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Gesellschaft Deutscher Chemiker

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

1,4-Dioxane

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(October 1991)

S. Hirzel
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on Existing Chemicals of Environmental Relevance (BUA)

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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 1,4-Dioxane

Summary and conclusions

Ecological aspects

Production and use

Annual production of dioxane in Europe amounts to about 4,000 - 5,000 tonnes in Germany and the Netherlands, each country producing about one half of the estimated total amount.

Most of the 1,4-dioxane produced at BASF AG Ludwigshafen is sold. A small quantity (about 30 tonnes a year) is employed as solvent within BASF.

According to an estimate by BASF AG Ludwigshafen, the annual usage of 1,4 in Germany is below 2,500 tonnes.

1,4-Dioxane was not produced in the former GDR.

The main use of 1,4-dioxane is as a solvent in the pharmaceuticals industry and in the dye, adhesive, textile processing etc. sectors.

1,4-Dioxane is also employed as stabilizer for chlorohydrocarbons, although this application is becoming less significant owing to the reduced use of chlorohydrocarbons. Another area of use is the production of magnetic pigment coatings of magnetic tapes.
While the amounts used are decreasing, there is only an estimate available for the pattern of use. It may be assumed that the amounts used will become smaller because of the decreasing demand as CHC stabilizer and the increasing recovery of dioxane in the pharmaceuticals industry.

There are no published statistics on exports and imports.

Entry into the environment

Entry from industrial production and use takes place mainly into waste water and to only a small extent into waste air. At BASF AG Ludwigshafen about 4 - 5 tonnes of dioxane enter the waste water from the production plant per year. Additional amounts derive from plants where 1,4-dioxane is a possible by-product of reactions involving ethylene oxide and its derivatives, inter alia. The amount entering the BASF treatment plant in 1990 was between 70 and 95 tonnes, and there was between 61 and 62 tonnes present in the effluent from the treatment plant. The elimination of 1,4-dioxane calculated for 227 days for which plausible values were obtained and the concentration entering was above the determination limit of 300 µg/l was above 58 %, which might be due to stripping.

Less than 8.7 tonnes of dioxane enter the Hüls treatment plant each year. There are no data available on other plants where ethoxylation reactions are carried out.

As an impurity in surfactants, 1,4-dioxane may be present in cosmetic products and thus enter the hydrosphere in amounts which cannot be quantified. The great decrease in the dioxane content of cosmetic products since 1986 suggests that less is entering the environment (see section 5.5).

The estimated use of surfactants in detergents and cleaners in Germany in 1989 was about 227,000 tonnes. The amount of 1,4-dioxane estimated to be present as impurity in some groups of surfactants is about 3 tonnes.

At BASF AG about 25 kg is emitted into the atmosphere each year during production (1 kg) and use (24 kg) as solvent.

There are no quantitative data on the amounts entering the hydrosphere or on waste incineration from solvent use.

The entry into the atmosphere on use of 1,4-dioxane as stabilizer for chlorohydrocarbons has been estimated at about 120 - 180 tonnes in 1990. About 60 tonnes of dioxane used for this purpose was incinerated with waste per year. The decline in this use means a simultaneous decrease in the entry into the atmosphere by this route. It is not possible to state the amounts entering the hydrosphere or waste water requiring treatment.

During magnetic tape production by the sole manufacturer, about 10 tonnes of 1,4-dioxane enter the atmosphere each year. None gets into the waste water from the plant.

All the waste resulting from manufacture and use is incinerated so that emissions are expected to be negligible.

Since a considerable amount of the dioxane entering the environment gets into the atmosphere directly, especially from its use as 1,1,1-trichloroethane stabiliser, the principal elimination route is presumably photochemical oxidation. Determined half-lives are 36 h (experimental) and 15 h (Atkinson‘s estimate).

With a Henry constant of 0.29 Pa · m^3/mol there is likely to be transport of any of the substance entering surface water from the water into the air by vaporization.

Sorption of 1,4-dioxane in the soil is low and thus it is mobile in soil.

The available results of studies suggest that there is no biodegradation either in soil or in the hydrosphere.

Occurrence in the environment

The amounts of dioxane in the atmosphere outside Germany have been found to average 0.036 - 0.07 µg/m^3 in city air (New Jersey, 1981, 1984), and 0.2 - 1.8 µg/m^3 for air around people without any information on the pollution level at the sites (California, 1984). Near an industrial zone they averaged 2 (daytime) and 3.3 (nighttime) µg/m^3 (Maryland, 1988), while exhalation studies over 2 days showed 0.3 to 0.4 µg/m^3.

The maximum levels of 1 ,4-dioxane found in various landfills in New Jersey were 0.62 and 0.33 µg/m^3 while the concentrations of trace organic substances, including dioxane, in the undiluted gas from a landfill in Germany (Schwalmtal) were in the ppm range.

