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Nitrous oxide
from agriculture



Tom Granli and
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Agricultural University of Norway – Advisory Service, Ås, Norway

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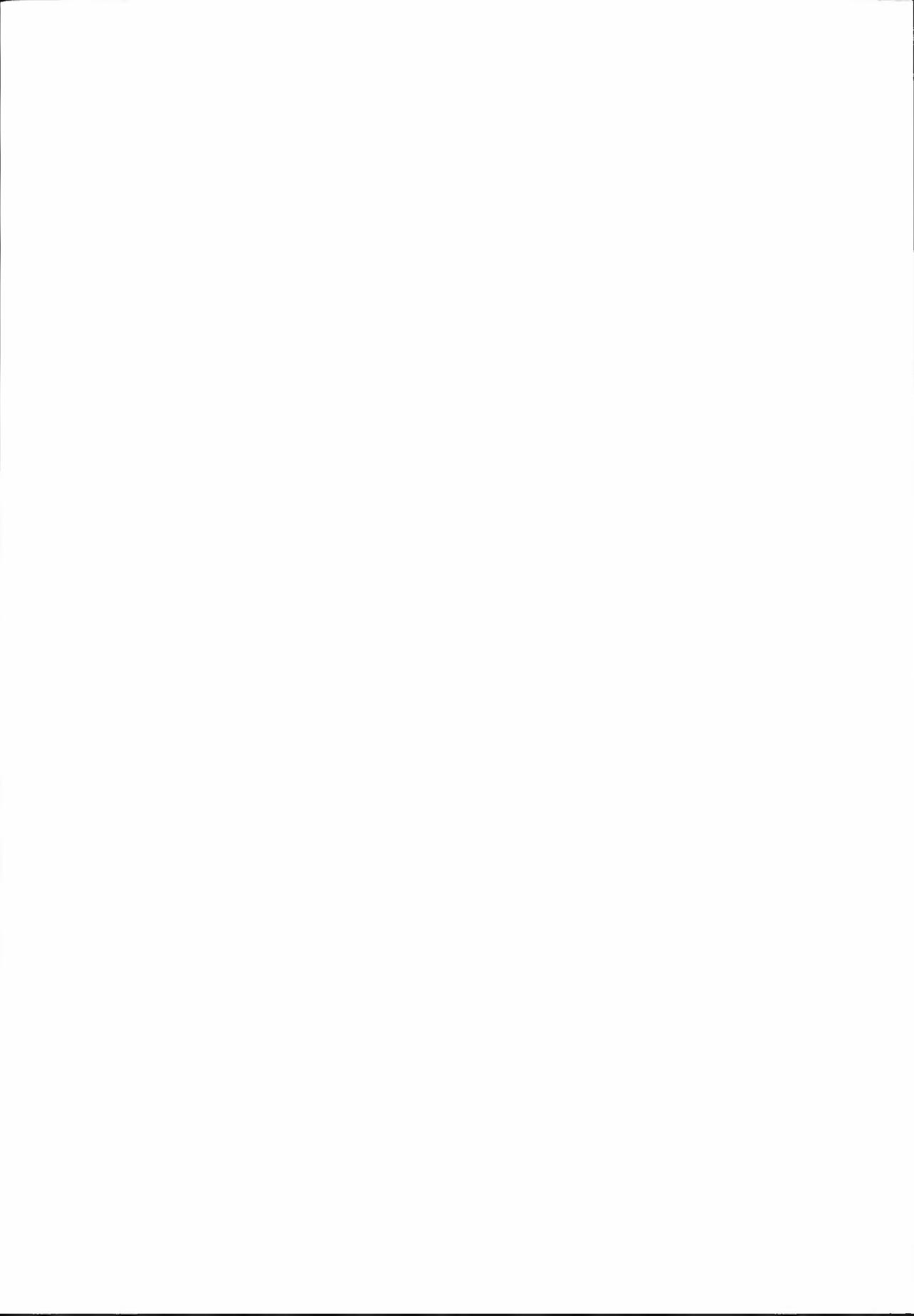
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Nitrous oxide from agriculture

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I. SUMMARY

Nitrous oxide (N_2O) is a greenhouse gas. Increasing atmospheric concentration may also be detrimental to the stratospheric ozone layer. The annual flux to the atmosphere has increased by 4.5 ± 0.6 Tg (= million tonnes) N_2O -N since preindustrial days – an increase of about 50%. Only rough estimates of amounts emitted from various sources can be made at present, but agriculture is a major source.

Most N_2O originates with soil processes, as an intermediate product from microbial nitrification and denitrification. Methods for measuring process and emission rates are reviewed. The rates vary greatly, and are larger from natural soils in tropical than in temperate climates.

The potential of a soil to form and emit N_2O increases with increasing availability of N, but the amounts emitted depends on interactions between soil properties, climatic factors and agricultural practices. Main controllers are:

- soil content of NH_4^+ and NO_3^- . As N inputs increase, so do N_2O losses. Application of fertilizers and manures, incorporation of crop residues rich in N and the growing of legumes, all tend to increase N_2O fluxes to an extent that depends on soil conditions
- soil aeration status and soil water content. N_2O emissions tend to be greatest when soils are wet, but not waterlogged
- presence of degradable organic material promotes microbial activity, tends to reduce the availability of O_2 and enhances N_2O emissions
- soil pH affects N_2O formation, but the outcome depends on other controllers
- soil temperature. Emissions tend to increase with increasing temperature.

Enhanced N_2O release from natural ecosystems due to increased anthropogenic N input is also discussed.

The possibilities for reducing N_2O emissions from agriculture through adherence to approved practice are surveyed. Since high levels of soil mineral N furthers N_2O formation those measures already in «Codes of Good Agricultural Practice» to minimize losses of NO_3^- to water systems should be useful also for diminishing N_2O emissions.

Topics that require further investigations are identified.

Key words: agriculture, ammonium, fertilization, management, manure, nitrate, nitrous oxide, organic material, soil, water.

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2. INTRODUCTION

The environmental issues relating to agriculture and fertilizer use were reviewed by Bøckman et al. (1990). One of these issues is an enhanced flux of N_2O to the atmosphere. The intensity of this flux varies greatly with circumstances. Identification of those conditions that lead to substantial production of N_2O seems a logical first step towards emission management. This review is a contribution towards that end.

The literature is covered to the end of 1992 by searches in databases for chemistry, biology, agriculture and environmental issues. Later publications are included where available, but the time delay before publications are listed in appropriate databases makes coverage of the scientific literature for 1993 incomplete.

2.1 N_2O in the atmosphere: The environmental issues

Increasing atmospheric content of some trace gases gives cause for serious environmental concern. One such gas is nitrous oxide (N_2O). Soil microbial processes, affected directly and indirectly by agriculture, are the principal sources. We will focus on these processes as sources of N_2O , and on agricultural practices that can influence N_2O emission.

The amount of N_2O present in the atmosphere is currently increasing at about 0.2 to 0.3% · year⁻¹. This increase gives concern on two counts:

- N_2O is one of the «greenhouse gases». It absorbs light in the infra-red region (at frequencies of 520–660, 1200–1350 and 2120–2270 cm⁻¹) and reduces atmospheric transparency to thermal radiation from the earth's surface. The present increase in atmospheric N_2O concentration contributes about 5% of the calculated anthropogenic greenhouse effect.
- N_2O , or rather nitrogen oxides produced from it by photochemical reactions in the stratosphere are involved in destruction of stratospheric ozone. However, nitrogen oxides also react with degradation products from volatile chlorinated carbon compounds and thus diminish their ability to cause ozone destruction. The influence of N_2O on the stratospheric ozone shield is thus complex. However, a slowly increasing atmospheric N_2O concentration may have an over-all detrimental effect on the total ozone content of the stratosphere, notably as the emissions of chlorofluorocarbons (CFC) are reduced.

The environmental concern with N_2O emissions from agriculture date from the early 1970's (Johnston 1972; Crutzen 1974). Earlier work on this topic was reviewed by Delwiche (1981), more recently by Cicerone (1987), McElroy & Salawitch (1989), IPCC (1990, 1992), Wuebbles & Edmonds (1991) Rubin et al. (1992) and Badr & Probert (1993a).

There is an extensive literature on adverse health effects (bone marrow depression and neurological abnormalities) of high concentrations of N_2O , that can be experienced in hospital operating theatres (DECOS 1991; Yagiela 1991). The adverse health effects are mainly due to a reaction between N_2O and the reduced form of vitamin B₁₂, thereby inhibiting important biochemical processes. The Norwegian

threshold limit value for occupational exposure to N_2O is 100 ppmv (DLI 1991). The small increase in ambient concentration (310 ppbv) which is taking place, is not regarded as having direct medical implications.

2.2 Units

Amounts of N_2O are reported in the literature both as N_2O and $\text{N}_2\text{O-N}$. We report amounts as $\text{N}_2\text{O-N}$, and use the conversion factor:

$$\text{N}_2\text{O-N} = 0.636 \cdot \text{N}_2\text{O}$$

Various units are used for N_2O emissions and concentrations, and the following conversion factors apply:

Emission measures:

$$\begin{aligned} 1 \text{ g N}_2\text{O-N} \cdot \text{ha}^{-1} \cdot \text{day}^{-1} &= 0.36 \text{ kg N}_2\text{O-N} \cdot \text{ha}^{-1} \cdot \text{year}^{-1} \\ &= 1.16 \text{ ng N}_2\text{O-N} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \\ &= 2.5 \cdot 10^9 \text{ molecules N}_2\text{O} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \end{aligned}$$

However, care should be exercised in converting results from short-term measurements into emissions over long time periods due to the large diurnal and seasonal variations in emission rates.

Concentration measures:

$$\begin{aligned} 1 \text{ ppmv N}_2\text{O} &= 1000 \text{ ppbv N}_2\text{O} \\ &= 10^{-4} \text{ vol-\% N}_2\text{O} \\ &= 4.1 \cdot 10^{-2} \text{ mmol N}_2\text{O} \cdot \text{m}^{-3} \text{ (at } 25^\circ\text{C)} \\ &= 1.14 \text{ mg N}_2\text{O-N} \cdot \text{m}^{-3} \text{ (at } 25^\circ\text{C)} \end{aligned}$$

Mass measures:

$$\begin{aligned} 1 \text{ Tg} &= 10^{12} \text{ g} = 10^6 \text{ tonnes} \\ 1 \text{ Gg} &= 10^9 \text{ g} \end{aligned}$$

2.3 Global sources and sinks of atmospheric N_2O

2.3.1 Sources

Ice core studies indicated that the concentration of N_2O in air was 285 ppbv before the year 1700 (Stauffer & Neftel 1988). This is the value currently used for the undisturbed background concentration, though Leuenberger & Siegenthaler (1992) reported a value as low as about 260 ppbv. The concentration has increased during the present century. The main increase has taken place since World War II, and in 1990 the ambient concentration of N_2O in air was 310 ppbv. Though there are large diurnal and seasonal variations in N_2O emissions, the amount present in the atmosphere is so large that seasonal variations in the atmospheric concentration are insignificant. However, the annual increment varies. Over 3 year periods the trends have ranged from $0.5 \pm 0.2 \text{ ppbv} \cdot \text{year}^{-1}$ to $1.2 \pm 0.1 \text{ ppbv} \cdot \text{year}^{-1}$ with a mean for 1977–88 of $0.80 \pm 0.02 \text{ ppbv} \cdot \text{year}^{-1}$ (Khalil & Rasmussen 1992b). The reason for this variation is unknown.

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The International Panel on Climate Change (IPCC 1992) estimates that the atmospheric lifetime of N₂O (mean residence time = atmospheric content/flux at steady state) is in the range of 110 to 168 years, best estimate about 130 years.

The atmosphere contains about 1500 Tg N₂O-N at present. The observed increase in atmospheric N₂O concentration represents an annual extra input due to human activities of about 3 to 4.5 Tg N₂O-N (Watson et al. 1990). Khalil & Rasmussen (1992b) found the increase to be 4.5 ± 0.6 Tg N₂O-N·year⁻¹. The natural background emission was about 9.5 Tg N₂O-N·year⁻¹, assuming a lifetime of 150 years and that the sinks have not changed significantly due to human activity. Prinn et al. (1990) calculated the total annual emission as 13.0 ± 1.5 Tg N₂O-N assuming a lifetime of 166 years. This corresponds closely with the estimate of Khalil & Rasmussen (1992b) when corrected for mean residence time.

The annual input of N₂O to the atmosphere has thus increased by about 50% since preindustrial times (IPCC 1990), and Khalil & Rasmussen (1992b) reported that the emissions seem to be increasing. Even with no further increase in emissions the concentration should reach about 340 ppbv in the year 2040.

Emission estimates are based on studies of ecosystems and sources that are assumed to be typical. Such studies usually give a wide range of results. Consequently it is still only possible to make rough estimates of regional and global emissions, despite the substantial amount of work already done, see Bouwman (1990), Badr & Probert (1992a,b) and Khalil & Rasmussen (1992b).

Two recent examples illustrate how estimates of regional N₂O sources and their relative importance vary:

Galbally et al. (1992) estimated the Australian N₂O emissions as:

	N ₂ O-N	
	<u>Gg year⁻¹</u>	<u>% of total</u>
<i>Natural:</i>		
Biomass burning	9	1.5
Natural ecosystems	488	80.0
Termites	22	3.6
Subtotal	<u>519</u>	<u>85.1</u>
<i>Anthropogenic:</i>		
Crops	38	6.2
Legume pasture	51	8.4
Motor vehicles	2	0.3
Subtotal	<u>91</u>	<u>14.9</u>
Total	<u>610</u>	<u>100</u>

K. Robertson (1991) estimated the emissions in Sweden as:

	<u>N₂O-N</u>	
	<u>Gg year⁻¹</u>	<u>% of total</u>
<i>Natural:</i>		
Agricultural land	3.7	8.0
Wetlands and waters	8.2	17.7
Forest and other land	13.9	30.0
Subtotal	<u>25.8</u>	<u>55.7</u>
<i>Anthropogenic:</i>		
Fertilizer use	2.4	5.2
Animal manure	2.8	6.1
Eutrophication and atmospheric deposition	6.9	14.9
Combustion and traffic	6.6	14.3
Fertilizer production	1.5	3.2
Others	0.3	0.6
Subtotal	<u>20.5</u>	<u>44.3</u>
Total	<u>46.3</u>	<u>100</u>

K. Robertson (1991) indicated that the flux from combustion and traffic may be an overestimate, and that each estimate has a wide range of uncertainty. The only exception was fertilizer production, where emissions were accurately known from measurements at the plants. Coastal and offshore N₂O formation was not included in this survey. Law & Owens (1990) estimated that 0.62% of the N input to the rather shallow North Sea was lost as N₂O. Similar estimates have been published by Rubin et al. (1992).

The estimate made by IPCC (1992) provides a summary of known global sources and sinks of atmospheric N₂O:

Sources	<u>N₂O-N</u>
	<u>Tg·year⁻¹ (range)</u>
<i>Natural</i>	
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	?
Subtotal	<u>4.15 – 10.3</u>

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	<u>N₂O-N</u> Tg·year ⁻¹ (range)
Sources	
<i>Anthropogenic</i>	
Cultivated soils	0.03 – 3.0
Biomass burning	0.2 – 1.0
Stationary combustion	0.1 – 0.3
Mobile sources	0.2 – 0.6
Adipic acid production	0.4 – 0.6
Nitric acid production	0.1 – 0.3
Subtotal	<u>1.03 – 5.8</u>
Total	<u>5.18 – 16.1</u>
Sinks	
Removal by soils	?
Photolysis in the stratosphere	7 – 13
Atmospheric increase	<u>3 – 4.5</u>

This IPCC (1992) estimate provide a useful basis for comments on sources.

Natural sources

Agriculture and other human activities cause emissions of N compounds (NH₃ and NO_x) to the atmosphere and NO₃⁻ and sewage to waters. These emissions have probably enhanced N₂O formation in natural ecosystems such as forests, rivers and coastal areas.

Part of the N₂O emission from water ecosystems originate from ground water which is supersaturated with N₂O originating from soil microbial processes. Ronen et al. (1988) suggested that 0.5 to 1 Tg N₂O-N·year⁻¹ might come from groundwater. Ueda et al. (1991) confirmed that groundwater is supersaturated with N₂O, and concluded that this source may play a significant, but not crucial, role in the global N₂O cycle. They noted that groundwater N₂O was depleted in ¹⁵N compared to atmospheric N₂O. Hence, groundwater may be a comparatively minor source of atmospheric N₂O. This topic is further discussed in section 7.5.

Aquatic ecosystems, e.g. wetlands, estuarine and coastal areas seem to be important areas for denitrification (Seitzinger 1990; Devol 1991). N₂O is formed (Lindau & DeLaune 1991; Lindau et al. 1991; Naqvi & Noronha 1991; Franken et al. 1992; Law et al. 1992), though the emission rates from natural wetlands were among the lowest reported from terrestrial ecosystems (Bouwman 1990; Samuelsson & Klemetsson 1991). The topic of enhanced N₂O emissions from non-agricultural ecosystems due to enhanced N inputs is further discussed in section 16.1.2.

Some atmospheric processes may generate N₂O. Adema et al. (1990) claim that N₂O can be formed by reactions between NO₂, O₃ and NH₃, but the amounts produced are not known. N₂O can form in electrical discharges (Brandvold & Martinez 1988). Hill et al. (1984) estimated that lightning and point discharges beneath thunderclouds only produce about 2 to 9 Gg N₂O-N·year⁻¹, while Bhetanabhotla et al. (1985) reported the even lower estimate of 0.14 Gg N₂O-N·year⁻¹. Hence this natural source

of N_2O seems minute. Stratospheric production of N_2O through photochemical reactions takes place, but is also an insignificant source for stratospheric N_2O (Maric & Burrows 1992).

Anthropogenic emissions:

While background emission may have been enhanced as an indirect effect of pollution, emissions directly attributable to human activities probably constitute the major part of anthropogenic N_2O emissions.

Soil microbial processes are generally regarded as the major global source of N_2O (Banin 1986).

Soil air can have N_2O concentrations greatly in excess of that of ambient air. Concentrations as high as 1200 to 8300 ppmv have been observed (Amundson & Davidson 1990). IPCC (1992) give an estimate of 0.03 to 3 Tg N_2O -N \cdot year⁻¹ as the range of emissions from cultivated soil. This broad range reflects the great variability in agricultural conditions and practices. Fluxes of N_2O from cultivated land are further discussed in chapter 5, and the magnitude of these emissions forms the subject of section 16.1.1.

Earlier estimates of anthropogenic N_2O inputs regarded fossil fuel burning as the major source (McElroy & Wofsy 1986). However, it was later shown that the data from analysis of stack gases from power stations were in error due to reactions between NO_x , SO_2 and H_2O in the period between sampling and analysis (Muzio et al. 1989). Power generation is now considered to be a minor anthropogenic source, though some N_2O is formed in catalytic converters on boilers (De Soete 1991). The formation of N_2O during combustion was reviewed by Hayhurst & Lawrence (1992). There still remains the possibility of some N_2O formation in plumes from industrial combustion including power and steam generation and in areas of gross atmospheric pollution with NO_x and SO_2 (Khalil & Rasmussen 1992a).

Motor vehicles are a minor source of N_2O . Dasch (1992) calculated the global emissions as 0.13 Tg N_2O -N \cdot year⁻¹ or somewhat below the IPCC (1992) estimate. However, cars with catalytic converters emitted on average (depending on catalyst system) 8 to 16 times more N_2O -mile⁻¹ than cars without converters. Wide-spread adoption of catalyst cars to combat air pollution may thus substantially increase the N_2O emission from traffic unless this potential problem is addressed.

About 90% of global biomass burning takes place in tropical regions: Forest clearing, savanna and sugar cane field fires, burning of agricultural waste and firewood. Most N in the biomass is released as N_2 , NH_3 , NO_x and nitrates, but small amounts of N_2O are also formed (Lobert et al. 1990; Kuhlbusch et al. 1991). Fires can also have indirect effects on N_2O emissions through alteration of physical, chemical and biological processes in the soil (Winstead et al. 1991). Estimates of annual emissions range from 0.27 Tg N_2O -N (Hao et al. 1991) to 1 Tg N_2O -N (Cofer III et al. 1991). Unnecessary biomass burning should preferably be kept to a minimum, but this source will not be considered further as it was recently reviewed by Badr & Probert (1992b). Trash incineration is also a source of N_2O , but the global amounts emitted are not known (Khalil & Rasmussen 1992b, Ueno et al. 1992).

Nitric acid is mainly produced for use in fertilizer manufacturing. Current production (1993) is about 90 Tg HNO_3 \cdot year⁻¹ (20 Tg HNO_3 -N \cdot year⁻¹). Some N_2O is formed in the catalytic oxidation of NH_3 to NO which is a key step in nitric acid

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production. Measurements of N₂O concentration in vented gases from 15 plants (out of 500 to 600 plants currently in operation) together with experience from a pilot plant, indicate that global N₂O emission from nitric acid production is probably in the range of 0.3 to 0.6 Tg N₂O-N·year⁻¹, with 0.4 to 0.5 Tg N₂O-N·year⁻¹ as our best estimate (Bøckman 1993). The N₂O emissions can be substantially reduced at some cost through process and constructional changes (Kongshaug et al. 1990). This source should diminish gradually as plants are replaced or modernized, provided abatement techniques are used.

Adipic acid is a raw material for the production of nylon, plasticisers and industrial chemicals. It is produced from benzene through reduction and oxidation steps. Nitric acid is used as an oxidizer and converted to N₂O (Thiemens & Trogler 1991). Current world production is about 1.8 Tg adipic acid·year⁻¹. Techniques for abatement of N₂O emission suitable for adipic acid plants are being developed and installed (Bøckman 1993; Reimer et al. 1993). Current (1993) emissions should be about or below 0.25 Tg N₂O-N·year⁻¹.

Some additional anthropogenic sources not listed in IPCC (1992) are known, but most are small:

- medical and industrial use of N₂O is about 0.03 Tg N·year⁻¹, which is eventually vented to the atmosphere. Most is used for anesthesia in hospitals. Other uses, e.g. as propellant and foaming agent, are minor in comparison (Sherman & Cullen 1988; G. Hansen Belgau, pers. comm.)
- corona power loss from electric power transmission systems generate N₂O, about 10¹⁷ molecules N₂O·J⁻¹. The average corona losses from US powerlines in 1980 were 8·10¹⁵ J. This corresponds to about 0.04 Tg N₂O-N·year⁻¹ (Hill et al. 1984, 1988). Global estimates are not available, but this anthropogenic source is also likely to be minor
- fumes from explosives contain N₂O, in amounts that depend on the type of explosive, amounts detonated and site conditions. Charges greater than 150 g generate about 0.2 to 0.5 l N₂O·kg explosive⁻¹ (Roberts et al. 1992). World use of explosives is about 6 million tonnes·year⁻¹ (about 1.75 Tg N) (E.C. Nygaard, pers. comm.), with an N₂O emission probably below 0.004 Tg N₂O-N·year⁻¹
- N₂O can form in the reaction between nitric acid and metals. It is thus possible that some N₂O is formed e.g. in the processing of spent nuclear fuels, (R.A. Reimer, pers. comm.), but amounts emitted from such sources are not known. They are probably small.
- Kaspar & Tiedje (1981) and Bleakley & Tiedje (1982) found that N₂O is produced in the rumen of animals, and that human breath frequently showed a N₂O concentration about 30% above that of ambient air for some hours after eating a meal. This may supply small amounts of N₂O, but the data are insufficient for detailed calculations
- wastewater N removal in treatment plants and wetlands can produce N₂O (Russell et al. 1991; Samuelsson & Klemmedtsson 1991; Samuelsson & Ulfsparré 1991; Franken

et al. 1992; Hanaki et al. 1992; Samuelsson 1993). The global amounts produced are unknown.

Weiland et al. (1982) reported that plants stressed by high temperature or drought emitted enhanced amounts of oxidized forms of N. Their analytical system would not have detected N₂O, but Dean & Harper (1986) showed that leaves of soybean formed N₂O and NO during an assay for nitrate reductase, and Chen et al. (1990) reported that plants can emit N₂O when stressed. This subject invites further investigation.

In general, all environments where nitrogen compounds are transformed by biological processes are potential sources of N₂O.

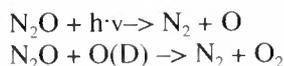
2.3.2 Sinks

N₂O is very stable in air, and chemical reactions in the stratosphere are regarded as the main (perhaps the only significant) processes for removal of N₂O from the atmosphere. These processes include those that control stratospheric ozone concentration. N₂O reacts with excited singlet oxygen atoms (O(D)) formed by photolysis of ozone; nitric oxide (NO) is the reaction product:



NO then participates in further reactions with ozone and other reactive molecules.

Two additional reactions in the stratosphere contribute to the removal of N₂O from the atmosphere:



A detailed description of the atmospheric chemical reactions of the oxides of N is given by Crutzen (1981), Warneck (1988) and Badr & Probert (1993a).

Soil can remove atmospheric N₂O under conditions favourable for N₂O reduction (Blackmer & Bremner 1976; Freney et al. 1978; Letey et al. 1980a; Ryden 1981; Silvola et al. 1992). This is probably only a minor sink on the global scale, but elimination of N₂O in the stratosphere is so slow that even a small soil sink can contribute significantly to reduction of the atmospheric residence time of N₂O (Cicerone 1989). The topic is further discussed in section 7.5.

Dowdell et al. (1979) reported that the N₂O content of rainwater was about 0.3 µg N₂O-N·l⁻¹. A rainfall of 1000 mm·year⁻¹ will therefore return only about 3 g N₂O-N·ha⁻¹·year⁻¹ to the soil.

Lensi & Chalamet (1981) reported that plants can take up and remove N₂O from air. This group also reported that ¹⁵N₂O is taken up by maize leaves and metabolized as a source of N (Grundmann et al. 1993). Acceptance of this process as a possible N₂O sink and N source requires independent confirmation and quantification.

2.4 The anthropogenic impact on the global nitrogen cycle

The multitude of forms in which N is found in nature are interrelated through a complex web of reactions: the N-cycle (Söderlund & Rosswall 1982; Sprent 1987; Jenkinson 1990). Atmospheric N_2 enters the cycle through fixation (Sprent & Sprent 1990), and exits as N_2 and N_2O through denitrification.

The input and movement of N in the N-cycle is greatly influenced by agriculture and other human activities. The observed increase in N_2O emission to the atmosphere is part of, and a consequence of this impact.

Man impacts the N-cycle mainly through land use. At present about 10% of all land is cultivated, while a further 14% is potentially cultivable (Bøckman et al. 1990). Land usage is changing (FAO 1992). The amount of forested area has declined from $4.2 \cdot 10^9$ ha in 1969-71 to $4.0 \cdot 10^9$ ha in 1990, while land devoted to permanent pasture has increased from 3.3 to $3.4 \cdot 10^9$ ha. The area used for arable and permanent crops has remained at about $1.4 \cdot 10^9$ ha, but is now more intensively used through fertilization and irrigation. The irrigated area increased by 25% between 1975 and 1990, from $0.189 \cdot 10^9$ ha to $0.237 \cdot 10^9$ ha.

