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Gesellschaft Deutscher Chemiker

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

Chloranil

(2,3,5,6-Tetrachloro-
2,5-cyclohexadiene-1,4-dione)

BUA Report 85
(February 1992)

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 Chloranil

(2,3,5,6-Tetrachloro-2,5-cyclohexadiene-1,4-dione)

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Occurrence and distribution in the compartments

In the Federal Republic of Germany, 2,3,5,6-tetrachloro-2,5-cyclohexandiene-1,4-dione (Chloranil) was manufactured until mid 1990 by the Hoechst AG in quantity of 400 - 500 t/a via chlorination of phenol. The quantity processed in the Federal Republic of Germany is estimated at about 400 t/a, 1989 included, 300 t/a being processed to pigments and 100 t/a to dyestuffs. Chloranil has not been used as a fungicide nor as a seed protectant in the Federal Republic of Germany.

Since the production at Hoechst AG has ceased, chloranil is manufactured by Rhône-Poulenc Chimie in France via chlorination of hydroquinone rendering a purer product than via the phenol process. In particular it contains less polychlorinated dibenzodioxins (PCDD) and dibenzofuranes (PCDF) (detectable toxicity equivalents TE approximately 6.35 µg/kg, non-detectable TEs inferior to 0.48 µg/kg). The existing analytical results, however, are not yet representative. Chloranil manufactured by the phenol process contained approximately 300 mg/kg of hepta- and octa chlorodibenzodioxins and -furanes.

The discharge of chloranil into the environment from the Hoechst manufacturing process corresponded to a maximum of 10 kg/a into the hydrosphere and less than 10 kg/a into the atmosphere.

The discharge of chloranil into the hydrosphere from processing to dyestuffs cannot be quantified but is supposed to be small because hydrolysis of chloranil takes place. Since the processing to pigments is carried out without the use of water, a small discharge of chloranil can take place only during plant cleansing operations. Waste from processing of chloranil to pigments is disposed of in an underground waste disposal unit. Used activated charcoal from production of dyestuffs is burnt up.

Sewage sludge from the treatment of chloranil processing effluents is discharged in authorized waste disposal units, there is no agricultural use.

Information on discharges of PCDD and PCDF into the environment cannot be given before there are reliable analytical data. Discharges into the hydrosphere are to be expected from the production of dyestuffs, from textile dyeing with the liquor-bath, and from paper recycling.

Chloranil is formed when tetrachlorohydroquinone is oxidized, the latter occurring as a metabolite of pentachlorophenol, hexachlorobenzene and lindane under ecologically relevant conditions.

Degradability

In the respirometric test chloranil proved to be not readily biodegradable. The test does not allow any conclusions whether biodegradation occurred or not owing to toxicity to bacteria. On the inherent biodegradability no studies are available.

At pH 7 chloranil is hydrolysed to trichlorohydroxybenzoquinone, at pH 9 to chloranilic acid, the reaction being accelerated by exposure to light. In aqueous buffer solution at 20 °C and pH 7 the half-life is about 2 days, whereas at pH 9 instantaneous elimination of chloranil takes place. Photolysis of chloranil in solvents produces tetrachlorobenzo-semiquinone as anionic radical.

As to the photochemically oxidative degradation of chloranil in the atmosphere, the half-life for the reaction with hydroxyl radical is calculated to be about 2 days; however, it is not environmentally relevant because of the low volatility of chloranil.

Accumulation

Basically a bioaccumulation potential must be taken into account because of calculated log P_{OW} values between 3 and 4.9, it is supposed not to be effective however, because of the instability and reactivity of chloranil.

Because of short-lasting sorption of chloranil onto the organic matter of the soil and rapid hydrolysis or metabolism only a temporary occurrence of chloranil in the environment has to be taken into account.

Ecotoxicology

In the respiration inhibition test the toxicity to bacteria of a mixed culture was determined to EC_{20} = 135 mg/l after 3-hour exposure, whereas the LC_{50} for *Pseudomonas fluorescens* amounted to 4.9 mg/l after exposure for 30 minutes.

Chloranil at a concentration of 1 mg/l causes 5 % growth inhibition in the algae *Chlorella pyrenoidosa* and *Phormidium inundatum*.

