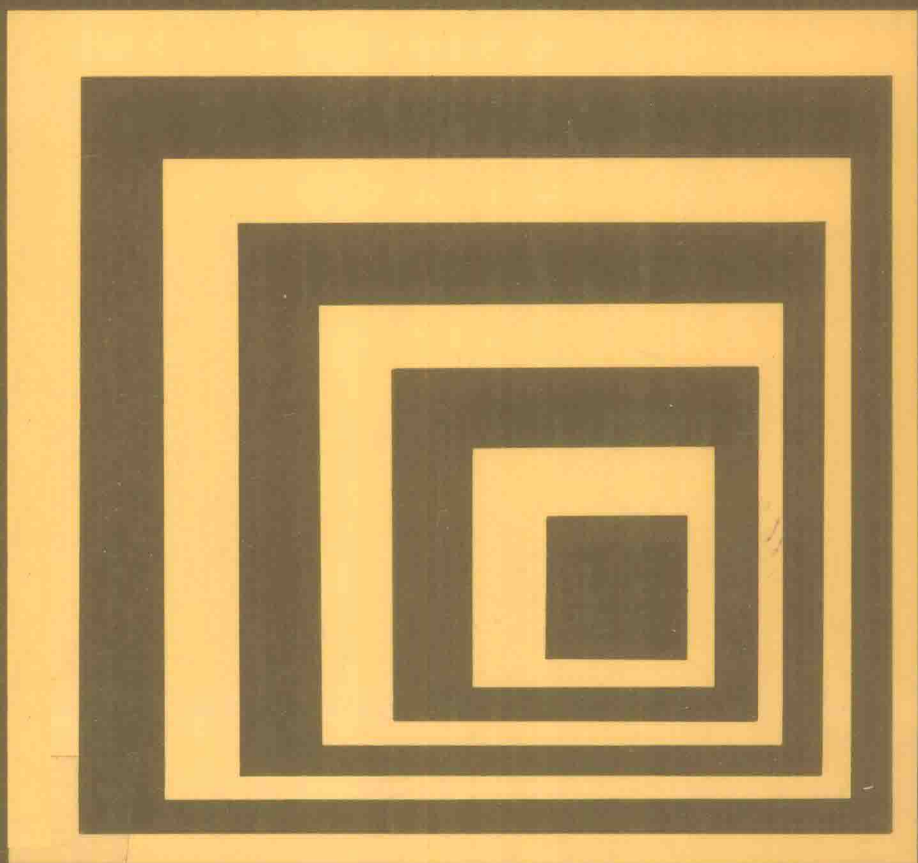


CAMBRIDGE STUDIES IN ECOLOGY

THE ECOLOGY OF THE NITROGEN CYCLE

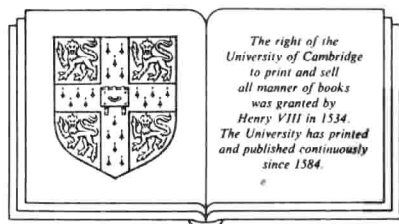
JANET I. SPRENT



The ecology of the nitrogen cycle

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Preface

Since the nitrogen cycle was discovered it has been the subject of intensive research. In the last ten years the scale of this research has increased dramatically, largely in parallel with worries over nitrate pollution and acid rain. As a result of these efforts many meetings have been held and many symposia volumes produced, dealing with nitrogen cycling in different areas of the world. It is thus timely to attempt an overall summary of the current situation within the confines of a single volume.

In attempting this I have of necessity been very selective. Although in an ecology series, the book begins on a rather biochemical note, but a knowledge of the reactions involved is necessary before the effects of environment on these reactions can be assessed. Because so many different organisms are involved, it is impossible to consider each of them in detail. The emphasis is necessarily on microorganisms and plants, since the major reactions take place in them. However, in view of the increasing awareness of the role of animals (especially invertebrates), examples involving these have been included.

The second part of the book is devoted to case histories from different environments. The selection of examples may seem rather subjective, but the aim has been to cover as wide a geographical range as possible. This has meant the omission of much first-rate work from certain areas, such as North America. I apologize to all those who are not included and hope that references to relevant symposia will enable readers with specialist interests to find more examples for their particular areas.

