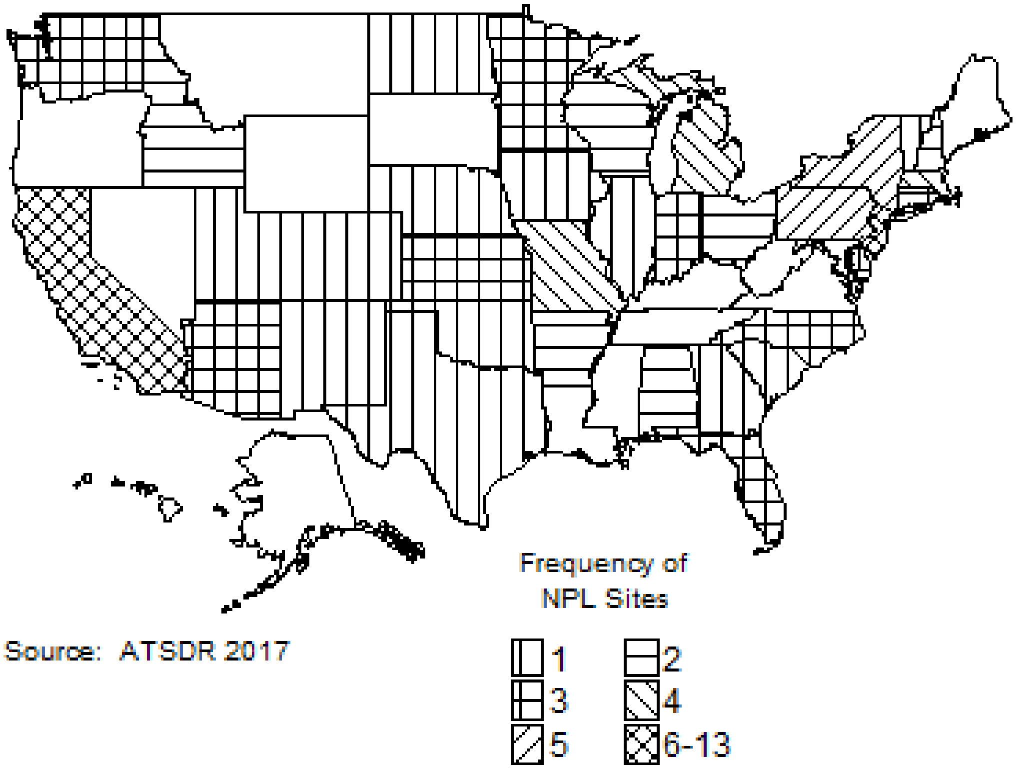
CHAPTER 5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Bromomethane has been identified in at least 94 of the 1,854 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (ATSDR 2017). However, the number of sites in which bromomethane has been evaluated is not known. The number of sites in each state is shown in Figure 5-1.

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



Source: ATSDR 2017

- The most likely route of human exposure is by inhalation because bromomethane exists as a gas at room temperature. Exposure to higher levels of inhaled bromomethane is more likely to occur in occupational settings; exposure of the general population is by bromomethane in ambient air.

- The general population is not likely to be exposed to bromomethane via the oral route; however, exposure to a small amount of bromomethane could occur via contaminated water or food.

- Bromomethane is a naturally occurring component of the environment, with oceans representing the largest natural source.
- Anthropogenic emissions of bromomethane recently have been markedly reduced due to restriction of bromomethane as a fumigant. Currently, the largest anthropogenic emission sources of bromomethane are biomass burning in agriculture and the use of biofuels.
- Bromomethane readily volatilizes into air from water and soil, with volatilization increasing with temperature.
- In air, the main degradation pathway for bromomethane is reaction with photochemically-generated hydroxyl radicals.
- Bromomethane degrades in water through a combination of abiotic (e.g., hydrolysis) and biotic processes.
- In soil, bromomethane degrades by three principle mechanisms: hydrolysis, methylation by organic matter, and biological oxidation by soil microorganisms.

Bromomethane is a naturally occurring component of the environment, with oceans representing the largest natural source (Butler and Rodriguez 1996). In the past, the primary anthropogenic source of bromomethane in the environment was from its use as a fumigant in fields and greenhouses to control a variety of pests and, to a lesser extent, by automobile exhaust. From 1995 to 1998, the use of bromomethane as a fumigant accounted for approximately 40% of all identified sources; however, by 2012, this use accounted for only about 10% of all sources of bromomethane (UNEP 2015). The use of bromomethane as a fumigant has declined about 80% since the mid-1990s. Today, the largest source of anthropogenically generated bromomethane arises from biomass burning and the use of biofuels (UNEP 2015).

Bromomethane has a high potential for volatilization and tends to partition to the atmosphere where it is slowly degraded. Bromomethane that has not degraded in the troposphere will gradually diffuse into the stratosphere where it will slowly degrade due to direct photolysis from high-energy UV radiation, which releases free bromine radicals, and contributes to the catalytic removal of stratospheric ozone. Because of its ozone-depletion and global warming potential, the United States and most other nations have gradually phased out its agricultural use as a fumigant. Bromomethane may only currently be used in the United States for two critical use exemptions and for quarantine and preshipment (QPS) purposes (EPA 2016a).

Levels of bromomethane in the troposphere have been decreasing at a rate of approximately 0.2–0.4 ppt per year due to the phase out of its use as an agricultural fumigant (WMO 2011). The 2008 annual mean levels of bromomethane were estimated to range from 7.3 to 7.5 ppt (WMO 2011). Prior to the widespread use of bromomethane as a fumigant, it was estimated that natural background levels in the atmosphere were approximately 5.3 ppt (UNEP 2015). Levels can be several orders of magnitude greater where it was applied as a fumigant. For example, bromomethane levels >12 mg/m^3 (3 ppm) were observed 4 hours postapplication above a field located in California in which it was applied (Yates et al. 1997).

5.2 PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.2.1 Production

Bromomethane is produced by reaction of methanol with hydrobromic acid, followed by distillation of the product (IARC 1986; Windholz 1983). Table 5-1 summarizes information on U.S. companies that reported the manufacture or use of bromomethane in 2017 (TRI17 2019). Toxics Release Inventory (TRI) data should be used with caution since only certain types of industrial facilities are required to report. This is not an exhaustive list.

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

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	1,000	9,999	1, 12, 13
AR	1	1,000,000	9,999,999	1, 2, 3, 4, 5, 9
CA	2	10,000	9,999,999	2, 3, 4, 7, 9
FL	1	100,000	999,999	7, 9
GA	1	100,000	999,999	7, 9
IL	1	100	999	1, 5
LA	1	1,000	9,999	1, 5, 13
MO	2	1,000	999,999	1, 5, 6
NC	1	100,000	999,999	7, 9
ND	1	1,000	9,999	12

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

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
NE	1	1,000	9,999	12
OH	1	1,000	9,999	12
SC	2	0	9,999	1, 5
TN	1	0	99	1, 5
TX	1	0	99	1, 5, 12

[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: TRI17 2019 (Data are from 2017)

According to the National Pesticide Information Retrieval System, there are nine companies in the United States manufacturing bromomethane (NPIRS 2016). Several of these products are mixtures of bromomethane with another pesticide. The companies, their bromomethane containing products, and the active ingredients are provided in Table 5-2. EPA also monitors the amount of bromomethane produced and used annually in the United States and releases data regarding its inventory for that calendar year. Because not all of the bromomethane that is produced is consumed annually, there may be a surplus at the end of the year. Data from 2003 to 2014 are provided in Table 5-3. Numerous countries have also phased out the use of bromomethane. Global production of bromomethane for all uses was estimated at 24,866 metric tons in 2013, which is nearly a 70% decrease in production from the early 1990s (UNEP 2015).

