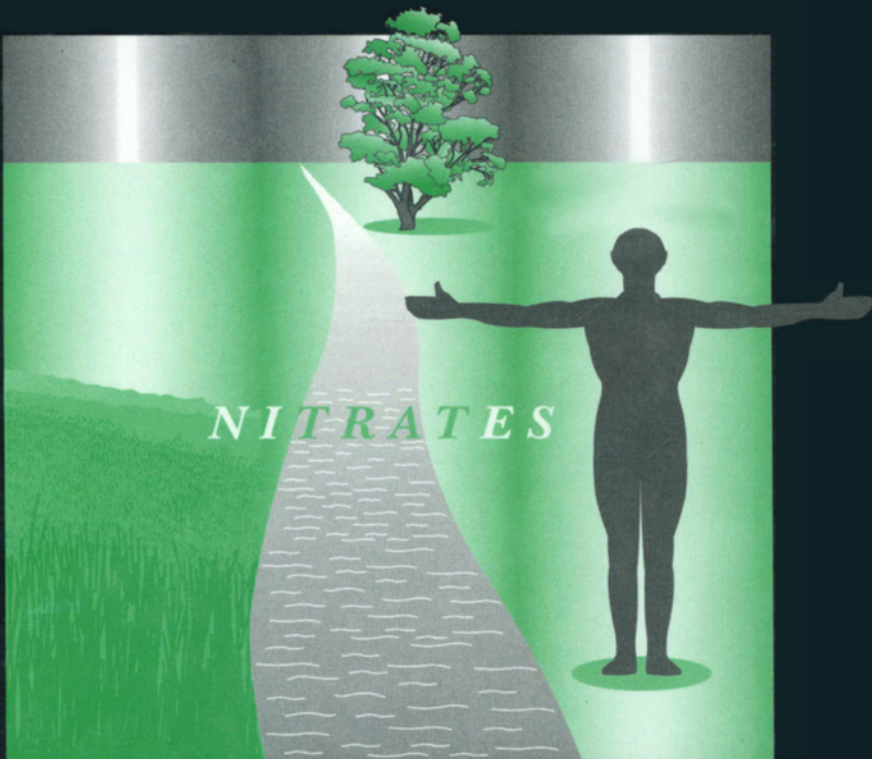


# MANAGING RISKS OF NITRATES TO HUMANS AND THE ENVIRONMENT



Edited by W.S. Wilson,  
A.S. Ball and R.H. Hinton

## **Managing Risks of Nitrates to Humans and the Environment**

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# Managing Risks of Nitrates to Humans and the Environment

Edited by

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The proceedings of a masterclass conference organised by the Agriculture Sector and Toxicology Group of The Royal Society of Chemistry on Managing Risks of Nitrates to Humans and the Environment at the University of Essex on 1-2 September, 1997.

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# Preface

Numerous scientific papers dealing with the so-called nitrate problem have been published during the past two or three decades. Usually these have taken the form of the Nitrate problem in Agriculture or the Nitrate problem in Water and have been set against the background of establishing limits such as those promulgated by the European Union and the World Health Organization. Frequently criticism is made of the dearth of rigorous scientific evidence or proof to justify these limits such as the European Union's upper limit of 11.3 mg NO<sub>3</sub><sup>-</sup>-N per litre in drinking water.

In view of the current public demands for thorough-going research in other problem issues such as Bovine Spongiform Encephalopathy (BSE), *E. coli* 0157 and Genetically Modified Organisms (GMOs), it was considered appropriate and opportune to review the wide range of nitrate research being carried out in key spheres such as agriculture, the environment and medicine. Thus, a masterclass conference on Managing the Risks of Nitrates to Humans and the Environment was organized by the Agriculture Sector and Toxicology Group of the Royal Society of Chemistry on 1–2 September 1997 at the University of Essex. Leading scientists in agricultural, environmental and medical aspects of nitrate research along with counterparts of young scientists engaged on research in the chemistry of terminal diseases, especially cancer, were invited to attend. This masterclass arrangement attracted generous financial support from The Angela and Tony Fish Bequest.

