

NATO ASI Series

Advanced Science Institutes Series

A series presenting the results of activities sponsored by the NATO Science Committee, which aims at the dissemination of advanced scientific and technological knowledge, with a view to strengthening links between scientific communities.

The Series is published by an international board of publishers in conjunction with the NATO Scientific Affairs Division

A Life Sciences	Plenum Publishing Corporation
B Physics	London and New York
C Mathematical and Physical Sciences	Kluwer Academic Publishers Dordrecht, Boston and London
D Behavioural and Social Sciences	
E Applied Sciences	
F Computer and Systems Sciences	Springer-Verlag Berlin Heidelberg New York
G Ecological Sciences	London Paris Tokyo Hong Kong
H Cell Biology	Barcelona Budapest
I Global Environmental Change	

NATO-PCO DATABASE

The electronic index to the NATO ASI Series provides full bibliographical references (with keywords and/or abstracts) to more than 30000 contributions from international scientists published in all sections of the NATO ASI Series. Access to the NATO-PCO DATABASE compiled by the NATO Publication Coordination Office is possible in two ways:

- via online FILE 128 (NATO-PCO DATABASE) hosted by ESRIN,
Via Galileo Galilei, I-00044 Frascati, Italy.
- via CD-ROM „NATO-PCO DATABASE“ with user-friendly retrieval software
in English, French and German (© WTV GmbH and DATAWARE
Technologies Inc. 1989).

The CD-ROM can be ordered through any member of the Board of Publishers or through NATO-PCO, Overijse, Belgium.



Series I: Global Environmental Change, Vol. 4

The ASI Series Books Published as a Result of Activities of the Special Programme on Global Environmental Change

This book contains the proceedings of a NATO Advanced Research Workshop held within the activities of the NATO Special Programmen on Global Environmental Change, which started in 1991 under the auspices of the NATO Science Committee.

The volumes published as a result of the activities of the Special Programme are:

- Vol. 1: **Global Environmental Change**. Edited by R. W. Corell and P. A. Anderson. 1991.
- Vol. 2: **The Last Deglaciation: Absolute and Radiocarbon Chronologies**. Edited by E. Bard and W. S. Broecker. 1992.
- Vol. 3: **Start of a Glacial**. Edited by G. J. Kukla and E. Went. 1992.
- Vol. 4: **Interactions of C, N, P and S Biogeochemical Cycles and Global Change**. Edited by R. Wollast, F. T. Mackenzie and L. Chou. 1993.

Interactions of C, N, P and S Biogeochemical Cycles and Global Change

Edited by

Roland Wollast

Laboratoire d'Océanographie Chimique
Université Libre de Bruxelles, Brussels, Belgium

Fred T. Mackenzie

Department of Oceanography
School of Ocean and Earth
Science and Technology
University of Hawaii, Honolulu, Hawaii, USA

Lei Chou

Laboratoire d'Océanographie Chimique
Université Libre de Bruxelles, Brussels, Belgium



Springer-Verlag

Berlin Heidelberg New York London Paris Tokyo

Hong Kong Barcelona Budapest

Published in cooperation with NATO Scientific Affairs Division

Proceedings of the NATO Advanced Research Workshop on Interactions of C, N, P
and S Biogeochemical Cycles held at Melreux, Belgium, March 4–8, 1991

Additional material to this book can be downloaded from <http://extra.springer.com>.

ISBN-13: 978-3-642-76066-2 e-ISBN-13: 978-3-642-76064-8
DOI: 10.1007/978-3-642-76064-8

Library of Congress Cataloging-in-Publication Data

Interaction of C, N, P, and S biogeochemical cycles and global change / edited by Roland Wollast, Fred T. Mackenzie, Lei Chou.

(NATO ASI series. Series I, Global environmental change ; vol. 4)

"Proceedings of the NATO Advanced Research Workshop on Interactions of C, N, P, and S Biogeochemical Cycles held at Melreux, Belgium, March 4–8, 1991" – T.p. verso. "Published in cooperation with NATO Scientific Affairs Division." Includes bibliographical references and index.

