

# The Handbook of Environmental Chemistry

Volume 1 Part C

Edited by O. Hutzinger

# The Natural Environment and the Biogeochemical Cycles

With Contributions by  
G. G. Choudhry, E. T. Degens, M. Ehrhardt,  
R. D. Hauck, S. Kempe, L. W. Lion,  
A. Spitzzy, P. J. Wangersky

With 55 Figures



Springer-Verlag  
Berlin Heidelberg GmbH 1984

Professor Dr. Otto Hutzinger  
University of Bayreuth  
Chair of Ecological Chemistry and Geochemistry  
Postfach 3008, D-8580 Bayreuth  
Federal Republic of Germany

Library of Congress Cataloging in Publication Data

Main entry under title: The Natural environment and the biogeochemical cycles. (The Handbook of environmental chemistry; v. 1, pt. A-C)

Includes bibliographical references and index.

1. Biogeochemical cycles. 2. Environmental chemistry. I. Craig, P. (Peter), 1944-. II. Series.

QD31.H335 vol. 1, pt. A-C 574.5'22s [574.5'222] 80-16608 [QH344]

ISBN 978-3-662-15235-5 ISBN 978-3-540-38829-6 (eBook)

DOI 10.1007/978-3-540-38829-6

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically those of translation, reprinting, re-use of illustrations, broadcasting, reproduction by photocopying machine or similar means, and storage in data banks. Under § 54 of the German Copyright Law where copies are made for other than private use, a fee is payable to „Verwertungsgesellschaft Wort“, Munich.

© by Springer-Verlag Berlin Heidelberg 1984

Originally published by Springer-Verlag Berlin Heidelberg New York in 1984.

Softcover reprint of the hardcover 1st edition 1984

The use of registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

2154/3140-543210

## Preface

Environmental Chemistry is a relatively young science. Interest in this subject, however, is growing very rapidly and, although no agreement has been reached as yet about the exact content and limits of this interdisciplinary discipline, there appears to be increasing interest in seeing environmental topics which are based on chemistry embodied in this subject. One of the first objectives of Environmental Chemistry must be the study of the environment and of natural chemical processes which occur in the environment. A major purpose of this series on Environmental Chemistry, therefore, is to present a reasonably uniform view of various aspects of the chemistry of the environment and chemical reactions occurring in the environment.

The industrial activities of man have given a new dimension to Environmental Chemistry. We have now synthesized and described over five million chemical compounds and chemical industry produces about hundred and fifty million tons of synthetic chemicals annually. We ship billions of tons of oil per year and through mining operations and other geophysical modifications, large quantities of inorganic and organic materials are released from their natural deposits. Cities and metropolitan areas of up to 15 million inhabitants produce large quantities of waste in relatively small and confined areas. Much of the chemical products and waste products of modern society are released into the environment either during production, storage, transport, use or ultimate disposal. These released materials participate in natural cycles and reactions and frequently lead to interference and disturbance of natural systems.

Environmental Chemistry is concerned with *reactions in the environment*. It is about distribution and equilibria between environmental compartments. It is about reactions, pathways, thermodynamics and kinetics. An important purpose of this Handbook is to aid understanding of the basic distribution and chemical reaction processes which occur in the environment.

Laws regulating toxic substances in various countries are designed to assess and control risk of chemicals to man and his environment. Science can contribute in two areas to this assessment; firstly in the area of toxicology and secondly in the area of chemical exposure. The available concentration ("environmental exposure concentration") depends on the fate of chemical compounds in the environment and thus their distribution and reaction behaviour in the environment. One very important contribution of Environmental Chemistry to the above mentioned toxic substances laws is to develop laboratory test

methods, or mathematical correlations and models that predict the environmental fate of new chemical compounds. The third purpose of this Handbook is to help in the basic understanding and development of such test methods and models.

The last explicit purpose of the Handbook is to present, in concise form, the most important properties relating to environmental chemistry and hazard assessment for the most important series of chemical compounds.

At the moment three volumes of the Handbook are planned. Volume 1 deals with the natural environment and the biogeochemical cycles therein, including some background information such as energetics and ecology. Volume 2 is concerned with reactions and processes in the environment and deals with physical factors such as transport and adsorption, and chemical, photochemical and biochemical reactions in the environment, as well as some aspects of pharmacokinetics and metabolism within organisms. Volume 3 deals with anthropogenic compounds, their chemical backgrounds, production methods and information about their use, their environmental behaviour, analytical methodology and some important aspects of their toxic effects. The material for volume 1, 2 and 3 was each more than could easily be fitted into a single volume, and for this reason, as well as for the purpose of rapid publication of available manuscripts, all three volumes were divided in the parts A and B. Publisher and editor hope to keep materials of the volumes one to three up to date and to extend coverage in the subject areas by publishing further parts in the future. Readers are encouraged to offer suggestions and advice as to future editions of "The Handbook of Environmental Chemistry".

