Nitrogen in the Marine Environment

Edited by

EDWARD J. CARPENTER
DOUGLAS G. CAPONE

NITROGEN IN THE MARINE ENVIRONMENT

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NITROGEN
IN THE
MARINE ENVIRONMENT

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To our parents,
Charles and Adelaide Carpenter
and
Louis and Marie Capone

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FOREWORD

Investigations of the bases of marine biological productivity logically center on nitrogen, a necessary structural component of living cells, and the element limiting primary production over most of the world ocean. This compilation of the major results and efforts of a decade of intensive investigation into the many aspects of the nitrogen cycle attests to the importance of nitrogen as a central focus of nutrient-based productivity studies. Since the publication of this book represents a milestone in ocean productivity research, it may be helpful to briefly review how this burgeoning field of research arrived at this point, thus providing a guide to future directions.

Brandt's original speculations on nutrient limitation of biological production in the sea, made at the turn of the last century, were based on very few analyses of nutrient concentrations in seawater, the methods available being both tedious and difficult. Phosphorus occupied the center of the nutrient stage for several subsequent decades after relatively simple analytical methods for its determination became available. Nitrogen investigations were held back for lack of suitable analytical procedures, especially for ammonium. Nevertheless, Harvey's "Chemistry and Fertility of Sea Water," published in 1955, presented a useful framework for further studies of the chemical basis of primary production in the sea.

With improved capability to analyze seawater for the primary micronutrients, especially nitrate and ammonium, the realization developed largely through the efforts of John Ryther that inorganic nitrogen limits primary production over much of the world ocean. However, the complexity of the nitrogen cycle with multiple active pathways made it difficult to make further progress with purely chemical, mass balance experiments, especially in the ocean itself. At about that time, in the early 1960s, when John Neess and I began to use the stable isotope of nitrogen, ^{15}N, in the aquatic environment, mass spectrometers were rare and there were few laboratories such as that of Robert Burris at the University of Wisconsin, where this extremely useful tracer was used in biological experiments and where these facilities were made available to aquatic ecologists. In little more than another decade, mass spectrometers have become readily available, and the techniques for sample preparation have been improved and simplified with the result that there has been an explosion of new knowledge as many capable new investigators have directed their attention to marine nitrogen cycling. Their efforts have been based not only upon advances in primary nutrient analyses and stable isotope tracer techniques, but upon a vast array of methodologies that have been developed to probe the activities of living cells. As a result, early hypotheses have been discarded or been modified and new ideas developed to inspire and guide new experimental approaches. Naturally, greater understanding has led to the need for greater accuracies and sensitivities in laboratory instruments and procedures. This volume presents a well-balanced treatment of both the present state of knowledge and techniques that may be used to investigate new and old hypotheses.

What benefits to oceanography as a whole can be envisioned as a result of this newfound wealth of knowledge represented between the covers of this volume and from the research to follow? Beyond the obvious point that marine ecosystem studies generally benefit from advances in the understanding of nitrogen cycling there are some more specific topics that will benefit also. For example, we are entering a period where an understanding of phytoplankton processes and attributes will contribute toward unraveling the nature of some physical processes such as mixed layer dynamics. The intense activity exhibited by bacteria and phytoplankton in eastern boundary regions may conceivably be found to influence world climate through interaction with the carbon dioxide cycle. The local aberrations in sea surface temperature observed in conjunction with intense blooms of migrating phytoplankton populations may be found to have effects that propagate for unexpected distances. Improved understanding of phytoplankton processes may lead also to the development of "phytoplankton engineering" approaches to managing, for example, large anthropogenic introductions of nitrogen into the sea, and to mass culturing of specific phytoplankton species for aquaculture with improved predictability. Reliable simulation models and improved theory are needed if engineering solutions are to be realized. Early attempts to model nitrogen flow suffered from the lack of detailed knowledge of nitrogen processes, some of which is now available from the results of research reported in this volume. The nitrogen story is really just beginning to unfold and with the publication of this volume, we begin a new period of exciting research on ocean production processes.

RICHARD C. DUGDALE

PREFACE

The perception that nitrogen is an important and dynamic ecological factor has roots going back over 200 years. Soon after its discovery in 1772 by Rutherford (or possibly Cavendish or Scheele), in 1784, Berthollet identified "azote" as a component of animal tissue and excreta. Boussingault proposed in 1838 its role as a major controlling factor in plant nutrition and productivity. And although it was long suspected that atmospheric nitrogen was utilized by living organisms, Hillreigel and Wilfarth provided the first definitive evidence in 1880. The pioneering work of Beijernick and Winogradsky in the 1890s confirmed the biological basis of N_2 fixation as well as another suspected bacterial process, nitrification. Thus, by the turn of the century, the rudiments of the nitrogen cycle had been established.

The supposition that nitrogen might also play a crucial role in the ecology of the sea dates back to the early 1900s (see Nixon and Pilson, Chapter 16, for a historical perspective). Research on nitrogen in the sea followed a rather casual course for the first half of the century, a result of minimal scientific interest, limited resources, and inadequate means to investigate the subject.