Two aspects of nitrogen cycling have been largely excluded. First, the numerous models currently being drawn up have not been discussed as these alone could form a whole volume: one field example is included. Second, methodology is covered only in passing. It is one of the regrettable facts of current science that accurate field measurement of most nitrogen cycle reactions, but particularly nitrogen fixing and denitrifica-

tion, is impossible because of limits in methodology. For these reasons amongst others, including the sheer volume of work involved, very few studies of nitrogen cycling include all descriptive (organisms, environments) and quantitative (rates of reaction, pool sizes) components. It has thus not been possible to adopt a uniform approach when discussing examples.

The book is intended for advanced undergraduates, early post-graduates and researchers in allied areas.

I should like to thank Professor John Harper FRS and Cambridge University Press for inviting me to write this volume. Discussions with many colleagues in various countries have assisted me greatly and I am particularly indebted to my Dundee colleagues Professor John A. Raven, Dr Linda Handley-Raven and Dr Rod Herbert. Members of my research group have shown great patience at my frequent absences when working at home. Without the help and encouragement of my husband Peter, who interrupted the writing of his own books to do all the word processing of the final version of the manuscript, the book would still be incomplete. I am indebted to the staff of Cambridge University Press for making the production of this book remarkably painless.

Janet I. Sprent

Dundee, Scotland
February 1987

Contents

	<i>Preface</i>	vii
Part I	General features of the nitrogen cycle	1
1	<i>Introduction</i>	3
	Forms of nitrogen in the biosphere	3
	The processes of the nitrogen cycle	5
2	<i>Evolutionary and current constraints on the nitrogen cycle</i>	29
	Evolutionary considerations	29
	Current constraints	31
3	<i>Shortened and open nitrogen cycles: effects of environment</i>	49
	Open and shortened cycles	49
	Environmental effects	56
Part II	Case histories from particular environments	67
4	<i>Nitrogen cycling in dry areas</i>	69
	Introduction	69
	Arid areas	70
	Semi-arid areas	77
5	<i>Terrestrial areas not subject to regular drought</i>	85
	Introduction	85
	Tussock tundra	85
	Forests	88
	Peat soils	96
	Effects of flooding	100
6	<i>Aquatic ecosystems</i>	101
	Introduction	101
	Lakes	103
	Marshes	107
	Other saline systems	110
7	<i>Impact of man</i>	118
	Introduction	118
	Agriculture	118
	Forestry	130
	Acid rain and related phenomena	134
	<i>References</i>	136
	<i>Index</i>	148

PART I

General features of the nitrogen cycle

Introduction

Nitrogen is one of many elements involved in cyclical transformations in the world. However, after the carbon cycle, the nitrogen cycle is arguably the most important to living organisms. Organic compounds of nitrogen are probably as diverse as those of carbon, but, in addition, there are several inorganic forms of importance, compared with one – carbon dioxide or its hydrated form carbonic acid. Before considering the reactions of the nitrogen cycle, it is thus pertinent to consider what these compounds of nitrogen are and also where they are, in the major global compartments.

Forms of nitrogen in the biosphere

Atmosphere

Nitrogen gas

The dinitrogen molecule, N_2 , makes up about 79% of the extant atmosphere, although this has not always been so. It is a very stable substance and a considerable quantity of energy is needed to break its inter-atomic bonds.

Nitrogen oxides

All possible molecules of nitrogen with oxygen may be found, i.e. N_2O (nitrous oxide), NO (nitric oxide) and NO_2 (nitrogen dioxide). These may be free or associated with either water or solid particles in the atmosphere.

Reduced nitrogen

Ammonia is the main form, but various organic compounds may be present and even be locally abundant – consider, for example, the aroma around fish processing plants or when pig slurry is put on to fields or the smell of rotting invertebrates at low tide on a warm day.

Water

All the above nitrogen-containing gases may be present in solution, often at saturation, but sometimes at sub- or super-saturated concentrations. Because the volume of water, particularly in oceans, is so great, its total content of nitrogen-containing dissolved gases is greatly in excess of that in the atmosphere. Water may also contain low concentrations of urea, ammonia and low molecular mass organic compounds such as amino acids.

