Nitrous oxide emission from intensively managed grasslands

G.L. Velthof

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Stellingen

1. Het afstemmen van de stikstofmeststofkeuze op de actuele vochttoestand van de bodem en de te verwachten neerslag voor de eerstvolgende dagen is een efficiënte maatregel om de lachgasemissie uit grasland te beperken.
    Dit proefschrift

2. Het terugdringen van het stikstofoverschot van melkveehouderijen leidt tot een vermindering van de lachgasemissie.
    Dit proefschrift

3. Een goede kwantificering van de lachgasemissie die door nitraatuitspoeling wordt veroorzaakt, is dringend noodzakelijk om de totale lachgasemissie uit de landbouw nauwkeurig te kunnen schatten.
    R.J. Dowdell, J.R. Burford and R. Crees (1979) Losses of nitrous oxide dissolved in drainage water from agricultural land. Nature 278: 342-343.
    Dit proefschrift

4. De grootte van de gerapporteerde lachgasemissie, verkregen via fluxkamerstudies, wordt niet alleen bepaald door verschillen in bodem- en klimaatfactoren, maar vooral ook door de toepassing van verschillende rekenmethodieken om de (gemiddelde) emissie te berekenen.
    Anthony, W.H., G.L. Hutchinson and G.P. Livingston (1995) Chamber measurement of soil-atmosphere gas exchange: linear vs. diffusion-based flux models. Soil Science Society of America Journal 59: 1308-1310.
    Dit proefschrift

5. Het omzetten van cultuurgrasland op veengrond in nat natuurgrasland zal de lachgasemissie doen afnemen maar de methaanemissie doen toenemen.

6. Het invoeren van het mineralen-aangiftesysteem (MINAS) in de akkerbouw zal tot een stijging van het mestoverschot in Nederland leiden.

7. Beleid waarin voor alle zware metalen geldt dat de aanvoer via meststoffen gelijk of lager is dan de afvoer via oogstproducten kan alleen worden geëffectueerd na aanpassing van de bemestingsadviezen of na verandering van de meststoffen-samenstelling.

8. Door het steeds groter wordende aantal wettelijke en landbouwkundige eisen die aan bemesting worden gesteld, zijn computerprogramma's een onmisbaar hulpmiddel voor boeren bij het opstellen van een passend meststoffenplan.

9. De voortgang van het afronden van het proefschrift door promovendi met jonge kinderen wordt sterk bepaald door de hoeveelheid slaap die de kinderen nodig hebben en die de ouders krijgen.

10. De concentratie waarbij lachgas een narcotiserende werking heeft, is meer dan een factor 10.000 hoger dan de lachgasconcentratie boven beweid grasland, zodat niet gevreesd hoeft te worden dat door beweiding veroorzaakte lachgasemissie leidt tot sufheid van de boer en het vee.

11. De vaak onduidelijke affiches die langs de snelweg zijn geplaatst om veiliger rijgedrag te stimuleren, leiden tot onveilig rijgedrag indien de weggebruiker ze daadwerkelijk tracht te lezen.

12. Het grote aantal versnellingen waarmee veel fietsen worden uitgerust, heeft meer voordelen voor de fietshandel bij de verkoop dan voor de gebruiker bij het fietsen.

13. Goede kinderopvang is onontbeerlijk voor werkende ouders én hun kinderen.

Stellingen behorende bij het proefschrift van G.L. Velthof: 'Nitrous oxide emission from intensively managed grasslands', 27 mei 1997.

Voorwoord

Het onderzoek dat in dit proefschrift staat beschreven, is uitgevoerd in het kader van het onderzoekprogramma van het Nutriënten Management Instituut (NMI) en werd gedeeltelijk gefinancierd door het Nationaal Onderzoek Programma Mondiale Luchtverontreiniging en Klimaatverandering. Het onderzoek werd verricht bij de NMI-sectie, die gedetacheerd is bij de vakgroep Bodemkunde en Plantenvoeding van de Landbouwuniversiteit in Wageningen (LUW). Veel mensen hebben op een of andere manier een bijdrage geleverd aan dit proefschrift. Enkele wil ik hier met name noemen.

