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Gesellschaft Deutscher Chemiker

GDCh-Advisory Committee
on Existing Chemicals of
Environmental Relevance (BUA)

1,2-Dichloropropane

BUA Report 155

(October 1994)



S. Hirzel

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Committee on Existing Chemicals
of Environmental Relevance

Beratergremium für
Umweltrelevante Altstoffe (BUA)



S. Hirzel

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Foreword

The German Chemicals Act (Chemikaliengesetz - ChemG) of 1980 stipulates that certain existing chemicals must be reported to the competent authority, if they exhibit properties which indicate that they may be hazardous, either alone or in combination with other substances.

In the summer of 1982, an Advisory Committee on Existing Chemicals of Environmental Relevance (BUA) was set up by the German Chemical Society (Gesellschaft Deutscher Chemiker - GDCh). It brings together representatives from the scientific community, the chemical industry and the governmental authorities. This Advisory Committee is responsible for elaborating appropriate solutions for substances of relevance for health and the environment on the basis of voluntary measures. It selects and examines existing chemicals from the aforementioned angles. The testing and evaluation are based on scientific criteria alone.

It was, therefore, necessary to develop priority setting procedures. In a first phase reports were only prepared for priority chemicals. Within the framework of a first priority setting procedure, chemicals were compiled from several priority lists and 135 chemicals were selected for detailed substance reports.

In a second priority setting procedure the survey of the German Chemical Industry Association (VCI) on all substances with a production volume of more than 10 tons per year was used as a starting list. Since this survey covered 4,600 chemicals, BUA decided to process the corresponding list in several stages. The first stage included approx. 1,050 substances with a production volume of more than 1,000 tons per year.

Detailed reports are drawn up on chemicals suspected of having a hazard potential and abridged reports on those presenting only a minor hazard potential, according to the current state of knowledge.

The detailed BUA reports take in both the published literature and data from industry. If data for the evaluation of the chemicals are not available, additional studies are recommended and the results are published as updates to the reports. The reports serve as a basis for the instigation of administrative measures, when there are indications of risks to health or the environment.

Tübingen, May 1993

Ernst Bayer
Chairman of the Advisory Committee
on Existing Chemicals
of Environmental Relevance

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BUA Report on 1,2-Dichloropropane

Summary and conclusions

Ecological aspects

Occurrence and distribution in the compartments

1,2-Dichloropropane (1,2-DCP) is formed in the Federal Republic of Germany as a by-product (about 4 - 8 %) in the 1,2-propylene oxide production (propylene chlorohydrin procedure). Furthermore, 1,2-DCP occurs as a by-product (9 %) during the high-temperature chlorination of propene to allyl chloride. 1,2-DCP is not directly manufactured as such in the Federal Republic of Germany.

Approximately 77,662 t 1,2-DCP were yielded in 1992 as a by-product in the Federal Republic of Germany. Of this amount, about 7,000 t 1,2-DCP were incinerated and approx. 7,868 t were recycled for thermal and material use. Approximately 7,500 t were temporarily stored at a waste landfill. About 10,000 t 1,2-DCP were exported annually. Approximately 45,694 t were further processed (mostly to tetrachloroethene/tetrachloromethane) as well as 8,500 t which were used for perchlorination within the EU. Less than 100 t were marketed (no data about their further use). The sale of < 100 t within the Federal Republic of Germany was terminated in 1992.

1,2-DCP is used as a solvent for oil, fats, rubber, gum, wax and resin as well as a spot remover for textiles, paraffin remover, component of abrasive agents, metal cleaner and galvanization agent. Earlier 1,2-DCP was found as a production-related contaminant in nematicides. Other application possibilities for 1,2-DCP cited in the literature are the use as a scavenger, as a flame retardant in the production of flame-retardant rubber mixtures as well as an impregnating agent.

In 1992, about 285 t 1,2-DCP/a were emitted into the atmosphere. The emission into the hydrosphere ranged from about 3 t/a to a maximum of 8 t/a. 1,2-DCP-containing wastes do not occur.