Table 5-2. U.S. Companies Manufacturing Bromomethane

Company	Registered product	Active ingredients
Albermerle Corp.	M-B-R 98 Technical. EPA registration number 3377-27	98% bromomethane
Great Lakes Chemical Corp.	MEH-O-GAS 100. EPA registration number 5785-11	100% bromomethane
	TERR-O-GAS 70 preplant soil fumigant. EPA registration number 5785-19	70% bromomethane, 30% chloropicrin
	TERR-O-GAS 98. EPA registration number 5785-22	98% bromomethane, 2% chloropicrin
	TERR-O-GAS 67. EPA registration number 5785-24	67% bromomethane, 33% chloropicrin

Table 5-2. U.S. Companies Manufacturing Bromomethane

Company	Registered product	Active ingredients
	TERR-O-GAS 57. Preplant soil fumigant. EPA registration number 5785-28	57% bromomethane, 43% chloropicrin
	TERR-O-GAS 75. EPA registration number 5785-40	75% bromomethane, 25% chloropicrin
	METH-O-GAS Q. EPA registration number 5785-41	100% bromomethane
	TERR-O-GAS 80. EPA registration number 5785-47	80% bromomethane, 20% chloropicrin
	TERR-O-GAS 50. EPA registration number 5785-48	50% bromomethane, 50% chloropicrin
	Methyl bromide. EPA registration number 5785-51	100% bromomethane
	67-63 EPA registration number 5785-52	67% bromomethane, 33% chloropicrin
	98-2 EPA registration number 5785-56	98% bromomethane
Soil Chemicals Corp.	PIC-BROM 33. EPA registration number 8536-5	67% bromomethane, 32.8% chloropicrin
	PIC-BROM 55. EPA registration number 8536-6	45% bromomethane, 54.7% chloropicrin
	PIC-BROM 43. EPA registration number 8536-7	43% bromomethane, 56.7% chloropicrin
	PIC-BROM 59. EPA registration number 8536-9	50% bromomethane, 49.7% chloropicrin
	PIC-BROM 25. EPA registration number 8536-11	75% bromomethane, 24.9% chloropicrin
	Methyl bromide 100. EPA registration number 8536-15	100% bromomethane
	Methyl bromide 98. EPA registration number 8536-19	98% bromomethane
	PIC-BROM 67. EPA registration number 8536-20	33% bromomethane, 66% chloropicrin
	Methyl bromide quarantine fumigant. EPA registration number 8536-29	100% bromomethane
ICP-IL America, Inc.	METABROM 100. EPA registration number 8622-16	100% bromomethane
	METABROM Q. EPA registration number 8622-55	100% bromomethane
Trical Inc.	TRI-CON 57/43. EPA registration number 11220-4	57% bromomethane, 43% chloropicrin
	TRI-CON 67/33. EPA registration number 11220-7	67% bromomethane, 33% chloropicrin
	TRI-CON 75/25. EPA registration number 11220-8	75% bromomethane, 25% chloropicrin
	TRI-CON 50/50. EPA registration number 11220-10	50% bromomethane, 50% chloropicrin
	TRI-CON 45/55. EPA registration number 11220-11	45% bromomethane, 54.7% chloropicrin
	Methyl bromide 89.5. EPA registration number 11220-17	89.5% bromomethane, 10.5% chloropicrin
	MBC concentrate soil fumigant. EPA registration number 11220-32	98% bromomethane

Table 5-2. U.S. Companies Manufacturing Bromomethane

Company	Registered product	Active ingredients
Bromine Compounds LTD	Methyl bromide 100. EPA registration number 15298-4	100% bromomethane
Shadow Mountain Products Corp.	TRI-CON 80/20. EPA registration number 58266-1	80% bromomethane, 19.9% chloropicrin
Triest AG Group, Inc.	MBC soil fumigant. EPA registration number 87994-1	68.6% bromomethane
	MBC-33. EPA registration number 87994-2	67% bromomethane, 32.8% chloropicrin
Mebrom Corp.	MEBROM 100. EPA registration number 89816-2	100% bromomethane
	MEBROM 70-30. EPA registration number 89816-3	70% bromomethane, 30% chloropicrin

Source: NPIRS 2016

Table 5-3. Bromomethane Inventory in the United States from 2003 to 2014

Year	Amount of inventory at the end of the year (metric tons)
2003	16,422
2004	12,994
2005	9,974
2006	7,941
2007	6,458
2008	4,271
2009	3,064
2010	1,803
2011	1,249
2012	627
2013	357
2014	158

Source EPA 2016c

5.2.2 Import/Export

In 1990, the world consumption of bromomethane was >6.7×10^7 kg (WHO 1994). Global bromomethane sales for 1984 to 1990 totaled 389,814 tons, ca. 3.9×10^8 kg (WHO 1995). According to Chemical Data Reporting Submissions Database (EPA 2016e), one reporting facility, a confidential manufacturing company, reported 0 pounds of imports for 2012. Two reporting facilities, Albemarle Corporation and Chemtura Corporation, reported import volumes as ‘withheld’ for 2012 through 2015 (EPA 2016e). More detailed data regarding the import and export of bromomethane were not located.

5.2.3 Use

In the past, the primary use of bromomethane was as a soil or space fumigant for the control of insects (insecticide), fungi (fungicide), and rodents (EPA 1986b; IARC 1986). It also had previous applications as an acaricide, antimicrobial, herbicide, and nematicide. Space fumigation was usually performed by enclosing the structure in a sealed tent and releasing bromomethane gas inside, while soil fumigation was usually performed by injecting bromomethane into the soil underneath a nonporous covering. Bromomethane was used in pre-planting soil fumigation, quarantine and commodity fumigation, and structural fumigation (WHO 1995). Bromomethane is classified as an 8A fumigant by the Insecticide Resistance Action Committee; it is a non-specific (multi-site) inhibitor (IRAC 2019). Bromomethane was also used in fire extinguishers in Europe from the 1920s through the 1940s (WHO 1995; IARC 1986; O'Neil et al. 2014), but never gained widespread use as a fire extinguishing agent in the United States (Alexeeff and Kilgore 1983). In the 1960s, use of bromomethane in fire extinguishers was stopped after causing fatal accidents (WHO 1995). Bromomethane has been used in ionization chambers; wool degreasing; oil extraction of nuts, seeds, and flowers; as a soil or space fumigant for insects, fungi, and rodents; and as a methylating agent in the chemical industry (Larrañaga et al. 2016; O'Neil et al. 2014). Bromomethane has also been used for the disinfection of potatoes, tomatoes, and other crops (Larrañaga et al. 2016). EPA has restricted the use of bromomethane to critical uses (EPA 2016a).

Because bromomethane is considered an ozone-depleting substance, the EPA phased out its use under the Clean Air Act in 2005; however, some critical use exemptions are still allowed to eliminate quarantine pests and for agricultural use where there are no technically or financially feasible alternatives (EPA 2014a, 2016a). The application of bromomethane is deemed critical if two strict criteria are met: a lack of bromomethane availability would result in a significant market disruption and no feasible alternative substances are available (EPA 2016a). Only two critical use exemptions were approved by the EPA for 2016: strawberry farmers in the state of California and dry cure pork producers (EPA 2016a, 2016b). The EPA denied critical use exemptions in 2016 for Michigan cucurbit, eggplant, pepper, and tomato growers; Florida eggplant, pepper, strawberry, and tomato growers; the California Association of Nursery and Garden Centers; California stone fruit, table and raisin grape, walnut, and almond growers; ornamental growers in California and Florida; and the U.S. Golf Course Superintendents Association (EPA 2015a). For 2016, the EPA is allowing the production and import of 141 metric tons of bromomethane for these two critical uses (EPA 2016b). A separate exemption under the Clean Air Act exists for the production and consumption of bromomethane for QPS purposes in order to prevent the spread of quarantine pests that may cause disease or result in significant environmental problems (e.g., fumigation of logs to control wood-boring pests from imported wood products). Since 1999, global consumption of bromomethane for QPS has remained steady at approximately 10,000 metric tons annually; however, non-QPS consumption of bromomethane has decreased from approximately 50,000 metric tons in 1999 to <3,000 metric tons in 2013 (UNEP 2015).

