



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

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

**Trichloroacetic acid,**  
**Sodium trichloroacetate**

BUA Report 167  
(August 1995)



S. Hirzel

Wissenschaftliche Verlagsgesellschaft 1997

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**Trichloroacetic acid,  
Sodium trichloroacetate**

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(August 1995)

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Committee on Existing Chemicals  
of Environmental Relevance

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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 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 update 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

## Contents

<b>Summary and Conclusions .....</b>	<b>XI</b>
--------------------------------------	-----------

<b>Recommendations .....</b>	<b>XXII</b>
------------------------------	-------------

### **Trichloroacetic Acid and Sodium Trichloroacetate**

<b>1. Chemistry of Trichloroacetic Acid and Sodium Trichloroacetate .....</b>	<b>1</b>
1.1 Chemical Identity .....	1
1.1.1 Trichloroacetic Acid .....	1
1.1.2 Sodium Trichloroacetate .....	2
1.2 Composition of the Technical Product .....	2
1.3 Chemical Properties .....	3
1.3.1 Trichloroacetic Acid .....	3
1.3.2 Sodium Trichloroacetate .....	4
<b>2. Physical Properties .....</b>	<b>5</b>
2.1 Trichloroacetic Acid .....	5
2.2 Sodium Trichloroacetate .....	8
<b>3. Analysis .....</b>	<b>9</b>
3.1 Determination in Air .....	10
3.2 Determination in Water .....	11
3.3 Determination of Trichloroacetic Acid in Soil, Sediment and Biological Material .....	12
<b>4. Emission into the Environment during Production, Processing, Use and Waste Disposal .....</b>	<b>23</b>
4.1 Production Methods .....	23
4.1.1 Trichloroacetic Acid .....	23
4.1.2 Sodium Trichloroacetate .....	23
4.2 Manufacturers and Processors, Production Quantities, Export, Import, Total Consumption .....	24
4.2.1 Trichloroacetic Acid .....	24

4.2.2	Sodium Trichloroacetate .....	25
4.3	Processing, Use and Quantities Consumed .....	26
4.3.1	Processing .....	26
4.3.1.1	Trichloroacetic Acid .....	26
4.3.1.2	Sodium Trichloroacetate .....	27
4.3.2	Use .....	27
4.3.2.1	Trichloroacetic Acid .....	27
4.3.2.2	Sodium Trichloroacetate .....	28
4.4	Emission into the Atmosphere .....	29
4.4.1	Emission during Production, Processing and Use .....	29
4.4.2	Emission from Other Areas .....	29
4.5	Emission into the Hydrosphere .....	32
4.5.1	Emission during Production, Processing and Use .....	32
4.5.2	Emission from Other Areas .....	34
4.6	Emission into the Geo- and Biosphere .....	36
4.6.1	Emission into Soil .....	36
4.6.2	Emission into Plants .....	38
4.7	Emission through Wastes and Their Treatment .....	38
4.8	Balance of Emissions into the Environment .....	39
<b>5.</b>	<b>Environmental Occurrence .....</b>	<b>40</b>
5.1	Atmosphere .....	40
5.2	Hydrosphere .....	41
5.2.1	River Water .....	41
5.2.2	Groundwater, Spring-, Lake- and Consumption Water .....	43
5.2.3	Soil Leachate .....	45
5.2.4	Rainwater .....	45
5.2.5	Drinking Water .....	49
5.3	Geosphere .....	50
5.4	Biosphere .....	51
5.4.1	Occurrence in Plants .....	51
5.4.2	Occurrence in Humans and Mammals .....	55
5.5	Natural Sources .....	58
6.	Environmental Behaviour .....	59
6.1	Transformation, Degradation and Degradation Products .....	59
6.1.1	Biodegradation .....	59