In agriculture N availability is enhanced over the natural level to enable crops to give high and preferentially optimal yields:

- mineral fertilizers are applied
- legumes may be included in the rotation
- crop residues and animal manure are returned to the land
- soil reserves of N are mobilized by tillage.

The increased availability of N benefits the crop but it also implies that N is made available for soil processes that generate N_2O .

N mobility and losses are also enhanced:

- food and animal feed is traded and transported
- NH_3 and NO is lost to the atmosphere where NO is converted to NO_2 . Such emissions enter the global circulation of these gases. Some is returned to agricultural land by atmospheric deposition and precipitation, this represents an internal N circulation in agriculture. But the remainder constitutes an increased N input to forests, grasslands and waters
- NO_3^- is leached from agricultural land to ground and surface water, and is eventually lost to rivers and coastal areas.

The mobility and losses of N imply that N moves from agriculture to other parts of the N-cycle where N_2O production may differ from what it would have been in farmland.

The magnitude of the human impact can be appraised from data about important parts of the N-cycle:

- world fertilizer N application is now about $77 \text{ Tg N} \cdot \text{year}^{-1}$ (IFA 1992). It was $32 \text{ Tg N} \cdot \text{year}^{-1}$ in 1970 (ISMA 1973). Fertilizer use has levelled off in the last few years

and is decreasing in Europe, but is expected to increase in developing nations with their burgeoning populations. The application rates vary greatly depending on local yield potential, crop requirements and, in developing nations, also on accessibility and socio-economic factors. But fertilizer is a major agricultural N source

- biological N fixation yields, at a rough estimate, some 140 Tg N·year⁻¹. Estimates range from 42 to 200 Tg·N·year⁻¹ (Söderlund & Rosswall 1982, Sprent & Sprent 1990), a substantial part of this is man-managed through growing of forage and grain legumes
- combustion and fires produce NO_x. Badr & Probert (1993b) lists 16 estimates for this emission, ranging from 16 to 76 Tg NO_x-N·year⁻¹. Most estimates are within the range of 20 to 50 Tg NO_x-N·year⁻¹
- the global flux of NO from soil may be about 20 Tg NO-N·year⁻¹ (Davidson 1991). The contribution of soils to atmospheric NO_x is small compared with emissions from combustion in the industrialized nations (Conrad 1990; Pacyna et al. 1991; Shepherd et al. 1991; Skiba et al. 1992) and around major urban areas in the developing nations, but is of importance in predominantly rural areas (Williams et al. 1992a). The processes that generate NO in soil were reviewed by Conrad (1990) and by Williams et al. (1992b)
- global NH₃ emission to the atmosphere was estimated by Schlesinger & Hartley (1992) to about 75 Tg N·year⁻¹ (range 50 to 128 Tg N·year⁻¹), of which 52 Tg NH₃-N·year⁻¹ comes from anthropogenic sources. About 32 Tg NH₃-N·year⁻¹ (range 24 to 40 Tg NH₃-N·year⁻¹) originates with domestic animals, with cattle as the main source (about 20 Tg NH₃-N·year⁻¹). About 20 Tg NH₃-N·year⁻¹ comes from biomass burning, decomposition of surface applied urea fertilizer and other human sources. Details about the loss processes can be found in Asman (1992) and ECETOC (1994). However, only part of the NH₃ emissions are of recent origin, as NH₃ losses from farm animals and their wastes must have been substantial also in earlier times. Thus Asman et al. (1987) estimated that European NH₃ emissions in 1950 were about 62% of those in 1980
- the vast global reserves of N in soil organic material (e.g. about 3000 to 7000 kg N·ha⁻¹ for arable land and 12000 to 20000 kg N·ha⁻¹ for old grassland in the UK) is probably slowly declining due to soil cultivation, though regional differences are likely
- NO₃⁻ is leached from agricultural land and lost to ground- and surface waters. The leachage losses are substantial, but less than the annual N inputs. This topic is discussed in section 16.1.2.

The need for producing food for an increasing world population implies that large-scale anthropogenic alterations of the N-cycle will remain necessary, but the long-term environmental consequences also imply that the N-cycle should be managed wisely. Good agricultural practices for keeping N₂O emissions from agriculture at a low level form the topic of section 16.2.

3. PROCESSES THAT FORM N_2O IN SOILS

3.1 Background

Two microbial processes contribute most of the emission of N_2O from soils: denitrification and nitrification. The emission depend on numerous interacting circumstances:

- denitrification is an anaerobic process while nitrification is aerobic. Their reaction rates usually respond differently to changes in soil conditions
- the process rates and the fraction of N_2O in the products are often inversely related. In most cases N_2O is a minor reaction product
- release of N_2O from soil to air depends on diffusion through the soil and the soil's capacity for consumption of N_2O . This depends on several factors, e.g. site of production in the soil profile, soil texture and soil water content.

Much is known about N_2O forming processes and N_2O emissions (Bremner & Blackmer 1981; Sahrawat & Keeney 1986; G.P. Robertson 1989; Bouwman 1990; K.S. Smith & Arah 1990; Sharp 1991; Badr & Probert 1992b; Batjes 1992). However, soil is a heterogenous material, different processes can proceed at the same time, and the N_2O flux tends to have a complicated pattern of response to regulating factors. The limiting factor for N_2O production can change, sometimes rapidly.

Until about 1980 denitrification was regarded as the supreme source of atmospheric N_2O , but work reported by Bremner & Blackmer (1978, 1980a,b, 1981) showed that nitrification also can be a significant source of N_2O . The relative importance of these processes varies with local circumstances.

The concept of N_2O formation in, and emission from, soil can be illustrated by the «hole-in-the-pipe» model of Davidson (1991), fig. 3-1.

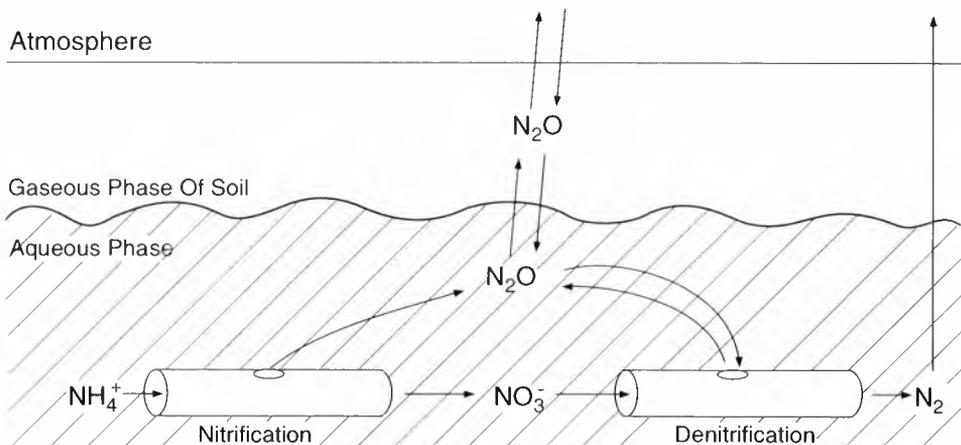


Figure 3-1. Three levels of regulation of N_2O flux: (i) the rates of nitrification and denitrification (amount of N flowing through the pipes); (ii) the ratios of end products (the size of the holes and orifices of the pipes); and (iii) diffusion and consumption of N_2O prior to escape from the soil to the atmosphere (Redrawn from Davidson 1991).

The various N transformation processes differ in their isotopic fractionation. Detailed studies of this effect may provide information on their relative importance for N₂O generation on the global scale (Yoshinari 1990).

We will discuss how physical, chemical and biological factors influence:

- the rates of denitrification and nitrification
- the ratio of N₂O to the other (often main) reaction products (N₂ and NO₃⁻) from these two processes
- the resulting combined N₂O emission

Some repetition is unavoidable in the presentation of a subject where all factors interact. For this we ask for our readers patience.

3.2 Denitrification

Denitrification is the last step in the N-cycle, where fixed N is returned to the atmospheric pool of N₂. It is an anaerobic process. Many microorganisms can use NO₃⁻ as their primary electron acceptor for obtaining energy from organic compounds when low O₂ availability restricts their metabolism (heterotrophic denitrification):



Some microorganisms can obtain energy by using NO₃⁻ for oxidation of inorganic compounds, e.g. S²⁻, Fe²⁺ (autotrophic denitrification). This occurs where NO₃⁻ diffuses into zones rich in FeS, e.g. sediments in shallow waters (Golterman 1991). However, heterotrophic denitrification is the most important of the two processes as a source for N₂O. It occurs stepwise:



There has been some doubt if NO is a true intermediate or a byproduct (Amundson & Davidson 1990) in the process, but a bacterial nitric oxide reductase has recently been characterized: *Pseudomonas stutzeri* loses the ability to denitrify if the genes for this enzyme are blocked (Braun & Zumft 1991). That N₂O is an obligatory intermediate in denitrification is widely accepted (Payne 1981; Zumft & Kroneck 1990). N₂O is reduced to N₂ by the labile enzyme nitrous oxide reductase (Stouthamer 1988). The reduction can also be carried out by the even more labile enzyme nitrogenase (the enzyme that reduce N₂ to NH₃, Hardy & Knight 1966). The enzymes associated with denitrification have been reviewed by Hochstein & Tomlinson (1988).

Depending on conditions, intermediate products can accumulate and eventually escape. The majority of soil bacteria seem able to denitrify (Umarov 1990, 1993), but denitrifying bacteria exhibit a variety of incomplete reduction pathways: Some bacteria produce only N₂, while others give a mixture of N₂O and N₂, and some only N₂O (Kaplan & Wofsey 1985; Stouthamer 1988; L.A. Robertson & Kuenen 1991). The rate of denitrification is usually rather low under environmental conditions reported to favour production of N₂O relative to N₂ (e.g., low temperature, low pH,

presence of O₂). Thus, N₂O is the favoured reaction product under conditions marginal for denitrification. This does not imply that the emissions are greatest under such conditions, as the total amount of products may be small.

Denitrification is usually thought of as a bacterial process, but Shoun et al. (1992) reported that many fungi are capable of evolving N₂O under anaerobic conditions.

Some microorganisms reduce NO₃⁻ to NH₄⁺. They use the N in production of biomass (assimilatory reduction), but the process can also serve other purposes (dissimilatory reduction) e.g. as a source of energy or for detoxification of NO₂⁻. N₂O can escape during these processes (Scott Smith & Zimmerman 1981; Kaplan & Wofsy 1985; Cole 1988; Stouthamer 1988; Tiedje 1988).

Heterotrophic denitrification requires both anaerobic conditions and presence of organic material that the bacteria can utilize. Topsoils can be anaerobic after heavy rain or thaw, but anaerobic microsites are often present in otherwise aerobic soil. In mineral soils lack of degradable organic material can be the principal factor that restricts denitrification, especially in the subsoil (McCarty & Bremner 1992, 1993).

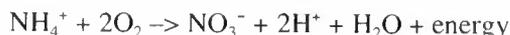
For further details on denitrification and related processes the reader is referred to Delwiche (1981), Knowles (1982), Fillery (1983), Kuenen & Robertson (1988), Tiedje (1988), Revsbeck & Sørensen (1990), Stouthamer (1991) and Matêjù et al. (1992). N losses from agricultural soils through denitrification have been reviewed by Rheinbaben (1990).

Chemodenitrification is a non-biological process. NO₂⁻ can react with organic compounds (e.g. amines) to form N₂, NO₂ and N₂O (Bremner & Nelson 1968). N₂O can also form in reactions between NO₃⁻/NO₂⁻ and some inorganic compounds (e.g., Fe²⁺, Cu²⁺). These reactions may be important for slow denitrification of groundwater (Van Cleemput et al. 1987) and have been discussed by Chalk & Smith (1983), Van Cleemput & Baert (1983), Van Hecke et al. (1990) and Sharp (1991). NO₂⁻ can also react with galvanized steel to produce N₂O (Parkin & Codling 1988).

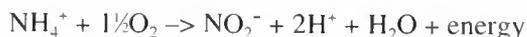
3.3 Nitrification

Nitrification is an aerobic process, performed both by autotrophs and heterotrophs in soils. Autotrophic nitrification is by far the most studied process (Prosser 1986; Umarov 1990).

Autotrophic nitrifiers use CO₂ as a carbon source and obtain their energy by oxidation of NH₄⁺. The NH₄⁺ can originate from mineralization of soil organic material by other organisms or from fertilizer:



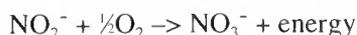
Nitrification takes place in two separate steps (Haynes 1986). In the first one, NH₄⁺ is oxidized to NO₂⁻ with NH₂OH as an intermediate. The over-all reaction can be formulated as:



Bacteria that transform NH₄⁺ to NO₂⁻ are called ammonium oxidizers, and they are

given names with the prefix *Nitroso*-. Species of *Nitrosomonas* are the best known in this group.

In the second step, NO_2^- is oxidized further to NO_3^- :



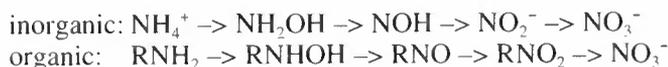
This step is carried out by nitrite oxidizers designated with the prefix *Nitro*-. Species of *Nitrobacter* are the best known in this group.

The mechanism of N_2O formation from nitrification has been a subject of debate. It now seems established that two processes are responsible (Groffman 1991):

- ammonium oxidizers can use NO_2^- as an alternative electron acceptor when O_2 is limiting and produce N_2O (Nõmmik 1956; Poth & Focht 1985; Firestone & Davidson 1989). This process is called nitrifier denitrification
- intermediates between NH_4^+ and NO_2^- , or NO_2^- itself, can chemically decompose to N_2O , especially under acidic conditions (a type of chemodenitrification).

Nitrite oxidizers do not usually produce N_2O (Goreau et al. 1980).

Heterotrophic organisms use organic substances as both a carbon and an energy source. They can obtain part of their energy from oxidation of NH_4^+ or organic nitrogen compounds. Fungi are apparently the most important of these. Different pathways have been postulated, but their role in fungal metabolism is largely unknown (Killham 1986):



Heterotrophic nitrification has not been extensively studied. As the rates of nitrification by heterotrophs appeared to be very low compared with those of the autotrophs, the phenomenon was regarded as of little significance outside the laboratory. However, Kuenen & Robertson (1988) found that a heterotrophic nitrifier could also denitrify, and accumulated little or no NO_3^- or NO_2^- . For such organisms nitrification rate cannot be estimated from the accumulation of NO_2^- . Thus, it seems possible that N_2O can also be produced by heterotrophic nitrifiers in significant amounts. However, this subject needs further investigation.

Heterotrophic nitrification may dominate over autotrophic under certain conditions. A low pH is one factor that seems to strongly restrict autotrophic nitrification. Nitrification is probably heterotrophic in soils such as acid coniferous forest soils, where the microbial biomass is often dominated by fungi. The low nitrification potential per unit biomass observed for heterotrophic nitrifiers may be more than offset by the huge fungal biomass in these soils (Killham 1986).

The relative significance of autotrophic and heterotrophic nitrification in regard to pH is also addressed in section 10.4.

For further details on heterotrophic and autotrophic nitrification, the reader is referred to Prosser (1986), Haynes (1986) and Kuenen & Robertson (1988).

3.4 Microbial diversity

Microbial species vary in their ability to produce N_2O . Soil conditions affect the composition of the microbial flora, but the flora also influence soil conditions, e.g. pH and O_2 level. The microbial flora and the soils ability to nitrify and produce N_2O can differ markedly between soil layers (Lång & Martikainen 1993). Microbial population dynamics in soil may be an important factor in N_2O production, perhaps more important than physical and chemical conditions (Abou Seada & Ottow 1985; Martin et al. 1988; Powlson et al. 1988; Schmidt et al. 1988; Munch 1989, 1991). Kromka et al. (1991) and Stepanov (1993) reported that denitrification proceeded mainly to N_2O in a saline soil because the soil contained few bacteria that could reduce N_2O to N_2 . This effect deserves further investigation as salinisation can be a problem in irrigated areas.

Microbial population dynamics is a difficult topic to study, and is often ignored in investigations of N_2O emissions. However, some of the discrepancies in results and conclusions between published studies may originate from differences in microbial populations.

4. THE EXPERIMENTAL BASIS

4.1 Background

Scientific arguments require a sound experimental basis. The study of N_2O emissions from soils is complicated by experimental difficulties. The amounts emitted per unit of area and time are small, show large variation and are cumbersome to measure. This makes it difficult to compare published data.

In this chapter we present a brief overview of the methods used in measuring emissions of N_2O and investigating the underlying processes. The experimental methods can broadly be classified into field and laboratory studies. Comprehensive field studies provide the best basis for emission estimates, whereas laboratory studies (e.g., pot incubation experiments) can give valuable insight into the relative importance of factors affecting emissions.

Laboratory studies are useful as a first step in development of methodology for field studies. Denitrification and nitrification can be measured by laboratory incubation of soil under conditions (aerobic or anaerobic) that favour one or the other of these processes. Denitrification is then measured by evolution of N_2O (and N_2), and nitrification by changes in NO_2^- , NO_3^- and/or NH_4^+ concentration.

4.2 Denitrification

Denitrification is difficult to measure directly in the field due to the large concentration of the major product, N_2 , in air. Various methods of indirect measurements are available (Hauck & Weaver 1986; Nieder et al. 1989; Leonardson 1992). The most common one is using acetylene as an enzyme inhibitor (the acetylene inhibition method, AIM), but N budget studies are also used. Use of isotope methods (marking the fertilizer N with ^{15}N and measuring the isotopic enrichment in the

products) permits direct measurement of denitrification rates, but is not in so common use as the AIM due to cost.

4.2.1 Acetylene inhibition method (AIM)

This method has been reviewed by Ryden & Rolston (1983), Tiedje et al. (1989), Klemetsson et al. (1990) and Knowles (1990).

Acetylene inhibits the enzymatic reduction of N_2O to N_2 (Balderston et al. 1976; Okereke 1984). 1 to 10 vol% is usually sufficient for this to occur. Denitrification can thus be measured as the amount of N_2O produced in soil treated with acetylene. The ratio of N losses as N_2O and as N_2 can be estimated by measuring N_2O emissions from both untreated and treated soils. The AIM method has several advantages:

- it is robust and reliable, the cost is low and the method can be used in a variety of conditions
- it has high sensitivity; loss of about $1 \text{ g N}\cdot\text{ha}^{-1} \text{ day}^{-1}$ can be measured.

However, the method also presents some problems (Keeney 1986; Arah et al. 1993a). The most important are:

- restricted gas diffusion in soil may lead to insufficient acetylene concentration. Diffusion of gases in the soil are dramatically reduced at high water contents (near field capacity and above), in heavy-textured soil (high clay content) or upon compaction
- acetylene as it emerges from cylinders contains some acetone. Acetone is easily degradable and stimulates denitrification. The gas should be purified before use (Gross & Bremner 1992), but this has not always been done
- increased demand for electron acceptors (e.g., high organic carbon- and/or low NO_3^- content) may lead to an incomplete inhibition of the N_2O reduction step
- S^{2-} can reverse the inhibitory effect of acetylene on N_2O reduction. This may restrict the usefulness of the AIM method in some special cases (Evans et al. 1985; Jones & Knowles 1992)
- the inhibitory effect decreases with time, but is usually sustained for days rather than hours. Long-time or repeated measurements on the same plot should be avoided.

These problems can result in an erroneous estimation of the denitrification rate. They can be overcome with appropriate care except where restricted gas diffusion is the main problem. In most circumstances the acetylene inhibition method gives acceptable results.

4.2.2 Methods based on N budgets or the use of isotopes

A traditional method for field measurements of denitrification is the N budget for a lysimeter or a drained field plot, as discussed by Ryden & Rolston (1983). The amount of N leached and that removed with the harvested parts of crops is determined and compared with the N input. Unaccounted N is assumed to be lost by denitrification. This method is valid only for systems where the soil reserves of N are the same at the beginning and the end of the experiment, and where losses from volatilization (e.g. NH_3) can be ignored. Complications arise if these conditions are not fulfilled, for instance where the soil N reserves undergo gradual and usually unmeasurable changes.

Various isotope methods are also used (Ryden & Rolston 1983; Mosier 1989; Tiedje et al. 1989; Myrold 1990; Arah 1992b; Arah et al. 1993a). Usually $^{15}\text{NO}_3^-$ is added to the soil and emitted N_2 is collected and isotopic composition ($^{30}\text{N}_2$) measured. The background concentration of $^{30}\text{N}_2$ in air is very low. Measurements of ^{15}N enriched N_2O and N_2 can also be made with emission spectrometry. This gives a random distribution of the N_2 isotopes and makes measurement of $^{30}\text{N}_2$ unnecessary (Eriksen & Holtan-Hartwig 1993).

The problems associated with isotope methods are:

- additions of NO_3^- can increase the denitrification rate and change the $\text{N}_2\text{O}/\text{N}_2$ ratio
- dilution of $^{15}\text{NO}_3^-$ with soil NO_3^- by various soil processes. This will cause an underestimate of denitrification rates if not corrected for
- uniform distribution of added $^{15}\text{NO}_3^-$ is difficult, and usually restricted to the upper part of the soil profile
- high cost due to the high ^{15}N enrichment required
- disturbance of the soil during application.

The AIM and ^{15}N -methods have been directly compared only in a few studies. These are summarized by Tiedje et al. (1989). Overall, the methods give similar results, and both methods, when used correctly, are acceptable for quantitative measurements of denitrification rates. Isotope methods are preferable to the AIM on heavy-textured soils where acetylene diffusion is hindered (Arah et al. 1993a).

4.3 Nitrification

Nitrification can be studied by following changes in concentration of NH_4^+ , NO_2^- and NO_3^- . Interpretation of such measurements can be difficult, as NH_4^+ and NO_3^- are also produced and consumed by other soil processes. ^{15}N methods can also be used for studies of nitrification, but similar limitations apply as for denitrification studies.

The first step in autotrophic nitrification is mediated by ammonium oxidase, an enzyme inhibited by acetylene at low pressure (0.001 to 0.01 vol-%) (Pedrazzini & Nannipieri 1982; G.P. Robertson & Tiedje 1987). Thus small amounts of acetylene can be used to prevent N_2O production by the ammonium oxidizers (Bremner & Blackmer 1980a; Blackmer et al. 1980; Aulakh et al. 1984a; Klemedtsson et al. 1987). Heterotrophic nitrifiers of the species *Arthrobacter* form an exception (Klemedtsson et al. 1990). The difference in inhibitory acetylene concentration for ammonium

oxidase and nitrous oxide reductase permits estimation of the rates of nitrification, denitrification and N_2O production from each of these processes. This is the PPM method (use of ppm levels of acetylene to inhibit nitrification) discussed by Klemmedtsson et al. (1990). Other nitrification inhibitors have also been used, as discussed by Bremner & Yeomans (1986), Keeney (1986), Kuenen & Robertson (1988) and Miller et al. (1993). Nitrapyrin and dicyandiamide (DCD) are to some extent in practical use. They are discussed further in section 8.6.2.

4.4 Field measurements of N_2O emission

4.4.1 Background

Methods for field measurements of N_2O emissions from agriculture have been reviewed by Mosier (1990) and are described in a manual from the IAEA (1992).

A problem in measuring N_2O emissions from soils is the large spatial and diurnal variations commonly observed (Matthias et al. 1979; Bremner et al. 1980; Folorunso & Rolston 1984; Christensen et al. 1990b,c; Brumme & Beese 1992; Heinemeyer & Kaiser 1992; Papen et al. 1993). Sitaula & Bakken (1993) found that a spruce forest soil showed comparatively low spatial variation in soil content of organic carbon and total N, but large spatial variations in N_2O release and in rates of nitrification and N-mineralization. Positions within a field can differ in the amounts of

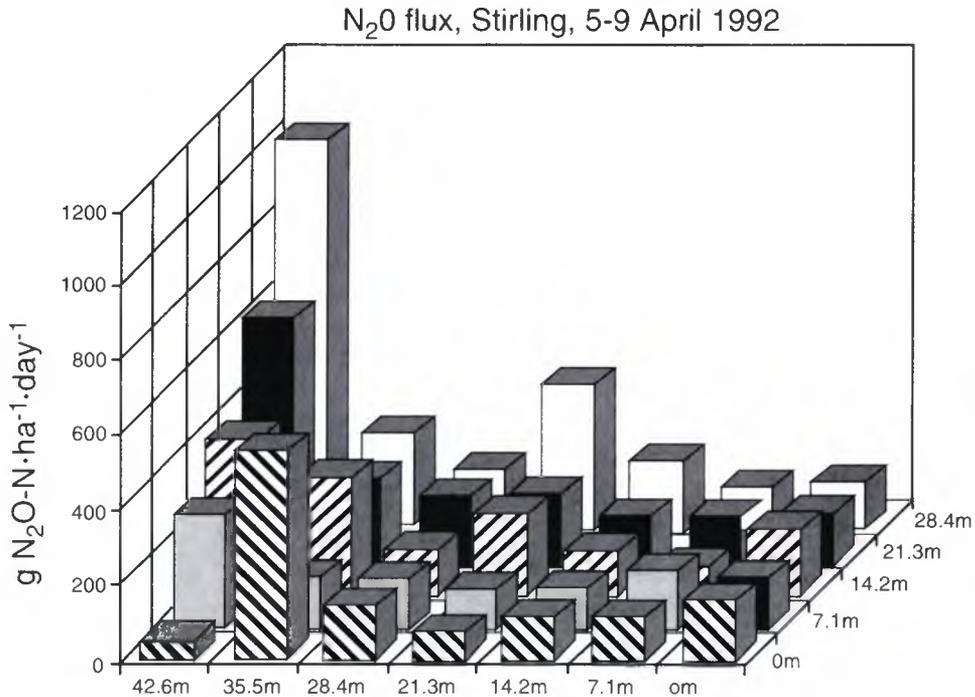


Figure 4-1. N_2O fluxes from a fertilized grassland measured at 7.1 m nodes within a regular 28.4 m x 42.6 m grid. Each bar represent mean fluxes from 10 cm diameter static chambers that were sampled daily from 5 to 9 April 1992 following application of 150 kg NH_4NO_3 - N·ha⁻¹ on 3 April. Source: P. Ambus ©, University of Copenhagen.

N₂O emitted by a factor of 10 or more (fig. 4-1). This variability makes it advisable to extend measurements over sufficiently long time spans, preferably over a whole season or year.

Determination of N₂O concentrations in air is central in studies of N₂O emissions. Analytical methods have been reviewed by Sharp (1991). Gas Chromatography (GC) is the most used method and permits convenient analysis of N₂O and other greenhouse gases (CH₄, CO₂) in the sample (Sitaula et al. 1992).

Usually gas samples are taken and analyzed in a laboratory. The most sensitive detector for N₂O can achieve a precision of ± 1 ppbv on concentrations of the order of 310 ppbv. This is more than sufficient for chamber methods and can also be used for micrometeorological stations when the N₂O flux is adequate. N₂O absorbs IR-light and the resulting photoacoustic effect can be used for measuring the N₂O concentration providing it is well above ambient levels (e.g. in closed chambers) and that care is taken to avoid interference with H₂O and CO₂. Sensitivity is less than with GC, but greater simplicity is an advantage for field studies. Long path IR spectrometers mounted in ultra-large chambers have now been shown to give results comparable to those obtained from GC analysis of samples from conventional closed chambers (IAEA 1992; Clayton et al. 1992, 1993; K.A. Smith et al. 1993).