5.2.4 Disposal

National or local regulations must be observed when disposing of bromomethane (WHO 1994). For large quantities, controlled incineration is recommended; incineration is hazardous for untrained personnel and therefore, only minimal amounts should be released into well-ventilated outdoor air (WHO 1994). Incineration requires dilution with additional fuel. Safe, efficient methods for loading this toxic gas into the combustion chamber must be employed. If an appropriate combustion chamber is unavailable, clearly labeled waste containers must be returned to the supplier (UN Hazard Class 2.3, UN Subsidiary Risks 6.1; National Fire Protection Association Code: Health 3; Flammability 1; Instability 0) (NOAA 2019; WHO 1994). Spills may accumulate in lowered spaces as this gas is heavier than air; disposal of spills by trained experts includes personal protection requiring complete protective clothing and self-contained breathing apparatus; ventilation is critical, and a direct water jet should never be used on spills containing bromomethane (WHO 2009). Disposal of fumigant products containing bromomethane, equipment wash-waters, or rinsate must not contaminate or be released to water as this pesticide is toxic to mammals and birds (EPA 2008a).

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).

5.3.1 Air

Estimated releases of 294,930 pounds (~133.78 metric tons) of bromomethane to the atmosphere from 19 domestic manufacturing and processing facilities in 2017, accounted for about 99.98% of the estimated total environmental releases from facilities required to report to the TRI (TRI17 2019). These releases are summarized in Table 5-4.

Table 5-4. Releases to the Environment from Facilities that Produce, Process, or Use Bromomethane[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
AK	1	41,653	0	0	0	0	41,653	0	41,653
AL	2	20,000	0	10	0	0	20,010	0	20,010
CA	2	639	0	0	0	0	639	0	639
FL	1	608	0	0	0	0	608	0	608
GA	1	10,601	0	0	0	0	10,601	0	10,601
IL	1	11,345	0	0	0	0	11,345	0	11,345
LA	1	0	0	0	0	0	0	0	0
MO	2	891	0	0	0	0	891	0	891
NC	1	3,000	0	0	0	0	3,000	0	3,000
ND	1	2,383	0	0	0	0	2,383	0	2,383
NE	1	7,350	0	0	0	0	7,350	0	7,350
OH	1	0	0	0	0	0	0	0	0
SC	2	102,966	0	0	0	0	102,966	0	102,966
TN	1	93,494	15	0	31	0	93,540	0	93,540

Table 5-4. Releases to the Environment from Facilities that Produce, Process, or Use Bromomethane[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
TX	1	0	0	0	0	0	0	0	0
Total	19	294,930	15	10	31	0	294,986	0	294,986

[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, waste water 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: TRI17 2019 (Data are from 2017)

Since bromomethane is highly volatile, nearly all environmental releases of bromomethane are into the air. EPA’s National Emission Inventory (NEI) database contains data regarding sources that emit criteria air pollutants and their precursors, and hazardous air pollutants (HAPs) for the 50 United States, Washington DC, Puerto Rico, and the U.S. Virgin Islands. The NEI database derives emission data 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. In 2011, approximately 5,596 metric tons of bromomethane were emitted to the environment in the United States according to data submitted to the NEI (EPA 2015b). For 2013, the United Nations Environmental Program (UNEP) estimated that total anthropogenic global emissions of bromomethane from non-QPS usage (e.g., agricultural soil fumigation practices) amounted to 1,673 metric tons and QPS emissions were 7,108 metric tons (UNEP 2015). The largest QPS emission (3,874 metric tons) was estimated to arise from usage on timber and wood packaging, followed by emissions on durable goods, preplant fumigation, and perishable items (UNEP 2015).

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

Due to the phase-out of leaded gasoline and the restrictions on bromomethane use as a fumigant, anthropogenic emissions of bromomethane are lower than the amount produced from natural sources. Currently, the largest estimated anthropogenic emission sources of bromomethane are biomass burning in agriculture and the use of biofuels (UNEP 2015). The ocean is both a major source and a sink for bromomethane. Estimates suggest that about 56 Gg (56,000 metric tons) of bromomethane are emitted from the ocean and uptake is about 77 Gg (77,000 metric tons) annually, resulting in a net sink of about 21 Gg (21,000 metric tons) (Baker et al. 1999). Others have offered slightly different estimates, but still concluded that the ocean acts as a net sink for bromomethane (Butler and Rodriguez 1996; WMO 2011). Approximately 10–40 Gg (10,000–40,000 metric tons) of bromomethane are released each year from the burning of biomass (Butler and Rodriguez 1996; WMO 2011). Coastal salt marshes have also been identified as a natural terrestrial source of bromomethane, with emissions of about 14 Gg (14,000 metric tons) annually, and the production of bromomethane and methyl chloride was demonstrated in laboratory studies using a variety of terrestrial plants and wood rot fungi (Rhew et al. 2003). A summary of all of the different sources and sinks of bromomethane were presented by the World Meteorological Organization in its 2010 Scientific Assessment of Ozone Depletion. The UNEP (2015) Report of the Methyl Bromide Technical Options Committee also provides a comprehensive review on the emissions of this substance from both anthropogenic and natural sources. Estimates of the various sources for two different temporal periods are provided in Table 5-5.

Table 5-5. Estimated Anthropogenic and Natural Sources of Bromomethane (Gg/Year) 1996–1998 and 2008

Sources[a]	1996–1998 (Gg/year)	Range (Gg/year)	2008 (Gg/year)	Range (Gg/year)
Fumigation-dispersive (soils)	41.5	28.1–55.6	6.7	4.6–9.0
Fumigation quarantine and preshipment	7.9	7.4–8.5	7.6	7.1–8.1

Table 5-5. Estimated Anthropogenic and Natural Sources of Bromomethane (Gg/Year) 1996–1998 and 2008

Sources[a]	1996–1998 (Gg/year)	Range (Gg/year)	2008 (Gg/year)	Range (Gg/year)
Ocean	42	34–49	42	34–49
Biomass burning	29	10–40	29	10–40
Leaded gasoline	5.7	4.0–7.4	<5.7	No data
Temperate peatlands	0.6	-0.1–1.3	0.6	-0.1–1.3
Rice paddies	0.7	0.1–1.7	0.7	0.1–1.7
Coastal salt marshes	7	0.6–14	7	0.6–14
Based on California salt marshes	14	7–29	14	7–29
Based on Scottish salt marshes	1	0.5–3.0	1	0.5–3.0
Based on Tasmania salt marshes	0.6	0.2–1.0	0.6	0.2–1.0
Mangroves	1.3	1.2–1.3	1.3	1.2–1.3
Shrublands	0.2	0–1	0.2	0 to 1
Rapeseed	4.9	3.8–5.8	5.1	4.0–6.1
Fungus (litter decay)	1.7	0.5–5.2	1.7	0.5–5.2
Fungus (leaf-cutter ants)	0.5	No data	0.5	No data

[a] Potential terrestrial sources (tropical trees, temperate woodlands, tropical ferns, and abiotic decomposition) were not quantified.

Source: WMO 2011

5.3.2 Water

Estimated releases of 15 pounds (~0.01 metric tons) of bromomethane to surface water from 19 domestic manufacturing and processing facilities in 2017, accounted for <1% of the estimated total environmental releases from facilities required to report to the TRI (TRI17 2019). This estimate includes releases to waste water treatment and publicly owned treatment works (POTWs) (TRI17 2019). These releases are summarized in Table 5-4.

Some bromomethane may leach from fumigated soil into surface water (EPA 1986b; IARC 1986). Most of this would be expected to quickly volatilize into air, although some could migrate downward into groundwater where evaporation is not significant.

5.3.3 Soil

Estimated releases of 31 pounds (~0.02 metric tons) of bromomethane to soil from 19 domestic manufacturing and processing facilities in 2017, accounted for <1% of the estimated total environmental releases from facilities required to report to the TRI (TRI17 2019). An additional 10 pounds (~0.005 metric tons), accounted for <1% of the total environmental emissions, were released via underground injection (TRI17 2019). These releases are summarized in Table 5-4.