Living organisms***Nitrogen gas***

This will always be present in solution in the cell, normally in equilibrium with the surrounding atmosphere. Possible exceptions include animals moving rapidly with respect to changing outside pressure – seen when divers suffer from the ‘bends’ when they rise from depth to the surface too quickly.

Oxidized nitrogen

Nitrate may be present in various concentrations in plants, micro-organisms and the alimentary systems of herbivores and omnivores, including man.

Reduced nitrogen

Ammonia may be present in low concentrations in all organisms. At physiological pH values most of it is normally protonated, since the pK of the reaction



is 9.25 at 25°C (ranging from 10.08 at 0°C to 8.56 at 50°C). Organic reduced nitrogen occurs in many forms, including urea, organic bases such as purines and pyrimidines, amino compounds and their polymers (peptides, proteins), polymers of amino sugars (e.g. chitin in exoskeletons of some arthropods and fungal cell walls, cell walls of bacteria) and various secondary products made by plants for defence against herbivores and other problems. All animals have nitrogenous excretory products (Table 1.1) and these will contribute to any of the environmental pools (water, air, soil) of nitrogen.

Table 1.1. *Nitrogenous compounds excreted by major groups of animals*

Compound	Animal group
Ammonia	Aquatic invertebrates, including some molluscs Some fish, especially those living in fresh water Amphibians in water
Trimethylamine oxide	Some marine teleosts (bony fish)
Urea	Some molluscs Elasmobranchs (cartilaginous fish) Some amphibians Mammals
Purines, for example uric acid	Some terrestrial molluscs Insects Spiders Reptiles Birds

Soil

Since soil has a solid, a liquid and a gas phase, all of the substances listed above may be present. In addition, vast amounts of N_2 are occluded in rocks. Ammonium is the principal form of inorganic nitrogen in many undisturbed soils: it may exchange with cations on soil colloids in a reversible way or form more stable complexes which account for up to 5% of total nitrogen in soil (Smith, 1982b). The exchangeable ammonium continually replenishes that taken from the soil solution by microorganisms and plants. Further losses from soil may occur due to leaching (generally small, because of the complexing with soil colloids) or due to volatilization (generally small, except under special, usually alkaline, conditions). A further fraction, known as humic acid, is unique to soils. Humic acid is a generic term used to cover a wide range of complex substances formed by the condensation of aromatic compounds (degradation products of lignin and tannin; flavonoids) with proteins or amino acids. The molecular mass of humic acid varies greatly (from less than 1 kilodalton to several hundred kilodaltons) as does the difficulty with which it is broken down by microorganisms. Large quantities of soil nitrogen may be in this form.

The processes of the nitrogen cycle

It is possible to construct diagrams of the nitrogen cycle from many standpoints, emphasizing, for example, the organisms or the