N₂O can be selectively adsorbed on molecular sieves ($5 \cdot 10^{-10}$ m) after removal of H₂O and CO₂ from the air, and desorbed with water for GC analysis. This technique for collecting N₂O has been used with open chambers for sampling soil emissions (Benckiser et al. 1986; Van Cleemput et al. 1992).

Emissions of trace gases from soils should preferably be measured without any disturbance either of the soil or of the process that form or remove N₂O, and with the required sensitivity. At present, chamber methods are preferred for measuring N₂O emissions from soils. Although these methods can disturb the soil and the emission process, they combine good detection sensitivity with practical simplicity. They are presently the reference method, but other methods (ultra-large chambers with IR instruments, micrometeorological methods and soil air analysis) are now also to hand. Hence the equipment necessary for extensive field studies of N₂O emissions is now available, but such studies will be expensive both in equipment and labour cost.

4.4.2 *Chamber methods*

Descriptions of chamber methods are found in Ryden & Rolston (1983), Mosier (1989), IAEA (1992) and K.S. Smith & Arah (1992). Two main types of chambers are used; open and closed.

Closed chambers

In closed chambers air inside the chamber is separated from outside air. N₂O flux (F) is calculated from the change in concentration (Δc) over a period of time (Δt):

$$F = \frac{V}{A} \frac{\Delta c}{\Delta t}$$

where V is the volume of the chamber above the enclosed soil with surface area (A).

Typically, chambers are closed for 1 hour, and develop N₂O concentrations within the

range of 1 to 50 times the ambient concentration. Opening and closing of chambers can be automated (Loftfield et al. 1992). The main benefits of closed chambers are:

- simple instrumentation which is easy to handle
- high sensitivity permitting measurement of fluxes of $0.3 - 1 \text{ g N}_2\text{O-N}\cdot\text{ha}^{-1}\cdot\text{day}^{-1}$ (Sharp 1991).

Recently, Brooks et al. (1993) described a method where N_2O is sorbed on zeolite, then thermally desorbed and analyzed by an isotope ratio mass spectrometer. They reported that N_2O derived from $^{15}\text{NO}_3^-$ could be measured at fluxes as low as $40 \mu\text{g N}_2\text{O-N}\cdot\text{ha}^{-1}\cdot\text{hour}^{-1}$ (about $1 \text{ mg N}_2\text{O-N}\cdot\text{ha}^{-1}\cdot\text{day}^{-1}$).

The main problems associated with closed chambers are:

- a high N_2O concentration inside the chamber may restrict N_2O diffusion from the soil
- air inside the chamber is stagnant without outside pressure- and wind fluctuations. As a consequence, N_2O is transported only by molecular diffusion. This will lead to underestimation of the flux. A closed loop with forced air movement can partly compensate for this
- solar irradiation can cause temperature differences in soil and air between the inside and outside of the chamber
- changes in pressure inside the chamber may occur due to gas fluxes and temperature changes. A small vent will eliminate this problem without inducing significant mixing with outside air
- presence of plants can create practical difficulties in the siting and operation of the chambers
- chambers are labour demanding.

Open chambers

In this set-up outside air is drawn continuously through the chamber and the N_2O flux (F) is calculated from the difference between test and background N_2O concentration:

$$F = Q \cdot \frac{\Delta c}{A}$$

where Q is the volumetric air flow rate. The flow rate should be balanced between holding Δc at a minimum (to avoid the effects of N_2O accumulation), but well above the detection limits.

The main advantages of open rather than closed chambers are:

- effects of N_2O accumulation are reduced or eliminated. This permits longer periods of measurements

- conditions outside and inside the chamber can be more similar than for closed chambers.

However, there are several disadvantages with the use of open chambers:

- N₂O concentrations are lower than in closed chambers, thus the method is less sensitive
- Drawing the air through the chamber can reduce pressure inside which may increase N₂O flux from the soil. This can be prevented by having an inlet orifice much larger than the outlet.

Ambus et al. (1993) reported that two closed and one open chamber systems gave similar results for N₂O fluxes.

Owing to their limited size, standard chambers give spot measurements. Parallel measurements are needed to obtain mean emission rates from a field. An insight into spatial variations can be advantageous, and chamber methods are better in this respect than micrometeorological studies.

N₂O emissions from soil vary with conditions. It is essential that climatic data are recorded and desirable that soil conditions (e.g. soil porosity and aeration) also are measured.

4.4.3 Measurements of N₂O concentration in soil

This approach has been used by Rolston et al. (1976), Mosier & Hutchinson (1981), Egginton & Smith (1986b), Benckiser et al. (1987) and Arah et al. (1991). The N₂O concentration in the soil air is measured at various depth intervals (e.g., 0,5,20 and 40 cm). Independently, the gas diffusivity, D, is calculated with respect to the soil's texture and water content (Ball et al. 1981). The N₂O flux, F is calculated by Fick's law:

$$F = -D \cdot \frac{\Delta c}{\Delta S}$$

where Δc is the difference in N₂O concentration between two points in the soil profile, and ΔS is the distance between them.

The necessary equipment is relatively cheap, and the soil is nearly undisturbed except for the insertion of the probes at the beginning of the experiment.

Mosier & Hutchinson (1981) found a good correlation between N₂O emissions from a cornfield measured by closed chamber technique and N₂O concentrations in the soil air. However, in the study of Arah et al. (1991) the shape of the concentration profile indicated significant N₂O consumption in the upper 5 cm of the soil. Reduction of N₂O in the surface soil was also reported by Blackmer & Bremner (1976). Use of Fick's law for calculating the flux under such circumstances is unsatisfactory, and the usefulness of the method seems to depend on the soil conditions. However, flux measurements at various depths permit determination of the most significant zones of N₂O production and consumption. This offers some insight into the mechanism of N₂O production (Goodroad & Keeney 1985).

Other disadvantages of this method are (Sharp 1991):

- large number of samples must be collected
- uncertainty in the value of the soil-gas diffusivity
- minimal spatial and temporal resolution
- the method is not appropriate for long-term monitoring on unattended sites. It requires attention and is labour demanding.

4.4.4 *Micrometeorological methods*

Micrometeorological methods measure gas emissions from fields without disturbing the gas exchange between the atmosphere and the soil/crop system. Wind speed, temperature and trace gas concentration are measured at one or more heights above the field, where the vertical flux can be assumed to be constant and horizontal gradients can be neglected. Three different approaches are used: eddy correlation, flux gradient and mass balance calculations. They are described by Thom (1975), Denmead (1983) and Fowler & Duyzer (1989). The technique is well established for measurement of NH_3 and CH_4 losses (Denmead 1983, Schütz & Seiler 1989). Hauck & Weaver (1986) reviewed the method used for N_2O emissions.

Measurement of N_2O losses from fields by micrometeorological techniques is difficult because:

- small concentration gradients that are difficult to measure with the required precision (preferably ± 0.1 to 1 ppbv)
- a need for large uniform fields with a minimum of air turbulence
- a need for appropriate weather conditions as periods of turbulence can give erroneous results. This limits the usefulness of micrometeorological techniques as N_2O emissions can show marked daily variations and periods with conditions suitable for measurements may not be representative for the whole season.

Further, the instrumentation is expensive, about ECU 10 000 for a micrometeorological station and more for the analytical unit.

Matthias et al. (1979) sampled air at different heights above a soybean field and found that the mean concentration of N_2O was 323 ppbv 0.02 m above the soil, 316 ppbv at 0.12 m height and ambient (310 ppbv) at about 4 m.

Mosier & Hutchinson (1981) sampled air at various heights above a cropped field and measured the N_2O concentration by standard GC methods. Only peak emission rates could be measured. Recently, Arah et al. (1993b) described a system for collecting air samples from various heights in plastic bags followed by GC analysis. They could measure fluxes down to 15 to 20 g $\text{N}_2\text{O-N}\cdot\text{ha}^{-1}\cdot\text{day}^{-1}$ under favourable conditions. This is about 10 times better sensitivity than possible with the equipment available to Mosier & Hutchinson (1981).

Where fluxes are large and the meteorological conditions suitable, micrometeorological methods give results similar to those obtained by chamber methods (Matthias et al. 1993). New, more sensitive, instrumentation based on tunable lasers should make micrometeorological techniques more useful for N_2O emission studies in the future, but work remains to be done in developing instruments and validating their use.

5. N₂O FLUXES FROM AGRICULTURAL LAND

As discussed in chapter 2 the observed increase in atmospheric N₂O concentration implies that global emissions have increased in recent years by about 4.5 Tg N₂O-N·year⁻¹. About 2 Tg N₂O-N·year⁻¹ originates from known non-agricultural sources (biomass burning and other forms of combustion, industry). Hence some 2 to 3 Tg N₂O-N·year⁻¹ should derive from other emitters, with agriculture regarded as the main source.

Of a total land area of $13.4 \cdot 10^9$ ha, about $1.44 \cdot 10^9$ ha is cultivated as arable land or under permanent crops. Most of this ($1.35 \cdot 10^9$ ha) is arable land. An enhanced emission of 2 to 3 Tg N₂O-N·year⁻¹ from cultivated land implies that the global average N₂O flux has increased since World War II by about 1.4 to 2.1 kg N₂O-N·ha⁻¹·year⁻¹. This is a very crude estimate, as no allowance is made for pasture management, for any increase in emissions from natural ecosystems due to unintentional anthropogenic increase in N inputs, nor from other indirect anthropogenic sources such as deforestation. However, it provides some background for the evaluation of published emission rates.

Surveys of emission rates are provided by Bouwman (1990), Campbell et al. (1990) and Badr & Probert (1992b). Emission rates vary greatly. Bouwman list estimated fluxes from uncultivated lands and natural ecosystems. The emissions ranged from 0.1 to 9.1 kg N₂O-N·ha⁻¹·year⁻¹ in temperate regions (22 sets of reported fluxes), but were mostly below 1 kg N₂O-N·ha⁻¹·year⁻¹. Tropical ecosystems seemed to have somewhat higher emissions: 7 quoted measurements ranged from 0.2 to 2.6 kg N₂O-N·ha⁻¹·year⁻¹, but were mostly below 2 kg N₂O-N·ha⁻¹·year⁻¹.

N₂O emissions were generally higher and more variable from agricultural land than from uncultivated land or natural ecosystems. Of the 36 sets of measurements listed by Bouwman (1990), 17 fluxes were above 3 kg N₂O-N·ha⁻¹·year⁻¹. The highest of these, ranging from 7 to 165 kg N₂O-N·ha⁻¹·year⁻¹, were associated with cropping on peat soils. However, so large fluxes are probably exceptional (section 11.5). Other soil types gave fluxes up to 10 kg N₂O-N·ha⁻¹·year⁻¹, and a set of measurements from irrigated and heavily fertilized horticultural crops had emissions ranging from 19.6 to 41.8 kg N₂O-N·ha⁻¹·year⁻¹. In contrast, 17 of the sets of measurements gave fluxes at or below 2.5 kg N₂O-N·ha⁻¹·year⁻¹. There is a considerable degree of uncertainty with these results:

- emissions are variable and can be episodic. It is difficult to calculate representative annual fluxes.
- reported instances may cover special conditions that are not representative for agriculture
- the number of observations is rather small.

In spite of such limitations, the results listed by Bouwman (1990) provides indications for what constitute large fluxes and what can be regarded as minor emissions.

That N is available for microbial transformation is a prerequisite for N₂O formation. The potential of a soil to form and emit N₂O increases with increasing availability of N, but the amounts emitted depends on complex interactions between soil properties, climatic factors and agricultural practices. The large spread of estimated fluxes from various types of agricultural land gives hope that management

practices can be defined that reduce N_2O emissions where these are at a markedly elevated level.

The remainder of this review deals with physical, chemical and biological factors that influence N_2O emissions and how they interact:

- soil content of air and water (chapter 6 and 7)
- soil content of NH_4^+ and NO_3^- (chapter 8)
- soil types and pH (chapter 9 and 10).
- organic carbon content of soil (chapter 11)
- crops and vegetation (chapter 12)
- temperature and season (chapter 13 and 14)

Some of the principal factors that influence N_2O emissions are outside the farmers control: soil type, rainfall, season and temperature. Nevertheless, some can be influenced by the farmer, at least partially. Such factors are:

- soil aeration, which is affected by tillage methods
- water status, which can be controlled by irrigation and drainage
- time, type, amounts and application method of fertilizers and manure
- soil pH which can be adjusted by liming
- supply of easily degradable organic material
- cropping patterns

Management practices that would be preferred or avoided in order to reduce N_2O emissions from agricultural soils to a practical minimum and a survey of topics where better basis for recommendations are desirable, are discussed in the final and most important chapter of this review.

6. SOIL AERATION

6.1 Summary

Soil is heterogenous and commonly has both aerobic and anaerobic sites.

Denitrification requires anaerobic conditions, hence the observation that the rate of denitrification decreases and is eventually inhibited in the presence of O_2 . Reduction of N_2O to N_2 is more prone to inhibition by O_2 than reduction of NO_3^- to N_2O , thus the N_2O/N_2 ratio decreases with decreasing O_2 concentration.

Nitrification is an aerobic process producing N_2O and NO_3^- . The process rate decreases and the product ratio N_2O/NO_3^- increases as the O_2 supply is reduced.

Thus, in both processes, N_2O is the product favoured at intermediate aeration. This is illustrated by the work of Khdyer & Cho (1983). In a soil column nitrification occurred in the aerobic region in the upper part of the column, close to the surface. Denitrification occurred in the lower part where conditions were anaerobic, and N_2O was mainly formed in the aerobic-anaerobic interface.

6.2 Background

K.A. Smith (1990) discussed the elements which determine the aeration status of soils. The O_2 content depends on:

- soil water content, with water displacing air
- diffusion of O_2 into the soil
- consumption of O_2 by soil microorganisms and plant roots.

Diffusion of O_2 in soil is mainly determined by texture, management (e.g. tillage) and water content. O_2 consumption by microbes is controlled by the availability of oxidizable substrates. The influence of each of these factors is considered in more detail in later chapters. This chapter is devoted to studies which explicitly have investigated the effect of O_2 concentration on the soil processes in question.

6.3 Denitrification

6.3.1 Rate

The inverse relationship between the rate of denitrification and O_2 concentration has been demonstrated in many studies (e.g. Focht 1974; Betlach & Tiedje 1981; Burton & Beauchamp 1985). This is illustrated by the results of Arah et al. (1991), fig.6-1.

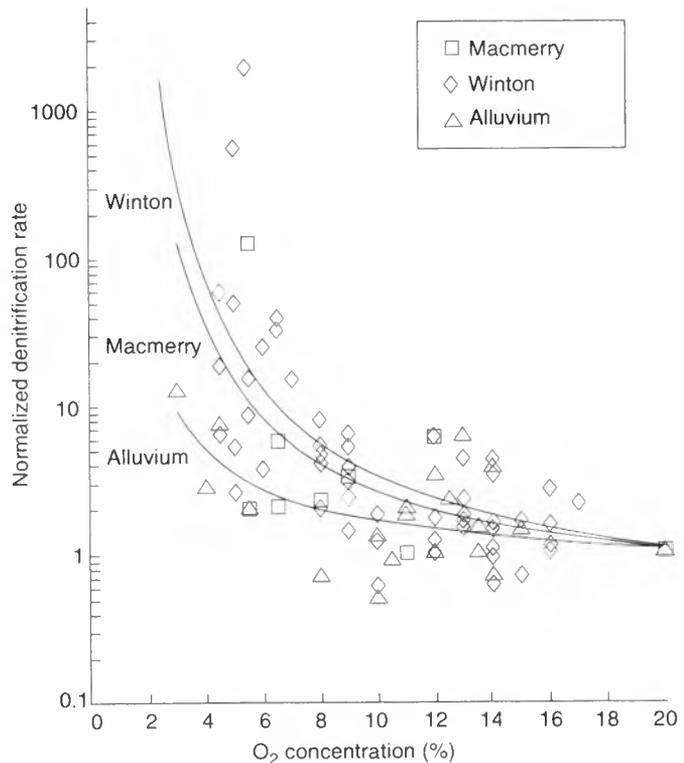


Figure 6-1. Relationship between denitrification rates for three Scottish soils determined by core incubation and the O_2 concentration in the incubation vessel. Source: Arah et al. (1991).

Similar results were obtained by Parkin & Tiedje (1984): Denitrification rates in their soil cores remained low, less than 2% of the anaerobic rate, as long as the O₂ concentration in the gas was greater than 3%. At lower O₂ concentrations the rates increased, and rapidly approached anaerobic rates when the O₂ concentration decreased below 0.5%.

The inverse relationship between denitrification rate and O₂ concentration is more pronounced at high (34.5°C), rather than at low (19.5°C), temperature (Focht & Verstraete 1977).

The role of O₂ diffusion in soil for denitrification was described in the model of K.A. Smith (1980). This model calculates concentrations in soil and describes how O₂ diffuses down the soil profile and into aggregates, and the fraction of the soil volume that is anaerobic. The diffusion of O₂ into the aggregates rather than down the soil profile appears to be the main rate-determining step for denitrification in this model.

6.3.2 N₂O/N₂ ratio

When denitrification occurs, the composition and the quantity of products formed are both influenced by O₂ availability. The presence of O₂ reduces the activity and delays the synthesis of nitrous oxide reductase relative to nitrate reductase and nitrite reductase, so that the N₂O/N₂ ratio increases with increasing O₂ concentration (Focht 1974; Smirnov et al. 1979; Firestone et al. 1980; Betlach & Tiedje 1981; C.J. Smith et al. 1983; Erich & Bekerie 1984; Tiedje 1988; Bonin et al. 1989; Masscheleyn et al. 1993). The N₂O/N₂ ratio can vary widely, and N₂O or N₂ can in some cases be the sole gaseous product of denitrification.

6.4 Nitrification

N₂O is produced when NO₂⁻ is used as electron acceptor by ammonium oxidizers in O₂-limited environments (Groffman 1991). Goreau et al. (1980) grew pure cultures of the ammonium oxidizer *Nitrosomonas* sp. in liquid cultures under headspace with O₂ partial pressures between 0.005 and 0.2 atm (0.18 to 7 mg O₂·l⁻¹ in the liquid). The relative rates and yields (20% O₂ = 1) were:

	20% O ₂	0.5% O ₂
Rate of N ₂ O evolution	1	4.3
Rate of NO ₂ ⁻ production	1	0.14
N ₂ O/NO ₂ ⁻ ratio	0.003	0.09

The nitrite oxidizer *Nitrobacter* sp. did not produce detectable amounts of N₂O during growth.

Keeney et al. (1985) incubated aerobic soil samples amended with NH₄⁺ in atmospheres where the air was partly replaced by CO₂. They found that nitrification rate decreased with increasing CO₂-concentration from 0.3 to 100%. No nitrification occurred at 100% CO₂. N₂O production tended to increase as CO₂ concentration increased from 0.3 to 2.6%. At higher CO₂ concentrations, up to 73% CO₂ corresponding to about 5% O₂, the rate of N₂O production was nearly constant.

6.5 N₂O emission

The influence of aeration on N₂O emissions from soils is complex and dependent on interacting factors. The dominant impression from the literature is that N₂O emission increases as aeration becomes restricted, up to the point when gaseous exchange between soil and air is severely hindered. Then N₂ becomes the main and ultimately the sole product of denitrification. N₂O production and emission is usually greatest when the average soil conditions are such that both aerobic and anaerobic sites are abundant. This has been found in several laboratory studies, e.g. by Focht (1974) who also found a combined effect of pH and aeration: At pH 6.0 and 8.0 N₂O evolution increased as the fraction of aerated pores increased to a maximum at ca. 12% air-filled pore space (AFPS). At higher aeration N₂O evolution rapidly declined. At pH 4.35 N₂O evolution decreased with increasing aeration over the whole range of fraction of aerated pores.

Masscheleyn et al. (1993) reported on N₂O emissions from rice paddy soils at various redox potentials, ranging from +500 to -250 mV. Two maxima for N₂O evolution were found, at +400 mV when nitrification was the source, and at 0 mV when N₂O was produced by denitrification.

Kralova et al. (1992) got similar results in a study on denitrification in a soil suspension amended with NO₃⁻. The maximum amount of N₂O was evolved at a redox value of 0 mV, while denitrification rates and N₂ emissions continued to increase with lower redox levels.

C.J. Smith & Patrick (1983) showed that alternate anaerobic-aerobic cycling increased N₂O evolution by a factor of 10 to 20 relative to constant aerobic conditions for soil suspensions amended with NH₄⁺. No N₂O evolved during constant anaerobic conditions. The redox potential fluctuated during cycling, but was always lower than the redox potential for constant aerobic, and much higher than for constant anaerobic, conditions. The enhanced N₂O emissions associated with cycling O₂ conditions are further discussed in sections 7.3.1 and 7.5.

Egginton & Smith (1986b) monitored N₂O and O₂ concentrations in an imperfectly drained grassland soil over a 2 year period and found them to be inversely related. Similar results were obtained on two clay soils by Dowdell & Smith (1974).

7. SOIL WATER CONTENT

7.1 Summary

Microbial processes that produce N₂O require water, and water in soil pores controls aeration and hinders gas diffusion. Generally, denitrification rate increases as soil water content rises. Nitrification rate also increases with water content up to a level where O₂ availability is restricted. The product ratio N₂O/N₂ from denitrification decreases and the product ratio N₂O/NO₃⁻ from nitrification increases as the soil becomes more anaerobic with increasing soil moisture content. N₂O emissions generally increase with increasing water content until the soil becomes very wet, then the emission declines. N₂O emissions are notably high when the soil alternates between dry and wet conditions.

7.2 Background

7.2.1 Physical terminology

Literature evaluation is complicated by the lack of uniformity in the use of terms for soil water content. The following definitions are used here:

- **Total pore space (TPS):** Total volume of soil not occupied by mineral or organic material. Soil porosity ($= \text{TPS} \cdot \text{soil volume}^{-1}$) is usually in the range 0.3 to 0.6 for mineral soils (Singer & Munns 1992).
- **Air-filled pore space (AFPS):** The fraction of TPS that is filled with air. Air-filled porosity ($= \text{AFPS} \cdot \text{TPS} \cdot \text{soil volume}^{-1} = \text{vol-}\%$ air) is also used.
- **Water-filled pore space (WFPS):** The fraction of TPS that is filled with water. Flooded soils have WFPS > 100%.
- **Field capacity (FC):** In laboratory studies, FC is the amount of water that a given volume of soil can hold against the force of gravitation. This is not a unique definition as values depend on drainage time and the height of the freely drained soil profile. In field situations, a soil is at FC when it is fully wetted and more rain would cause water loss by drainage. In well-drained soils FC is a natural reference, as by definition water content does not exceed that level, except temporarily during and soon after heavy rain.

The relationship between WFPS and FC varies considerably between soils, depending on texture, organic carbon content, mineralogy and management. Typically:

- heavy clay soil at FC has about 90% WFPS
- clay soil « « « « 80% WFPS
- silt soil « « « « 70% WFPS
- sandy soil « « « « 40% WFPS
- coarse sandy soil « « « 20% WFPS

- **Gravimetric water content (Weight-%):** Weight of the water in a given soil volume as a percent of the weight of dry soil.
- **Volumetric water content (Vol-%):** Water volume as percent of total soil volume.

AFPS or even better «air-filled porosity» are in principle the factor(s) that best describe the conditions that determine the production and emission of N_2O . But WFPS is a more commonly used factor. Where possible, literature values are transformed into WFPS and given in parentheses after the original figure. Aulakh et al. (1991b) found that denitrification loss in three soils with very different textures was better indicated by WFPS than by either gravimetric or volumetric water content.

In pot experiments soil water content is often reported as WFPS or as a percentage of FC. This is impractical in field experiments where water content is often expressed as weight-% or vol-%. These differences enhance the difficulty of comparing results of pot and field experiments.

7.2.2 *Soil water content variation*

Soil water status depends on:

- water supply by precipitation and irrigation
- water removal by drainage, evaporation from the soil surface, and uptake and transpiration by plants
- the soils capacity to store water.

These factors are governed by topography, soil texture, climate, plant growth and management practices. The water status can vary within a field, and usually varies through the profile, where the topsoil gradually dries out during dry spells. After rain the topsoil can be above FC for a short period, but the water content gradually diminishes as the water percolates to deeper layers or evaporates. Water distribution in the soil profile is rarely determined though it clearly influences the outcome of soil microbial processes.

Soil water content also varies with region, season and climate. A few examples are given as an illustration:

In southeast Norway, soil water content is often below field capacity between early May and mid-September. The soil dries up during the spring and the first part of the summer with episodes of wetting of topsoil after rain. Later, the water content gradually increases to reach FC by the middle of September. Similar patterns with the soil mostly well below FC during most of the growing season, and wet or perhaps frozen in the remainder of the year are common in temperate regions.

In coastal areas with maritime climates (e.g. western Norway, parts of the British Isles) and a mean annual rainfall of more than 1000 mm the soil is likely to remain wet for extended periods throughout the year. Pasture and forage production are the dominant form of agriculture in such areas.

Around the Mediterranean, rainfall is usually restricted to the winter, and FC may only be reached in the late winter/early spring. «Black earth» regions where organic material tends to accumulate, e.g. in the Ukraine and parts of the US mid-west, have little surplus precipitation. In tropical and subtropical regions climates are warm all year round, and range from continually wet, seasonally wet or dry, to arid conditions.

7.2.3 *The effect of water on soil processes*

Addition of water to soil influences soil processes in various ways:

- aeration is reduced. This stimulates denitrification and reduces nitrification
- if the soil is thoroughly wetted to a water content at or above FC, the pores are filled with water and can also close due to swelling of clay and humus and settling out of suspended particles. Such physical barriers limit N₂O emission (Christensen 1985b; Shepherd et al. 1991). The probability of N₂O reduction increases with its residence time in soil. Thus, N₂O derived in the surface soil is more likely to be emitted to the atmosphere than N₂O formed deeper in the soil profile
- soil air commonly contains 1 to 1000 ppmv N₂O. Topsoil (upper 30 cm) with

WFPS of 30%, total porosity 50% and 10 ppmv N_2O holds about 12 g $N_2O-N \cdot ha^{-1}$ in the pores. Displacement of soil air with this content of N_2O by rain or irrigation water can give an emission peak. For comparison, daily N_2O emissions from agricultural soils are reported to range from 0.1 to 125 g $N_2O-N \cdot ha^{-1}$ (Eichner 1990)

- water can act as a carrier for N_2O . The solubility of N_2O (1 atm. partial pressure) is 0.7 g $N_2O-N \cdot l^{-1}$ at 25°C (Wilhelm et al. 1977). Soil air with a N_2O concentration of 10 ppmv (10^{-5} atm) is in equilibrium with 7 μg $N_2O-N \cdot l^{-1}$ in soil water if Henry's law is valid for these conditions. Hence, such topsoil contains about 5 g $N_2O-N \cdot ha^{-1}$ dissolved in the water down to 0.3 m, assuming a water content of 25 vol-%. A content of 1 to 300 μg $N_2O-N \cdot l^{-1}$ in soil water is reported by several authors (Dowdell et al. 1979; Terry et al. 1981b; Minami & Fukushi 1984; Minami 1987; Minami & Ohsawa 1990), but concentrations up to 500-10000 μg $N_2O-N \cdot l^{-1}$ have also been observed (Amundson & Davidson 1990). Dissolved N_2O may follow percolating water towards ground or drainage water in wet seasons, or be released to the atmosphere during drying periods
- water is necessary for microbial activity. Increasing water content can, up to a point, increase the rate of mineralization and the availability of nutrients. Increased microbial activity enhances O_2 consumption. The effect of soil water on soil processes through its influence on aeration and microbial activity is illustrated by Linn & Doran (1984). With increasing water content up to 60% WFPS nitrification increased with enhanced microbial activity. An increase in WFPS from 60 to 100% gives a marked reduction in nitrification, some reduction in microbial activity and an increase in denitrification rate as conditions become more anaerobic. Thus, at low water content, microbial processes are limited by water availability, while aeration status is the most important regulating factor at high water content. The association between soil water content and production of N_2O and N_2 is illustrated by Davidson (1991), fig. 7-1 (section 7.5)
- water distribution in soil influences the movement of solutes, e.g. NO_3^- salts, their concentration and availability to organisms.