Most chapters in the Handbook are written to a fairly advanced level and should be of interest to the graduate student and practising scientist. I also hope that the subject matter treated will be of interest to people outside chemistry and to scientists in industry as well as government and regulatory bodies. It would be very satisfying for me to see the books used as a basis for developing graduate courses on Environmental Chemistry.

Due to the breadth of the subject matter, it was not easy to edit this Handbook. Specialists had to be found in quite different areas of science who were willing to contribute a chapter within the prescribed schedule. It is with great satisfaction that I thank all 52 authors from 8 countries for their understanding and for devoting their time to this effort. Special thanks are due to Dr. F. Boschke of Springer for his advice and discussions throughout all stages of preparation of the Handbook. Mrs. A. Heinrich of Springer has significantly contributed to the technical development of the book through her conscientious and efficient work. Finally I like to thank my family, students and colleagues for being so patient with me during several critical phases of preparation for the Handbook, and to some colleagues and the secretaries for technical help.

I consider it a privilege to see my chosen subject grow. My interest in Environmental Chemistry dates back to my early college days in Vienna. I received significant impulses during my postdoctoral period at the University of California and my interest slowly developed during my time with the

National Research Council of Canada, before I could devote my full time to Environmental Chemistry, here in Amsterdam. I hope this Handbook may help deepen the interest of other scientists in this subject.

O. Hutzinger

## **Preface to Parts C of the Handbook**

Parts C of the three series

- The Natural Environment and the Biogeochemical Cycles (Vol. 1)
- Reactions and Processes (Vol. 2)
- Anthropogenic Compounds (Vol. 3)

are now either available or in press. During their preparation it became obvious that further parts will have to follow to present the respective subject matters in reasonably complete form.

The publisher and editor have further agreed to expand the Handbook by three new series: Air Pollution, Water Pollution and Environmental Trace Analysis.

Again, I thank all authors as well as collaborators at the Springer Publishing House for their cooperation and help. Thanks are also due to many environmental chemists and reviewers in particular for their critical comments and their positive reception of the Handbook.

Bayreuth, December 1983

Otto Hutzinger

## Contents

### **Humic Substances. Structural Aspects, and Photophysical, Photochemical and Free Radical Characteristics**

*G. G. Choudhry*

Background . . . . .	1
Definitions . . . . .	1
Occurrence and Origin . . . . .	2
Structural Aspects . . . . .	2
Molecular Weights . . . . .	2
Elemental Composition . . . . .	3
Functional Groups . . . . .	3
NMR Spectrometry . . . . .	4
Products Obtained by Degradation and Physical Separation . . . . .	5
Working Hypotheses on Chemical Structure . . . . .	9
Visible and Ultraviolet Light Absorbing Characteristics . . . . .	13
Fluorescent Characteristics . . . . .	14
Free Radical Characteristics . . . . .	15
Irradiations . . . . .	18
References . . . . .	22

### **Organic Material in Sea Water**

*P. J. Wangersky*

Introduction . . . . .	25
Sampling Methods . . . . .	25
The Surface Film . . . . .	26
The Constituents of the Water Column . . . . .	27
The Volatile Fraction . . . . .	27
The Particulate Fraction . . . . .	28
The Dissolved Fraction . . . . .	28
Analytical Methods . . . . .	30
Organic Carbon . . . . .	31
Organic Nitrogen and Phosphorus . . . . .	32

Analysis by Compound Class . . . . .	32
Analysis for Specific Compounds . . . . .	33
Distributions . . . . .	35
Horizontal Distributions of Organic Materials . . . . .	35
Estuaries . . . . .	36
Coastal Zones . . . . .	36
The Open Ocean . . . . .	37
Vertical Distribution of Organic Materials . . . . .	39
The Surface Microlayer . . . . .	39
The Mixed Layer . . . . .	40
The Deep Water . . . . .	41
Sediment-Water Interface . . . . .	42
The Sediment . . . . .	43
Sources of Organic Materials . . . . .	44
Terrestrial Sources . . . . .	44
Estuaries and Coastal Zones . . . . .	45
The Open Ocean . . . . .	46
Sinks . . . . .	47
Photodecomposition . . . . .	48
Heterotrophy . . . . .	48
Larger Organisms . . . . .	48
Phytoplankton . . . . .	49
Bacteria . . . . .	49
Removal to the Sediment . . . . .	50
Incorporation of DOM Into POM . . . . .	50
The Large Particle Problem . . . . .	51
Sinking of POM . . . . .	51
Heterotrophy at the Sea Floor . . . . .	52
The Cycle of Organic Carbon in the Sea . . . . .	53
Acknowledgements . . . . .	54
References . . . . .	54

## **Marine Gelbstoff**

*M. Ehrhardt*

Early Observations – the Origin of the Concept . . . . .	63
Isolation of Marine Gelbstoff . . . . .	64
Sources of Marine Gelbstoff . . . . .	65
Differentiation Between Terrestrial and Marine Gelbstoff Based on Spectroscopic Properties . . . . .	71
Attempts at Structure Elucidation . . . . .	72
Some Indications of Ecological Consequences of Gelbstoff in the Sea . . . . .	75
References . . . . .	75



