

Emissions of nitrous oxide from soil

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Nitrous oxide (N₂O) accounts for approximately 5% of the total greenhouse effect. It also plays an important role in the destruction of the stratospheric ozone, which protects the earth from ultraviolet radiation from the sun. The atmospheric concentration of N₂O increased from 280–290 ppbv before industrial revolution to 350 ppbv at present. Soil is considered to be one of the major contributors with 65% of the total global emission. Various soil, climate and management factors control the N₂O emission. They include soil moisture regime, temperature, pH, N content of soil, soil organic carbon and presence of crops. Emission of N₂O could be reduced using nitrification inhibitors and modifying crop management practices. However, the economic feasibility of using these technologies needs to be evaluated in the farmer's field.

NITROUS oxide (N₂O) with its present concentration in the atmosphere (350 ppbv) is one of the important greenhouse gases accounting for approximately 5% of the total greenhouse effect¹. Atmospheric N₂O along with carbon dioxide (CO₂), methane (CH₄), water vapour, etc. absorbs and reflects back some of the thermal radiation emitted from the earth and increases its temperature. It is also responsible for destruction of the stratospheric ozone². A doubling of atmospheric N₂O would cause a 10% decrease in the ozone layer that would increase ultraviolet radiation reaching the earth surface by about 20% (ref. 3). Shea⁴ estimated that there would be 4–6% increase in cases of skin cancer with every 1% drop in ozone. Apart from its effects on the atmosphere, emission of N₂O from soil results in a diminution of the pool of soil-N available to the plants.

N₂O was first discovered and prepared in 1793 by an English scientist and clergyman, Joseph Priestley. Nitrous oxide (N^o N=O), also known as laughing gas, a term coined by Humphrey Davy of the Pneumatic Institute, Bristol, England, is a colourless, almost odourless gas with a molecular weight of 44, a specific gravity of 1.53, and a boiling point of –89°C. Atmospheric abundance, lifetime, sources, and sinks of N₂O as compared to other greenhouse gases are given in Table 1. Concentration of N₂O in the atmosphere before the industrial revolution was 280–290 ppbv (ref. 5). Increase by about 8% since then and the current increase (approximately 0.2–0.4% annually) are attributed mainly to anthropogenic

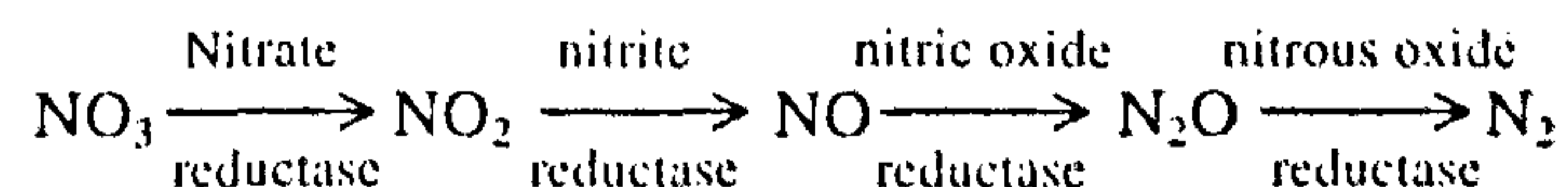
processes⁶. Soil is considered to be one of the major sources of N₂O emission contributing 65% of total global emission⁷. Soils receiving industrially and biologically fixed N contribute to this emission during denitrification⁸ and nitrification^{9,10}. Due to the advent of modern agriculture, consumption of nitrogenous fertilizer has risen sharply all over the world. This is expected to increase every year as the third world countries are using larger amounts of fertilizer to meet their food demand. Consequently, emission of N₂O from the soil will also increase. Any attempt to reduce its emission will be of great significance as it not only will reduce the atmospheric pollution but also increase fertilizer use efficiency. The prerequisite of developing management practices to minimize N₂O emission from managed ecosystems is an understanding of the source and factors controlling N₂O emission. The current paper deals with recent developments in the field of N₂O emission from soils.

Mechanism of N₂O emission

Biological processes (denitrification, nitrification, dissimilatory nitrate reduction and assimilatory nitrate reduction) as well as abiological reactions (chemodenitrification) are possible mechanisms of N₂O emission from the soil¹¹. However, it has been established that denitrification and nitrification are the most important mechanisms¹², others contributing very little to this pool (1% of total production)¹³.

Denitrification

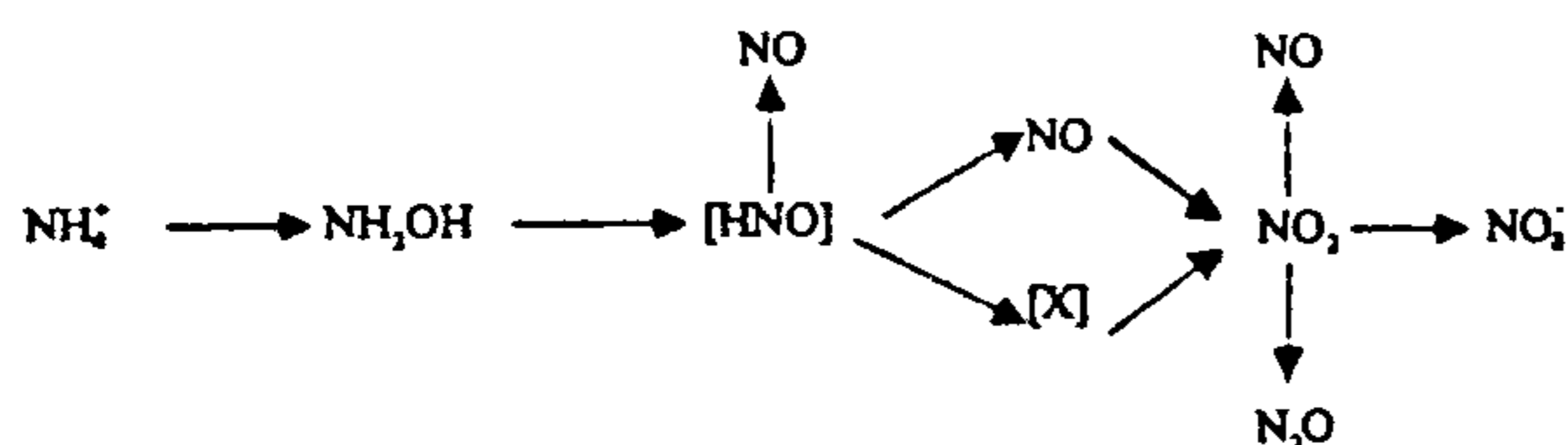
The simplest scheme of denitrification can be shown as



