



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

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

**Dichloroaniline**

(2,4-, 2,5- and 3,4-Dichloroaniline)

BUA Report 140

(October 1993)



S. Hirzel

Wissenschaftliche Verlagsgesellschaft 1996

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

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

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## **BUA Report on 2,4-, 2,5- and 3,4-Dichloroaniline**

( benzeneamine, 2,4-dichloro-  
benzeneamine, 2,5-dichloro-  
benzeneamine, 3,4-dichloro-)

### **Summary and conclusions**

#### **Ecological aspects**

##### **1. Entry into the environment and occurrence in environmental compartments**

###### **Amounts entering the environment**

In the Federal Republic of Germany in 1990 and 1991, < 200 t 2,4-dichloroaniline/a, approx. 1,000 resp. 550 t 2,5-dichloroaniline/a and approx. 8,500 resp. 7,000 t 3,4-dichloroaniline/a were produced. On the basis of known import-export data, annual consumption in the Federal Republic of Germany in 1990 and 1991 was thus < 180 t 2,4-dichloroaniline, approx. 350 resp. 250 t 2,5-dichloroaniline and approx. 9,000 resp. 8,000 t 3,4-dichloroaniline.

All 3 isomers are used solely as intermediates. 100 % of the 2,4- and 2,5-dichloroaniline was used as a precursor for the synthesis of dyestuffs and pigments in 1990/91, whereas only 0.2 % of the 3,4-dichloroaniline was used for this purpose. 99.8 % of the 3,4-dichloroaniline was converted into 3,4-dichlorophenyl isocyanate, 63 % of which was exported. 34 % of the isocyanate was processed in the Federal Republic of Germany to herbicides such as Linuron, Diuron and Propanil, and 3 % to a bactericide used in the cosmetics industry.

The amount of 2,4-, 2,5- and 3,4-dichloroaniline entering the atmosphere due to production and processing by the two German producers, who process 100 % (2,4-) and > 99 % (2,5-, 3,4-) of the indicated consumption, was < 25 kg/a per isomer in 1990/91 in each of the factories concerned.

Two factories handle 2,4-, three 2,5- and four 3,4-dichloroaniline. The amounts entering the hydrosphere due to production and processing were < 2 kg 2,4-dichloroaniline/a, approx. 0.1 t 2,5-dichloroaniline/a (as far as could be quantified) and a maximum of 2.74 t (1990) or 1.56 t (1991) 3,4-dichloroaniline. Some of the sludge from the biological sewage plants treating the waste water is incinerated and some is dumped in special landfills. Production and processing wastes containing dichloroaniline are disposed of in incineration plants for "special waste" ("besonders überwachungsbedürftiger Abfall").

3,4-Dichloroaniline is introduced by certain crop protection agents into the soil, from which it can also enter the biosphere and hydrosphere with or via these agents. Only the herbicides Linuron and Diuron are permitted for use in the Federal Republic of Germany. In the Federal Republic of Germany the estimated maximum amount of 3,4-dichloroaniline entering the soil in the form of an impurity in these agents is 0.31 t 3,4-dichloroaniline/a in 1990/91. Quantification of the amounts of 3,4-dichloroaniline entering the soil due to degradation of these agents is not feasible.

An unquantifiable amount of 3,4-dichloroaniline is to be expected in surface waters polluted with 3,4-dichloronitrobenzene due to microbial reduction of the nitro group.

### **Occurrence**

There are no available data on the occurrence of 2,4-, 2,5- and 3,4-dichloroaniline in the atmosphere. The amounts of these isomers entering the air in the Federal Republic of Germany are of an order of magnitude (kg range, see above) which would lead one to expect concentrations below current detection limits.

