**German Chemical Society**
**Gesellschaft Deutscher Chemiker**

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

# BUA Reports 150 and 151

## Methyl chloroacetate

BUA Report 150
(April 1994)

## Ethyl chloroacetate

BUA Report 151
(December 1993)

S. Hirzel
Wissenschaftliche Verlagsgesellschaft 1996

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on Existing Chemicals of Environmental Relevance (BUA)

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# BUA Reports 150 and 151

## Methyl chloroacetate

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(April 1994)

## Ethyl chloroacetate

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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

# Methyl chloroacetate

BUA Report 150

(April 1994)

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

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# BUA Report on acid methyl ester

## Summary and conclusions

## Ecological aspects

### Occurrence and distribution in the compartments

In the Federal Republic of Germany, methyl chloroacetate is actually (as of 1990/91) produced in a quantity of 1 000 — 5 000 t/a by esterification of monochloroacetic acid with methanol and partially processed at home, partially exported.

The quantity processed in the Federal Republic of Germany, imports included, is distributed among the consecutive products dimethyl malonate (about 58 %), chloroacetamide and derivatives (about 40 %) and a series of minor use areas (< 1.6 %), e.g. flavours and fragrances.

During the production of methyl chloroacetate, about 300 kg/a are emitted into the atmosphere.

When it is processed to chloroacetamide, no emission is to be expected because the vent air is scrubbed.

The discharge into the hydrosphere from production and processing to chloroacetamide is < 75 kg/a.

The release caused by residual contents in this product can be estimated at < 70 kg/a.

During processing to dimethyl malonate, < 10 kg/a are discharged into the hydrosphere according to routine measurements of AOX, whereas practically nothing is emitted into the atmosphere.

No data are available on the discharges from other areas of use.

The wastes (about 200 and 50 kg/a, respectively) resulting from production and processing to dimethyl malonate are incinerated.

No wastes remain from processing to chloroacetamide other than the charge of the effluent. No data are available on the other areas of use.

There are no data available an occurrence in the environment.

According to the Henry‘s Law Constant of 1.47 Pa · $m^3$ · $mol^{-1}$, methyl chloroacetate is moderately volatile from aqueous solution.

**Degradability**

In a test on potential biodegradability according to OECD 302 B, 98 % of the substance were eliminated within 10 days when measured as COD, whereas only 78 % of the chlorine bound organically were transformed to chloride, i.e. about 20 % of the substance had volatilized on aeration.

The half-life time of hydrolysis of methyl chloroacetate in neutral aqueous solution yielding chloroacetic acid and methanol was derived from calculated reaction enthalpies to be 22 days and was calculated, respectively, on the basis of a measured reaction rate constant to be about 39 days. Yet, hydrolysis is likely to be accelerated also in neutral or weakly acid solution by general base catalysis.

The half-life time of the photochemical-oxidative degradation in the atmosphere was calculated to be 74 days.

**Accumulation**

No studies are known on bio- and geoaccumulation. With respect to the (calculated) n-octanol-water partition coefficient (log $P_{OW}$ = 0.76), a relevant bioaccumulation potential is not to be expected.

**Ecotoxic Effects**

A 24 h $EC_{10}$ of 35 mg/l was determined in *Pseudomonas putida* for the inhibition of cell proliferation.

In facultatively anaerobic bacteria no inhibition of gas production was observed after 24 hours exposure to methyl chloroacetate in concentrations ranging up to 200 mg/l.

The toxic limit concentration (24 h $EC_3$ for the growth of a green alga is 0.19 mg/l.

There are no studies known regarding the effect an higher plants.

Testing the acute toxicity to the *Daphnia* resulted in a 24 h $EC_0$ of 3.2 mg/l and a 24 h $EC_{50}$ of 5.5 mg/l for inhibition of the swimming capability.

The 48 h and 96 h $LC_0$ in the zebra fish was 1.13 mg/l.

For the rainbow trout, 48 h $LC_0$ < 2.5 mg/l and 48 h $LC_{100}$ of 6 mg/l are reported.