An average of 0.85 - 3.10 µg 1,2-DCP/m³ ambient air was detected in 1981/82 and 1986/87 in cities of the Federal Republic of Germany. Annual mean values of 0.9 - 2.0 µg 1,2-DCP/m³ are available from April 1986 to 1987 from Hamburg city areas with heavy traffic (19,000 - 72,000 cars/day). Annual mean 1,2-DCP concentrations

between $0.9 \mu\text{g}/\text{m}^3$ (nearby one gum factory) and $1.6 \mu\text{g}/\text{m}^3$ (nearby one dry cleaner) were measured in the vicinity of industrial firms.

1,2-DCP in a concentration of 1 - $198 \mu\text{g}/\text{m}^3$ was found in the soil spacial air above one approx. 12-year old random landfill (no further data).

An average of $2.00 \mu\text{g}$ 1,2-DCP/ m^3 was measured in 1982 in the ambient air of clean-air areas (unpolluted continental troposphere: Allgäu as well as Swiss Alps).

A maximum 1,2-DCP concentration of 7.1 - $14.1 \mu\text{g}/\text{m}^3$ (mean: 0.28 - $0.65 \mu\text{g}/\text{m}^3$ was specified for the ambient air of industrially polluted cities in the Netherlands.

An average daily 1,2-DCP concentration of $0.752 \mu\text{g}/\text{m}^3$ (median: $0.1 \mu\text{g}/\text{m}^3$ was cited for residential and industrial areas in the U.S.A.

1,2-DCP in a concentration of $1.4 \mu\text{g}/\text{m}^3$ was determined in 1978 in the room air of cellars in apartment houses nearby one waste landfill in Niagara Falls, New York (U.S.A.).

In 1983 - 1988, 1,2-DCP in concentrations of 2 - $198 \mu\text{g}/\text{m}^3$ were measured in over 200 samples of soil spacial air in landfill gas of a former industrial sludge landfill near Bielefeld.

1,2-DCP was measured in October 1978 in the Rhine near Lobith in concentrations ranging from undetectable to $3 \mu\text{g}/\text{l}$ and in 1986 - 1989 in concentrations of up to $\leq 1 \mu\text{g}/\text{l}$ in the upper, lower and middle course of the Rhine (FRG). It was also found in 1988 and 1989 in concentrations of up to $< 0.1 \mu\text{g}/\text{l}$ in the section near Hagestein.

Between 1986 and 1989, 1,2-DCP concentrations of up to $\leq 1 \mu\text{g}/\text{l}$ were measured in the Rhine tributaries Sieg, Erft, Ruhr, Emscher and Lippe.

During 1980 - 1982, $< 7 - 87 \mu\text{g}$ 1,2-DCP/l were measured in the Elbe, near Schnackenburg up to $< 0.15 \mu\text{g}/\text{l}$ in 1981 and 1982.

The 1,2-DCP concentrations for the Ems, Leine and Weser were below $7 \mu\text{g}/\text{l}$ for 1980, 1981 and 1982.

Monthly mean values of 200, 300 and $< 100 \mu\text{g}$ 1,2-DCP/l were determined in 1991 in Haringvliet water near Stellendam (Netherlands) during January - March, April and May as well as June and July, respectively.

1,2-DCP in concentrations of 0.2 - $0.4 \mu\text{g}/\text{kg}$ sediment (wet weight) was determined in sediment samples of Pontchartrain Lake (Mississippi

Delta, U.S.A.).

Between October 1988 and May 1990, 0.02 - 0.43 mg 1,2-DCP/kg dry weight were measured in river sediment along the Grand Calumet River (Indiana, U.S.A.) and the Indiana Harbor Ship Canal.

From July 1985 to December 1986, 1,2-DCP in concentrations of 0.05 - 5.1 µg/l was detected in groundwater of mostly shallow wells in 206 agricultural areas of the Federal Republic of Germany.