Today there are active investigations of nitrogen transformations in literally all environments. Increased worldwide demand for nitrogenous fertilizers has paralleled dramatic increases in the cost of their synthesis. Major efforts in the agricultural sectors have been aimed at more efficient fertilizer use, prevention of fertilizer loss, and greater exploitation of biological N_2 fixation to offset requirements for synthetically produced ammonia. An important offshoot of this research has been an elaboration of methods to undertake quantitative studies and a refined understanding of the nitrogen cycle.

The patterns and quantities of nitrogen discharged to the environment have also changed dramatically with increasing population and technological advancement. Along with agricultural leachates, considerable combined nitrogen is released to the environment in industrial and domestic sewage effluents as well as from automobile emissions. Accelerated eutrophication has occurred in some coastal waters as a direct result of nitrogen loading. Furthermore, concern has been expressed over the possible depletion of the atmospheric ozone layer as a result of increased emissions of nitrogen oxides. Hence, there has been considerable stimulus to examine the natural cycling of nitrogen in the biosphere in order to provide a framework to evaluate the interactions and effects of human activities.

Given these factors, the last fifteen years have understandably seen a dramatic surge in research on nitrogen dynamics in the sea. Much of the direct impetus for this interest may be traced to a perceptive monograph written by R. C. Dugdale in 1967 and entitled "Nutrient Limitation in the Sea: Dynamics, Identification, and Significance," (*Limnol. Oceanogr.* **12,** 685–695). Further stimulation and provocation arose from the report of Ryther and Dunstan in 1971 (*Science* **171,** 1008) describing nitrogen as the primary limiting nutrient in coastal waters.

The research interest in nitrogen in the recent past relative to another crucial plant nutrient, phosphorus, is reflected in Figure 1. A substantial divergence in the annual rate of published reports on the two elements in marine ecosystems has occurred over the last decade. An analysis of freshwater ecosystems did not uncover a similar trend.

While nitrogen cycling in the sea is predominantly a biologically oriented subject, the geological, physical, and, in particular, chemical disciplines of the marine sciences have made important contributions to our understanding as well. We have especially profited in oceanic nitrogen cycling studies from the "interdisciplinary" approach.

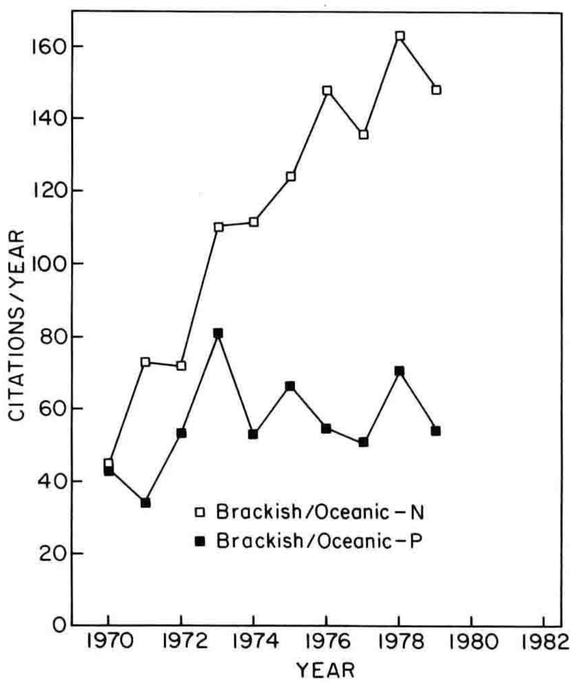

Fig. 1. Comparison of citations in Bibliographic Retrieval Services' Biosis® Data Base for marine-oriented research on nitrogen or phosphorus.

In view of the recent intensity and breadth of research and heightened concern over global nitrogen cycling, we perceived a major need for a synthesis volume on nitrogen cycling in the sea. Given the nature of the topic and its development in the marine sciences, the organization of the volume was straightforward. The volume centers on the role of microbes in nitrogen transformations with excursions to higher trophic levels. We have tried to provide a comparison of the nitrogen cycling of various ecosystems within the marine environment. Furthermore, we have included chapters on chemical distributions and methodology as an aid to those entering the field. We hope this book will provide fresh input and insights by which to align our future directions.

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CONTENTS

Chapter 1

THE DISTRIBUTIONS OF INORGANIC NITROGEN AND DISSOLVED AND PARTICULATE ORGANIC NITROGEN IN THE SEA

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I. PERSPECTIVE

Nitrogen is found in the sea primarily in five oxidation states: -3(NH_4^+, NH_2), 0(N_2), +2(N_2O), +3(NO_2^-), and +5(NO_3^-). The micronutrients have been reviewed by Spencer (1975) and the organic nitrogen compounds by Williams (1975). By far the most abundant species of nitrogen in the sea is N_2, but it is essentially unreactive (see Chapters 3 and 4). Nitrogen gas (N_2) is found throughout most oceanic and coastal waters at very near saturation values (Kester, 1975). It is considered separately (Chapter 2) and is referred to here only for comparative purposes (Table I). The next most abundant species, and a biologically active one, is the nitrate ion (NO_3^-). The other bioactive inorganic ions, nitrite (NO_2^-) and ammonium (NH_4^+) are less abundant overall, but are of local significance. Ammonia gas (NH_3) is lumped with NH_4^+ for discussions in this chapter; NH_3 along with nitrous oxide (N_2O) are

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