

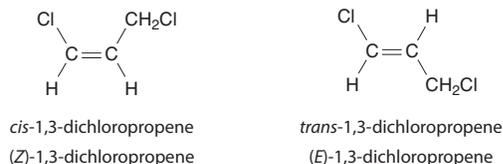
## 1,3-Dichloropropene (Technical Grade)

### CAS No. 542-75-6

Reasonably anticipated to be a human carcinogen

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

Also known as Telone II soil fumigant, a registered trademark of Dow Agrosciences



### Carcinogenicity

Technical-grade 1,3-dichloropropene (containing 1.0% epichlorohydrin as a stabilizer) is *reasonably anticipated to be a human carcinogen* based on sufficient evidence of carcinogenicity from studies in experimental animals. The technical-grade 1,3-dichloropropene used in the cancer studies in experimental animals was a mixture of *cis*- and *trans*-isomers and varied in purity and the stabilizer used (see Properties).

#### Cancer Studies in Experimental Animals

Oral exposure to technical-grade 1,3-dichloropropene (Telone II, approximately 89% pure, containing 1.0% epichlorohydrin as a stabilizer) caused tumors at several different tissue sites in rats and mice. Administered by stomach tube, technical-grade 1,3-dichloropropene caused benign and/or malignant tumors of the forestomach (squamous-cell papilloma or carcinoma) in rats of both sexes and in female mice. It also caused urinary-bladder cancer (transitional-cell carcinoma) and benign lung tumors (alveolar/bronchiolar adenoma) in female mice and benign liver tumors (adenoma) in male mice. The same types of tumors observed in female mice (forestomach, urinary-bladder, and lung tumors) also were observed in male mice; however, the evidence for carcinogenicity in males was considered to be inadequate because of low survival in the vehicle-control group (NTP 1985). *cis*-1,3-Dichloropropene administered by subcutaneous injection caused tumors at the injection-site (fibrosarcoma) in female mice (Van Duuren *et al.* 1979).

Since technical-grade 1,3-dichloropropene was listed in the *Fifth Annual Report on Carcinogens*, studies in rodents have been identified that evaluated the carcinogenicity of technical-grade 1,3-dichloropropene without the stabilizer epichlorohydrin. Inhalation exposure to technical-grade 1,3-dichloropropene (92.1% pure, stabilized with 2% epoxidized soybean oil) caused benign lung tumors (alveolar/bronchiolar adenoma) in male mice (Lomax *et al.* 1989, IARC 1999). Dietary exposure to 1,3-dichloropropene (Telone II, 96% pure, stabilized with 2% epoxidized soybean oil) microencapsulated in a starch-sucrose matrix caused benign liver tumors (hepatocellular adenoma) in rats of both sexes (Stebbins *et al.* 2000).

#### Cancer Studies in Humans

The data available from epidemiological studies are inadequate to evaluate the relationship between human cancer and exposure specifically to 1,3-dichloropropene. Two cases of malignant histiocytic lymphoma were reported among nine firemen accidentally exposed to 1,3-dichloropropene six years before diagnosis, and one case of leukemia was reported in a farmer exposed to 1,3-dichloropropene (IARC 1986, 1987). Since technical grade 1,3-dichloropropene was listed in the *Fifth Annual Report on Carcinogens*, an ecological case-

control study of pancreatic cancer mortality (from 1989 to 1996) and exposure to organochlorine pesticides was reported. The authors reported an increase in pancreatic cancer mortality among long-term residents in areas with high application rates of 1,3-dichloropropene after adjustment for the use of other pesticides (Clary and Ritz 2003).

### Properties

1,3-Dichloropropene, a chlorinated alkene, exists at room temperature as a clear colorless to straw-colored liquid with a chloroform-like odor (NTP 1985, IARC 1986). It is slightly soluble in water and soluble in methanol, chloroform, acetone, diethyl ether, toluene, benzene, *n*-heptane, and octane. It is stable at normal temperatures in closed containers, but is considered highly flammable (Akron 2009). Technical-grade formulations of 1,3-dichloropropene contain mixtures of *cis* (Z) and *trans* (E) isomers (EPA 2000). Physical and chemical properties of 1,3-dichloropropene are listed in the following table.

Property	Technical	Cis	Trans
Molecular weight	111.0	111.0	111.0
Specific gravity	1.220 at 25°C	1.224 at 20°C	1.224 at 20°C
Melting point	< -50°C	NR	NR
Boiling point	108°C	104°C	112°C
Log $K_{ow}$	1.82	2.06	2.03
Water solubility	2.8 g/L at 20°C	2.7 g/L at 25°C	2.8 g/L at 25°C
Vapor pressure	34 mmHg at 25°C	26 mmHg at 20°C	34 mmHg at 25°C
Vapor density relative to air	3.8	1.4	1.4

Source: HSDB 2009. NR = not reported.

