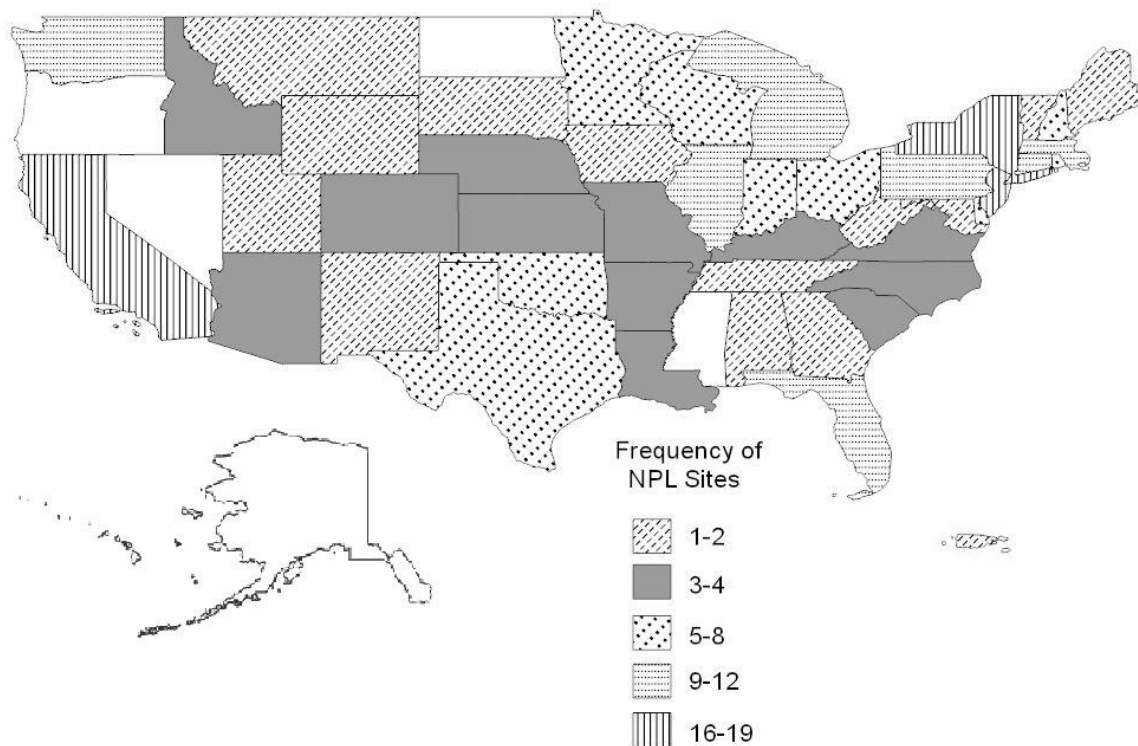


CHAPTER 5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Chloromethane has been identified in at least 236 of the 1,867 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (ATSDR 20179). However, the number of sites evaluated for chloromethane is not known. The number of sites in each state is shown in Figure 5-1.

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



Source: ATSDR 2019

- The most likely route of exposure for the general public to chloromethane is through inhalation; the general public is not expected to be exposed to concentrations of chloromethane much above 1-3 ppbv in urban locations.
- The population with the highest potential exposures would include those people who work in chloromethane manufacturing or use industries.
- Chloromethane is mostly found in the air due to releases from processing facilities, and in the air and ocean from natural processes.

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Chloromethane 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 a product of 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 a component in vinyl chloride (PubChem 2021; WHO 1999), 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 with various estimates in the range of 0.6-3 years (see Section 5.4). 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 H.B. 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 2019; IPCC 1995).

In water, chloromethane is expected to volatilize rapidly (Mabey and Mill 1978). It is not expected to sorb to sediments or to bioaccumulate. 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 (Elliot and Rowland 1995; Mabey and Mill 1978). Air concentrations of chloromethane are generally in the low parts 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 1.22 ppbv in urban locations (Mohamed et al. 2002). In rural locations, the exposure concentration is expected to be ≈ 0.7 -0.9 ppb. The database for occupational exposure is outdated (late 1980s or earlier). The OSHA PEL allows for a TWA 100 ppm, a ceiling exposure of 200 ppm and a peak exposure of 300 ppm (5-minute maximum peak in any 3 hours) (OSHA 2018). Also, no sufficiently comprehensive data on current applications of the substance are known so as 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, such as those that produce chloromethane as an intermediary product.

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

Chloromethane is both an anthropogenic and naturally occurring chemical. Chloromethane is a volatile organic compound (VOC) and is a halocarbon. Anthropogenic sources include industrial production, polyvinyl chloride burning, and wood burning; natural sources include the oceans (biogenic emissions from phytoplankton), normal human exhalation, microbial fermentation, and biomass fires (e.g., forest fires, grass fires). Chloromethane is produced industrially by reaction of methanol and hydrogen chloride (HCl) or by chlorination of methane (Edwards et al. 1982a; Key et al. 1980). While the reaction of methanol with HCl is the most common method, the choice of process depends, in part, on the HCl balance at the site (the methane route produces HCl, the methanol route uses it) (Edwards et al. 1982a). Typically, manufacturing plants that produce chloromethane also produce higher chlorinated methanes (methylene chloride, chloroform, and carbon tetrachloride).

The methanol-HCl process involves combining vapor-phase methanol and HCl at 180-200 °C, followed by passage over a catalyst where the reaction occurs (Key et al. 1980). Catalysts include alumina gel, gamma alumina, and cuprous or zinc chloride on pumice or activated carbon. The exit gases from the reactor are quenched with water to remove unreacted HCl and methanol. The quench water is stripped of the dissolved methanol and chloromethane, and the remaining dilute HCl solution is used in-house or treated and discharged (Key et al. 1980). The chloromethane is then dried by treatment with concentrated sulfuric acid, compressed, cooled, and stored.

In the methane chlorination process, a molar excess of methane is mixed with chlorine, and the mixture is then fed to a reactor, which is operated at 400 °C and 200 kPa pressure (Key et al. 1980). The exit gases can then be scrubbed with chilled chloromethanes (mono- to tetrachloromethane) to remove most of the reaction chloromethanes from unreacted methane and HCl. The by-product HCl is removed by water wash, stripped of any chloromethanes, and either used in-house or sold; the unreacted methane is recycled through the process. The condensed chloromethanes are scrubbed with dilute NaOH to remove any HCl, dried, compressed, cooled, and then fractionally distilled to separate the four chloromethanes.

It is difficult to estimate the total production levels for chloromethane at specific industrial plants because many of the producers consume their output internally as a feedstock for other chemicals, including silicones and higher chlorinated methanes. The nine sites reported in CDR manufacturing information are: (1) Occidental Chemical Corp Geismar Plant in Geismar, Louisiana; (2) Occidental Chemical Corporation in Wichita, Kansas; (3) Momentive Performance Materials in Waterford, New York; (4) Praxair Distribution, Inc. in Toledo, Ohio; (5) Formosa Plastics Corp. in Point Comfort, Texas; (6) Dow

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Corning Corp in Carrollton, Kentucky; (7) Olin Blue Cube in Freeport, Texas; (8) Solvay USA Inc. in Princeton, New Jersey; and (9) Blue Cube Operations LLC in Plaquemine, Louisiana (CDR 2016). The production volume at each of these sites is withheld as it is considered confidential business information (CBI). The on-site quantities of chloromethane reported by facilities to the EPA are shown in Table 5-1. In 2015, national aggregate production volume of chloromethane was between 1,000,000,000 and 5,000,000,000 pounds (CDR 2016). National aggregate production volumes of chloromethane from 2012 to 2014 were also between 1,000,000,000 and 5,000,000,000 pounds (CDR 2016). National aggregate production volumes in 2011 were 1,396,155,238 pounds (CDR 2012).