Denitrification occurs when nitrate is present in anaerobic microsites developed wherever microbial demand for O₂ exceeds diffusion-mediated supply¹⁴. This may well occur where O₂ diffusion is impeded by water, either at the centers of soil aggregates¹⁵ or in water-saturated regions¹⁶, or wherever local O₂ demand is exceptionally high¹⁷. Denitrification in soils also consumes N₂O through the reduction of N₂O to N₂ (ref. 18). Hence, this bacterial process may serve either as a source or as a sink of N₂O.

Nitrification

Nitrification also contributes to N₂O emission following ammonium fertilizer or ammonia forming fertilizer addition to soils during the oxidation of NH₄⁺ or NH₂OH to NO₃⁻ (refs 9, 19–21). Definitive evidences are available on N₂O release from even aerobic soils treated with ammoniacal fertilizers⁹. The pathway of N₂O production during nitrification can be depicted as follows¹¹.



(Dashed lines and square brackets indicate incompletely known processes and intermediates.)

The relative importance of either of these processes in N₂O emission from the soil is difficult to assess and is likely to vary appreciably with the type of N fertilizer, land management, climate and other factors affecting soil conditions²². At present, there are no laboratory manipulations which permit delineation of these two processes as sources of N₂O. However, Stevens *et al.*²³ have made an attempt by differentially ¹⁵N-labeling the NO₃⁻ and NH₄⁺ pools in soils. They proposed that by periodically measuring and comparing the enrichments of N₂O, NH₄⁺ and NO₃⁻ pools, relative importance of the two processes could be quantified.

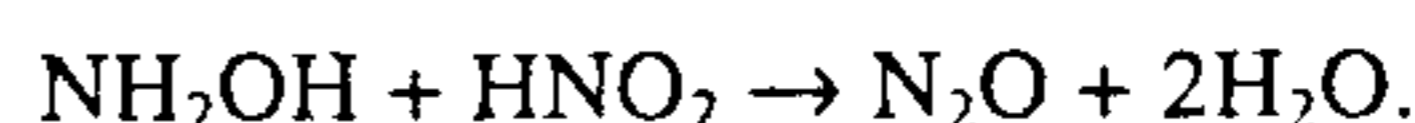
Other microbial processes

Nitrous oxide production is reported in micro-organisms with dissimilatory NO₃ reduction, with respiratory NO₃

reduction to N₂O and with assimilatory NO₃ reduction to NH₄. All these metabolic pathways typically produce N₂O but not N₂ and they do not gain energy by producing N₂O. They have thus been named nonrespiratory N₂O producers in contrast to respiratory N₂O producing denitrifiers²⁴. N₂O seems to be produced also by nitrate reductase acting on NO₂. However, this evidence is still restricted to *E. coli*²⁵ and to bean leaves²⁶.

Chemical formation of N₂O

Nitrous oxide can also be formed by chemical reactions when NO₂ or NH₂OH are decomposed in acid soils.



However, formation of N₂O by chemical reaction of NO₂ and hydroxyl amine does not seem to be important since there was no significant increase in the rate of N₂O production by the addition of NO₂⁻ or NH₂OH in soils²⁷. Yoshinari²⁸ also reported that chemical production of N₂O in soil and other ecosystems is of minor importance as a source of N₂O since the reaction becomes significant only in the presence of relatively high NO₂ concentration (> 1 mM), which is not commonly found in natural environments.

In spite of lot of work on the mechanism of N₂O emission, the primary source of observed soil emission is often uncertain. It is generally assumed that a majority of N₂O production occurs in proximity to the surface of soil²⁹. However, Burton and Beauchamp³⁰ observed a significant sub-surface N₂O production. They emphasized the need to examine the soil as a three-dimensional body for production, transport and storage of N₂O. Seiler and Conrad³¹ concluded that N₂O produced at depths are likely to be consumed in upper soil layer during upward transport by a diffusive process. This process of N₂O