Soil fumigation was the primary use of bromomethane in the United States, historically accounting for approximately 65% of total consumption (EPA 1987; IARC 1986). However, the use of bromomethane applied to soils as a fumigant has been decreasing rapidly since the late 1990s. Soil fumigation of California strawberry crops is still allowed for 2016 and the EPA is allowing 141 metric tons of bromomethane to be used for this and one other critical use exemption (EPA 2016b).

5.4 ENVIRONMENTAL FATE

5.4.1 Transport and Partitioning

Bromomethane is a readily volatile compound, with a boiling point of 3.6°C (Windholz 1983) and a vapor pressure at 20°C of 1,420 mmHg (EPA 1982). Consequently, bromomethane has a strong tendency to volatilize into air from other media (soil, water). Because bromomethane is quite soluble in water (approximately 13–18 g/L) (EPA 1986b), some bromomethane in air may partition into clouds and rain, where it may be redeposited to the earth by wet deposition.

Anderson et al. (1996) used soil column studies to assess the volatilization rate of bromomethane applied as a pressurized liquid to the surface of a sandy clay loam (53% sand, 29% silt, 17% clay, 3.1% organic matter, pH 6.6) as a function of temperature and moisture content. The results indicated that volatilization of bromomethane from the soil surface was rapid and positively correlated with increasing temperature and moisture content. At a constant soil moisture tension of 0.3 bar, 27.3, 30.4, and 50.9% of the applied bromomethane was volatilized after 3 hours at temperatures of 15, 25, and 35°C, respectively. After 119 hours, 32.2, 35.2, and 54.4% of the applied bromomethane was lost to volatilization at 15, 25, and 35°C, respectively. At a constant incubation temperature of 25°C, 4.0, 28.7, 28.0, and 66.3% of the applied bromomethane was volatilized at 3, 1, 0.3, and 0.03 bar tension, respectively, after 2 hours. After 72 hours, 4.1, 28.9, 34.7, and 66.7% was volatilized at 3, 1, 0.3, and 0.03 bar tension, respectively

(Anderson et al. 1996). Volatilization of bromomethane from three soils consisting of different organic matter content showed large variations in the amounts volatilized versus the amounts degraded (Gan et al. 1996, 1997). Forty mL of bromomethane gas was injected to a depth of 30 cm into packed columns of low organic matter containing soils: a Greenfield sandy loam (0.92% organic matter) or a Carsitas loamy sand (0.22% organic matter). Similar experiments were conducted using Linne clay loam with greater organic matter content (2.99% organic matter). Cumulative volatilization losses from the two low organic matter containing soils were approximately 90%; however, only 44% of the applied bromomethane was volatilized from the Linne clay loam, with about half being degraded. Only about 10% degradation occurred in the two low organic matter containing soils. Additional experiments were conducted to determine the effect of moisture content on the rate of volatilization. Increasing the volumetric moisture content of the Greenfield sandy loam from 0.058 to 0.180 cm^3/cm^3 resulted in a 17% decrease in the amount of bromomethane that was volatilized (Gan et al. 1996). It was concluded that as the moisture content increased, the effective diffusion coefficient of bromomethane in the soil decreased, resulting in a lower surface volatilization flux and greater degradation (Gan et al. 1996, 1997); these results are in contrast to the findings of Anderson et al. (1996). Similarly, it was observed that soils with higher bulk density tended to have lower volatilization rates since the effective diffusion coefficient of bromomethane and other gasses in these soils are lower as compared to soils with lower bulk density.

It is common practice to cover treated fields with tarps immediately following fumigation in order to limit volatilization loss of the fumigant and maximize the impact of fumigant vapors on the treated soils. Historically, high-density polyethylene (HDPE) tarps were used in agriculture as the standard barrier film; however, HDPE is semi-permeable to gases such as bromomethane and other fumigants. The development of high barrier totally impermeable film tarps (TIF) (HDPE-based films containing multilayer polymers composed of ethylene vinyl alcohol) or virtually impermeable films (VIF) (HDPE or low-density polyethylene [LDPE] films containing nylon or vinyl polymers) have shown better performance at reducing volatilization losses of bromomethane and other fumigants (Fennimore and Ajwa 2011; Freeman 2015). Volatilization losses from soil columns treated with bromomethane and methyl iodide were monitored using HDPE tarps or high-barrier TIF tarps, or left completely uncovered following fumigation (Gan and Yates 1996; Gan et al. 1997). In each experiment, it was observed that greater volatilization losses occurred in soils that were left uncovered and contained the lowest amounts of organic matter. The authors also observed that under similar conditions, a greater percentage of methyl iodide was volatilized as compared to bromomethane due to the relatively slow rate of degradation of methyl iodide when compared to bromomethane (Gan and Yates 1996; Gan et al. 1997). Using a Greenfield sandy loam with approximately 0.92% organic matter, the cumulative volatilization loss of bromomethane injected as a cooled liquid to a depth of 30 cm below the surface was 75, 68, and 45% for an uncovered soil column, a soil column covered with HDPE, and a soil column covered with a TIF tarp, respectively (Gan et al. 1997). Volatilization was significantly decreased in similar experiments using soils containing a higher percentage of organic matter. For example, only 30% of the applied bromomethane was volatilized from a nursery potting soil containing 9.60% organic matter and covered with a HDPE film. Packed soil column experiments using a low organic Arlington sandy loam (0.92% organic matter, pH 7.2) indicated that approximately 88% of the injected bromomethane was volatilized if the soil surface was left uncovered (Gan et al. 2000). Volatilization losses were 83 and 55% of the nominal concentration when the soil columns were covered with a HDPE tarp and a high-barrier TIF tarp, respectively (Gan et al. 2000). The addition of soil amendments rich in organic matter was also shown to reduce volatilization losses of bromomethane by enhancing the rate of degradation (Gan et al. 1998). Applying 5% composted manure to soil columns treated with bromomethane reduced volatilization approximately 12% as compared to unamended soil columns (Gan et al. 1998).

Majewski et al. (1995) monitored postapplication volatilization losses of a bromomethane/chloropicrin (67%/33%) fumigant in field experiments in Monterey County, California in which bromomethane was injected into the soil and then the fields were either left uncovered or were covered with tarps (Majewski et al. 1995). The fumigant was injected to a depth of 25–30 cm in pressurized liquid form at an application rate of 392 kg/ha to fields located approximately 6 km away from one another. One field was immediately covered with a high-barrier TIF plastic tarp, while the other field was left uncovered. Both fields were Salinas clay loam with similar physical properties and moisture content. The primary difference between the properties of the soils was that the non-tarped field contained a greater content of organic carbon (2.30%) than the tarped field (1.40%) and possessed higher clay content, but a lower silt content. Cumulative volatilization losses of bromomethane were approximately 22 and 32% at 5 and 9 days postapplication, respectively, for the tarp-covered field, while the cumulative volatilization loss of bromomethane from the uncovered field was about 89% 5 days postapplication (Majewski et al. 1995). The maximum volatilization flux of bromomethane from the covered field occurred about 20 hours postapplication and was 91 $\mu g/m^2$-second, while the maximum volatilization flux from the uncovered field was about 4 times greater and occurred at <3 hours postapplication.

Field studies conducted in California demonstrated the effectiveness of deep injection depths, irrigation, and postapplication tarping practices at reducing bromomethane volatilization from treated fields (Wang et al. 1997). Bromomethane was injected into Arlington fine sandy loam (64% sand, 29% silt, 7% clay) in experimental plots constructed at the University of California Agricultural Experimental Station in

Riverside, California. When bromomethane was applied as a gas at an injection depth of 25 cm, cumulative volatilization losses were 87, <42, and 59% for uncovered plots, plots that were immediately irrigated and covered by HDPE tarps, and non-irrigated plots covered by HDPE tarpaulins, respectively. At a deeper injection depth of 60 cm, the volatilization losses decreased to 60, 15, and <15% for uncovered plots, HDPE covered plots, and plots covered by a Hytibar plastic tarp, respectively.