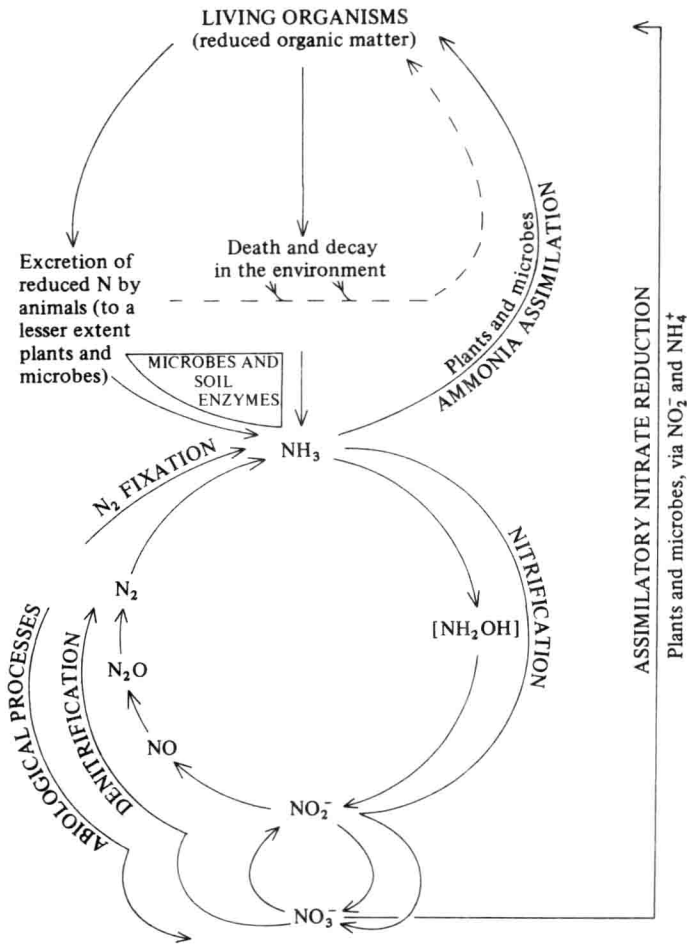


Figure 1.1. A summary of the major reactions of the nitrogen cycle.

chemistry. Figure 1.1 is yet another form, in which the cycle is considered as three interlocking component cycles with a major bypass. The upper cycle is the only one which can operate on its own, for example in some forest climax situations. The central cycle can only operate in association with the upper part, since the organisms which carry out its key reactions must contain organic nitrogen. The smallest section, which contains only nitrate and nitrite, usually operates with the other two parts, but at least in theory, may operate without the central part. The route from nitrate to plant or microbial biomass is shown as a separate branch, since, although

nitrite and ammonia are intermediates, the whole process occurs within individual cells in a series of coupled reactions. A dissimilatory pathway from NO_3^- to NH_3 (see pp. 25 and 43) is not included in the figure, as details are unclear.

Figure 1.1 is purely descriptive, giving no indication of the total quantities of the different components nor of the energy contained within them. The former will be considered in the next chapter. In order to know whether reactions are likely to occur, it is necessary to know how much energy is required by, or lost during, those reactions. Table 1.2 gives values for the major reactions of the nitrogen cycle. The actual energetics are more complex for a number of reasons. First, the rate of reactions must be considered – if a reaction is thermodynamically possible, but occurs very slowly, it is generally of little use to living organisms. Biological catalysts (enzymes) are the common way of speeding up reactions: their synthesis and maintenance require energy. Additionally, some of the available energy may be used to drive the reaction. Second, where reactions are required to occur at low substrate concentration (for example if little substrate is available, or if the substrate is toxic) it may be more advantageous (competitive) to use energy (usually as adenosine triphosphate, ATP) to help drive that reaction, so that a more rapid reaction rate is achieved. An example of this in the nitrogen cycle is the assimilation of ammonium by the GS: GOGAT system, discussed below. Third, the partial reactions may have different energies associated with them, so that an overall reaction which is energetically feasible may not occur at finite rates in practice. The classic example of this in the nitrogen cycle is the reduction of nitrogen gas to ammonia. Fourth, living organisms have various potential energy sources available to them and these sources vary considerably in the fraction of their energy available to drive reactions. This means, for example, that the actual energy used by organisms to fix nitrogen varies greatly. Fifth, energy available for oxidation–reduction reactions (i.e. all the reactions of the nitrogen cycle) will vary according to whether the environment is oxidative or reducing. Some of these aspects are considered later in this chapter. Quantitative details are given in Harris (1982).

Each of the steps in the cycle is subject to constraints related to the physical and biological environment. Thus the actual pathway followed and its rate-limiting steps, vary with geographical location and season. The purpose of this book is to explore these variations, but first it is necessary to look at the reactions themselves.

Table 1.2. *Standard free energy changes ($\Delta G'_0$) associated with some of the major reactions of the nitrogen cycle. A negative sign indicates net energy loss. More details of individual reactions can be found in Table 1.3. From various sources including Harris (1982) and Rosswall (1982)*

