacific NW	3/11/76	34[c]	Grab	GC/ECD	428–611[d]	569	100	Cronn et al. 1977

Table 5-2. Detection of Chloromethane in Air[a] (continued)

Media type/location	Sampling dates	No. of samples	Sample type	Analytical method	Concentration (ppt) Range	Concentration (ppt) Mean	Percent occurrence	Reference
Point Arena, CA	12/8/79–2/18/81	NS	Continuous[f]	GC/ECD	674–898	754	100	Singh et al. 1981b
Point Reyes, CA	12/2–12/75	NS	Grab	GC/ECD	680–1,700[a]	1,260	100	Singh et al. 1977a
Yosemite Park, CA	5/12–17/75	NS	Grab	GC/ECD	654–999	713	100	Singh et al. 1977a
Palm Springs, CA	5/24–27/76	NS	Grab	GC/ECD	645–2,128	1,058	100	Singh et al. 1977a

[a] Marine air may influence levels.
[b] Samples were taken in downtown Pullman, Washington State University campus, 1.2, 1.8, 2.4, 3.0, and 3.6 km in altitude.
[c] Samples were taken at altitudes up to 14.5 km.
[d] Read from a graphical presentation of the data.
[e] Samples were taken at altitudes up to 4.3 km.
[f] 4–6 samples were taken in a 24-hour period on each of 17 sampling days.

GC/ECD = gas chromatography/electron capture detection; GC/MS = gas chromatography/mass spectroscopy; ND = not detected; NS = not specified

In accordance with provisions of the Clean Air Act Amendments (CAAAs) of 1990, chloromethane (or methyl chloride) was among 189 compounds designated as hazardous air pollutants (HAPS). Aside from the public health impacts from direct exposures to these chemicals, most of the HAPS are VOCs that, in combination with other air pollutants, can lead to the formation of ozone and photochemical smog. The EPA has collected available ambient measurements to compile an HAP database (Kelly et al. 1994). This database adds monitoring information to earlier databases that focused on VOCs. The national median ambient air concentration from the HAP database for chloromethane is 1.3 $\mu g/m^3$ (629 ppt [v/v]).

5.4.2 Water

Chloromethane has been detected in surface water, groundwater, drinking water, municipal and hazardous waste landfill leachate, and industrial effluents (Table 5-3). When detected, concentrations appear to be in the ppb-ppt range, possibly due to the rapid volatilization of chloromethane. Chloromethane apparently is formed during the chlorination of drinking water. It was 1 of 13 compounds found in the drinking water of all five cities (Philadelphia, Pennsylvania; Miami, Florida; Seattle, Washington; Ottumwa, Iowa; and Cincinnati, Ohio) studied as part of the EPA National Organics Reconnaissance Survey (NORS) (Coleman et al. 1976). Most of the compounds detected were reported to be highly specific to the locality and raw water supply. Those compounds found in all supplies studied may be widespread.

No specific information concerning sources of chloromethane in fresh surface water was located in the literature. Chloromethane concentrations in surface water may be the result of rain as well as human activity (e.g., industrial effluents, chlorinated secondary effluent from POTWs). Industrial effluents may be a significant source. Seven positive detections of chloromethane in industrial effluents out of more than 4,000 samples from 46 industrial categories and subcategories were reported in the EPA database (Bursey and Pellizzari 1982). Concentrations ranged from 6 to 4,194 mg/L in these effluents. Thirty-four species of fungi can produce chloromethane biosynthetically (Harper et al. 1988). The presence of these fungi near lakes and streams may be a source of chloromethane. The significance of this source to surface water, however, cannot currently be estimated.