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Arie Brader, jij hebt een groot deel van de veldmetingen uitgevoerd. Bedankt, dat je ondanks de soms extreme omstandigheden altijd de metingen nauwgezet hebt verricht. Ook bedankt, dat je altijd goed gezorgd hebt voor de voor het project onmisbare, maar niet altijd even betrouwbare, 'meetbus'.

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metingen gedurende twee jaar.

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De promovendi uit de methodologie-discussiegroep van de C.T. de Wit Onderzoekschool voor Productie Ecologie, onder de leiding van prof. dr. ir. A. Stein, bedank ik voor het commentaar op twee manuscripten. Alfred, ook bedankt voor je bijdrage aan één van de publicaties uit dit proefschrift.

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Gerard Velthof,
Barneveld, mei 1997

Abstract

The aims of this thesis are to quantify nitrous oxide (N_2O) emission from intensively managed grasslands in the Netherlands, to increase the insight in the factors controlling N_2O emission from intensively managed grasslands and to explore the possibilities to reduce N_2O emission from intensively managed grasslands. The study was part of the integrated project 'N$_2$O emissions from grassland', with laboratory experiments, field measurements, field monitoring studies, and modelling at process and field levels. The focus of the present study was predominantly on field monitoring studies using vented closed flux chambers and a photo-acoustic spectroscopic infra-red gas analyzer. Emissions of N_2O from unfertilized and mown grasslands ranged from 1 to 9 kg N ha^{-1} yr^{-1} and were larger on peat soils than on sandy and clay soils. The large emissions from peat soils were attributed to the high mineralizable organic carbon (C) and nitrogen (N) contents, in combination with the shallow groundwater levels. Application of N fertilizer increased N_2O emission; on an annual basis 1.0% of the N applied as calcium ammonium nitrate (CAN) was emitted from mineral soils and 1.9 to 3.9% from peat soils. Emission of N_2O from N fertilized and grazed grasslands ranged from 10 to 39 kg N ha^{-1} yr^{-1}. On annual basis, 1.5 to 9.8% of the N excreted as urine and dung during grazing was emitted as N_2O. Spatial and temporal variability of N_2O fluxes were large and mainly controlled by variations in contents of mineral N and moisture. During wet conditions, N_2O emissions from nitrate fertilizers were much larger than those from ammonium fertilizers. Total N_2O emissions from dairy farming systems in the Netherlands were estimated at 13.7 ± 5.1 Gg N yr^{-1}. Model calculations of N_2O budgets for three dairy farming systems on sandy soil with different nutrient management indicate that the potentials to reduce N_2O emission from dairy farming systems are large. Improving the N fertilizer use efficiency and choosing the N fertilizer type depending on the soil moisture status were shown to be effective measures to reduce N_2O emissions.

Key words: ammonium, calcium ammonium nitrate, dairy farming systems, denitrification, emission, flux chamber method, grassland, grazing, greenhouse gas, groundwater level, mineral soils, nitrate, nitrogen fertilizer, nitrous oxide, nutrient management, peat soils, spatial variability, temporal variability.

Contents

CHAPTER 1

General introduction

General introduction

Background

Nitrous oxide (N_2O) is a natural trace gas in the atmosphere of the earth. The present atmospheric N_2O concentration is about 310 μl m^{-3}, but is increasing at a rate of 0.6 to 0.9 μl m^{-3} yr^{-1} during the recent years (Khalil and Rasmussen, 1992). This increase is of concern because N_2O contributes i) to the enhanced greenhouse effect (Wang _et al._, 1976), which may lead to global warming and climate change, and ii) to the destruction of stratospheric ozone (Crutzen, 1970), which may increase biologically harmful ultraviolet radiation onto the earth. On a molecular basis N_2O has a global warming potential of about 250 times that of carbondioxide (CO_2). Nitrous oxide in the atmosphere accounts for about 6% of the direct radiative forcing of the long-lived greenhouse gases (Houghton _et al._, 1996).