The objective of the conference was *inter alia* to investigate the developments whereby nitrate, a simple anion, had become the centrepiece of a furious debate in which farmers and growers were accused of obtaining large profits through the excessive use of nitrogenous fertilizers. The resulting increases in nitrate concentration in natural waters, it was claimed, threatened both the public's health and the environment. The timely and unique conference was asked to assess the foregoing allegations by answering such basic questions as:

- What really happens to nitrogenous fertilizer applied to crops?
- Which environmental problems have nitrate as a primary cause?
- Is nitrate a problem or a solution where our health is concerned?

The answers to these questions proved not only very interesting but rather surprising, particularly where the third question was concerned.

The paper and poster sessions were arranged in three logical sessions and

chaired by persons of wide experience. This was augmented by discussion groups and reference to an expert panel and a working party. This procedure was applied to maximize the amount of new knowledge extractable from the work reported.

The book is effectively an account of the proceedings of the conference. It comprises three sections signifying the areas covered. Each section is headed by introductory comments which guide and correlate the constituent chapters. New knowledge in each section proved enlightening to specialists in the other sections. Undoubtedly, the greatest amount of salient knowledge came from the section on medical aspects of nitrates. Most of the total work reported indicated that the time had arrived for a major reassessment of the generally accepted negative attitude to nitrate and, by implication, the need to review the European Union's severe limit for nitrate in drinking water.

The fair balance of new research information contained in this volume will provide scope for persons and organizations involved in policy-making and purveying essential information on nitrates. In this connection active participation of representations from various branches on the Ministry of Agriculture, Fisheries and Food, the Ministry of Health and the Department of the Environment, Transport and the Regions, was significant. Contributions from Agricultural, Horticultural, Environmental, Ecological and Water Research institutes provided full scientific coverage. Representatives from Europe, United States of America and India indicated the universality of the issues discussed. The value and timeliness of the event and the projected publication was acknowledged by Stephen Spivey, Director of Technology Foresight, representing the Office of Science and Technology.

W S Wilson, University of Essex  
A S Ball, University of Essex  
R H Hinton, University of Surrey

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# Section 1

## The Nitrate Problem in Agriculture Introductory Comments

by T. Batey, University of Aberdeen

Although agricultural activity is a major contributor, it is not the only source of nitrates in waters. Rainfall and organic waste of human origin also contribute significant amounts directly and indirectly to waters derived from both anthropic and natural ecosystems. However, the turnover of nitrogen in most agricultural systems is much greater than under natural ecosystems and the potential for loss as nitrate correspondingly higher. As shown by Powlson, the direct contribution of fertilizer N to losses of nitrate is low. During the growing season losses of N are mainly gaseous; it is during autumn and winter that most nitrate is leached from the land. Much is known about the complex dynamics of the N cycle in the soil (Jarvis, Powlson, Stockdale) and on predicting nitrogen losses as nitrate. We know which soils are most vulnerable, the role of rainfall and of crop type and tillage. These factors can be assessed leading to the formulation of a rotation which minimizes the risk of loss (Glendining & Smith). Crops which are likely to contribute high amounts are those which receive large amounts of nitrogen either as fertilizers or as manures and which are relatively shallow rooting, for example potatoes. As discussed by Wilson, there may be scope for reducing the amount of nitrogen applied as fertilizer or altering the timing of applications to crops. Situations at most risk are those where the land is devoid of plant cover or where the growth of crops (and thereby their uptake of nitrogen) has been reduced by drought, pest, disease or the deficiency of another nutrient.

Other questions addressed at this Conference include the role of soluble organic nitrogen. This has been shown in recent work by Murphy *et al.* to constitute a significant proportion (up to 60%) of total soluble nitrogen in the soil. Some aspects of the effects of increasing levels of atmospheric carbon dioxide are discussed by Ball & Pocock. The possible benefits of nitrate to the health of ruminant livestock are evaluated by Hill.

It is clear from the papers and posters presented that agriculture does not appear to be the bogey which is profligate in its use of fertilizer nitrogen thereby contributing to excessive losses ending up as nitrate in waters. Nevertheless, much still needs to be done to provide a scientific and practical basis to find a system of nitrogen management which continues to provide mankind with crops of satisfactory yield and quality and at the same time minimizes losses as nitrate leaving the land and entering waters.