In Schleswig-Holstein, 1,2-DCP in concentrations ranging from < 0.05 to 5.1 µg/l were measured between October 1985 and November 1986 in 40 samples from 5 wells (various depths). In the period from September 1992 to June 1993, 91 individual wells were examined of which one showed a maximum concentration of 94.3 µg 1,2-DCP/l.

1,2-DCP was found in concentrations of up to 9.3 µg/l in mainly deeper groundwater in the Netherlands (1987).

Studies of the Lower Rhine from November 1975 to January 1976 resulted in 1,2-DCP concentrations of 0.40 µg/l in shore filtrate and 0.09 µg/l in pure filtrate.

In 1979 - 1986, < 0.1 µg 1,2-DCP/l was detected in drinking water prepared from Rhine water of the Netherlands.

Data are available from waterworks surveys (Schleswig-Holstein, 1990) which show 0.3 µg 1,2-DCP/l drinking water.

In 1988, 1,2-DCP in concentrations of 1.1 µg/l and 650 µg/l were found in leachate water from German hazardous waste landfills and in another hazardous waste landfill, respectively.

A daily uptake of 18.5 µg 1,2-DCP (Δ 0.13 µg/kg body weight with 50 % absorption) was estimated for a person weighing 70 kg with an average respiratory volume of 20 m³/day and at an average 1,2-DCP concentration in the ambient air (Netherlands: 1980) of 0.3 - 0.7 µg/m³.

1,2-DCP was detectable in various foodstuff samples in the following concentrations: apple Juice: 103 µg/kg; ginger ale: 94 µg/kg, limonade: 91.3 µg/kg; milk with 0.1 % butter fat: 67.6 µg/kg; flour containing foodstuffs: 66.9 µg/kg; decaffeinated tea: 27.3 µg/kg; decaffeinated coffee: 60.0 µg/kg; onion flakes: 80.5 µg/kg.

Natural sources of 1,2-DCP are unknown.

Because of its physicochemical properties, 1,2-DCP is considered to be a substance which is volatile from water. A high mobility of 1,2-DCP in soil is expected.

Degradability

1,2-DCP is not readily biodegradable in the closed bottle test. A significant hydrolytic degradation for 1,2-DCP could not be determined. The half-lifetime in demineralized water (pH-value: 6.9) was approx. 24 years and in seawater (pH value: 8.3), approx. 5 years. Half-lifetimes of 16.6 hours and 50.9 hours can be estimated for the photochemical degradation of 1,2-DCP in demineralized water under the existing test conditions. An extrapolation to environmental conditions is impossible.

A degradation of 1,2-DCP emitted into the air is feasible by reaction with photochemically formed OH-radicals, for which a half-lifetime of 24.3 days was calculated.

Accumulation

The calculated n-octanol/water partition coefficients ($\log P_{OW}$) of 1.99 to 2.16 infer moderate bioaccumulation. The experimentally determined bioconcentration factor (BCF) of 0.5 - 6.9 suggests no or only a slight bioaccumulation.

Calculated on the basis of the n-octanol/water partition coefficients, the soil sorption coefficients K_{OC} ranging from 288 to 414 indicate a very low or moderate soil sorption.

No significant geoaccumulation is expected on the basis of the measured soil sorption coefficients.

Ecotoxicology

For activated sludge microorganisms, an EC_{50} value of 520 mg 1,2-DCP/l was determined after 30 minutes of contact.

EC_{50} values of 83, 62 and 50 mg 1,2-DCP/l are available for the acute toxicity of 1,2-DCP in the unicellular freshwater green algae *Chlamydomonas reinhardi* after 4, 7 and 10 days, respectively.

In the halophilic silica algae *Skeletonema costatum*, a NOEC (no-observed-effect concentration) of 18 mg 1,2-DCP/l was estimated, based on the nominal concentration (parameter: cell count).