6.1.1.1	Aerobic Biodegradation.....	59
6.1.1.2	Aerobic Biodegradation of Sodium Trichloroacetate in Soil .....	61
6.1.1.3	Anaerobic Biodegradation .....	74
6.1.1.4	Degradation in Plants .....	74
6.1.2	Decomposition in Aqueous Medium .....	76
6.1.3	Photochemical Degradation .....	77
6.2	Accumulation .....	78
6.2.1	Bioaccumulation .....	78
6.2.1.1	Bioaccumulation in Animals .....	78
6.2.1.2	Uptake, Distribution, Accumulation and Residues of Sodium Trichloroacetate in Plants .....	80
6.2.2	Geoaccumulation .....	86
6.3	Distribution Behaviour and Transport Processes within and between Environmental Compartments .....	86
6.3.1	Henry's Law Constant .....	86
6.3.2	n-Octanol/Water Partition Coefficient .....	87
6.3.3	Soil Sorption Coefficients .....	88
6.4	Environmental Fate .....	92
<b>7.</b>	<b>Ecotoxicology .....</b>	<b>94</b>
7.1	Effects on Aquatic Organisms .....	94
7.1.1	Microorganisms .....	94
7.1.2	Plants .....	96
7.1.3	Invertebrates .....	98
7.1.4	Vertebrates .....	101
7.2	Effects on Terrestrial Organisms .....	104
7.2.1	Microorganisms .....	104
7.2.2	Plants .....	106
7.2.3	Invertebrates .....	114
7.2.4	Vertebrates .....	115
7.3	Effects on Ecosystems .....	116
<b>8.</b>	<b>Toxicity in Warm-Blooded Organisms .....</b>	<b>117</b>
8.1	General Effects .....	117
8.2	Mode of Action .....	117
8.3	Metabolism, Toxicokinetics .....	118
8.4	Acute Toxicity .....	119

8.5	Skin and Mucous Membrane Tolerance .....	121
8.6	Sensitizing Effect .....	121
8.7	Subacute, Subchronic and Chronic Toxicity .....	122
8.8	Genotoxicity .....	128
8.8.1	<i>In vitro</i> .....	128
8.8.2	<i>In vivo</i> .....	133
8.9	Carcinogenicity .....	141
8.10	Reproductive Toxicity .....	144
8.11	Effect on the Immune System .....	145
8.12	Other Effects .....	145
8.13	Experiences for Humans .....	147
<b>9.</b>	<b>Substance-Specific Legal Regulations .....</b>	<b>148</b>
<b>10.</b>	<b>Literature .....</b>	<b>153</b>



# **BUA Report on Trichloroacetic acid and Sodium trichloroacetate**

## **Summary and conclusions**

### **Ecological aspects**

### **Production and Use**

Trichloroacetic acid (TCA) is produced in the Federal Republic of Germany on a technical base by exhaustive chlorination of the chloroacetic acid mother liquor which results during the synthesis of monochloroacetic acid. Sodium trichloroacetate (Na-TCA) is obtained by neutralization of TCA with 50 % sodium hydroxide solution. The only manufacturer of TCA and Na-TCA in the Federal Republic of Germany is Hoechst AG.

Around 1,000 t TCA were produced in 1993 in the Federal Republic of Germany.

With an export of 670 t TCA, about 330 t TCA remained in the country, of which around 250 t and 50 t were processed respectively to Na-TCA and ethyl trichloroacetate (which is exported to 100 %) and about 30 t TCA sold to manufacturers of pharmaceuticals and retailers.

Only summary import and export data are available for mono-, di- and trichloroacetic acids and their salts and esters. In 1991, approximately 12,600 t were imported and around 15,300 t were exported. The import for 1993 was 9,064 t, and the export was not documented.

Around 300 t Na-TCA were manufactured in 1993, about 190 t thereof were exported and 110 t sold nationally

Approximately 100 t of the herbicide NaTA (Na-TCA), the license of which has expired since 1989 in the Federal Republic of Germany, were exported in 1993 from storage inventories. Production and trade have thus been terminated.