Measurement of the dioxane concentration in the air in production plants were far below the MAC of 180 mg/m^3 both in Germany (max. 14 mg/m^3 BASF AG Ludwigshafen, 1986) and abroad (max. 80 mg/m^3 Dow Chemical Co., Texas).

There are few data on dioxane contents in surface water. Concentrations below 1 ng/l (effluent from a treatment plant in Great Britain) to a maximum of 1 µg/l (Chicago ship canal; effluent from two treatment plants near Lake Michigan, USA) have been found. Samples of ground water from the vicinity of various landfills (Canada, 1983 - 1986) contained less than 1 µg of dioxane per liter. The levels in the vicinity of a landfill (USA) were between 0.1 and 2.4 (max.) µg of dioxane per liter, and a maximum of 500 µg/l was found in the ground-water underneath a landfill (Canada). The low log P_{OW} of -0.27 means that there is little sorption of 1,4-dioxane in soil and thus it can be washed out into the groundwater.

Tests on drinking water in the USA showed dioxane contents of 0.01 µg/l (Lawrence) and, in a contaminated drinking water fountain (Massachusetts) in about 1976, 2,100 µg of dioxane per liter.

There are no data on the occurrence in the geosphere and biosphere.

One source for the occurrence in the environment is the presence of dioxane as impurity in ethoxylates. This means that it may be present as by-product in raw materials for cosmetic products (surfactants).

In the USA (1979) the dioxane contents in 47 % of the tested cosmetic products exceeded 10 mg/kg. Colgate-Palmolive products contained up to 0.423 % by weight of dioxane and were thus below the limit of 1 % recommended at this time (1979) for subsidiary components.

Investigations by a chemical testing agency in the Federal Republic of Germany (Hagen, 1987) showed that cosmetics such as shampoos, shower gels, herbal bath oils and hand cleansers had a dioxane content between less than 50 and 300 mg/kg.

Investigations carried out in the same year by the federal state chemical testing agencies showed that the dioxane content in cosmetics was generally below 100 mg/kg and frequently below 10 mg/kg. The cosmetic product committee of the German health authorities therefore specified a residual dioxane content of less than 10 mg/kg, which ought to be achievable for all cosmetic products and was set as the goal to aim at. Until recently these contaminations need not to be predicted as safely avoidable, which occur up to 500 ppm in shower bath, bubble bath, shampoos and similar products containing alkyl ether sulfates as foaming compounds. Meanwhile reduction of the residual Dioxan contents has been reached.

While the levels in anti-dandruff shampoos in 1986 were between 10 and 390 mg/kg, investigations in 1990 showed that dioxane was no longer detectable specifically in such shampoos.

The residual dioxane contents in normal shampoos (1986) ranged from undetectable to 487 mg/kg, while in 1989 dioxane was no longer detectable in 50 % of the samples and the content was much lower in the remaining samples (5 - 101 mg/kg).

There is no information available on natural sources.

Degradability

Dioxane underwent no biodegradation either in standardized tests (OECD) or in non-standardized tests, and the elimination from open systems is partly physical by stripping.

The photochemical oxidation of 1,4-dioxane by OH radicals in the atmosphere has a half-life of 36 hours (determined experimentally) or 15 hours according to Atkinson.

The half-life for a possible degradation reaction in the hydrosphere, reaction with ozone, is 60 hours.

Bioaccumulation

The log P_{OW} values of -0.27 and -0.42 (measured) and -0.492 (calculated) and the information in the 1986 MITI list indicate that 1,4-dioxane is among the substances with little or no accumulation.

Ecotoxicological effects

Investigations of the bacteriostatic and bactericidal effects of 1,4-dioxane on an adapted activated sludge population showed a bacteriostatic effect in the range 20 - 40 g/l dioxane and a bactericidal effect at 160 g/l dioxane.

Tests of the inhibition of respiration by dioxane on various adapted activated sludges and treatment plant effluent showed no inhibition either in the short-term respiration test or in the Sapromat test up to the highest tested concentration of 2,000 mg/l.

Even in longer-term tests with addition to the normal treatment plant effluent (14 days) or in a continuous treatment plant model, a toximeter, no inhibition of respiration was found at a dioxane concentration of 200 mg/l. Elimination takes place by stripping.

Exposure of anaerobic bacteria to 1,4-dioxane for 24 hours revealed an EC_0 (inhibition of gas production) of 10 g/l.

Investigations of the adverse effects of 1,4-dioxane on a number of model organisms of biological self-purification in a standard test of the inhibition of cell growth (closed system) showed the following results:

The limiting toxic concentration (LTC), at which inhibition of cell growth starts, was 2,700 and 575 mg/l respectively for bacteria (*Pseudomonas putida*, 16 h; cyanobacterium *Microcystis aeruginosa* 8 d) and 5,340, 5,620 and over 10,000 mg/l respectively for protozoa (*Entosiphon sulcatum* 72 h; *Uronema parduczi* 20 h; *Chilomonas paramecium* 48 h).

