



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

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

Chairman:

Prof. Dr. E. Bayer, Institut für Organische Chemie der Universität Tübingen

Members:

Dr. G. Alfke, Mineralölwirtschaftsverband e. V., Hamburg

Prof. Dr. K. Ballschmiter, Abteilung Analytische Chemie und Umweltchemie der Universität Ulm

Dr. R. Bias, BASF AG, Emissionsüberwachung und Ökologie, Ludwigshafen a. Rh.

Dr. B. Broecker †, HOECHST AG, Abteilung Umweltchemikalien/Verbrauchersicherheit, Frankfurt am Main

Prof. Dr. O. Fränzle, Geographisches Institut der Universität Kiel

Prof. Dr. F. H. Frimmel, DVGW-Forschungsstelle am Engler-Bunte-Institut der Universität Karlsruhe

Prof. Dr. H.-P. Gelbke, BASF AG, Toxikologie, Ludwigshafen a. Rh.

Prof. Dr. H. Greim, GSF - Institut für Toxikologie, Neuherberg (Vice Chairman)

Dir. und Prof. Dr. J. Hahn, Institut für Wasser-, Boden- und Lufthygiene des Umweltbundesamtes, Berlin

Dr. H. Jungen, Deutsche Wissenschaftliche Gesellschaft für Erdöl, Erdgas und Kohle e. V., Hamburg

Dir. und Prof. Dr. D. Kayser, Bundesinstitut für gesundheitlichen Verbraucherschutz und Veterinärmedizin, Berlin

Dr. W. Mühlhölzl, Bayerische Landesanstalt für Wasserforschung, München

Prof. Dr. P. Müller, Institut für Biogeographie, Universität des Saarlandes, Saarbrücken

Dir. und Prof. Dr. E. Offhaus, Umweltbundesamt, Berlin

Dr. R. Ott, Deutsche Shell Chemie GmbH, Eschborn/Ts.

MinRat Prof. Dr. U. Schlottmann, Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit, Bonn

Dr. N. Schön, BAYER AG, Umweltschutz/Produktsicherheit, Leverkusen

Vizepräsident Dr. A. Troge, Umweltbundesamt, Berlin

Collaborators and Guests:

Dr. K. H. Adlfinger, Initiative Umweltrelevante Altstoffe, Frankfurt am Main

Priv.-Doz. Dr. J. Ahlers, Fachgebiet IV 1.2 des Umweltbundesamtes, Berlin

Dr. S. Ettel, Institut für Organische Chemie der Universität Tübingen

Frau Dipl.-Geoökol. A. Geschke, BAYER AG, Toxikologie, Wuppertal

Dr. R. F. Hertel, Fachgruppe 821 des Bundesinstituts für gesundheitlichen Verbraucherschutz und Veterinärmedizin, Berlin

Dr. J. Koppenhöfer, Institut für Organische Chemie der Universität Tübingen

Prof. Dr. R. Kümmel, Institut für Umwelt- und Sicherheitstechnik der Fraunhofer Management-Gesellschaft, Oberhausen

Frau Dr. I. Mangelsdorf, GSF - Institut für Toxikologie, Neuherberg

Dr. J. Oberhansberg, BG Chemie, Heidelberg

Frau Dr. H. Sterzl-Eckert, GSF - Institut für Toxikologie, Neuherberg

Dr. D. Vogel, Institut für Organische Chemie der Universität Tübingen

Frau Dipl.-Biol. L. Weis, Institut für Organische Chemie der Universität Tübingen

Frau Dr. K. Widmann, Institut für Organische Chemie der Universität Tübingen

Frau Chr. Wötzel, BAYER AG, Umweltschutz, Leverkusen

GDCh Office:

Dr. H. Behret, GDCh, Frankfurt am Main

Dichloroaniline

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

BUA Report 140

(October 1993)

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

Beratergremium für
Umweltrelevante Altstoffe (BUA)



S. Hirzel

Wissenschaftliche Verlagsgesellschaft 1996

Dr. H. Behret
Gesellschaft Deutscher Chemiker
Postfach 90 04 40
D-60444 Frankfurt am Main

Translated by P. Karbe

This book was carefully produced. Nevertheless, authors, editors and publisher do not warrant the information contained therein to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

The use of general descriptive names, trade names, trademarks, etc. in a publication, even if not specifically identified, does not imply that these names are not protected by the relevant law and regulations.

