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

Hexachlorobutadiene

BUA Report 62
(August 1991)

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

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Beratergremium für Umweltrelevante Altstoffe (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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Ecological aspects

In the Federal Republic of Germany hexachlorobutadiene (HCBD) is not purposefully produced by the chemical industry. It is obtained as a by-product during low-pressure chlorolysis in the production of tetrachloroethene and tetrachloromethane. HCBD could not be detected in the raw products obtained during high-pressure chlorolysis or chlorination of methane, which are exclusively used for the production of tetrachloromethane.

Based on the German production capacities of tetrachloroethene/tetrachloromethane the maximum amount of HCBD obtained as a by-product is calculated to be 550—1400 tonnes per annum. Import figures on tetrachloroethene are not yet available (BUA-report on tetrachloroethene in preparation). Until 1990 300 tonnes HCBD per annum were highly purified and exported. Beginning 1991 HCBD is no longer exported. The remaining 250 - 1100 tonnes are recycled within the production process.

There are no indications that HCBD is still used within the EEC.

Due to process improvements of the tetrachloroethene/tetrachloromethane production, which resulted in emission reductions, the formation of HCBD was considerably reduced. Previous entries of HCBD into the environment during production of tetrachloroethene/tetrachloromethane and former uses of HCBD cannot be quantified because of lack of data.

Potential HCBD emissions from the production of tetrachloroethene/tetrachloromethane are incinerated (1200 °C) after passing a vent collecting system.*

There are no data on the HCBD emission during the incineration of HCBD-containing waste. The amount of HCB entering the atmosphere during use of terachloroethene is estimated at less than 0.56 kg per annum. Possible tetrachloroethene imports are not taken into account (BUA-report on tetrachloroethene in preparation). The amount of HCBD entering the atmosphere from use of tetrachloromethane in the Federal Republic of Germany is negligible, because 99 of the tetrachloromethane produced is used for the production of fluorochlorocarbons.

The maximum amount of HCBD entering the hydrosphere during production of tetrachloroethene/tetrachloromethane and processing of HCBD-containing chlorinated hydrocarbons (e. g hexachlorocyclopentadiene) in the Federal Republic of Germany is estimated at 620 kg HCBD per annum. Discharge of HCBD into the Rhine River and the Elbe River amount to approximately 70 and 150 kg per annum respectively.

HCBD may enter the geosphere and the hydrosphere by wash out from the atmosphere and through drainage water of waste disposal sites.

* Data on possible HCBD emissions from the terachloroethen/tetrachloromethane production of Wacker Chemie are not yet available.

Systematic investigations of the occurrence of HCBD in the atmosphere of the Federal Republic of Germany have not been performed. Atmospheric HCBD levels over urban sites of the United States amounted to n.d. - 1648 ng/m^3 in 1980. In the northern and southern hemisphere HCBD levels of 0.2 - 3.2 ng/m^3 and 0.8 ng/m^3 respectively, were determined in 1982 - 1985.

In surface waters of the Federal Republic of Germany average HCBD concentrations were found to be < 0.1 - 13.2 µg/l in 1976/77 (maximum 47.1 µg/l). HCBD concentrations measured in recent years were usually below 0.01 µg/l. In some locations, however, considerably higher levels were determined. Bank filtrate and dune filtrate of the Rhine River contained < 0.01 and 0.03 µg HCBD/l respectively. In 1982 - 89 levels of HCBD ranged from < 0.1 - 300 µg/kg dry weight in the sediment and from < 1 - 18 µg/kg dry weight in suspended matter; in sediment and suspended matter of other surface waters in the Federal Republic of Germany HCBD concentrations amounted to 0.1 - 220 µg/kg.

