

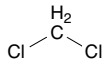
Dichloromethane

CAS No. 75-09-2

Reasonably anticipated to be a human carcinogen

First listed in the *Fifth Annual Report on Carcinogens* (1989)

Also known as methylene chloride



Carcinogenicity

Dichloromethane is *reasonably anticipated to be a human carcinogen* based on sufficient evidence of carcinogenicity from studies in experimental animals.

Cancer Studies in Experimental Animals

Exposure to dichloromethane by inhalation caused tumors in two rodent species and at several different tissue sites. In mice of both sexes, it caused tumors of the lung (alveolar/bronchiolar tumors) and liver (hepatocellular tumors), and in rats of both sexes, it caused benign mammary-gland tumors (fibroadenoma) (NTP 1986).

Cancer Studies in Humans

The data available from epidemiological studies are inadequate to evaluate the relationship between human cancer and exposure specifically to dichloromethane (IARC 1982). In 1999, the International Agency for Research on Cancer reviewed additional epidemiological studies published after dichloromethane had been listed in the *Fifth Annual Report on Carcinogens*, including seven cohort studies (six of which were small) and three case-control studies (of brain cancer, breast cancer, and rectal plus lung cancer). Although cancer risk was increased for some tissue sites, including the pancreas in two cohort studies, the breast in one case-control and one cohort study, and the liver, prostate, rectum, and brain in one study each, IARC concluded that the evidence for carcinogenicity was too inconsistent to support a causal interpretation (IARC 1987, 1999). Studies published since the IARC review include updates of previous studies (Hearne and Pifer 1999, Dumas *et al.* 2000, Radican *et al.* 2008) and new case-control studies of brain cancer (Cocco *et al.* 1999), lymphoma (Seidler *et al.* 2007), and renal-cell cancer (Dosemeci *et al.* 1999). As was found in the 1999 IARC review, excesses of cancer at specific tissue sites, including the pancreas, lymphohematopoietic system, brain and central nervous system, and breast, were reported in some but not all studies.

Properties

Dichloromethane is a chlorinated hydrocarbon that exists at room temperature as a colorless liquid with a sweet, pleasant odor similar to that of chloroform (NTP 1986). It is miscible with alcohol, ether, dimethyl formamide, and carbon tetrachloride. Dichloromethane is stable at normal temperatures and pressures, but it may form explosive compounds when in a high-oxygen environment (Akron 2009). Physical and chemical properties of dichloromethane are listed in the following table.

Property	Information
Molecular weight	84.9
Specific gravity	1.3255 20°C/4°C
Melting point	-95°C
Boiling point	39.75°C at 760 mm Hg
Log K_{ow}	1.25
Water solubility	13.0 g/L at 25°C
Vapor pressure	435 mm Hg at 25°C
Vapor density relative to air	2.93

Source: HSDB 2009.

Use

Dichloromethane is used as a solvent in paint strippers and removers (30%), in adhesives (20%), as a propellant in aerosols (10%), as a solvent in the manufacture of pharmaceuticals and drugs (10%), in chemical processing (10%), as a metal cleaning and finishing solvent (10%), and in urethane foam blowing (5%) (Holbrook 2003). Other uses make up the remaining 5%. Dichloromethane has also been used as a solvent in the production of triacetate fibers, in film processing, and as an extraction solvent for spice oleoresins, hops, and caffeine in coffee (NTP 1986). However, due to health concerns, dichloromethane's use as an extraction solvent in food products and coffee has declined greatly over the years (ATSDR 2000). It is also used as a low-pressure refrigerant, for air-conditioning installations, and as a low-temperature heat-transfer medium (Holbrook 2003). Current household products that may contain dichloromethane include lubricants, valve cleaners, and degreasers for automobiles, adhesive and varnish removers, paint strippers, and one household herbicide (HPD 2009). Dichloromethane is present in these products at percentages ranging from 1% to 90%. Dichloromethane was once registered for use in the United States as an insecticide for commodity fumigation of strawberries, citrus fruits, and a variety of grains (ATSDR 2000). It is no longer an active ingredient in any registered pesticide product in the United States (HSDB 2009).

