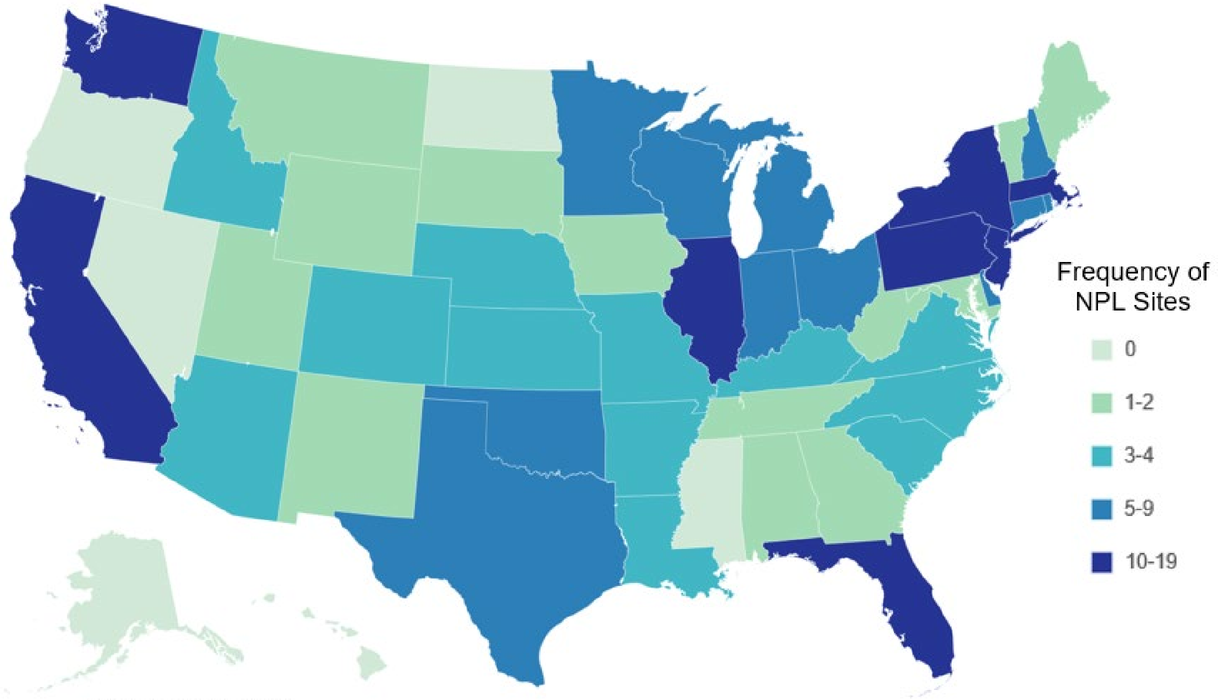
CHAPTER 5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Chloromethane has been identified in at least 236 of the 1,868 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (ATSDR 2022). However, the number of sites in which chloromethane has been evaluated is not known. The number of sites in each state is shown in Figure 5-1. Of these sites, 235 are located within the United States and 1 is located in Puerto Rico (not shown).

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



Source: ATSDR 2022

- The most likely route of exposure for the general population to chloromethane is through inhalation; the general population 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.

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 of 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 (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 estimated half-lives ranging from 0.6–3 years (see Section 5.4). Chloromethane is the dominant organochlorine species in the atmosphere. In the upper atmosphere, chloromethane is involved in the 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 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. Chloromethane is expected to volatilize from soil surfaces; however, when present in a landfill, it has the potential to 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 pbb 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 approximately 0.7–0.9 ppb.

The database for occupational exposure is outdated (late 1980s or earlier). The Occupational Safety and Health Administration (OSHA) permissible exposure limit (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, precluding reliable predictions of average or probable occupational exposure levels. The population with the highest potential for exposure would likely include people who work in chloromethane manufacturing or use industries, such as those that produce chloromethane as an intermediary product.

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 HCl or by chlorination of methane (Edwards et al. 1982a; EPA 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 (EPA 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 (EPA 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 (EPA 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 byproduct 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 Chemical Data Reporting (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, with a 2015 production volume of 815,774,608 pounds; (4) Praxair Distribution, Inc. in Toledo, Ohio, with a 2015 production volume of 293,216 pounds; (5) Formosa Plastics Corp. in Point Comfort, Texas, with a 2015 production volume of 86,327 pounds; (6) Dow 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 (EPA 2022a). The production volume at the sites without values listed here 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 (EPA 2022a). National aggregate production volumes of chloromethane from 2012 to 2014 were also between 1,000,000,000 and 5,000,000,000 pounds (EPA 2022a). National aggregate production volumes in 2011 were 1,396,155,238 pounds (EPA 2022a).