Bromomethane, either as a gas or dissolved in water, has relatively low affinity for soils (Brown and Rolston 1980; Fuhr et al. 1948). K_{oc} values in the ranges of 1–10 (EPA 1986b; Roy and Griffin 1985) and 9–22 (Yates et al. 2003) suggest that this compound possesses high mobility and could ultimately leach into groundwater. However, the rapid volatilization and degradation rates of bromomethane in soil will reduce the potential of this chemical to leach. The lack of detection of bromomethane in groundwater (see Section 5.5.2 water monitoring data) strongly suggests that although bromomethane is very mobile in soils, it is either volatilized or degraded before migrating to lower soil horizons and contaminating groundwater.

Bromomethane is not expected to bioconcentrate in aquatic organisms because of its low octanol/water partition coefficient (K_{ow}) (estimated to be about 13) (EPA 1979a). The bioconcentration factor (BCF) for bromomethane has not been measured experimentally. However, based on an empirical relation between the BCF and the K_{ow} (Neely et al. 1974), the estimated BCF for bromomethane is about 3. This low estimated BCF indicates that bromomethane is not likely to bioconcentrate in aquatic organisms (EPA 1986b).

5.4.2 Transformation and Degradation

Air. The main degradation pathway for bromomethane in the troposphere is reaction with photochemically-generated hydroxyl radicals. The rate constant for this reaction has been measured to be 4.02×10^{-14} cm^3/molecule-second at 25°C (Atkinson 1989), which corresponds to an atmospheric half-life of about 266 days, assuming a hydroxyl radical concentration of 1.5×10^6 molecules/cm^3 and a 12-hour day. Due to the long atmospheric half-life, some bromomethane will gradually diffuse into the stratosphere above the ozone layer where it will slowly degrade due to direct photolysis from high-energy UV radiation and contribute to the catalytic removal of stratospheric ozone. The direct photolysis half-life in the stratosphere is estimated to be about 35 years (Butler and Rodriguez 1996). The total lifetime of atmospheric bromomethane is calculated by summing its reciprocal lifetime due to each major sink as shown in the equation below (Butler and Rodriguez 1996; WMO 2011; Yvon and Butler 1996):

$$\frac{1}{\tau_{total}} = \frac{1}{\tau_{p}} + \frac{1}{t_{o}} + \frac{1}{\tau_{s}}$$

where t_{total} is the total lifetime of atmospheric bromomethane, t_p is the lifetime in the troposphere and stratosphere, t_o is the lifetime due to ocean uptake, and t_s represents the lifetime due to terrestrial uptake. Using lifetimes of 1.7, 2.7, and 3.4 years for t_p, t_o, and t_s, the total atmospheric lifetime of bromomethane (t_{total}) was estimated as 0.8 years (Shorter et al. 1995; Yvon and Butler 1996). There is a great deal of uncertainty in this estimate, however, since all of the sources and sinks of bromomethane are not thoroughly understood; therefore, this lifetime can only be considered a best estimate for the global lifetime of atmospheric bromomethane.

Water. Bromomethane degrades in water through a combination of abiotic and biotic processes. Hydrolysis of bromomethane takes place by S_N2 nucleophilic substitution reaction, yielding methanol, the bromide anion, and the hydrogen ion as hydrolysis products. At neutral pH and a temperature of 25°C, the half-life of bromomethane in nonsterile purified deionized water was reported as 20 days (Papiernik et al. 2000). The hydrolysis half-life of bromomethane was studied in distilled water over a pH range of 3–8, and at temperatures of 18 and 30°C (Gentile et al. 1989). At 18°C, the hydrolysis half-lives of bromomethane were reported as 29, 19, 12, and 9 days at pH 3, 5, 7, and 8, respectively. When the temperature was increased to 30°C, the observed half-lives were 28, 18, 10, and 8 days at pH 3, 5, 7, and 8, respectively, in the distilled water. Slightly longer hydrolysis half-lives were observed in groundwater with a pH of 7.5–7.8. Half-lives ranging from 36 to 50 days were observed at 18°C, and half-lives ranging from 15 to 19 days were observed in the groundwater at 30°C (Gentile et al. 1989). A 6–7-fold increase in the rate of hydrolysis was observed when an aqueous solution of bromomethane maintained at neutral pH was irradiated with UV light at 254 nm (Castro and Belser 1981). The enhanced degradation was attributed to hydrolysis of an excited state of bromomethane, but since this compound has only weak absorption above 290 nm, it is uncertain whether this enhanced hydrolysis rate is important under environmental conditions.

Goodwin et al. (1998) studied the microbial oxidation of bromomethane in freshwater, estuary water, coastal seawater, and hypersaline-alkaline water by monitoring the production of $^{14}CO_2$ from samples of $^{14}CH_3Br$ incubated in the different water types. Calculated half-lives were approximately 5, 36, 82, and 298 days for the freshwater, estuary water, coastal seawater, and hypersaline-alkaline water samples, respectively (Goodwin et al. 1998). No $^{14}CO_2$ production was observed for sterilized controls. These data suggest that biotic degradation processes will occur at a rate similar to the hydrolysis rate in freshwater, but microbial degradation appears to be slower in seawater given these results. Bromomethane was shown to be oxidized using water samples obtained at different depths from Mono Lake, California (Connell et al. 1997). Oxidation only occurred in nonsterilized lake water samples, suggesting microbial-induced degradation as opposed to abiotic degradation mechanisms.

Sediment and Soil. Bromomethane degrades in soil by three principle mechanisms: hydrolysis, methylation by organic matter, and biological oxidation by microorganisms in the soil. For soils rich in organic matter, degradation by reaction with nucleophilic sites in the organic matter is thought to be the primary mechanism responsible for the consumption of bromomethane, whereas hydrolysis and microbially mediated oxidation are the main degradation mechanisms for soils of low organic matter content.

Evidence suggests that bromomethane undergoes nucleophilic substitution with sites in soil organic matter, resulting in the methylation of the organic matter and the release of the bromide anion (Papiernik et al. 2000). To study its abiotic degradation mechanisms, bromomethane was incorporated in an Arlington sandy loam (74.6% sand, 18.0% silt, 7.4% clay, 9.2 g/kg organic carbon, pH 6.73) and a Linne clay loam (36.7% sand, 32.0% silt, 31.3% clay, 25.1 g/kg organic carbon, pH 6.80) under sterile and nonsterile conditions (Papiernik et al. 2000). The half-lives of bromomethane in the Arlington sandy loam were approximately 38.5 and 46.2 days in non-autoclaved and autoclaved samples, respectively. Shorter half-lives of approximately 3.6 and 4.2 days were observed in non-autoclaved and autoclaved Linne clay loam samples, respectively. Because the rates of degradation were similar in the autoclaved and the non-autoclaved soil experiments, the authors concluded that abiotic processes were largely responsible for the observed loss rather than microbial activity. The greater content of organic matter in the Linne clay loam also resulted in much greater degradation rates as compared to the lower organic containing Arlington sandy loam. This observation is consistent with the data of Gan and Yates (1996), which observed a similar correlation between the consumption of bromomethane and soil organic matter content. In four soils containing 0.92, 2.51, 2.99, and 9.60% organic matter, the half-lives of bromomethane were reported as 22, 6, 6, and 6 days, respectively, and there was no statistically significant difference in degradation rates in sterilized versus nonsterilized soils, which again suggests the importance of abiotic transformations rather than microbially mediated degradation (Gan and Yates 1996).