Na-TCA is used primarily as a selective herbicide against grassy and winter-resistant weeds in crops (grain, potatoes, beets, vegetables) and for growth control of reeds and crab grass in ponds and irrigation canals. No TCA- or Na-TCA-containing pesticide is permitted currently (state: 1994) in the Federal Republic of Germany. Na-TCA is also used as a component of dyeing aids (fixing agents) in the textile industry (about 1.5 t Na-TCA were used in the Federal Republic of Germany).

## **Emission into the Environment**

### **Atmosphere**

The quantifiable release of TCA into the atmosphere during the production, processing and use of TCA was < 20 kg/a in 1993.

Further emissions into the environment take place through the degradation of readily volatile chlorinated hydrocarbons in the atmosphere to TCA (estimated emission at about 53-225 t TCA/a). The resulting TCA can reach the earth's surface with rain or fog and further enter soil leachate and ground water by means of transport processes.

### **Hydrosphere**

The quantifiable release of TCA into the hydrosphere during production, processing and use was approximately 2.350 t/a in 1993. No data are available about the fate of 1.5 t Na-TCA used for formulating of dyeing aids.

TCA can be emitted into the hydrosphere with precipitation through wet deposition of the TCA formed in the atmosphere (estimated at about 256 t/a on the basis of measured TCA concentrations in rainwater).

Further emissions of TCA into the environment are expected through chlorination of drinking water (about 13 t/a) as well as through waste waters from the pulp industry and from outdoor and indoor swimming pools. The discharged quantity is unquantifiable.

### **Geo- and Biosphere**

An unquantifiable amount of Na-TCA can be released into soil by use of end Stocks of the herbicide NaTA (Na-TCA). TCA can likewise be discharged into the geosphere through wet deposition, whereby the value of 256 t/a estimated for the rainfall emission of TCA for the hydrosphere is distributed among the hydrosphere and geosphere.

TCA can be formed and excreted as a metabolite in humans, animals and plants after exposure to volatile chlorinated hydrocarbons (tetrachloroethene, trichloroethene, 1,1,1-trichloroethane). An estimation of this emission is impossible.

TCA is present mainly in the compartment water, while Na-TCA is divided up among the compartments water and soil. On the basis of the physicochemical properties, a transfer of TCA from water into the atmosphere is unexpected, whereas a leaching out from the atmosphere with rain is feasible.

### **Occurrence in the Environment**

In the atmosphere east of the Black Forest in the Federal Republic of Germany 0.4 - 3 ng TCA/m<sup>3</sup> were detected in 1992.

#### XIV

Quantities of 2 - 3 µg TCA/l were found in the Rhine River in 1983; measurements in 1989 showed average TCA concentrations of 0.3 - 2.5 µg/l (maximum: 109.8 µg/l).

In two Austrian rivers on which wood pulp mills were located, values of 3 - 558 µg TCA/l and 42 - 104 µg TCA/l were measured in January 1990 for the rivers Pöls and Mur, respectively.

Spring water from forest areas in Hessen (Federal Republic of Germany) showed the following TCA levels in the period of 1988/89: Königstein 0.02 - 0.06 µg/l, Grebenau 0.01 - 0.92 µg/l and Witzenhausen 0.052 - 0.09 µg/l. Groundwater from the same forest regions contained an average of 0.03 - 0.04 µg/l near Mörfelden, 0.3 µg/l near Grebenau and 0,05 µg/l near Witzenhausen.

In Switzerland, 0.2 - 0.3 µg TCA/l were measured in spring water and < 0.4 - 0.6 µg TCA/l in groundwater.

Soil leachate in Hessian forests contained 0.36 - 1.3 µg TCA/l beneath spruce groves and 0.14 - 5.0 µg TCA/l in the open field.