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

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
AL	2	100	9,999	1, 5, 13
AR	2	0	99,999	1, 5
FL	1	10,000	99,999	6
GA	1	1,000,000	9,999,999	2, 3, 6
IA	1	100	999	1, 13, 14
IL	4	1,000	999,999	6
KS	2	1,000,000	9,999,999	1, 4, 6
KY	2	100,000	9,999,999	1, 3, 6
LA	11	100	99,999,999	1, 3, 4, 5, 6, 7, 9, 10, 12, 13, 14
MI	5	10,000	49,999,999	1, 3, 4, 5, 6, 10, 12, 13
MS	2	0	99	1, 5
NC	2	0	99	1, 5
NJ	1	100	999	14
NY	1	1,000,000	9,999,999	1, 3, 6
OH	4	1,000	999,999	6, 9, 12, 14
PA	1	100,000	999,999	6

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

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
SC	4	0	99,999	1, 5, 6, 10
TX	9	0	9,999,999	1, 3, 4, 5, 6, 10, 11, 12, 13, 14
WI	2	100,000	999,999	6
WV	1	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. Produce
2. Import
3. Used Processing
4. Sale/Distribution
5. Byproduct
6. Reactant
7. Formulation Component
8. Article Component
9. Repackaging
10. Chemical Processing Aid
11. Manufacture Aid
12. Ancillary
13. Manufacture Impurity
14. Process Impurity

Source: TRI21 2022 (Data are from 2021)

5.2.2 Import/Export

Exports of chloromethane from the United States are considerably larger than imports. In the period from 2014 to 2018, general imports and imports for consumption of chloromethane were equal. General imports are total physical arrivals of chloromethane to the United States from other countries that either enter consumption channels immediately or enter 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. 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). 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 exports of chloromethane fluctuated from 2014 to 2018, ranging from 22,042,539 kg in 2015 to 10,430,816 kg in 2017 (USITC 2019). 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). U.S. total exports of chloromethane also fluctuated from 2014 to 2018. 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). 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 2022; 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 2022). 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 2022). 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 individuals who were being exposed (McNally 1946). At the present time, virtually all 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 (EPA 2022a). Industry function categories include laboratory chemicals, intermediates, adhesives and sealant chemicals, paint additives, and coating additives not described by other categories (EPA 2022a).

According to CDR data for 12 sites, 4 report chloromethane use for commercial and 3 report for both commercial and consumer use (EPA 2022a). Product categories for consumer and commercial use include adhesives and sealants; fabric, textile, and leather products not covered elsewhere; paints and coatings; personal care products; and plastic and rubber products not covered elsewhere (EPA 2022a). Of these 12 sites, 6 reported that chloromethane is not intended for use in children’s products (EPA 2022a).

5.2.4 Disposal

Of 22 sites that reported industrial processing and use of chloromethane in 2016, 4 reported that the chemical was recycled and 4 reported that it was not (EPA 2022a). In 2012, 1 of 22 sites reported that chloromethane was recycled while 5 of 22 reported that it was not (EPA 2022a).

Of 12 sites that reported consumer and commercial use of chloromethane in 2016, 1 reported that the chemical was recycled while 7 reported that it was not (EPA 2022a). In 2012, one of nine sites reported that chloromethane was recycled while five of nine reported that it was not (EPA 2022a).

Limited information was identified 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).

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 2005). 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 is included in Standard Industrial Classification (SIC) Codes 10 (except 1011, 1081, and 1094), 12 (except 1241), 20–39, 4911 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4931 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4939 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4953 (limited to facilities regulated under RCRA Subtitle C, 42 U.S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited to facilities primarily engaged in solvents recovery services on a contract or fee basis); and if their facility produces, imports, or processes ≥25,000 pounds of any TRI chemical or otherwise uses >10,000 pounds of a TRI chemical in a calendar year (EPA 2005).

Table 5-2 lists the amounts of chloromethane released to the environment in each state (TRI21 2022).

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

		Reported amounts released in pounds per year[b]							
							Total release		
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
AL	2	470	0	0	0	0	470	0	470
AR	2	47,095	0	0	10	0	47,105	0	47,105
FL	1	50	1	0	0	0	50	1	51
GA	1	5,500	4	0	0	0	5,504	0	5,504
IL	4	54,336	7	0	4	0	54,337	10	54,347
IA	1	151	0	0	0	0	151	0	151
KS	2	8,759	0	259,040	0	0	267,799	0	267,799
KY	2	19,080	56	0	0	0	19,136	0	19,136
LA	11	33,224	1,029	62,000	0	0	96,253	0	96,253
MI	5	37,901	110	0	0	0	38,011	0	38,011
MS	2	68,621	0	0	0	0	68,621	0	68,621
NJ	1	1	0	0	0	0	1	0	1
NY	1	4,150	21	0	0	0	4,171	0	4,171
NC	2	81,214	2	0	1	0	81,216	0	81,216
OH	4	20,754	0	0	0	0	20,754	0	20,754
PA	1	376	0	0	0	0	376	0	376
SC	4	63,911	0	0	0	0	63,911	0	63,911
TX	9	218,709	28	9,773	8,285	0	228,514	8,281	236,795
WV	1	7,309	30	0	0	0	7,339	0	7,339