7.3 Denitrification

7.3.1 Rate

As mentioned above and illustrated below, soil water content is a major factor determining the rate of denitrification (Bremner & Shaw 1958; Grundmann & Rolston 1987; Myrold 1988). Thus, rainfall and irrigation usually cause an increase in the denitrification rate as the soil water content peaks provided other factors (e.g. degradable organic material) are not limiting (Ryden et al. 1979; Rolston et al. 1982; Ryden 1983; Aulakh et al. 1983; Mosier et al. 1986; Jarvis et al. 1991). Some authors find no, or only a weak, correlation between soil water content and rate of denitrification (Limmer & Steele 1982; Hixson et al. 1990), but most demonstrate a strong and positive correlation (Benckiser et al. 1986; Mosier et al. 1986; Murakami & Kumazawa 1987; Mancino et al. 1988; Myrold 1988; Malhi et al. 1990; K.S. Smith & Arah 1990; Giambiagi et al. 1990; Parsons et al. 1991; Groffman & Tiedje 1991;

Weier et al. 1993). Increasing denitrification rate with increasing soil water content seems most marked above about 60% WFPS (Terry et al. 1981b; Linn & Doran 1984; Aulakh et al. 1984a; Mulvaney & Kurtz 1984; Heinemeyer et al. 1988; Vinther 1990; Nugroho & Kuwatsuka 1992a).

Denitrification may cease if the soil remains wet for some time, and higher denitrification rates are observed where soils are going through wetting/drying cycles than where soil water content is constantly high (sections 6.5 and 7.5) (Mulvaney & Kurtz 1984). Groffman & Tiedje (1988) showed that the rate of denitrification did not depend on water content in a simple manner. They dried intact soil cores and found that denitrification rates decreased markedly when water content declined from flooding to field capacity. With further drying the decline was less rapid. However, when water content was increased from dry conditions, the sharpest increase in rate of denitrification occurred at low water content. Others have also found that denitrification rates depend on the history of the sample (Galsworthy & Burford 1978; Letey et al. 1980a).

Other factors influence the effect of soil water on denitrification rate. Especially important are:

- temperature (Vinther 1990; Mancino et al. 1988)
- NO_3^- concentration (Rolston et al. 1978)
- soil texture (Mancino et al. 1988; Groffman & Tiedje 1991)
- compaction, e.g. tractor traffic (Bakken et al. 1987; Hansen et al. 1993).

These factors are discussed in later chapters.

7.3.2 $\text{N}_2\text{O}/\text{N}_2$ ratio

The $\text{N}_2\text{O}/\text{N}_2$ ratio usually decreases with increasing soil water content and tends to be high when the denitrification rate is low (Murakami & Kumazawa 1987; Rolston et al. 1978; Rolston et al. 1982; Terry et al. 1981b; Christensen 1985b; Aulakh et al. 1984b; Schuster & Conrad 1992; Weier et al. 1993). However, N_2O emissions from denitrification are mainly determined by the denitrification rate and not by the $\text{N}_2\text{O}/\text{N}_2$ ratio as long as the soil is not so wet that escape of gases from soil is hindered and most of the N_2O is reduced to N_2 .

7.4 Nitrification

Nitrification is an aerobic process and the microbial activity will be maximal at a soil water content where the limiting effects of NH_4^+ and O_2 diffusion are equal. Both theoretical calculations (Skopp et al. 1990) and laboratory and field experiments (Linn & Doran 1984) indicate maximal nitrification rates at a water content about 50 to 60% WFPS. The product ratio $\text{N}_2\text{O}/\text{NO}_3^-$ increase as aeration becomes restricted.

Goodroad & Keeney (1984c) reported the effect of soil water content on nitrification and N_2O production in aerobic soils amended with NH_4^+ . Three levels of water content were studied, 10, 20 and 30 vol-% (= 18, 36 and 54% WFPS), and the relative rates (calculated from their tabulated means) were (18% WFPS = 1):

	18% WFPS	36% WFPS	54% WFPS
Rate of nitrification	1.0	1.5	1.7
Rate of N ₂ O production	1.0	1.6	7.4
N ₂ O-N/NO ₃ -N ratio (in %)	0.1	0.1	0.5

Similarly, Tietema et al. (1992) found the nitrification rate to increase with moisture content in the organic layer of an acid forest soil.

7.5 N₂O emission

Fig. 7-1 illustrates schematically the relationship between soil water content (expressed as WFPS) and N₂O (and N₂) emission due to denitrification and nitrification.

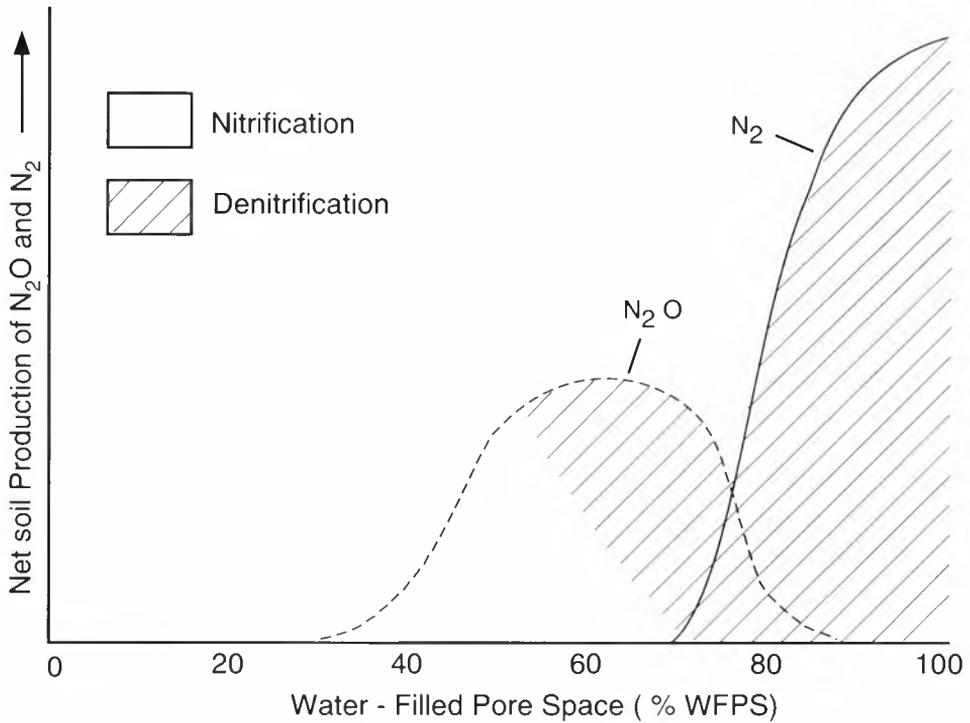


Figure 7-1. Model of the relationship between WFPS of soil and relative fluxes of N₂O and N₂. The emitted N₂O derives both from nitrification and denitrification. Source: Davidson (1991).

Caveat: While the figure indicates the general relationship between fluxes, the position of the maximum can vary with soil type and conditions.

At low soil water content, N_2O emission is low because microbial activity is low and the O_2 supply is ample so that nitrification goes all the way to NO_3^- , and denitrification rates are low. With increasing water content mineralization rate increases and nitrification increasingly produces N_2O . Also denitrification becomes significant with a high N_2O/N_2 ratio as O_2 diffusion becomes impeded. At high soil water content gas diffusion is severely hindered, denitrification proceeds increasingly towards N_2 and N_2O emission declines. Thus, a soil water content where both denitrification and nitrification can proceed, will generally give the maximum emission of N_2O . The range of this soil water content is normally 45 to 75% WFPS though some studies have indicated a higher level (Klemetsson et al. 1988; Hansen et al. 1993). This soil water content associated with maximum N_2O emission is normally close to FC. Either nitrifiers or denitrifiers may be the main N_2O generators within this range (Parton et al. 1988; Klemetsson et al. 1988; Schuster & Conrad 1992; Davidson 1992). Except for the topsoil after heavy rain or irrigation and for soils with a high clay content, agricultural soils are usually below FC during the growing season. Accordingly, except for prolonged very wet conditions (Terry et al. 1981b), most authors find a strong and positive correlation between N_2O emission and soil water content when either

- denitrification (Heinemeyer et al. 1988; Davidson 1992) or
- nitrification (Freney et al. 1979; Goodroad & Keeney 1984c; Klemetsson et al. 1988; Hutchinson & Brams 1992; Davidson et al. 1993)

is the main N_2O generating process. This is so in:

- unfertilized and fertilized soils (Conrad et al. 1983)
- pastures (Denmead et al. 1979b)
- arable land (Rolston et al. 1978; Ryden & Lund 1980b; Mosier et al. 1986)
- undisturbed soils (Mosier et al. 1981; Hao et al. 1988; Garcia-Méndez et al. 1991)
- organic soils (Terry et al. 1981a)
- mineral soils (Eaton & Patriquin 1989).

However, two studies have found little or no significant relationship between N_2O emission and soil water content: For extremely well drained grassland (Cates & Keeney 1987a) and for 6 forest sites (Schmidt et al. 1988).

The high rates of denitrification that occur when soils pass through wetting/drying cycles also show up as high N_2O emissions. This can be due to

- drying kills part of the soil microbial population and increases availability of degradable organic carbon (Ayanaba et al. 1976; Patten et al. 1980). Both nitrifying and denitrifying bacteria seem well adapted to survive extreme drought and are active within minutes of the wetting of dry soil (Davidson 1992; Rudaz et al. 1991)
- O_2 stimulates microbial activity in general and especially nitrification (Groffman & Tiedje 1988; Nishio & Fujimoto 1991)
- when a soil is wetted sufficiently by rain or irrigation water to cause anoxic conditions and to initiate denitrification, N_2O will be produced more rapidly than it

is reduced. If the soil dries within 24 to 72 hours, insufficient time will have elapsed for the development of nitrous oxide reductase, thereby preventing N_2O reduction to N_2 (Letey et al. 1981; Murakami et al. 1987; Cates & Keeney 1987b)

– NO_2^- can accumulate in soil during a dry season (Davidson et al. 1993).

The relationship between soil moisture content and N_2O emission rate is also often seen in field studies as an association between corresponding values of N_2O emission and water content obtained over a period of time, e.g. season or year and over a wide range of water content levels (Guthrie & Duxbury 1978; Foluronso & Rolston 1985; Duxbury & McConnaughey 1986; Parton et al. 1988; Skiba et al. 1992). This is illustrated by Mosier et al. (1981) who found N_2O emissions from a native shortgrass steppe during a summer sampling period to be positively correlated with soil water content in the upper 5 cm. Emissions were some 10-fold higher at 18 vol-% (36% WFPS) than at 10 vol-% (20% WFPS). Conrad et al. (1983) made similar observations at water contents of 10 to 20 weight-% (weight of water/weight of moist soil, that is up to approximately 60% WFPS). Maximal N_2O fluxes from soils are reported shortly after irrigation or rainfall (Conrad et al. 1983; Cates & Keeney 1987b; Hao et al. 1988; Hansen et al. 1993).

Terry et al. (1981a) investigated emissions from organic soils in Florida. These ranged from 4 g $\text{N}_2\text{O-N}\cdot\text{ha}^{-1}\cdot\text{day}^{-1}$ during dry periods to the extremely high value of 4500 g $\text{ha}^{-1}\cdot\text{day}^{-1}$ following rainfall events.

Davidson et al. (1993) studied N_2O emissions in a dry tropical forest. Emissions were higher in the wet season than in the dry season, but addition of water to dry soil caused rapid formation of NH_4^+ from mineralization and large pulses of N_2O emissions.

Currently much effort is placed on increasing food production in the developing countries through more extensive use of irrigation. However, this may increase the N_2O emissions (Hao et al. 1988; Vitousek et al. 1989).

Frenay et al. (1985) found that emissions increased by 1 to 2 orders of magnitude following heavy irrigation of a field cropped with sunflower and fertilized with urea. Most of the urea had been converted to NO_3^- at the time of the emission measurements. The irrigation increased soil water content in the 10–20 cm profile from 27 to 41 weight-%. In the upper 2 cm the soil water content was increased from 10 to 70 weight-%.

Ryden & Lund (1980a) reported peak emissions from Californian horticultural fields after each irrigation. The flux diminished as the soil dried up. Mosier & Hutchinson (1981) reported that an irrigated field of maize lost 59% of the seasons loss of N_2O during the week following the first irrigation, when restricted O_2 diffusion favoured denitrification.

It is possible to obtain good crop yields with irrigation strategies that keep water consumption low (Riley 1989), but the influence of water usage strategy on N_2O emissions has not been adequately studied.

Drainage stimulates nitrification (S.C. Jarvis, pers. comm.) and diminishes denitrification. The $\text{N}_2\text{O}/\text{N}_2$ ratio can also change. Hence, the effect of drainage on N_2O emissions varies with circumstances (Colbourn & Harper 1987).

Large emissions of N_2O requires that soil inorganic N and organic C supply is adequate (Mosier & Hutchinson 1981; Ryden 1983; Ryden & Lund 1980b; Frenay et

al. 1985; Li et al. 1992a,b). High emissions associated with rainfall/irrigation are favoured when fertilizer is applied simultaneously with, or soon before, the event (Burford & Hall 1977; Ryden et al. 1979; Mosier & Hutchinson 1981; Webster & Dowdell 1982; Su et al. 1990; Hutchinson & Brams 1992).

Waterlogged conditions are mostly undesirable in agriculture, except for paddy rice. These fields usually emit only small amounts of N_2O while flooded (Buresh & Austin 1988; Bouwman 1990; Lindau et al. 1990b; De Datta et al. 1991; Buresh et al. 1991; Freney & Denmead 1992). However, Minami (1987) reported emissions ranging from 0.27 to 0.55 kg $N_2O-N \cdot ha^{-1}$ during about 4 months from 3 Japanese paddy rice fields. N_2O can form and escape if appreciable amounts of NO_3^- is present in the soil before flooding (Freney & Denmead 1992). Emissions may also increase when the soil dries up.

It has been proposed that the soil may act as a sink for N_2O (Blackmer & Bremner 1976; Bremner 1978; Freney et al. 1978; Letey et al. 1980a; see also section 2.3.2). Silvola et al. (1992) also observed occasional uptake of N_2O in field studies on Finnish peat soils. Soil absorption of N_2O is illustrated by the result of Ryden (1981), fig. 8-2 for a fertilized grassland. He observed that the unfertilized control invariably removed atmospheric N_2O when the water content exceeded 20 weight-%. However, wet field conditions suitable for extensive N_2O reduction, are also the conditions that will restrict N_2O movement from the air into soil. This suggests that there is little removal of atmospheric N_2O by reduction in the soil to N_2 , but the topic cannot be regarded as settled.

Drainage together with surface run-off and groundwater seepage carry leached NO_3^- to surface waters. A major part of the NO_3^- in European surface and coastal waters originate with agriculture. Labroue et al. (1991) reported that the N_2O/N_2 ratio for summertime denitrification, determined with the AIM, was as high as 39% in a lake where the average NO_3^- concentration was 60 mg $NO_3^- \cdot l^{-1}$, compared with 4% in a lake where this concentration was 8 mg $NO_3^- \cdot l^{-1}$. The formation of N_2O varied greatly with season, with the highest N_2O concentrations in the lakes during summer.

Denitrification in aquatic sediments have been reviewed by Seitzinger (1990). She concluded that the magnitude of the increase in N_2O production on a global scale as a result of eutrophication of aquatic systems is uncertain and warrants quantification.

As mentioned in section 2.3.1, groundwater can contain up to three orders of magnitude higher concentrations of N_2O than the amounts expected as a result of equilibrium with the atmosphere (Dowdell et al. 1979, Ronen et al. 1988). This N_2O may eventually escape to the atmosphere (Bowden & Bormann 1986). Ueda et al. (1991) reports that groundwater N_2O in Japan is depleted in ^{15}N , as is observed for N_2O derived from nitrification. Lind & Eiland (1989) found that N_2O formation by nitrification was limited to the topsoil. This suggests that in temperate climates N_2O in groundwater originates from mineralization and nitrification in the upper part of the soil in the autumn, followed by downward movement of N_2O enriched drainage during the cold season.

8. NITROGEN AVAILABILITY

8.1 Summary

The denitrification rate, N_2O/N_2 ratio and N_2O emission all increase with increasing soil NO_3^- concentrations. Production of N_2O by nitrification is also enhanced as the soil concentration of the substrate, NH_4^+ , increases. Hence, application of N fertilizers or manures is usually followed by an increase in N_2O emission. The amounts emitted vary greatly depending on circumstances, and some conditions seem to be associated with notably high N_2O emission rates.

8.2 NH_4^+ and NO_3^- in soil

Availability of mineral N (NH_4^+ and NO_3^-) to bacteria are important controllers for the microbial processes that produce N_2O .

Different methods exist for expressing this availability of NH_4^+ and/or NO_3^- :

- soil N content: $kg\ N \cdot ha^{-1}$, in a defined soil profile or as input
- soil N concentration: $mg\ N \cdot kg\ dry\ soil^{-1}$.

They are related through the formula:

$$kg\ N \cdot ha^{-1} = h \cdot \frac{p_s}{10} \cdot mg\ N \cdot kg\ dry\ soil^{-1}$$

where h is the profile depth (in cm) and p_s is the soil bulk density. p_s varies with soil type and soil depth. Østergaard & Mamsen (1990) reported that it was usually in the range of 1.30 to 1.65, typically about 1.4, for mineral topsoils in Denmark.

The expressions of N availability that are most directly related to the microbial processes are the concentrations of NO_3^- and NH_4^+ (or combined as «mineral N») in soil water. This is the notation used in laboratory studies of microbial cultures. However, it is impractical to use N concentration in soil water as a measured parameter in field studies as this concentration varies greatly with soil water content. However, the use of soil N content or soil N concentration instead of the N concentration in soil water makes it difficult to compare results from different types of studies. We will conform to common practice by referring to soil N content and soil N concentration, but the problems with this approach should be borne in mind.

Danish results (Østergaard & Mamsen 1990) can be used as an illustration of the amounts and concentrations of mineral N found in fields. They reported average values for soil N content or concentration for a 100 cm profile after the growing season (in Nov.-Dec.) on land where animal manures had not recently been applied:

		<u>arable</u>	<u>grassland</u>
NO_3^-	as $kg\ N \cdot ha^{-1}$	32	15
	as $mg\ N \cdot kg\ soil^{-1}$	2.1	1.0
	as $mg\ N \cdot l\ water^{-1}$	14	6
NH_4^+	as $kg\ N \cdot ha^{-1}$	13	26
	as $mg\ N \cdot kg\ soil^{-1}$	0.8	1.7

During the growing season the concentration of mineral N in soil water should preferably not be below that required for optimal crop growth. Barraclough (1986) reported this to be at least 3 mg $\text{NO}_3^- \cdot \text{N} \cdot \text{l}^{-1}$ for winter wheat, while Robinson et al. (1991) found a higher value for spring wheat, about 22 mg $\text{NO}_3^- \cdot \text{N} \cdot \text{l}^{-1}$.

NH_4^+ and NO_3^- in soil derive from mineralization of soil organic material, manures, fertilizers and atmospheric deposition. Mineralization can be a slow process that does not normally cause high NH_4^+ or NO_3^- concentrations. Exceptions can occur following the incorporation of easily mineralizable crop residues rich in N, e.g. from rape and legumes, and following the ploughing of grassland.

Application of animal manure as slurry increases NH_4^+ concentration in soil, because about 60 to 70 % of the N in slurry is present as NH_4^+ , urea and uric acid. Patches of soil with high urea concentrations occur where grazing animals urinate. Urea is rapidly hydrolyzed to NH_4^+ in soil, usually within a few hours to a few days (Haynes & Williams 1992).

Solid fertilizers are mostly applied as particles on the soil surface. They absorb water and dissolve, usually within a few hours, and initially form spots, about 1 cm in diameter, where the soil solution is nearly saturated with nutrients. Further distribution of the nutrients in the soil is by diffusion and mass flow. NH_4^+ binds to clays and humus through ion exchange and moves initially at a slower rate than NO_3^- , but is often nitrified within a few days, though the process can take a few weeks. The dispersion pattern of fertilizer N depends on the soil water content (Saxena & Chaudhary 1991). Dispersion was more extensive if originally the soil was wet than if it was dry before the soil was irrigated after application (Tillman et al. 1991).

It follows that the concentrations of NH_4^+ and NO_3^- in soil can vary widely. This variability also can have other causes:

- dilution by rain or irrigation, concentration through evapotranspiration and uptake by plants and microbes
- seasonal variations: NH_4^+ and NO_3^- are rapidly taken up by arable crops during the first part of the growing season, while mineralization of roots, crop residues and soil biomass after harvest release NH_4^+ that is converted to NO_3^-
- apparently uniform fields can show substantial spatial variation in mineral N content (Van Meirvenne & Hofman 1989). This can be due to differences in soil and subsoil texture, past history etc.

8.3 NO_3^- and denitrification

8.3.1 Rate

Fig. 8-1 illustrates the principal relationship between soil NO_3^- content and gaseous N losses. Denitrification rate increases with increasing soil NO_3^- content up to a certain level, then becomes constant.

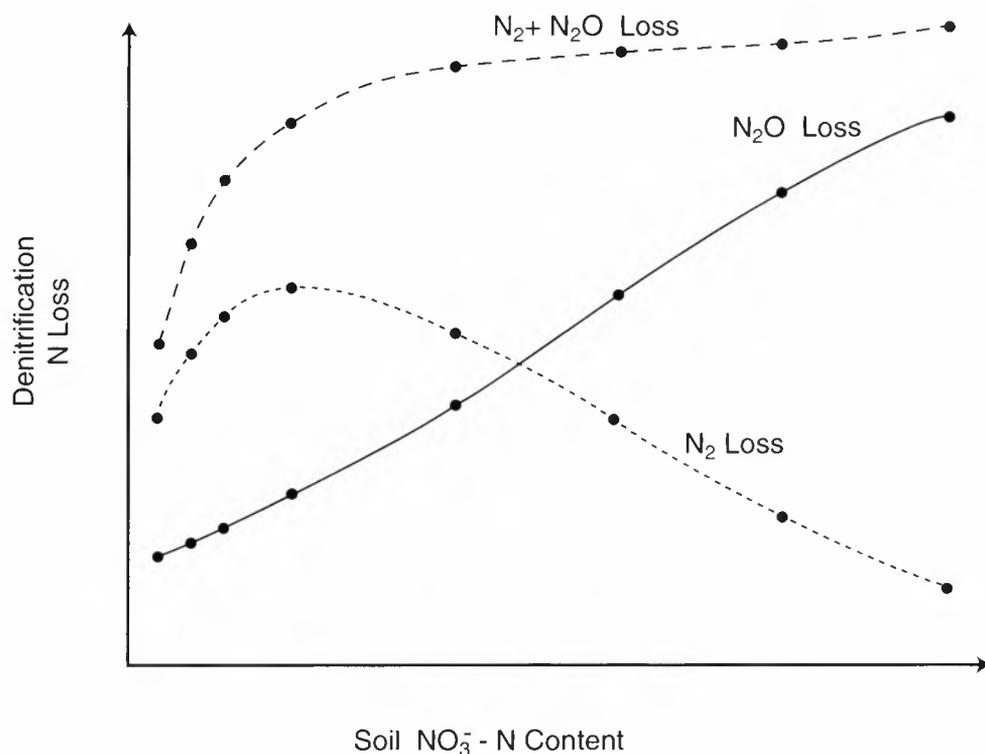


Figure 8-1. The idealized effect of soil NO_3^- on N_2 and N_2O losses associated with denitrification. Source: Mosier et al. (1983).

This type of relationship is common for microbiological processes, and is described by Michaelis-Menten kinetics:

$$V = \frac{V_m S}{S + K_M}$$

where: V : denitrification rate
 V_m : maximum rate
 S : NO_3^- concentration
 K_M : constant.

K_M is in this case the soil NO_3^- concentration that gives a denitrification rate of 50% of the maximal value. The denitrification rate is first order for NO_3^- concentration only when this is well below K_M , but reported apparent K_M values for denitrification vary greatly:

- Klemetsson et al. (1977): 4 mg NO_3^- -N·kg soil⁻¹
- Murray et al. (1989): 0.025-0.2 mg NO_3^- -N·kg soil slurry⁻¹
- Malhi et al. (1990): 117-138 mg NO_3^- -N·kg soil⁻¹.

Hence, the soil NO_3^- concentration that gives the maximum denitrification rate varies. The rate remains at this maximum value when the soil NO_3^- concentration increases further. Limmer & Steele (1982) found denitrification potential to be independent of NO_3^- concentration above $25 \text{ mg NO}_3^- \cdot \text{N} \cdot \text{kg}^{-1}$ in a range of soils.

The NO_3^- concentration in topsoil is commonly between 2 and $10 \text{ mg N} \cdot \text{kg}^{-1}$ in arable land for most of the year, and should therefore be in the range where denitrification rate increases with increasing NO_3^- concentration. However, after application of fertilizer or manure or incorporation of crop residues the denitrification rate may be at NO_3^- saturation level for some time.

The rate of denitrification is also influenced by other factors, as discussed in detail in other chapters. When such other factors are limiting, the denitrification rate can be rather insensitive to variations in soil NO_3^- concentrations. This has been found in studies by Bremner (1978), Cho & Mills (1979), Aulakh et al. (1983) and Kroeze et al. (1989). There is usually no effect of increased NO_3^- concentration if organic carbon is in short supply (Limmer & Steele 1982; McCarty & Bremner 1992, Nugroho & Kuwatsuka 1992a). However, the principal trend is that the denitrification rate increases after NO_3^- additions (Ryden 1983; Vinther 1984; Colbourn & Harper 1987; G.P. Robertson et al. 1987; Samson et al. 1990; Schloemer 1990; Ambus & Lowrance 1991). Sufficient numbers of microorganisms capable of denitrification must also be present. It can take a short time, some hours to a few days before the microbial population and process rate adjust to the changed circumstances (e.g. after rain, Hansson et al. 1990) so that denitrification can proceed at maximum rate.

The denitrification rate can be reduced if the concentration of N_2O in soil increases to high levels (Van Cleemput et al. 1988).

