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Gesellschaft Deutscher Chemiker**

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

**Carbon disulfide**

BUA Report 83  
(August 1991)



S. Hirzel

Wissenschaftliche Verlagsgesellschaft 1993

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# **Carbon disulfide**

BUA Report 83

(August 1991)

edited by the GDCh-Advisory  
Committee on Existing Chemicals  
of Environmental Relevance

Beratergremium für  
Umweltrelevante Altstoffe (BUA)



S. Hirzel

Wissenschaftliche Verlagsgesellschaft 1993

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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 Carbon disulfide**

## **Summary and conclusions**

### **Ecological aspects**

#### **Production, processing and application**

In the Federal Republic of Germany (territory of former West Germany), 52,700 tonnes of CS<sub>2</sub> were produced in 1990; 13,100 tonnes were imported and 22,900 tonnes exported. This amounts to local consumption of 42,900 tonnes. Consumption in Western Europe was 223,500 tonnes in 1986; in 1990, world consumption was about 900,000 tonnes. In the industrialised countries of the West, consumption has been on a falling trend for years.

At present, roughly half of the CS<sub>2</sub> used in the Federal Republic goes to the viscose industry; 25 % is used for the production of agricultural chemicals (thiocyanates excepted), 14 % for the production of thiocyanates, 5 % for rubber chemicals, and the remainder for various other purposes.

#### **Discharge into the environment**

The known discharge of anthropogenic CS<sub>2</sub> into the environment in the old Federal States presently amounts to a maximum of 13,110 tonnes per annum. Over 99 % of this is emitted into the air, with the viscose industry -- with a share of 96.7 % -- by far the largest contributor. The remainder of the CS<sub>2</sub> in the air comes mainly (max. 3 %) from Claus units used in gas desulphurising, from various other uses (32 tonnes per annum), and from CS<sub>2</sub> production (1 tonne per annum).

The emissions in the Unterrhein district were reduced from 1,226 tonnes in 1981 to 569 tonnes in 1990; in Greater Wiesbaden, they dropped from 4,474 tonnes (1977) to 772 tonnes (1988). The high CS<sub>2</sub> emissions in the Merseburg and Bitterfeld districts (former GDR) no longer exist, due to the shutdown of the viscose plants there in 1990.

The discharge figures for treatment plants receiving CS<sub>2</sub> sewage peak at 0.1 mg/l. The max. annual volume released into the hydrosphere is therefore 14 tonnes, coming only from the viscose industry.

Nothing is known about the direct discharge of CS<sub>2</sub> into the soil, apart from local soil gassing for the control of phylloxera (vine pest) in viticulture. Some CS<sub>2</sub> can originate from microbial decomposition of pesticides based on dithiocarbamic acid, but just how much CS<sub>2</sub> is formed by this mechanism it is impossible to say.

The total global emission of CS<sub>2</sub> (stated in terms of the sulphur content\*) in 1984 is estimated at between 0.4 and 7.6 million tonnes. One author puts the anthropogenic share of this emission at 18 % of the total figure, assumed by him to be 2 million tonnes. The biogenic CS<sub>2</sub> share of the global sulphur emission is estimated at about 5 %; the anthropogenic emission makes an additional contribution of about 0.2 to 0.6 %.

### **Occurrence in the environment**

Because it is produced by microbial processes, CS<sub>2</sub> can be viewed as a natural, ubiquitous substance. Due to lack of data, a specific statement about the base pollution in the Federal Republic is not possible.

An extremely volatile substance with low water solubility, CS<sub>2</sub> is mainly found in the atmosphere. The atmospheric base pollution in low-pollution areas (over oceans) lies between 1 and 100 ng/m<sup>3</sup>, elsewhere between 60 and 320 ng/m<sup>3</sup> and in certain industrialised areas it is as high as 1,000 ng/m<sup>3</sup> or over. In the Federal Republic, the short-time immission values officially registered for the Rhine/Main District in 1986/87 varied between limits of < 6,000 and 38,000 ng/m<sup>3</sup>. For this district, a considerable drop in the immission load from 1977 to 1986/87 has been officially recorded. In Austria in 1984, values up to 1,580,000 ng/m<sup>3</sup> were measured near emission sources.