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

		Reported amounts released in pounds per year[b]							
							Total release		
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
WI	2	7,315	15	0	0	0	7,315	15	7,330
Total	58	678,926	1,302	330,813	8,300	0	1,011,035	8,306	1,019,341

[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 are included in releases to air by a given facility.
[f] Surface water discharges, wastewater treatment (metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).
[g] Class I wells, Class II-V wells, and underground injection.
[h] Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other onsite landfills, land treatment, surface impoundments, other land disposal, other landfills.
[i] Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown.
[j] The sum of all releases of the chemical to air, land, water, and underground injection wells.
[k] Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI21 2022 (Data are from 2021)

5.3.1 Air

Estimated releases of 678,926 pounds (~307.96 metric tons) of chloromethane to the atmosphere from 58 domestic manufacturing and processing facilities in 2021, accounted for about 67% of the estimated total environmental releases from facilities required to report to the TRI (TRI21 2022). These releases are summarized in Table 5-2.

The reportable air discharges reported in the TRI 2021 data have dropped from the estimated releases of 757,156 pounds reported for 2020 (TRI20 2021). Chloromethane has been identified in air at 23 of the 236 NPL hazardous waste sites at which it was detected in one or more environmental media (ATSDR 2022). The geometric mean of maximum concentrations at these sites was approximately 0.033 mg/L (3.29 ppbv).

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 wastewaters 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 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 (Cox et al. 2004; Rhew et al. 2000), wetlands (Keppler et al. 2005), dead or senescent plant material (Derendorp et al. 2012) and tropical vegetation (Yokouchi et al. 2000, 2002, 2007). Emissions of chloromethane were previously known to come from animals such as cattle, and recent studies have shown that humans also exhale chloromethane in the range of 2.5–33 ppbv or <0.03% 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 4,000 and 5,000 Gg (8,818,490,487–11,023,113,109 pounds) (Keppler et al. 2005). Greater 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 <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) estimated 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 g 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 μg/m^3) (Woodruff et al. 1998) to 0.87 ppm (1.8 μg/m^3) (Logue et al. 2012). 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.

EPA's National Emission Inventory (NEI) database contains information regarding sources that emit criteria air pollutants (CAPs) and their precursors, and hazardous air pollutants (HAPs) for the 50 United States, Washington DC, Puerto Rico, and the U.S. Virgin Islands. Emissions are estimated from multiple sources, including state and local environmental agencies; the TRI database; computer models for on- and off-road emissions; and databases related to EPA's Maximum Achievable Control Technology (MACT) programs to reduce emissions of HAPs. Chloromethane emissions estimated from the 2017 inventory are summarized in Table 5-3.

Table 5-3. Estimated Annual Chloromethane Emissions in the United States[a]

Emission sector	Pounds of chloromethane emitted
Fires, wildfires	18,950,991.39
Fires, prescribed fires	10,299,194.09
Waste disposal	15,377,95.697
Industrial processes, chemical manufacturing	484,200.14
Industrial processes, pulp and paper	425,652.70
Fuel combustion, electric generation, coal	127,064.91

Table 5-3. Estimated Annual Chloromethane Emissions in the United States[a]

Emission sector	Pounds of chloromethane emitted
Industrial processes, not elsewhere classified	70,708.94
Fuel combustion, industrial boilers, internal combustion engines, other	39,733.34
Fuel combustion, industrial boilers, internal combustion engines, biomass	16,166.54
Solvent, degreasing	10,831.38

[a]Emissions are estimated from the 2017 inventory.

Source: EPA 2022b

5.3.2 Water

Estimated releases of 1,302 pounds (~0.59 metric tons) of chloromethane to surface water from 58 domestic manufacturing and processing facilities in 2021, accounted for about < 1% of the estimated total environmental releases from facilities required to report to the TRI (TRI21 2022). This estimate includes releases to wastewater treatment and publicly owned treatment works (POTWs) (TRI21 2022). These releases are summarized in Table 5-2.

The reportable surface water discharges reported in the TRI 2021 data have increased from the estimated releases of 258 pounds reported for 2020 (TRI20 2021). Most of the amount released in 2021 was reported from Louisiana accounting for 1,029 pounds released to waters. 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 2022). The geometric mean of maximum concentrations at these sites was approximately 0.013 mg/L (12.9 ppb).

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 several 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 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 likely 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 wastewater effluents, possibly as a result of its formation (EPA 1975) or incomplete removal during industrial wastewater 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).

5.3.3 Soil

Estimated releases of 8,300 pounds (~3.76 metric tons) of chloromethane to soil from 61 domestic manufacturing and processing facilities in 2021, accounted for about < 1% of the estimated total environmental releases from facilities required to report to the TRI (TRI21 2022). An additional 330,813 pounds (~150 metric tons), accounting for about 33% of the total environmental emissions, were released via underground injection (TRI21 2022). These releases are summarized in Table 5-2.