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

State ^a	Number and Name of facilities	Minimum amount on site in pounds ^b	Maximum amount on site in pounds ^b	Activities and uses ^c
AL	2	1,100	10,998	1, 5, 13
	AMVAC CHEMICAL CO	1,000	9,999	1, 5
	EVONIK CORP	100	999	1, 13
AR	2	10,000	100,098	1, 5
	EVERGREEN PACKAGING	0	99	1, 5
	FUTUREFUEL CHEMICAL CO	10,000	99,999	1, 5
CA	1	No data	No data	No data
	AMVAC CHEMICAL CORP	No data	No data	No data
FL	2	1,000	10,098	1, 5, 6
	SIVANCE LLC	1,000	9,999	6
	WESTROCK CP LLC (FORMERLY ROCK-TENN & SMURFIT-STONE)	0	99	1, 5
GA	1	1,000,000	9,999,999	6
	CHEMTALL INC	1,000,000	9,999,999	6
IL	4	1,200,000	11,999,997	6
	RHO CHEMICAL CO INC	No data	No data	No data
	AKZO NOBEL SURFACE CHEMISTRY LLC	100,000	999,999	6
	EVONIK CORP	1,000,000	9,999,999	6
	LONZA INC	100,000	999,999	6
KS	1	1,000,000	9,999,999	1, 4, 6
	OCCIDENTAL CHEMICAL CORP	1,000,000	9,999,999	1, 4, 6
KY	2	1,100,000	10,999,998	1, 3, 6
	DOW SILICONES CORP	1,000,000	9,999,999	1, 3, 6

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

State ^a	Number and Name of facilities	Minimum amount on site in pounds ^b	Maximum amount on site in pounds ^b	Activities and uses ^c
	PMC ORGANOMETALLIX INC	100,000	999,999	6
LA	12	51,441,100	114,410,988	1, 3, 4, 5, 6, 9, 10, 12, 13, 14
	AXIALL LLC	10,000	99,999	1, 5, 12
	BASF CORP	100,000	999,999	6
	BLUE CUBE OPERATIONS LLC - PLAQUEMINE SITE	100,000	999,999	9, 12, 14
	ECO-SERVICES OPERATIONS	10,000	99,999	12
	EXXONMOBIL BATON ROUGE CHEMICAL PLANT (PART)	10,000	99,999	10
	GALATA CHEMICALS LLC - GALATA TAFT FACILITY	1,000,000	9,999,999	6
	HONEYWELL INTERNATIONAL INC-BATON ROUGE PLANT	10,000	99,999	1, 13
	MONSANTO LULING	1,000	9,999	1, 13
	OCCIDENTAL CHEMICAL HOLDING CORP - GEISMAR PLANT	50,000,000	99,999,999	1, 3, 4, 6
	SHINTECH PLAQUEMINE PLANT	100	999	1, 4, 5
	SOLVAY USA INC	100,000	999,999	6
	THE DOW CHEMICAL CO - LOUISIANA OPERATIONS	100,000	999,999	1, 5, 6, 12, 13
MD	1	100	999	1, 5
	VERSO LUKE LLC	100	999	1, 5
MI	2	110,000	1,099,998	1, 3, 5, 6, 10, 12, 13
	EES COKE BATTERY LLC	10,000	99,999	1, 5
	THE DOW CHEMICAL CO	100,000	999,999	1, 3, 5, 6, 10, 12, 13
MO	1	10,000	99,999	6
	BCP INGREDIENTS INC	10,000	99,999	6
MS	2	0	198	1, 5

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

State ^a	Number and Name of facilities	Minimum amount on site in pounds ^b	Maximum amount on site in pounds ^b	Activities and uses ^c
	GEORGIA-PACIFIC MONTICELLO LL C	0	99	1, 5
	INTERNATIONAL PAPER-VICKSBURG MILL	0	99	1, 5
NC	2	0	198	1, 5
	BLUE RIDGE PAPER PRODUCTS LLC	0	99	1, 5
	INTERNATIONAL PAPER RIEGELWOOD MILL	0	99	1, 5
NJ	2	1,100	10,998	1, 12, 13, 14
	DUPONT CHAMBERS WORKS	1,000	9,999	1, 12, 13, 14
	VEOLIA - MORSES MILL	100	999	14
NY	1	1,000,000	9,999,999	1, 3, 6
	MPM SILICONES LLC	1,000,000	9,999,999	1, 3, 6
OH	4	121,000	1,209,996	6, 9, 12, 14
	CHEMTRADE REFINERY SOLUTIONS LP	10,000	99,999	14
	HERITAGE THERMAL SERVICES	1,000	9,999	12
	PRAXAIR DISTRIBUTION INC	100,000	999,999	9
	SOLVAY SPECIALTY POLYMERS USA LLC	10,000	99,999	6
PA	1	10,000	99,999	6
	CRODA INC	10,000	99,999	6
SC	4	20,000	200,097	1, 5, 6
	SANTOLUBES MANUFACTURING LLC DBA BLACKMAN UHLER SPECIALTIES	No data	No data	No data
	HALOCARBON PRODUCTS CORP	10,000	99,999	6
	INTERNATIONAL PAPER GEORGETOWN MILL	0	99	1, 5

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

State ^a	Number and Name of facilities	Minimum amount on site in pounds ^b	Maximum amount on site in pounds ^b	Activities and uses ^c
	SUN CHEMICAL BUSHY PARK FACILITY	10,000	99,999	6
TN	1	1,000	9,999	6
	ALBEMARLE US INC	1,000	9,999	6
TX	11	3,511,000	35,110,089	1, 3, 4, 5, 6, 7, 10, 12, 13, 14
	AKZO NOBEL FUNCTIONAL CHEMICALS LLC	10,000	99,999	6
	ALBEMARLE CORP PASADENA PLANT	100,000	999,999	6
	BAKER PETROLITE BAYPORT FACILITY	100,000	999,999	6, 7
	BASF CORP - BEAUMONT	1,000,000	9,999,999	6
	EASTMAN CHEMICAL CO TEXAS OPERATIONS	0	99	1, 13
	EXXONMOBIL BAYTOWN CHEMICAL PLANT (PART)	100,000	999,999	1, 5, 10, 12, 14
	FORMOSA PLASTICS CORP TEXAS	100,000	999,999	1, 5, 13, 14
	NALCO CHAMPION - AN ECOLAB CO	1,000,000	9,999,999	6
	OLIN BLUE CUBE FREEPORT TX	1,000,000	9,999,999	1, 3, 4, 6
	SACHEM INC	100,000	999,999	6
	VEOLIA ES TECHNICAL SOLUTIONS LLC PORT ARTHUR FACILITY	1,000	9,999	12
UT	1	10,000	99,999	12
	CLEAN HARBORS ARAGONITE LLC	10,000	99,999	12
WA	1	1,000,000	9,999,999	1, 5
	LONGVIEW FIBRE PAPER & PACKAGING INC	1,000,000	9,999,999	1, 5
WI	4	210,100	2,100,996	1, 5, 6
	CHEMDESIGN PRODUCTS INC	10,000	99,999	6

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

State ^a	Number and Name of facilities	Minimum amount on site in pounds ^b	Maximum amount on site in pounds ^b	Activities and uses ^c
	EVONIK INDUSTRIES	100,000	999,999	6
	EVONIK MATERIALS CORP	100,000	999,999	6
	WISCONSIN RAPIDS PULP MILL	100	999	1, 5
WV	1	10,000	99,999	1, 5, 6
	MPM SILICONES LLC	10,000	99,999	1, 5, 6

^a Post office state abbreviations used.

^b Amounts on site reported by facilities in each state.

^c Activities/Uses:

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

Source: TRI17 2018; Data are from 2017

5.2.2 Import/Export

Exports of chloromethane from the U.S. are considerably larger than imports. In the period from 2014 to 2018, general imports² and imports for consumption³ of chloromethane were equal. U.S. imports of chloromethane increased from 228,303 kg in 2014 to 3,246,844 kg in 2018 (USITC 2019). Between 2016 and 2017, imports more than doubled from 1,157,708 kg to 2,598,670 kg (USITC 2019). U.S. domestic

² General imports are total physical arrivals of chloromethane to the United States from other countries that either enter consumption channels immediately or enter into bonded warehouses or Foreign Trade Zones (FTZs) (U.S. Census Bureau 2018). A bonded warehouse is an approved private warehouse used to store imports until duties or taxes are paid (U.S. Census Bureau 2018). FTZs are specially licensed commercial and industrial areas in or near ports of entry where goods may be brought in without paying customs duties. Imports brought to FTZs can be manipulated (i.e. sold, stored, exhibited, repacked, cleaned, manufactured, etc.) prior to re-export or entry (U.S. Census Bureau 2018).

³ Imports for consumption are the total amount of merchandise that has physically cleared through customs by either entering consumption channels immediately or leaving bonded warehouses or FTZs (U.S. Census Bureau 2018).