Table 1. Abundance, lifetime and sources of greenhouse gases

	CO	CO ₂	CH ₄	N ₂ O	NO _x	SO ₂	CFCs
Average concentration 100 years ago (ppbv)	40–80	290,000	900	285	0.001–?	0.03–?	0
Current concentration (ppbv)	40–200	350,000	1700	350	0.001–50	0.03–50	3
Projected conc. in year 2030 (ppbv)	?	400,000–500,000	2,200–2,500	330–350	0.001–50	0.03–50	2.4–6
Atmospheric lifetime	Months	100 yr	10 yr	170 yr	Days	Weeks	75 yr
Anthropogenic/Total emission (Tg yr ⁻¹)	700/2200	5500/~ 5500	350/550	6/25	25/40	115/175	~ 1/1
Main sources	Fossil fuel combustion, biomass burning	Fossil fuel combustion, deforestation	Rice fields, cattle, landfills, fossil-fuel production	Nitrogen fertilizers, deforestation, biomass burning	Fossil fuel combustion, biomass burning	Fossil fuel combustion, ore smelting	Aerosol sprays, refrigerants, foams
Main sinks	Oxidation in troposphere, soil	Green plants, soil, ocean	Soil (aerobic) troposphere	Oxidation in stratosphere	Oxidation in troposphere	Oxidation in troposphere	Breakdown in stratosphere

(Source – refs 129, 130).

reduction to N_2 during diffusion would be enhanced if the soil were wet, since diffusion coefficient of N_2O is much less than that of N_2 (ref. 32).

Factors affecting the emission of N_2O

A range of soil, climate and management factors affect emission of N_2O from the soils^{12,13,33,34}. Some of the important findings are presented here.

Moisture regime

Soil water can directly/indirectly influence denitrification through: (1) provision for suitable conditions for microbial growth and activity; (2) restricting supply of O_2 to microsites by filling soil pores; (3) release of available C and N substrates through wetting and drying cycles; and (4) providing a diffusion medium through which substrates and products are moved to and away from soil micro-organisms³⁵. However, the primary effect of water on N_2O production in aerobic and partially aerobic soils is to restrict O_2 levels by reducing the air-water interfacial area within air-filled pores, thus producing an anaerobic condition³⁶. Generally, an increase in denitrification rates following irrigation and precipitation is commonly observed³⁷. Henault *et al.*³⁸ and Freney *et al.*³⁹ reported that N_2O emission increased with increase in soil water from air dry to field capacity. MacKenzie *et al.*⁴⁰ also observed that emission increased with increased soil water content, NO_3 concentration and fertilizer N rates. When water content is greater than field capacity, N_2O gets reduced to N_2 (refs 41, 42). Duxbury *et al.*⁴³ and Goodroad and Keeney⁴⁴ found that N_2O fluxes from mineral and organic soils were many times lower during dry periods than shortly after rainfall events when the soils were saturated. Ryden and Lund³⁷ recorded the maximum flux of N_2O with soil water content between 75 m bars and 150 m bars tensions. Smith and Patrick⁴⁵ studied the effect of several anaerobic and aerobic cycles on N_2O emission from ammonium sulphate amended soil suspensions and found that no N_2O evolved from continuously anaerobic samples. Continuously aerobic samples produced small amounts of N_2O , whereas alternate anaerobic and aerobic cycles of varying duration increased emission of N_2O by several folds. Drying of soils increases the capacity to denitrify by increasing the amount of readily available organic C (ref. 46). Hysteresis was observed whereby a decrease in denitrification occurred when moist soils were dried, whereas wetting dry soils resulted in an increase in the amount of N denitrified and the amount of N was dependent on the antecedent moisture conditions.

Oxygen

Oxygen is considered to be inhibitory for denitrifying enzymes⁴⁷ although the critical limit of O_2 varied among

different species of denitrifying bacteria. The N_2O yield during nitrification activity is inversely correlated with the concentration of dissolved O_2 (ref. 48). Firestone *et al.*⁴⁹ found that increased O_2 content enhanced production of N_2O relative to N_2 during denitrification. Under anaerobic conditions, N_2O production was initially found to increase, but this was followed by N_2O consumption in the system and its conversion to N_2 by N_2O reductase. This was also confirmed by Letey *et al.*⁵⁰ who reported that the soil can act as a N_2O sink under anoxic conditions. They also reported that N_2O emissions were higher in soils with fluctuating redox potential established by alternate wetting and drying cycles.

Soil pH

The optimum pH for N_2O emission via denitrification varies with species and age of the organism and NO_3 concentration, but most denitrifiers have optimum pH for growth between 6 and 8. Although the process is favoured at slightly alkaline pH, it proceeds up to pH as low as 3.5 and can account for significant N losses in acid soils³⁵. Soil acidity through various mechanisms may modulate the emission of N_2O . Firstly, increased soil acidity may lower the decomposition rate of soil organic matter⁵¹, hence reducing the availability of N substrate for N_2O production. Secondly, higher soil acidity directly reduces nitrification and denitrification⁵². Thirdly, acidification may severely inhibit N_2O reductase with the result that denitrification yields more N_2O than N_2 (ref. 53). Fourthly, decreasing pH reduces the availability of molybdenum that in turn may reduce the synthesis of NO_3 reductase, a molybdo-protein enzyme. Fifthly, with decreasing pH, NO_2 formed by NO_3 reduction would become toxic and solubilization of aluminium or manganese might cause toxicity effects⁵⁴. Finally, severe acidification may induce chemical production of N_2O from NO_2 . However, the actual mechanism of controlling NO_2 emission in acid soils is still unknown. Firestone *et al.*⁴⁹ reported that the influence of soil acidity is exerted through or its effect on NO_3 or NO_2 formation. Sitaula *et al.*⁵⁵ reported that N_2O fluxes were significantly reduced at pH 3, increased when the pH was increased to 4 but at pH 5.5 decreased with no fertilizer as well as with the application of 90 kg N ha⁻¹. It is generally accepted that evolution of N_2O relative to N_2 increases with increase in pH (refs 13, 54, 56).

Soil texture

The effect of soil texture on N_2O emission likely results from physical variations in air and water proportions. Water infiltration rate and gas diffusion rates are greatly influenced by soil texture and hence N_2O emission³⁵. Chaterpaul *et al.*⁵⁷ reported greater rates of N_2O emission in finely textured soils.