The reportable soil discharges reported in the TRI 2021 data have decreased from the estimated release of 9,596 pounds reported for 2020 (TRI20 2021). Chloromethane has been identified in soil at 11 of the 236 NPL hazardous waste sites at which it was detected in one or more environmental media (ATSDR 2022). The geometric mean of maximum concentrations at these sites was approximately 0.058 mg/L (58.3 ppb).

Chloromethane may be 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 may be released to the environment due to abiotic and biotic formation of chloromethane in soils and sediments, which may occur at both ambient and higher temperatures (Keppler et al. 2020; Moore et al. 2005). A source of release of chloromethane to soils comes from abiotic and enzymatic production in certain plants (e.g., *Osmunda regalis; Salicornia europaea)* and wood-rotting fungi (Bringel et al. 2019; Jaeger et al. 2018; Keppler et al. 2020; Kröber et al. 2022; Moore et al. 2005). *O. regalis* has been reported to produce chloromethane at rates of 0.6–128 μg/g/day and *S. europaea* can produce chloromethane at rates of 0.2±0.04 ng/g/hour at 20°C and 2.1±0.8 ng/g/h at 40°C (Jaeger et al. 2018; Keppler et al. 2020). However, it has been shown that some lignin-degrading fungi (*Coriolus versicolor, Phanerochaete chrysosporium, Phlebia radiata*), plants and their associated microbiomes, and phyllospheric and other bacteria (*Arabidopsis thaliana, Cyathea australis, Cyathea cooperi, Methylobacterium extorquens*) also can degrade chloromethane, limiting its release to the environment (Bringel et al. 2019; Farhan Ul Haque et al. 2017; Kröber et al. 2021).

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 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 identified in the literature.

Water. The dominant transport process from water will be volatilization. The results of two model runs of the Exposure Analysis Modeling System (EXAMS) 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 wastewater and in the air above the wastewater at the Memphis North Wastewater Treatment Plant in Memphis, Tennessee. Based on chloromethane's log K_{ow} and its estimated bioconcentration factor (BCF) (see Table 4-2), chloromethane is not expected to bioconcentrate in aquatic species.

Sediment and Soil. In soil, the dominant transport mechanism for chloromethane present near the surface will be volatilization (based on its Henry's law constant, water solubility, and vapor pressure), but no experimental information was identified in the literature to confirm this. The actual volatilization rate for a chemical in soil is influenced by several factors, including surface roughness, soil type, rainfall, leaching, depth of incorporation, temperature, and ground cover (Jury et al. 1987). Based on its estimated K_{oc} (see Table 4-2), chloromethane is not expected to sorb to soils or sediments. 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, CO_2, HCOCl (formyl chloride), and H_2O_2 (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 et al. 1979). These studies estimate the half-life to range 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. Tsai (2017) estimates that chloromethane has an atmospheric lifetime of 1 year. In a laboratory study where degradation of chloromethane was evaluated at 20°C using photolitically generated hydroxyl and chloride radicals, over 70% degradation was observed within 6–10 hours (Keppler et al. 2020). These data suggest that although abiotic degradation may occur, there is potential for atmospheric transport.

Water. In water, chloromethane can degrade via hydrolysis or biodegradation. Available data on the abiotic and biotic degradation of chloromethane in water suggest that neither hydrolysis nor biodegradation is a dominant fate process when compared with volatilization. Chloromethane hydrolysis proceeds via an S_N2 mechanism (involving the nucleophilic substitution of chlorine with water) in which no intermediate ions are formed, where methanol and HCl are the two degradation products. The kinetics of chloromethane hydrolysis have been measured by Heppolette et al. (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} second^{-1}, with a half-life of 10.6 days. When extrapolated to 20°C and neutral conditions using the thermodynamic constants calculated by Heppolette et al. (1959), a rate constant was calculated of 1.04×10^{-8} second^{-1} with a half-life of approximately 2.1 years. Other 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: $k(\text{in second}^{-1})=9.5 \times 10^{10}e^{-12,800/T}$. 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). In a test conducted in a manner similar to EPA Office of Toxic Substances (OTS) 796.3500 (hydrolysis as a function of pH) in compliance with Good Laboratory Practices (GLP), the half-life in water at pH 7 and 25.5°C was determined to be 62 days (EPA 2022a; ECHA 2022). A laboratory study evaluating the hydrolysis of chloromethane in distilled water at 23°C resulted in a rate constant of 0.0015 day^{-1}, corresponding to a half-life of approximately 577 days (Horst et al. 2019). Based on these data, the rate of hydrolysis is slow and is not considered to be of environmental significance in surface waters, considering the rapid volatilization of chloromethane from surface water (Mabey and Mill 1978).