8.3.2 $\text{N}_2\text{O}/\text{N}_2$ ratio

NO_3^- usually inhibits or retards N_2O reduction to N_2 (Blackmer & Bremner 1978; Cho & Mills 1979), although there are exceptions for some strains of bacteria (Betlach & Tiedje 1981). As a result, the $\text{N}_2\text{O}/\text{N}_2$ ratio strongly increases with increasing NO_3^- concentration in soil (Nömmik 1956; Blackmer & Bremner 1978; Bremner 1978; Cho & Sakdinan 1978; Firestone et al. 1980; Terry & Tate 1980; Erich & Bekerie 1984; Vinther 1984; Christensen 1985b; Ottow et al. 1985; Kroeze et al. 1989). This is also illustrated in fig. 8-1. Concentrations in the range of 10 to $30 \text{ mg NO}_3^- \cdot \text{N} \cdot \text{kg}^{-1}$ is usually sufficient for this retardation. This is in the upper range of what is common in arable land, but can be exceeded at least locally after application of fertilizers or manures and during autumn mineralization of crop residues. As denitrification and plant and microbial uptake proceed and the NO_3^- concentration falls, the $\text{N}_2\text{O}/\text{N}_2$ ratio also declines (Rosswall 1979).

It is not clear if the effect of NO_3^- on the last step in denitrification is due to true inhibition of N_2O reduction or simply because NO_3^- is preferred as an electron acceptor over N_2O during denitrification, or whether both processes occur simultaneously (Cho & Sakdinan 1978). The effect and the required concentration depend on several other factors (e.g. pH, aeration, organic carbon content, type of soil and water content). Under highly reducing conditions (e.g. flooded organic soils) the inhibitory effect of NO_3^- on N_2O reduction is strongly decreased or nullified due to the increased demand for electron acceptors (Terry & Tate 1980; Terry et al. 1981b; Aulakh et al. 1984b; Bouwman 1990).

Generally, when the soil water content is sufficiently high, a large amount of N_2O is produced and evolved immediately after addition of NO_3^- . After a period of time, typically a few hours or days, N_2O evolution decreases, and N_2 evolution increases. As a result, the N_2O/N_2 ratio is initially high, but decreases with time (Cho & Sakdinan 1978; Rolston et al. 1978; Aulakh et al. 1984b). A marked peak in N_2O emissions after fertilization is commonly seen in field studies (fig. 8-2).

It has been proposed that while the enzyme nitrate reductase develops rapidly after anoxic conditions are initiated, development of nitrous oxide reductase requires more time (Letey et al. 1980b). The duration of this lag period increases with NO_3^- concentration (Galsworthy & Burford 1978; Nõmmik et al. 1984; Colbourn & Harper 1987; Kroeze et al. 1989), but eventually N_2O reduction occurs even in the presence of relatively high concentrations of NO_3^- and may even be more rapid than NO_3^- reduction (Letey et al. 1981). Consequently, N_2O accumulated in the soil profile during the early stages of denitrification can be reduced later, provided it has not escaped.

Firestone et al. (1980) showed that the effect of NO_3^- depends on pH. Addition of 10 mg NO_3^- -N·kg soil⁻¹ gave a N_2O/N_2 ratio of 4 at pH 4.9 and 0.2 at pH 6.5. Similar effects have been reported by others (Blackmer & Bremner 1978; Cho & Sakdinan 1978; Gaskell et al. 1982). This is further discussed in section 10.3.2.

Firestone et al. (1980) also reported that NO_2^- can be more inhibitory for N_2O reduction than NO_3^- , and suggested that the apparent effect of NO_3^- may be due to microbial reduction of NO_3^- to NO_2^- or NO. That NO_2^- inhibits N_2O reduction was also reported by Van Cleemput et al. (1988). However, Gaskell et al. (1982) measured N_2O reduction in soils incubated with various mixtures of NO, NO_3^- and NO_2^- , and found that NO_3^- *per se* inhibited N_2O reduction. The inhibitory effect of NO was much smaller than that of NO_3^- and NO_2^- .

NO_3^- is thus, under most circumstances, an inhibitor of N_2O reduction. But at low concentrations, e.g. 5 mg NO_3^- -N·kg soil⁻¹, NO_3^- can also stimulate formation and activity of nitrous oxide reductase (Blackmer & Bremner 1979; SooHoo & Hollocher 1990).

8.3.3 N_2O emission

Because NO_3^- enhances the N_2O/N_2 ratio and stimulates the denitrification rate, N_2O emission generally increases with increasing NO_3^- content of the soil (Mosier et al. 1983; Lind 1985; Murakami 1987; Eaton & Patriquin 1989; Matson et al. 1990). A high soil water content (e.g. following rainfall) is also usually required (Ryden 1983; Skiba et al. 1992).

NO_2^- is a key intermediate in both nitrification and denitrification, and increased soil NO_2^- concentration may also increase N_2O emissions (Minami & Fukushi 1986; Baumgärtner & Conrad 1992). However, significant NO_2^- concentrations in soils are usually transient, though in soils with pH > 7 concentrations in the range of 6 to 15 mg NO_2^- -N·kg soil⁻¹ have been measured for a few days after urea application of 100 mg urea-N·kg soil⁻¹ (O. Van Cleemput, pers. comm.).

8.4 NH_4^+ and nitrification

Oxidation of NH_4^+ proceeds more rapidly than formation of NH_4^+ through mineralization, so nitrification is usually NH_4^+ limited. Similarly, NO_2^- is so rapidly oxidized that it usually does not accumulate in soil (Macdonald 1986). However, when low O_2 supply limits nitrification, ammonium oxidizers may use the intermediate NO_2^- as an alternative electron acceptor. N_2O is formed in that reaction.

In older literature denitrification was regarded as the only significant N_2O generating microbial process in soil. However, results by Bremner & Blackmer (1981) indicated that nitrification also produced N_2O , notably in fields fertilized with urea or fertilizers that contain NH_4^+ .

Compared to the many studies that have explicitly investigated the control of NO_3^- on denitrification, only a few have been published on the control of NH_4^+ on nitrification and associated N_2O formation.

Yoshida & Alexander (1970) and Blackmer et al. (1980) demonstrated in liquid cultures and in soil that *Nitrosomonas europaea* form N_2O from NH_4^+ . The part of the nitrified N that was evolved as N_2O increased with increasing NH_4^+ concentration up to about 1 g $\text{NH}_4^+ \cdot \text{N} \cdot \text{l}^{-1}$, and was on average 1 to 2%.

However, the relevance of these studies to field situations may be limited as the NH_4^+ concentrations were 10 to 100 times those values normally occurring in cultivated fields (Ryden 1981; C.J. Smith et al. 1982; Lockman & Storer 1990). Exceptions are the high concentration spots formed around fertilizer granules shortly after fertilizer application (section 8.2) and possibly in urination patches in grazed pastures (section 8.5.3).

Hutchinson & Brams (1992) found that N_2O (and NO) emissions from a pasture peaked following fertilization with NH_4^+ fertilizer and precipitation. The emissions then declined at a rate that closely paralleled the nitrification rate indicating that the N_2O came from nitrification rather than from denitrification.

Two N_2O emission peaks separated by time have been seen following N application as NH_4^+ compounds (Freney et al. 1985; Murakami et al. 1987). The two peaks were thought to represent N_2O from nitrification followed in time by denitrification.

In the model of Mosier et al. (1983) based on measurements of N_2O emissions from cropped and native soils, emissions increased exponentially with NH_4^+ concentrations between 1 and 6 mg $\text{NH}_4^+ \cdot \text{N} \cdot \text{kg soil}^{-1}$. Emissions were constant above 10 mg $\text{NH}_4^+ \cdot \text{N} \cdot \text{kg soil}^{-1}$.

8.5 N_2O emissions from fertilized land

The influence of fertilizer application on N_2O emission from soils is discussed in several reviews (Bouwman 1990; Byrnes 1990; Eichner 1990; Mosier & Schimel 1991).

8.5.1 *The origin of increased N_2O emissions from cultivated land*

A soil's potential for N_2O emission increases when the amount of N available for microbial transformation is enhanced: through fertilizer N application, cropping of legumes, return to soil of manures and crop residue, and mineralization of soil

biomass and other forms of soil organic material. Hence, it is generally found that N_2O emissions from fertilized cultivated land are greater than from native soils (chapter 5).

Application of fertilizer N is almost always followed by a notable short-term increase in N_2O emission (Breitenbeck et al. 1980; Bremner & Blackmer 1980b; Bremner et al. 1981a; Duxbury et al. 1982; Conrad et al. 1983; Su et al. 1990; Tsuruta et al. 1993). An example is shown in fig. 8-2. This increase is usually immediate, but a lag period of some days may occur. Duration of the peak emission usually lasts for one or a few weeks and is often ended by a sharp decrease. The magnitude of the peak emission can vary greatly as is shown by fig. 8-2.

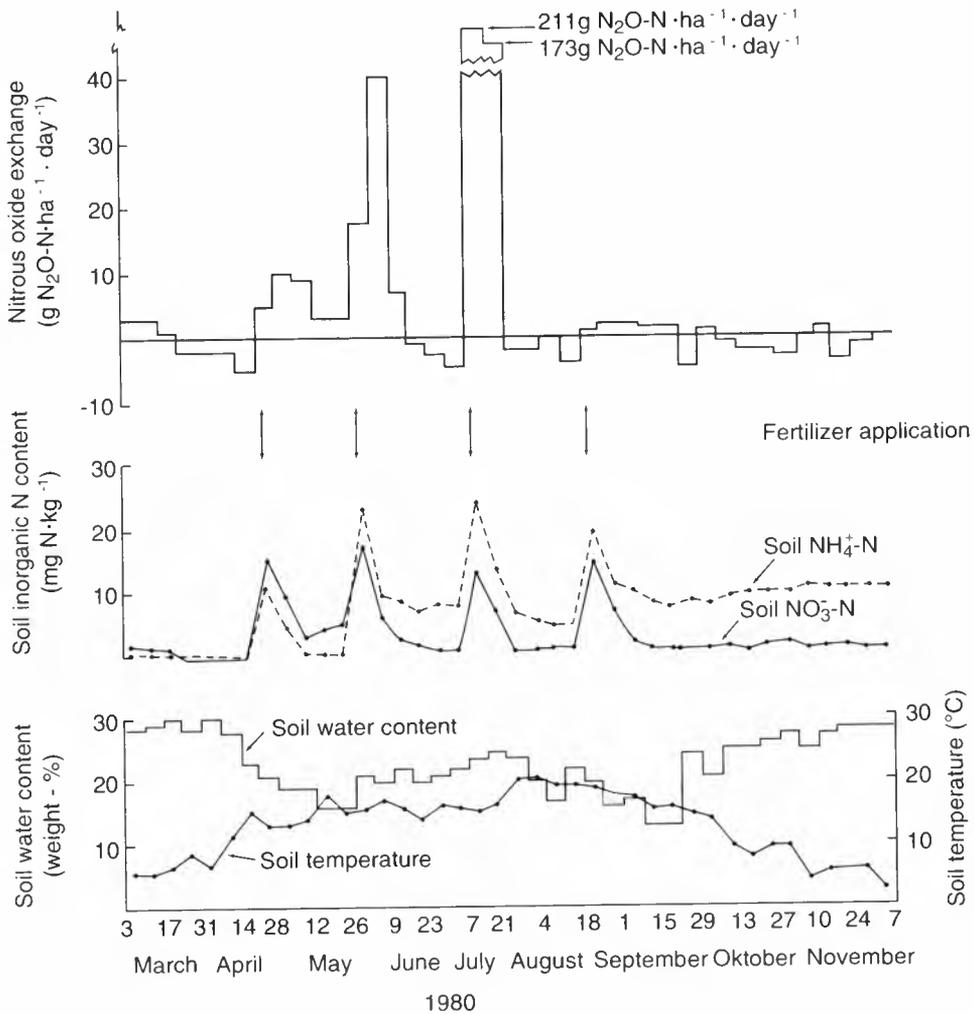


Figure 8-2. N_2O exchange, soil NH_4^+ , NO_3^- , and water content (0–20 cm), and soil temperature (2 cm) in grassland receiving $250\ kg\ N \cdot ha^{-1} \cdot year^{-1}$ as NH_4NO_3 . Fertilizer was applied in four equal amounts on the dates indicated with an arrow. Source: Ryden (1981).

Published N₂O yields following fertilization with various types of fertilizer have been discussed by Byrnes (1990) and summarized in 5 recent reports. These reviews cover to some extent the same material, but there are also differences in coverage. The observations are summarized as median values and ranges for each review, table 8.1.

The N₂O yields that have been reported vary within a wide range, indicating that attention to circumstances of fertilizer use and other management practices may reduce emissions.

Most data in table 8.1 derive from temperate agriculture. There are reasons to believe that some tropical soils emit more N₂O than is typical for temperate regions (see section 9.4).

Table 8.1. Median N₂O yields (%) for different fertilizer types (with ranges) from reviews by five authors.

	A	B	C	D	E
NO ₃ ⁻	0.07 (0.01-1.8)	0.04 (0.001-1.3)	0.07/0.04 (0.001-0.5)	0.05	0.04
NH ₄ ⁺	0.12 (0.03-0.9)	0.15 (0.03-1.5)	0.15 (0.05-1.8)	0.1 ¹⁾	0.17 ³⁾
Urea	0.11 (0.07-0.2)	0.1 (0.01-0.6)	0.2/0.6 ¹⁾ (0.1-2.1)	0.5 ²⁾	
NH ₄ NO ₃	0.1/0.4 (0.04-1.7)	0.7 (0.3-1.6)			
NH ₃	1.2/1.4 (0.9-6.8)	0.1 (0.05-1.3)			5.0
Organic		1.0 (0.01-2.05)			
A:	Eichner (1990)	¹⁾ NH ₄ NO ₃ included			
B:	Bouwman (1990)	²⁾ NH ₃ included			
C:	Keller et al. (1988)	³⁾ urea included			
D:	Galbally (1985)				
E:	Bolle et al. (1986)				

With this reservation the table indicates that the N₂O yield is (except for anhydrous NH₃) usually within a range of about 0.1 to 2%, though higher values have been reported. Thus, Shepherd et al. (1991) found that 5.3% of the N in NH₄NO₃ applied to a fine sandy loam soil in Canada was lost as N₂O.

The N₂O yields are used in the assessment of global N₂O fluxes from cultivated land. This topic is discussed in the concluding chapter, section 16.1.

The literature indicate that some situations can be associated with high N₂O yields:

- application of urea/ NH_4^+ compounds under conditions favouring N_2O production by both nitrification and denitrification, e.g. in moist, but well-aerated soil (Bremner & Blackmer 1978, 1980a,b; Blackmer et al. 1980; Conrad & Seiler 1980; Seiler & Conrad 1981; Conrad et al. 1983; Duxbury & McConnaughey 1986; Van Breemen & Feijtel 1990). However, only small amounts of N_2O should form where plant uptake is rapid and nitrification slow, e.g. in spring on grassland in wet climates. This has recently been observed (K.A. Smith, pers. comm.)
- use of NO_3^- fertilizers where denitrification is favoured, e.g. on clay soils in wet climates (Egginton & Smith 1986b). Also, NO_3^- compounds produced higher N_2O emissions than NH_4^+ fertilizers in humid tropical soils (Keller et al. 1988; Livingston et al. 1988)
- injection of anhydrous (but not aqueous) NH_3 seems to give markedly higher N_2O emissions than any other fertilizer type in studies where different N sources are compared (Hutchinson & Mosier 1979; Bremner & Blackmer 1980b; Bremner et al. 1981a; Breitenbeck & Bremner 1986a,b). The underlying mechanism is unknown, but results reviewed by Focht & Verstraete (1977) suggest it could be the inhibition of *Nitrobacter* activity by NH_3 and hence NO_2^- accumulation at the high pH in the injection zone. Another possibility is the death and decomposition of soil microbes in this zone, which should further N_2O producing processes when the zone is recolonized. However, not all authors find that application of anhydrous NH_3 results in large N_2O emissions (Cochran et al. 1981). Further work is required to clarify the situation. However, this is mainly a North-American issue. In the US about 37% of fertilizer-N is applied as NH_3 , in Canada 31% and in Mexico 22%, while in the rest of the world only about 1% of fertilizer N is applied in this form. In Europe, Denmark is the only country where NH_3 is used to any extent as fertilizer (about 16% of the N application) (IFA 1992)
- application to compacted soils in wet climates (Hansen et al. 1993)
- soils rich in organic carbon are especially prone to produce N_2O when fertilized (chapter 11). High N_2O emissions are observed on:
 - fertilizer application to organic soils (Guthrie & Duxbury 1978; Duxbury et al. 1982).
 - use of mineral fertilizers together with manure or manure alone (Christensen 1985a; Christensen 1983; Cates & Keeney 1987b)
 - fertilizer application to grasslands (Ryden 1981; Webster & Dowdell 1982; Christensen 1983).

8.5.3 Application method and N_2O emission

Most fertilizers are applied by surface spreading. In arable crops, sowing and fertilization are sometimes combined in one operation, with the fertilizer placed near the seeds. Later applications are spread on the surface. Injection of anhydrous and aqueous NH_3 into the soil using special equipment and the spreading of fertilizers dissolved or suspended in water are also used in some regions.

Manure is also usually surface applied, but regulations designed to reduce

losses of NH_3 increasingly specify that manure should be injected or rapidly ploughed into the soil. N_2O emissions following application of animal manures are discussed in section 11.5.

N_2O emitted from soil is mostly produced in the topsoil. Fertilizer and manure application primarily influence topsoil conditions, but reports on the effect of application method on N_2O emission are few. Stefanson (1976) found that placement of $\text{Ca}(\text{NO}_3)_2$ at 5, 15 and 25 cm depths gave similar N_2O production rates, but Breitenbeck & Bremner (1986a) reported the N_2O yield from anhydrous NH_3 to increase with injection depth:

Depth (cm)	N_2O yield ¹⁾	
	112 kg N	225 kg N
10	0.7	0.9
20	1.2	1.1
30	1.5	1.2

¹⁾ Based on total emissions in 156 days.

C.J. Smith et al. (1982) found that on average twice as much N_2O was emitted from a wetland rice field when urea was drilled at sowing than where the urea was applied as two topdressings during the growing season. However, emissions were at a rather low level, $< 6 \text{ g N}_2\text{O-N}\cdot\text{ha}^{-1}\cdot\text{day}^{-1}$.

Conclusions on the relationship (if any) between fertilizer application method and N_2O emission cannot be drawn at present due to lack of data.

Droppings and urine from grazing cattle form patches with high soil concentrations of soluble N. Several studies (Sherlock & Goh 1983; Colbourn 1992; Spatz et al. 1992) have indicated that appreciable amounts of N_2O can be emitted from urine patches on grazed pasture. Monaghan & Barraclough (1993) found that this was due to a combination of increased availability of solubilized soil organic material and high NH_3 concentrations. Both deposited and mineralized N contributed to the N_2O flux. Parton et al. (1988) found that the N_2O flux from such urine patches were on average three to four times greater than that from controls, with a wide spread in the results. In extensive cattle operations the area affected by urine is too small to have a significant impact on the flux of N_2O per ha, but in intensive pasture management urine patches can cover about 40% of the area in a grazing season (W. Bussink, pers. comm.). Then the N_2O flux from the pasture can be significantly enhanced.

8.6 Chemical modifiers

8.6.1 Phosphate and other nutrients

Yoshida & Alexander (1970) studied NH_4^+ oxidation in cultures of *Nitrosomonas europaeae* at pH 8.0. Their results indicated that phosphate in extremely high concentration (for soil conditions) of 0.01 to 0.03 M = 310 to 930 mg $\text{P}\cdot\text{l}^{-1}$ slightly stimulated N_2O formation. Some stimulatory effect by phosphate on N_2O formation has also been seen in soils (Minami & Fukushi 1983; Martikainen 1985; Keller et al.

1988). By contrast, Sahrawat et al. (1985) found no significant effect of P addition ($100 \text{ mg P} \cdot \text{kg soil}^{-1}$) to acid forest soils, on nitrification, ammonification or N_2O emission.

The effect of phosphate, where observed, seems to be due mainly to a general stimulation of microbial activity in P deficient soils as suggested by Keller et al. (1988). It should be of importance only in situations where the soil is deficient in P, but data confirming this assumption are not available.

Rapid crop uptake of applied N should counteract N_2O losses. A balanced and adequate supply of the other nutrients should therefore contribute to reduced N_2O losses compared with situations where deficiencies occur, but studies on this topic are lacking.

8.6.2 *Nitrification inhibitors*

When nitrification is inhibited, less N might be lost by leaching, and more immobilized or taken up by plants. The use of nitrification inhibitors in agriculture is at present very limited, questions can be raised both as to their short and long term efficiency and to the ecological acceptability of their large scale use.

Nitrapyrin (2-chloro-6-(trichloromethyl)-pyridine or N-serve®) inhibits the NH_4^+ oxidation step and has been used in field and laboratory studies of nitrification (Bremner & Blackmer 1978, 1980a; Aulakh et al. 1984a; Livingston 1988). Nitrapyrin will inhibit nitrification for a period of up to four to eight weeks. Thus, where NH_4^+ fertilizers, urea or anhydrous NH_3 are used, nitrapyrin may reduce N_2O emissions (Bremner et al. 1981b; McElhannon & Mills 1981; Magalhães et al. 1984; Bronson et al. 1992; Vermoesen et al. 1992).

Dicyandiamide (DCD, Didin) is marketed as a fertilizer and fertilizer component that inhibits the first step of nitrification. It is also used as an additive to manure slurries (Amberger 1989). The effect of this compound on N_2O formation has been less studied than that of nitrapyrin. Willison & Anderson (1991) reported that DCD reduced N_2O emission rates from forest soils amended with glucose and NO_3^- and that DCD may thus also suppress denitrification.

Calcium carbide reacts with water, producing acetylene. Calcium carbide coated with wax and shellac has been used as a nitrification inhibitor, resulting in reduced N_2O emissions from flooded rice fertilized with urea in laboratory and field studies (Bronson & Mosier 1991; Keerthisinghe et al. 1993). Freney et al. (1992) used coated calcium carbide in a field experiment with irrigated wheat fertilized with urea. The inhibitor limited NH_4^+ oxidation and denitrification loss for 75 days, but the N_2O emission was not measured.

Sallade & Sims (1992) recently demonstrated that thiosulphate inhibited nitrification in manure.

Miller et al. (1993) found that methyl fluoride and dimethyl ether inhibited nitrification and N_2O production in laboratory studies, and azides (N_3^-) are general inhibitors of nitrification (Aulakh & Rennie 1985). These products have been used in some laboratory studies. They are not used in agriculture. By contrast to nitrapyrin, addition of azides seems to stimulate N_2O emission. This may be due to inhibition of N_2O reduction (Freney et al. 1979; Kristjansson & Hollocher 1980) or stimulation of denitrification (Aulakh & Rennie 1985).

9. SOIL: TYPES, TEXTURE, TILLAGE

9.1 Summary

On the whole, fine-textured soils seem to emit more N_2O than light soils, but this tendency can be masked or reversed by other factors, especially soil water content. Organic soils and soils in humid tropical climates tend to be high N_2O emitters. Soil compaction increases emissions.

9.2 Type and texture

A soil's propensity for generating and emitting N_2O varies with soil physical characteristics, but the relationship is not simple. Clay soils can maintain a higher WFPS for longer periods than can light easily drained sandy soils. Clay soils can have a higher potential for sustained N_2O formation than sandy soils, but N_2O can escape more easily from coarse-textured soil types. N_2O produced at depth can be reduced to N_2 as it moves upwards through the soil profile, especially when diffusion is slow as in heavy textured soils (Arah et al. 1991). The most important factors affecting diffusion of gases in soil are porosity and water content. As air-filled porosity (vol-% of air in the soil) declines, diffusion becomes increasingly restricted (Amundson & Davidson 1990).

Nitrification requires access to air (O_2) and then takes place under conditions where the N_2O formed can escape easily, while the anaerobic conditions required for denitrification can be associated with presence of diffusional barriers to N_2O emission. The two N_2O generating processes may therefore differ in their dependence on soil type, texture and conditions (Byrnes 1990).

Nitrification is usually most rapid in light soils while denitrification is favoured in heavy soils. The resulting N_2O emission depends on the balance between these processes, where in the soil profile N_2O is generated, and the ease of release into the atmosphere. Overall, there seem to be higher N_2O emission rates from fine-textured clay soils than from coarse-textured sandy soils, but reports differ.

McKenney et al. (1980) found N_2O emissions generally to be one to two orders of magnitude greater from a clay soil than from a sandy loam soil fertilized with NH_4NO_3 , KNO_3 or urea. Webster & Dowdell (1982) applied $400 \text{ kg N}\cdot\text{ha}^{-1}$ as $Ca(NO_3)_2$ to two soils and found the annual N_2O emission to be slightly greater from the clay (6 to $8 \text{ kg N}_2O\text{-N}\cdot\text{ha}^{-1}$) than from the lighter and better drained silt loam soil (4 to $6 \text{ kg N}_2O\text{-N}\cdot\text{ha}^{-1}$). Matson et al. (1990) found 6-fold higher N_2O emissions from clay than from sandy soil samples from a humid tropical forest. Skiba et al. (1992) and Vinther (1992) also found the highest rates of N_2O emission to be associated with fine-textured soils.

However, reduction of N_2O to N_2 is favoured in soils with very high clay content. Such soils can show low N_2O emission rates compared to coarser soils (Arah et al. 1991).

Recous et al. (1992) found that virtually all $^{15}NO_3^-$ applied to a chalky (75% $CaCO_3$) soil planted to wheat was found in the plants, roots and soil organic material, and none was lost. N losses came exclusively from the NH_4^+ part of applied fertilizers. This indicates a low rate of denitrification and possibly a low rate of N_2O emission

following $\text{Ca}(\text{NO}_3)_2$ fertilizer application to such soils presumably provided the soil is not so wet at the time of application that denitrification will be favoured. Vermoesen et al. (1992) found that N_2O emissions can be high from calcareous soils when nitrification is the source. The effect of pH is further discussed in chapter 10.

Organic soils tend to be high emitters of N_2O . This is further discussed in chapter 11.

The size of the soil aggregates has a profound effect on denitrification and N_2O emission. Large aggregates will more easily become anaerobic than small ones under otherwise equal conditions, but penetration of NO_3^- and degradable organic materials into large aggregates can be slow. Seech & Beauchamp (1988) observed that the denitrification rate was 2 to 3 times higher in small aggregates (< 0.25 mm) than in large (5-20 mm). This was ascribed to low carbon substrate availability in the larger aggregates. Nõmmik (1956) found denitrification and N_2O production rate to be higher in soil aggregates < 0.3 mm and > 4 mm than in aggregates of intermediate size. Arah & Smith (1989) included aggregate size in their mathematical model for denitrification. Model calculations indicated that soil texture, structure and water content affect denitrification rate more than NO_3^- concentration. Denitrification rate increased strongly due to O_2 limitation as aggregate size increased from 5 mm to 30 mm.

9.3 Tillage, compaction and erosion

Ploughing and cultivation increase aeration, ease moisture evaporation and enhance accessibility of crop residues for soil microbes. Undisturbed and direct drilled soils usually have more water and smaller total pore space than cultivated land, but they may have more earthworm channels and can have increased structural and pore channel stability. Some soils may therefore have higher O_2 concentrations in the surface soil after direct drilling than after ploughing (Ross 1990). Further, earthworm casts are active microsites for denitrification and N_2O production (Svensson et al. 1986; Elliott et al. 1990; Knight et al. 1992).