In the stretch of the Rhine flowing through North Rhine Westphalia and in the mouths of its tributaries, the concentrations of 2,4- and 2,5-dichloroaniline (1990/91) and

3,4-dichloroaniline (1985-1991) were, with the exception of two samples, below the detection limits of 0.5 µg/l (1985), 0.1 µg/l (1986-1989 and 1991 in the Wupper) and 1 µg/l (1990/91) (exceptions: 2 out of 209 samples in 1991: 0.3 and 1.1 µg 3,4-dichloroaniline/l). The maximum concentrations of 2,4- plus 2,5-dichloroaniline in the Rhine between Lake Constance and the German-Dutch border (isomers not resolved) were 0.3\* µg/l (1989) and 0.2\* µg/l (1990/91). In 1990/91 no 2,4- plus 2,5-dichloroaniline was detected in approx. 40 % of the samples (< 0.05 µg/l).

In the Main in 1986 - 1988 the concentrations of 2,4-, 2,5- and 3,4-dichloroaniline were below the detection limits of 0.5 µg/l (1986/87) and 0.1 µg/l (1988). Between 1989 and 1991 the maximum levels of 2,4- plus 2,5-dichloroaniline were 0.5 - 0.7 µg/l\* (measured at Bischofsheim).

Very large amounts of herbicides, including Diuron, were used on Hawaii in the sixties and seventies (a total of 1,730 t in 1968). These substances entered the ocean by way of surface runoff. Besides Diuron, 3,4-dichloroaniline was found in sediment in concentrations of up to 0.95 mg/kg (dry weight) in 1972/73.

On the basis of a seepage study employing radiolabelled 3,4-dichloroaniline, 3,4-dichloroaniline is not expected to occur in soil seepage water.

In the US in 1978, 0.2 µg 3,4-dichloroaniline/l was found in the groundwater near a waste water treatment pond into which waste water contaminated with 6.11 µg 3,4-dichloroaniline/l had been discharged (97 % elimination).

In the Federal Republic of Germany in 1973/74 approx. 0.01 - 0.02 µg 3,4-dichloroaniline/l was found in drinking water obtained from surface water contaminated with 3,4-dichloroaniline (approx. 0.2 - 0.7 µg/l) (90 - 98 % elimination).

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\* values rounded off to one decimal place

In 1989 the Bundesgesundheitsamt (German Federal Health Authority) issued a recommendation that the testing of drinking water should be extended to include 3,4-dichloroaniline. In the Netherlands the concentrations of 3,4-dichloroaniline in drinking water between 1976 and 1986 were 0.03 - 1 µg/l.

3,4-Dichloroaniline is expected to occur in soils treated with herbicides which release 3,4-dichloroaniline. Field trials were carried out in the US with Linuron, Diuron and Propanil to determine soil concentrations of 3,4-dichloroaniline. 15 days to 3 years after the final application the maximum levels were < 0.1, 1 and 6 mg/kg respectively (the last two values comprising free plus bound substance; see below). In a field trial carried out in the Federal Republic of Germany by the Bayerische Landesanstalt für Bodenkultur und Pflanzenbau (Bavarian Institute of Soil Culture and Plant Cultivation) with herbicides (no details given) which release 3,4-dichloroaniline, the concentrations of free plus bound 3,4-dichloroaniline were below the detection limit of 0.005 mg/kg in 85 % of the 352 samples; the maximum level was 0.08 mg/kg.

The detection of traces of 3,4-dichloroaniline is to be expected in plants treated with herbicides which release 3,4-dichloroaniline, or in plants growing in treated soils:

Numerous studies carried out in the sixties and seventies with Linuron revealed 3,4-dichloroaniline concentrations at harvest of between 0.007 and 0.1 mg/kg in most cases and 0.1 - 0.7 mg/kg in some cases.

## **2. Behaviour in environmental compartments**

### **Atmosphere**

Half-lives  $t_{1/2}$  of 13 hours (2,4-) and 9 hours (2,5- and 3,4-dichloroaniline) have been calculated for the reaction with OH radicals in the troposphere.

## Hydrosphere

2,4- and 3,4-dichloroaniline are to be classified as sparingly volatile in water at 20 °C and 2,5-dichloroaniline as volatile.