In a study of groundwater samples from 479 active waste disposal sites, chloromethane was detected at 20 of these sites (Plumb 1991). Information from HazDat (1998) documents at least 100 current or past NPL sites with detections in groundwater. There is virtually no reporting of actual concentration values or ranges for groundwater detections in the available literature. The presence of chloromethane in groundwater may

Table 5-3. Detection of Chloromethane in Water and Sediments[a]

Media type/location	Sampling dates	No. of samples	Sample type	Analytical method	Concentration (ppt)		Percent occurrence	Reference
					Range	Mean		
Surface water								
Delaware River and Raritan Canal	NS	NS	Grab	NS	ND	NS	0	Grantsrom et al. 1984
Lake Ontario	7/82–5/83	10[a]	Grab	GC/MS	<1	≤ 1	0	Otson 1987
Lake Ontario	NS	NS	NS	NS	Detected	NS	NS	Great Lakes Water Quality Board 1983
Surface waters in New Jersey	NS	605	NS	NS	<0.1–222	NS	4	Page 1981
Groundwater								
New Jersey	NS	1,058[b]	NS	NS	<0.1–6	NS	0.3	Page 1981; Greenberg et al. 1982
Minnesota[c]	NS	13	NS	NS	Detected	NS	69	Sabel and Clark 1984
Minnesota	NS	7	NS	NS	Detected	NS	29	Sabel and Clark 1984
Massachusetts	NS	NS	NS	NS	Detected	44	NS	Burmaster 1982
Drinking water								
Miami, FL	NS	NS	Grab	GC/MS	Detected	NS	NS	Coleman et al. 1976
Seattle, WA	NS	NS	Grab	GC/MS	Detected	NS	NS	Coleman et al. 1976
Ottumwa, IA	NS	NS	Grab	GC/MS	Detected	NS	NS	Coleman et al. 1976
Philadelphia, PA	NS	NS	Grab	GC/MS	Detected	NS	NS	Coleman et al. 1976
Cincinnati, OH	NS	NS	Grab	GC/MS	Detected	NS	NS	Coleman et al. 1976; Kopfler et al. 1977
Landfill leachate								
Minnesota[d]	NS	6	NS	NS	Detected	NS	66	Sabel and Clark 1984
Wisconsin[d]	NS	5	NS	NS	170	170	20	Sabel and Clark 1984
Love Canal, NY[e]	NS	NS	NS	NS	180	180	NS	Shuckrow et al. 1982
Kin-Buc Landfill, NJ[e]	NS	NS	NS	NS	3.1	3.1	NS	Shuckrow et al. 1982

Table 5-3. Detection of Chloromethane in Water and Sediments[a] (continued)

Media type/location	Sampling dates	No. of samples	Sample type	Analytical method	Concentration (ppt)		Percent occurrence	Reference
					Range	Mean		
Hazardous waste sites	NS	NS	NS	GC/MS	5.4–500	115	NS	CLPSBD 1987
11 National Priority List sites	NS	NS	NS	NS	Detected	NS	NS	NPLTDB 1989
Urban Runoff								
15 U.S. cities	NS	86	Grab	GC/MS	ND	ND	0	Cole et al. 1984
Effluents								
Petroleum refinery effluents[f]	NS	17	Grab	GC/MS	<100–>100	NS	NS	Snider and Manning 1982
Petroleum refinery effluents[g]	NS	17	Grab	GC/MS	<10	NS	NS	Snider and Manning 1982

[a] 10 locations on Lake Ontario.
[b] 408 wells.
[c] Groundwater under municipal solid waste landfills.
[d] Municipal solid waste leachate.
[e] Industrial landfill.
[f] Biotreatment effluents.
[g] Final effluent.

GC/ECD = gas chromatography/electron capture detection; GC/MS = gas chromatography/mass spectroscopy; ND = not detected; NS = not specified.

result from both natural and anthropogenic sources. Since chloromethane has been detected in the groundwater near municipal waste sites containing the chemical (Sabel and Clark 1984), waste deposits of chloromethane on land may lead to groundwater contamination. Chloromethane appears to be a constituent of both municipal and industrial waste landfills. In these landfills, volatilization may be hindered and leaching to groundwater could become an important transport pathway. Chloromethane may also be a product from the anaerobic metabolism of higher chlorinated methanes present in the soil (Vogel et al. 1987).

5.4.3 Sediment and Soil

Information from HazDat (1998) documents the presence of chloromethane in soils at 34 waste sites and in sediments at 13 waste sites. Information on background levels in soils and sediments is very limited in the available literature. The only information located in the literature concerning the presence of chloromethane in soil was the natural formation of chloromethane by a number of fungi (Harper et al. 1988) and its presence in both landfill leachate and groundwater.