Temperature

Temperature plays a significant role in the process of N_2O emission. Emission of N_2O increased with increase in soil temperature from 5 up to 40°C (ref. 58). However, optimum temperature for denitrification should be in the range of 60–70°C (refs 59, 60). It is argued that the high optimum temperature for denitrification is actually due to a combination of biological and chemical reactions. As thermophilic temperature is approached, thermophilic nitrate respirers and chemodenitrification reactions dominate⁵⁹. The thawing of frozen soil can lead to a temporal increase in N_2O production^{40,60}. Christensen and Tiedje⁶¹ reported brief and vigorous N_2O fluxes during rapid thaw events during spring in a sandy loam soil. Peak flux rates of 486 g N ha⁻¹ d⁻¹ as N_2O were observed in NO_3 -amended soils. They observed that field production of N_2O was two orders of magnitude higher at thaw during spring than at any other time during the rest of the year. This may be due to changes in solubility, production near the soil surface and diffusion from depth⁶². However, Nyborg *et al.*⁶³ though observed that large amounts of soil nitrate may be denitrified, there was smaller amounts of N_2O emitted as the soil thawed. Kamp *et al.*⁶⁴ determined the effects of increased soil temperature resulting from global warming and concluded that more N_2O will be released in case global temperature increases.

Fertilizer application

Production of N_2O from soil during denitrification and nitrification increased in N-fertilized systems⁶⁵. Blackmer *et al.*⁵⁸ reported that the amount of N_2O evolved from plots treated with $(NH_4)_2SO_4$ or urea markedly exceeded those from plots receiving the same amount of N as $Ca(NO_3)_2$. Bremner and Blackmer⁹ observed that emission of N_2O was more with application of urea followed by ammonium sulphate and nitrate fertilizers at 60% water holding capacity. These are evidences that most of the N_2O evolved from soils is generated by nitrifying microorganisms⁶⁶. In another study, Clayton *et al.*⁶⁷ observed that loss of N_2O -N was higher with urea than ammonium sulphate as fertilizers in grasslands. However, Ryden and Lund³⁷ observed no unique dependence of N_2O emission on fertilizer N application that was applied in the form of ammonium. It has also been observed that the N_2O emission is larger from soils fertilized with anhydrous NH_3 than those of fertilizers with NO_3 and NH_4 sources⁶⁸. Breitenbeck and Bremner⁶⁹ also reported that on an average, the emission of N_2O -N induced by anhydrous ammonia was 13 times more than that induced by aqueous ammonia or urea and represented 1.2% of the anhydrous ammonia-N applied. They attributed this to the fact that the customary method of applying anhydrous ammonia by injection into soil produces highly alkaline zones and

results in high N_2O emission. Lindau *et al.*⁷⁰ reported that the emission of N_2O due to fertilizer addition was low in lowland rice and there was no increase of N_2O emission with urea addition above control. In maize field, however, the emission of N_2O with urea was about two times that of $Ca(NO_3)_2$ (ref. 71). Eichner⁷² summarized the data from 104 field experiments and estimated that 2.7% of anhydrous ammonia, 0.44% of ammonium nitrate, 0.25% of ammonium type, 0.11% of urea and 0.05% of nitrate were lost as N_2O . However, his estimation differed significantly from that of Galbally⁷³, who estimated that 0.5% of anhydrous ammonia, 0.1% of ammonium nitrate, 0.1% of ammonium type, 0.5% of urea and 0.05% of nitrate were emitted as N_2O . Addition of nutrients such as P and liming materials such as $CaCO_3$ can also affect N_2O evolution from soils in some situations. Minami and Fukushi⁷⁴ found that application of P or $CaCO_3$ increased emission of N_2O under aerobic conditions. However, P-induced emission were larger than those obtained with $CaCO_3$. Sahrawat *et al.*⁷⁵ also observed that addition of $CaCO_3$ increased emission but the addition of P had no effect.

Amendment with organic manure

Denitrifiers as well as nitrifiers use organic C compounds as electron donors for energy and synthesis of cellular constituents. Plant residues, green manure and farm-yard manure have been reported to increase rates of denitrification^{35,76,77}. However, if the soil is N limiting, denitrification losses may be reduced due to immobilization of N caused by the decomposition of residues having wider C : N ratios⁷⁸. Cabrera *et al.*⁷⁹ observed that maximum rates of N_2O emission occur within the first 4 days after poultry litter application. The highest emission rate occurred with fine poultry litter particle followed by palletized litter. Rolston *et al.*⁸⁰ estimated the emission of N_2O from a field which received cow dung manure and reported that maximum emission occurred with manure application.

Plants

Plants affect the emission of N_2O by influencing nitrate and carbon content of the soil and partial pressure of oxygen. Plants can directly influence nitrate availability through uptake and assimilation making it unavailable to denitrification. An indirect effect of nitrate levels arises from the supply of organic matter of root origin. Mineralization and nitrification of this material can potentially provide more nitrate for denitrification and conversely immobilization can reduce nitrate levels. Another indirect effect is the ability of few plants, e.g. rice to supply O_2 at the rhizosphere, which can enhance the nitrate content by promoting nitrification. Plant species might differ

in their effect on denitrification. Higher denitrification rates in soils grown with a legume rather than with a monocotyledonous plant have been observed^{81,82}.