Other differences relevant to the formation and emission of N_2O have also been reported (Randall et al. 1985): Soils under continuous no-till management accumulate organic material in the top layer, and the rate of temperature increase in springtime is reduced, compared with tilled soils.

There seems to be a general observation that the rates of denitrification and N_2O losses are higher from undisturbed than from ploughed soils (Aulakh et al. 1984b; Linn & Doran 1984; Rice & Scott Smith 1982; Staley et al. 1990). This is illustrated by one soil where annual emissions were estimated to be within the range of 5.4 to 8.6 $\text{kg N}_2\text{O-N}\cdot\text{ha}^{-1}$ from the no-tilled plots compared with 0.9 to 5.6 $\text{kg N}_2\text{O-N}\cdot\text{ha}^{-1}$ from the ploughed plots (Burford et al. 1981).

Mechanical disturbance of the soil can increase N_2O emission for a short period of time due to release of soil air enriched in N_2O (section 7.2.3) (Matthias et al. 1980; Bremner & Blackmer 1980b).

Tractor traffic causes compaction. Hence, compaction can gradually develop in direct drilled soils until they are ploughed. Soil compaction can increase both denitrification rate (Bakken et al. 1987; Torbert & Wood 1992) and N_2O emission rate (Hansen et al. 1993) by a factor of 1.5 to 6.

Cropland degradation through erosion is a serious sustainability issue in agriculture. Erosion of arable land occurs in all regions of the world, but the problem seems most serious in some subtropical and tropical areas (Pimentel 1993). Erosion gradually removes clay particles and organic material, soil structure deteriorates, and the nutrient reserves and productivity decreases. As a result, the need for nutrient inputs are enhanced and more land must be cultivated to maintain crop production. There are no specific studies on the influence of soil erosion on N₂O emissions, but it seems likely from the effects that erosion indirectly contribute to enhanced global N₂O emissions.

9.4 Soils in tropical regions

The tropics cover 38% of the total land surface of the earth and include a very broad range of soil types (Richter & Babbar 1991; Lal & Sanchez 1992). In the humid tropics soils are often acidic (pH < 6.0), while soils with pH > 7 are common in dryer regions. Tropical soils are warm throughout the year. Seasonal variations are mainly due to variations in rainfall. Wet seasons have high microbial activity and fast biomass turnover. Such activity can be substantially reduced during the dry season.

Most studies of N₂O emissions from soils have been done in temperate regions where the wet season is rather cool and mostly outside the growing period. A limited number of studies from the tropics indicate that these regions have a substantially greater propensity for N₂O loss from soil compared to temperate climates. This is especially so when high temperatures are combined with a humid climate for extended periods of the year, and where large amounts of mineralizable N is available (Matson & Vitousek 1990). N₂O emissions tend to increase as the temperature rises (chapter 13) and acidic soil conditions common in the humid tropics favour a higher N₂O/N₂ ratio than more neutral conditions (chapter 10). Bouwmann et al. (1993) made a mathematical model for N₂O production in natural soils. Their model combined information on soil types with data for inputs of organic material, soil fertility, temperature, moisture and soil oxygen status. The calculations supports earlier conclusions that the major natural source regions of N₂O are the tropics (Prinn et al. 1990). N₂O emissions from tropical soil also depend on the vegetation. This is discussed in section 12.3.

10. SOIL pH

10.1 Summary

The rate of both denitrification and nitrification increase with pH from acidic conditions (pH 3 to 5) to neutral or slightly alkaline conditions. The product ratio N₂O/N₂ from denitrification falls as the soil pH exceeds 5 to 6. There is no general trend in the product ratio N₂O/NO₃⁻ from nitrification with increasing pH.

The effect of pH on N₂O emission from soils is complex. Conflicting results are reported. Where denitrification is the main source of N₂O, emissions tend to decrease with increasing pH, at least in acid soils (pH below 5 to 6). Where nitrification is the main source of N₂O, emissions tend to increase with increasing pH, at least in the

range of pH 6 to 8. However, the rate of N_2O production from autotrophic nitrification decreases with increasing pH in acid soils up to a pH of about 5.

10.2 Background

10.2.1 *pH in agricultural and forest soils*

Acidification of soils is a natural process, caused by the formation of inorganic and organic acids through microbial activity, and by loss of soil bases through ion exchange and leaching. Root uptake of cations (e.g., NH_4^+ , K^+ , Ca^{2+}) is accompanied by excretion of H^+ and thus contributes to soil acidity while uptake of anions (e.g. NO_3^-) has an alkalizing effect due to excretion of HCO_3^- . Denitrification consumes H^+ and increase pH, while nitrification converts NH_4^+ to HNO_3 and decrease pH. Any input or process that increases the supply of NH_4^+ tends to promote soil acidity. Mineral-N fertilizers generally have an acidifying effect, mainly due to the NH_4^+ content. $Ca(NO_3)_2$ is an exception, also the calcium gives it some liming value (Bøckman et al. 1990).

Liming (the addition of ground limestone or similar materials) is a standard method to increase pH in acid soils. Arable land should preferably have a pH in the range of 6 to 7. On calcareous and some clay soils pH will commonly be in the range of 7 to 8, but values in the range 8 to 9 do occur in some areas. For grassland a pH of 5.5 to 6.0 is acceptable. The pH of forest soils and some tropical soils used for agriculture can be acidic, occasionally (e.g. under coniferous forests) as low as 3.5 to 4.5.

The pH is not homogenous throughout the soil. Owing to uptake and excretion of ions and organic acids, the pH in the immediate surroundings of plant roots (the rhizosphere) can deviate from that of the bulk of the soil by 1 pH unit or more (Marschner et al. 1986). Decomposing organic material (e.g. crop residues) acidifies surrounding soil somewhat while the pH in urine patches from grazing animals can be increased by one unit or more due to liberation of NH_3 (Doak 1952; Haynes & Williams 1992). The pH then falls as nitrification takes place. The injection zone for anhydrous NH_3 will have very high pH.

10.2.2 *Experimental factors*

Soil pH is measured in the solution obtained by shaking a soil sample with pure water or a solution of salts (e.g. 1-2 M KCl, 0.01 M $CaCl_2$) that release H^+ bound to soil particles. The pH values in salt solutions (pH_{CaCl_2} , pH_{KCl}) are in most cases lower than are those in pure water (pH_{H_2O}) by about 0.5 to 1.0 pH units (Minami & Fukushi 1983; Skinner et al. 1992). It is not always clear in reports what method or procedure has been used. This creates some uncertainty when reports from different laboratories are compared. We use a subscript to denote the method when reported.

Most studies on the effect of pH on denitrification, nitrification and N_2O production in soils are by laboratory incubation of soil samples at natural or adjusted pH. Field studies are few.

Microbial processes generally are markedly influenced by the pH of the medium. Large and rapid changes in soil pH can create unnatural microbial populations and conditions that influence N_2O formation. It cannot be assumed that observations shortly after a major soil pH change in a laboratory study is representative for a soil at that pH. This should be borne in mind when laboratory studies are evaluated.

10.3 Denitrification

10.3.1 Rate

Denitrification rate increases with pH, with an optimum pH in the range of 7.0 to 8.0 (Bremner & Shaw 1958; Bryan 1981). Weier & Gilliam (1986) studied the effect of acidity on denitrification in six soils from North Carolina. Flooded soil samples amended with NO_3^- were incubated for periods up to 21 days. Denitrification rates (measured as NO_3^- lost) increased on average 2 to 3-fold as pH increased with liming from 3.6-5.0 to 7.2-7.8. The effect was most noticeable at $\text{pH} > 6.5$. Focht (1974) used results obtained by others and showed that the rate of NO_3^- reduction increased in a linear way with pH from 4 to 8. The increase was 3-fold between pH 5 and 8.

10.3.2 $\text{N}_2\text{O}/\text{N}_2$ ratio

The reduction of N_2O is much more sensitive to acidic conditions than is that of NO_3^- . The $\text{N}_2\text{O}/\text{N}_2$ ratio strongly decreases when pH increases. In the study by Weier & Gilliam (1986) the ratio of N_2O evolved to NO_3^- lost decreased from 0.63-0.93 at pH 4.2-5.0 to almost zero at a $\text{pH} > 5.8$ in 5 out of 6 soils. Nõmmik (1956) measured $^{29}\text{N}_2$ and $^{45}\text{N}_2\text{O}$ in the headspace of soil samples incubated for 12 days with $^{15}\text{NO}_3^-$ (as KNO_3). At $\text{pH}_{\text{H}_2\text{O}}$ 3.8 to 5.0, N_2O was the sole or dominant gas throughout the experiment. At pH 5.6 to 6.6 N_2O dominated in the first 5 to 9 days, and at pH 6.9 to 8.0 N_2 was the dominant or sole gas throughout the experiment. Similar trends were seen by Koskinen & Keeney (1982). Burford & Bremner (1975) reported a study of 17 different American soils incubated anaerobically for 7 days where the average $\text{N}_2\text{O}/\text{N}_2$ ratio was higher (1.4) in soils with pH 5.8 to 6.6 than in those with pH 6.7 to 7.8 (0.38). Eaton & Patriquin (1989) found N_2O to be the main gas evolved from infertile soil samples of lowbush blueberry stands at the natural pH of the soils (4.0 to 5.5). Raising soil pH resulted in increased rates of denitrification and more conversion of N_2O to N_2 . Similarly, Cho & Sakdinan (1978) found that liming had a positive effect on the reduction of N_2O to N_2 . C.J. Smith et al. (1983) reported the effect of pH (range 5 to 8.5) and redox potential on N_2O reduction in soil/water suspensions and found the maximum rate to occur at pH between 6 and 7.

The influence of soil pH on the $\text{N}_2\text{O}/\text{N}_2$ ratio is especially great when the NO_3^- concentration in the soil is high (Blackmer & Bremner 1978; Firestone et al. 1980). This is discussed in section 8.3.2.

10.4 Nitrification

The growth and metabolism of autotrophic nitrifying bacteria is optimal in the neutral to slightly alkaline range (pH 7 to 8) (Focht & Verstraete 1977; Bock et al. 1986). Autotrophic nitrification is reported to proceed slowly in acid soils with $\text{pH}_{\text{H}_2\text{O}}$ 5.5 to 6.0, very slowly in acid soils with $\text{pH}_{\text{H}_2\text{O}}$ 4.5 to 5.5 and generally ceases below $\text{pH}_{\text{H}_2\text{O}}$ 4.5 (Duggin et al. 1991). However, Martikainen (1985) found enhanced autotrophic nitrification in forest soils in the $\text{pH}_{\text{H}_2\text{O}}$ range of 4.1 to 4.7, possibly due to aggregation of ammonium oxidizers (*Nitrosospira*) (Martikainen & De Boer 1993).

The pH range for NO_2^- oxidation is restricted to about 5 to 8, largely due to the toxicity of free NH_3 (at alkaline pH) and HNO_2 (under acidic conditions). HNO_2 inhibits nitrification when the concentration in soil water in soil water exceeds 2.8 mg

$\text{HNO}_2\text{-N}\cdot\text{l}^{-1}$. This corresponds to a NO_2^- concentration of about $50 \text{ mg NO}_2^-\text{-N}\cdot\text{l}^{-1}$ at pH 5. The inhibitory concentration of $\text{NH}_3\text{-N}$ is $1 \text{ mg}\cdot\text{l}^{-1}$ corresponding to about $20 \text{ mg NH}_4^+\text{-N}\cdot\text{l}^{-1}$ at pH 8 (Focht & Verstraete 1977).

Goodroad & Keeney (1984c) studied the nitrification process by aerobic incubation of silt loam soil samples for 5 days after addition of $(\text{NH}_4)_2\text{SO}_4$ at different pH, temperature and water content. With the nitrification rate at pH 4.7 taken as basis, the rate was 47% higher at pH 5.1 and 80% higher at pH 6.7. The $\text{N}_2\text{O}/\text{NO}_3^-$ ratio also increased, with 36% and 23%, respectively.

Similarly, liming of soil samples from six acid tropical climax forest floors ($\text{pH}_{\text{CaCl}_2}$ 3.9 to 5.1), incubated aerobically, generally increased both ammonification and nitrification rates (Sahrawat et al. 1985).

In contrast, Martikainen & De Boer (1993) found the nitrification rate to be slightly higher and the $\text{N}_2\text{O}/\text{NO}_3^-$ ratio to be 4 to 8 times higher at pH 4 than at pH 6 in samples from a Dutch coniferous forest incubated aerobically.

The large and diverse group of heterotrophic microorganisms is capable of nitrification over a broad pH range, and are probably the dominant nitrifiers in some acid soils (e.g. some forest soils, section 3.3) (Kuenen & Robertson 1988; Killham 1986).

The relative importance of heterotrophic and autotrophic nitrification in an acid forest soil was studied by Duggin (1991) by laboratory incubation of soil samples with nitrapyrin, a selective inhibitor for autotrophic nitrification. Autotrophic and heterotrophic nitrifiers were about equally important in NO_3^- production in fresh forest soil ($\text{pH}_{\text{H}_2\text{O}}$ 3.9). When $\text{pH}_{\text{H}_2\text{O}}$ was increased to 4.4 by adding lime, autotrophic nitrification rate almost doubled while heterotrophic nitrification was not affected. When $\text{pH}_{\text{H}_2\text{O}}$ was increased to 6.6 by heavier applications of lime, heterotrophic nitrification was eliminated, and NO_3^- production was solely autotrophic. The total NO_3^- production increased 3 times. Acidification to $\text{pH}_{\text{H}_2\text{O}}$ 3.5 reduced NO_3^- production by completely inhibiting autotrophic nitrification and reduced heterotrophic nitrification by about 50%. Nitrification does not take place when pH drops below 3.5 (Tietema et al. 1992).

10.5 N_2O emission

The influence of soil pH on N_2O emission is complex, and reported results differ.

Denitrification rate increases with pH, while the $\text{N}_2\text{O}/\text{N}_2$ ratio decreases. The net effect on N_2O emission is unclear, though there may be a minimum in N_2O emissions around pH 6. Further studies addressing this point are desirable.

Weier & Gilliam (1986) found in a laboratory study that N_2O evolution decreased dramatically when pH was increased by liming from 4.2-5.0 to 6.6-7.6 in samples of six soils saturated with water and amended with NO_3^- . Focht (1974) reported that N_2O evolution rate increased up to pH about 4.5, but remained constant at higher pH.

There seems to be no obvious trend in the product ratio $\text{N}_2\text{O}/\text{NO}_3^-$ from nitrification with changing pH. As the rate increases with increasing pH, the emission of N_2O derived from nitrification should increase with pH. Yoshida & Alexander (1970) demonstrated that increasing pH from 6 to 8 strongly increased N_2O evolution in cell suspensions of *Nitrosomonas europaea*. Bremner & Blackmer (1978) investigated 3 Iowa soils used for maize and soybean production. They found

approximately 3-fold higher N_2O emissions from a soil with pH 7.8 than from soils with pH_{H_2O} 6.8 and 5.4. The soils were well-aerated, incubated for 30 days and amended with $(NH_4)_2SO_4$ or urea. Similarly, in another study Bremner & Blackmer (1980a) found N_2O production to be 6 to 8-fold higher in two soils of pH_{H_2O} 8.1 to 8.2 than in two soils at pH 6.2 to 6.8 when incubated under aerobic conditions and treated with NH_4^+ (as $(NH_4)_2SO_4$). Bremner & Blackmer (1981) also reported a laboratory study where alfalfa residues had been added to well-aerated soils. N_2O emissions were 2.7 and 20 times higher at pH_{H_2O} 7.1 and 8.3, respectively, relative to that from a soil at pH 5.9. Soil amended with $(NH_4)_2SO_4$ and incubated under aerobic conditions (60% of FC) at 30°C for 20 days evolved about 9 times more N_2O at pH_{KCl} about 7 than it did at a pH_{KCl} of about 5 (Minami & Fukushi 1983). The observations were explained by increased accumulation of NO_2^- and stimulation of the nitrifying population and enzymatic activity responsible for N_2O formation.

If nitrification originally occurs at a low rate as has been found in Swedish coniferous forests, then liming can increase N_2O emissions (L. Klemetsson, pers. comm.). Sahrawat et al. (1985) reported that liming of acid soil samples increased N_2O emission in 5 out of 6 cases on average by a factor of 2 to 3.

However, liming of acid forest soils in Germany where N availability was not a limiting factor, decreased the emissions (Brumme & Beese 1992). Martikainen (1985) reported higher N_2O emissions from pine forest soils fertilized with urea at pH_{H_2O} 4.1 than at 4.7. Sitaula & Bakken (1993) also found that N_2O release from a spruce forest stand was negatively correlated with pH from 3.4 to 4.1. However, soils with very low pH are relevant for forestry, but not so much for agriculture.

The effect of pH on N_2O emission is further complicated by the fact that denitrification and nitrification generates N_2O simultaneously in soil.

Goodroad & Keeney (1984c) found in a laboratory study that N_2O production was 4 times greater at pH 5.1 and 3 times greater at pH 6.7 compared to that at pH 4.7 in soils amended with NH_4^+ (as $(NH_4)_2SO_4$) and incubated at 30°C and at a water content of 30 vol-%. But at lower temperatures (10 or 20°C) and water contents (10 or 20 vol-%) the effect of pH was less pronounced.

Nägele & Conrad (1990) showed that NO and N_2O release decreased as pH_{H_2O} was raised from 4 to 7 by $NaOH$ in an acid forest soil amended with $NaNO_3$ or NH_4Cl . The release rate of N_2O increased when pH_{H_2O} in an alkaline agricultural soil was reduced from 7.8 to 6.5 by HCl , but decreased when pH_{H_2O} was further reduced to 4.

Goodroad et al. (1984) measured N_2O emissions from different plots on a silt loam soil fertilized with NH_4NO_3 in a long-term experiment. They found about 50% higher N_2O emissions at pH 4.7 than at pH 5.1 and 6.7, but the differences were not statistically significant.

11. ORGANIC MATERIAL

11.1 Summary

Input of degradable organic material to soil can create conditions favourable for N_2O formation: Microbial activity is enhanced, O_2 is consumed, and anaerobic sites can develop.

Similarly, soils with high levels of organic carbon content have greater propensity for N₂O formation than soils with low levels, notably after application of N. Very high emission rates have been observed from peat soils. Where availability of degradable organic material is a limiting factor for N₂O formation, application of manure can lead to production of more N₂O than application of mineral fertilizer N.

11.2 Background

Soil content of organic material is reported either as soil organic carbon or soil organic matter, where:

$$\text{organic matter in \%} = 1.72 \cdot \text{organic carbon in \%}$$

We express soil content of organic material as «organic carbon». Organic material in soil consists of:

- living plant roots, bacteria, fungi, fauna
- exudates from plant roots and soil organisms
- dead plant tissue and other organisms in various stages of decay, ranging from recent roots to stable humus.

Examples of annual carbon inputs to arable land are:

- exudates, roots and stubble from fertilized barley contribute 1.5 to 1.8 t C·ha⁻¹ (Andrén et al. 1990)
- application of pig slurry at a common rate of 30 m³·ha⁻¹ provides about 0.5 t C·ha⁻¹. About a third of this can degrade within one or two weeks (H. Høyvik, pers. comm.).

The rate of microbial transformation of these different types of organic material varies greatly. Thus soluble plant exudates will be metabolized within minutes to hours, manure and crop residues degrade within days to a few months or years, while humus may persist for centuries.

Most soil microorganisms get their energy and substance from organic materials. These materials exerts a major influence on the types and intensity of soil microbial processes, including those leading to the formation and reduction of N₂O. More specifically:

- organic material provides reducing agents (electron donors) for denitrification
- organic material is a substrate for respiration, and may induce O₂-limitation. In an otherwise aerobic soil, pockets with high organic carbon content may consume O₂ at a rate greater than can be compensated for by diffusion, thus creating anoxic conditions (Parkin 1987).
- increased input of organic material can increase the number of potential denitrifiers through general stimulation of microbial activity (Drury et al. 1991; Parsons et al. 1991; Yeomans et al. 1992)
- the amount of organic material in soil depends on soil origin and history, inputs of manures and plant residues and their rate of decomposition, and develops towards an equilibrium value that depends, inter alia, on management practices.

The distribution of organic material in soil varies. It is highest in the uppermost layer of undisturbed soil, but is well distributed throughout the plough layer in arable land. Forests, grassland and land under no tillage management accumulate organic material that is mineralized when cultivated. Denitrification in subsoil can be low due to lack of degradable organic carbon (Lind & Eiland 1989; McCarty & Bremner 1992).

11.3 Denitrification

11.3.1 Rate

Burford & Bremner (1975) studied denitrification capacity in the laboratory on addition of NO_3^- (as KNO_3 solution) in 17 surface soils of different pH, texture and organic carbon content. They found denitrification rate to be correlated with total organic carbon and even more closely correlated to water-soluble or mineralizable carbon. This relationship has also been expressed in mechanistic models (Grundmann & Rolston 1987; Malhi et al. 1990) and found in laboratory and field studies (Limmer & Steele 1982; Pedrazzini & Nannipieri 1982; Colbourn et al. 1984; Ottow et al. 1985; Bijay-Singh et al. 1988; Lowrance & Smittle 1988; Paul & Beauchamp 1989; Eaton & Patriquin 1989; El-Habr & Golterman 1990; Drury et al. 1991; Iqbal 1992). Others have demonstrated the increase in rate of denitrification when plant residues are incorporated into the soil (Aulakh et al. 1991a; Schloemer 1991). Dorland & Beauchamp (1991) showed that incorporation of alfalfa or glucose increased denitrification rates at least up to a temperature of 25°C , and lowered the threshold temperature for the process. Several authors have shown that the large spatial variability in soil denitrification is due in part to differences in available organic carbon (Burton & Beauchamp 1985; Parkin 1987; Seech & Beauchamp 1988; Christensen et al. 1990b; Fujikawa & Hendry 1991), especially at high water contents (Christensen et al. 1990c).

Webster & Goulding (1989) reported from an experiment with long-term continuous cropping with spring barley. Both autumn denitrification rate and denitrifying biomass was markedly higher in those parts of the field where the soil carbon content was high due to long-term manure application than where it was low and the N was supplied as fertilizer. Nugroho & Kuwatsuka (1992b) found that the size of the bacterial population in rice fields depended mainly on the input of organic material.

Soil content of available organic carbon is thus an important determinant for denitrification rate (Beauchamp et al. 1989; Weier et al. 1993), but the relationship also depends on other factors.

Hixson et al. (1990) found that denitrification rate in four subalpine natural plant communities depended on an interplay between controlling factors that included, but was not dominated, by availability of organic substances.

Growing crops provide the soil with degradable organic carbon but also remove NO_3^- . Under such conditions availability of organic material may not be the limiting factor for denitrification. This was reported by Benckiser et al. (1986), and Schloemer (1990) found denitrification rate to be negatively correlated to water-soluble carbon in the growing season in a field study on loamy sand cropped with celery.

11.3.2 N_2O/N_2 ratio

Several authors (Nömmik 1956; Smirnov et al. 1979; Elliot et al. 1990; Vinther 1990) have reported that easily degradable organic carbon (e.g. glucose) promote full reduction to N_2 and lower the N_2O/N_2 ratio in laboratory studies.

Dissimilatory NO_3^- reduction to NH_4^+ may give higher N_2O yields than denitrification (Samuelsson & Klemetsson 1991). This process is favoured over denitrification in the special situations where the C/N ratio (more properly C/ NO_3^- ratio) is very high, e.g. in the rumen of animals, in estuarine sediments and possibly in organic soils or in soils after organic amendments (Tiedje 1988).

11.4 Nitrification

Organic carbon input stimulates microbial activity in an aerobic environment. This can create O_2 -limitation and so reduce autotrophic nitrification. Reduction of aeration in this way may enhance N_2O production.

Organic material with a high C/N ratio can stimulate immobilization of free NH_4^+ and hence restrict nitrification by substrate competition. In contrast, N can be mobilized in excess of microbial needs on decomposition of organic material with a low C/N ratio. Such mineralization can create conditions suitable for generation of N_2O .

The mechanism of heterotrophic nitrification is largely unknown. The effect (if any) of degradable organic carbon on this process and associated N_2O production has not, to our knowledge, been addressed in experimental studies.

11.5 N_2O emission

Several investigators have reported that N_2O production in various soils showed positive correlation with soil organic carbon content (Bremner & Blackmer 1981; G.P. Robertson & Tiedje 1984; Arcara et al. 1985; Eaton & Patriquin 1989; Iqbal 1992). N_2O emissions from organic soils have been reported to be one order of magnitude or more higher than that from mineral soils (Duxbury et al. 1982; Duxbury 1984). However, the very high emission rates reported by Duxbury (up to 167 kg $N_2O-N \cdot ha^{-1} \cdot year^{-1}$ from peat soils in Florida) seem to be exceptional.

Soils with a high content of organic carbon are not common in Europe and generally cover only a few percent of the land, but there are exceptions. Thus in Finland 21% and in the Netherlands 11% of the soils are peat soils. Soils with more than 3% organic carbon are markedly more common in North-Western Europe than in the Southern and Eastern regions (W. de Vries & G.J. Reinds, pers. comm.). There are thus marked regional differences in the soils capacity for producing N_2O without soil organic material appearing as a major limiting factor.

Inputs of degradable organic material can also increase N_2O emissions. This has been found for glucose (Eaton & Patriquin 1989; Schuster & Conrad 1992) and glycerol (Denmead et al. 1979a) in laboratory experiments. The laboratory study of Murakami et al. (1987) indicated that the relationship is complex. In soils treated with NO_3^- (as KNO_3), additions of 0.1 and 1.0% glucose increased emissions 5-fold and

1.5 to 2.5-fold relative to the samples without added glucose. The N_2O that was formed derived from the fertilizer. In this experiment the higher glucose amendment produced less N_2O than the lower. Emissions of N_2O from samples amended with NH_4^+ (as $(NH_4)_2SO_4$) were 1 to 2 orders of magnitude lower, and the N_2O derived partly from the soil, partly from the fertilizer.

Organic fertilizers (sewage sludge, animal and green manure) contain both organic materials and easily mineralizable N. This combination promotes denitrification when manure is injected or worked into the soil (Comfort et al. 1990). Hence, N_2O can be formed unless the decomposition of the organic material creates sufficient anaerobic conditions to cause reduction to N_2 or the temperature is so low that extensive formation of N_2O does not take place before the crop (often grass) has taken up the N. Application of manure or sludge to the surface can form a crust on the soil beneath which conditions favourable for denitrification develop easily, but where escape of N_2O is obstructed (Burford 1976). The combination of manure and mineral (NO_3^-) fertilizers can lead to high N_2O emission rates: Rolston (1977) reported that application of NO_3^- fertilizer to manured soil gave higher N_2O emission than application to grassland (section 8.5.2). Acidification of slurry with nitric acid reduce NH_3 losses after spreading, but may increase N_2O losses (Velthof & Oenema 1993).