Production

In 2009, dichloromethane was produced by 26 manufacturers worldwide, including 4 in the United States (SRI 2009), and was available from 133 suppliers, including 58 U.S. suppliers (ChemSources 2009). Reports filed under the U.S. Environmental Protection Agency's Toxic Substances Control Act Inventory Update Rule indicated that U.S. production plus imports of dichloromethane totaled 500 million to 1 billion pounds in 1986 and 1990 and 100 million to 500 million pounds between 1996 and 2006 (EPA 2004, 2009). From 1989 to 2008, U.S. exports of dichloromethane exceeded imports; in 2008, imports were over 19.8 million pounds, and exports were 136.9 million pounds (USITC 2009).

Exposure

The routes of potential human exposure to dichloromethane are inhalation, ingestion, and dermal contact (NTP 1986). However, absorption is slower after dermal contact than after ingestion or inhalation. The general population is exposed mainly through inhalation of ambient air. Inhalation exposure might also occur through the use of consumer products containing dichloromethane, such as paint removers, which results in relatively high concentrations in indoor air (IPCS 1996, ATSDR 2000). Dichloromethane was found in 43.7% of 1,159 consumer household products tested and in 74.3% of paint-related products, at an average concentration of 33.5% (Sack *et al.* 1992). According to EPA's Toxics Release Inventory, environmental releases of dichloromethane totaled nearly 139 million pounds in 1988. In 2007, over 5.9 million pounds was released by 297 facilities, including over

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5 million pounds to air, for a decrease of over 95% since 1988 (TRI 2009). In rural and remote areas, dichloromethane was measured in ambient air at concentrations of 0.07 to 0.29 $\mu\text{g}/\text{m}^3$; in suburban areas, the average concentration was less than 2 $\mu\text{g}/\text{m}^3$, while in urban areas it was no more than 15 $\mu\text{g}/\text{m}^3$. Near hazardous-waste sites, concentrations of up to 43 $\mu\text{g}/\text{m}^3$ were recorded (IPCS 1996).

Dichloromethane occurs in groundwater, finished drinking water, commercially bottled artesian-well water, and surface water in heavily industrialized river basins. Higher levels of dichloromethane typically are found in groundwater than surface water. Dichloromethane was the sixth most frequently detected organic contaminant in groundwater from hazardous-waste sites in 1987, occurring at 19% of the sites (ATSDR 2000). In a study published in 2007, dichloromethane was detected in 3% of over 5,000 groundwater samples taken in the United States between 1985 and 2002. The concentrations ranged from 0.02 to 100 $\mu\text{g}/\text{L}$, with a median well below the Safe Drinking Water Act maximum contaminant level of 5 $\mu\text{g}/\text{L}$ (Moran *et al.* 2007).

Occupational exposure to dichloromethane occurs during its production and shipping, primarily during filling and packaging. Because of its use in paint strippers, exposure also occurs during formulation of paint removers, original equipment manufacture, and commercial furniture refinishing (IPCS 1996). In the 1980s, dichloromethane was found in the air at an Israeli workplace at a concentration of 5.22 ppm and in urine samples from seven workers at a maximum concentration of 0.06 mg/L (Hoffer *et al.* 2005). In the 1990s, health-hazard investigations by the National Institute for Occupational Safety and Health found workplace air concentrations of 0.17 ppm to 525 ppm, with a median of 5 ppm (Armstrong and Green 2004). In field monitoring of workers in a waste-repackaging facility, dichloromethane was detected in 7 of 16 samples of exhaled breath at concentrations of up to 573 ppm (Thrall *et al.* 2001). In 2003, the American Conference of Governmental Industrial Hygienists recommended that a urinary concentration of 200 $\mu\text{g}/\text{L}$ at the end of a shift be used to monitor the threshold limit value of 50 ppm in workplace air (Imbriani and Ghittori 2005). The National Occupational Exposure Survey (conducted from 1981 to 1983) estimated that 1,438,196 workers, including 352,536 women, potentially were exposed to dichloromethane (NIOSH 1990). No more recent large occupational exposure surveys were identified.

Regulations

Coast Guard, Department of Homeland Security

Minimum requirements have been established for safe transport of dichloromethane on ships and barges.

Consumer Product Safety Commission (CPSC)

Products containing dichloromethane must be labeled to indicate that inhalation of vapor has produced cancer in laboratory animals and must also specify precautions.

Department of Transportation (DOT)

Dichloromethane is considered a hazardous material, and special requirements have been set for marking, labeling, and transporting this material.

Environmental Protection Agency (EPA)

Clean Air Act

National Emissions Standards for Hazardous Air Pollutants: Listed as a hazardous air pollutant.