ISBN-13: 978-3-642-76066-2

1. Biogeochemical cycles–Congresses. 2. Global temperature changes–Congresses. 3. Man–Influence on nature–Congresses. I. Wollast, R. II. Mackenzie, Fred T., 1934- . III. Chou, Lei, 1953- . IV. North Atlantic Treaty Organization. Scientific Affairs Division. V. NATO Advanced Research Workshop on Interactions of C, N, P, and S Biogeochemical Cycles (1991 : Melreux, Belgium) VI. Series. QH344.I53 1993 574.5'222–dc20

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilm or in any other way, and storage in data banks. Duplication of this publication or parts thereof is permitted only under the provisions of the German Copyright Law of September 9, 1965, in its current version, and permission for use must always be obtained from Springer-Verlag. Violations are liable for prosecution under the German Copyright Law.

© Springer-Verlag Berlin Heidelberg 1993
Softcover reprint of the hardcover 1st edition 1993

Typesetting: Camera ready by authors
31/3145 - 5 4 3 2 1 0 - Printed on acid-free paper

TABLE OF CONTENTS

PREFACE	VIII
GENERAL	
C, N, P, S GLOBAL BIOGEOCHEMICAL CYCLES AND MODELING OF GLOBAL CHANGE <i>F. T. Mackenzie, L. M. Ver, C. Sabine, M. Lane and A. Lerman</i>	1
TERRESTRIAL	
THE COUPLING OF CARBON AND ION CYCLES INCLUDING N, P AND S IN SOILS OF TERRESTRIAL ECOSYSTEMS <i>B. Ulrich and M. Bredemeier</i>	63
TERRITORIAL, CONTINENTAL AND GLOBAL ASPECTS OF C, N, P AND S EMISSIONS FROM AGRICULTURAL ECOSYSTEMS <i>K. Isermann</i>	79
RIVERS	
C, N, P EXPORT DYNAMICS IN THE AMAZON RIVER <i>J. E. Richey and R. L. Victoria</i>	123
THE PHISON RIVER SYSTEM: A CONCEPTUAL MODEL OF C, N AND P TRANSFORMATIONS IN THE AQUATIC CONTINUUM FROM LAND TO SEA <i>G. Billen</i>	141
C, N, P AND S IN RIVERS: FROM SOURCES TO GLOBAL INPUTS <i>M. Meybeck</i>	163
OCEAN	
INTERACTIONS OF CARBON AND NITROGEN CYCLES IN THE COASTAL ZONE <i>R. Wollast</i>	195
PRODUCTIVITY AND NEW PRODUCTION OF THE OCEANIC SYSTEM <i>G. A. Knauer</i>	211

AIR-SEA

AIR-SEA CO ₂ EXCHANGE IN COASTAL ECOSYSTEMS <i>M. Frankignoulle and J.-P. Gattuso</i>	233
AIR-SEA EXCHANGE OF CO ₂ AND ITS RELATION TO PRIMARY PRODUCTION <i>A. J. Watson, J. E. Robertson and R. D. Ling</i>	249
AIR-SEA EXCHANGE OF SULPHUR AND NITROGEN AND THEIR INTERACTION IN THE MARINE ATMOSPHERE <i>P. S. Liss and J. N. Galloway</i>	259

ATMOSPHERE

ORIGINS, ATMOSPHERIC TRANSFORMATIONS AND FATE OF BIOLOGICALLY EXCHANGED C, N and S GASES <i>R. H. Gammon and R. J. Charlson</i>	283
MULTI-PHASE PROCESSES IN THE ATMOSPHERIC SULFUR CYCLE <i>J. Lelieveld</i>	305

SEDIMENTS

ORGANIC MATTER OXIDATION IN MARINE SEDIMENTS <i>D. E. Canfield</i>	333
THE NATURE OF PHOSPHORUS BURIAL IN MODERN MARINE SEDIMENTS <i>R. A. Berner, K. C. Ruttenberg, E. D. Ingall and J.-L. Rao</i>	365
RECYCLING EFFICIENCIES OF ORGANIC CARBON, NITROGEN, PHOSPHORUS AND REDUCED SULFUR IN RAPIDLY DEPOSITING COASTAL SEDIMENTS <i>C. S. Martens</i>	379
BIOGEOCHEMICAL TRANSFORMATIONS IN SEDIMENTS: KINETIC MODELS OF EARLY DIAGENESIS <i>P. Van Cappellen, J.-F. Gaillard and C. Rabouille</i>	401

HISTORY

NONLINEARITIES IN PHOSPHOGENESIS AND PHOSPHATE-CARBON COUPLING AND THEIR IMPLICATIONS FOR GLOBAL CHANGE <i>K. B. Föllmi, H. Weissert and A. Lini</i>	447
---	-----