Die Deutsche Bibliothek - CIP-Einheitsaufnahme

Dichloroaniline (2,4-, 2,5- and 3,4-Dichloroaniline) / GDCh
Advisory Committee on Existing Chemicals of Environmental
Relevance (BUA). – [Transl. by P. Karbe]. - (October 1993). -
Stuttgart: Hirzel ; Stuttgart : Wiss. Verl.-Ges., 1996
(BUA report; 140)
Dt. Ausg. u.d.T.: (2,4-Dichloranilin, 2,5-Dichloranilin and 3,4-
Dichloranilin)
ISBN 3-7776-0715-0
NE: Karbe, P.. [Übers.]; Gesellschaft Deutscher Chemiker /
Beratergremium für Umweltrelevante Altstoffe: BUA report

All rights reserved. No part of this publication may be translated, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without permission in writing from the publisher.

© 1996 S. Hirzel Verlag, Birkenwaldstraße 44, 70191 Stuttgart

Printed in acid-free and low-chlorine paper.

Printing and binding: Druckhaus Beltz, Hemsbach
Printed in F.R. Germany

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

Contents

Summary and Conclusions	XI
--------------------------------------	-----------

Recommendations	XX
------------------------------	-----------

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

(1-amino-2,4-dichlorobenzene, 1-amino-2,5-dichlorobenzene,
1-amino-3,4-dichlorobenzene)

1. Chemistry of 2,4-, 2,5- and 3,4-Dichloroaniline aniline	1
1.1 Chemical Identity	1
1.2 Composition of the Technical Product	2
1.3 Chemical Properties	2
2. Physical Properties	4
3. Analysis	9
3.1 General Information	9
3.2 Determination in Air	12
3.3 Determination in Water	13
3.4 Determination in Soil, Sediment and Biological Material	25
4. Introduction into the Environ through Production, Processing, Application and Waste Disposal	31
4.1 Production Methods	31
4.2 Manufacturers and Processors, Production Quantities, Export, Import, Total Consumption	32
4.3 Processing, Application, Consumption Quantities	35
4.4 Introduction into the Atmosphere	40
4.4.1 Introduction through Production and Processing	40
4.4.2 Introduction through Application	41
4.5 Introduction into the Hydrosphere	41
4.5.1 Introduction through Production and Processing	41
4.5.2 Introduction through Application	44
4.5.3 Introduction of 3,4-Dichloroaniline through the Application of Crop Protection Active Ingredients	44
4.5.4 Introduction through Reduction of Dichloro-nitrobenzenes	46

4.6	Introduction into the Geosphere and Biosphere	47
4.6.1	Introduction of 3,4-Dichloroaniline through the Application of Crop Protection Active Ingredients	47
4.7	Introduction through Wastes and Their Treatment	53
4.8	Balance of Environmental Introduction	54
5.	Environmental Occurrence	57
5.1	Atmosphere	57
5.2	Hydrosphere	57
5.2.1	Waters	57
5.2.1.1	The Rhine and Its Tributaries	57
5.2.1.2	The Main River	63
5.2.2	Sediment	63
5.2.3	Seepage Water	64
5.2.4	Groundwater	65
5.2.5	Drinking Water	65
5.3	Geosphere	67
5.4	Biosphere	68
5.5	Natural Sources	69
6.	Environmental Behavior	70
6.1	Transformation, Degradation, Degradation Products	70
6.1.1	Air	71
6.1.1.1	Photochemical Transformation	71
6.1.2	Water	71
6.1.2.1	Photochemical Transformation	71
6.1.2.2	Sorption from the Aqueous Phase to the Sediment	82
6.1.2.3	Microbial Transformation (Aerobic)	82
	1. Activated Sludge and Waste Water as Inoculum	82
	2. Water Samples as Inoculum	86
6.1.2.4	Hydrolysis	87
6.1.2.5	Transformation in Model Aquatic Ecosystems	87
6.1.3	Sediment	89
6.1.3.1	Microbial Transformation (Anaerobic)	89
6.1.4	Soil	91
6.1.4.1	Covalent Binding to the Organic Substance of the Soil (Aerobic/Anaerobic)	91
6.1.4.2	Transformation of Dichloroaniline, Free and Bound in the Soil (Aerobic/Anaerobic)	99
6.1.4.2.1	Biodegradation in the Soil (Aerobic)	99
	1. Bacterial Pure Cultures as Inoculum	99
	2. Fungal Pure Cultures as Inoculum	105
	3. Mixed Cultures as Inoculum	109
	4. Soil Samples as Inoculum	111