Gan et al. (1994) studied the degradation of bromomethane in four California surface soils: Greenfield sandy loam (9.5% clay, 0.921% organic matter, pH 7.39), Wasco sandy loam (4.3% clay, 0.646% organic matter, pH 6.98), Linne clay loam (25.1% clay, 2.989% organic matter, pH 7.23), and Carsetas loamy sand (0.1% clay, 0.222% organic matter, pH 8.02) under moist, air-dried, and oven-dried conditions (Gan et al. 1994). The authors determined that the degradation of bromomethane was highly correlated with the amount of organic matter and nitrogen content contained in moist and air-dried soils, but not oven-dried soils. Half-lives of approximately 11–33 and 6–39 days were calculated for the four soils under moist and air-dried conditions, respectively, while half-lives of roughly 27–59 days were estimated in the oven-dried soil experiments.

Accelerated rates of bromomethane degradation were observed in experiments conducted employing six soils used to grow strawberries in California (Trikey-Dotan and Ajwa 2014). A bromomethane (67%)/chloropicrin (33%) mixture was applied at a rate of 100 mg/kg to 100 g of soil from the six different plots in sealed glass vials. In order to test the dissipation rates after repeated applications, soils were chosen from three locations (Oxnard, Salinas, and Watsonville) that either had been previously fumigated with chloropicrin or had never been fumigated. Half-lives ranged from under an hour to approximately 15 hours in the six soils. The half-lives of bromomethane in the Salinas and Watsonville soils were significantly shorter in the nontreated soils as compared to the previously fumigated soils. In contrast, a slightly longer half-life (14.5 hours) was observed in the nontreated soil from Oxnard as compared to the previously treated soil (half-life 11.6 hours). Unlike other studies, the authors did not find any significant correlation between soil properties and the degradation rate of bromomethane in these soils and surmised that the accelerated degradation rates of bromomethane observed in these soils was the result of biotic processes.

The bacterial oxidation of bromomethane under aerobic conditions in methanotrophic soils (soils containing bacteria that readily oxidize methane) has been demonstrated (Ou 1998). Using an application rate of 1,000 mg/g, bromomethane was completely degraded within 40–90 hours under aerobic conditions in methanotrophic soils. At an application rate of 10 mg/g, bromomethane was completely degraded in 5 hours under aerobic conditions, but degraded very slowly under anaerobic conditions (Ou 1998). Formaldehyde and the free bromide anion were reported as the primary degradation products (Ou 1998). The authors remarked that the majority of agricultural soils in the United States are not methanotrophic and have low methane oxidizing capabilities, so this may not be a particularly important environmental fate process. Low levels of bromomethane were shown to be rapidly degraded by an agricultural (corn field) soil and highly organic forest soil obtained from southern New Hampshire under aerobic conditions

(Hines et al. 1998). Bromomethane applied to vials of soil at 10 ppb was completely consumed in the forest soil in a matter of minutes, and in the agricultural soil in a matter of hours. Almost no degradation occurred in autoclaved soils or soils that had previously been sterilized by the addition of antibiotics 12 hours earlier, confirming that the source of degradation was biological. Experiments conducted using high levels of bromomethane (10–10,000 ppm) resulted in toxicity to the microbes and much slower degradation rates. Experiments conducted under a nitrogen-rich environment also showed little degradation of bromomethane for any of the soils tested, suggesting that biodegradation is very slow under anaerobic conditions. Although biodegradation under anaerobic conditions is considered to occur slowly in the environment, Oremland et al. (1994) demonstrated that bromomethane may react with free sulfide commonly found in anaerobic sediments and salt marshes, resulting in the production of methylated sulfur reaction products, which in turn are degraded by sulfate-reducing bacteria.

5.5 LEVELS IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to bromomethane depends, in part, on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of bromomethane 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 bromomethane 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 5-6 shows the lowest limit of detections that are achieved by analytical analysis in environmental media. An overview summary of the range of concentrations detected in environmental media is presented in Table 5-7.

Table 5-6. Lowest Limit of Detection Based on Standards[a]

Media	Detection limit	Reference
Air	0.2 ppb	LeFevre et al. 1989
Drinking water	0.01 μg/L	EPA 1988c
Surface water and groundwater	0.01 μg/L	EPA 1988c
Whole blood	3 ng/mL blood	Pellizzari et al. 1985

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

Table 5-7. Summary of Environmental Levels of Bromomethane

Media	Low	High	For more information
Outdoor air (ppbv)[a]	Not reported	0.46[b]	Section 5.5.1
Outdoor (ppbv)[c]	0.04	8.7	Section 5.5.1
Surface water (ppb)	Not detected		Section 5.5.2
Ground water (ppb)	0.50	6.4	Section 5.5.2
Drinking water (ppb)	Detected but not quantified		Section 5.5.2
Food (ppb)	Not detected		Section 5.5.4
Soil	No data	No data	Section 5.5.3

[a] Ambient air, non-agricultural areas.
[b] Data collected 2015 (EPA 2019a); median: 0.007 ppbv.
[c] Agricultural areas near bromomethane use.

Detections of bromomethane in air, water, and soil at NPL sites are summarized in Table 5-8.

Table 5-8. Bromomethane Levels in Water, Soil, and Air of National Priorities List (NPL) Sites

Medium	Median[a]	Geometric mean[a]	Geometric standard deviation[a]	Number of quantitative measurements	NPL sites
Water (ppb)	7.00	11.5	10.9	10	10
Soil (ppb)	10.9	11.8	2.68	4	4
Air (ppbv)	0.700	0.325	10.4	4	4

[a] Concentrations found in ATSDR site documents from 1981 to 2017 for 1,854 NPL sites (ATSDR 2017). 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

The global annual mean mixing ratio of bromomethane in the troposphere for 2008 was reported to range from about 7.3 to 7.5 pptv (0.0073–0.0075 ppbv), which is a decrease of about 20% from the estimates from 1996 to 1998, prior to the large-scale phase-out of bromomethane’s use as an agricultural fumigant (WMO 2011). Background atmospheric levels of bromomethane were estimated to be approximately 5.3 pptv (0.0053 ppbv) prior to the introduction of this substance as a fumigant in the 1940s (UNEP 2015).

Data from the EPA Air Quality System (AQS) database are consistent with current estimates for levels of bromomethane in the atmosphere provided by the WMO and UNEP. Table 5-9 shows the annual mean 24-hour percentile distributions of bromomethane from multiple monitoring locations across the nation for the years 2010–2018 (EPA 2019a).

Table 5-9. Percentile Distribution of Annual Mean Bromomethane Concentrations (ppbv) Measured in Ambient Air at Locations Across the United States

Year	Number of U.S. locations	25th	50th	75th	95th	Maximum
2010	257	0.0046	0.0088	0.013	0.043	0.14
2011	231	0.0028	0.0068	0.011	0.039	0.21
2012	231	0.00	0.0081	0.011	0.027	0.14
2013	217	0.00	0.0040	0.0089	0.021	0.13
2014	197	0.00	0.0090	0.011	0.024	0.90
2015	175	0.00	0.0034	0.012	0.026	0.40
2016	159	0.00	0.005	0.018	0.049	0.26
2017	124	0.00	0.00	0.00	0.022	0.31
2018	105	0.00	0.00	0.00	0.017	0.14

Source: EPA Air Quality System (AQS) annual summaries (EPA 2019a)

The 2013 National Monitoring Program sponsored by the EPA compiled 24-hour air sample data from 66 monitoring sites located in 26 states across the United States (EPA 2015c). Samples from 34 sites were assessed for volatile organic compounds, including bromomethane. Bromomethane was detected above the detection limits in 1,404 out of 1,883 samples collected at a maximum concentration of 3.37 ppbv (EPA 2015c). The arithmetic mean was reported as 0.014 ppbv and the median value was 0.011 ppbv.