Elimination from surface waters by means of sorption in sediment, mainly chemisorption, can play a significant role: At equilibrium after 50 hours, 93 % of 1 mg 3,4-dichloroaniline/l had been sorbed. Similar values can be expected for 2,4- and 2,5-dichloroaniline. In sediment, which is predominantly anaerobic, dichloroanilines are reductively dehalogenated by microorganisms, however the resulting monochloroanilines accumulate (confirmed for 2,4- and 3,4-dichloroaniline).

Photodegradation plays a significant role as an elimination path in surface waters: Half-lives  $t_{1/2}$  for the phototransformation of 2,4-dichloroaniline in natural solar radiation (latitude of 30° north) ranges from 26 hours in summer to 68 hours in winter. The values for the phototransformation of 3,4-dichloroaniline in natural solar radiation (latitude of 40 - 50° north) ranges from > 90 % in 5 hours at the surface of rice-paddy water to half-lives of  $t_{1/2}$  3.2 - days in a pond 1 m deep. No experimental results are available for 2,5-dichloroaniline. The position of the chlorine atoms in the benzene ring would lead one to expect somewhat slower photodegradation.

2,4-, 2,5- and 3,4-dichloroaniline are to be categorised as not readily biodegradable on the basis of the standard laboratory tests for readily biodegradability under aerobic conditions. No primary biodegradation of 2,4-dichloroaniline was determined in samples of Rhine water within 35 days. However, half-lives  $t_{1/2}$  of 49 days (Summer) to 92 days (Winter) were obtained for mineralisation, i.e. a combination of phototransformation of the 2,4-dichloroaniline and subsequent

photodegradation and biodegradation of the photoproducts. Low concentrations of 2,5-dichloroaniline in Rhine water samples (10 µg/l) showed 80 % primary biodegradation in 35 days. In surface water samples, no biodegradation of 3,4-dichloroaniline was measured over a period of 42 days at 12 °C in North Sea water, whereas primary degradation of up to ≥ 95 % was measured in samples of Rhine water at 22 °C over a period of 50 days. Using adapted inoculum, 3,4-dichloroaniline was degraded at a rate of 82 % in 28 days up to > 99 % in a continuous bioreactor for a residence time of 2 hours at 30 °C.

2,4-, 2,5- and 3,4-dichloroaniline are not expected to undergo significant elimination by hydrolysis under environmental conditions.

The elimination rates of 3,4-dichloroaniline were 8.5 - 15.5 % in 2 days and 50 % in 4.1 - 6 days (half-lives  $t_{1/2}$ ) in various model aquatic ecosystems.

## **Geosphere**

Overall, 2,4-, 2,5- and 3,4-dichloroaniline can be assumed to show a strong sorption tendency in soil.

3,4-Dichloroaniline is covalently bonded to the organic soil substance in a purely chemical reaction. Under aerobic conditions, 75 - 96 % of the 3,4-dichloroaniline was bonded at concentrations of 1 - 10 mg/kg. The bonding processes were for the most part complete in 1 - 2 days. The lower the soil pH and the higher the organic carbon content, the stronger the chemisorption will be. Somewhat weaker chemisorption is to be expected under anaerobic conditions. 2,4- and 2,5-dichloroaniline are expected to behave analogously.

Under aerobic conditions, primary degradation up to ring cleavage (92 - 100 % in 8 - 14 days) has been found in studies on 2,4-dichloroaniline with pure and mixed soil cultures adapted to structurally related substance

Primary degradation (ring cleavage and oxidative dehalogenation of both chlorine atoms) by mixed cultures adapted to structurally related substances has been detected under aerobic conditions in the case of 3,4-dichloroaniline. The metabolisation, including mineralisation to CO<sub>2</sub> of free 3,4-dichloroaniline and 3,4-dichloroaniline bonded to humic acid or lignin has been widely documented: The mineralisation rates in soil without added stimulators (1.9 - 11.9 % in 50 - 187 days at concentrations of 1 - 5 mg 3,4-dichloroaniline/kg) were within the range of humic acid mineralisation rates without bound 3,4-dichloroaniline (3.3 % in 100 days).