Several chloromethane-degrading bacteria have been isolated from various marine and freshwater sources, and pure culture experiments have indicated the potential for aerobic biotransformation of chloromethane (Bringel et al. 2019). In studies using the bacteria, *Methylococcus capsulatus,* formaldehyde was a product of chloromethane biodegradation (Stirling and Dalton 1979). *Acetobacterium dehalogenans* has been shown to use chloromethane as a sole source of carbon under anoxic conditions (Bringel et al. 2019). Hartmans et al. (1986) reported that pure cultures of a *Hyphomicrobium sp.* isolated from a sewage treatment plant were obtained with a chloromethane-minima1 medium and demonstrated the ability to use chloromethane as a sole source of carbon under aerobic conditions. Abiotic hydrolytic dehalogenation was not significant, while the observed microbial cell growth and chloride formation confirmed biodegradation as the predominant transformation process (Hartmans et al. 1986). These species may not degrade chloromethane in the environment to any significant degree; however, there is potential for biodegradation of chloromethane under some environmental conditions based on the available information. In a closed bottle test according to Organisation of Economic Co-operation and Development (OECD) guideline 301D, chloromethane reached 77% biodegradation after 28 days (ECHA 2022).

Based on carbon isotope analysis during aerobic chloromethane degradation using bacterial strains from both marine and terrestrial environments, microbial degradation is likely by S_N2 type reactions resulting in dehalogenation and 51–86% loss of chloromethane after 29 hours of bacterial growth (Keppler et al. 2020), and degradation rates of approximately 0.2–1.4 µg/g dry weight/day in various soils at pH values of 4.7–7.1 (Jaeger et al. 2018).

Sediment and Soil. Limited information on transformation and degradation of chloromethane in soil was identified 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 indicates that certain white rot fungi and lignin-degrading fungi, such as *P. chrysosporium*, *P. radiata*, and *C. versicolor* can degrade (metabolize) chloromethane (Bringel et al. 2019; Harper et al. 1990). These fungi (especially *P. 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.

Several chloromethane-degrading bacteria have been isolated from various soils and sediments, and pure culture experiments have indicated the potential for anaerobic and aerobic biotransformation of chloromethane (Bringel et al. 2019). Doronina et al. (1996) isolated eight strains of non-methane-utilizing bacteria that can utilize 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

CO2 or assimilated through icl+ or icl-variants of the serine pathway. Vannelli 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, suggesting that under the experimental conditions of the test, chloromethane was readily biodegradable (ECHA 2022). 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.

Biodegradation of chloromethane, with and without addition of methanol, was observed in forest topsoil microcosms under aerobic conditions where mineralization to CO_2 occurred at rates of 0–0.3 mmol/$g_{dry\ soil}$/day (Chaignaud et al. 2018). Addition of chloromethane to microcosms representing forest compartments resulted in first-order degradation rates constants of 0.19–2.35 $hour^{-1}$ in leaf litter, 2.00–6.96 $hour^{-1}$ in various soil horizons, and 0.06–2.76 $hour^{-1}$ in fresh beech leaves. *Alphaproteobacteria sp.*, and *Actinobacteria sp.* were identified as the prominent degraders in the soil and the addition of methanol-enhanced biodegradation suggests that co-metabolism may be preferred for methanotrophs.

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. Enzymatic dehalogenation of chloromethane was demonstrated using a bacterial strain (*Acetobacterium dehalogens*) from a river sediment mixed culture that could use chloromethane as a sole carbon source under anaerobic conditions (Chen et al. 2017).

Other Media. Several microbial strains including *Hyphomicrobium* sp., *Aminobacter* sp., a Gram-positive isolate related to *Nocardiodides* sp., *Alphaproteobacteria sp.*, *Methylorubrum extorquens*, and *Leisingera methylohalidivorans* from a variety of terrestrial, freshwater, estuarine, and marine environments were determined as chloromethane-utilizing bacteria (Keppler et al. 2020; Kröber et al. 2022; McAnulla et al. 2001). Degradation rates of 0.3–17 µg/g/day have been determined for chloromethane degradation in certain ferns (Jaeger et al. 2018). *C. australis* and its associated microbiome have demonstrated the ability to consume (degrade) chloromethane at rates of 7–15 ppm/day (µg/g/day) (Kröber et al. 2021).

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 5-4 shows the limit of detections typically achieved by analytical analysis in environmental media. Presented in Table 5-5 is a summary of the range of concentrations detected in environmental media of NPL Sites.

Table 5-4. 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 1986
Secondary treated effluent	0.066 μg/L	Rodriguez et al. 2012
Exhaled Air	243 pptv/200 mL	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	1 mg/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 5-5. 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

Table 5-5. 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
Air (ppbv)	1.04	3.29	24.0	32	23

[a]Concentrations found in ATSDR site documents from 1981 to 2022 for 1,868 NPL sites (ATSDR 2022). Maximum concentrations were abstracted for types of environmental media for which exposure is likely. Pathways do not necessarily involve exposure or levels of concern.