In Berlin, the concentration of TCA in rainwater in 1990/91 lay at 0.1 - 20 µg/l. Measurements of the TCA concentrations in rainwater in Germany conducted in 1993/94 showed mean values of 0.197 µg/l in the open field, 0.733 µg/l in spruce groves (maximum: 2.204 µg/l), 0.278 µg/l in beech groves and 0.253 µg/l in mixed forests.

Concentrations of 18 - 136 µg TCA/l were measured in water samples from Bremen swimming pools.

Values between < 1 and 3 µg TCA/l were detected in 1983 in drinking water of various places in the Federal Republic of Germany.

TCA is widely found in soil, unless even ubiquitous. In Hessian forest soils concentrations of 0.02 - 0.4 mg TCA/kg were measured.

TCA is detectable in plant roots, leaves and fruits, whereby the amount greatly varies with the time elapse between the Na-TCA application and sowing or harvest. After use of normal application amounts, TCA is mostly no longer detectable in the fruits during harvest time.

TCA was measured, for example, at concentrations of 30 µg/kg in the youngest needles and 80 µg/kg in the older needles of a spruce branch. TCA in concentrations of 0.7 - 175 µg/kg was found in conifer needles near Berlin and 22 - 33 µg/kg in the needles of conifers from the Rhine-Main plain.

TCA levels of up to 682 µg/l were detected in urine of persons employed at a dry-cleaning factory (tetrachloroethene used as a solvent), and concentrations of still up to 105 µg TCA/l were found in the urine of residents living nearby. The 24 h mean value of urine of North-Rhine Westphalian women, who were not occupationally exposed to chlorinated hydrocarbons, was 7.6 µg TCA/l.

### **Degradability**

TCA and Na-TCA are partially biodegradable under aerobic conditions. After adaptation, a microbic degradation (lag phase of up to 15 days) can take place in natural water bodies and soils, the degree and rate of which depend on the substance concentration, the climatic conditions (mainly moisture and heat) and the microorganism population. With repeated application of Na-TCA on the same soil, the biodegradation is accelerated, whereby this effect of adapted microorganisms lasts for at least one year. Bacteria strains of genus Arthrobacter sp., Pseudomonas sp.

and Actinomyces as well as various species of fungi such as Trichoderma viride are microorganisms capable of metabolizing both substances. A degradability ranging from 0 % to 46 % was found in the standardized Zahn-Wellens test and in the MITI II test. In the water of a river, a half-life of 50.3 days was calculated for the biodegradation of Na-TCA.

Under normal application conditions, Na-TCA can be persistent for up to 12 months in soil, whereby the phytotoxic effect has mostly ended already after 3 months.

No data are available about the anaerobic biodegradation of TCA and Na-TCA.

In plants, TCA is degraded only very slowly. For example, the half-lives were 11.3 days in a wheat sprout, 7.9 days in an oat sprout and 10 days in spruce needles.

In aqueous solutions, TCA and Na-TCA are hydrolyzed only very slowly at normal temperature: a 50 % aqueous solution of Na-TCA is hydrolyzed to 1 % within 4 - 6 weeks at 20 - 25 °C.

Photochemical degradation and adsorption to mineral soils play only a subordinate role in the elimination of Na-TCA from soil.

For the reaction of trichloroacetic acid with OH-radicals in the troposphere, a reaction rate constant of  $3.6 \cdot 10^{-14} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$  was calculated from which a half—life of about 446 days is derived.

### **Accumulation**

A bioaccumulation of TCA is not very likely due to the low  $P_{OW}$  value of 1.33.

Tests on the bioaccumulation (OECD Guideline 305E) of TCA in carp until equilibration (6 weeks) resulted in bioconcentration factors of 0.4 - 1 (TCA concentration of 0.2 mg/l) and < 1.7 (TCA concentration of 2 mg/l). According to MITI, TCA is classified into the substance group "non-accumulating or weakly accumulating".