An EC_{50} value of 50 mg 1,2-DCP/l seawater is available for the unicellular silica algae *Phaeodactylum tricornutum* for inhibition of ^{14}C -assimilation.

A 48 h- LC_{50} value of > 100 mg 1,2-DCP/l exists for the adult brown

shrimp (*Crangon crangon*).

Based on the effective concentration, a 96 h-LC₅₀ value of 24.79 mg/l as well as a 24 h-LC₅₀ value of > 26.65 mg/l were calculated for the acute toxicity of 1,2-DCP in a few hours-old (< 24 hours) marine shrimp (*Mysidopsis bahia*). A 96 h-LC₅₀ value of > 26.65 mg/l was estimated for 3 - 4 day-old animals.

A 48 h-LC₅₀ value of 53 mg 1,2-DCP/l seawater is available for the acute toxicity of 1,2-DCP in nauplii of marine crustaceans such as e.g. the barnacle (*Elminius modestus*).

Based on the nominal concentration, the 24 h- and 48 h-LC₅₀ values for the water flea (*Daphnia magna*) were 99 and 52 mg 1,2-DCP/l, respectively. The NOEC is < 22 mg 1,2-DCP/l.

A 48 h-IC₅₀ value of 45 mg 1,2-DCP/l, based on the nominal concentration, was ascertained for the water flea (*Daphnia magna*).

In the 28 d life-cycle test with < 24 hour-old marine shrimp (*Mysidopsis bahia*), the NOEC was 4.09 mg 1,2-DCP/l, based on the effective concentration (parameters: parental mortality and F₁-mortality, growth in length of the parents and reproduction).

Based on the effective concentrations, a NOEC of 8.3 mg 1,2-DCP/l, a LOEC (lowest-observed-effect concentration) of 15.8 mg 1,2-DCP/l and a MATC (maximum acceptable toxic concentration) of 11.4 mg 1,2-DCP/l were determined for reproduction of the water flea (*Daphnia magna*). For the bluegill sunfish (*Lepomis macrochirus*), a 24 h-LC₅₀ value of 360 or < 560 mg 1,2-DCP/l was established as well as a 96 h-LC₅₀ value of 280 or 320 mg 1,2-DCP/l.

For the tidewater silverside (*Menidia beryllina*), the 24 h- and 96 h LC₅₀ values were > 240 and 240 mg 1,2-DCP/l, respectively.

The 96 h-LC₅₀ value for the fathead minnow (*Pimephales promelas*) was 127 mg 1,2-DCP/l. Furthermore, 24 h-, 48 h-, 72 h- and 96 h-LC₅₀ values of 194, 154, 141 and 140 mg 1,2-DCP/l are available for this fish species.

A 96 h-LC₅₀ value of 61 mg 1,2-DCP/l seawater exists for the dab (*Limanda limanda*).

During a 28-day early-life-stage test (ELS test) with 2 - 5 hour-old eggs of the fathead minnow (*Pimephales promelas*), a MATC of 6 ± 1 mg 1,2-DCP/l to 11 ± 2 mg 1,2-DCP/l was established (parameter: reduced larva weight).

A LC₅₀ value of 116 mg 1,2-DCP/l was determined in the prolonged fish toxicity test on 2 - 3 month-old guppies (*Poecilia reticulata*).

There are indications that 1,2-DCP is very phytotoxic.

Toxicological aspects *)

1,2-DCP is absorbed well through the respiratory and gastrointestinal tracts. The primary metabolites of 1,2-DCP identified in the urine of F344 rats after oral or inhalative application were mainly glutathione adducts such as N-acetyl-S-(2-hydroxypropyl)-L-cysteine, N-acetyl-S-(2-oxopropyl)-L-cysteine and N-acetyl-S-(1-carboxyethyl)-L-cysteine. 1,2-DCP is exhaled through the lung mainly unchanged or as CO₂. After oral application of radioactively labeled 1,2-DCP, a rapid elimination of the radioactivity was observed, whereby 80 - 90 % were excreted within 24 hours via the urine, feces and respiratory tract.