No altitude gradient could be established for the CS<sub>2</sub> concentration. CS<sub>2</sub> is produced under natural conditions in soil, salt marshes and lakes, and is released into the atmosphere. Volcanoes also emit CS<sub>2</sub>. The figures for this natural production vary considerably from one author to the next. For soil, the values lie between 0.04 and 170 mg CS<sub>2</sub>-S/m<sup>2</sup>/a. Old studies (1979—81) state figures which are about one order of magnitude higher than those in more recent studies. Marshlands, in particular salt marshes, have a relatively high CS<sub>2</sub> production capacity, with emission rates up to 1,380 mg CS<sub>2</sub>-S/m<sup>2</sup>/a. For a general estimate including the oceans, an emission rate of 22 mg CS<sub>2</sub>-S/m<sup>2</sup>/a is assumed. The natural CS<sub>2</sub> emissions from the oceans alone are estimated at one order of magnitude lower.

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\* written CS<sub>2</sub>-S throughout this article

In 1987, the workplace concentration of CS<sub>2</sub> in West German viscose spinning plants averaged 12 mg/m<sup>3</sup> for operators changing spinnerettes, and 17 mg/m<sup>3</sup> for operators doffing spools.

No reports were found on CS<sub>2</sub> in German inland surface waters. In sea water, concentrations between 0.09 and 4.6 ng/l were measured, and in mud from the seabed, 29.5 ng/l. In the United States, industrially polluted rivers were tested for CS<sub>2</sub> from 1980 to 1983. At one point of discharge, 25,000 ng/l was measured. In the majority of the samples no CS<sub>2</sub> was detected, however.

Soil does not only emit CS<sub>2</sub> but also absorbs CS<sub>2</sub> and COS from the air. It can therefore serve as a natural sink for atmospheric CS<sub>2</sub> and COS. Apparently no data on the CS<sub>2</sub> content in soil have been published yet.

### **Decomposition in the environment**

CS<sub>2</sub> can, in principle, be eliminated by sulphur and methane bacteria. The ability to degrade the compound seems to be limited to just a few species or phyla of microorganisms, however.

Aerobic degradation of CS<sub>2</sub> in the biological stage of sewage treatment plants is possible, but a considerable portion of the dissolved CS<sub>2</sub> is likely to evaporate into the air during passage through the treatment plant.

In water, there is practically no hydrolysis of CS<sub>2</sub> at pH values between 4 and 10.

In the atmosphere, CS is decomposed photochemically. This process starts with the OH radicals. The estimated half-life of CS<sub>2</sub> in the atmosphere is something in between 2.1 and 15 days. The reaction products are mainly COS and SO<sub>2</sub>. For the reaction of COS with OH radicals, a tropospheric half-life of 22 years can be calculated. The reaction of COS with NO<sub>3</sub> radicals proceeds with an estimated half-life of more than 32 days. The most important sink for COS is probably dry deposition on plants, with stratospheric photolysis coming second. The global half life of COS is reported as 1.5 to 4.4 years. Oxidation of CS<sub>2</sub> contributes an estimated 22 - 38 % to global COS emissions.

## Accumulation

There are no figures on record for bio-accumulation. The value found for  $\log P_{OW}$  is 1.94. Based on this value, only a low bio-accumulation potential can be expected.

Because of the very low sorption tendency of  $CS_2$  in soil, geo-accumulation seems unlikely.

## Ecotoxicology

In water, an incipient effect is observed on microbial respiration at a concentration of 4.6 mg  $CS_2/l$  and on nitrification at 17.8 mg  $CS_2/l$ . The growth of *Chlorella pyrenoidosa* is reduced by 50 % at 21 mg/l. With regard to *Daphnia magna*,  $CS_2$  has an acute 48 h  $EC_{50}$  of 2 mg/l. For fish, acute  $LC_{50}$  values start at 4 mg/l. An Early Life-Stage Test over 7 days on Zebra fish (*Brachydanio rerio*) found an NOEC of 1 mg  $CS/l$ . The embryonic development of frogs was disturbed at a concentration of 126 mg  $CS_2/l$  with no hatching taking place (100 % mortality).