In 1976 - 78 drinking water contained HCBD amounts from 0.01 µg/l up to a maximum of 0.8 µg/l. Recent data are not available. In contaminated ground and well water (Switzerland, USA) average HCBD concentrations ranged from 0.15 to 0.3 µg/l (maximum 2.53 µg/l). Drainage water samples collected from Dutch waste disposal sites in 1973/74 contained HCBD at concentrations from n. d. to 55 µg/l. In soil from the Hamburg area HCBD concentrations were below limit of detection of 0.1 µg/kg in 1984. In the United States maximum soil concentrations of HCBD in the Vicinity of tetrachloroethene and tetrachloromethane producing plants were reported to be 980 mg/kg before 1979.

HCBD was particularly detected in aquatic organisms.

Depending on the contamination of the sampling site marine algae and plankton contained n. d. - 8.9 and n. d. - 0.09 µg HCBD/kg wet weight respectively (limit of detection not indicated). In marine and freshwater evertebrates HCBD concentrations ranged from 0.06 to 2410 µg/kg wet weight. In marine and freshwater fish HCBD was measured at concentrations of n. d. - 16205 µg/kg wet weight (limit of detection not indicated). In 1988 American and Canadian investigations of freshwater organisms report HCBD concentrations of 0.1 µg/kg wet weight in plankton, 0.1 - 60 µg/kg wet weight in evertebrates and n. d. - 3960 fig/kg wet weight in fish (limit of detection not indicated). In human adipose tissue and liver HCBD levels of 0.8 - 13.7 µg/kg wet weight were measured in 1976. In 1975 foodstuff and feeding stuff contained n. d. - 42 µg HCBD/kg wet weight (limit of detection not indicated). Foodstuff samples collected from the vicinity of tetrachlorethene and tetrachloromethane producing plants contained up to 1320 µg HCBD/kg wet weight.

Presumably HCBD is neither aerobically nor anaerobically biodegradable. There are, however, no conclusive results from tests on the potential aerobic biodegradability. Data on the biodegradability in soil have not been published. Hydrolysis or appreciable photochemical degradation under environmental conditions are not to be expected. Assuming a first order kinetic the half-life of HCBD in the hydrosphere is calculated to be 3 - 30 days in rivers and 30 - 300 days in lakes and groundwater (including volatilisation and adsorptive processes). The half-life for degradation in the atmosphere by reaction with photochemically produced OH radicals is calculated according to Atkinson to be 716 days.

According to its physico-chemical properties HCBO has to be regarded as being highly volatile from the hydrosphere. Despite of its high volatility entry into the atmosphere is expected to be insignificant due to sorption of HCBD to suspended matter and to sediments.

In view of the high log P_{OW} of 4.78 and 4.9 (measured) bioaccumulation must be expected. Following 7 days exposure a bioconcentration factor of 160 was determined for green algae. Bioconcentration factors up to 2000 have been measured in evertebrates. Bioconcentration factors in fish reached up to 19000 following a 105-days exposure period. There is no evidence of biomagnification. In the hydrosphere sorption to the sediment must be expected. For sediments of surface waters concentration factors were estimated to be 10 - 10800. In food plants significant accumulation did not occur. As HCBD binds strongly to the organic matter of soils, geoaccumulation must be expected. In soils containing very little organic matter HCBD is considerably more mobile.

The toxicity threshold of HCBD in the cell multiplication inhibition test was 0.017 mg/l for bacteria after 24 hours. The EC_{10} values were found to be > 0.9 and > 100 mg HCBD/l after 30 minutes. Inhibition of an anaerobic culture (municipal primary sludge) following an exposure period of 12 days was measured via the reduction of methane production and was observed at HCBD levels from 50 mg/l. The toxicity threshold for flagellates was found to be > 8 mg HCBD/l (72 h) and > 10 mg HCBD/l (48 h). For algae a toxicity threshold of > 25 mg HCBD/l (8 days) and a 4 h LC_{10} of 2 mg HCBD/l were reported. In outdoor ponds a concentration of 0.7 mg HCBD/l resulted in the disappearance of the test algae after 8 to 12 days. For Daphnia the acute toxicity (24 h EC_{50}) and the 24 h EC_0 were 0.5 and 0.08 mg HCBD/l respectively. For a brackish water and a marine crustacean 96 h LC_{50} values of 1.2 and 0.059 mg HCBD/l, respectively, have been reported. 24 - 96 h LC_{50} values for fish ranged from 0.09 to 4.5 mg HCBD/l for freshwater species and from 0.399 to 3.6 mg HCBD/l for marine species. In the 14-day fish test the threshold concentration for lethal effects was determined to be 0.16 mg HCBD/l. The threshold concentration for non-lethal effects was 0.014 mg HCBD/l and the NOEC was found to be 0.005 mg HCBD/l. In the early life stage toxicity test using 2 - hours old fish embryos the maximum acceptable toxicant concentration lay between 0.0065 and 0.013 mg HCBD/l.