In agricultural areas where bromomethane is applied as a fumigant, ambient air levels are often higher than in non-agricultural areas. Average concentrations at five monitoring sites in Ventura County, California were 0.02–0.39 ppbv with a highest 1-day concentration of 3.90 ppbv at one location over the monitoring period August 22 to September 30, 2005, which coincided with high bromomethane usage for this county (Cal EPA 2008). Average concentrations of 0.22–0.88 ppbv with a highest 1-day concentration of 5.92 ppbv were reported for Ventura County for sampling period June 14 to August 6, 2006 (Cal EPA 2008). Bromomethane was detected in all 23 samples of air obtained from urban communities in California that had high use of 1,3-dichloropropene and secondary use of bromomethane at a mean concentration of 0.69 μg/m^3 (0.17 ppbv) and in all 30 samples of air from urban communities that had high use of bromomethane and secondary use of 1,3-dichloropropene at a mean concentration of 5.2 μg/m^3 (1.3 ppbv) (Lee et al. 2002). In rural communities that had high use of 1,3-dichloropropene and secondary use of bromomethane, bromomethane was detected in 117 out of 118 air samples at a mean concentration of 2.5 μg/m^3 (0.63 ppbv) and in rural communities with high bromomethane usage and secondary usage of 1,3-dichloropropene, it was detected in 149 out of 149 air samples at a mean of 12 μg/m^3 (3.0 ppbv) (Lee et al. 2002). Table 5-10 shows some monitoring data for bromomethane at various communities in California where it was applied as a fumigant.

Table 5-10. Ambient Air Concentrations in Parts per Billion Near Areas of Bromomethane Use

Concentration (ppbv)	Location (California)	Date	Sampling details	Reference
0.2–8.7	Camarillo/Oxnard	2010–2014	Data represents the highest 1-day concentration for each of the years	Cal EPA 2015
0.1–1.8	Watsonville	2010–2014	Data represents the highest 1-day concentration for each of the years	Cal EPA 2015
0.6–3.8	Santa Maria	2010–2014	Data represents the highest 1-day concentration for each of the years	Cal EPA 2015
0.13	Watsonville	2012	1-Year overall average concentration	Cal EPA 2014
0.45	Watsonville	2013	1-Year overall average concentration	Cal EPA 2014
0.26	Salinas	2011	1-Year overall average concentration	Cal EPA 2014
0.09	Salinas	2012	1-Year overall average concentration	Cal EPA 2014
0.39	Salinas	2013	1-Year overall average concentration	Cal EPA 2014
0.20	Santa Maria	2011	1-Year overall average concentration	Cal EPA 2014
0.09	Santa Maria	2012	1-Year overall average concentration	Cal EPA 2014
0.15	Santa Maria	2013	1-Year overall average concentration	Cal EPA 2014
0.17	Ripon	2011	1-Year overall average concentration	Cal EPA 2014
0.08	Ripon	2012	1-Year overall average concentration	Cal EPA 2014
0.11	Ripon	2013	1-Year overall average concentration	Cal EPA 2014

Table 5-10. Ambient Air Concentrations in Parts per Billion Near Areas of Bromomethane Use

Concentration (ppbv)	Location (California)	Date	Sampling details	Reference
0.23	Camarillo/Oxnard	2011	1-Year overall average concentration	Cal EPA 2014
0.10	Camarillo/Oxnard	2012	1-Year overall average concentration	Cal EPA 2014
0.06	Camarillo/Oxnard	2013	1-Year overall average concentration	Cal EPA 2014
0.11	Shafter	2011	1-Year overall average concentration	Cal EPA 2014
0.06	Shafter	2012	1-Year overall average concentration	Cal EPA 2014
0.04	Shafter	2013	1-Year overall average concentration	Cal EPA 2014
0.631	Parlier	2006	Highest 1-day concentration	Wofford et al. 2014
1.02	Monterey	1986	Mean concentration	Baker et al. 1996
1.10	Monterey	1986	Maximum concentration	Baker et al. 1996

Highest air levels of bromomethane are usually observed locally at field sites shortly following its application or at facilities where it is used as a fumigant. These situations appear to be the greatest acute exposure scenarios for humans. Bromomethane peak concentrations of 12.4 and 13.4 mg/m^3 (3.14 and 3.39 ppmv) were observed 4 hours postapplication above a field located in Moreno Valley, California in which bromomethane was injected at a depth of 25 cm (Yates et al. 1997). At a deeper injection depth (68 cm), the maximum concentration measured at 0.5 m above the field was 0.625 mg/m^3 (0.158 ppmv) and occurred roughly 12 hours postapplication. Bromomethane levels as high as 20 ppmv were observed in sealed trailers used to transport grapes that had been fumigated with bromomethane and 7 ppmv inside the refrigerated area at a facility (O'Malley et al. 2011). Table 5-11 summarizes bromomethane levels under high exposure scenarios.

Table 5-11. Bromomethane Levels Following Fumigation

Concentration (ppmv)	Sampling details	Reference
10–20	Inside trailer transporting grapes fumigated with bromomethane with vent doors closed	O'Malley et al. 2011
2.0–4.0	Enclosed refrigerated building storing fumigated grapes	O'Malley et al. 2011

Table 5-11. Bromomethane Levels Following Fumigation

Concentration (ppmv)	Sampling details	Reference
3.14–3.39	Peak concentration above a treated field when bromomethane was injected at a shallow 25 cm depth	Yates et al. 1997
~45	Peak concentration inside of a greenhouse shortly after fumigation	De Vreede et al. 1998

5.5.2 Water

Bromomethane occurs in ocean waters at a concentration of about 1–2 ng/L (0.001–0.002 μg/L) (Lovelock 1975; Singh et al. 1983), but is not a common contaminant in fresh waters in the United States. It was not detected in storm water runoff from 15 U.S. cities (Cole et al. 1984) or in influents to sewage treatment plants in four cities (EPA 1979b), and was detected in only 1.4% of >900 surface water samples recorded in the STORET database (Staples et al. 1985). The median concentration in these positive samples was <10 μg/L. Bromomethane was not detected in 297 surface water samples for which it was analyzed for in 2015 in the STORET database (EPA 2016d). Bromomethane has been identified, but not quantified, in drinking water supplies of several U.S. cities (Coleman et al. 1976; EPA 1975; Kool et al. 1982; Kopfler et al. 1977; EPA 1976). Bromomethane in drinking water is presumably generated as an inadvertent byproduct following chlorination. Bromomethane was monitored as part of the Unregulated Contaminant Monitoring Rule (UCMR-3) program to collect data for contaminants suspected to be present in drinking water, but that do not have health-based standards set under the Safe Drinking Water Act (SDWA). Bromomethane was detected above its minimum reporting level (0.2 μg/L) but not above its reference concentration (140 μg/L) in 115 out of 36,848 samples of drinking water obtained from public water systems (PWSs) (EPA 2017). It was detected above its minimum reporting level but not above its reference concentration in 49 out of 4,916 PWSs that reported results.

Observation of bromomethane in groundwater is somewhat more likely than in surface water, since evaporation is restricted. Bromomethane was detected at a concentration of 0.50 μg/L in groundwater at 1 out of 1,831 sites sampled by the U.S. Geological Survey (USGS) in monitoring studies conducted from 1992 to 1996 (Kolpin et al. 2000). Bromomethane was not detected in any of the 40 principal aquifers in the United States that are used for drinking water during a USGS assessment from 1991 to 2010. However, it was detected in 1 of the 22 urban aquifers (0.09% of total) at 0.29 μg/L. The laboratory reporting levels ranged from 0.1 to 0.4 μg/L (USGS 2015). A review of the EPA Pesticides in Groundwater Database showed that bromomethane was detected in only 2 out of 20,429 groundwater wells sampled from 1971 to 1991 (EPA 1992). Both detections occurred at sampling locations in California at levels of 1.5 and 6.4 µg/L. There were no detections of bromomethane in 15,119 wells sampled in Florida and no detections in 93 wells sampled in Hawaii over the 2-decade study period. Plumb (1992) analyzed the occurrence of bromomethane and other contaminants in wells at active and abandoned hazardous waste sites for different regions of the country. Bromomethane was not detected in any wells covering EPA Regions 1, 2, 4, 5, 6, 7, 8, and 10; however, it was detected in 3.2% of groundwater wells in EPA Region 3 (Pennsylvania, West Virginia, Maryland, District of Columbia, and Delaware) and 0.8% of the groundwater wells in EPA Region 9 (California, Nevada, Utah, Hawaii, Guam, Samoa, Northern Mariana Islands, and Trust Territories). Bromomethane was not detected in 1,174 community wells or 617 private wells located in Wisconsin (Krill and Sonzogni 1986).