In laboratory experiments, 3,4-dichloroaniline can be converted into higher-molecular compounds such as 3,3', 4,4'-tetrachloroazobenzene (TCAB), 1,3-bis(3,4-dichlorophenyl)-triazene and di-, tri- and tetrachlorobiphenyls by isolated soil bacteria and fungi and in soil samples. A prerequisite for this conversion in soil is the presence of special NO<sub>3</sub><sup>-</sup>-reducing bacteria and NO<sub>3</sub><sup>-</sup> or the presence of peroxidases, e.g. fungal peroxidases, it being necessary to add H<sub>2</sub>O<sub>2</sub> in the latter case for laboratory experiments. The experiments which resulted in the formation of significant amounts of TCAB in soil samples involved high concentrations of 3,4-dichloroaniline: 50 - 2,000 mg/kg soil. At the lowest concentrations of 3,4-dichloroaniline tested, namely 1 - 30 mg/kg soil, 0.008 - 0.2 mg TCAB/kg was detected in laboratory tests after 7 - 31 days. Field trials with appropriate amounts of herbicides which release 3,4-dichloroaniline gave the following results: Depending on the kinetics of cleavage of the 3,4-dichloroaniline from the agent, temporarily higher concentrations of 3,4-dichloroaniline are to be expected. For example, the 3,4-dichloroaniline concentration in rice-paddy soil 3 days after the last application of Propanil showed a maximum of 29 mg/kg due to rapid degradation of the Propanil. During a 3-year treatment of a rice paddy with Propanil, a maximum of 0.06 mg TCAB/kg soil was measured. 15 days to 3 years after the

last application, the concentrations of 3,4-dichloroaniline and TCAB were as follows:

Linuron (single application) :	< 0.1 mg 3,4-DCA /kg;	<0.1 mg TCAB/kg
Diuron (4- to 12-year ) : application	max. 1 mg 3,4-DCA*/kg;	<0.1 mg TCAB/kg
Propanil (3-year application) :	approx. 6 mg 3,4-DCA*/kg;	<0.004 mg TCAB/kg

\* free plus bound 3,4-dichloroanilin

When finishing the treatment of the fields with these agents, slow biodegradation should also be assumed for the residual concentrations of 3,4-dichloroaniline (see above).

On the basis of studies on the bonding of 3,4-dichloroaniline to the organic soil substance, on the aerobic biodegradation of bonded 3,4-dichloroaniline in the soil and on seepage water transport, a temporary geoaccumulation of chemically bonded 3,4-dichloroaniline is to be expected, given a constant entry rate of 3,4-dichloroaniline and a fairly slow mineralisation of about the order of magnitude of the humic acid parent substances. Field trials with appropriate amounts of crop protection agents, however, do not reveal any geoaccumulation of free or bonded 3,4-dichloroaniline, even after several years of application. Taking into account the different reactivities, a similar behaviour in soils is to be expected for the structural isomers 2,4- and 2,5-dichloroaniline, with some limitations.

## **Biosphere**

2,4-, 2,5- and 3,4-dichloroaniline are to be categorised as minimally bioaccumulative on the basis of the BCF values for fish (4 - 95) and the log  $K_{OC}$  values. This also applies to dichloroaniline which may be chemically bound.

Although cultivated plants are able to readily absorb 3,4-dichloroaniline through their roots, the availability of the 3,4-dichloroaniline in soil is considerably reduced by

rapid bonding to the organic soil substance. The bulk of the amount absorbed remains in the roots, where most of it is bonded. In rice plants this amount was approx. 66 %, approx. 56 % of which was bonded to extractable lignin. Approx. 90 % of the 3,4-dichloroaniline was bonded in soya bean cell suspensions and wheat cell suspensions. Approx. 67 % was bonded to polar substances in soya bean cells and 52 % in wheat cells, mostly sugar conjugates and amino acid conjugates being formed. The rest was bonded to non-extractable cell wall constituents in different proportions according to plant type lignin (10 – 60 %), pectin (15 - 30 %), starch (5 - 40 %), protein (5 - 20 %), hemicellulose (5 - 10 %) and cellulose (0.2 - 5 %).