Paddy soils

Paddy soils used for growing rice, are also major contributors of N_2O . Puddling eliminates water transmission pores, reduces the percolation rate and drastically reduces gaseous exchange between the soil and the outer atmosphere. Lindau *et al.*⁸³ reported that from a flooded Crowley silt loam rice soil of USA, emission of N_2O-N was about $4 \text{ g ha}^{-1} \text{ d}^{-1}$. Smith *et al.*⁸⁴ estimated N_2O emission following urea application in wetland rice and observed that the emission was correlated with the exchangeable ammonia-N content of the soil and nitrous plus nitrate-N content of floodwater. The emission of N_2O ranged from 90 to 171 g N ha^{-1} . Cai *et al.*⁸⁵ observed that emission increased with the increase in N application and it was higher from ammonium sulphate than from urea treatments at the same application rates. Buresh and De Dutta⁸⁶ observed that total loss due to denitrification was around 2.2% of applied N during a period of 20 days and N_2O constituted about 10% of it. Mosier *et al.*⁸⁷ recorded 10% loss of applied N due to denitrification ($N_2 + N_2O - N$). Studies conducted in India⁸⁸ revealed 12.4% loss of added N as ($N_2 + N_2O$)-N.

Secondary interactions affecting N_2O emission

Organic carbon, oxygen and nitrate content of the soil are three important factors that exert a direct effect on N_2O emission. The effects of these primary factors are influenced by a number of secondary interactions. Soil water content exerts diffusional constraints on soil oxygen. It also influences the availability of organic carbon release through wetting and drying cycles. Organic carbon has an effect on nitrate availability, which is manifested through mineralization/immobilization reactions. Nitrate availability is also subjected to diffusional constraints imposed by soil water content. Soil texture and structure can also influence N_2O emission. Finally, microbial respiration of the available organic carbon can have a dramatic effect on oxygen levels at the microsite level. Thus, heterogeneous nature of the soil matrix makes the relationships more complex and difficult to quantify. In order to deal more effectively, the factors and their interactions need to be identified for estimations. Interactions of various factors regulating denitrification, the major contributor of N_2O , in soil have been depicted in Figure 1 (ref. 89).

Use of nitrification inhibitors

One strategy to limit N_2O emission from fertilized fields is the use of nitrification inhibitors. These inhibitors can

slow NH_4^+ oxidation to NO_3^- and thereby reduce N_2O losses during both nitrification and denitrification^{37,90}. Application of nitrapyrin, a nitrification inhibitor, reduced N_2O emission in an incubation study with ammonium sulphate and urea⁹. Blackmer *et al.*⁹¹ reported that nitrapyrin as well as acetylene reduced the emission of N_2O from urea and ammonium-fertilized soil. Similarly, nitrification inhibitors such as DCD, 2-amino-4-chloro-6-methylpyrimidine (AM) and 2-sulfanilamide-thiazole, were also effective in reducing N_2O emission from the soils^{89,92}. Bremner and Yeomans⁹³ studied the influence of 28 nitrification inhibitors on N_2O emission in anaerobic soil conditions. They observed that except potassium azide and 2,4-diamino-6-trichloromethyl-s-triazine, the inhibitors either had no appreciable effect or enhanced the emission when applied at the rate of 10 mg g^{-1} soil or 50 mg g^{-1} soil. Recently, cycloheximide was tried to block N_2O emission⁹⁴. It was observed that between 0.5 and 2.5 mg g^{-1} cycloheximide almost completely blocked the emission.

Methods of measuring N_2O emission

There are two steps for measurement of N_2O emission from soil, i.e. collection of N_2O and its quantification.

Collection

Two methods have been employed for collection of N_2O from soil in the field, viz. soil cover method^{95,96} and micrometeorological method^{97,98}. However, due to simplicity of measurement, the soil cover method is widely used.

Soil cover method: In this method, N_2O flux from soil is estimated by measurement of N_2O concentration in the atmosphere beneath a soil cover, e.g. glass jars or a box of acrylic sheets placed over the soil for a certain period⁹⁹. Each cover is inserted about 2 cm into the soil and then fitted with a styrofoam cover to minimize internal heating