1,2-DCP possesses a low acute toxicity with oral, intraperitoneal and dermal LD₅₀ values of 860 - 10,115 mg/kg b.w. and LC₅₀ values of 2,250 - 14,000 mg/m³ air for a 10 and 8 hour period, respectively. The symptoms of intoxication are characterized by sialorrhoea, lacrimation, lethargy, hemolytic anemia as well as by liver and kidney damage.

1,2-DCP does not cause any skin irritation in rabbits, but does slightly irritate the mucosa.

Animal studies on the sensitizing effect of 1,2-DCP are unavailable. 1,2-DCP can act sensitizing in humans (see below).

Liver and kidney changes primarily occurred after repeated application of 1,2-DCP. Pathological liver alterations reported were in particular a centrilobular necrosis, inflammatory cell infiltration, fibroblast proliferation as well as fatty degeneration. Kidney damage was manifested primarily in a necrosis of the brush border, glomerular nephritis as well as fatty degeneration. A toxic effect on the hematopoietic system was likewise observed. The NOEL for the rat after oral application by gavage (13 weeks) was 20 mg/kg b.w./day and was below 71 mg/m³ air after inhalative uptake (13 weeks, 5

*) See Annex: "Toxikologisch-arbeitsmedizinische Begründungen von MAK-Werten (1993)"

days/week, 6 hours/day), with very slight local effects on the olfactory epithelium in the lowest tested dosage.

In vitro, 1,2-DCP was proven to be mutagenic in *Salmonella typhimurium* strains TA 100 and TA 1535 (with and without metabolic activation), in *Aspergillus nidulans* (without metabolic activation) and in the thymidine kinase test on mouse lymphoma cells (with S9-mix). In further *in vitro* studies, an increased chromosome aberration rate on ovarian cells of the Chinese hamster (CHO-cells, with S9 mix) and an increased sister chromatid exchange rate in CHO- and V79-cells were described (with and without metabolic activation). A weak DNA-binding in the liver could be detected *in vivo*. 1,2-DCP did not trigger any dominant lethal mutations in rats and no sex-linked recessive lethal mutations in *Drosophila melanogaster*.

With oral application by gavage in a 2-year study, 1,2-DCP caused liver tumors in the male and female mouse in the highest dosage group. A dosage-dependent, insignificantly increased incidence of adenocarcinomas in the mamma occurred in the female rat. Raised mortality and decreased body weight gain were observed in both species depending on the dosage.

In reproductive toxicological studies on rats and rabbits, a fetotoxic effect was exhibited only with simultaneous maternal toxicity, but no increased rate of teratogenicity was noted. In one 2-generation study on rats, fertility and litter parameters were unchanged at high dosages.

After occupational dermal exposure to 1,2-DCP, an allergic contact dermatitis was observed in some individuals.

Absorptive intoxication in humans by 1,2-dichloropropane have become mainly known through accidental oral uptake and in one case through inhalative uptake. The symptoms are marked by functional liver and kidney damage, hemolytic anemia, metabolic acidosis, cardiac muscle weakness as well as shock. The oral uptake of larger amounts of 1,2-DCP (about 50 ml/70 kg b.w.) can be lethal. Postmortally liver necroses have been determined thereby.

Recommendations

Ecology

With respect to the generally low exposure, further studies on ecotoxicology, e.g. on phytotoxicity, are not considered to be a priority. Insofar as currently relevant emissions into the atmosphere still take place, the success of the planned reduction measures should be monitored and documented.

Toxicology

The substance was classified by the MAK (maximum work place concentration)-Commission into Group III B (substance with a founded carcinogenic potential). From observations on humans, there are indications of a sensitizing effect which nonetheless is insufficient for making a final decision about whether the substance has a sensitizing potential. Animal experimental studies on this end point are missing. The performance of corresponding studies is not seen as a priority when this hazard potential is properly indicated on the basis of the findings in humans.