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exports⁴ of chloromethane fluctuated from 2014 to 2018, ranging from 22,042,539 kg in 2015 to 10,430,816 kg in 2017 (USITC 2019). U.S. total exports⁵ of chloromethane also fluctuated from 2014 to 2018. Total exports range from 22,048,825 kg in 2015 to 11,115,446 kg in 2017 (USITC 2019). In 2018, there were 13,332,060 kg of chloromethane domestic exports and 14,640,606 kg of total exports (USITC 2019).

5.2.3 Use

Chloromethane is used mainly (89%) in the production of silicones (PubChem 2019; Tsai 2017). Chloromethane has also been used in the production of methyl cellulose ethers (3%), quaternary ammonium compounds (3%), herbicides (3%), butyl rubber (1%), and miscellaneous uses (2%) (PubChem 2019). It has also been used in the past as a foam blowing agent (e.g., in producing polystyrene foams), as a refrigerant, and as aerosol propellant (PubChem 2019). At some time after a series of chloromethane related deaths in 1928 and 1929, acrolein was added to chloromethane refrigerants as a nasal irritating tracer to help warn individual who were being exposed (McNally 1946). At the present time, virtually all of the commercial uses for chloromethane are consumptive in that the chloromethane is reacted to form another product during use. Thus, almost all chloromethane will be consumed when used and will no longer be available for release, disposal, or reuse.

Chloromethane is reported in the most recent CDR data for both industrial and consumer uses. Sectors that use chloromethane in industrial processing include plastic material and resin manufacturing, all other basic organic chemical manufacturing, and paint and coating manufacturing (CDR 2016). Industry function categories include laboratory chemicals, intermediates, adhesives and sealant chemicals, paint additives, and coating additives not described by other categories (CDR 2016).

According to CDR data for 12 sites, 4 report chloromethane use for commercial and 3 report for both commercial and consumer use (CDR 2016). Product categories for consumer and commercial use include adhesives and sealants; fabric, textile, and leather products not covered elsewhere; paints and coatings;

⁴ Domestic exports are goods that are grown, produced, or manufactured in the United States, or goods of foreign origin that have been changed, enhanced in value, or improved in condition in the United States (U.S. Census Bureau 2018).

⁵ Total exports are the sum of domestic exports and foreign exports, which are goods of foreign origin that are in the same condition at the time of export as they were in when imported (U.S. Census Bureau 2018).

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personal care products; and plastic and rubber products not covered elsewhere (CDR 2016). Of these twelve sites, six reported that chloromethane is not used in children's products (CDR 2016).

5.2.4 Disposal

Of 22 sites that reported industrial processing and use of chloromethane in 2016, four reported that the chemical was recycled and four reported that it was not (CDR 2016). In 2012, one of 22 sites reported that chloromethane was recycled while five of 22 reported that it was not (CDR 2012).

Of 12 sites that reported consumer and commercial use of chloromethane in 2016, one reported that the chemical was recycled while seven reported that it was not (CDR 2016). In 2012, one of nine sites reported that chloromethane was recycled while five of nine reported that it was not (CDR 2012).

Limited information was located in the literature concerning the disposal of chloromethane. Since most chloromethane is used consumptively, little remains to be disposed. Nonetheless, some chloromethane is present in waste, and chloromethane has been detected in hazardous waste landfills. Its presence in hazardous waste sites may result from the landfilling of still bottoms (accumulated solvent wastes) or other residues from the manufacture and use of chloromethane. Its presence in municipal waste landfills suggests that consumer products containing chloromethane were landfilled (e.g., propellants for aerosol cans, old refrigerators). Since chloromethane is an impurity in vinyl chloride, the disposal of vinyl chloride may also lead to chloromethane contamination. Like other chlorinated hydrocarbons, chloromethane can inhibit the combustion of such fuels as methane. Chloromethane has a considerable inhibitory effect on combustion when mixed with methane, the principal component of natural gas (Philbrick et al. 1993). Changes in the amounts of chloromethane added to the methane fuel stock did not affect combustion in a concentration-dependent or consistent manner. Such phenomena would complicate the disposal of chloromethane using incineration technologies. When incineration was attempted under oxygen-starved conditions (Taylor and Dellinger 1988), chloromethane was shown to combine with other components of the combustion mixture to form, among other compounds, chlorinated ethanes, hexachlorobenzene, and octachlorostyrene.

Chloromethane is listed as a toxic substance under Section 313 of the Emergency Planning and Community Right to Know Act (EPCRA) under Title III of the Superfund Amendments and Reauthorization Act (SARA). Disposal of wastes containing chloromethane is controlled by a number of federal regulations (see CHAPTER 7.).

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5.3 RELEASES TO THE ENVIRONMENT

The Toxics Release Inventory (TRI) data should be used with caution because only certain types of facilities are required to report (EPA 2018). This is not an exhaustive list. Manufacturing and processing facilities are required to report information to the TRI only if they employ ≥ 10 full-time employees; if their facility's North American Industry Classification System (NAICS) codes is covered under EPCRA Section 313 or is a federal facility; and if their facility manufactures (defined to include importing) or processes any TRI chemical in excess of 25,000 pounds, or otherwise uses any TRI chemical in excess of 10,000 pounds, in a calendar year (EPA 2018).

According to the Toxics Release Inventory (TRI), in 2017, a total of 1,094,537 pounds (496,474 kilograms) of chloromethane was released to the environment from 66 processing facilities (TRI17 2018). This total consists of chloromethane released to air (955,937 pounds), water (6661 pounds), soil (31 pounds), and via underground injection (131,890 pounds). Table 5-2 lists the amounts released to the environment in each state. In addition, there were no releases from manufacturing and processing facilities to POTWs and an estimated 5,811 pounds (2,636 kg) were transferred off-site (TRI17 2018).

Chloromethane has been identified in a variety of environmental media (air, surface water, groundwater, soil, and sediment) collected at 236 of the 1,867 current and former NPL hazardous waste sites (ATSDR 2019).

Table 5-2. Releases to the Environment from Facilities that Produce, Process, or Use Chloromethane^a

State ^c	RF ^d	Reported amounts released in pounds per year ^b						Total Release	
		Air ^e	Water ^f	UI ^g	Land ^h	Other ⁱ	On-site ^j	Off-site ^k	On and off-site
TX	11	349,041	21	14,800	5,806	0	363,878	5,790	369,668
LA	12	46,208	3	74,660	0	0	120,871	0	120,871
MS	2	76,976	434	0	0	0	77,410	ND	77,410
SC	4	68,714	0	0	0	0	68,714	ND	68,714
WI	4	57,298	0	0	0	0	57,298	ND	57,298
AR	2	56,112	0	0	10	0	56,122	ND	56,122
IL	4	51,260	0	0	4	0	51,260	4	51,264
KS	1	5,602	0	42,430	0	2	48,032	2	48,034
NC	2	47,920	1	0	1	0	47,922	ND	47,922
FL	2	46,413	0	0	0	16	46,413	16	46,429
NY	2	35,372	15	0	0	0	35,387	ND	35,387
KY	2	30,340	49	0	0	0	30,389	ND	30,389
WA	1	26,790	0	0	0	0	26,790	ND	26,790
MI	2	25,100	130	0	0	0	25,230	ND	25,230
OH	4	19,250	0	0	0	0	19,250	ND	19,250
GA	1	6,500	7	0	0	0	6,507	ND	6,507

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Table 5-2. Releases to the Environment from Facilities that Produce, Process, or Use Chloromethane^a

State ^c	RF ^d	Air ^e	Reported amounts released in pounds per year ^b				Total Release		
			Water ^f	UI ^g	Land ^h	Other ⁱ	On-site ^j	Off-site ^k	On and off-site
WV	1	5,311	211	0	0	0	5,522	ND	5,522
NJ	2	703	0	0	0	0	703	ND	703
TN	1	609	0	0	0	0	609	ND	609
UT	1	238	0	0	0	0	238	0	238
PA	1	167	0	0	0	0	167	ND	167
AL	2	13	0	0	0	0	13	ND	13
MO	1	0	0	0	0	0	0	ND	0
CA	1	ND	ND	ND	ND	ND	ND	ND	ND
Total	66	955,937	871	131,890	5,821	18	1,088,725	5,812	1,094,537

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

^b Data in TRI are maximum amounts released by each facility.

^c Post office state abbreviations are used.

^d Number of reporting facilities.