**The Surface of the Ocean***L. W. Lion*

Introduction: Why are we Interested in the Surface of the Ocean? . . . . .	79
An Atmospheric Perspective . . . . .	80
A Chemical Perspective . . . . .	80
A Biological Perspective . . . . .	80
Measurement: The Characterization of the Ocean Surface . . . . .	81
The Different Meanings of „Surface“ . . . . .	81
Sampling and the Nature of the Sample Obtained . . . . .	82
The Composition of Surface Films . . . . .	84
Organics . . . . .	86
Inorganics . . . . .	88
Organisms . . . . .	90
The Origin of Surface Films . . . . .	93
Transport from the Ocean . . . . .	93
Transfer from the Atmosphere . . . . .	96
Characteristics of Surface Films Which May Have Geochemical Impact . . . . .	98
Transfer to the Atmosphere . . . . .	98
Transfer to the Ocean . . . . .	99
Special Opportunities for Biological-Chemical Interactions . . . . .	100
Conclusions . . . . .	100
List of Symbols and Abbreviations . . . . .	100
References . . . . .	101

**Atmospheric Nitrogen. Chemistry, Nitrification, Denitrification, and their Interrelationships***R. D. Hauck*

Introduction . . . . .	105
Abiological Reactions of Atmospheric Nitrogen . . . . .	105
The Atmosphere . . . . .	105
Nitrous Oxide . . . . .	106
Tropospheric Nitric Oxide and Nitrogen Dioxide . . . . .	107
Stratosphere: Nitrogen Oxides and Ozone Balance . . . . .	109
Atmospheric Ammonia and its Salts . . . . .	110
Total Nitrogen Fluxes . . . . .	111
Nitrification . . . . .	111
Ammonium Oxidation . . . . .	111
Nitrite Oxidation . . . . .	112
Energy Relationships . . . . .	113
Heterotrophic Nitrification . . . . .	113
Important Ecological Considerations . . . . .	114
Denitrification . . . . .	115
Reaction Conditions . . . . .	117
Freshwater and Marine Environments . . . . .	118

Chemodenitrification . . . . .	118
Sources and Sinks . . . . .	120
Comment . . . . .	120
Precipitation-Volatilization Cycle . . . . .	121
Dinitrogen Fixation-Denitrification Cycle . . . . .	121
Concluding Remark . . . . .	122
References . . . . .	123

### **Carbon Dioxide: A Biogeochemical Portrait**

*E. T. Degens, S. Kempe, and A. Spitzzy*

Introduction . . . . .	127
History of CO <sub>2</sub> . . . . .	127
Cosmic Molecular Clouds . . . . .	127
Meteorites . . . . .	129
Solid Earth . . . . .	131
Juvenile CO <sub>2</sub> . . . . .	134
Today's Carbon Cycle . . . . .	139
Sinks, Sources and Fluxes . . . . .	139
Volcanic Emanations . . . . .	141
Carbon in the Sea . . . . .	143
Carbon on Land . . . . .	149
Carbon in the Air . . . . .	155
Man-Made Carbon Dioxide . . . . .	162
Boundary Phenomena . . . . .	167
Weathering and Erosion . . . . .	168
Air-Sea-Exchange . . . . .	182
Mid-Water Stratification . . . . .	186
Biomineralization . . . . .	190
Sediment-Water Interface . . . . .	196
Chemoclines . . . . .	196
Environmental Scenarios . . . . .	199
Carbon Cycle Modelling . . . . .	199
Radiation Balance . . . . .	203
Outlook . . . . .	206
Acknowledgements . . . . .	207
References . . . . .	207
<b>Subject Index . . . . .</b>	<b>217</b>

## List of Contributors

Dr. Ghulam Ghaus Choudhry  
Laboratory of Environmental  
and Toxicological Chemistry  
University of Amsterdam  
Nieuwe Achtergracht 166  
NL-1018 WV Amsterdam,  
The Netherlands

Prof. Dr. E. T. Degens  
Universität Hamburg  
SCOPE/UNEP  
International Carbon Center  
D-2000 Hamburg 13  
Federal Republic of Germany

Dr. Manfred Ehrhardt  
Institut für Meereskunde  
an der Universität Kiel  
Düsternbrooker Weg 20  
D-2300 Kiel 1  
Federal Republic of Germany

Dr. Roland D. Hauck  
Division of Agricultural Development  
Tennessee Valley Authority  
Muscle Shoals, AL 35660, USA

Dr. Stephan Kempe  
Universität Hamburg  
SCOPE/UNEP  
International Carbon Center  
D-2000 Hamburg 13  
Federal Republic of Germany

Prof. Dr. Leonard W. Lion  
Cornell University  
Department of  
Environmental Engineering  
Hollister Hall  
Ithaca, NY 14853, USA

Dr. A. Spitzky  
Universität Hamburg  
SCOPE/UNEP  
International Carbon Center  
D-2000 Hamburg 13  
Federal Republic of Germany

Prof. Dr. Peter J. Wangersky  
Department of Oceanography  
Dalhousie University  
Halifax, Nova Scotia B3H 4J1  
Canada