Na-TCA is a moderately persistent compound in soil with half-lives between 20 and 100 days (based on all elimination processes).

No geoaccumulation is expected on the basis of the possible biodegradation and other distribution processes.

### **Ecotoxicology**

The ecotoxicology of TCA and, in particular, Na-TCA was studied quite extensively because of the temporary use as a herbicide. Aside from the application of microbial test procedures, largely studies on aquatic vertebrates and terrestrial plants predominated.

The effect on prokaryotes at concentrations of mostly above 1,000 mg/l was manifested by an inhibition of cell multiplication or by a delayed spore germination. For Pseudomonas putida, the toxic threshold value for Na-TCA was > 1,000 mg/l. Photobacterium phosphoreum (EC<sub>50</sub> value: 35 mg TCA/l) and various cyanobacteria (Spirulina platensis: 14 d-LC<sub>50</sub> = 5 mg TCA/l) were proven to be particularly sensitive.

The statements on the toxicity in green algae (in particular Chlorella sp. are contradictory. The lowest effective concentration (for Chlorella pyrenoidosa was cited at

0.3 mg Na-TCA/l (14 d-EC<sub>50</sub>) while other authors could not detect any effects on this and other Chlorella species at 100 mg/l. Differences in toxicity between TCA (24 h-EC<sub>0</sub> = 78 mg/l; 24 h-EC<sub>50</sub> = 110 mg/l) and Na-TCA (EC<sub>0</sub> = 2,500 mg/l; 24 h-EC<sub>50</sub> = 8,370 mg/l) were ascertained on Daphnia magna as well an effect increase with increasing temperature. For dragonfly nymphes (Somatochlora cingulata) a significant effect on the oxygen consumption and the ammonia excretion was detected at 1 mg TCA/l (8 h). The effect of higher TCA concentrations on fish was shown primarily by reduced motility and respiration (Poecilia reticulata: 48 h-LC<sub>50</sub> = 9,160 mg TCA/l; Esox lucius fry: 48 h-LC<sub>50</sub> < 100 mg Na-TCA/l). Chronic tests on carp (Cyprinus carpio), however, produced indications of a noteworthy effect of Na-TCA concentrations which approach values relevant to practice (63 d-EC<sub>10</sub> = 7 mg/l).

Whereas Azotobacter sp. under natural terrestrial conditions were shown to be mostly TCA-resistant (EC<sub>0</sub> > 1,000 mg/kg soil), cultivated methanogenic bacteria were more sensitive by several orders of magnitude (2 d-IC<sub>50</sub> < 0,001 mg/l). Aerobic soil bacteria accepted Na-TCA and its biotransformation products as the C-source under release of chloride ions (Arthrobacter sp.: partial retention of the dehalogenase activity at concentrations up to 46,350 mg/l was tested).

TCA was shown to be relatively toxic to plants (especially monocotyledons). Although it was found that the toxicity in terrestrial plants is generally expected to be lower in solid substrates than in nutrient solutions due to adsorption effects, a prolongation of the germination period and a 10 % reduction of the yield of plant material was determined for wheat (Triticum aestivum) at a substrate charge of 3 mg TCA/kg (22 d-EC<sub>50</sub> < 3 mg/kg). The 14 d-LC<sub>50</sub> for oats was 4.6 mg/kg loam and, in another study, 31.6 mg/kg standard soil. Developmental disturbances on conifer

seedlings, which partially caused death, were detectable at  $\geq 1$  mg Na-TCA/kg soil (spruce: 60 d-LC<sub>50</sub> about 16 mg/kg).

Frequent symptoms of a phytotoxic TCA/Na-TCA effect were: inhibition of root growth, metabolic changes, inhibition of cuticular formation processes with increased transpiration, morphological changes in the vegetative and reproductive plant parts.

Earthworms were frequently used as terrestrial invertebrates for toxicity testing. The 7 d-LC<sub>50</sub> value for *Eisenia fetida* was specified at 1,139.9 mg Na-TCA/kg soil.