^e The sum of fugitive and point source releases by a given facility.

^f The sum of on-site surface water discharges, and off-site transfers to wastewater treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).

^g The sum of on-site and off-site disposal to underground injection wells (Class I wells and Class II-V).

^h The sum of on-site and off-site disposal to: Resource Conservation and Recovery Act (RCRA) subtitle C landfills, other landfills, RCRA subtitle C surface impoundments, other surface impoundments, land treatment, other land disposal.

ⁱ Includes the sum of off-site transfers to: storage only, solidification/stabilization (metals only) disposal, other off-site management, waste broker for disposal, unknown.

^j Total on-site disposal or other releases of the chemical including emissions to air, surface water discharges, land and underground injection wells.

^k Total amount of chemical transferred off-site for disposal or other releases, including to POTWs.

ND = No data; RF = Reporting Facilities; UI = Underground Injection

Source: TRI17 2018; Data are from 2017

5.3.1 Air

Estimated releases of 955,937 pounds (~434 metric tons) of chloromethane to the atmosphere from 64 domestic manufacturing and processing facilities in 2017, accounted for about 87% of the estimated total environmental releases from facilities required to report to the TRI (TRI17 2018). These releases are summarized in Table 5-3.

Table 5-3. Releases to the Atmosphere from Facilities that Produce, Process, or Use Chloromethane^a

Facility	Reported amounts released in pounds per year ^b		
	State	Fugitive Air Emissions	Point Source Air Emissions
EASTMAN CHEMICAL CO TEXAS OPERATIONS	TX	63	233,920

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Table 5-3. Releases to the Atmosphere from Facilities that Produce, Process, or Use Chloromethane^a

Facility	Reported amounts released in pounds per year ^b		
	State	Fugitive Air Emissions	Point Source Air Emissions
EXXONMOBIL BAYTOWN CHEMICAL PLANT (PART)	TX	86,000	1,200
MONSANTO LULING	LA	1,888	7,000
INTERNATIONAL PAPER GEORGETOWN MILL	SC	0	68,714
EVERGREEN PACKAGING	AR	8	56,084
GEORGIA-PACIFIC MONTICELLO LLC	MS	5	48,696
OCCIDENTAL CHEMICAL CORP	KS	3,831	1,771
WESTROCK CP LLC	FL	2	46,371
INTERNATIONAL PAPER RIEGELWOOD MILL	NC	17	38,929
WISCONSIN RAPIDS PULP MILL	WI	0	35,797
AKZO NOBEL SURFACE CHEMISTRY LLC	IL	12,823	19,219
VERSO LUKE LLC	NY	0	30,022
INTERNATIONAL PAPER-VICKSBURG MILL	MS	0	28,275
DOW SILICONES CORP	KY	7,100	20,100
LONGVIEW FIBRE PAPER & PACKAGING INC	WA	0	26,790
SOLVAY SPECIALTY POLYMERS USA LLC	OH	12,793	6,237
FORMOSA PLASTICS CORP TEXAS	TX	0	17,991
NALCO CHAMPION - AN ECOLAB CO	TX	1,566	250
EXXONMOBIL BATON ROUGE CHEMICAL PLANT (PART)	LA	14,000	2,500
GALATA CHEMICALS LLC - GALATA TAFT FACILITY	LA	1,167	4,523
THE DOW CHEMICAL CO	MI	1,100	12,000
EVONIK CORP	IL	1,614	11,080
EES COKE BATTERY LLC	MI	0	12,000
EVONIK MATERIALS CORP	WI	229	9,830
BASF CORP - BEAUMONT	TX	3,501	234
BLUE RIDGE PAPER PRODUCTS LLC	NC	4	8,970
LONZA INC	IL	157	6,367
CHEMTALL INC	GA	2,900	3,600
THE DOW CHEMICAL CO - LOUISIANA OPERATIONS	LA	756	5,337
OCCIDENTAL CHEMICAL HOLDING CORP - GEISMAR PLANT	LA	3,669	2,419
EVONIK INDUSTRIES	WI	905	5,108
MPM SILICONES LLC	WV	4,907	404
CHEMDESIGN PRODUCTS INC	WI	86	5,343

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Table 5-3. Releases to the Atmosphere from Facilities that Produce, Process, or Use Chloromethane^a

Facility	Reported amounts released in pounds per year ^b		
	State	Fugitive Air Emissions	Point Source Air Emissions
MPM SILICONES LLC	NY	250	5,100
PMC ORGANOMETALLIX INC	KY	494	2,646
OLIN BLUE CUBE FREEPORT TX	TX	1,851	83
BLUE CUBE OPERATIONS LLC - PLAQUEMINE SITE	LA	1,392	374
ALBEMARLE CORP PASADENA PLANT	TX	1,622	21
DUPONT CHAMBERS WORKS	NJ	0	702
ALBEMARLE US INC	TN	609	0
SACHEM INC	TX	589	6
HONEYWELL INTERNATIONAL INC-BATON ROUGE PLANT	LA	262	235
SOLVAY USA INC	LA	424	0
CLEAN HARBORS ARAGONITE LLC	UT	238	0
PRAXAIR DISTRIBUTION INC	OH	41	169
CRODA INC	PA	10	156
BASF CORP	LA	57	98
AKZO NOBEL FUNCTIONAL CHEMICALS LLC	TX	37	86
AXIALL LLC	LA	42	11
SHINTECH PLAQUEMINE PLANT	LA	0	41
SIVANCE LLC	FL	0	40
FUTUREFUEL CHEMICAL CO	AR	13	7
BAKER PETROLITE BAYPOR FACILITY	TX	0	15
ECO-SERVICES OPERATIONS	LA	12	0
CHEMTRADE REFINERY SOLUTIONS LP	OH	5	5
AMVAC CHEMICAL CO	AL	5	5
VEOLIA ES TECHNICAL SOLUTIONS LLC PORT ARTHUR FACILITY	TX	6	0
EVONIK CORP	AL	1	2
VEOLIA - MORSES MILL	NJ	1	0
HERITAGE THERMAL SERVICES	OH	0	0
SUN CHEMICAL BUSHY PARK FACILITY	SC	0	0
HALOCARBON PRODUCTS CORP	SC	0	0
BCP INGREDIENTS INC	MO	0	0
SANTOLUBES MANUFACTURING LLC DBA BLACKMAN UHLER SPECIALTIES	SC	No data	No data
RHO CHEMICAL CO INC	IL	No data	No data

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Table 5-3. Releases to the Atmosphere from Facilities that Produce, Process, or Use Chloromethane^a

Facility	Reported amounts released in pounds per year ^b		
	State	Fugitive Air Emissions	Point Source Air Emissions
AMVAC CHEMICAL CORP	CA	No data	No data

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

^b Data in TRI are maximum amounts released by each facility.

Source: TRI17 2018; Data are from 2017

Chloromethane has been identified in air samples collected at 23 of the 236 NPL hazardous waste sites at which it was detected in one or more environmental media (ATSDR 2017/ATSDR 2019). The geometric mean of maximum concentrations in air at these sites was 0.0029 ppm (0.006 mg/m³).

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 will be released from manufacturing and use (fugitive emissions) as well as from production resulting from human and natural activities. Anthropogenic sources include burning plastic (Lestari et al. 2011), cigarette smoke (Filipiak et al. 2012; Novak et al. 2008; Sleiman et al. 2014), biomass burning (Keppler et al. 2005), the manual process of dismantling television printed circuit boards using electric heating furnaces during e-waste recycling (Liu et al. 2017), and interior materials in vehicles (Xing et al. 2018). Recently, chloromethane has been found in VOC emissions from laundry products (Steinemann 2015). Chloromethane present in waste waters also may be released to air during aeration (Pincince 1988). Chloromethane has also been detected in atmospheric emissions from municipal solid waste landfills (Manca et al. 1997) and from artificial waterfalls using reclaimed water (Ma et al. 2008).

An anthropogenic source of chloromethane may be cigarette smoke as estimated by (Novak et al. 2008). Novak et al. (2008) collected smoke samples from burning cigarettes in special smoking adaptors into 2 L canisters and analyzed the smoke for chloromethane using gas chromatography. The chloromethane concentrations were about 30–500 ppmv (1.5–5.3 mg/cigarette) compared with about 500 pptv (parts per trillion) in typical urban air. The chloromethane levels from some brands of cigarettes exceeded the EPA's maximum exposure limit of 200 ppmv (Novak et al. 2008).