Investigations on the green alga *Scenedesmus quadricauda* showed a limiting toxic concentration of 5,600 mg/l after 8 days.

The EC_{50} values in the acute toxicity test (open system) on waterfleas *Daphnia magna* were 4,700 and 8,450 mg/l in investigations using different methods; investigations on a minute crustacean *Ceriodaphnia dubia* showed EC_{50} values of 163 - 299 mg/l at 48 and 24 h.

In acute toxicity tests on various species of fish (static test method) the 48 h LC_{50} values for golden orfe *Leuciscus idus* were 8,450 and 9,630 mg/l, for fathead minnows *Pimephales promelas* above 100 mg/l

(72 and 96 h), for the tidewater silverside *Menidia beryllina* (96 h) 6,700 mg/l and for the bluegill sunfish *Lepomis macrochirus* above 10,000 mg/l (96 h).

Another acute toxicity test on young fathead minnows *Pimephales promelas* showed a 96 h LC_{50} of 13,000 mg/l. Statistical analysis of the chronic toxicity on fathead minnow embryos (32 d) showed no significant differences in the average daily hatching rate, the number of deformed larvae or of surviving larvae and the larval weight at each concentration tested. The MATC (maximum acceptable toxicant concentration) is above 145 mg/l.

Investigations of the effects of 1,4-dioxane on plants showed complete loss of viability of the pollen of the composite *Gallardia aristata* after storage in dioxane for 3 hours.

With lettuce *Lactuca sativa* in a closed system there was 50 % inhibition of germination compared with the control at a dioxane concentration of 16.5 ± 3 mol/m^3.

Investigations of the effect of dioxane as potential stimulant of the initial development of the blowfly *Sarcophaga crassipalpis* in the pupal dormant stage (diapause) showed that 32 % of the pupae prematurely terminated the diapause on administration of dioxane (5 µl); 56 % of these developed normally into adult flies.

Toxicological aspects

Dioxane is an organic solvent which can be absorbed in toxic amounts by inhalation or through the skin. Death cases have been observed upon excessive occupational exposure. The data from animal experiments indicate that the acute toxicity is low, the LD_{50} being > 2,000 mg/kg, but there is a risk of short-term accumulation on repeated uptake of high doses. The potential for skin irritation is low, while pronounced irritant effects on the eye have been observed.

No investigations have been carried out on sensitization.

Dioxane may cause liver and kidney damage. Chronic exposure in animal experiments caused tumors, probably via chronic organ damage and increased cell turn over. In particular, liver tumors were found on administration in the drinking water to rats and mice and, less clearly, guinea pigs. Tumors also occurred in the nose of rats. They were seen at dioxane-concentrations of 0.5 - 2.0 % in drinking water (about 500 - 2,000 mg/kg body weight and day). Organotoxic effects stilll occurred at 0.1 % (about 100 mg/kg and day), but not at 0.01 % (about 10 mg/kg body weight and day).

The German committee for examining industrial substances which arc a hazard to health placed dioxane in group IIIB of substances with a carcinogenic potential. The IARC has placed dioxane in group IIB of carcinogens.

Dioxane showed positive results in the ed-transformation test and in tumor promotion studies.

Dioxane had no genotoxic effect in most of the test systems. At high doses exerting cytotoxic or organotoxic effects (> 1,000 mg/kg) *in vitro* or *in vivo* there was found to be damage to genetic material, such as DNA strand breaks, sister chromatid exchange (SCE) or micronuclei. A relation to the cytotoxic effects is assumed.

Signs of some retardation, but no teratogenic effects, were found in rats at the dose of 1,000 mg/kg and day which is weakly toxic for the dams. No valid studies of the effect on fertility are available.

Retrospective studies on several cohorts of chemical workers (maximum cohort size 165 employees) who had inhaled dioxane concentrations up to 180 mg/m^3 (50 ppm) for years revealed no evidence of occupational disease or of an increased tumor incidence compared with the general population. The chromosome aberration rate in 6 active dioxane-exposed workers was in the control range.

Assessment of the potential hazard must take account of the saturation kinetics: low doses of dioxane (eg. inhalation of 50 ppm (180 mg/m^3) for 6 hours or oral intake of 10 mg/kg and day) are completely converted via 1st order kinetics into β-hydroxyethoxyacetic acid and excreted in the urine without detectable toxic effects. These kinetics have been found at 50 ppm for humans too. At higher doses (above about 100 mg/kg and day) there is a change to zero order kinetics associated with a disproportionated increase in dioxane levels and temporary accumulation of dioxane in the blood and tissues, and cytotoxic damage to the liver and kidneys.

Recommendations

Further investigations of the ecotoxicology are not regarded as necessary.

On the toxicity in warm-blooded species:

Assessment is possible of all the toxicological endpoints with the exception of the sensitizing properties of dioxane. For this reason it is proposed that further investigations of cutaneous sensitization be carried out.