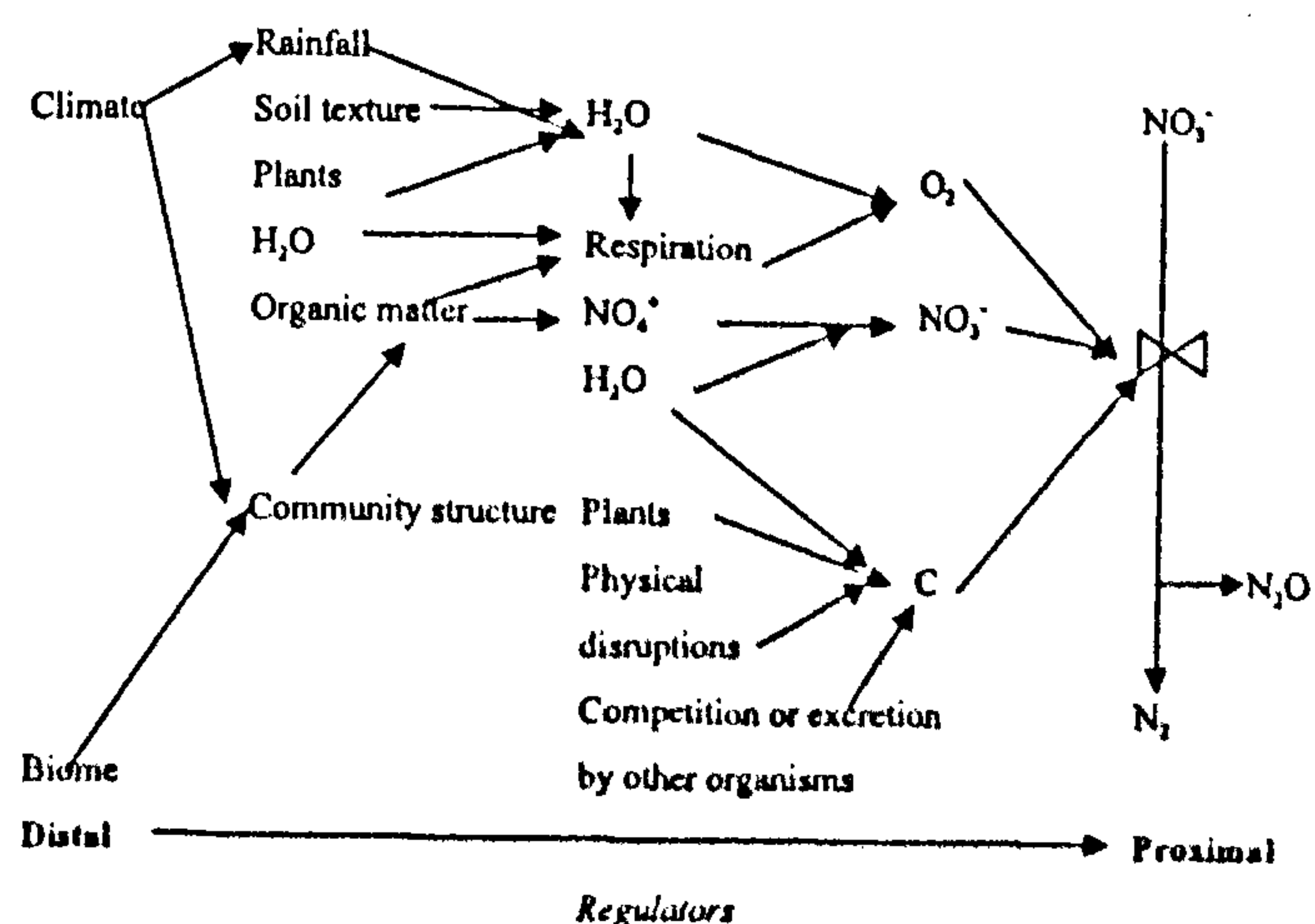


Figure 1. Interactions of various factors regulating denitrification.

by solar radiation. After certain time intervals, air samples are withdrawn from the covers and analysed. Rolston *et al.*⁸⁰ directly measured the flux of N₂O by placing covers over the soil surface and sampling the atmosphere beneath the covers after 1 or 2 h. However, in some measurements, chambers are put for even 2 days⁹. Measurement of flux in this method, however, has to be corrected for the effects of increasing N₂O concentration in the enclosed air space on the rate of N₂O diffusion from the soil surface^{98,100}. Furthermore, a closed soil cover isolates the soil surface from atmospheric influences, particularly pressure fluctuations, experienced by the external soil surface. Ryden *et al.*⁹⁵ suggested that it would be preferable to use the soil cover method coupled to external atmosphere through an air inlet vent. Such an approach, they argued, is expected to minimize the differences between conditions at the enclosed and open soil surface, as the enclosed air will be continuously replaced with external air. Moreover, the inlet vent will allow external pressure variation to be reflected within the enclosure. They absorbed the N₂O swept from the air space on a quantity of 5 Å molecular sieve¹⁰¹ placed in an air-flow line connected to one end of the enclosure. Based on the principles of Hutchinson and Mosier¹⁰² and Conrad *et al.*¹⁰³, an automated static chamber system has been developed by Loftfield *et al.*¹⁰⁴ for measurement of N₂O, although with several modifications. They measured fluxes by monitoring increases in N₂O in double-walled plexiglas chambers at 30 and 60 min intervals after the chamber lids are closed. Opening and closing of the chamber lids, gas sampling operations, and data collection and analyses are all controlled by a personal computer.

Micrometeorological method. Originally described by Thom¹⁰⁵, it requires vertical profiles of wind, temperature, and N₂O concentration in the first few meters of free air stream above the vegetation. Mosier and Hutchinson⁹⁷ used this technique and measured vertical wind speed profiles using C.W. Thorthwaite Associates cup anemometers and temperature by linear thermistoes. N₂O concentration profiles were determined by using a modified Harvard Apparatus 975 constant rate syringe pump to simultaneously fill eight of the syringes, each with air from a different sampling height. Air samples accumulated over 1 h period were then returned to laboratory for analysis. They measured emission of N₂O from corn field by the soil cover method as well as by the micrometeorological method and noticed that both the methods gave identical estimations of N₂O emission. Recently, Skiba *et al.*¹⁰⁶ successfully used this technique to measure N₂O emission from a wheat crop.

Quantification

Gas samples are analysed for N₂O by gas chromatography (GC) fitted with electron capture detector (ECD). In case

of the soil cover method, N₂O flux can be computed from the concentration increase using the equation given by Hutchinson and Mosier¹⁰², which corrects for the reduction in soil N₂O concentration gradient with time as the gas accumulates. Corrections should be made for solubility of N₂O in water and effect of temperature on the solubility¹⁰⁷.

Problems associated with quantification of N₂O emission

Measurement of N₂O emission in the field is complicated by phenomena like (1) diurnal, temporal and spatial variability; (2) entrapment in soil; (3) transmission of gas through plants; and (4) dissolution of N₂O in soil water.