Natural sources include the oceans, forest fires, burning wood, burning coal, volcanoes (Keppler et al. 2005; Moore 2008), biomass burning (Rudolph et al. 1995), fungi (Saxena et al. 1998), coastal salt marshes (Rhew et al. 2000; Cox et al. 2004), wetlands (Keppler et al. 2005), dead or senescent plant material (Derendorp et al. 2012) and tropical vegetation (Yokouchi et al. 2002; Yokouchi et al. 2000; Yokouchi et al. 2007). Emissions of chloromethane were previously known to come from animals such as

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cattle, and recent studies have shown that humans also exhale chloromethane in the range of 2.5 to 33 ppbv or less than .03% of the total annual global atmospheric source strength (Keppler et al. 2017).

Various estimates of average global annual production rates and 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 Keppler et al. (2005) and are used primarily to emphasize the overwhelming contributions from nonindustrial production.

Chloromethane is the most abundant halocarbon in the atmosphere, and its total atmospheric burden is between 4000 to 5000 Gg (8,818,490,487 to 11,023,113,109 pounds) (Keppler et al. 2005). Total releases to environmental media estimated from the 2018 TRI are around 955,937 pounds (~433,606 kg) (TRI17 2018). Thus, more than 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. Gases contributed by industrial and other anthropogenic sources tend to result in higher concentrations in middle northern latitudes (Khalil and Rasmussen 1999). Khalil and Rasmussen (1999) estimate that there is more chloromethane in the atmosphere in the tropical latitudes than at higher latitudes, which may be a result of more chloromethane being emitted from natural sources. McCulloch et al. (1999) estimated the global distribution of chloromethane from coal and waste combustion and industrial processes. In the United States, it appears that these emissions were higher in the east, with emissions nearing 0.022 grams of equivalent chlorine emissions per square meter per year in the Northeast and Midwest.

Typical estimates for the natural background concentrations of chloromethane in ambient air are 0.58 ppm ($1.2 \mu\text{g}/\text{m}^3$) (Woodruff et al. 1998) to 0.87 ppm ($1.8 \mu\text{g}/\text{m}^3$) (Logue et al. 2012). Chloromethane concentrations are often in excess of rural background concentrations in the ambient air of cities in the United States (Singh H.B. et al. 1982; Singh H.B. et al. 1983) (see Section 5.5.1). 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. However, concentrations of chloromethane in air monitored by EPA in 2018 show that mean concentrations were highest in Florida, Michigan, Arizona, Delaware, and Washington D.C. (EPA 2018), while only Florida and Michigan are accounted for in TRI (TRI17 2018). This suggests that emissions from sources aside from manufacturing contribute to chloromethane in the air in many states. Other than data from the TRI or rough estimates based on global budgets, no studies

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were identified that attempt to make quantitative estimates for natural or anthropogenic releases of chloromethane to the air in the United States.

5.3.2 Water

Estimated releases of 871 pounds (~.40 metric tons) of chloromethane to surface water from 14 domestic manufacturing and processing facilities in 2017, accounted for about 0.08% of the estimated total environmental releases from facilities required to report to the TRI (TRI17 2018).

Chloromethane has been identified in water at 38 of the 236 NPL hazardous waste sites at which it was detected in one or more environmental media (ATSDR 2017ATSDR 2019). The geometric mean of maximum concentrations at these sites was 0.013 mg/L.

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 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 (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, application, and fate of process water were not found in the available literature; however, spent process water is probably treated (including aeration) prior to discharge. Chloromethane has also been detected in recycled water (Rodriguez et al. 2007). In a study to determine the concentration of volatile organic compounds in secondary treatment effluent (STE) and post-reverse osmosis (RO) treatment, chloromethane was found in 57.6% of STE samples and 62.9% of RO samples (Rodriguez et al. 2012). It is possible that chloramination may play a role in the detection of chloromethane in RO permeate, given that chloromethane has shown increases in concentration during MF/RO (micro filtration/reverse osmosis) (Linge et al. 2012).

Chloromethane has been found in waste water effluents, possibly as a result of its formation (EPA 1975) or incomplete removal during industrial waste water treatment (Snider and Manning 1982).

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).

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5.3.3 Soil

Estimated releases of 31 pounds (~.014 metric tons) of chloromethane to soils from 8 domestic manufacturing and processing facilities in 2017, accounted for about 0.003% of the estimated total environmental releases from facilities required to report to the TRI (TRI17 2018). An additional 131,890 million pounds (~60 metric tons), constituting about 12% of the total environmental emissions, were released via underground injection (TRI17 2018). These releases are summarized in Table 5-4.

Table 5-4. Releases to Soil from Facilities that Produce, Process, or Use Chloromethane^a

Facility	State	Reported amounts released in pounds per year ^b	
		Underground Injection Class I Wells	Underground Injection Class II-V Wells
EASTMAN CHEMICAL CO TEXAS OPERATIONS	TX	0	0
EXXONMOBIL BAYTOWN CHEMICAL PLANT (PART)	TX	0	0
MONSANTO LULING	LA	67,000	0
INTERNATIONAL PAPER GEORGETOWN MILL	SC	0	0
EVERGREEN PACKAGING	AR	0	0
GEORGIA-PACIFIC MONTICELLO LLC	MS	0	0
OCCIDENTAL CHEMICAL CORP	KS	42,430	0
WESTROCK CP LLC	FL	0	0
INTERNATIONAL PAPER RIEGELWOOD MILL	NC	0	0
WISCONSIN RAPIDS PULP MILL	WI	0	0
AKZO NOBEL SURFACE CHEMISTRY LLC	IL	0	0
VERSO LUKE LLC	NY	0	0
INTERNATIONAL PAPER-VICKSBURG MILL	MS	0	0
DOW SILICONES CORP	KY	0	0
LONGVIEW FIBRE PAPER & PACKAGING INC	WA	0	0
SOLVAY SPECIALTY POLYMERS USA LLC	OH	0	0
FORMOSA PLASTICS CORP TEXAS	TX	0	0
NALCO CHAMPION - AN ECOLAB CO	TX	14,800	0
EXXONMOBIL BATON ROUGE CHEMICAL PLANT (PART)	LA	0	0
GALATA CHEMICALS LLC - GALATA TAFT FACILITY	LA	7,660	0
THE DOW CHEMICAL CO	MI	0	0
EVONIK CORP	IL	0	0
EES COKE BATTERY LLC	MI	0	0
EVONIK MATERIALS CORP	WI	0	0
BASF CORP - BEAUMONT	TX	0	0

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Table 5-4. Releases to Soil from Facilities that Produce, Process, or Use Chloromethane^a

Reported amounts released in pounds per year ^b			
Facility	State	Underground Injection Class I Wells	Underground Injection Class II-V Wells
BLUE RIDGE PAPER PRODUCTS LLC	NC	0	0
LONZA INC	IL	0	0
CHEMTALL INC	GA	0	0
THE DOW CHEMICAL CO - LOUISIANA OPERATIONS	LA	0	0
OCCIDENTAL CHEMICAL HOLDING CORP - GEISMAR PLANT	LA	0	0
EVONIK INDUSTRIES	WI	0	0
MPM SILICONES LLC	WV	0	0
CHEMDESIGN PRODUCTS INC	WI	0	0
MPM SILICONES LLC	NY	0	0
PMC ORGANOMETALLIX INC	KY	0	0
OLIN BLUE CUBE FREEPORT TX	TX	0	0
BLUE CUBE OPERATIONS LLC - PLAQUEMINE SITE	LA	0	0
ALBEMARLE CORP PASADENA PLANT	TX	0	0
DUPONT CHAMBERS WORKS	NJ	0	0
ALBEMARLE US INC	TN	0	0
SACHEM INC	TX	0	0
HONEYWELL INTERNATIONAL INC- BATON ROUGE PLANT	LA	0	0
SOLVAY USA INC	LA	0	0
CLEAN HARBORS ARAGONITE LLC	UT	0	0
PRAXAIR DISTRIBUTION INC	OH	0	0
CRODA INC	PA	0	0
BASF CORP	LA	0	0
AKZO NOBEL FUNCTIONAL CHEMICALS LLC	TX	0	0
AXIALL LLC	LA	0	0
SHINTECH PLAQUEMINE PLANT	LA	0	0
SIVANCE LLC	FL	0	0
FUTUREFUEL CHEMICAL CO	AR	0	0
BAKER PETROLITE BAYPOR FACILITY	TX	0	0
ECO-SERVICES OPERATIONS	LA	0	0
CHEMTRADE REFINERY SOLUTIONS LP	OH	0	0
AMVAC CHEMICAL CO	AL	0	0
VEOLIA ES TECHNICAL SOLUTIONS LLC PORT ARTHUR FACILITY	TX	0	0
EVONIK CORP	AL	0	0
VEOLIA - MORSES MILL	NJ	0	0
HERITAGE THERMAL SERVICES	OH	0	0
SUN CHEMICAL BUSHY PARK FACILITY	SC	0	0
HALOCARBON PRODUCTS CORP	SC	0	0
BCP INGREDIENTS INC	MO	0	0