The 48 h LC_{50} for HCBD evaluated in the earthworm contact test was calculated to be 0.01 mg/cm².

Toxicological aspect

Due to its lipophilic properties HCBD is well absorbed through the skin, the gastro-intestinal tract and the lung. HCBD is extremely lipophilic. It is mainly distributed in the liver, the kidneys and the brain. HCBD is biotransformed in these organs and exhaled without being metabolized. The greater part of HCBD is excreted via the feces. The main metabolite in the liver is the HCBD-glutathion-conjugate, which is further metabolised in the rat kidney and cleaved by β-lyase to yield the toxic en-thiol.

Both acute and chronic animal studies revealed the kidney as the target organ of the toxic effects of HCBD. Primarily the renal proximal tubules are damaged dependent on the dose, leading to degeneration/regeneration processes, necrosis and finally the formation of neoplasms. Apart from general clinical changes histologically detectable alterations of the liver tissue, lymphatic tissue, testicular tissue and nerval tissue have been observed in addition at higher dose levels.

HCBD irritates the skin.

Data on possible sensitization effects are not available.

HCBD is non-mutagenic in the Standard Ames test with and without metabolic activation. Only after bioactivation in the presence of glutathion did the resulting HCBD glutathion-conjugate and its metabolites react mutagenic in the presence of different enzymes (glutathion-S-transferase, ß-lyase and γ-glutamyltranspeptidase). HCBD and its oxidation product pentachlorobutenoic acid, which can be produced synthetically, are mutagenic in the DNA repair test. Oral and inhalative HCBD-exposure resulted in an in vivo increase in chromosome aberrations in bone marrow cells in mice and to a lesser extent in rats. In the Drosophila test HCBD did not exhibit any genotoxic effect.

HCBD is nephrocarcinogenic in rats. Positive results were obtained from a cell transformation test with HCBD and its metabolite pentachlorobutenoic acid.

It can be concluded from the described results of animal studies that HCBD is not teratogenous in the rat and that it is feto- and embryotoxic only in doses which are maternally toxic.

Data on possible effects on the immune System are not available.

Epidemiological studies or other relevant data on the effect of HCBD on humans have not come in.

<u>Recommendations</u>

Ecology

Because of lack of data on the potential biodegradability suitable biodegradation tests with adapted inoculum should be conducted. Additionally, the contradictory results the bacterial toxicity tests should be examined.

In order to estimate the amount of HCBD entering the atmosphere from waste incineration of tetrachloroethene/tetrachloromethane emission measurements should be performed.

If there is no vent collecting system, emission measurements should be performed in order to estimate the amount of HCBD entering the atmosphere during the production of tetrachloroethene/tetrachloromethane.

In case of appreciable emissions into the atmosphere, which will result in wash out of HCBD from the atmosphere into the soil, the HCBD levels in soil should be monitored by the official authorities.

HCBD binds strongly to the organic matter of soils. It is not known, however, if HCBD is degradable in soil. If HCBD exhibits an aerobic biodegradation potency in the tests recommended above and if there are measurable HCBD levels in soil, the biodegradability in soil should be investigated.

Toxicology

There is a lack of investigations on the sensitizing properties and eye irritating effects of HCBD. Furthermore, the carcinogenic potential for humans is not finally clarified. As HCBD, an undesired by-product, is recycled into the production process and consequently not used, these investigations do not have priority in view of the exposure situation.