Green manure from legumes is recommended as a N source in tropical and subtropical agriculture where the supply of fertilizer can be difficult (Peoples & Craswell 1992), and growing of catch crops to minimize NO_3^- leaching is a recommended practice. However, decomposition of crop residues rich in N may produce N_2O . It is not clear if there are conditions where the use of green manures or catch crops are inappropriate due to N_2O emissions. This topic invites studies.

Where decomposition takes place under highly aerobic conditions (e.g. cereal straw, sugarcane tops deposited on the soil surface) N_2O emissions are not likely to be substantial. However, conditions during surface decomposition, can also be partly anaerobic, and Tietema et al. (1991) suggested that wet litter generates N_2O .

A given amount of N applied in organic fertilizers may generate more N_2O than the same amount of N applied as mineral fertilizers, especially in mineral soils where organic carbon can be limiting for denitrification. Several studies support this deduction (Christensen 1983; Benckiser et al. 1987; Bouwman 1990; Van Cleemput et al. 1992). Christensen (1985a) found the number of denitrifying bacteria as well as N_2O emission to be greater in an acid sandy loam soil (limed to pH 5.4) when supplemented with liquid manure than where supplemented with NO_3^- .

However, Sanders (1980), Egginton & Smith (1986b) and Hansen et al. (1993) found higher N_2O emissions from mineral (NO_3^-) fertilizer than from slurry applied to grassland where availability of organic carbon is unlikely to be rate limiting for denitrification (Elliot et al. 1991).

Several other studies indicate that the C/N ratio in the amendment, or rather in the soil after addition, is important. Bremner & Blackmer (1981) reported that the nitrification rate, N_2O/NO_3^- ratio and the N_2O emission rate all increased with decreasing C/N ratio in organic amendments ($10 \text{ g C kg soil}^{-1}$) to a well-aerated soil:

Amendment	C/N-ratio	N ₂ O-N evolved ($\mu\text{g}\cdot\text{kg soil}^{-1}$)	NO ₃ ⁻ -N produced ($\text{mg}\cdot\text{kg soil}^{-1}$)
none	–	4	16
cattle manure A	35.0	24	4
maize residue	34.4	106	5
sheep manure	18.0	124	5
cattle manure B	16.7	163	20
swine manure	11.3	2400	250
alfalfa residue	10.1	4519	316
rye residue	6.3	9510	490
chicken manure	5.7	20500	562

Their soil samples were incubated at 50% of FC and 30°C for 13 days.

Goodroad et al. (1984) showed that addition of manure or alfalfa residue (which have readily available N and C) to field plots resulted in a much larger N₂O output than did the addition of digested sewage sludge or high C residues (straw, rye).

The maintainance of a certain level of soil organic material is necessary to prevent a decline in soil productivity. Thus return of manure and crop residues is desirable and conserves resources. However, these commendable practices have potential for increasing N₂O emissions, but guidelines for good management practice that limit N₂O emissions from use of organic amendments are not presently available.

Some N₂O is formed when manure or crop residues are composted, especially when the aeration is poor (Brink et al. 1992). Further study on this topic is desirable.

As discussed in section 8.5.3, animals at pasture can cause appreciable N₂O emissions originating from urine patches. Cattle in feedlots defecate and urinate on highly compacted soil where high NO₃⁻ concentration together with high input of organic carbon can be found (Ellis et al. 1975). Such conditions should favour production of N₂O. Khalil & Rasmussen (1992b) reported that N₂O concentrations were highly elevated in milking sheds and barns after cattle were brought in. The levels around feedlots and manure piles were also elevated. They estimate that these aspects of cattle operations could produce 0.2 to 0.5 Tg N₂O-N·year⁻¹ worldwide. Details about this study have not yet been published. However, Sibbesen & Lind (1993) reported that dungheaps release N₂O, but that the rate is low. Stored pig manure released only 0.26 g N₂O-N·m⁻³·day⁻¹. Manure from pigs generated more N₂O than manure from cattle. The topic of N₂O emissions from animal husbandry requires further clarification.

12. CROPS AND VEGETATION

12.1 Summary

Plants provide an input of degradable organic material to soil and remove NH₄⁺ and NO₃⁻. Plants generally increase soil denitrification and N₂O emission rates in laboratory studies, but this is not confirmed in field studies. An increase in N₂O emission usually occurs when plants are cut or damaged and the roots remain in the soil.

Growing legumes seems usually to result in enhanced N_2O emissions. No consistent trend is reported for other crops. Temperate forests produce N_2O at a low rate. In contrast, the warm and moist conditions with rapid N turnover in humid tropical forests result in high emissions.

12.2 Effect on denitrification

The presence of plants influences soil microbial processes including denitrification and N_2O emission in several ways:

- release of root material and exudates stimulates general microbial activity (Klemetsson et al. 1987; Christensen et al. 1990a)
- the activity of plant roots consumes O_2 (Cribbs & Mills 1979; Klemetsson et al. 1987) and can change the soil pH in their immediate surroundings (Marschner et al. 1986)
- growing plants gradually deplete the soil of NO_3^- and NH_4^+ (Scott Smith & Tiedje 1979; Heinemeyer et al. 1988)
- growing plants consume water, and reduce soil water content
- root growth influences soil structure and creates channels through which gases can escape
- plant cover reduces diurnal soil temperature fluctuations by shielding the soil from solar irradiation during the day and from heat loss during the night
- some plants, notably rice, have internal gas channels through which gases produced in the soil profile may escape to the atmosphere (Mosier et al. 1990).

There are differences between plant species regarding these effects.

Most studies have reported higher denitrification rates and losses in the presence than in the absence of growing plants (Cribbs & Mills 1979; Rolston et al. 1979; Klemetsson et al. 1987; Lindau et al. 1990a; Mosier et al. 1990). However, Scott Smith & Tiedje (1979) and Heinemeyer et al. (1988) demonstrated the importance of taking soil NO_3^- concentration into account. Where denitrification rate is limited by availability of NO_3^- , root activity can decrease the rate as roots and microorganisms compete for NO_3^- . Hence, fallow fields can emit more than cropped fields, as reported by Terry et al. (1981a). Where NO_3^- is present in excess, any supplement of organic carbon from plants to the rhizosphere will stimulate denitrification. Stefanson (1972) found that the stimulating effect of plants on denitrification was influenced by soil organic carbon content, with the greatest effect in soil where the content was low. Soil water content was also important, the effect being most marked close to field capacity. Bakken (1988) found that plants increased denitrification rate only at high soil moisture content. At moderate and low moisture content the effect was slightly negative.

High denitrification rates are found in soils where the plants have been cut or damaged, and the roots remain in the soil (G.P. Robertson et al. 1987; Dutch & Ineson 1990; Beck & Christensen 1987). Reports on the influence of plants on the N_2O/N_2 ratio differ. Klemedtsson et al. (1987), Stefanson (1972) and Hauck (1984) reported that plants tend to reduce this ratio, while Scott Smith & Tiedje (1979) and Rolston et al. (1979) found no clear trend.

12.3 N_2O emission

Cribbs & Mills (1979) incubated humic peat soil with and without tomato plants and with addition of $100 \text{ mg NO}_3^- \cdot \text{N} \cdot \text{kg soil}^{-1}$ for 8 days. N_2O evolution in the presence of plants was almost twice the level found in the absence of plants, suggesting higher N_2O emissions from cropped soils than from bare soils. The laboratory study of Klemedtsson et al. (1987) supports this, but not that of Stefanson (1973). Duxbury et al. (1982) found higher annual N_2O emissions (2 to 5 times) from fallow organic soil than from comparable soils cropped with sugarcane or St. Augustine-grass. The difference may have been the result of wetter soil and higher soil NO_3^- levels in the absence of plants. Emissions from soils under St. Augustine grass were about twice those from the sugarcane fields. Matson et al. (1992b) reported that young sugarcane fields emit more N_2O than fields with old cane. The latter have an established root system that rapidly depletes the soil of NO_3^- .

The study of Beck & Christensen (1987) indicated that mature roots may supply more organic carbon to the soil than do young roots. They also found that removal of the above-ground plant material in grass-covered pots gave an immediate long-lasting increase in N_2O production in the soil. The increase was especially noticeable during the first hours after cutting, when the emission increased by a factor of 10 or more. They suggested that easily available organic carbon had leaked out from the roots after the plants were damaged. Higher N_2O emissions from grass-covered soils after the grass was cut were also demonstrated in a field study by Conrad et al. (1983). These authors indicated that an additional explanation of this phenomenon could be the increased temperature (or temperature fluctuations) due to increased irradiation absorbance of the soil when grass was removed. However, Hutchinson & Brams (1992) reported that emission of N_2O from pasture was not stimulated by clipping and removal of the grass.

Permanent grassland develops a surface layer rich in organic material with potential for denitrification and N_2O formation when fertilized or when urine and droppings are deposited during grazing (Ryden 1985).

Grasslands constitute an important part of agriculture, but most of the world's pastures are under low intensity management. Only about 7% of all N applied is spread on grass (FAO-IFA-IFDC 1992). It is only in the former USSR and the northern half of Europe that more than 20% of the fertilizer N used is applied to grasslands. About 10% of applied N in USA is used on grass, while fertilization of pastures is uncommon in most developing nations. Application of $> 250 \text{ kg N} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$ occur in a few nations with highly intensive grassland management (e.g. the Netherlands), but such rates are exceptional on the global scale (FAO-IFA-IFDC 1992). Bouwman (1990) summarized published N_2O emissions from fertilized crops and grassland in graphs. On the whole, there seem to be no consistent and major

difference, between grasslands and arable land, in N_2O losses following N application at common application rates.

Some authors have found greater N_2O emissions from some arable crops than from others, but such differences do not seem consistent. The impression is that crop type is not a major factor in emission of N_2O , with the possible exception of leguminous crops. However, the timing of emissions can vary with that of N uptake, which varies among crops.

Mosier et al. (1986) monitored N_2O emissions from irrigated fields in two consecutive years. In the first year, the soil was cropped with maize. Total N_2O emission was about 4 times that from the barley crop in the following year. Emission rates were greatest during the spring for barley and during the summer for maize. Similar trends were seen in an earlier study (Mosier & Hutchinson 1981) when much higher N_2O emissions (on some occasions 1 to 2 orders of magnitude) were found from a clay soil cropped with maize than from a nearby clay loam soil cropped with sugarbeet. However, there were substantial differences in conditions (e.g. fertilizer type and amounts) between the two sites, and it is doubtful if the variations in N_2O emissions were mainly due to the cropping differences.

Lind (1985) measured N_2O concentration in soil air throughout three consecutive growing seasons in a soil cropped with barley the first and third year and with beet the second year. With the barley crop, periods with increased concentrations of N_2O were seen in the spring and the early autumn. She found the N_2O concentration to be low in the early summer corresponding with the crops main period for NO_3^- uptake. For the beet crop the highest concentrations were found in the summer. This difference was mainly ascribed to the later start of the major uptake of NO_3^- by beet compared with barley.

N_2O emission differences between crops were also found in field studies by Findlay & McKenney (1979). They were low from soils cropped with bluegrass or clover, 5 to 8 times higher from continuous maize and from non-agricultural marsh land and almost 40-times higher from maize in rotation following alfalfa. However, the number of measurements was small.

Van Cleemput et al. (1992) reported emissions of N_2O under different cropping systems. Emissions from grasslands were on average about 15% higher than those from maize, potato, sugarbeet and wheat. Emissions from forest ecosystems were on average only 25% of those from arable land.

N_2O emission from intensive horticulture deserves scrutiny though the area under cultivation is rather small. In the EU vegetables cover only 2.4% of the arable land, but fertilization levels and NO_3^- concentrations tend to be high, so possibilities exist for significant N_2O formation (chapter 8). Thus, Ryden & Lund (1980b) found that annual N_2O emissions ranged from as high as 19.6 to 41.8 kg $N_2O-N \cdot ha^{-1}$ from irrigated land in California cropped with vegetables and fertilized with applications that ranged from 176 to 528 kg $N \cdot ha^{-1}$.

Another crop with potential for enhanced N_2O emission is bananas and plantains. This crop covers about $4.3 \cdot 10^6$ ha in the humid tropics and subtropics (F. Pariboni, pers. comm.). This crop is well fertilized, 100 to 800 kg $N \cdot ha^{-1} \cdot year^{-1}$, in some cases with more than 1000 kg $N \cdot ha^{-1} \cdot year^{-1}$ (Martin-Prevel 1992). After harvest the mass of leaves are cut and left on the surface to decompose under warm, moist conditions. However, there are no reports on measurements of N_2O emissions in banana plantations.

Temperate forests are among the ecosystems with low fluxes of N_2O (Matson et al. 1992a), while humid tropical forests are regarded as one of the major emitters (Keller et al. 1983; Sharp 1991; Bouwman et al. 1993). Tropical forests seem to emit considerably more N_2O per ha than temperate forests. Fluxes listed by Keller et al. (1983) are at or somewhat above those from arable land. High emission rates from tropical forests probably originate with the high rate of litter deposition (commonly 8 to 10 $\text{t}\cdot\text{year}^{-1}$, Greenland et al. 1992), with rapid year-round turnover under warm and moist conditions. No special processes are involved which are unique to tropical conditions. The tropical forests cover about 10% of the global land area. Most studies in the tropics relate to south- and central America with a special emphasis on the Amazonian rain forest, and have been reviewed by Vitousek & Matson (1992). N_2O emissions from tropical soils are also discussed in section 9.4.

Earlier estimates of global N_2O flux from tropical forests (7.4 Tg $\text{N}_2\text{O}\text{-N}\cdot\text{year}^{-1}$, McElroy & Wofsy 1986) seem to have been too high. The IPCC (1992) estimate is 2.2 to 3.7 Tg $\text{N}_2\text{O}\text{-N}\cdot\text{year}^{-1}$. Vitousek & Matson (1992) estimated that these forests emitted 2.4 Tg $\text{N}_2\text{O}\text{-N}\cdot\text{year}^{-1}$ prior to extensive human disturbance. Though the numbers are uncertain, there seems to be agreement that tropical forests are a major global source of N_2O emissions, though not a dominant source.

Lensi et al. (1992) found that soil samples from a West African savanna produced less N_2O than samples of forest soils, and Sanhueza et al. (1990) reported that emissions from savannas in Venezuela were lower than from forested soils. However, Hao et al. (1988) found no marked difference at another Venezuelan site, and Garcia-Mendéz et al. (1991) reported similar N_2O emission from a tropical deciduous forest and pasture in Mexico.

Hao et al. (1988) also reported that burning the savanna had little influence on the N_2O emission rate, but that the emission increased when the rain started to fall. The area covered by savannas is about twice the forested area, their overall contribution may be considerable (Bouwman 1990; Matson et al. 1991).

The rapid conversion of tropical forests to pasture and other types of agricultural land is a major environmental issue. Studies have indicated that human disturbance of native tropical ecosystems (forest clearing for arable agriculture and pasture) will initially increase N_2O emissions from these sites, at least for some time (Matson et al. 1990; Keller et al. 1991; Steudler et al. 1991). Luizao et al. (1989) found that the annual N_2O emission from a tropical pasture that had been converted from tropical forest was about 3-fold higher than from a paired forest site. Keller et al. (1993) reported that emissions from pastures in Costa Rica exceeded forest soil emissions by a factor of 5 to 8 for the first decade after deforestation. The emission rate then declined, and pastures older than 20 years emitted less N_2O than forest soil.

Wetland rice fields are flooded most of the season, gases tend to be trapped in the soil, and any N_2O formed can be reduced to N_2 . Hence, emissions of N_2O are generally low (Lindau et al. 1990a). However, soil gases can be vented through the vascular system of rice plants, and higher N_2O and N_2 emission rates have been measured in the presence than in the absence of rice plants (Mosier et al. 1990).

Leguminous crops fix nitrogen. Decomposition of their residues can increase the amounts of N_2O emitted. Enhanced concentrations of NO_3^- can develop in soil cropped with legumes after the growing season, but this seems to be more marked with forage than with grain legumes (Scott Angle 1990). Duxbury et al. (1982) measured annual N_2O emissions from mineral soils cropped with alfalfa in two

consecutive years. Emissions were 4.2 and 2.3 kg N₂O-N·ha⁻¹·year⁻¹. Comparable emissions from a weedy pasture of timothy grass were 1.7 and 0.9 kg N₂O-N·ha⁻¹·year⁻¹. Neither of these sites was fertilized. The N₂O emissions from the alfalfa site were about equal to those from maize sites receiving 130 kg fertilizer-N·ha⁻¹ (NH₄NO₃ + urea or manure). Similar results were obtained in a later study (Duxbury 1984).

Galbally et al. (1992) reported from Australia that an unfertilized summer sunflower crop, sown in a field previously cropped for 8 years with lucerne had higher emission rates than a subterranean clover pasture. Hence, breaking swards for arable crops could result in enhanced emissions, about 4 kg N₂O-N·ha⁻¹·year⁻¹ in this case. Ploughing of grassland results in the formation of substantial amounts of NO₃⁻ from mineralization and nitrification (Addiscott et al. 1991), with increased potential for N₂O emissions. However, the extensive cultivation of prairies in the USA and elsewhere in the last century does not seem to have increased atmospheric N₂O levels.

Bremner et al. (1980) found that 6 different unfertilized soils in Iowa cropped with soybeans emitted between 0.34 and 1.97 kg N₂O-N·ha⁻¹·year⁻¹ with an average of 1.2 kg N₂O-N·ha⁻¹·year⁻¹. Comparisons with non-leguminous crops or uncultivated soil were not included in this study. However, these emissions were in general larger than most of those reported from fertilized Iowa soils, except where anhydrous NH₃ was used (Eichner 1990).

In contrast, Su et al. (1992) reported N₂O fluxes from winter wheat and alfalfa in northern China to be the same when soil conditions were similar.

Based on the limited number of studies available Eichner (1990) tentatively concluded that «Total N₂O emissions from fields of cultivated legumes are estimated to be in the range of 23 to 315 Gg N₂O-N in 1986. This does not include emissions from legumes that are not harvested, emissions from seedlings, or emissions from fertilizer applied to the field before planting. If leguminous fields are found to emit more N₂O than fertilized fields, dual cropping with legumes, or rotating hectares under cultivation with legumes as an alternative to fertilizer use could raise the atmospheric burden of N₂O».

There are reports that plants can produce N₂O as a metabolic product (section 2.3.1), and also that plants can remove and metabolize N₂O from air (section 2.3.2). These proposed processes requires further study before they can be accepted and evaluated as sources and sinks for atmospheric N₂O.

13. TEMPERATURE

13.1 Summary

Microbial activity, denitrification and nitrification rates all increase with temperature. The denitrification product ratio (N₂O/N₂) falls with increasing temperature, while that from nitrification (N₂O/NO₃⁻) tends to rise. The combined effect is that N₂O emission rates increase with temperature.

13.2 Background

Soil temperature depends on location, climate, weather, soil type and soil cover. Temperature variations in the soil profile throughout the year are mainly determined by variations in ambient air temperature and by depth. The soil surface temperature will follow temperature variations in ambient air, while temperature deeper in the soil profile will more closely reflect the average temperature of the day, week, month or season.

The mean temperature in the tropics can be almost constant throughout the year (e.g. Manaus: about 27-28°C), while it fluctuates markedly with season in temperate zones (e.g. Oslo: -5 to 18°C) (Pearce & Smith 1990).

The solubility of N₂O in water depends on temperature. It is about 3 times higher at 5°C than at 40°C (Wilhelm et al. 1977, section 7.2.3). This may explain some of the diurnal variations in N₂O emissions with temperature (section 4.4.1 and section 13.5).

Microbial activity varies with temperature. The rate of biochemical processes is negligible below a threshold temperature, but increases rapidly as this is exceeded.

The relationship between microbial processes and temperature is often given as $Q_{\Delta n}$, defined as:

$$Q_{\Delta n} = r(T_n)/r(T_0)$$

where $r(T_n)$ and $r(T_0)$ are the activity, rate etc. of the process at the absolute temperatures T_0 and T_n (in Kelvin, K), respectively, and $\Delta n = T_n - T_0$.

Only $Q_{\Delta n}$ values for the same temperature interval are directly comparable. It is common practice to use a 10°C (= 10 K) interval as basis for comparisons. Results of $Q_{\Delta n}$ where n differs from 10 can be transformed into values of Q_{10} using the Arrhenius equation that leads to the relationship:

$$\ln(Q_{10}) = \ln(Q_{\Delta n}) \cdot \frac{1/T_0 - 1/T_{10}}{1/T_0 - 1/T_n}$$

where $T_{10} = T_0 + 10$. We have used this equation to transform $Q_{\Delta n}$ values into Q_{10} where n differs from 10.

All $Q_{\Delta n}$ values are given as Q_{10} , but where reported Δn differs from 10, the original result is given in a separate column.

13.3 Denitrification

13.3.1 Rate

Low rates of denitrification have been reported at temperatures as low as -2°C (Dorland & Beauchamp 1991) and -4°C (Malhi et al. 1990), but higher temperatures, > 5°C, are usually required for a significant denitrification rate (Nömmik 1956; Aulakh et al. 1983; Benckiser et al. 1986; Vinther 1990). The effect of increasing soil temperature on denitrification rate has been investigated in many laboratory studies. These have all found a positive, though variable, correlation:

Study	Q_{10}	Temperature range ($^{\circ}\text{C}$)	$Q_{\Delta n}$
Nõmmik (1956)	15.3-19.5	3-13	
	9.4-17.1	13-22	7.6-13.0
	1.7-2.4	22-45	3.2-6.7
Keeney et al. (1979)	1.1	7-15	1.1
	3.7	15-25	
	2.4	25-40	3.7
Mancino et al. (1988)	8.3	22-30	5.5
	0.8-1.0	30-35	0.9-1.0
Malhi et al. (1990)	2.4-2.8	(-4)-4	2.0-2.3
	6.1-12.3	4-10	3.0-4.6
	1.4-1.9	10-20	
	1.5	20-40	2.2
Vinther (1990)	0.1-3.5	2-10	
	1.9-15.8	10-25	
Dorland & Beauchamp (1991)	3.8-3.9	0-15	7.2-7.5
	2.0-2.2	15-25	

A Q_{10} of about 2 is common for biochemical reactions. A Q_{10} greatly different from 2 indicates that other factors than temperature also affect the reaction rates. Such factors can be:

- physical (e.g. changes in gas solubility in water)
- biological (changes in microbial populations)
- both (e.g. increasing temperature furthers O_2 consumption, thus extending anaerobic zones (Smith & Dowdell 1974)).

The optimum temperature for denitrification seems to range from 30 to 67 $^{\circ}\text{C}$ (Nõmmik 1956; Bremner & Shaw 1958; Keeney et al. 1979; Mancino et al. 1988; Malhi et al. 1990). The reported differences reflect to some extent bacterial adaption to local conditions (Powlson et al. 1988; Malhi et al. 1990). At temperatures > 50 $^{\circ}\text{C}$ chemodenitrification may be the major mechanism (Keeney et al. 1979). Denitrification stops at temperatures of 75 to 85 $^{\circ}\text{C}$ (Nõmmik 1956; Bremner & Shaw 1958; Keeney et al. 1979). However, such high temperatures are of little practical interest as soil temperatures will mostly be below 60 $^{\circ}\text{C}$, at least where water is present.

13.3.2 $\text{N}_2\text{O}/\text{N}_2$ ratio

As the temperature increases, the $\text{N}_2\text{O}/\text{N}_2$ ratio declines. This inverse relationship has been demonstrated by several authors in laboratory incubations of soil (Nõmmik 1956; Keeney et al. 1979; Vinther 1990).

13.4 Nitrification

The optimum temperature range for nitrification in soils is usually between 25 and 35°C (Bock et al. 1986; Haynes 1986). However, it seems that indigenous nitrifiers have temperature optima adapted to their climatic regions. Heterotrophic nitrification can probably occur at even higher temperatures (Haynes 1986). In contrast to what is found for denitrification, for nitrification N₂O becomes more important as a reaction product as temperature increases (Bremner & Blackmer 1981; Goodroad & Keeney 1984c; Yoshida & Alexander 1970).

13.5 N₂O emission

Laboratory studies of both denitrification and nitrification indicate that N₂O production rate increases strongly with increasing temperature up to 20-40°C:

Study:	Time	Q ₁₀	Temperature range (°C)	Q _{Δn}
Nõmmik (1956)	2 days	17.1	13-22	13
		1.5	22-45	2.3
	6 days	14	3-13	
		10.3	13-22	8.2
Yoshida & Alexander (1970)	3 hours	0.3	22-45	0.1
		3.9	15-30	7.5
Freney et al. (1979)	45 hours	1.3	30-45	1.4
		1.7	4-18	2
		4.7	18-25	3
Keeney et al. (1979)	4 days	1.8	25-37	2
		0.9	7-15	0.9
		1.5	15-25	
	16 days	4.4	25-40	8.9
		1.3	7-15	1.2
Goodroad & Keeney (1984c)	5 days	1.4	15-25	
		3.3	10-20	
		3.1	20-30	

Diurnal, daily and seasonal variations in N₂O emission in a field can at least partly be explained by variations in temperature (Denmead et al. 1979a,b; Bremner & Blackmer 1980b; Bremner et al. 1980; Blackmer et al. 1982; Armstrong 1983; Christensen 1983; Goodroad et al. 1984; Slemr et al. 1984; Mosier & Parton 1985; Su et al. 1990, 1992).

Conrad et al. (1983) measured daily N₂O emissions from a lawn and found rates to be related to soil surface temperature according to the Arrhenius equation:

$$\text{N}_2\text{O evolution} = e^{-k/T} + k'$$

k and k' are constants and T is absolute temperature. In their data Q₁₀(13-23°C) was 2.8.

Cates & Keeney (1987b) found that an increase in surface soil temperature from 11 to 24°C in a fertilized and manured maize field was associated with a marked N₂O emission peak.

14. SEASON

14.1 Summary

N₂O emission is favoured by warm and wet conditions and is affected by the timing of fertilizer applications. Generally emission rates are highest in the summer provided that the weather is not too dry, higher in the spring than in the autumn and lowest in the winter. Spring thaw usually is associated with high emission rates.

14.2 Background

N₂O emission rates generally show large variations throughout the year, between months, but also, from week to week, day to day and even within the day. As the processes leading to such variations have been considered in previous chapters, the discussion here will be limited to their combined effect as they appear in observed seasonal variation.

14.3 N₂O emission

Bremner et al. (1980) illustrated the general trend in seasonal variations in N₂O emissions from soils. They studied six unfertilized agricultural soils in Iowa and found that the emission ranged:

<u>season:</u>	<u>% of annual emission:</u>
summer (June-August)	55-83
autumn (September-November)	6-32
winter (December-February)	<1 - 5
spring (March-May)	9-26

The variations could not be explained entirely by corresponding variations in temperature or water content. The content of nitrifiable N also played a major role. Goodroad & Keeney (1984a) investigated 7 natural ecosystems in Wisconsin. Peak N₂O emissions were generally associated with periods following heavy rainfall in the summer when the average soil temperature was at its highest. They claimed the mechanism responsible for N₂O emission seemed to be a complex combination of environmental conditions and factors that control mineralization of N as well as subsequent nitrification and possibly denitrification. Similar explanations for N₂O emission peaking in summer were given by Parton et al. (1988) who measured emissions from both unfertilized and urea-fertilized soils.