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Table 5-4. Releases to Soil from Facilities that Produce, Process, or Use Chloromethane^a

Reported amounts released in pounds per year ^b			
Facility	State	Underground Injection Class I Wells	Underground Injection Class II-V Wells
SANTOLUBES MANUFACTURING LLC DBA BLACKMAN UHLER SPECIALTIES	SC	No data	No data
RHO CHEMICAL CO INC	IL	No data	No data
AMVAC CHEMICAL CORP	CA	No data	No data

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

^b Data in TRI are maximum amounts released by each facility.

Source: TRI17 2018; Data are from 2017

Chloromethane is probably released into the soil during the landfilling of sludge and other wastes (e.g., still bottoms) generated from industrial processes and municipal sewage treatment. Chloromethane has been detected in the leachate of both municipal (Sabel and Clark 1984; Manca et al. 1997) 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 the soil of 11 of the 236 NPL hazardous waste sites at which it was detected in one or more environmental media (ATSDR 2019). The geometric mean of maximum concentrations at these sites was 0.058 mg/kg.

A significant source of release of chloromethane to soil in tropical locations comes from wood-rotting fungi (Moore et al. 2005).

5.4 ENVIRONMENTAL FATE

5.4.1 Transport and Partitioning

Air. Most chloromethane discharged into the environment will be released into the air, where it will be subjected to transport and diffusion into the stratosphere (Tsai 2017). The relatively uniform concentration of chloromethane in the northern and southern hemispheres (Singh H.B. et al. 1979; Singh H.B. et al. 1982; Singh H.B. et al. 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.

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Water. 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 embedded scenarios for a typical pond and lake developed by the Athens Environmental Research Laboratory of the EPA, half-lives for volatilization were calculated to be 2.5 hours and 18 days, respectively. The rate of disappearance of chemicals in the model is assumed to be driven by transformation and transport processes and by hydraulic and hydrological processes in the water bodies (Smith et al. 1977). For different water bodies, data on physical, chemical, and biological processes are integrated by the model, resulting in different half-lives for volatilization. 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 estimated log octanol/water partition coefficient and the sorption coefficient and BCF calculated from it (see Table 4-2.), chloromethane is not expected to concentrate in sediments or in biota.

Sediment and Soil. 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. 1982; Jury et al. 1987; Page 1981).

5.4.2 Transformation and Degradation

Air. The chemical and physical properties of chloromethane indicate that when it is released to the environment, it will partition predominantly to the atmosphere (Tsai 2017). The atmospheric degradation reaction of chloromethane is initiated by a hydroxyl radical attack (Tsai 2017). The main degradation products of chloromethane include HCl, CO, CO₂, HCOCl (formyl chloride), and H₂O₂ (Tsai 2017).

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 1999; Singh H.B. et al. 1979). These studies estimate

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the half-life to be in the neighborhood of 1 year, 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. Additionally, Tsai et al. (2017) estimates that chloromethane has an atmospheric lifetime of 1 year. Such values suggest that transport is likely.

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 SN2 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 Heppollette 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 $7.6 \times 10^{-7} \text{ sec}^{-1}$, with a half-life of 10.6 days. When extrapolated to 20 °C and neutral conditions using the thermodynamic constants calculated by Heppollette and Robertson (1959), a rate constant was calculated of $1.04 \times 10^{-8} \text{ sec}^{-1}$ 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: $k(\text{in s}^{-1}) = 9.5 \times 10^{10} e^{-12,800/T}$. This relation was used to estimate the values at 25 and 15 °C given in Table 4-2. 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-minimal 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

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information. As with reactions of other chloroalkanes, chloromethane may degrade anaerobically via reductive dechlorination to form methane (Vogel et al. 1987).

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 CMI, 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 HCl and formaldehyde. The formaldehyde was oxidized via formate to CO₂ or assimilated through icl⁺ or icl⁻ variants of the serine pathway. Vannelli et al. (1998) found that *Methylbacterium* 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).

Other Media. Six new *Hyphomicrobium* strains, strain CMC related to *Aminobacter* spp, two previously isolated bacteria CC495 and IMB-1, and a Gram-positive isolate related to *Nocardiodides* spp. from a variety of pristine terrestrial, freshwater, estuarine, and marine environments were determined as chloromethane utilizing bacteria (McAnulla et al. 2001).

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5.5 LEVELS 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.

Concentrations of chloromethane in unpolluted atmospheres and in pristine surface waters are often so low as to be near the limits of current analytical methods. In reviewing data on 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.

Table 5-5 shows the limit of detections typically achieved by analytical analysis in environmental media. Presented in Table 5-6 is a summary of the range of concentrations detected in environmental media (Table 5-5 and Table 5-6).

Table 5-5. Lowest Limit of Detection Based on Standards^a

Media	Detection limit	Reference
Outdoor Air	0.01 µg/sample	NIOSH 1994
	0.02 ppb	Hsu et al. 2018
	<0.5 ppbv	Mohamed et al. 2002
Indoor Air	~1 µg/m ³	Weisel et al. 2008
Surface water and groundwater	52 pg/L	USGS 2015
Drinking water	0.03 µg/L	EPA 1995
Water, soil, solid waste	0.03 µg/L	EPA 1986c
Secondary treated effluent	.066 µg/L	Rodriguez et al. 2012
Exhaled Air	243 pptv/200mL	Keppler et al. 2017
E-waste	2.42 µg/M ³	Liu et al. 2017
Vehicle interior	0.042 µg/m ³	Xing et al. 2018
Urine	1mg/L	DeKok and Anthenius 1981

^a Detection limits based on using appropriate preparation and analytics. These limits may not be possible in all situations.

Table 5-6. Chloromethane Levels in Water, Soil, and Air of National Priorities List (NPL) Sites

Medium	Median ^a	Geometric mean	Geometric standard deviation	Number of quantitative measurements	NPL sites
Water (µg/L)	13.0	12.9	8.19	54	38
Soil (ppb)	52.0	58.3	9.09	12	11
Air (ppbv)	1.04	3.29	24.0	32	23

^a Concentrations found in ATSDR site documents from 1981 to 2019 for 1,867 NPL sites (ATSDR 2019). Maximum concentrations were abstracted for types of environmental media for which exposure is likely. Pathways do not necessarily involve exposure or levels of concern.

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5.5.1 Air

Chloromethane has been the subject of numerous studies conducted to determine the atmospheric chloride balance. A volatile organic carbon (VOC) database reported by Shah and Singh (Shah and Singh 1988) contained 706 data points (300 cities from 42 states). The average value is higher than the upper quartile (75% value) and may be skewed because of a few high values or because the underlying distribution is approximately lognormal as are many distributions of environmental concentration values. Thus, the median may be a better summary representation of chloromethane concentration. The data were also grouped by types of air mass so that the influence of urban centers could be estimated. 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. (Singh H.B. et al. 1982; Singh H.B. et al. 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.

In accordance with provisions of the Clean Air Act Amendments (CAAA) 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 $\mu\text{g}/\text{m}^3$ (629 ppt [v/v]).

Data from the EPA Air Quality System (AQS) database were used to calculate the annual mean percentile distributions of chloromethane from multiple monitoring locations across the nation for the years 2014–2018 (EPA 2018b). The results of these data are summarized in Table 5-7. The AQS database is EPA's source of criteria air pollutant and hazardous air pollutant (HAP) monitoring data. Monitoring data for other years may be obtained directly from the EPA AQS website.