**Toxicological Aspect** *)

Chloroacetic acid methyl ester is toxic on acute oral or dermal exposure ($LD_{50}$ rat oral 107 and 140 mg/kg body weight; rat dermal 136.6 mg/kg and approx. 470 mg/kg body weight; rabbit dermal 318 mg/kg body weight). Both non-specific signs of toxicity and clear irritant effects are observed. Comparable symptoms also occur after intraperitoneal injection ($LD_{50}$ mouse i.p. 200 to 460 mg/kg body weight) and vapour inhalation. Marked irritation

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*) With permission of BG Chemie taken from:
Toxikologische Bewertungen Nr. 76 „Chloressigsäuremethylester“.
Berufsgenossenschaft der chemischen Industrie, Heidelberg (1994).
Kapitel 1: Summary and assessment

of the respiratory tract and eyes is also observed on inhalation exposure ($LC_{50}$ rat > 945 < 1 418 mg/$m^3$).

After repeated inhalation exposure to chloroacetic acid methyl ester for 28 days at concentrations of 10, 33 or 100 ppm (equivalent to 44, 146 and 443 mg/$m^3$, respectively), adverse effects on the breathing (irregular breathing) and on movement (uncoordinated gait) as well as irritant effects (closing together of the eyelids, sneezing, increased frequency of cleaning) and an increase in relative lung weight occurred in rats at the highest concentration. These effects, though less pronounced, were also observed in males in the 33 ppm group. In contrast, no such effects were detected in the 10 ppm group. Body weight gain was markedly impaired in both sexes at the highest concentration. Thus in this study, the no effect level is 10 ppm in male rats and 33 ppm in female rats.

Chloroacetic acid methyl ester is corrosive to rabbit 5km and is absorbed through the skin (0.5 ml undiluted substance/rabbit leads to death). The substance is severely irritating to the rabbit eye.

In guinea-pigs, chloroacetic acid methyl ester induces sensitization. Cross— sensitization with chloroacetic acid ethyl ester has been observed in this species.
Chloroacetic acid methyl ester is not mutagenic in the Salmonella/microsome test in five strains of *Salmonella typhimurium* or in *Escherichia coli* either with or without metabolic activation. No induction of micronuclei has been observed in the micronucleus test in the mouse.

No increase in the incidence of lung tumours has been established after intraperitoneal administration to strain A mice.

In man, delayed occurrence of irritation of the conjunctiva is observed after exposure to the vapour.

## Recommendations

### Ecology

In order to clarify the ecological relevance, tests on biodegradability (test on ready biodegradability) are to be carried out.

### Toxicology

Data are lacking especially on prolonged toxicity and reproductive toxicity.

On the basis of the use pattern the emissions into the environment seem to be small. From the view of BUA clarification of the open questions on toxicology may be deferred if the minor environmental exposure is confirmed by the test on biodegradability.

# Ethyl chloroacetate

BUA Report 151

(December 1993)

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**Toxicological Assessment no. 190 of the BG Chemie (1992).** Appendix
(German Employers Liability Insurance Association for the Chemical Industry)

# BUA Report on Chloroacetic acid ethyl ester

## Summary and conclusions

## Ecological aspects

### Occurrence and distribution among the compartments

In the Federal Republic of Germany, ethyl chloroacetate is actually (as of 1990/91) produced in a quantity of 1000—5000 t/a by esterification of monochloroacetic acid with ethanol and partially processed at home, partially exported.

88 % of the ethyl chloroacetate processed in the Federal Republic of Germany, which is partially imported, are used for the production of diethyl malonate, approx. 5 % are processed to phosphonoacetic acid triethyl ester for plastics additives, approx. 4 % to the herbicide benazolin-ethyl. The rest of 3 % is distributed among a series of minor use areas, e.g. flavours and fragrances.

During the production of ethyl chloroacetate, 120 kg/a are emitted into the atmosphere and less than 75 kg/a are discharged into the hydrosphere.

Practically nothing of the substance is emitted into the atmosphere when it is processed to diethyl malonate; < 11 kg/a are discharged into the hydrosphere according to routine measurements of AOX and conversion into the ester. The emission into the atmosphere during processing to triethyl phosphonoacetate is negligible, the discharge into the hydrosphere is not quantified. During processing to benazolin-ethyl < 1 kg ethyl chloroacetate/a is emitted into the atmosphere; there is no release into the hydrosphere because the resulting effluent is incinerated.