5.5.3 Sediment and Soil

No data were found on bromomethane levels in soil. Bromomethane is not expected to be a stable constituent of soil, since it either evaporates or reacts with organic soil components releasing the bromide ion. The background bromide content of soils normally is about ≤10 mg/kg depending upon the soil type (WHO 1995). Bromide ion concentrations were measured in greenhouse soil before and after the application of bromomethane at a rate of 80 g/m^2. Prior to fumigation, bromide levels were about 5 mg/kg. Two months post treatment, bromide levels of >30 mg/kg were observed; however, these levels decreased to <10 mg/kg 3 months later. The total bromide ion concentrations in two soils containing 2.81 and 0.93% organic carbon were 9 and 5 mg/kg, respectively, before application of bromomethane (IARC 1986). Following the application of bromomethane at a rate of 500 mg/kg to both soils, the bromide ion concentration increased to 63 mg/kg for the soil containing 2.81% organic carbon and 25 mg/kg for the soil containing 0.93% organic carbon after 24 hours (IARC 1986).

5.5.4 Other Media

Although bromomethane was used extensively as a fumigant for grains and other food products, it is rarely detected unchanged as a residue in foods. Most of the fumigant is rapidly lost to the atmosphere, and the remaining portion reacts with the food components, producing residues of inorganic bromide (IARC 1986; NAS 1978). Daft (1987, 1988, 1989) reported that bromomethane was not detected in hundreds of tested food products. The tolerances for residues on agricultural commodities and processed foods that have been set by EPA and FDA are for bromide ion, not bromomethane (EPA 2014b). Bromide ion is a frequently detected component in food samples. For example, it was detected in 27.9%

of lettuce samples, 27% of tomato samples, and 37.3% of rye tested in a European Union report on pesticide residues in food (EFSA 2015); however, bromide ion is a naturally occurring component in plants and it is not a unique indicator for bromomethane usage.

5.6 GENERAL POPULATION EXPOSURE

Inhalation of bromomethane in ambient air is the predominant exposure route for most people in the United States. Singh et al. (1981) calculated that average daily doses of bromomethane from air in three U.S. cities ranged from 4.5 to 24.5 μg/day, based on total air intake of 23 m^3/day by an adult. These estimates were based on 1979 monitoring data in urban areas that had mean concentrations well above current levels. Using the same air intake rate and ambient air levels of 7.3–7.5 pptv from the WMO for 2008 (WMO 2011), current intake is roughly 0.66–0.68 μg/day. Based on the very low levels of bromomethane in water and the negligible levels in food, it appears that exposure of the general population to bromomethane from sources other than air is likely to be insignificant under normal circumstances.

The Fourth National Report on Human Exposures to Environmental Chemicals, published and updated by the Centers for Disease Control and Prevention reporting biomonitoring data from the National Health and Nutrition Examination Survey (NHANES) for survey years 2005–2012 does not include data for bromomethane or the bromide ion (CDC 2018).

Exposure of workers to bromomethane is highly variable, depending on conditions. The highest exposures are most likely to occur during fumigation activities, especially when bromomethane is first released to the environment after fumigation ends. Exposure levels under these conditions could reach from 25 to 2,500 ppmv (IARC 1986; NIOSH 1984; Van Den Oever et al. 1982), which would correspond to a dose of 100–10,000 mg/hour for an exposed worker.

Occupational exposure to bromomethane was examined in a 17-year study of 124 employees at a chemical factory primarily manufacturing bromomethane (Yamano et al. 2011). Workers aged 18–64 years were grouped based upon their responsibilities: synthesis group, filling group, and other group. The geometric mean workplace levels in the synthesis and filling areas were 0.68 and 0.77 ppmv, respectively. The median urinary concentration of bromide ion for all employees over the 17-year period was 11 μg/mg CRE (creatinine corrected). The synthesis group had urinary concentrations of bromide ion ranging from 2.5 to 51.8 μg/mg, with a median of 13.0 μg/mg. The filling group and other group had median values of 11.9 and 7.2 μg/mg, respectively. Levels were ≥30 μg/mg in 16.3% of the workers in the synthesis group, 6.9% of the workers in the filling group, and in none of the workers of the other group. Exposure to bromomethane may have occurred during work procedures, such as the exchange of reaction equipment for maintenance or cleaning, during operations to adjust weights after filling canisters, or during canister recycling.

Concentrations of bromide in blood samples from six storage room workers (four females, two males) ages 32–54 years were examined (Baur et al. 2015; Kloth et al. 2014). The workers were accidentally exposed to fumigant offgassing while unloading and unpacking at a European company importing goods from overseas. Exposure incidents were reported 3 times during a 2-year period (2010–2012). Bromomethane was found in ambient air of the storage room at concentrations ranging from 2.5 to 200 ppmv (mean 125 ppmv) measured after the occurrence of the first incident, and also detected in the air after the second incident (concentration not reported). Serum bromide levels in the analyzed samples were similar to background levels; however, low levels of bromomethane were detected in the serum of one worker (0.24 μg/L) 5 days following the second incident.

Data were not located on the exposure of children to bromomethane. Children are likely to be exposed to low levels of bromomethane from inhalation of ambient air. Children residing in agricultural areas where a critical use exemption for bromomethane has been granted may be exposed to slightly greater levels.

5.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

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

Although bromomethane has been banned for use in homes or residential settings, a pest control company fumigated a resort in the U.S. Virgin Islands in the spring of 2015 with bromomethane, resulting in severe illness for a family of four persons staying at the resort (Kulkarni et al. 2015). Sampling of the housing units detected bromomethane at levels of 0.59–1.12 ppmv several days after the initial fumigation. In addition to the four individuals of the family who became ill, 37 individuals were identified who had potentially been exposed to bromomethane after the fumigation in the spring of 2015 or from a previous fumigation in the fall of 2014.

Two produce inspectors became ill when they were intermittently exposed to high levels of bromomethane while performing routine inspections of fumigated grapes inside a cold storage unit at a produce facility located in California (O'Malley et al. 2011). The measured serum bromide level for one worker was 4.4 mg/dL 5 days after working in the cold storage unit. A peak serum bromide level of 58 mg/dL was estimated on his last day of potential exposure by assuming a 12-day half-life for inorganic bromide. A second inspector had measured bromide levels of 1.5 mg/dL more than a month after his last day of work at the facility, which corresponded to a peak estimated level of approximately 85 mg/dL 1 month prior. Air samples obtained at three locations that either stored or transported the grapes showed median levels of bromomethane ranging from <0.4 to 15 ppmv, with a maximum level of 20 ppmv in trailers responsible for transporting the grapes.

The exposure to workers using bromomethane for quarantine purposes was evaluated by measuring ambient air levels during the fumigation process and monitoring urinary bromine levels of 251 employees involved in the fumigation of logs and grain products (Tanaka et al. 1991). Workers fumigated logs both inside the sealed holds of a transport ship and in sealed polyvinyl sheets at the shipyard. Additionally, other workers fumigated grains in a closed warehouse and a silo. Exposure periods for both the dispersion and degassing processes were roughly 120 minutes/day over a 6-day work week. Ambient concentrations during the bromomethane dispersion process averaged 1.1–3.8 ppmv and ambient levels averaged 0.5–74.6 ppmv during the degassing process. Urinary bromine levels of workers engaged in the fumigation activities ranged from 7.8 to 9.0 mg/L (0.78–0.90 mg/dL) and a control group of 379 workers who were not involved in the use of bromomethane averaged 6.3 mg/L (0.63 mg/dL) (Tanaka et al. 1991). Even though workers used full facepiece gas masks with a respiratory canister to limit inhalation exposure during the fumigation process, bromomethane was detected in the exhaled breath of a sampling of workers who fumigated logs aboard the ship and in the shipyard and fumigated grains in the closed warehouse.