For water fleas (*Daphnia magna*) the 24-hr EC_{65} (immobilisation) is 0.36 mg/l.

For the golden ide, the 96-hr LC_0 amounts to 2.5 mg/l, the NOEC to 1.6 mg/l.

Following exposure to 0.5 to 2 mg/l for 1 to 10 days, larvae of the clawed toad *Xenopus laevis* showed abnormalities of the otolith, optic cup and pigmentation as well as sporadically convulsive and unbalanced movements. The LC_{50} was about 1.6 mg/l.

In the terrestric environment the lowest concentration completely inhibiting growth of most of the investigated moldlike and yeastlike fungi was greater than 500 mg/l medium except one species in which it amounted to 246 mg/l.

Rhizobium japonicum showed no growth inhibition up to 1000 mg/l in the filter paper disc inhibition test on agar. Complete growth inhibition was reported for *Rhizobium phaseoli* exposed to a suspension of chloranil at a concentration of 50 mg/l medium.

No or minor germination disturbances in wheat were observed at application rates of 2 to 6 g/kg seed. Chromosomal abnormalities, mitotic disturbances and damages to seedlings appeared in the onion *Allium cepa* following contact with a suspension of 15 g/l water.

In soybeans, germination behavior was not impaired by chloranil up to a rate of application of 5 g/kg seed. Growth of fungi which has been found to be pathogenic to the soybean was inhibited with IC_{50} values between 415 and 3200 mg/l agar.

In vitro inhibition of photosynthesis by chloranil is proven.

Toxicological Aspects

Apparently chloranil is not absorbed percutaneously. There are no studies available on the metabolism.

The irritating action to the skin is weak. To the eye, chloranil causes strong irritation and irreversible damage.

Characteristic of the acute oral intoxication of the rat by chloranil were watery diarrhoea, convulsions and, following lethal doses, depression of the central nervous system. For the rat, the oral LD_{50} lies between 4.0 and 7.1 g/kg body weight.

Changes in blood pattern and pathologic findings in liver and kidney were observed in the rat following subacute and chronic oral administration.

In an insufficiently described 30-day inhalation study with chloranil dust, changes in the lung and histologic findings in brain, liver, kidney, heart and testicles were reported.

In plant tissues, chloranil induces changes of the chromosome form and aneuploid states. The Ames test performed at only low concentration of the chemical per plate gave no indication of a mutagenic effect. In the micronucleus test no increase in the number of micronuclei in polychromatic erythrocytes of mice has been observed.

A cancerogenicity study in mice administered a single dosage level of 215 mg chloranil/kg body weight/day with the feed for 18 months, indicated a tumorigenic effect in liver and lung of male animals. The numbers of individuals, however, were relatively small.

In an insufficiently documented study no indications of adverse effects to fertility following treatment of male rats were reported. In another study which cannot be validated, either, dystrophic changes of the spermatogenic epithelium were proven in rats after inhalation exposure to chloranil dust.

Recommendations

Ecology

A study on the inherent biodegradability is recommended. Because of the low solubility of chloranil in water, a respirometric test after an adaptation period of 4 weeks shall be performed instead of a standard test. Furthermore, a study on the acute toxicity to aquatic organisms, preferably to fish, with measurements of the effective concentrations is recommended, since the results of the available studies on toxicity to daphnids and fish are based only on nominal concentrations.

The manufacturers of dioxazine pigments and dyestuffs in the Federal Republic of Germany have promised to provide in the not-too-distant future representative analytical data concerning the dioxin contents of their products in order that the discharge of dioxins into the environment from those sources can be assessed. In addition determinations of the dioxin contents of representative batches of choranil imported should be carried out.

Toxicology

A 28-day feeding study should be performed in order to determine target organs and NOEL, and to clarify indications e.g. of testicular injuries observed in previous studies.

For a further clarification of the genotoxicity the performance of a point mutation assay on mammalian cells (HGRPT test) is recommended. Thereupon it has to be considered whether further studies are necessary to verify the indications of a carcinogenic effect.

Well documented information on metabolism, sensitisation and reproductive toxicity is lacking. Since only minor exposure to this chemical is to be expected, these studies are not regarded as having priority.