The technical-grade formulation of 1,3-dichloropropene (Telone II) used in the National Toxicology Program cancer studies in rodents contained 88% to 90% 1,3-dichloropropene (41.6% *cis*, 45.9% *trans*), 2.5% 1,2-dichloropropene, 1.5% of a trichloropropene isomer, other impurities, and 1% epichlorohydrin as stabilizer (NTP 1985). The inhalation-exposure study (Lomax *et al.* 1989) used a formulation containing 92.1% 1,3-dichloropropene (49.5% *cis*, 42.6% *trans*), 0.7% 1,2-dichloropropane, and mixtures of hexanes and hexadienes, stabilized with 2% epoxidized soybean oil. The formulation used in the dietary-exposure study (Stebbins *et al.* 2000) contained 96% 1,3-dichloropropene (50.7% *cis*, 45.1% *trans*), stabilized with 2% epoxidized soybean oil; no information on impurities was reported. Other formulations of pesticides based on 1,3-dichloropropene may also contain 1,2-dichloropropane, trichloronitromethane, 1,2-dibromoethane, or methyl isothiocyanate (IARC 1986, HSDB 2009).

### Use

1,3-Dichloropropene (a technical-grade mixture of the *cis*- and *trans*-isomers) is used as a preplanting fumigant, mainly for the control of nematodes affecting the roots of plants, selected plant diseases, garden centipedes, wireworms, and weeds; as a solvent; and as an intermediate in the manufacture of 3,3-dichloro-1-propene and other pesticides. It is registered for use on all vegetable, fruit, and nut crops, all forage crops, tobacco, all fiber crops, and all nursery crops (EPA 1998). In Hawaii, 1,3-dichloropropene is used to control nematodes on pineapples at planting (Albrecht 1987). In 2009, three products containing 1,3-dichloropropene as an active ingredient were registered for restricted, non-residential use in the United States (EPA 2009). No products containing 1,3-dichloropropene are registered for use by homeowners (EPA 1998).

### Production

1,3-Dichloropropene was first synthesized in 1872, and commercial production in the United States started in 1955 (NTP 1985, IARC 1986). Before 1978, annual U.S. production was 25 million kilograms

(55 million pounds) (NTP 1985). In 2009, 1,3-dichloropropene was produced by one manufacturer each in the United States and East Asia and two manufacturers in Europe (SRI 2009) and was available from 21 suppliers, including 14 U.S. suppliers (ChemSources 2009). No data on U.S. imports or exports of 1,3-dichloropropene or Telone II were found. Reports filed from 1986 to 2002 under the U.S. Environmental Protection Agency's Toxic Substances Control Act Inventory Update Rule indicated that U.S. production plus imports of 1,3-dichloropropene totaled 1 million to 10 million pounds (EPA 2004).

## Exposure

The primary routes of potential human exposure to 1,3-dichloropropene are inhalation, dermal contact, and ingestion (NTP 1985, ATSDR 1992, EPA 1998). In 1978, 1 million kilograms (2.2 million pounds) of pesticide containing 1,3-dichloropropene was reportedly used in California (ATSDR 1992). In Hawaii, estimated usage on pineapple fields based on the usual application rate for Telone II was nearly 0.9 million kilograms (2 million pounds) in 1985 (Albrecht 1987). Although the data are incomplete, it has been estimated that from 1987 to 1995, over 23 million pounds of 1,3-dichloropropene was applied as a soil fumigant nationwide (EPA 1998). 1,3-Dichloropropene has not been detected in food crops grown in treated soils.

EPA's Toxics Release Inventory reported environmental releases of almost 55,000 lb of 1,3-dichloropropene in 1988. Releases have steadily declined since then; in 2009, 16 industrial facilities released 5,695 lb. Most releases have been to air (TRI 2009). 1,3-Dichloropropene can also be formed from chlorination of organic material during water treatment. In air, 1,3-dichloropropene is degraded by photochemically produced hydroxyl radicals, with a half-life of 7 hours for the *trans*-isomer and 12 hours for the *cis*-isomer. It is also degraded by reaction with ozone, with a half-life of 12 to 52 days. Volatilization of 1,3-dichloropropene from a model river was estimated to occur with a half-life of 4 hours (HSDB 2009). In field studies, 25% of 1,3-dichloropropene volatilized within two weeks after soil injection (EPA 1998). The 1,3-dichloropropene remaining in moist soils may hydrolyze at rates depending on temperature; the reported half-life was 13.5 days at 20°C, 2 days at 29°C, and 100 days at 2°C. Absorption by soil and sediment is expected to be low, based on physical and chemical properties and laboratory data. Monitoring data show that 1,3-dichloropropene is highly mobile in soils (ATSDR 1992, EPA 1998, HSDB 2009). Biodegradation by *Pseudomonas* spp. is expected to occur in soil, with a half-life of 1 to 3 days (NTP 1985). Hydrolysis and biodegradation products are mostly 3-chloroallyl alcohol and, to a lesser extent, 3-chloroacrylic acid (NTP 1985, ATSDR 1992, EPA 1998). The potential for 1,3-dichloropropene or its degradation products to bioaccumulate in terrestrial or aquatic organisms is low, based on physical and chemical properties. This is consistent with the finding that only 1% of radiolabeled 1,3-dichloropropene administered orally remained in rats after 4 days (NTP 1985, HSDB 2009).