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Table 5-7. Percentile Distribution of Annual Mean Chloromethane Concentrations (ppbv) Measured in Ambient Air at Locations Across the United States

Year	Number of US locations	25 th	50 th	75 th	95 th	Maximum
2014	230	0.53	0.60	0.63	0.73	1.86
2015	180	0.54	0.59	0.63	0.71	2.24
2016	163	0.52	0.57	0.61	0.81	2.33
2017	156	0.52	0.56	0.62	0.71	1.35
2018	127	0.51	0.60	0.63	1.12	1.41

Source: EPA 2018b

Several studies have been conducted to measure chloromethane concentrations in outdoor air at specific locations. The results of these studies are summarized in Table 5-8.

Table 5-8. Outdoor Air Monitoring Data for Chloromethane

Location(s)	Geographic type	Date(s)	Range	Mean concentration	Reference
Del Norte, Albuquerque, NM	Not specified	Not specified	0.1-15.3 ppbv	1.1 ppbv	Kavouras et al. 2015
North Valley, Albuquerque, NM	Not specified	Not specified	0.4-5.1 ppbv	1.1 ppbv	Kavouras et al. 2015
South Valley, Albuquerque, NM	Not specified	Not specified	0.1-2.7 ppbv	0.7 ppbv	Kavouras et al. 2015
Baton Rouge, LA	Urban	9/96-8/97	Not specified	0.537 ppbv	Mohamed et al. 2002
Brownsville, TX	Urban	9/96-8/97	Not specified	1.222 ppbv	Mohamed et al. 2002
Brattleboro, VT	Urban	9/96-8/97	Not specified	0.511 ppbv	Mohamed et al. 2002
Burlington, VT	Urban	9/96-8/97	Not specified	0.495 ppbv	Mohamed et al. 2002
Camden, NJ	Urban	9/96-8/97	Not specified	0.542 ppbv	Mohamed et al. 2002
El Paso, TX	Urban	9/96-8/97	Not specified	0.676 ppbv	Mohamed et al. 2002
Garyville, LA	Urban	9/96-8/97	Not specified	0.641 ppbv	Mohamed et al. 2002
Galveston, TX	Urban	9/96-8/97	Not specified	0.952 ppbv	Mohamed et al. 2002
Hahnville, LA	Urban	9/96-8/97	Not specified	0.576 ppbv	Mohamed et al. 2002
Port Neches, TX	Urban	9/96-8/97	Not specified	1.093 ppbv	Mohamed et al. 2002
Rutland, VT	Urban	9/96-8/97	Not specified	0.483 ppbv	Mohamed et al. 2002
Underhill, VT	Urban	9/96-8/97	Not specified	0.481 ppbv	Mohamed et al. 2002
Winooski, VT	Urban	9/96-8/97	Not specified	0.526 ppbv	Mohamed et al. 2002
Flag Plaza, Pittsburgh, PA	Not specified	2/4/06-1/19/08	1.14-1.57 µg/m ³	0.00065 ppm (1.34 µg/m ³)	Logue et al. 2012
South Fayette, Pittsburgh, PA	Not specified	2/4/06-1/19/08	1.03-1.47 µg/m ³	0.0006 ppm (1.23 µg/m ³)	Logue et al. 2012

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Table 5-8. Outdoor Air Monitoring Data for Chloromethane

Location(s)	Geographic type	Date(s)	Range	Mean concentration	Reference
Avalon, Pittsburgh, PA	Not specified	2/4/06-1/19/08	1.03-1.40 $\mu\text{g}/\text{m}^3$	0.00059 ppm (1.22 $\mu\text{g}/\text{m}^3$)	Logue et al. 2012
Stowe, Pittsburgh, PA	Not specified	2/4/06-1/19/08	1.04-1.44 $\mu\text{g}/\text{m}^3$	0.00061 ppm (1.25 $\mu\text{g}/\text{m}^3$)	Logue et al. 2012
Houston, TX	Urban/suburban	5/15-24/80	531-1,015 ppt	955 ppt	Singh H.B. et al. 1982
St. Louis, MO	Urban/suburban	5/30/80-6/8/80	519-1,157 ppt	732 ppt	Singh H.B. et al. 1982
Denver, CO	Urban/suburban	6/16-26/80	437-1,593 ppt	763 ppt	Singh H.B. et al. 1982
Riverside, CA	Urban/suburban	7/2-12/80	437-1,593 ppt	703 ppt	Singh H.B. et al. 1982
Staten Island, NY	Urban/suburban	3/27/80-4/5/80	466-1,280 ppt	701 ppt	Singh H.B. et al. 1982
Pittsburgh, PA	Urban/suburban	4/8-16/80	450-852 ppt	665 ppt	Singh H.B. et al. 1982
Chicago, IL	Urban/suburban	4/21-30/80	575-1,311 ppt	856 ppt	Singh H.B. et al. 1982
Los Angeles, CA	Urban/suburban	4/29/76-5/4/76	708-944 ppt	834 ppt	Singh H.B. 1977
Stanford Hills, CA	Urban/suburban	11/24-30/75	700-1,700 ppt	1,022 ppt	Singh H.B. 1977
Pullman, WA	Rural/remote	12/74-2/75	503-566 ppt	530 ppt	Grimsrud and Rasmussen 1975
Alaska	Rural/remote	5/24-30/75	505-970 ppt	Not specified	Robinson et al. 1977
Point Barrow, AK	Rural/remote	5/7 & 13/82	634-660 ppt	647 ppt	Rasmussen and Khalil 1983
Pacific Northwest	Rural/remote	3/11/76	428-611 ppt	569 ppt	Cronn et al. 1977
Point Reyes, CA	Rural/remote	12/2-12/75	680-1,700a ppt	1,260 ppt	Singh et al. 1977
Yosemite Park, CA	Rural/remote	5/12-17/75	654-999 ppt	713 ppt	Singh et al. 1977
Palm Springs, CA	Rural/remote	5/24-27/76	645-2,128 ppt	1,058 ppt	Singh et al. 1977

Chloromethane is also present in indoor air. In a study to quantify and compare health impacts from indoor air pollutants, the population-average concentration of chloromethane in the United States was assumed to be 0.00087 ppm (1.8 $\mu\text{g}/\text{m}^3$), and chloromethane was estimated to result in 10,000 DALYs lost due to indoor inhalation (Logue et al. 2012). Weisel et al. (2008) measured indoor VOC air concentrations in 100 suburban and rural homes in New Jersey, and found that the average concentration of chloromethane was 0.00072 ppm (1.49 $\mu\text{g}/\text{m}^3$). Van Winkle and Scheff (2001) found that the average concentration of chloromethane in 10 urban homes in Southeast Chicago 0.00097 ppm (2,000 ng/m^3).

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5.5.2 Water

Chloromethane has been detected in surface water, groundwater, drinking water, municipal and hazardous waste landfill leachate, and industrial effluents. When detected, concentrations appear to be in the ppb to ppt range, possibly due to the rapid volatilization of chloromethane. Chloromethane apparently is formed during the chlorination of drinking water. Chloromethane is a List 1 contaminant and was monitored by EPA as part of UCMR3. In samples taken from 2013 to 2015, chloromethane was found at concentrations above the minimum reporting level of 0.2 µg/L in less than 1 percent of the 36,845 samples (EPA 2017b). In a study of tap water at residential and workplace sites, Bradley et al. (2018) found chloromethane at 6 of the 26 sites sampled. Concentrations ranged from not detected to 0.269 µg/L (Bradley et al. 2018).

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 (Burse and Pellizzari 1983). 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 natural 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 (Plumb Jr. 1991). There is little reporting of actual concentration values or ranges for groundwater detections in the available literature. The presence of chloromethane in groundwater may 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 methane present in the soil (Vogel et al. 1987).

In a study at the Kwinana Water Reclamation Plant, recycled water was tested at four points during the reclamation process. Chloromethane was detected in all samples after reverse osmosis (Rodriguez et al. 2007). Table 5-9 shows surface water monitoring data for chloromethane, Table 5-10 represents groundwater monitoring data for chloromethane. Table 5-12 contains most recent data from landfill

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leachate monitoring data for chloromethane and Table 5-13 contains effluent monitoring data for chloromethane.