### 3. Ecotoxicology

#### Effects on aquatic organisms

A study of the cell proliferation of representatives of the common bacterium *Pseudomonas* gave an 8 h-NOEC of 10 mg 2,4-dichloroaniline/l and a 16 - 18 h-“TGK“ (toxic threshold concentration) of 19 or 23 mg 3,4-dichloroaniline/l. Whereas the respiration of *Pseudomonas* was not inhibited at a level of 125 mg 2,5-dichloroaniline/l following 30 minutes of exposure, the 3 h-IC<sub>50</sub> for 3,4-dichloroaniline was 100 mg/l when activated sludge was used. The cell proliferation of a cyanobacterium reacted more sensitively to 2,4-dichloroaniline, the 96 h-NOEC being 1 mg/l in this case.

The 22 h-“TGK“ for the cell proliferation of a protozoan was 1.6 mg 3,4-dichloroaniline/l and the 24 h- of another representative was 9 mg 3,4-dichloroaniline/l and 31 mg 2,4-dichloroaniline/l.

The cell proliferation of yeast fungi showed widely differing, species-dependent levels of sensitivity to 2,4-dichloroaniline. The 24 h-IC<sub>50</sub> values were 18 - 191 mg/l.

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0.7 - 3.2 mg 2,4-dichloroaniline/l, 3.2 or 5 mg 2,5-dichloroaniline/l and 1 - 2.4 mg 3,4-dichloroaniline/l had either no influence (96 h-NOEC) or a small influence (48 to 168 h-IC<sub>50</sub>) on the cell proliferation of single-cell algae. The 48 to 168 h-IC<sub>50</sub> values were 11 and approx. 17 mg/l for 2,4- and 2,5-dichloroaniline respectively. 3,4-dichloroaniline showed a very steep dose-effect relationship: The 48 - 96 h IC<sub>50</sub> values were 2.2 - 6.8 mg/l. A single 96 h-IC<sub>50</sub> value - for a saltwater alga - was 0.45 mg 3,4-dichloroaniline/l.

The photosynthesis of a single-cell green alga was influenced as follows by 2,4-dichloroaniline after 2 - 3 hours of exposure: IC<sub>10</sub> 0.6 mg/l; IC<sub>50</sub> = 5.1 mg/l.

1 mg 2,4-dichloroaniline/l had no influence on the growth of an aquatic plant (7 d-NOEC).

10 mg 2,4-dichloroaniline/l had no effect on the development and survival rate of insect larvae (mosquitoes) living in water (25 d-NOEC). *Chironomus* larvae reacted with greater sensitivity to 3,4-dichloroaniline with a 10 d-LC<sub>50</sub> of 4.2 mg/l.

In tests according to standard or equivalent procedures in which larvae are used at the beginning of the tests, the following values were recorded for *Daphnia magna* [mg/l]:

		2,4-DCA	2,5-DCA	3,4-DCA
Ability to swim	24/48 h-EC <sub>0</sub>	0.63 - 1.3	2.6	0.14/0.6
	24/48 h-EC <sub>50</sub>	2.8 - 4.4	4.1	3/6
Mortality or mortality and ability to swim	24-96 h-LC <sub>50</sub> or -EC <sub>50</sub>	0.85	-	0.16 - 0.5*
Mortality and reproduction rate	14/21 d-NOEC	0.032	0.16	0.0056 - 0.012

\* *Daphnia longispina*: 0.44 mg/l

In tests with other freshwater or saltwater crustaceans, the 24 - 96 h-LC<sub>50</sub> values for 3,4-dichloroaniline were 1.3 - 36 mg/l with larvae, young or adults. A 28 d-NOEC of 0.032 mg/l was determined for the reproduction and mortality of *Artema salina* larvae.