5.4.4 Other Environmental Media

As presented in Section 5.2.1, chloromethane is released from wood smoke, burning coal, volcanoes, and burning plastic (Chopra 1972; Crutzen et al. 1979; Edgerton et al. 1984, 1986; Fabian 1986; Kadaba et al. 1978; Khalil et al. 1985; Kleindienst et al. 1986; Palmer 1976; Rasmussen et al. 1980; Singh et al. 1982; Tassios and Packham 1985). Palmer (1976) suggested that 1 cm^3 of chloromethane gas (2.2 mg) was produced for each gram of cellulose burned (glowing combustion). Concentrations of chloromethane in smoke from combustion processes, however, are highly variable and depend on both the fuel (i.e., the amount of inorganic chlorine present in the fuel) and the temperature of the bum. Thus, quantification of chloromethane in these media will be representative of the specific source and the exact conditions of the burn rather than of general emission levels. Chloromethane has not been detected in auto exhaust (detection limit of 1 ppm) (Hasanen et al. 1979).

Chloromethane was present in the expired air of all 3 tested groups of 62 nonsmoking adults, including a control, a prediabetic, and a diabetic group (Krotoszynski and O’Neill 1982). Since chloromethane is a ubiquitous constituent of air, it is reasonable that it would be found in the expired air of virtually all humans. The chlorine solutions used to chlorinate drinking water did not contain chloromethane, but other higher chloromethanes were present (Otson et al. 1986).

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

Chloromethane is a ubiquitous low-level constituent of air and is probably found at very low concentrations in many drinking water supplies that have used chlorine treatment for disinfection. As such, the general population will be exposed to low background levels at all times, while those living in urban centers may be exposed to slightly higher levels.

According to one report, persons living in Los Angeles, California; Phoenix, Arizona; and Oakland, California; would have daily intakes of ≈ 140.4, 108.6, and 59.7 μg/day, respectively (Singh et al. 1981a), based on a total respirable air volume of 23 m^3/day at 25 °C and 1 atm pressure. Using the data of Shah and Singh (1988) for remote, rural, suburban, and urban air masses, daily intakes are estimated to be = 31, 40, 28, and 35 μg/day, respectively. The intakes for rural and remote air masses are based on very small sample sizes and may be inaccurate. Dermal exposure and exposures from drinking water containing chloromethane are more difficult to estimate from the available information. Drinking water concentrations are not well described in the literature and may vary considerably both seasonally and geographically.

Historically (30 years ago or longer), large exposures could have been associated with leaking refrigerators that used chloromethane as a refrigerant. While refrigeration-grade chloromethane may still be available, it is not known whether it is currently used to any significant degree in refrigeration equipment. Without this information, potential exposures cannot be estimated.

Chloromethane is an impurity in vinyl chloride when the vinyl chloride is produced from the thermal dehydrochlorination of 1,2-dichloroethane (Zaidman et al. 1991). Exposures to chloromethane could take place during the manufacture of vinyl chloride or when vinyl chloride wastes have been released to the environment or to waste sites. Information is lacking to make any firm estimates of such exposure potentials. Of the 172 current or past NPL sites in HazDat (1998) showing site contamination with chloromethane, 128 of these sites (about 75%) also showed site contamination related to vinyl chloride.

Current and empirically based estimates of exposures to chloromethane in various occupations are lacking. Some insights can be gleaned from the National Institute for Occupational Safety and Health's (NIOSH's)

National Occupational Hazard Survey (NOHS) database (the NOHS database is also called the National Occupational Exposure Survey or NOES database) that estimates the number of potentially exposed workers in a variety of manufacturing jobs (Sieber et al. 1991). Based on conditions typical of the mid-1970s it was estimated that 39,343 workers had potential exposures to chloromethane (NOES 1991). The majority of these potential exposures involved occupations where chloromethane could have been used as a cleaner or pest control fumigant. There is virtually no mention in NOHS of current applications such as use as a process chemical in the manufacture of silicone rubbers. While the NOHS data are of some historical value, it is therefore doubtful whether they accurately reflect the potential number of workers subject to current occupational exposures. A number of regulations, however, are in place to protect workers from exposure to levels of chloromethane that are considered harmful.