# 1

## Nitrogen Dynamics in Natural and Agricultural Ecosystems

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### Abstract

Nutrient cycling within ecosystems is influenced by the nature of the element concerned, edaphic and environmental conditions, inputs to the system, and managerial influence. The physico-chemical and biological processes that control cycling are basically the same, whatever the system; some become more influential under different circumstances. For some nutrients, the cycle is relatively 'closed', *i.e.* there are few losses from the system. Most ecosystems, however, whether natural or managed, lose various forms of N. Nitrogen differs from many other nutrients in that it is 'leaky' and can, at various stages within the cycle, change valence and form: this contributes to a large degree of mobility and potential for loss either as gases or into water as  $\text{NO}_3^-$ , and thus form part of a larger global cycle.

A number of microbiological processes control the flow of N. These contribute to the available pool of 'available' soil mineral N, the form in which it exists and the extent of conversion into gases. In the first instance, mineralization and nitrification are the controlling processes. These are influenced by soil moisture, temperature, pH and other properties, the microbial communities present, and in the case of mineralization, by the 'quality' of the soil organic matter and any returned residues. All of these factors differ between different ecosystems and, depending upon the management, differ between agricultural and natural systems, and contribute to differences in the dynamics of N change. In agricultural systems, there are also large direct inputs into the available pool and large quantities of N recycling within the system. This increases the potential for loss as  $\text{NO}_3^-$ .

Nitrate leaching varies with soil and rainfall and on the interaction with competitive removal processes, *i.e.* those of uptake/assimilation and denitrifi-

cation. The extent to which these occur varies with the size of the relevant pools at any one time and their interactions with the soil and weather conditions and plant uptake potential. These obviously differ substantially between different systems (including different natural ecosystems) and will have impact on the amounts of  $\text{NO}_3^-$  leached from soils into water courses or aquifers.

## 1 Introduction

Nitrogen (N) cycling processes operate over a wide range of different physical scales from cellular to global and with reaction times from milliseconds to 1000s of years. There can be near instantaneous transfer of N from, for example, inorganic pools in terrestrial or aquatic environments into organic forms or into the atmosphere, and also long-term processes, for example controlling the release of N from stable organic forms in the soil with half-lives of centuries. In a global sense, the important processes which regulate the cycle are those which regulate the fixation or removal of N from the large atmospheric reservoir of dinitrogen gas and those which influence its return, ultimately through denitrification (Fig 1). Within an ecosystem, the processes

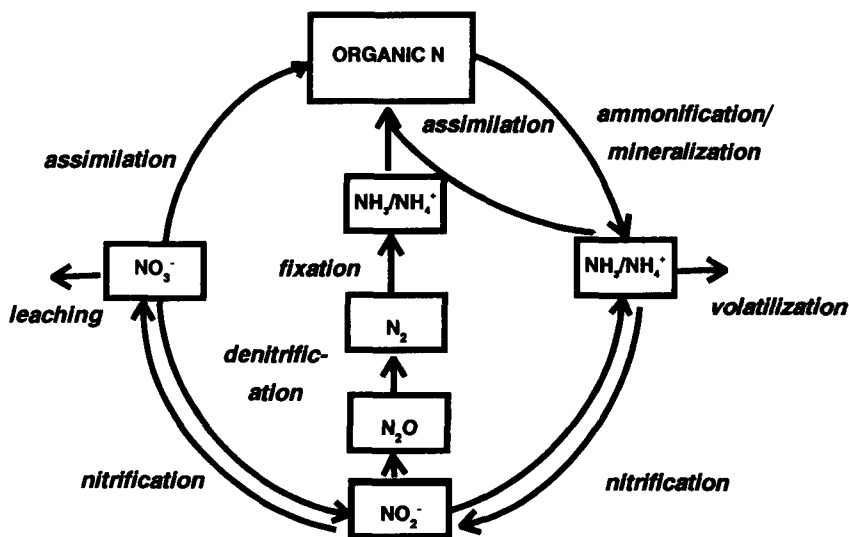


Figure 1 Global N cycle

which interact with the global scale are those which introduce N into the system (largely as the result of biological or chemical fixation), assimilation into biomass, ammonification/mineralization (releasing mobile forms) and denitrification (returning stable  $\text{N}_2$  back to the atmosphere). These and the other contributory processes which take place, especially in the soil-plant system (Figs 2 and 3), occur in both natural and agricultural environments.