New Source Performance Standards: Manufacture is subject to certain provisions for the control of volatile organic compound emissions.

Urban Air Toxics Strategy: Identified as one of 33 hazardous air pollutants that present the greatest threat to public health in urban areas.

Clean Water Act

Effluent Guidelines: Listed as a toxic pollutant.

Water Quality Criteria: Based on fish or shellfish and water consumption = 4.6 $\mu\text{g}/\text{L}$; based on fish or shellfish consumption only = 590 $\mu\text{g}/\text{L}$.

Comprehensive Environmental Response, Compensation, and Liability Act

Reportable quantity (RQ) = 1,000 lb.

Emergency Planning and Community Right-To-Know Act

Toxics Release Inventory: Listed substance subject to reporting requirements.

Resource Conservation and Recovery Act

Listed Hazardous Waste: Waste codes for which the listing is based wholly or partly on the presence of dichloromethane = U080, F001, F002, F024, F025, K009, K010, K156, K157, K158.

Listed as a hazardous constituent of waste.

Safe Drinking Water Act

Maximum contaminant level (MCL) = 0.005 mg/L.

Food and Drug Administration (FDA)

Maximum permissible level in bottled water = 0.005 mg/L.

Dichloromethane may be used as an extraction solvent to prepare modified hop extract, spice oleoresins, and coffee, with limitations prescribed in 21 CFR 172 and 173.

Dichloromethane is banned from use in cosmetic products.

Polyester-carbonate resins may be safely used in articles intended for use in producing, packaging, or holding foods with residual methylene chloride levels not to exceed 5 ppm.

Occupational Safety and Health Administration (OSHA)

While this section accurately identifies OSHA's legally enforceable PELs for this substance in 2010, specific PELs may not reflect the more current studies and may not adequately protect workers.

Permissible exposure limit (PEL) = 25 ppm.

Short-term exposure limit (STEL) = 125 ppm.

Comprehensive standards for occupational exposure to this substance have been developed.

Guidelines

American Conference of Governmental Industrial Hygienists (ACGIH)

Threshold limit value – time-weighted average (TLV-TWA) = 50 ppm.

Consumer Products Safety Commission (CPSC)

Requests that manufacturers eliminate the use of hazardous chemicals, including dichloromethane, in children's products.

National Institute for Occupational Safety and Health (NIOSH)

Immediately dangerous to life and health (IDLH) limit = 2,300 ppm.

Listed as a potential occupational carcinogen.

References

- Akron. 2009. *The Chemical Database*. The Department of Chemistry at the University of Akron. <http://ull.chemistry.uakron.edu/erd> and search on CAS number. Last accessed: 12/10/09.
- Armstrong SR, Green LC. 2004. Chlorinated hydrocarbon solvents. *Clin Occup Environ Med* 4(3): 481-496.
- ATSDR. 2000. *Toxicological Profile for Methylene Chloride*. Agency for Toxic Substances and Disease Registry. <http://www.atsdr.cdc.gov/toxprofiles/tp14.pdf>.
- ChemSources. 2009. *Chem Sources - Chemical Search*. Chemical Sources International. <http://www.chemsources.com/chemonline.html> and search on methylene chloride. Last accessed: 11/9/09.
- Cocco P, Heineman EF, Dosemeci M. 1999. Occupational risk factors for cancer of the central nervous system (CNS) among US women. *Am J Ind Med* 36(1): 70-74.
- Dosemeci M, Cocco P, Chow WH. 1999. Gender differences in risk of renal cell carcinoma and occupational exposures to chlorinated aliphatic hydrocarbons. *Am J Ind Med* 36(1): 54-59.
- Dumas S, Parent ME, Siemiatycki J, Brisson J. 2000. Rectal cancer and occupational risk factors: a hypothesis-generating, exposure-based case-control study. *Int J Cancer* 87(6): 874-879.
- EPA. 2004. *Non-confidential IUR Production Volume Information*. U.S. Environmental Protection Agency. <http://www.epa.gov/oppt/iur/tools/data/2002-vol.html> and search on CAS number.
- EPA. 2009. *Non-confidential 2006 IUR Records by Chemical, Including Manufacturing, Processing and Use Information*. U.S. Environmental Protection Agency. http://cfpub.epa.gov/iursearch/2006_iur_natlcheminfo.cfm?id=4942.
- Hearne FT, Pifer JW. 1999. Mortality study of two overlapping cohorts of photographic film base manufacturing employees exposed to methylene chloride. *J Occup Environ Med* 41(12): 1154-1169.
- Hoffer E, Tabak A, Shcherb I, Wiener A, Bentur Y. 2005. Monitoring of occupational exposure to methylene chloride: sampling protocol and stability of urine samples. *J Anal Toxicol* 29(8): 794-798.
- Holbrook MT. 2003. Methylene chloride. In *Kirk-Othmer Encyclopedia of Chemical Technology*, vol. 16. Online edition. New York: John Wiley & Sons. pp. 371-380.
- HPD. 2009. *Household Products Database*. National Library of Medicine. <http://hpd.nlm.nih.gov/ingredients.htm> and search on CAS number. Last accessed: 11/9/09.
- HSDB. 2009. *Hazardous Substances Data Bank*. National Library of Medicine. <http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB> and search on CAS number. Last accessed: 11/9/09.
- IARC. 1982. Dichloromethane. In *Chemicals, Industrial Processes and Industries Associated with Cancer in Humans*. IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Humans, suppl. 4. Lyon, France: International Agency for Research on Cancer. pp. 111-112.
- IARC. 1987. Dichloromethane. In *Overall Evaluations of Carcinogenicity*. IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Humans, suppl. 7. Lyon, France: International Agency for Research on Cancer. pp. 194-195.