Reaction	$\Delta G'_0$ (kJ mol ⁻¹)	Comment
1. $\text{NO}_3^- \rightarrow \text{NO}_2^-$	-161	Nitrate respiration, anaerobic
2. $\text{NO}_3^- \rightarrow \text{NO}_2^-$	-142 to -161	Assimilatory nitrate reduction: value depends on electron donor (see Table 1.3)
3. $\text{NO}_2^- \rightarrow \text{NH}_4^+$	-374 to -433	Anaerobic nitrite reduction: value depends on electron donor (see Table 1.3)
4. $\text{NO}_3^- \rightarrow \text{NH}_4^+$	+348	The sum (2 + 3) taking into account the energy required to produce the electron donor (see also Sprent & Raven, 1985)
5. $\frac{1}{2}\text{N}_2 \rightarrow \text{NH}_4^+$	-40	Theoretical value for overall nitrogen fixation reaction. Initial step requires energy (see text)
	+480	Taking into account energy needed to produce electron donors, wasted in H_2 evolution, etc. (see Sprent & Raven, 1985)
6a. $\text{NH}_4^+ \rightarrow \text{NH}_2\text{OH}$	+15	} As carried out by <i>Nitrosomonas</i>
6b. $\text{NH}_2\text{OH} \rightarrow \text{NO}_2^-$	-244 to -353	
7. $\text{NO}_2^- \rightarrow \text{NO}_3^-$	-65 to -88	} As carried out by <i>Nitrobacter</i>
8. $\text{N}_2\text{O}^- \rightarrow \text{N}_2\text{O}$	-230	
9. $\text{NO} \rightarrow \frac{1}{2}\text{N}_2\text{O}$	-153	
10. $\text{NO}_2^- \rightarrow \text{NO}$	-76	
11. $\frac{1}{2}\text{N}_2\text{O} \rightarrow \frac{1}{2}\text{N}_2$	-170	
12. $\text{NO}_3^- \rightarrow \frac{1}{2}\text{N}_2$	-560	An overall figure, based on denitrification by <i>Pseudomonas aeruginosa</i> Nitrate fermentation (dissimilatory), anaerobic: as carried out by <i>Clostridium</i> <i>perfringens</i>
13. $\text{NO}_3^- \rightarrow \text{NH}_4^+$	-591	

Abiological processes

Nitrogen fixation can occur naturally, or as a result of industrial reactions. In either case, because of the strength of the nitrogen–nitrogen bond, energy is required. Suitable energy sources are short wavelength light (photochemical reactions) and electric discharge (thunderstorms),

either of which may be sufficient to cause nitrogen and oxygen to combine, forming one or more of the nitrogen oxides described above. Industrially, the Haber–Bosch process in which nitrogen and hydrogen are combined under pressure and at high temperature (these together providing the necessary energy) to form ammonia is the most widespread way of producing nitrogen fertilizer. Free ammonia may be used or it may be further processed to ammonium salts or urea. Unintentional industrial ‘fixation’ of nitrogen occurs during various high-temperature combustion processes. According to the fuel (coal, wood, diesel oil, aviation spirit, etc.), the temperature and pressure of the combustion, and the rate of air supply, the products may be nitrogen oxides, ammonia or even hydrogen cyanide. The quantities of nitrogen involved in this component of the abiological cycle have increased greatly in recent years and because of further reactions which may result there is cause for concern about possible adverse effects on the environment. This topic will be discussed in chapter 7.

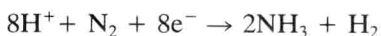
In addition to that from industrial processes, a considerable amount of nitrogen, both free and combined, is passed to the atmosphere from natural (wild) or man-made fires (for example burning of straw).

Enzymic reactions

Most of these occur in living organisms, but some important reactions are catalysed by soil enzymes, of which urease is the most important in the context of nitrogen cycling. Table 1.3 lists the major enzymes of the nitrogen cycle.

Biological nitrogen fixation

The enzyme complex known as nitrogenase is found only in certain microorganisms. These were formerly known as prokaryotes, but have recently been divided into two kingdoms, prokaryotes and archaeobacteria (also known as metabacteria), see, for example, Stackebrandt & Woese (1984): the occurrence of nitrogenase in eukaryotes has been reported from time to time, but none of these reports has been confirmed. Nitrogenase catalyses two simultaneous and, in living organisms, inseparable reductions, those of dinitrogen gas and protons:



Note that, for every nitrogen molecule reduced, one molecule of hydrogen is produced; under some circumstances, considerably more hydrogen is formed. The details of the reactions are very complex and not fully