In acute tests, freshwater and saltwater worms (larvae and adults) reacted to 3,4-dichloroaniline less sensitively than the daphniae with 24 - 96 h-LC<sub>50</sub> values of 4 - 62 mg/l. In a chronic test on one chaetopod, however, the 38 d-NOEC for mortality, reproduction and growth was 0.003 mg/l.

The 48 h and 7 d LC<sub>50</sub> for snail eggs or larvae was > 32 and 18 mg 3,4-dichloroaniline/l respectively. 1 mg 2,4-dichloroaniline/l had no influence on the reproduction and mortality of adult Lymnaeids (40 d-NOEC).

The 96 h to 28 d-LC<sub>50</sub> values for adult freshwater and salt water mussels were in the range 6.5 - 22 mg 3,4-dichloroaniline/l.

The following values were recorded for freshwater fish in acute tests according to standard or equivalent procedures using young fish [mg/l]:

		2,4-DCA	2,5-DCA	3,4-DCA
Mortality, behaviour, color	: 96 h-NOEC	5.6	-	1/1.8
Mortality	: 96 h-LC <sub>0</sub>	-	1	10
	: 24 - 96 h-LC <sub>50</sub>	5.7-16	(10.8)*	7 - 13 : 20 values for 5 different fish species 1.94 : rainbow-trout
	: 7-28 d-LC <sub>50</sub>	1.66/11.7	6.3	0.18 - 8.5

\* no indication of whether young were used

Young and adult fish tested in saltwater (3 species) showed 48 and 96 h LC<sub>50</sub> values of 2.4 - 6.5 mg 3,4-dichloroaniline/l.

In chronic tests, including early-life-stage and life-cycle tests, the threshold concentrations (NOEC, LOEC) for the effect of 3,4-dichloroaniline on body length, body weight, deformation, mortality and reproduction, following 4 to a maximum of 16 weeks of exposure, were 0.002 - 0.2 mg/l as tested on 4 fish species, among them the rainbow trout.

In a model freshwater ecosystem at the lowest tested concentration of 0.01 mg 2,4-dichloroaniline/l, this substance brought about a permanent change in the ecosystem after 5 or 23 days in that it established a new equilibrium in terms of the biomass of the algae and the number of daphniae and polyps.

3,4-Dichloroaniline significantly inhibited the birth rate of *Daphnia longispina* beginning on day 1 and the population density beginning on day 14 or 7 in a model freshwater ecosystem in which, after the selected concentrations had been maintained at a constant level for 28 days (0.045 and 0.45 mg/l), the levels then dropped between days 28 and 40 or 45 to < 10 %. In all cases, the control values had been reached again by the end of the experiment (day 85) and at the earliest by day 31. 0.045 mg/l had no significant influence on the population density of copepods up to the end of the experiment and neither concentration level had a significant influence on the diversity of mollusc and insect species by day 29 or 32.

Concentrations of 0.002, 0.01 and 0.025 mg 3,4-dichloroaniline/l did not disturb the microcosm of a model marine ecosystem (phytoplankton, zooplankton, bacteria) within the 33-day exposure period. 0.1 mg/l caused a temporary inhibition or change in 4 out of 9 criteria following the 38 day exposure period and 1 mg/l led to inhibition or change in 8

out of 9 criteria, persisting up to the end of the exposure period. The concentrations at the end of the experiment were approx. 50 % of the nominal initial concentrations.

On the basis of the validated biodegradation, bioaccumulation and aquatotoxicity data listed in this report, 2,4-, 2,5- and 3,4-dichloroaniline, according to EC guideline 93/21/EEC on the 18th technical progress amendment of guideline 67/548/EEC of the Commission on Categorisation, Packaging and Labelling of Hazardous Materials, are environmentally hazardous for the aquatic compartment, are toxic (2,4- and 2,5-dichloroaniline) or highly toxic (3,4-dichloroaniline) to aquatic organisms and may have longer-term damaging effects in surface waters.