Variability in N₂O measurement: The spatial as well as temporal variability exhibited by N₂O emission from the soil are very high. Spatial variability may partly be due to heterogeneity of the soil system. Temporal variability has been reported to be much greater than spatial variability^{108,109}. This can be related to the fact that the rate of N₂O reduction increases rapidly following longer periods of incubation of the soil in the presence of N₂O (ref. 110) or anaerobic preincubation⁹⁵. The variability of the N₂O flux measurement could be reduced by intensive sampling¹⁰⁸.

Entrapment of the gas in soil: N₂O generated in the soil can be entrapped in the soil itself, resulting in underestimation of flux measurement. In dry soils, diffusion of the gas is quicker as compared to wet soils. Therefore, in wet soils, more than a week is required to collect all the gas produced within the soil¹¹¹.

Transmission of N₂O through plants: Transmission of gas through internal voids in roots and stems occurs in several plants¹¹². Mosier *et al.*⁸⁷ obtained greater recovery of N₂O produced in the soils when the chambers were placed over rather than between rice plants and demonstrated that N gas produced in the soil can be transported through rice plants to the atmosphere. The N gas flux was not only greater but also faster in the planted system.

N₂O dissolved in water: In wet soils, N₂O remains entrapped in the soil pore water. In high moisture condition, serious errors may be encountered in the measurement of N₂O if dissolved gas is not taken into account. Temperature and the ratio of solution volume to atmosphere volume in the incubation vessel influence the quantity of dissolved N₂O (ref. 107).

Estimates of N₂O emission from soil

The tentative global estimate of N₂O emission is 9.7 Tg N yr⁻¹ to 12.0 Tg N yr⁻¹ for natural ecosystems and

2.3 Tg N yr⁻¹ to 3.7 Tg N yr⁻¹ for cultivated lands¹¹³. Yoshinari²⁸ predicted that the global budget of N₂O emission should be 14–17 Tg yr⁻¹. The methodologies adopted in N₂O collection at field level are not yet precise and hence, there is considerable uncertainty in N₂O estimates. Eichner⁷² estimated that the global release of N₂O from fertilized soils to the atmosphere ranged from 0.2 Tg N₂O–N yr⁻¹ to 2.1 Tg N₂O–N yr⁻¹. Inter-Governmental Panel on Climate Change (IPCC)¹¹⁴ reported that total global emission of N₂O from the soil are 5–15 Tg N₂O–N yr⁻¹ (Table 2). For lack of data on N₂O emission from individual fields, the earlier estimates assumed that about 7% of the nitrogen lost by denitrification are emitted as N₂O (ref. 115). Now with the advent of sensitive N₂O detection equipment it is possible to measure N₂O production directly in the field. Various researchers^{95,101,116} indicated N₂O emission ranging from < 0.001 kg N₂O–N ha⁻¹ day⁻¹ to 1 kg N₂O–N ha⁻¹ day⁻¹ depending on nitrogen fertilization rate, source of N, soil water content, tillage practices and prevailing soil temperature. Ryden and Lund³⁷ quantified N₂O flux from irrigated land cropped to vegetables in California and it ranged from 0.0038 to 1.06 kg N ha⁻¹ per day. Mosier and Hutchinson⁹⁷ estimated N₂O emission from an irrigated corn field to be only 2.5 kg N ha⁻¹ during mid-May to mid-September. In a field study¹¹⁷, the amount of N₂O evolved varied from nil to 8 kg N ha⁻¹ day⁻¹. The highest emissions were reported in summer from experimental plots maintained in a wet state and treated with manure. Duxbury and McConnaughey¹¹⁸ observed 2% of the applied N as N₂O in corn systems.

Yoshinari²⁸ concluded that loss of fertilizer N as N₂O is generally in the range of 0.01–3%. Though Bremner *et al.*¹¹⁹ found the loss to be as much as 4–7% when the fields were fertilized with anhydrous ammonia. Duxbury *et al.*¹²⁰ found that the annual emission of N₂O–N from mineral soils ranged from 0.9 kg N ha⁻¹ to 0.42 kg N ha⁻¹, whereas for organic soils it ranged from 7 kg N ha⁻¹ to 165 kg N ha⁻¹. Emission of N₂O from various land use types is presented in Table 3.

N₂O emission studies in India

Requirement of sophisticated laboratory facility for N₂O emission restricted such studies to a few laboratories in India. Some measurements of N₂O from grassland and wasteland in India have been done by Parashar *et al.*¹²¹. Studies in the Division of Environmental Sciences, Indian Agricultural Research Institute (IARI), New Delhi showed that the emission of N₂O from rice fields fertilized with urea ranged from 0.06 to 0.8% of the applied fertilizers. Soils amended with urea emitted the highest amount of N₂O followed by ammonium sulphate and potassium nitrate amended soils of wheat crop. In case of paddy soils potassium nitrate-applied plots emitted the maximum amount of N₂O compared to ammonium sulphate¹²². Some studies also were conducted on the loss of nitrogen due to denitrification. At Central Rice Research Institute, Cuttack, a field study was conducted to determine the influence of rice plants on the transport of N₂ and N₂O from the soil to the atmosphere⁸⁷. For N₂O measurement gas chromatography was used, whereas for N₂ + N₂O

Table 2. Sources and sinks of N₂O (10¹² g N yr⁻¹)

Sources	Ref. 114	Ref. 130	Ref. 131	Ref. 132
Natural				
Oceans	1.4–2.6			
Tropical soils:				
Wet forests	2.2–3.7			
Dry savannas	0.5–2.0			
Temperate soils				
Forests	0.05–2.0			
Grasslands	?			
Anthropogenic				
Cultivated soils	0.03–3.0			
Biomass burning	0.2–1.0			
Stationary combustions	0.1–0.3			
Mobile sources	0.2–0.6			
Adipic acid production	0.4–0.6			
Nitric acid production	0.1–0.3			
Total	5.2–17	17–20	29	15
Total emissions from soil	5–15			
Sinks				
Photolysis in stratosphere	7–13	6–11		11
Removal by soils	?			
Atmospheric increase	3–4.5			

Contribution of irrigated and upland paddy fields of India 0.004–0.21 and 0.002–0.01 Tg/y (ref. 133).

measurement mass spectrophotometric method with ¹⁵N was used. The young rice plant facilitated the efflux of these gases from soil. Little N₂O gas was trapped in the rice planted soils but large quantities were trapped in the unplanted soils. In another study⁸⁸ conducted at IARI, New Delhi (N₂ + N₂O)-¹⁵N fluxes were determined, which revealed 12.4% recovery of added N as (N₂ + N₂O)-N.