From the use of benazolin-ethyl, < 150 kg ethyl chloroacetate/a are discharged into the environment.

No data are available on the discharges from other areas of use.

The wastes (approx. 26 t/a) resulting from production and processing are incinerated.

There are no data available on occurrence in the environment.

According to the Henry‘s Law Constant of 2.85 Pa · $m^3$ · $mol^{-1}$ ethyl chloroacetate is moderately volatile from aqueous solution.

**Degradability**

In a test on potential biodegradability according to OECD 302 8, 93 % of the substance were eliminated within 13 days when measured as COD, whereas only 74 % of the chlorine bound organically were transformed to chloride, i.e. about 20 % of the substance had volatilized on aeration.

The half-life time of hydrolysis of ethyl chloroacetate in neutral aqueous solution yielding chloroacetic acid and ethanol was calculated to be 74 days using the reaction rate constants of the base-catalysed hydrolysis at different base concentrations and extrapolating to infinite dilution of the bases.

The half—life time of the photochemical-oxidative degradation in the atmosphere was calculated to be 11.1 days.

**Accumulation**

No studies are known on bio- and geoaccumulation. With respect to the (calculated) n-octanol-water partition coefficient (log $P_{OW}$ = 1.28), a relevant bioaccumulation potential is not to be expected.

**Ecotoxic Effects**

In facultatively anaerobic bacteria, no inhibition of gas production was observed after 24 hours exposure to ethyl chloroacetate in concentrations ranging up to 900 mg/l.

There are no studies known an the effect of ethyl chloroacetate to algae. It is supposed to be similar to the homologous methyl chloroacetate. For the latter, a toxic limit concentration (24 h $EC_3$) of 0.19 mg/l was determined.

Testing the acute toxicity to the Daphnia resulted in a 24 h $EC_0$ of 1.9 mg/l for inhibition of the swimming capability.

The 48 h and 96 h $LC_0$ in the zebra fish was 1.0 mg/l.

The shoot fresh weights of different terrestrial plant species amounted to 83 - 125 and 70 - 120 %, respectively, of controls 14 days after 500 and 1000 mg/$m^2$ had been sprayed onto the plant substrate.

**Toxicological Aspect** *)

Chloroacetic acid ethyl ester is acutely toxic (oral $LD_{50}$ rat: 180 mg/kg body weight; dermal $LD_{50}$ rat: 161 mg/kg body weight, rabbit: 230—335 mg/kg body weight; $LC_{50}$ rat, 4 hours: 3.33 ml/$m^3$ air).

In the rabbit the substance is a moderate skin irritant and a strong eye irritant. Studies conducted in guinea-pigs according to Magnusson/Kligman provide evidence of sensitization (25 % of animals show a positive reaction). **)

In the Salmonella/microsome test, chloroacetic acid ethyl ester is not genotoxic when tested in *Saccharomyces cerevisiae* and *Escherichia coli*.

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*) With permission of BG Chemie taken from:
Toxikologische Bewertung Nr. 190 „Chloressigsäureethylester“.
Berufsgenossenschaft der Chemischen Industrie, Heidelberg (1992).
Kapitel 1: Summary and assessment.

**) Another, unpublished study has become known, in which 79 % of the animals show a positive reaction.

VIII

No tumorigenic effect is detected in two carcinogenicity studies where mice have received chloroacetic acid ethyl ester epicutaneously and subcutaneously. Nor is any evidence of a carcinogenic effect obtained in a further carcinogenesis study in mice (strain A).

In one case, chloroacetic acid ethyl ester has produced contact allergy in a human.

## Recommendations

### Ecology

In order to clarify the ecological relevance, tests on biodegradability (test on ready biodegradability) are to be carried out.

### Toxicology

Data are lacking especially on prolonged toxicity and reproductive toxicity.

On the basis of the use pattern the emissions into the environment seem to be small. From the view of BUA clarification of the open questions on toxicology may be deferred if the minor environmental exposure is confirmed by the test on biodegradability.