Cates & Keeney (1987b) measured N₂O emission rates throughout the year from maize fields in Wisconsin fertilized and manured at the beginning of May. May

was a very dry month whereas June and August were wet. Most of the N_2O was emitted in the period between mid-June and the end of July when the soil was warm and NH_4^+ was present, and at spring thaw when the soil was cold and near water-saturated. High N_2O emission rates also occurred during the growing season after rain.

Schmidt et al. (1988) found that the N_2O emissions were highest in spring and autumn in 6 German forests when the soil was wet. The fluxes were lower during summer when conditions generally were dry. Kaiser & Heinemeyer (1993) reported maximal fluxes in spring ($20 \text{ g N}_2\text{O-N}\cdot\text{ha}^{-1}\cdot\text{day}^{-1}$), while the annual mean rate was $3 \text{ g N}_2\text{O-N}\cdot\text{ha}^{-1}\cdot\text{day}^{-1}$ from two German agricultural soils.

The general tendency that much more N_2O is emitted from soils when they are warm and wet than when they are cold and dry has also been reported by others (Steele 1987; Luizao et al. 1989; Weier et al. 1991; Matson et al. 1992a).

Fertilizer application is a seasonal operation, and the effects of applications can mask those of other variables. This complicates the interpretation of field studies on seasonal variations in N_2O emissions from soils. Fertilizer application is one cause of N_2O emission peaks in spring and summer.

Ryden (1981), fig. 8-2 (section 8.5.1), reported on the interactions between soil temperature, water content and fertilizer application. From March to December grassland sown to perennial ryegrass was given NH_4NO_3 in equal amounts on four occasions: mid-April, end-May, June-July and mid-August. N_2O emission rates were high only for 2 to 3 weeks after fertilizer applications. At other times, the rate was below $0.0035 \text{ kg N}_2\text{O-N}\cdot\text{ha}^{-1}\cdot\text{day}^{-1}$. Highest rates were observed after the second and third application (0.04 to $0.21 \text{ kg N}_2\text{O-N}\cdot\text{ha}^{-1}\cdot\text{day}^{-1}$) which followed or were followed by periods of frequent rain and high soil water content. Generally, the highest rates were observed when the conditions in the upper 20 cm of the soil profile were:

- water content > 20 weight-% (= 34% WFPS)
- NO_3^- and NH_4^+ concentration > $10 \text{ mg N}\cdot\text{kg soil}^{-1}$
- temperature > 10°C .

Additional measurements indicated that the highest rates of N_2O emission were associated with water content well above FC in the upper 2.5 cm of the soil profile. Low rates of N_2O emission ($< 0.01 \text{ kg N}_2\text{O-N}\cdot\text{ha}^{-1}\cdot\text{day}^{-1}$) were observed following the first and fourth fertilizer applications. These periods coincided with appreciable drying of the soil. Low rates were also observed during the first weeks of the study even though the soil was at field capacity (about 50% WFPS), but with a soil temperature of $< 5^\circ\text{C}$ and a NO_3^- concentration $< 1 \text{ mg N}\cdot\text{kg soil}^{-1}$.

Egginton & Smith (1986a,b) measured N_2O concentrations in soil air in an imperfectly drained grassland soil in Scotland which was fertilized with slurry or $\text{Ca}(\text{NO}_3)_2$ in late summer, early and late autumn and spring for two consecutive years. N_2O concentrations increased during the winter months with a gradual return to near-ambient levels in the spring. NO_3^- fertilizer increased N_2O concentrations after applications in the autumn, but not in the summer or spring even though conditions were suitable for denitrification. Slurry applications always increased N_2O concentrations although in summer the effect was small.

Plants differ in the timing of their uptake of N and thus influence the seasonality of N_2O emissions (see section 12.3).

N_2O emitted during spring thaw can be a significant part of the total annual

input to atmospheric N₂O from temperate climates. The emission rates can be very high (occasionally higher than at any other time in the year) during thawing in the early spring. This has been reported for:

- natural ecosystems (Goodroad & Keeney 1984a)
- forests (Schmidt et al. 1988)
- unfertilized soils (Bremner et al. 1980; Egginton & Smith 1986b)
- fertilized agricultural soils (Goodroad et al. 1984; Egginton & Smith 1986b; Cates & Keeney 1987b).

Bremner et al. (1980) found that on average 14% of total annual N₂O was emitted from early March to mid-April, mostly in association with soil thawing. Goodroad & Keeney (1984b) and Christensen & Tiedje (1990) investigated the phenomenon in field and laboratory studies. They found that the high N₂O emission rates would not be explained solely by the physical release of accumulated N₂O. The principal cause was rapid development of conditions favourable for microbial activity: liberation of organic carbon, increase in temperature and high water content during the thaw. Christensen & Christensen (1991) showed that freeze/thaw cycles increased denitrification activity both in whole soil and in aggregates, largely due to release of carbon from organic material sources.

Breitenbeck & Bremner (1987) reported that storage of soils at -4°C for up to 30 days increased their capacity for denitrification compared with soils stored at 4°C, but this could not be solely attributed to the minor changes found in the availability of soil organic carbon.

An initially high N₂O emission is generally seen at the onset of denitrification as the microbial capacity to reduce NO₃⁻ develops more rapidly than the capacity to reduce N₂O. A relatively low temperature also favours N₂O over N₂ as a reaction product.

This topic invites further study, as management practices in the previous year (e.g. autumn tillage and manure spreading) may influence the spring emission (Goodroad et al. 1984; Cates & Keeney 1987b).

N₂O emissions are at their lowest in winter. However, snow protects soil against the extremes of low winter temperature, without preventing the escape of N₂O. Thus significant N₂O emissions can occur from fields covered by snow (Sommerfeld et al. 1993).

Since N₂O emissions vary greatly both within and between seasons, realistic measurement programmes should preferably cover the whole year. Measurement series that cover only short periods are of little value for making estimates of annual emissions.

15. MODELS

The previous chapters have shown that N₂O losses depend on many factors. The interaction of these factors is complex and incompletely known. The understanding of their relationships can be increased by constructing mathematical models that can be calibrated and validated by results from experiments and field studies. Such models seem necessary for the organization and rational use of existing knowledge, but they

are not yet at a stage where their predictive ability is satisfactory. It is usually not possible to obtain more than about 50% explained variance of the observed data, although up to 82% explanation has been achieved for a sandy soil where nitrification was the principal source of N₂O (Parton et al. 1988). The topic of modelling has recently been discussed by K.S. Smith & Arah (1990, 1992), Arah (1992a), Batjes (1992) and Li et al. (1992a,b) where details about the approaches currently attempted can be found.

16. CONCLUDING DISCUSSION: N₂O EMISSIONS FROM AGRICULTURE AND WAYS TO DECREASE THEM THROUGH GOOD AGRICULTURAL PRACTICE

16.1 The magnitude of direct and indirect N₂O emissions from agricultural land

16.1.1 N₂O emissions from agricultural land

Bouwman (1990) summarized published data on emissions from cropped soils by regression analysis which excluded data from poorly drained soils and following application of more than 250 kg N·ha⁻¹. The relationship between N₂O emission and fertilizer application rate was:

$$\text{N}_2\text{O} = 1.879 + 0.00417 \cdot \text{N}$$

where: N₂O = N₂O emission (kg N₂O-N·ha⁻¹·year⁻¹)
N = N fertilizer application rate (kg N·ha⁻¹·year⁻¹)

He used this equation to estimate that global emissions from cultivated land could be in the range 2.3 to 3.7 Tg N₂O-N·year⁻¹, though the estimate was subject to considerable uncertainty.

The equation indicates that the background emission rate of N₂O from cultivated land is about 1.9 kg N₂O-N·ha⁻¹·year⁻¹. Bouwman (1990) estimated the flux as 1 to 2 kg N₂O-N·ha⁻¹·year⁻¹ from a graphic presentation of his data. This seems to be higher than the rates usually found in natural ecosystems as discussed in chapter 5. Cultivated soils might be expected to emit more N₂O than land not used for agriculture because:

- historically it was the most fertile land that was taken for cultivation
- fertilization and other forms of N inputs increase the amounts of N in soil biomass and crop residues and enhance the availability of N for a few years
- cultivations increase the turnover rate of nutrients in the soil and enhance their availability.

Fertilizer applied in any one year is only one contributor to the total pool of soil N available for microbial transformation. The data summarized by the equation of Bouwman (1990) indicate that it takes rather high fertilizer input rates to markedly increase the N₂O emissions from cultivated land (Byrnes 1990). In arable agriculture application rates are commonly in the range of 50 to 250 kg N·ha⁻¹·year⁻¹ (FAO-IFA-

IFDC 1992). This should correspond with enhancements of N_2O emissions in the range of about 10 to 55%. Thus at fertilizer rates commonly used, the influence of other factors on N_2O emissions can mask effects of the application rate notably when studies are combined. This can be seen in fig. 8.3 (section 8.5.2) and indicates that factors other than fertilization rate exert an important influence on the emissions.

Data about pre-World War II levels of N_2O emissions from cultivated soils are lacking. This is unfortunate as it is not N_2O emissions from cultivated land *per se* that cause concern, but the probable increase in these emissions in recent times (chapter 2).

The IPCC (1992) estimated present N_2O emissions from cultivated land as 0.03 to 3.0 Tg $N_2O-N \cdot year^{-1}$ (section 2.3.1). This estimate was based mainly on reviews of Bouwman (1990) and Eichner (1990). N_2O yields are usually in the range of 0.1 to 2% (table 8.1, section 8.5.2). Presently global fertilizer N application is 77 Tg $N \cdot year^{-1}$ (IFA 1992). There seems to be no major systematic difference between types of fertilized crops in the amounts of N_2O formed after fertilization (section 12.3). Thus, N_2O emission following fertilizer application calculated from N_2O yields cover the range of 0.1 to 1.5 Tg $N_2O-N \cdot year^{-1}$. This range is unfortunately very broad, and also mostly based on measurements from temperate regions. Enhancement of background emissions from cultivated land due to a generally increased availability of N is not included in these figures.

Growing of legumes provide an additional but less well quantified input of N to cultivated land. N in legume roots and residues seems prone to N_2O formation, but there are not enough data for a reliable estimate of global N_2O fluxes from this source. However, pulses, soybeans and groundnuts were grown in 1991 on $146 \cdot 10^6$ ha (11% of the arable land, FAO 1992). In addition, much of the cereal production in Argentina and Australia is based on crop rotation between wheat and legume pastures, and intercropping with legumes is practiced and promoted in tropical regions. Hence, cultivation of legumes can be assumed to be a significant but probably minor source of N_2O from cultivated lands (section 12.3).

Domestic animals form an important part of agriculture. In western Europe (EU + EFTA nations) about 12 Tg $N \cdot year^{-1}$ was excreted as animal wastes in buildings and at pastures in 1990. About 25% (3 Tg $N \cdot year^{-1}$) was lost to the atmosphere as NH_3 , the rest (9 Tg $N \cdot year^{-1}$) returned to the soil. The amount of N returned was comparable with the amount of mineral fertilizer applied (10 Tg $N \cdot year^{-1}$) (ECETOC 1994). Global NH_3 losses from animals should be about 32 Tg $NH_3-N \cdot year^{-1}$ (section 2.4). Since only about 25% of the excreted N is lost, the implication is that the amounts of N returned annually to the soil with animal excretions may equal or exceed that applied as mineral fertilizers. Return of animal waste to the soil is associated with N_2O losses (section 11.5). However, data that can serve as a basis for global estimates of these losses are lacking.

Return of crop residues also constitute a probable but unquantified source of N_2O , especially when they are rich in N.

Both use of animal manures and return of crop residues to the soil have long been practiced in agriculture. Hence part of the N_2O emission associated with these sources must also have occurred before World War II. However, increased intensity in animal product production and larger animal populations should have increased N_2O emission also from these sources.

Catch crops are grown to a limited extent to diminish soil erosion and NO_3^- loss

by leaching. Only a minor part of the intercepted N is available for the next crop (Thorup-Kristensen 1993). Use of catch crops as green manure may result in N_2O emissions, but the amounts of NO_3^- available for N_2O forming processes in waters should be diminished. Hence catch crops may not give rise to net emissions, but this does not imply that utilization of green manures should be ignored when agricultural methods are scrutinized for practices that can reduce N_2O emissions.

16.1.2 Increased N_2O emission from natural ecosystems due to enhanced N inputs

N supply to non-agricultural land through atmospheric deposition have increased due to agriculture and other human activities, at least in some regions. However, there are marked differences between regions in the amounts of N deposited. In Europe increased depositions are most pronounced in central Europe, less so in the Iberian peninsula and in northern Europe (Sandnes & Styve 1992), and it seems likely that increased N depositions are only on a modest scale in most of Africa and South America.

N deposited from the atmosphere comes mainly from emissions of nitrogen oxides (NO_x) and NH_3 . Some is deposited on agricultural land and contributes to its background N_2O emission, some on waters, but most should be deposited on non-agricultural land. These emissions were outlined in section 2.4. The combined amount may equal or exceed that applied as fertilizer N. The majority of atmospheric NO_x originates with non-agricultural sources (mainly from combustion of fossil fuels). However, agriculture is the principal source of anthropogenic NH_3 in the atmosphere.

There are less data on N_2O yields from N inputs to natural ecosystems than from agricultural land. Brumme & Beese (1992) reported on N_2O emission from a heavily fertilized German beech forest that also received an atmospheric deposition of $35 \text{ kg N}\cdot\text{ha}^{-1}\cdot\text{year}^{-1}$. About 1.6% of the applied $140 \text{ kg N}\cdot\text{ha}^{-1}\cdot\text{year}^{-1}$ (as $(NH_4)_2SO_4$) was emitted as N_2O . This high N_2O yield was ascribed to N overloading of the system, perhaps also partly a result of soil acidification. However, such high N_2O yields seems exceptional. Bowden et al. (1991) reported that fertilization on a pine plantation and a mixed hardwood forest in the US only gave small increases in the annual N_2O fluxes. The maximal N_2O yield (about 0.2%) were on pine soil plots given 120 and $150 \text{ kg N}\cdot\text{ha}^{-1}\cdot\text{year}^{-1}$.

Similar results were reported by Matson et al. (1992a) who found that the N_2O -N flux from a fertilized ($200 \text{ kg N}\cdot\text{ha}^{-1}\cdot\text{year}^{-1}$ as NH_4NO_3) Douglas-fir forest represented 0.35% of added N. Also, these results are from experiments with rather heavy N inputs, $> 100 \text{ kg N}\cdot\text{ha}^{-1}\cdot\text{year}^{-1}$. This is much more than typical increases in N depositions. The reports indicate that lower application rates to these forest ecosystems results in lower N_2O yields than those quoted here, at least to soils under coniferous forests. Hence, it appears that N_2O yields from N deposited on non-agricultural land tend to lie in the lower range of that reported from cultivated soils. Matson et al. (1992a) concluded that increased N inputs to temperate forests only make a minor contribution to the current increase in atmospheric N_2O content.

Substantial amounts of N is also lost as NO_3^- from agricultural land to ground and surface waters. The NO_3^- concentration in ground water varies greatly with regions, but enhanced levels of NO_3^- are found in parts of Europe, the US and elsewhere (Spalding & Exner 1993). The NO_3^- originates mostly with mineralization of crop residues and soil biomass after harvest (Addiscott et al. 1991). The amounts

lost varies greatly from year to year, depending mainly on weather conditions, soil type and cropping pattern. Fertilizer application rates exerts only a minor influence on these loss rates as long as recommended application rates are not exceeded (Addiscott et al. 1991). Goulding & Poulton (1992) gauged NO_3^- losses from continuous arable cropping on sandy soils in Britain as about $20 \text{ kg NO}_3^- \cdot \text{N} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$, while Rossi et al. (1991) reported losses from cultivated soils in northern Italy of about $50 \text{ kg NO}_3^- \cdot \text{N} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$. N losses from agriculture to waters (in $\text{kg} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$) by leaching should be substantially less than customary N inputs to soils by fertilizers. Non-agricultural sources (urban sewers, N deposition to waters) also contribute considerably to N availability of river and coastal waters. Global estimates are not available, but Lidgate (1987) estimated that about 40% of the anthropogenic N input to the North Sea was of non-agricultural origin.

Unfortunately, data on the amounts of NO_3^- in waters that are converted to N_2O are too few to permit reliable quantification (Seitzinger 1990).

16.1.3 Summary and conclusions

This discussion serves more to illustrate the difficulties in presenting an estimate for the amounts of N_2O emitted, both directly and indirectly, from agriculture, rather than as a guide to a precise figure. However, the following conclusions can be drawn:

- agricultural land is probably a major source of atmospheric N_2O , since emission rates are enhanced compared to those from virgin soils, and the area under cultivation is very large (chapter 5)
- no precise estimate for the global input of N_2O from agricultural land can be given at present because reports on annual emission rates from field measurements are too few, with widely variable results and incomplete coverage of potentially important areas (e.g. tropical agriculture) and sources (e.g. animal wastes, legumes)
- N_2O emissions from fertilized land generally increase with increasing application rates of mineral fertilizer N, but the magnitude of the increase depends also on other factors, e.g. climate, soil and management practices
- enhanced N inputs to other ecosystems should enhance their N_2O emissions, but only a part of the enhanced inputs originate with agriculture. The contribution of enhanced deposition of N on non-agricultural land to the increase in global N_2O flux is probably minor. Increased N losses to waters as leached NO_3^- may lead to increased N_2O emissions, but the magnitude of this increase cannot be assessed due to lack of data
- though firm estimates cannot be made, the discussions on direct and indirect emissions indicate that the global N_2O emissions originating with agriculture probably are in the upper part of the IPCC estimate of 0.03 to 3 Tg $\text{N}_2\text{O} \cdot \text{N} \cdot \text{year}^{-1}$. Some of this is not of recent origin
- in order to decrease the emissions, attention should be directed to all those factors in land management that influence N_2O emission from soil, including but not

limited to fertilization practices. However, though there should be potential for reduction of current emissions, they cannot be eliminated altogether.

16.2 Good agricultural practice

Current and emerging food production and preservation capabilities are sufficient to ensure an adequate global supply of safe nutritious food, at least for the near future. About 10% of the human population suffers from malnutrition, but this is due to economic, political and social factors and not to limits in present agricultural productivity. However, the population is increasing while the amount of land available for food production is almost static, thus great efforts are required in agriculture to satisfy increased future needs for food (WHO 1992). Some regions (e.g. EU) have current food production in excess of market requirements, but there is no margin on the global scale for a decrease in future agricultural production level.

Crops must have an adequate supply of water and plant nutrients to give high yields. N availability is often the limiting factor, where yields are not restricted by lack of water.

As discussed in chapter 2, N is made available to crops as N fertilizer, from biological N fixation in legumes, by return of animal and crop waste to the land, and by mobilization of soil N reserves. All these ways of increasing nutrient availability raise environmental issues (Bøckman et al. 1990) and, as discussed in previous chapters, all contribute to enhanced N₂O emissions.

The magnitude of the N₂O emissions originating directly and indirectly from agriculture are largely unknown, but they seem to be substantial and may constitute the largest anthropogenic source of atmospheric N₂O. Lack of precise information about the amounts emitted should not discourage efforts to decrease the emissions where such actions appear reasonable and when their effect can be significant.

National authorities have addressed the issues of agricultural impact on the environment through statutory codes of good agricultural practice. Those for the protection of water emphasize actions that will keep the amounts of NO₃⁻ lost through leaching to a minimum, while those for the protection of air stress more efficient use of animal manures with reduced loss of NH₃ to the atmosphere. It can be deduced from the discussion in this report, mainly chapter 7, 8 and 11, that many of these measures also serve to restrain N₂O emission, by:

- keeping soil NO₃⁻ concentrations low outside the growing season
- encourage return of N wastes to the soil and thus reducing the need for new N inputs
- restricting N availability in the soil by limiting N input to that needed by crops
- creating soil conditions generally associated with low N₂O emissions
- reducing unintentional N transfer from agriculture to other ecosystems.

The codes of good agricultural practice for England and Wales (MAFF 1991, 1992) can be used as an illustration:

- fertilizer and manure application should be planned and limited to the plant's

requirement for N, taking soil reserves and residues of the previous crop into consideration

- fertilizer application should be timed to correspond with the crop's ability to make the best use of the N. Too late or too early applications should be avoided
- fertilizers and manures should be evenly applied, and they should not be spread on frozen or waterlogged soils
- fallow fields should be avoided by growing autumn-sown or catch crops, and ploughing should rapidly be followed by planting new crops
- ploughing of permanent grassland should be avoided if possible. When such land needs reseeding cultivation should be reduced to a minimum and done so that the field is covered with grass at the end of the growing season
- incorporation into the soil of crop residues rich in N (e.g. from vegetable crops) should be delayed until just before the next crop is sown
- irrigation should be even and restricted to the amounts necessary to ensure good plant and root development so that the crop can make good use of the applied fertilizer, and should not need to return the soil to field capacity during the growing season
- arable crops grown in rotation with grass leys should be sown as soon as possible after the grass is ploughed up
- pasture management should not be so intense that marked NO_3^- leaching occurs, and fertilizer use or grazing intensity should preferably be reduced in the autumn
- NH_3 emissions to the atmosphere and thus to other ecosystems should be reduced by cleanliness in stables, sufficient storage capacity of an approved type for animal wastes and incorporation of manure into soil at or very shortly after application

The advice specifically given for keeping N_2O emissions to a practical minimum reflects the most important points that should be taken into consideration by farmers:

« N_2O from farms comes from the reaction of N compounds in manures and soils especially in O_2 -free conditions. The most effective way for farmers to reduce releases of this gas is to avoid excess use of N fertilizer and manures and make sure that they are not applied to waterlogged soils.»

Further, the traditional advice of avoiding soil compaction and erosion can be included in the list of good practices that should restrain N_2O emissions (section 9.3).

What is regarded as good agricultural practice varies somewhat from region to region reflecting variations in local soil and climatic conditions. But the example from UK indicates that much advice to farmers on how to minimize N_2O losses from agricultural land is already found in existing codes.

16.3 Research opportunities

N_2O emissions vary greatly with circumstances. These can be managed to some extent. But crop yields also vary. Unfortunately, crop yields are not commonly reported in studies of N_2O emissions from agricultural land. Much is known about N_2O emissions in terms of $kg\ N_2O-N\cdot ha^{-1}$, but almost nothing about the losses as $kg\ N_2O-N$ ·unit of crop production⁻¹. This lack of information makes it impossible at present to include the crop yield factor in appraisals of best means to reduce N_2O emissions from agriculture. We suggest that this point should be given attention in future research.

Knowledge about the conditions that influence N_2O emissions from soil is considerable, but much work remains to be done to transform this basic knowledge into guidelines for good agricultural practice for low N_2O emissions that cover special situations:

- there may be an optimum combination of fertilizer application and irrigation practice. The very large scale of irrigated cereal production in developing nations ($32.5\cdot 10^6$ ha) points to the potential importance of this topic. To avoid fertilizer application when heavy rains are expected and to avoid irrigation in the first 1 to 2 weeks after the application may reduce N_2O emissions (chapter 7 and 8). However, this may be impractical, and losses of NH_3 can be substantial if the fields are not irrigated after fertilization with urea
- use of fertilizers on grassland in very wet (maritime) climates is associated with a marked potential for N_2O loss (section 8.5.2 and 12.3). It is not clear what fertilizer practice is appropriate under such circumstances
- intensively managed pastures:
 - are well fertilized
 - have a substantially part of the area affected by urine patches with high mineral N concentration (section 8.5.3 and 11.5)
 - have a topsoil enriched in organic material (section 11.5)
 - can be compacted by trampling of cattle (section 9.3)
 - the plants are frequently cut by the grazing (section 12.3).
 All these circumstances are associated with enhanced potential for N_2O emission.
- use of anhydrous NH_3 as a fertilizer is common in the USA and in a few other regions, but seems to give more N_2O loss than does the use of other N fertilizer types. The cause is unknown, and it is not clear if this higher emission occurs in all circumstances (chapter 8)
- worldwide, urea is the principal fertilizer, but application of urea under conditions favourable for nitrification can be associated with enhanced N_2O formation (section 8.5.2). Urea also gives rise to significant NH_3 volatilization that may contribute to N_2O formation from non-agricultural soils (section 2.4). It is not presently clear under what circumstances application of urea should or should not be recommended due to potential emission of N_2O

- there are indications (chapter 8, 9 and 10) that predominantly NO_3^- fertilizer, e.g. $\text{Ca}(\text{NO}_3)_2$, is the fertilizer type that gives the lowest emissions of N_2O when applied on well-aerated calcareous soils, while emissions can be high from wet clay soils (section 8.5.2). Fertilizer type (except anhydrous NH_3) does not seem to exert a major influence on N_2O emissions from neutral soils. It is not clear if this is also true for acid soils. The influence of soil type, pH and fertilization practice on N_2O emission requires further study before general recommendations can be given
- conclusions on the relationship (if any) between fertilizer application method and N_2O emission cannot be drawn at present due to lack of data (section 8.5.3)
- a high content of organic carbon in soil seems to dispose for high levels of N_2O emission, and peat soils seems to be especially prone to give high emission rates (chapter 11). Recommendations for cultivation practices that restrain N_2O emissions from such soils cannot be given at present
- injection of slurry or rapid incorporation by tillage rather than surface spreading is the recommended method for manure application in order to reduce NH_3 volatilization. However, incorporation may enhance N_2O formation. Also, incorporation of straw is recommended in the autumn in order to consume NO_3^- through microbial action, as is the growing of catch crops. However, addition of degradable organic material to soil can increase N_2O losses, notably where the soil is wet and the amount of NO_3^- in the soil is substantial. Composting is another operation that may emit N_2O . Crop residues and manures are unavoidable by-products and must be put to good use as nutrient sources, supplemented as appropriate with mineral fertilizers. However it is not clear what guidelines are appropriate for their use to achieve minimal N_2O emission (chapter 11)
- grains and forage legumes are important crops that provide a N input through biological fixation. However, decomposition of their roots and residues seems to result in relatively high N_2O emissions (section 12.3). It is not known what management practices are desirable to keep emissions to a minimum.
- reduced tillage and direct drilling with no tillage reduce soil erosion losses but may be associated with enhanced N_2O emissions (section 9.3). It is not clear if, and under what circumstances, this gives cause for concern
- there is insufficient information on N_2O emission from animal stables, feedlots and grazing, but reports indicate that these may be important sources (section 11.5)
- hot and humid conditions should promote N_2O emissions, but data from tropical agriculture are few. Investigation of this topic deserves priority
- some basic issues require clarification, e.g.:
 - if plants can emit or remove N_2O (section 2.3.1 and 2.3.2)
 - to what extent soils can act as a sink for N_2O (section 2.3.2 and 7.5)
 - the influence of soil salinity on N_2O production by denitrification (section 3.4)
 - the origin of the apparent variations in the annual N_2O increment in the atmosphere (section 2.3.1).

Much information is available about the processes that generate N_2O in soil, and the basic features seem now reasonably well known. Nevertheless, much remains to be done before advice for good agricultural practices can be given for every important management option. These issues should be addressed on a broad basis.

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18. LIST OF ACRONYMS

AFPS:	Air Filled Pore Space
AIM:	Acetylene Inhibition Method
FC:	Field Capacity
GC:	Gas Chromatography
IR:	Infra-red
TPS:	Total Pore Space
WFPS:	Water Filled Pore Space

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