5.6 EXPOSURES OF CHILDREN

This section focuses on exposures from conception to maturity at 18 years in humans and briefly considers potential pre-conception exposure to germ cells. Differences from adults in susceptibility to hazardous substances are discussed in Section 2.6, Children's Susceptibility.

Children are not small adults. A child's exposure may differ from an adult's exposure in many ways. Children drink more fluids, eat more food, and breathe more air per kilogram of body weight, and have a larger skin surface in proportion to their body volume. A child's diet often differs from that of adults. The developing human's source of nutrition changes with age: from placental nourishment to breast milk or formula to the diet of older children who eat more of certain types of foods than adults. A child's behavior and lifestyle also influence exposure. Children crawl on the floor; they put things in their mouths; they may ingest inappropriate things such as dirt or paint chips; they spend more time outdoors. Children also are closer to the ground, and they do not have the judgement of adults in avoiding hazards (NRC 1993).

Children are members of the general population and encounter the same exposures that are described in Section 5.5. No data were found on the measurement of chloromethane or its metabolites in amniotic fluid, meconium, cord blood, or neonatal blood that would indicate prenatal exposure. It is not known whether chloromethane in the body can cross the placenta and enter into the developing young. Since chloromethane is broken down and eliminated from the body quickly in adults, it is unlikely that chloromethane would be stored in maternal tissues or mobilized during pregnancy or lactation. Chloromethane was present in 2 of 8 samples of mothers' milk from Bayonne and Jersey City, New Jersey; Bridgeville, Pennsylvania; and Baton

Rouge, Louisiana (Pellizzari et al. 1982). No concentrations were reported and no information was given concerning the source of the chloromethane in the milk.

The levels that children could be exposed to through accidents involving chloromethane may be higher than levels affecting adults because chloromethane is heavier than air (i.e., greater concentrations near the ground).

Parents can inadvertently carry certain hazardous materials home from work on their clothes, skin, hair, tools and in their vehicles. However, since chloromethane is so volatile, it is unlikely that children would be exposed by this route. No incidents of home contamination by chloromethane were reported in the Workers' Home Contamination Study conducted under the Workers' Family Protection Act (29 U.S.C. 671a) (DHHS 1995).

5.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

All humans are probably exposed to low concentrations of chloromethane. Those with potentially higher than average exposures include workers employed in the manufacturing and use (by analogy) industries. In addition to individuals occupationally exposed to chloromethane (see Section 5.5), there are several groups within the general population that could have exposures higher than background levels. These populations include individuals living in proximity to sites where chloromethane was produced or disposed, and individuals living near one of the 172 NPL hazardous waste sites where chloromethane has been detected in some environmental media (HazDat 1998). Chloromethane may also be a constituent in other materials such as vinyl chloride. Chloromethane exposure risks may be of concern to individuals working or living in the vicinity of sites where vinyl chloride was produced or where there is evidence vinyl chloride has been disposed.

People with very old refrigeration equipment in which chloromethane is used as a refrigerant are a population with potentially very high exposures. These refrigerators can leak and result in very high local air concentrations of chloromethane. This population is, however, likely to be small since the number of refrigerators using chloromethane has been decreasing.

5.8 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 chloromethane 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 chloromethane.

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.

5.8.1 Identification of Data Needs

Physical and Chemical Properties. Data regarding physical and chemical properties are essential for estimating the partitioning of a chemical in the environment. Most of the necessary data on physical and chemical properties are available for chloromethane, and many of these have experimental descriptions accompanying them so that accuracy can be evaluated. The data on known physical and chemical properties form the basis of many of the input requirements for environmental models that predict the behavior of a chemical under specific conditions including hazardous waste landfills.

Production, Import/Export, Use, Release, and Disposal. Production methods for chloromethane are well-described in the literature (including the patent literature) and there does not appear to be a need for further information. Uses of chloromethane have been documented, although a detailed description of all uses is not available. This information is useful for estimating the potential for environmental releases from manufacturing and use industries as well as the potential environmental burden; however, it is difficult to obtain this information in the detail desired since generally it is considered to be confidential business information (CBI) for those industries that manufacture chloromethane. Release information, which can be used to estimate environmental burdens and potentially exposed populations, is also not obtained easily.