5.5.1 Air

Chloromethane is a pollutant monitored for in the national Air Quality System (AQS) database which contains ambient air pollution data collected by EPA, state, local, and tribal air pollution control agencies from monitors throughout the country. Table 5-6 shows the yearly mean 24-hour percentile distributions of chloromethane at monitoring stations across the United States.

Table 5-6. Summary of Annual Concentration of Chloromethane Measured in Ambient Air at Locations Across the United States[a,b]

Year	Number of samples	Average of the arithmetic mean at all locations	Maximum concentration (ppbv)
2018	198	0.5180	2.6
2019	145	0.5699	9.0
2020	154	0.6018	9.9
2021	208	0.6036	52.6
2022	34	0.5712	1.5

[a]24-hour sampling period.
[b]As of August 26, 2022.

Source: EPA Air Quality System (AQS) annual summaries (EPA 2022c)

Several studies have also been conducted to measure chloromethane concentrations in outdoor air at specific locations across the United States since 2000. The results of these studies are summarized in Table 5-7.

Table 5-7. Outdoor Air Monitoring Data for Chloromethane

Location(s)	Geographic type	Date(s)	Range	Mean concentration	Reference
Del Norte, Albuquerque, New Mexico	Not specified	Not specified	0.1–15.3 ppbv	1.1 ppbv	Kavouras et al. 2015
North Valley, Albuquerque, New Mexico	Not specified	Not specified	0.4–5.1 ppbv	1.1 ppbv	Kavouras et al. 2015
South Valley, Albuquerque, New Mexico	Not specified	Not specified	0.1–2.7 ppbv	0.7 ppbv	Kavouras et al. 2015
Baton Rouge, Louisiana	Urban	9/96–8/97	Not specified	0.537 ppbv	Mohamed et al. 2002
Brownsville, Texas	Urban	9/96–8/97	Not specified	1.222 ppbv	Mohamed et al. 2002
Brattleboro, Vermont	Urban	9/96–8/97	Not specified	0.511 ppbv	Mohamed et al. 2002
Burlington, Vermont	Urban	9/96–8/97	Not specified	0.495 ppbv	Mohamed et al. 2002
Camden, New Jersey	Urban	9/96–8/97	Not specified	0.542 ppbv	Mohamed et al. 2002
El Paso, Texas	Urban	9/96–8/97	Not specified	0.676 ppbv	Mohamed et al. 2002
Garyville, Louisiana	Urban	9/96–8/97	Not specified	0.641 ppbv	Mohamed et al. 2002
Galveston, Texas	Urban	9/96–8/97	Not specified	0.952 ppbv	Mohamed et al. 2002
Hahnville, Louisiana	Urban	9/96–8/97	Not specified	0.576 ppbv	Mohamed et al. 2002
Port Neches, Texas	Urban	9/96–8/97	Not specified	1.093 ppbv	Mohamed et al. 2002
Rutland, Vermont	Urban	9/96–8/97	Not specified	0.483 ppbv	Mohamed et al. 2002
Underhill, Vermont	Urban	9/96–8/97	Not specified	0.481 ppbv	Mohamed et al. 2002
Winooski, Vermont	Urban	9/96–8/97	Not specified	0.526 ppbv	Mohamed et al. 2002
Flag Plaza, Pittsburgh, Pennsylvania	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, Pennsylvania	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
Avalon, Pittsburgh, Pennsylvania	Not specified	2/4/06–1/19/08	1.03–1.40 μg/m^3	0.00059 ppm (1.22 μg/m$^{3)}$	Logue et al. 2012
Stowe, Pittsburgh, Pennsylvania	Not specified	2/4/06–1/19/08	1.04–1.44 μg/m^3	0.00061 ppm (1.25 μg/m^3)	Logue et al. 2012