1,3-Dichloropropene was measured in ambient air at distances of 0 to 800 m from treated fields at mean seven-day air concentrations ranging from 11 to 181 µg/m<sup>3</sup> (EPA 1998). In another study, the median air concentration of *cis*-1,3-dichloropropene was 23.9 ppb by volume in 148 urban air samples collected from representative locations (ATSDR 1992). During field application of the nematocide in the Netherlands, 8-hour time-weighted-average concentrations were up to 1,120 µg/m<sup>3</sup> for the *cis*-isomer and 910 µg/m<sup>3</sup> for the *trans*-isomer (van Welie *et al.* 1991). 1,3-Dichloropropene was measured in a drinking-water aquifer at average concentrations of up to 357 ppb (micrograms per liter) and in surface water at up to 1.8 ppb (EPA 1998). It was detected at very low levels (up to 18 µg/L) in groundwater contaminated by leachates from municipal landfills and was identified at

107 hazardous-waste sites on EPA's National Priorities List (ATSDR 1992). Samples of rainwater were reported to contain up to 12 ng/L of 1,3-dichloropropene (10 ng/L of the *cis*-isomer and 2 ng/L of the *trans*-isomer). In one study, water entering a treatment facility did not contain detectable levels of 1,3-dichloropropene, but after chlorination, 1,3-dichloropropene was found in the resulting liquid sludge at a concentration of 10 ppb (HSDB 2009).

Workers may be exposed to 1,3-dichloropropene during its manufacture or during formulation or application of the pesticide products. Measured exposure of agricultural workers was highest during loading (mean concentration = 10,833 µg/m<sup>3</sup>) and lower during application (mean concentration = 1,359 µg/m<sup>3</sup>) (EPA 1998). Dermal exposure has been shown to occur even with the use of most types of protective gloves (Zainal and Que Hee 2005). The National Occupational Exposure Survey (conducted from 1981 to 1983) estimated that 2,162 workers, including 33 women, potentially were exposed to 1,3-dichloropropene in the Chemical, Petroleum, and Coal Products industries (NIOSH 1990).

## Regulations

### Coast Guard (Dept. of Homeland Security)

Minimum requirements have been established for the safe transport of 1,3-dichloropropene on ships and barges.

### Department of Transportation (DOT)

Dichloropropenes are considered hazardous materials, and special requirements have been set for marking, labeling, and transporting these materials.

### Environmental Protection Agency (EPA)

#### Clean Air Act

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

*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

Designated a hazardous substance.

*Effluent Guidelines:* Listed as a toxic pollutant.

*Water Quality Criteria:* Based on fish or shellfish and water consumption = 0.27 µg/L; based on fish or shellfish consumption only = 12 µg/L.

#### Comprehensive Environmental Response, Compensation, and Liability Act

Reportable quantity (RQ) = 100 lb.

#### Emergency Planning and Community Right-To-Know Act

*Toxics Release Inventory:* Listed substance subject to reporting requirements.

#### Federal Insecticide, Fungicide, and Rodenticide Act

Tolerance for the combined residues of the fungicide *cis*- and *trans*-1,3-dichloropropene on grapes = 0.018 ppm.

#### Resource Conservation and Recovery Act

*Listed Hazardous Waste:* Waste code for which the listing is based wholly or partly on the presence of 1,3-dichloropropene = U084.

Listed as a hazardous constituent of waste.

## Guidelines

### American Conference of Governmental Industrial Hygienists (ACGIH)

Threshold limit value – time-weighted average (TLV-TWA) = 1 ppm.

Potential for dermal absorption.

### National Institute for Occupational Safety and Health (NIOSH, CDC, HHS)

Recommended exposure limit (time-weighted-average workday) = 1 ppm (5 mg/m<sup>3</sup>).

Potential for dermal absorption.

Listed as a potential occupational carcinogen.

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