### **Effects on terrestrial organisms**

Whereas 49 mg 3,4-dichloroaniline/l nutrient medium following 2 - 22 hours of exposure under aerobic conditions showed no significant influence (1 or 2 % inhibition) on the cell proliferation and respiration of a *Pseudomonas* strain isolated from soil, the inhibition of other soil bacteria was 57 and 95 % (cell proliferation), 30 and 33 % (respiration) and - for the above-mentioned *Pseudomonas* strain under anaerobic conditions - 35 and 52 %.

2,5- and 3,4-dichloroaniline showed no significant influence on bacterial nitrification in concentrations of 2.5 and 5 mg/kg soil (dry weight). 100 mg of 2,4-dichloroaniline delayed the onset of nitrification by 46 days, but did not influence the reaction rate.

49 mg 3,4-dichloroaniline/l inhibited the mycelial growth of fungi after 4 - 5 days of exposure to very variable extents of 18 to 80 %, depending on the species.

For the mycelial growth of white rot fungi, the toxic threshold concentrations after 12 days of exposure were between 10 and 30 mg/l.

In a growth inhibition test involving three species of higher plants, 2,4-dichloroaniline had less effect on growth in various soils than on growth in nutrient solution, due to rapid covalent bonding to the organic soil substance. Whereas in clay soil (1.4 % organic substance) the 14 d-NOEC was 10 mg/kg soil (dry weight) and the 14 d EC<sub>50</sub> was 18 and 28 mg/kg soil (dry weight), the values for sandy humus soil (3.7 % organic substance) were: 14 d-NOEC = 32 mg/kg soil (dry weight) and 14 d-EC<sub>50</sub> 68 - 136 mg/kg soil (dry weight).

The 14 d-LC<sub>50</sub> values for adult annelids, determined in various soils, were within the range 142 - 824 mg/kg soil (dry weight) for 2,4-dichloroaniline, depending on the organic substance content (3.7 - 15.6 %). The 14 d-LC<sub>50</sub> values for 3,4-dichloroaniline at an organic substance content of 1.7 - 7.7 % were within the range 100 - 320 mg/kg soil (dry weight). A study of the effect of 2,4-dichloroaniline on reproduction in artificial OECD soil (approx. 8 % organic substance) revealed a 21 d-NOEC of 56 mg/kg soil (dry weight) for egg laying. 100 mg/kg soil (dry weight) had no influence on egg development following the 21 day exposure period.

18 h-LD<sub>50</sub> values of 237 and 562 mg 3,4-dichloroaniline/kg body weight were determined for birds.

### **Toxicological aspects**

2,4-, 2,5-, and 3,4-dichloroaniline may be absorbed through the gastrointestinal tract, the skin and the lungs. *In vivo* tests showed hydroxylation of dichloroanilines in the ortho or para position relative to the amino group. The metabolites thus formed were identified in rabbit urine. Hydroxylation at the nitrogen atom was also observed *in vitro*. The rat rapidly excreted orally administered 3,4-dichloroaniline, predominantly in urine and, to a lesser extent, in faeces.

Like other chloroanilines, the primary toxic effect of 2,4-, 2,5-, and 3,4-dichloroaniline is methaemoglobin formation, which is attributed to the intermediate formation of hydroxylated metabolites. Acute intoxication is indicated by the symptoms of methaemoglobinaemia (cyanosis, fatigue, dyspnoea, muscle weakness). Judging by doses which had an effect in animal experiments, dichloroanilines showed moderate acute toxicity.

After occlusive application to experimental animals, 2,4-dichloroaniline was moderately irritant on skin. 3,4-dichloroaniline was not irritant on rabbit skin, and the results for irritancy in the eye varied from not irritant to irritant. The 2,5-isomer was not irritant on rabbit skin, but caused irritant effects in the eye; the effects were severe and not completely reversible. The hyperkeratogenous and acnegenic effects documented in the literature were attributed to 3,3', 4,4'-tetrachloroazobenzene and 3,3', 4,4'-tetrachloro-azoxybenzene, impurities formerly present in industrial 3,4-dichloroaniline.