### **Toxicological Aspect**

Trichloroacetic acid (TCA) acts caustic to the skin and mucous membranes and possesses a strong protein-precipitating effect. A 90 % Na-TCA solution also irritates the mucosa of the eyes. The dermal absorption of TCA is low. A sensitizing effect of TCA could be established neither in animal experiments nor for humans.

The retention time in the organism is relatively long, because TCA is strongly bound to plasma proteins. Most of the substance is excreted unchanged via the kidneys; a smaller fraction is metabolized to carbon dioxide and trichloromethane and is exhaled. Biliary excretion takes place as trichloroethanolglucuronide, whereby trichloroethanol is reabsorbed to a larger part from the intestine.

TCA administered in form of its sodium salt exhibits a low acute systemic toxicity. The LD<sub>50</sub> value for rats and mice is 3,000 mg/kg body weight after oral and subcutaneous administration and is 1,500 - 2,000 mg/kg body weight for the dog after oral administration. The acid itself possesses a high local toxicity.

XX

After repeated application of doses up to 800 mg TCA or Na-TCA/kg body weight to rats for 3-4 months (NOEL for TCA: about 4 mg/kg body weight; NOEL for Na-TCA: about 200 mg/kg body weight), no further toxic effects could be observed aside from reduced body weight gain and indications of an increased peroxisome proliferation. Regarding the kidneys, no histopathological changes were determined in a study other than an increase of the relative weights. In mice, chronic exposure led to an increased hepatotoxicity and also caused tumors in male mice which were supposedly attributed to an increased lipid peroxidation. Peroxisome proliferation was observed in male and female mice, whereby mice reacted more sensitively than rats with respect to this end point. Furthermore, no hepatic tumors occurred in rats after chronic administrations. The mechanism of tumor development in the male mouse, however, is not definitely clarified. The observed peroxisome proliferation after TCA administration is discussed as a possible cause. The relevance of the findings on mice to humans cannot be estimated until this question is finally clarified.

In dogs, however, damage to the liver, heart, skeletal muscle, blood picture and spermiogenesis was shown after 90 days as of dosages of 120 mg Na-TCA/kg body weight per day (NOEL: 30 mg/kg body weight).

TCA caused in vitro neither point mutations, chromosome damage nor DNA-strand breaks. However there are indications of a clastogenic as well as a DNA-damaging effect in vivo. The validity of these findings is limited by the lack of positive controls and, in part, by an absent dosage dependency. Other studies were negative, also with higher dosages. DNA single-strand breaks occurred in mice at a 10 time lower dosage than in rats. On the other hand, studies with application of higher oral doses are available in which no DNA-strand breaks occurred in the liver,

spleen, intestinal and stomach cells of the mouse or in liver cells of the rat. The nonuniformity of the available in vivo findings is not yet sufficiently explicable. Cytotoxic effects are discussed as a possible cause for positive results.

In rats, TCA led to fetotoxicity and malformations already in the lowest tested dosage of 330 mg/kg body weight, at which toxic effects also appeared in the dams. A NOEL could not be established. Studies in the maternally non-toxic range are not available. The fertility in rats was unaffected by increased TCA-levels in the reproductive Organs.

## **Recommendations**

### **Ecology**

The available results on the ecology and the behaviour of trichloroacetic acid and sodium trichloroacetate in the environment are considered to be sufficient for an evaluation of the environmental relevance.

### **Toxicology**

Studies on the genotoxic effect are not seen to be a priority, because the available data do not suggest any genotoxic mechanism. This is supported by carcinogenicity studies in which no indications of a carcinogenic effect were observed aside from an increased incidence of hepatic tumors in the male mouse, indication of a species-specific mechanism.

A study on the embryotoxicity in the rat after oral administration is recommended, because the available data are insufficient and do not allow any setting of a NOEL.