Table 5-7. Outdoor Air Monitoring Data for Chloromethane

Location(s)	Geographic type	Date(s)	Range	Mean concentration	Reference
Houston, Texas	Urban/suburban	5/15/80–5/24/80	531–1,015 ppt	955 ppt	Singh et al. 1982
St. Louis, Missouri	Urban/suburban	5/30/80–6/8/80	519–1,157 ppt	732 ppt	Singh et al. 1982
Denver, Colorado	Urban/suburban	6/16/80–6/26/80	437–1,593 ppt	763 ppt	Singh et al. 1982
Riverside, California	Urban/suburban	7/2/80–7/12/80	437–1,593 ppt	703 ppt	Singh et al. 1982
Staten Island, New York	Urban/suburban	3/27/80–4/5/80	466–1,280 ppt	701 ppt	Singh et al. 1982
Pittsburgh, Pennsylvania	Urban/suburban	4/8/80–4/16/80	450–852 ppt	665 ppt	Singh et al. 1982
Chicago, Illinois	Urban/suburban	4/21/80–4/30/80	575–1,311 ppt	856 ppt	Singh et al. 1982
Los Angeles, California	Urban/suburban	4/29/76–5/4/76	708–944 ppt	834 ppt	Singh 1977
Stanford Hills, California	Urban/suburban	11/24/75–11/30/75	700–1,700 ppt	1,022 ppt	Singh 1977
Pullman, Washington	Rural/remote	12/74–2/75	503–566 ppt	530 ppt	Grimsrud and Rasmussen 1975
Alaska	Rural/remote	5/24/75–5/30/75	505–970 ppt	Not specified	Robinson et al. 1977
Point Barrow, Alaska	Rural/remote	5/7/82 and 5/13/82	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, California	Rural/remote	12/2/75–12/12/75	680–1,700 ppt	1,260 ppt	Singh et al. 1977
Yosemite Park, California	Rural/remote	5/12/75–5/17/75	654–999 ppt	713 ppt	Singh et al. 1977
Palm Springs, California	Rural/remote	5/24/76–5/27/76	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 μg/m^3), and chloromethane was estimated to result in 10,000 disability-adjusted life-years (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 μg/m^3). Van Winkle and Scheff

(2001) found that the average concentration of chloromethane in 10 urban homes in Southeast Chicago was 0.00097 ppm (2,000 ng/m^3).

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 is apparently 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 <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). 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).

In a study of groundwater samples collected prior to 1991 from 479 active waste disposal sites, representing 178 Superfund sites, 173 RCRA sites, and 128 sanitary/municipal landfill sites, chloromethane was detected at 20 sites in 9 EPA Regions with 30 detectable events where concentration exceeded the detection limits in groundwater (Plumb 1991). 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. In landfills, volatilization may be hindered and leaching to groundwater could become a transport pathway. Chloromethane may also be a product from the anaerobic metabolism of higher chlorinated methane present in the soil (Vogel et al. 1987).

A national water quality study was done for contaminants including chloromethane over the period of 1991–2010 (USGS 2014). The study evaluated frequency of chloromethane detected at any concentration in principal aquifers in the United States. For the 40 aquifers used for drinking water and sampled for chloromethane, the percentage of all samples containing chloromethane was 3.37% (range 0–27.59%). For the 17 shallow groundwater aquifers beneath agricultural land, 1.81% of samples contained chloromethane (range 0–56.25%), and for the 22 shallow groundwater aquifers beneath urban land, 4.11% of samples contained chloromethane (range 0–20.0 %) (USGS 2014).

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. Additionally, 34 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.

Since recent water monitoring data are available, both recent and historical data water monitoring data are presented below. Table 5-8 shows surface water monitoring data for chloromethane, Table 5-9 represents groundwater monitoring data for chloromethane, Table 5-10 represents drinking water monitoring data for chloromethane, and Table 5-11 contains landfill leachate and effluent monitoring data for chloromethane.

Table 5-8. Surface Water Monitoring Data for Chloromethane

Location(s)	Type	Date(s)	Range (µg/L)	Mean concentration (µg/L)	Notes	Reference
Monitoring sites in 19 U.S. states	Surface water	Jan 2019–August 2022	<LOD–0.6	Not specified	78 samples were analyzed	WQP 2022
38 streams in 24 states and Puerto Rico	34 urban/ agricultural impacted sites 4 undeveloped sites	November 2012–June 2014	<LOD	<LOD		Bradley et al. 2017a, 2017b
Delaware River and Raritan Canal	Surface water	August 1979–January 1980	<LOD	<LOD	Samples collected at 12 sites and during several storms	Granstrom et al. 1984
Lake Ontario	Not specified	Late 1970s–early 1980s	Detected	Not specified		Great Lakes Water Quality Board 1983
New Jersey	Surface water	1977–1979	<LOD–222	<LOD	Detected in 24 of 605 samples	Page 1981

LOD = level of detection

Table 5-9. Groundwater Monitoring Data for Chloromethane

Location(s)	Type	Date(s)	Range (μg/L)	Mean concentration (μg/L)	Notes	Reference
Monitoring sites in 32 U.S. states	Groundwater	Jan 2019–August 2022	<LOD–360	16.6 (mean of samples with concentrations >LOD)	5527 samples were analyzed	WQP 2022
New Jersey	Groundwater	1977–1979	<LOD–6	Not specified	Detected in 3/1,058 samples	Page 1981
Minnesota	Groundwater (under municipal solid waste landfills)	Early 1980s	Detected	Not specified	Detected (but not quantified) in 11/20 samples	Sabel and Clark 1984

LOD = level of detection

Table 5-10. Drinking Water Monitoring Data for Chloromethane

Location(s)	Type	Date(s)	Range (μg/L)	Mean concentration (μg/L)	Notes	Reference
Tap water sites in California, Colorado, Florida, Iowa, Kansas, Michigan, New Jersey, Oklahoma, Oregon, South Carolina, and Virginia	Tap water	May–September 2016	<LOD–0.269	0.194	LOD=0.100 μg/L; chloromethane was detected in 6 of 26 sites	Bradley et al. 2018
Cincinnati, Ohio	Not specified	Not specified	Detected	Not specified		Kopfler et al. 1977