Use of models to predict N₂O emission

Presently, mathematical models are increasingly being

used to predict N₂O emission¹²³. Li *et al.*¹²⁴ developed a rainfall-driven model for simulating the evolution of N₂O. The model includes thermal-hydraulic, decomposition and denitrification sub-models and needs inputs of climate data, soil physical properties, initial soil chemical properties and agronomic management practices. They observed that the magnitudes of simulated N₂O emission were consistent with the results of field experiments¹²⁵. Parton *et al.*¹²⁶ presented a general model (NGAS) for N₂ and N₂O formation from nitrification and denitrification to simulate regional and global trace gas production as a function of climate, soil properties, and management.

Table 3. N₂O-N emission (g ha⁻¹ day⁻¹) from different land use types

Land use type	Fertilizer type	N level (kg/ha)	N ₂ O-N emission	Country	Soil texture	Org. C (%)	Ref.
Soil	Ammonium	180	31.4	USA	Medium	2.5	69
Soil	Ammonium	250	107.9	USA	Fine	4.6	119
Soil	Anhy. amm.	180	4.6	USA	Medium	2.5	69
Grass	Amm. nitrate	100	24.3	Denmark	Medium	1.9	130
Grass	Calcium nitrate	400	16.4	UK	Medium	2.3	132
Grass	Calcium nitrate	400	21.9	UK	Medium	4.0	132
Corn	Urea	140	29.4	USA	Medium	1.0	118
Corn	Manure/urea	273	14.2	USA	Fine	1.0	134
Corn	Urea	100	24.2	Pakistan	Medium	1.05	135
Barley	Amm. nitrate	112	6.7	USA	Medium	1.7	97
Barley	Amm. nitrate	224	9.2	USA	Medium	1.7	97
Wheat	Amm. nitrate	175	3.5	USA			72
Wheat	Amm. nitrate	175	6.5	USA			72
Wheat	Urea	100	28.6	Pakistan	Medium	1.05	135
Rye	Amm. nitrate	80	1.6	USA	Medium		44
Rye	Amm. nitrate	80	7.9	USA	Medium		44
Tobacco	Amm. nitrate	410	68.3	USA	Medium		44
Tobacco	Green manure		8.8	USA	Medium		44
Cauliflower	Urea	528	72.9	USA	Medium		37
Cauliflower	Urea	528	80.0	USA	Medium		37
Rice	Urea	120	1.3	Philippines	Fine	1.69	136
Rice	Green manure	60	0.56	Philippines	Fine	1.69	136
Rice	Urea	120	1.01	India	Fine	0.4	122
Rice	Urea + DCD	120	0.48	India	Fine	0.4	122

Table 4. Strategies to mitigate N₂O emission from agricultural soils

Practice followed	Estimated decrease in emission (Tg N yr ⁻¹)
1. Match N supply with crop demand:	0.24
a. Use soil/plant testing to determine fertilizer needs	
b. Minimize fallow periods to limit mineral N accumulation	
c. Optimize split application schemes	
d. Match N application to reduce production goals in regions of crop overproduction	
2. Tighten N flow cycles:	0.14
a. Integrate animal and crop production systems in terms of manure. Reuse in crop production	
b. Maintain plant residue N on the production site	
3. Use advanced fertilization techniques:	0.15
a. Controlled release fertilizers	
b. Place fertilizers below the soil surface	
c. Foliar application of fertilizers	
d. Use nitrification inhibitors	
e. Match fertilizer type to seasonal precipitation	
4. Optimize tillage, irrigation and drainage	0.15
Total	0.68

practices. Comparison of simulated emission with field data for several sites showed that the model compared well with the observed data ($R^2 = 0.62$). The model also suggested that about 0 to 59% of N_2O emission are a result of denitrification. Muller *et al.*¹²⁷ used Michaelis-Menten kinetics and observed that such models can successfully be used for prediction of N_2O emission.

Strategies to reduce emission of N_2O from soil

With the present knowledge, it appears that agriculture is the major source for N_2O emission. Mosier *et al.*¹²⁸ and Beauchamp¹²³ discussed the mitigation options that could result in significant decrease in N_2O emission from agricultural systems. They opined that if implemented they are more likely to increase rather than decrease crop and animal productivity. A list of such practices are given in Table 4.

Areas of further research

1. Simple and accurate technologies in quantifying N_2O emission need to be developed for different land use types.
2. The relative contribution of denitrification and nitrification towards emission of N_2O needs to be estimated.
3. Interactions of different factors involved in N_2O emission need to be studied.
4. Use of chemicals in controlling N_2O emission needs to be assessed for non-target effects and for economic feasibility.
5. Field measurements need to be carried out in our country for precise (accurate) estimations through simulation models.
6. Models capable of extrapolating N_2O emission estimates in local and regional scales need to be developed.

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