Six-hour exposure to 6.2 mg  $CS_2/m^3$  had no influence on the photosynthesis of dwarf beans and led to neither leaf necrosis nor leaf chlorosis.

Data on the effects on ecological systems, other than those on terrestrial bacteria communities, are not available.

## Toxicology

In all examined exposure routes,  $CS_2$  is easily absorbed and distributed to all organs. Depending on dose or exposure concentration, part of the compound is co-valently bound to amino acids, proteins and other biomolecules ("acid-unstable  $CS_2$ "). The elimination of free  $CS_2$  from the body is quick (half-life is in the order of hours); that of bound  $CS_2$  is slower (half-life is in the order of days).

Besides the oxidation products sulphate and carbon dioxide, thiocarbamates are detected as metabolites resulting from the decomposition of amino acid or protein-bound  $CS_2$ . The toxicological consequences of the accumulation cannot be estimated from the available data.

The causes of the toxic effects of CS<sub>2</sub> are the facility with which it binds to biomolecules, its metabolic activation to reactive sulphur, and the metal-chelating ability of the newly formed thiocarbamates.

In both animal and human tests, CS<sub>2</sub> produces acute toxic effects at relatively high doses or exposure concentrations only. Acute toxicity is mainly confined to neurotoxic effects. However, changes also occur in other organs, for example the inactivation of cytochrome P-450 in the liver.

CS<sub>2</sub> can elicit severe degenerative changes in the skin, however. The sensitising effects of CS<sub>2</sub> have not been studied. In spite of widespread human use, there is no literature on sensitisation, probably because of the high volatility.

The subchronic and chronic toxicity of CS appears in both laboratory animals and humans as morphological, physiological and biochemical changes in many organs. Particularly affected are the central nervous system, the peripheral nervous system, the eye (optic nerve), the cardiovascular system, and, less severely, liver and kidneys.

A NOEL for the most sensitive biological end-points is estimated to be in between 150 and 800 mg/m<sup>3</sup> for laboratory animals, and in between 10 and 60 mg/m<sup>3</sup> for humans. It has been established beyond doubt that the cardiovascular mortality rate of workers exposed to CS<sub>2</sub> is increased only at exposure concentrations of 60 mg/m<sup>3</sup> or more. Some differences between countries appear to exist.

CS<sub>2</sub> can affect male fertility in rats through changes in sperm count and mating behaviour. In humans, changes in Sperm morphology were observed. The NOEL in laboratory animals lies at > 1,000 mg/m<sup>3</sup> and in humans at > 30 mg/m<sup>3</sup>.

In laboratory animals CS<sub>2</sub> is embryotoxic at high doses or concentrations, which, however, are still below the maternal toxicity threshold. Teratogenic effects can be observed only at maternally toxic doses.

The available mutagenicity tests -- which admittedly are far from perfect -- did not reveal any evidence of genotoxic effects.

No proof of any carcinogenic potential of CS<sub>2</sub> was found, either in animal or in epidemiological studies.

## **Recommendations**

Significant gaps exist in our knowledge, suggesting the following recommendations.

1. Measurement values of the CS<sub>2</sub> content in inland surface waters in the Federal Republic are not available. It is therefore not possible to assess the hazard potential by comparing actual water pollution with the known effect levels. Hence it is recommended that representative data be compiled.
2. With respect to biodegradation in an aquatic environment, only information about the degradation of CS<sub>2</sub> as a sole substrate by certain pure bacterial strains is available. It is therefore difficult to draw valid conclusions about the degradation process under natural conditions (as in mixed bacterial population cultures). Hence it is recommended that CS<sub>2</sub> be subjected to the standardised Closed Bottle Biodegradation Test.
3. In view of the substantial CS concentrations near emission sources, it is recommended that standard phytotoxicity tests be conducted, using *Avena sativa* and *Brassica rapa*.
4. The amount of CS released into the environment from viscose industry waste should be determined.
5. Although data on toxicokinetics and metabolism of CS<sub>2</sub> are incomplete, further tests are not deemed necessary, since the risk for man can be sufficiently assessed from experiences at the workplace. The genotoxicity should, however, be tested in the usual standard assays at high dose levels/concentrations, and taking into account the volatility of the substance. It is recommended that an Ames test and a micronucleus test be carried out.