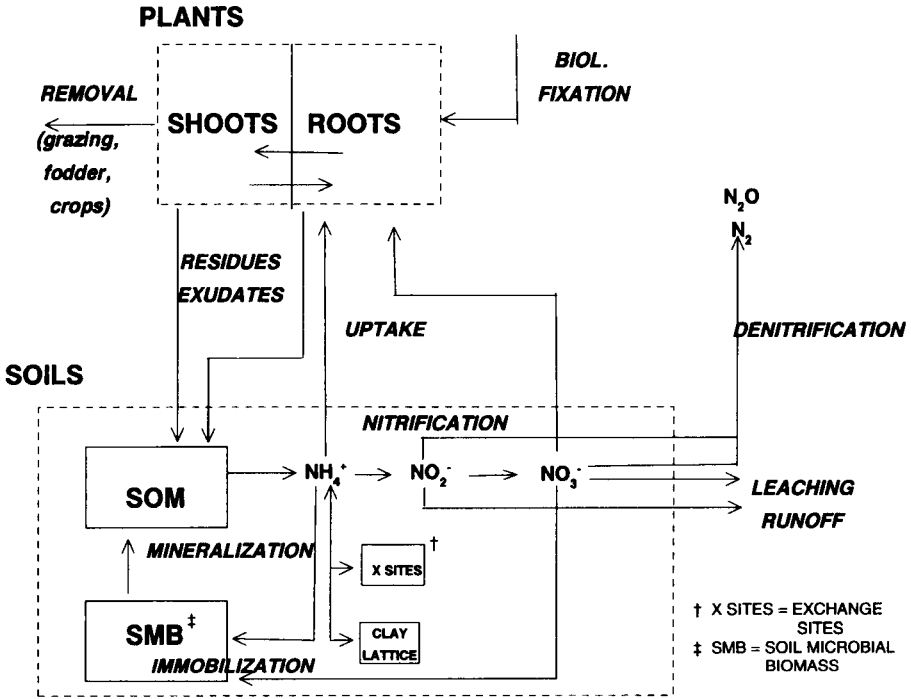


Figure 2 Nitrogen transformations and transfer in the soil plant system

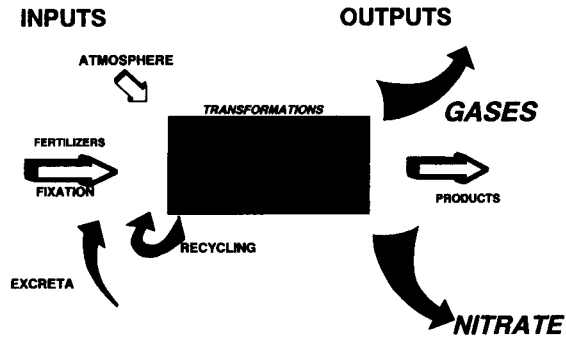


Figure 3 Inputs and outputs of N for terrestrial ecosystems

The same basic suite of interactive biological/chemical/physical controls operate in both systems to determine the rate at which N transformations take place. As the result of these transformations, all systems are 'leaky' to some extent or other and N is lost from the system. Nitrogen chemistry is such that a range of different states and chemical forms exist but, because of this, opportunities occur for 'escape' from the system to contribute to the larger cycle (Fig 1). Nitrate ( $\text{NO}_3^-$ ) is a key intermediary in this cycle, in that it is

highly mobile and takes part in many of the transfer processes at global (Fig 1) and smaller scales (Fig 2), *i.e.* through assimilation by biomass, denitrification to nitrous oxide ( $\text{N}_2\text{O}$ ) and/or  $\text{N}_2$ , and leaching into aquatic systems (for subsequent participation and contribution to the cycle within another ecosystem or removal by denitrification).