THE COUPLING OF THE CARBON AND SULFUR BIOGEOCHEMICAL CYCLES OVER PHANEROZOIC TIME <i>L. R. Kump</i>	475
WORKING GROUP REPORTS	
WORKING GROUP 1: C, N, P AND S BIOGEOCHEMICAL DYNAMICS AND CYCLING IN THE GEOLOGIC RECORD <i>L. R. Kump (Rapporteur), R. A. Berner (Chairperson)</i> <i>D. E. Canfield, K. B. Föllmi, J.-F. Gaillard, J. Lelieveld</i> <i>and F. T. Mackenzie</i>	491
WORKING GROUP 2: INTERACTIONS OF THE CYCLES OF C, N, P AND S IN THE RECENT PAST (THE QUATERNARY) AND PRESENT <i>A. J. Watson (Rapporteur), P. S. Liss and R. H. Gammon (Chairpersons)</i> <i>G. Gauwet, J.-P. Gattuso, G. A. Knauer and C. Rabouille</i>	495
WORKING GROUP 3: C, N, P and S BIOGEOCHEMICAL DYNAMICS AND CYCLING: FUTURE AND HUMAN DIMENSIONS <i>P. Van Cappellen (Rapporteur), P. Crutzen (Chairperson)</i> <i>G. Billen, P. Friedlingstein, G. Gravenhorst, J. Lelieveld,</i> <i>A. Lerman, M. Meybeck, J. E. Richey and R. Wollast</i>	501
LIST OF WORKSHOP PARTICIPANTS	509
SUBJECT INDEX	515

PREFACE

This book is a natural extension of the SCOPE (Scientific Committee of Problems on the Environment) volumes on the carbon (C), nitrogen (N), phosphorus (P) and sulfur (S) biogeochemical cycles and their interactions (Likens, 1981; Bolin and Cook, 1983). Substantial progress in the knowledge of these cycles has been made since publication of those volumes. In particular, the nature and extent of biological and inorganic interactions between these cycles have been identified, positive and negative feedbacks recognized and the relationship between the cycles and global environmental change preliminarily elucidated. In March 1991, a NATO Advanced Research Workshop was held for one week in Melreux, Belgium to reexamine the biogeochemical cycles of C, N, P and S on a variety of time and space scales from a holistic point of view. This book is the result of that workshop.

The biogeochemical cycles of C, N, P and S are intimately tied to each other through biological productivity and subsequently to problems of global environmental change. These problems may be the most challenging facing humanity in the 21st century. In the broadest sense, "global change" encompasses both changes to the status of the large, globally-connected atmospheric, oceanic and terrestrial environments (e.g. tropospheric temperature increase) and change occurring as the result of nearly simultaneous local changes in many regions of the world (e.g. eutrophication). Equally important, global change may be natural, part of the constant disturbance and variability so evident in the past history of the earth, or human-induced, novel changes in the state of the earth that are directly attributable to the activities of the expanding population of humans. Both natural changes in the cycles of C, N, P and S (e.g. atmospheric composition, temperature and sea level changes of the Pleistocene glacial-interglacial stages) and interference and distortion of these cycles by human activities (e.g. fossil fuel burning and accompanying problems of climate change and acid precipitation) will have impacts on ecosystems and human society.

The natural global earth-surface system -- the atmosphere, hydrosphere, biosphere, and the shallow crust -- and the coupled cycles of C, N, P and S are in a continuous state of disturbance and fluctuation; change and turmoil are more the rule than constancy and equilibrium. These natural fluctuations of the system typically vary within some limits. Each disturbance changes the future course of the system. Constant changes in external forcing functions, such as solar luminosity and orbital parameters, and in the internal forcing of plate tectonics, rarely, if ever, give the system a chance to settle into a stable state for long. There is no "perfect" state of total equilibrium to which the earth-surface system returns. This is true at many scales of time and space, from the epochal to the seasonal and from the global to the local. However, there are processes in the system that act as positive or negative feedbacks in a perturbed system. The latter feedbacks are of particular importance, because they prevent the system from going completely awry. *This book considers the natural system of the coupled biogeochemical cycles of C, N, P and S at various time and space scales and discusses relevant feedback mechanisms.*