LOD = level of detection

Table 5-11. Landfill Leachate and Effluent Monitoring Data for Chloromethane

Location(s)	Type	Date(s)	Range (μg/L)	Mean concentration (μg/L)	Notes	Reference
Monitoring sites in three U.S. states	Leachate; Municipal wastewater; industrial effluent	Jan 2019–August 2022	<LOD–2.5	All samples below reporting limits	24 samples were analyzed	WQP 2022
Minnesota	Leachate; under municipal solid waste landfills	Early 1980s	Detected	Not specified	Detected in 4/6 samples	Sabel and Clark 1984
Wisconsin	Leachate; under municipal solid waste landfills	Early 1980s	170	170	Detected (but not quantified) in 1/5 samples	Sabel and Clark 1984
Love Canal, New York	Leachate; industrial landfill	1970s	180	180		Shuckrow et al. 1982
Kin-Buc Landfill, New Jersey	Leachate; industrial landfill	1970s	3.1	3.1		Shuckrow et al. 1982
Petroleum refinery effluents	Wastewater feeds to biotreatment effluents	1970s	<100–>100	Not specified	Samples from 17 refineries were analyzed	Snider and Manning 1982
Petroleum refinery effluents	Final effluents	1970s	<10	Not specified	Samples from 17 refineries were analyzed	Snider and Manning 1982

LOD = level of detection

5.5.3 Sediment and Soil

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 several species of fungi (Harper 1985), and to its presence in both landfill leachate and groundwater.

Soils from coastal Antarctica were incubated to evaluate their potential as a source or sink of chloromethane. Experiments suggested that chloromethane consumption was predominantly microbial, while production was through abiotic processes. Results indicated that tundra soil acted as a chemical sink for chloromethane with chemical fluxes ranging from -18.1 to -2.8 pmol/g/day (Zhang et al. 2020).

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; Filipiak et al. 2012; Keppler et al. 2005; Liu et al. 2017; Novak et al. 2008; Sleiman et al. 2014; Steinemann 2015; Xing et al. 2018). 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). Chloromethane has been detected at a concentration of 860 μg/L as a pyrolysis product in simulated combustion experiments using plastic PVC pipes (Draper et al. 2022). Wood pulp and other cellulosic materials can release methane when burned that is converted to chloromethane by the chlorine in the material, producing 1 cm^3 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).

In a 2018 study, VOC emissions from two memory foam mattresses were evaluated over a 32-day period using passive 12- and 24-hour samples; chloromethane was detected at concentrations ranging from 1.0 to 2.0 μg/m^3. It was not detected in background samples (Beckett et al. 2022). Although not quantified, chloromethane has been identified as a chemical present or emitted from crumb rubber used in synthetic turf athletic fields (Perkins et al. 2019).

Chloromethane was present in the expired air of all three 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 nonsmokers and smokers, and suggest that concentrations are influenced by environmental pollutants, food and beverages, and smoking-related compounds (Filipiak et al. 2012). Keppler et al. (2017) estimates that based on testing of 31 human subjects ages 3–87 years, all subjects exhaled between 2.5 and 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 chloromethane intakes of approximately 140.4, 108.6, and 59.7 μg/day, respectively (Singh et al. 1981), 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 were estimated to be 31, 40, 28, and 35 μg/day, respectively.

Chloromethane is a ubiquitous low-level constituent of air and is likely found at very low concentrations as a disinfection byproduct 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 any time, 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 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/m^3, 95th percentiles ranged from 2.1 to 5 μg/m^3, and maximum values ranged from 4.2 to 260 μg/m^3.

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 10–100 mg/kg and is a degradation product (PubChem 2021; WHO 1999). 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 potential exposures.

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 GD 17 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 GD 19 to 1,500 ppm ^{14}C radiolabeled chloromethane. Both maternal and fetal tissues (lungs, heart, and brain) were found to contain ^{14}C, 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 detected in two of eight 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 potential source(s) of the chloromethane in the milk.

Parents can inadvertently carry certain hazardous materials home from work on their clothes, shoes, skin, hair, and tools, and in their vehicles. However, since chloromethane is highly 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).

All humans have the potential to be 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 NPL hazardous waste sites where chloromethane has been detected in environmental media (ATSDR 2022). The geometric mean of maximum concentrations in air at the sites where chloromethane was detected was 0.006 mg/m^3, or 0.0029 ppm. This is higher than estimates of background concentrations in ambient air, which are between 0.00058 and 0.00087 ppm (Logue et al. 2012; Woodruff et al. 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.

Some insights can be gleaned from the NIOSH 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 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). Most 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. Several regulations, however, are in place to protect workers from exposure to levels of chloromethane that are considered harmful.