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 1996, became available in May of 1998. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

Environmental Fate. The fate of chloromethane in air is well-described because extensive air photolysis and photo-oxidation studies are available that characterize these processes. Biodegradation studies in surface water and groundwater are not as complete. These kinds of studies are important because they would provide information about fundamental removal mechanisms for chloromethane in the environment and might aid in understanding the behavior of chloromethane at hazardous waste sites or municipal landfills. The vapor pressure of chloromethane and its presence in groundwater suggest that these processes are important, particularly at hazardous waste sites, and may account for some of the losses of chloromethane from the site. Limited research suggests that common soil fungi may be able to generate chloromethane as well as to dehalogenate, and thus degrade, it. Since these wood rot fungi can also break down other halogenated aliphatic compounds, there is the possibility that some of the chloromethane found at waste sites could have been produced through the action of such fungi on other waste compounds. More research is needed to document the importance of these biodegradation mechanisms and to determine whether the net effects tend toward a progressive reduction in the levels of chloromethane found in contaminated soils and sediments at waste sites.

Bioavailability from Environmental Media. Experimental inhalation studies in animals and humans indicate that chloromethane is bioavailable from the atmosphere. Studies for the oral and dermal routes of exposure may be of lesser research importance than studies on inhalation pathways and the bioavailability of chloromethane from water, soil, and other environmental media.

Food Chain Bioaccumulation. The log K_{ow} for chloromethane is in the range of 0.91 to 1.086 (see Chapter 3, Table 3-2). Such low values generally mean that the BCF will be low, suggesting that chloromethane will not tend to concentrate in aquatic organisms. However, no information was identified on experimental determinations of BCF levels for chloromethane. Determinations of BCF values for organisms at various trophic levels are needed to estimate human dietary intake of chloromethane.

Exposure Levels in Environmental Media. Extensive environmental monitoring data are available for chloromethane in air, while the available data are very limited for drinking water, surface water, and groundwater. The air monitoring data describe the concentrations that populations are exposed to through inhalation of ambient air. The data for water are not sufficient to accurately characterize the concentrations of chloromethane present in drinking water, surface water, or groundwater. Almost no data are available for soils. These data are needed to determine the ambient concentrations of chloromethane so that exposure of the general population as well as of terrestrial and aquatic organisms can be estimated.

Reliable monitoring data for the levels of chloromethane in contaminated media at hazardous waste sites are needed to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites.

Exposure Levels in Humans. The database for chloromethane exposure levels in humans is limited to determinations of chloromethane in breast milk. A more complete database is needed to determine the current exposure levels and to estimate the average daily dose associated with various scenarios (e.g., living near a hazardous waste site). An environmental media monitoring program may provide the necessary information for estimating environmental exposures, while workplace monitoring at use sites, using personal dosimeters and remote sensing devices, would probably provide useful workplace information. The available NOES database of potential occupational exposures was assembled in the late 1980s and is becoming outdated. An update to this statistically based database of potential occupational exposures is needed.

Exposures of Children. Chloromethane was present in 2 of 8 samples of mothers' milk from Bayonne and Jersey City, New Jersey; Bridgeville, Pennsylvania; and Baton Rouge, Louisiana (Pellizzari et al. 1982). No concentrations were reported and no information was given concerning the source of the chloromethane in the milk. Studies to determine current chloromethane residues and sources in breast milk of women in the general population and in the work force are needed. Well water surveys should be conducted in areas near landfills where chloromethane has been detected at significant levels. Ingestion of chloromethanecontaminated drinking water could be an important route of exposure in children.

Current information on whether children are different in their weight-adjusted intake of chloromethane via oral and dermal exposures was not available. A study to determine this information is needed.

Exposure Registries. An exposure registry for chloromethane is not available. The development of a registry of exposures is needed to assess exposure levels and frequency. In addition, a registry would allow assessment of variations in exposure resulting from such variables as geography, season, regulatory actions, presence of hazardous waste landfills, or presence of manufacturing and use facilities.

Although chloromethane is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry, it will be considered in the future. 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.

5.8.2 Ongoing Studies

A project carried out at Cambridge Analytical Associates, Inc., under the direction of Dr. Samuel Fogel with NSF support will study the biodegradation of chlorinated aliphatic compounds by methane-utilizing bacteria (FEDRIP 1998).