Table 5-9. Surface Water Monitoring Data for Chloromethane

Location(s)	Type	Date(s)	Range (ng/L)	Mean concentration (ng/L)	Notes	Reference
38 streams in 24 states and Puerto Rico	34 urban/agricultural impacted sites 4 undeveloped sites	November 2012 – June 2014	Not detected	Not detected		Bradley et al. 2017
Delaware River and Raritan Canal	Not specified	Not specified	Not detected	Not specified		Grantsrom et al. 1984
Lake Ontario	Not specified	Not specified	Detected	Not specified		Great Lakes Water Quality Board 1981
Surface Waters in New Jersey	Not specified	Not specified	<0.1-222	Not specified	605 samples were analyzed	Page 1981

Table 5-10. Groundwater Monitoring Data for Chloromethane

Location(s)	Type	Date(s)	Range (ng/L)	Mean concentration (ng/L)	Notes	Reference
New Jersey	Not specified	Not specified	<0.1-6	Not specified	1,058 samples from 408 wells were analyzed	Page 1981; Greenberg et al. 1982
Minnesota	Not specified	Not specified	Detected	Not specified	13 samples of groundwater were taken from under municipal solid waste landfills	Sabel and Clark 1984
Minnesota	Not specified	Not specified	Detected	Not specified	7 samples were analyzed	Sabel and Clark 1984
Massachusetts	Not specified	Not specified	Detected	44		Burmester 1982

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Table 5-11. Drinking Water Monitoring Data for Chloromethane

Location(s)	Type	Date(s)	Range (µg/L)	Mean concentration (µg/L)	Notes	Reference
Tap Water Sites in CA, CO, FL, IA, KS, MI, NJ, OK, OR, SC, and VA	Tap Water	May- September 2016	ND – 0.269	0.194	Limit of Quantification = 0.1 µg/L Chloromethane was detected in 6 of 26 sites	Bradley et al. 2018
Cincinnati, OH	Not specifi ed	Not specifi ed	Detect ed	Not specified		Kopfler et al. 1977

ND = not detected

Table 5-12. Landfill Leachate Monitoring Data for Chloromethane

Location(s)	Type	Date(s)	Range (ng/L)	Mean concentration (ng/L)	Notes	Reference
Minnesota	Not specified	Not specified	Detected	Not specified	Samples of municipal solid waste leachate were analyzed	Sabel and Clark 1984
Wisconsin	Not specified	Not specified	170	170	Samples of municipal solid waste leachate were analyzed	Sabel and Clark 1984
Love Canal, NY	Not specified	Not specified	180	180	Samples were from industrial landfill	Shuckrow et al. 1982
Kin-Buc Landfill, NJ	Not specified	Not specified	3.1	3.1	Samples were from industrial landfill	Shuckrow et al. 1982

Table 5-13. Effluent Monitoring Data for Chloromethane

Location(s)	Type	Date(s)	Range (ng/L)	Mean concentration (ng/L)	Notes	Reference
Petroleum refinery effluents	Not specified	Not specified	<100 - >100	Not specified	17 samples of biotreatment effluents were analyzed	Snider and Manning 1982
Petroleum refinery effluents	Not specified	Not specified	<10	Not specified	17 samples of final effluent were analyzed	Snider and Manning 1982

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5.5.3 Sediment and Soil

Information from ATSDR (2019) documents the presence of chloromethane in soils at 28 waste sites and in sediments at 16 waste sites. Information on background levels in soils and sediments is very limited in the available literature. Information located in the literature concerning the presence of chloromethane in soil refers to the natural formation of chloromethane by a number of fungi (Harper 1988), and to its presence in both landfill leachate and groundwater.

5.5.4 Other Media

As presented in Section 5.3.1, chloromethane is released from burning plastic, cigarette smoke, biomass burning, the process of dismantling e-waste, interior materials in vehicles, and laundry products (Lestari et al. 2011; Sleiman et al. 2014; Filipiak et al. 2012; Novak et al. 2008; Keppler et al. 2005; Liu et al. 2017; Xing et al. 2018; Steinemann 2015). When chlorine compounds are heated in contact with cellulose, gaseous chlorine compounds are produced by reactions involving the hydroxyl groups or the water formed *in situ* by dehydration (Palmer 1976). Wood pulp and other cellulosic materials can release methane when burned that is converted to chloromethane by the chlorine in the material, producing 1 cm³ of chloromethane gas (2.2 mg) for each gram of cellulose burned in glowing combustion (Palmer 1976). 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 burn. 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) (Häsänen 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. Recent studies confirm that chloromethane is expired in both non-smokers and smokers, and suggest that concentrations are influenced by environmental pollutants, food and beverages, and smoking-related compounds (Filipiak et al. 2012). Keppler (2017) estimates that based on testing of 31 human subjects ages 3 to 87, all subjects exhaled between 2.5 to 33 ppbv of chloromethane, which significantly exceeds the amount of chloromethane in the inhaled air.

5.6 GENERAL POPULATION EXPOSURE

According to one report, persons living in Los Angeles, California; Phoenix, Arizona; and Oakland, California; would have daily intakes of \approx 140.4, 108.6, and 59.7 μ g/day, respectively (Singh H.B. et al.

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1981a), based on a total respirable air volume of 23 m³/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 were estimated to be 31, 40, 28, and 35 µg/day, respectively.

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 may generally be exposed to low background levels at all times, while those living in urban centers may be exposed to slightly higher levels.

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.

Chloromethane in water volatilizes fairly rapidly; thus, there is potential for inhalation exposure during showering and bathing. ATSDR's three-compartment Shower and Household-Use Exposure (SHOWER) model predicts air concentrations in the shower stall, bathroom, and main house throughout the day by estimating the contribution from showering or bathing and the contribution from other water sources in the house, such as the dishwasher, clothes washer, and faucets. This information along with human activity patterns are used to calculate a daily time-weighted average exposure concentration via inhalation exposure and from dermal uptake from skin contact. ATSDR's SHOWER model is available by sending a request to showermodel@cdc.gov.

Vapor intrusion may also be a potential source of chloromethane exposure, as vapor intrusion has been observed for several volatile organic chemicals (VOCs) with similar properties. EPA's compilation of five studies of background indoor air concentrations found a 54–100% detection rate for chloromethane in 975 U.S. resident samples between 1994 and 2004 (EPA 2011). The background medians ranged from 0.5 to 1.69 µg/m³, 95th percentiles ranged from 2.1 to 5 µg/m³, and maximum values ranged from 4.2 to 260 µg/m³.

Historically (50 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 a trace component of vinyl chloride present at concentrations in the range of 10 to 100 mg/kg and is a degradation product (PubChem 2021; WHO 1999). Exposures to chloromethane could

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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 potential exposures. Of the 236 current or past NPL sites (ATSDR 20179) showing site contamination with chloromethane, 174 (about 74%) also showed site contamination related to vinyl chloride.

No data were found on the measurement of chloromethane or its metabolites in amniotic fluid, meconium, cord blood, or neonatal blood in humans that would indicate prenatal exposure. It is not known whether chloromethane in the body can cross the placenta and enter into the developing young. However, Wolkowski-Tyl et al. (1983a) noted from unpublished observations that rat dams exposed to 500, or 1,500 ppm but not 100 ppm chloromethane for 6 hours on gestation day17 had significant NPSH concentration reductions in both dams and fetuses, indicative of transplacental passage of chloromethane or its metabolites. The case for placental transfer is also supported by their unpublished work (1983a) in which maternal animals were exposed for 6 hours on gestation day19 to 1500 ppm ¹⁴C radiolabeled chloromethane. Both maternal and fetal tissues (lungs, heart, and brain) were found to contain ¹⁴C, with fetal concentrations twice those of the dams. 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.

Parents can inadvertently carry certain hazardous materials home from work on their clothes, shoes, 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

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 for several decades (UNEP 1999). People who smoke cigarettes and those exposed passively to the smoke have a higher exposure to chloromethane than the general population as noted by Novak et al. (2008) and Sleiman et al. (2014).

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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, 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 236 NPL hazardous waste sites where chloromethane has been detected in environmental media (ATSDR 2017ATSDR 2019). The geometric mean of maximum concentrations in air at the 23 sites where chloromethane was detected was 0.006 mg/m³, or 0.0029 ppm. This is higher than estimates of background concentrations in ambient air, which are between 0.00058 and 0.00087 ppm (Woodruff et al. 1998; Logue et al. 2012). 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.

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) which estimates the number of potentially exposed workers in a variety of manufacturing jobs (Sieber Jr. et al. 1991). An estimated 10,003 employees in 10 industries were potentially exposed to chloromethane according to survey results from 1981 to 1983 (NIOSH 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 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.