3,4-dichloroaniline had no photoallergic effect on the mouse. The maximisation test on the guinea pig revealed that 3,4- and 2,5-dichloroaniline had skin sensitising potential. There are no data on the sensitising effect of the 2,4-isomer.

Like after acute application, haematological changes become evident after repeated application of dichloroanilines. An increase in both haemoglobin break-down and haematopoiesis was observed in the rat after subacute oral administration of 2,5-dichloroaniline at doses of 150 mg/kg body weight and above. The NOEL was 30 mg/kg body weight per day. After repeated administration of 3,4-dichloroaniline by inhalation (6 h/d, 5 d/w over 2 weeks), there was evidence of slight methaemoglobin formation at an exposure concentration of 10 mg/m<sup>3</sup> and above, histopathological changes in the spleen (haemosiderin deposits) at 45 mg/m<sup>3</sup> and above and extramedullary haematopoiesis at 200 mg/m<sup>3</sup>.

Most of the mutagenicity tests carried out did not indicate any genotoxic effects of dichloroanilines. None of the isomers considered here was mutagenic in the numerous Ames tests, either with or without metabolic activation, or when Norharman was added.

2,5-dichloroaniline did not cause any chromosomal damage to V79 cells in the chromosome aberration test, it was not mutagenic in *E. coli* WP2uvrA, and it did not damage DNA in the UDS test on hepatic cells.

Similarly, 3,4-dichloroaniline did not have any mutagenic activity in mammalian cells in the HGPRT test. A positive result was recorded in the fungus *Aspergillus nidulans* and in the pol A<sub>1</sub><sup>-</sup>-test on *E. coli*. Several UDS tests on hepatic cells showed that 3,4-dichloroaniline did not damage DNA; one UDS test recorded a weak positive result. There was no increase in the frequency of sister chromatid exchanges in lymphocytes without metabolic activation, but an increase was observed when S9 mix was added. There was no indication of chromosomal damage in *Allium cepa*, in mammalian cells during the chromosome aberration test and *in vivo* in the mouse during the micronucleus test for 3,4-dichloroaniline.

There are no studies on carcinogenicity.

3,4-dichloroaniline was not teratogenic in animal experiments and was embryotoxic only at distinctly maternotoxic doses.

Methaemoglobinaemia occurred in workers exposed to dichloroanilines. Cases of chloracne recorded in previous years after exposure to industrial 3,4-dichloroaniline are attributed to contamination with 3,3', 4,4'-tetrachloroazobenzene or 3,3', 4,4'-tetrachloroazoxybenzene. Since the introduction of 3,4-dichloroaniline containing virtually no 3,3', 4,4'-tetrachloroazobenzene or 3,3', 4,4'-tetrachloroazoxybenzene, there have been no more cases of chloracne in Germany.

## **Recommendations**

### **Ecology**

The ecotoxicological and environmental behaviour data provided in the present report are considered to be a sufficient basis for assessment of the environmental impact of 2,4-, 2,5- and 3,4-dichloroaniline.

### **Toxicological aspect**

The toxicologically relevant properties of 3,4-dichloroaniline have largely been clarified. There are no data available on carcinogenicity. Although most of the data on genotoxicity are negative, a genotoxic and carcinogenic effect cannot be ruled out with certainty because of the structure. In order to clarify these remaining questions, the Trade Association of the Chemical Industry (BG Chemie) is currently assessing mononuclear aromatic amines, and a decision on any further studies will thus be deferred until the results are available.

Studies on 2,5-dichloroaniline and particularly on 2,4-dichloroaniline are not available for all relevant end points. The structural affinity with 3,4-dichloroaniline and comparison of the available toxicological data for the three substances suggest that all three isomers are likely to have a similar toxicological profile. Further studies are therefore not necessary at the present time.