In many senses, uptake/assimilation, denitrification and leaching can be seen as competing processes within the soil/plant system. The amount of  $\text{NO}_3^-$  present in the soil is a reflection of the interaction between removal processes and those which are responsible for its presence, *i.e.* generation through the mineralization/nitrification pathway or by external additions. Again, the same controlling factors (Table 1) for these interactions operate in both natural and agricultural systems. However, by definition, because conditions (*i.e.* extent of input, soil, climate) differ, the equilibria achieved between the interactions differ and as a consequence the rates and dynamics of the transfers and transformations and effects on  $\text{NO}_3^-$  in soil/plant systems will also differ.

**Table 1** Key processes in controlling N dynamics

Process	Outcome	Major controlling factors
Uptake into biomass and assimilation	Removal of mobile, mineral N from soil available pools	<ul style="list-style-type: none"> <li>• environmental (<math>\text{H}_2\text{O}</math> and temperature)</li> <li>• carbon fixation</li> <li>• soil type and conditions</li> <li>• biomass community structure and populations</li> </ul>
Mineralization/immobilization	Release/removal of mobile mineral N into available pools	<ul style="list-style-type: none"> <li>• soil type and conditions (temperature and <math>\text{H}_2\text{O}</math>)</li> <li>• organic matter/residue quality/quantity</li> <li>• system stability and equilibrium</li> </ul>
Nitrification	Transfer from relatively immobile ( $\text{NH}_4^+$ ) to highly mobile ( $\text{NO}_3^-$ ) form (some release of $\text{N}_2\text{O}$ and $\text{NO}_x$ )	<ul style="list-style-type: none"> <li>• substrate (<math>\text{NH}_4^+</math>) concentration</li> <li>• soil aerobicity (and other environmental conditions)</li> <li>• nitrifying populations</li> <li>• other soil (<i>e.g.</i> pH) conditions</li> </ul>
Volatilization	Transfer from terrestrial state to short-lived atmospheric forms ( $\text{NH}_3^\circ$ and particulate $\text{NH}_4^+$ )	<ul style="list-style-type: none"> <li>• substrate [<math>\text{NH}_4^+/\text{NH}_3</math> (dissolved)] concentration</li> <li>• soil pH</li> <li>• environmental conditions (including windspeed)</li> <li>• enzymic activities</li> </ul>
Denitrification	Transfer from terrestrial and aquatic states to atmosphere [ $\text{N}_2\text{O}$ ( $\text{NO}_x$ ) and $\text{N}_2$ ]	<ul style="list-style-type: none"> <li>• substrate (<math>-\text{NO}_3^-</math>) concentration</li> <li>• anoxia</li> <li>• environmental conditions (temperature)</li> <li>• energy source</li> </ul>
'Leaching'	Transfer of mobile $\text{NO}_3^-$ (also $\text{NO}_2^-$ , dissolved organic forms and some $\text{NH}_4^+$ ) from terrestrial to aquatic systems	<ul style="list-style-type: none"> <li>• <math>\text{NO}_3^-</math> concentration</li> <li>• hydrological pathways</li> <li>• soil type/conditions</li> <li>• other N cycling processes</li> </ul>



The dynamics of N transfer within systems will vary according to many contributory factors (for example, the extent of physical disturbance of the soil system and the degree to which equilibria have been reached). By and large, however, the potential to generate, transform and transfer  $\text{NO}_3^-$  within and from the system is a reflection of the rate of N input. This increase may take place as the result of transformation processes acting directly on the input itself, leaching or denitrification of added fertilizer N for example. In general, unless management practices are badly timed, *direct* leaching losses from fertilizers are relatively small but those from denitrification can be substantial. The major consequences of N added into any system, whether derived from fertilizer, biological fixation or atmospheric deposition, is to enhance the flows (*via* plant residues, animal excreta for example) through the system. Fertilizer inputs to intensively managed systems can be large (Table 2): it should be emphasized that these are recommended optimum rates of application and are not universally applied. Excesses of N in any system arise when the capacity to be assimilated into biomass is limited: if this happens in combination with the appropriate favourable conditions for particular transformation processes then these will be accelerated and result in increased losses (Fig 3).