Human activities are interfering in the "workings" of the global earth-surface system and the functioning of the C, N, P and S biogeochemical cycles. Agricultural, industrial and urbanization activities are adding new disturbances to the system, changing the rates at which C, N, P, S and other natural materials circulate in the environment, and are resulting in additions of new and synthetic chemicals. Some of the waste products of human society, such as carbon dioxide, nitrogen oxides, sulfur dioxide and chlorofluorocarbons, are modifying the chemical processes and composition of the atmosphere. Some substances, like

nitrogen and phosphorus compounds, organic carbon, and other organic compounds like pesticides, and trace metals (often connected to the cycles of C, N, P and S because of their bioessential nature) like Co, V, and Zn, are modifying the chemistry of aquatic systems. Human activities, themselves, such as deforestation and urbanization, are leading to degradation of ecosystems, loss of forests, habitats, species diversity and arable land, and increased erosion rates and ultimately desertification. These latter activities modify the biogeochemical cycles of C, N, P and S, and in turn, these modifications affect other cycles and the environment as a whole. *This book discusses how the interactive web of C, N, P and S biogeochemical cycling has been affected by human activities.*

The book is arranged starting with a general paper dealing with the global biogeochemical cycles of C, N, P and S and geochemical modeling of these cycles (Mackenzie, Ver, Sabine, Lane and Lerman). The arrangement, thereafter, follows a pattern whereby individual and coupled cycles are considered first in the terrestrial realm (Ulrich and Bredemeier; Isermann) and then linked to the ocean reservoir via the rivers (Richey and Victoria; Billen; Meybeck). Processes and fluxes internal to the coastal (Wollast) and open (Knauer) ocean involving C and N are then discussed. This section is followed by one dealing with the exchange of C, N, and S gases between the sea surface and atmosphere (Frankignoulle and Gattuso; Watson, Robertson and Ling; Liss and Galloway) and the chemical reactions involving transformations of compounds of these elements in the atmosphere (Gammon and Charlson; Lelieveld). Besides the atmosphere and land linkages, the ocean is also coupled to the sediment reservoir by processes of sedimentation, accumulation and diagenesis. Biogeochemical transformations and recycling of C, N, P and S compounds involved with these processes are the principal subject of the section on sediments (Canfield; Berner, Ruttenberg, Ingall and Rao; Martens; Van Cappellen, Gaillard and Rabouille). Finally, the coupling of the C-P (Föllmi, Weissert and Lini) and the C-S (Kump) biogeochemical cycles over geological time and implications for global change are explored.

A perusal of the chapters in this book will inform the reader of the status of knowledge concerning the C-N-P-S global biogeochemical cycles, their degree of coupling and their relationship to global change. Global environmental change is a subject that is discussed today by scientists, policy makers and lay-people. It has even reached the ultimate of expression, the comic pages. All of this discussion gives the subject of global change a sense of respectability, a sense we know what it is all about and can even make predictions of the future state of the global environment. The reader of this book, however, will probably come away with a different feeling of how far we have come, but how little we know, and how far we have to go in obtaining a realistic understanding of the cycling behavior of four major elements involved with global change. This understanding is necessary for any future scenario of global change. The editors of this book hope that it provides at least a basis for understanding the global biogeochemical cycles of C, N, P and S and their relationship to global change and that it acts as a framework for future studies.

The book concludes with statements of the three working groups established at the Melreux meeting. The statements emphasize problems related to lack of knowledge of the interactive behavior of the biogeochemical cycles of C, N, P and S and point out potential research directions. Three time scales are considered: the long-time, geologic scale; the recent past (Quaternary) and present; and the future.

Acknowledgements

The organizing committee of the NATO Advance Research Workshop on

"Interactions of C, N, P and S Biogeochemical Cycles and Global Change", Roland Wollast, Lei Chou and Fred T. Mackenzie, acknowledge with thanks the financial support received from the NATO Scientific Affairs Division (Brussels). Financial support during editing of this volume for FTM was in the form of a Visiting Scientist Fellowship, State Secretary of Brussels Capital, and is gratefully acknowledged. LC and RW would like to thank the Belgian State - Prime Minister's Service - Science Policy Office in the framework of the Impulse Programme "Global Change" (contract No. GC/11/009) for the financial support for editing of this book.

Fred T. Mackenzie
Brussels, July 1992

Lei Chou

Roland Wollast

References

- Bolin B. and Cook R. B. (1983) *The Major Biogeochemical Cycles and their Interactions*. John Wiley and Sons, N.Y., 532 p.
- Likens G. E. (1981) *Some Perspectives of the Major Biogeochemical Cycles*. John Wiley and Sons, N.Y., 175 p.