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- IARC. 1999. Dichloromethane. In *Re-evaluation of Some Organic Chemicals, Hydrazine, and Hydrogen Peroxide*. IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Humans, vol. 71. Lyon, France: International Agency for Research on Cancer. pp. 251-315.
- Imbriani M, Ghittori S. 2005. Gases and organic solvents in urine as biomarkers of occupational exposure: a review. *Int Arch Occup Environ Health* 78(1): 1-19.
- IPCS. 1996. *Environmental Health Criteria No. 164. Methylene Chloride*. International Programme on Chemical Safety. <http://www.inchem.org/documents/ehc/ehc/ehc164.htm>.
- Moran MJ, Zogorski JS, Squillace PJ. 2007. Chlorinated solvents in groundwater of the United States. *Environ Sci Technol* 41(1): 74-81.
- NIOSH. 1990. *National Occupational Exposure Survey (1981-83)*. National Institute for Occupational Safety and Health. Last updated: 7/1/90. <http://www.cdc.gov/noes/noes1/47270sic.html>.
- NTP. 1986. *Toxicology and Carcinogenesis Studies of Dichloromethane (Methylene Chloride) (CAS No. 75-09-2) in F344/N Rats and B6C3F₁ Mice (Inhalation Studies)*. Technical Report Series no. 306. Research Triangle Park, NC: National Toxicology Program. 208 pp.
- Radican L, Blair A, Stewart P, Wartenberg D. 2008. Mortality of aircraft maintenance workers exposed to trichloroethylene and other hydrocarbons and chemicals: extended follow-up. *J Occup Environ Med* 50(11): 1306-1319.
- Sack TM, Steele DH, Hammerstrom K, Remmers J. 1992. A survey of household products for volatile organic compounds. *Atmos Environ Part A — General Topics* 26(6): 1063-1070.
- Seidler A, Mohner M, Berger J, Mester B, Deeg E, Elsner G, Nieters A, Becker N. 2007. Solvent exposure and malignant lymphoma: a population-based case-control study in Germany. *J Occup Med Toxicol* 2: 2-12.
- SRI. 2009. *Directory of Chemical Producers*. Menlo Park, CA: SRI Consulting. Database edition. Last accessed: 11/9/09.
- Thrall KD, Callahan PJ, Weitz KK, Edwards JA, Brinkman MC, Kenny DV. 2001. Design and evaluation of a breath-analysis system for biological monitoring of volatile compounds. *Am Indust Hyg Assoc J* 62(1): 28-35.
- TRI. 2009. *TRI Explorer Chemical Report*. U.S. Environmental Protection Agency. <http://www.epa.gov/triexplorer> and select Dichloromethane. Last accessed: 11/9/09.
- USITC. 2009. *USITC Interactive Tariff and Trade DataWeb*. United States International Trade Commission. http://dataweb.usitc.gov/scripts/user_set.asp and search on HTS no. 290312. Last accessed: 11/9/09.