6.1.4.2.2	Biotransformation to High-Molecular Compounds in the Soil (Aerobic/Anaerobic)	116
1.	Bacterial Pure Cultures am Inoculum	116
2.	Fungal Pure Cultures am Inoculum and Investigations with Isolated Fungal Enzymes	119
3.	Soil Samples as Inoculum	121
6.1.5	Plants	125
6.1.6	Fate of 3,4-Dichloroaniline Released from Herbicides in Water, Soil and Plants	129
6.1.7	Summary (Biodegradation)	132
6.2	Accumulation	133
6.2.1	Bioaccumulation	133
6.2.2	Geoaccumulation	136
6.3	Partitioning Behavior and Transport Processes within and between Environmental Compartments	137
6.3.1	Henry's Law Constant	137
6.3.2	n-Octanol/Water Partition Coefficient	138
6.3.3	Soil Sorption Coefficients	138
6.3.4	Distribution in the Soil/Plant System	144
6.4	Environmental Fate	146
7.	Ecotoxicity	153
7.1	Effects on Aquatic Organisms	153
7.1.1	Microorganisms	154
-	Bacteria	155
-	Protozoa	157
-	Unicellular Fungi	157
7.1.2	Plants	159
-	Unicellular Algae	159
-	Seed Plants	161
7.1.3	Invertebrates	162
-	Insect Larvae	162
-	Crustaceans - Water Fleas (Daphniae)	162
-	Crustaceans - (Except Daphniae)	170
-	Worms	173
-	Hydrozoa and Mollusks	174
7.1.4	Vertebrates	175
-	Fish	175
7.2	Effects on Terrestrial Organisms	185
7.2.1	Microorganisms	185
-	Bacteria	185
-	Fungi	187
7.2.2	Plants	189
7.2.3	Invertebrates	192
-	Worms	192
7.2.4	Vertebrates	195
-	Birds	195
7.3	Effects on Ecosystems (Model Ecosystems)	196
-	Freshwater Ecosystems	196
-	Marine Ecosystem	198

8.	Toxicity in Warm-Blooded Animals	201
8.1	General Effects	201
8.2	Mode of Action	201
8.3.	Metabolism, Toxicokinetics	202
8.3.1	Absorption	202
8.3.2	Distribution in Tissue	202
8.3.3	Biotransformation	202
8.3;4	Macromolecular Binding	203
8.3.5	Elimination	203
8.4	Acute Toxicity	204
8.5	Skin and Mucous Membrane Tolerance	207
8.6	Sensitization	211
8.7	Subacute, Subchronic and Chronic Toxicity	212
8.8	Genotoxicity	213
8.8.1	Gene Mutations	218
8.8.2	DNA Damage	218
8.8.3	Chromosome Damage	219
8.8.4	Other Studies	219
8.9	Carcinogenicity	225
8.10	Reproductive Toxicity	225
8.11	Other Effects	226
8.11.1	Methemoglobin Formation	226
8.11.2	Effects on the Metabolic Functions of the Liver	234
8.11.3	Hyperkeratogenic Effects of Impurities in 3,4-Dichloroaniline	235
8.12	Human Cases	236
9.	Substance-Specific Legal Regulations	239
9.1	Chemicals Act and Hazardous Substances Order	239
9.2	Safety Rules at the Workplace	239
9.3	Federal Clean Air Act and "TA-Luft"	239
9.4	Water Supply Act and Regulations on Water-Polluting Substances	240
9.5	Drinking Water Regulations and Recommend- tions of the German Health Agency	242
9.6	Waste Act and "TA-Abfall"	242
9.7	Transport Regulations	243
10	References	245