**Table 2** *Optimum rates of N fertilizer application for intensive systems: values are  $\text{kg ha}^{-1} \text{ year}^{-1}$  (from ref. 2)*

Soil fertility	Grassland for intensive dairying			
	Silage <sup>a</sup>	Grazing <sup>b</sup>		
low	420	380		
medium	380	340		
high	340	320		
Soil N status (index) <sup>c</sup>	Tillage systems			
	Winter wheat	Potatoes	Brussel sprouts	
	0	196	230	255
	1	136	180	185
2	56	115	115	

<sup>a</sup> 4 cuts

<sup>b</sup> rotational grazing. 6+ grazings

<sup>c</sup> on average, for mineral soils

## 2 Process Influencing $\text{NO}_3^-$ Contents in Soils

### 2.1 Nitrate Generation

**2.1.1 Mineralization/immobilization.** The microbial activities responsible for the release, in the first instance of  $\text{NH}_4^+$  (ammonification/mineralization: Fig 2, Table 1), are the main controlling determinants of the rate of supply of mineral N from internal sources and recycling. In many natural situations where there are no legumes and negligible atmospheric deposition, they will

provide the only means for delivering N in a form that is accessible for uptake by plants and so assume considerable importance in ecosystem regulation. The processes involved are complex and interactive (1) and dependent in the first instance on macro-faunal activity to initiate the breakdown process, but then the microbial community determines the dynamics of the release of N into available pools. The net effect in terms of available N – net mineralization – supply is an expression of the balance between gross N mineralization and gross immobilization. Gross mineralization rates depend on the nature of the soil and the history of the background organic matter inputs: Fig. 4 demonstrates an 8–9 fold difference in cumulative gross mineralization in two different soils over a 9 week period. There are also fundamental differences in immobilization rates depending upon the background nature of the system. As illustrated in Table 3, the effects of different grassland managements (from extensive semi-natural to intensive high N input) result in substantial differences in the balance of the patterns in mineralization and immobilization and therefore in the net release of N into the soil available (mineral)-N pool. It is also apparent that even in the semi-natural, low intensity system, microbial activity is releasing substantial amounts of mineral N. This is confirmed by other field based measurements of net mineralization (5) and will be an important feature of other systems in other circumstances, including other semi-natural vegetation types.

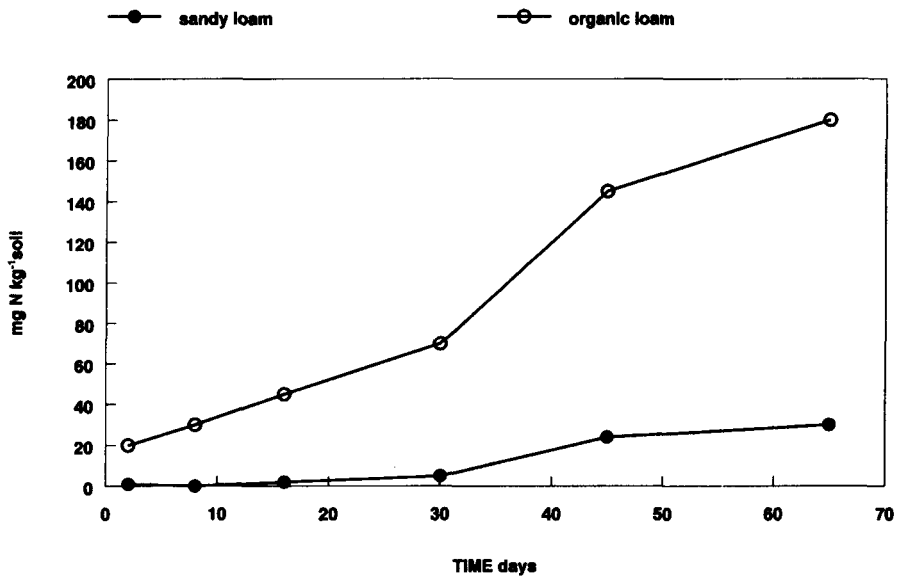


Figure 4 Cumulative gross mineralization rates from two soil types (3).

The dynamics of this release depend upon the activities of the soil microbial biomass community structure which will be determined by the nature and extent of the inputs and management (6), the soil type and environmental