A recent estimate of the global N_2O budget by Prather _et al._ (1995) indicates that the identified natural and anthropogenic N_2O sources account for 10 to 17 Tg N_2O-N per year (Table 1). Cultivated soils are a major source of N_2O: 1.8-5.3 Tg N yr^{-1} (Table 1). The atmospheric N_2O concentration increases at a rate of 3.1 to 4.7 Tg N yr^{-1} (Prather _et al._, 1995). Chemical reactions in the stratosphere are the major (perhaps the only) sink of N_2O. The magnitude of this sink of N_2O was estimated at 9 to 16 Tg N yr^{-1} (Prather _et al._, 1995).

The uncertainties in the estimates of Prather _et al._ (1995) indicate that there are still considerable uncertainties in the N_2O budget. Clearly, there is a need to quantify the sources and sinks of N_2O to obtain a more accurate estimate of the global N_2O budget. Moreover, there is a need to develop strategies to reduce the increase in the atmospheric N_2O concentration. Stabilisation of the atmospheric N_2O concentration at today's level would involve a reduction in the anthropogenic N_2O emissions of more than 50% (Houghton _et al._, 1996).

Emission of N_2O from soils

The biological soil processes nitrification and denitrification are considered to be the major source of N_2O (Prather _et al._, 1995). Nitrification is the aerobic process in which ammonium (NH_4^+) is oxidized into nitrate (NO_3^-). Production of N_2O during nitrification mainly occurs when the oxygen concentration is relatively low

(Firestone and Davidson, 1989). Denitrification is the anaerobic process in which NO_3^- is reduced to the gaseous N compounds N_2O and dinitrogen (N_2). The ratio of the amount of N_2O and N_2 produced during denitrification may strongly vary and is dependent on factors as the oxygen concentration, NO_3^- concentration, temperature and pH (Firestone and Davidson, 1989). A third process contributing to N_2O emission is chemical denitrification. In this process is nitrite (NO_2^-) chemically reduced to gaseous N compounds (Chalk and Smith, 1983; Van Cleemput and Samater, 1996). It is generally assumed that chemical denitrification is only a minor source of N_2O, in comparison to biological nitrification and denitrification.

Table 1. Estimated magnitude of identified sources of N_2O typical of the last decade, in Tg N yr^{-1} (From Prather *et al.*, 1995).

Source	Range	Likely
Natural		
oceans	1 - 5	3
tropical soils		
wet forests	2.2 - 3.7	3
dry savannas	0.5 - 2.0	1
temperate soils		
forests	0.1 - 2.0	1
grasslands	0.5 - 2.0	1
Total natural	6 - 12	9
Anthropogenic		
cultivated soils	1.8 - 5.3	3.5
biomass burning	0.2 - 1.0	0.5
industrial sources	0.7 - 1.8	1.3
cattle and feed lots	0.2 - 0.5	0.4
Total anthropogenic	3.7 - 7.7	5.7
Total sources	10 - 17	14.7

Important factors controlling production of N_2O during nitrification and denitrification in soils are the contents of NH_4^+, NO_3^-, NO_2^-, mineralizable carbon (C),

oxygen, moisture and temperature (e.g. Firestone _et al._, 1980; Blackmer and Bremner, 1978; Blackmer _et al._, 1980; Burford and Bremner, 1975 and Keeney _et al._, 1979). Generally, largest production of N_2O in soils is found when mineral N content is high and the soil is wet. When the soil is strictly anaerobic, production of N_2O is low, because then the aerobic process nitrification is hampered, and because under strictly anaerobic conditions N_2O is only a minor end product of denitrification (e.g. Davidson, 1991). Besides the production of N_2O in the soil, also the diffusion rate of N_2O in the soil strongly affects the emission of N_2O from the soil towards the atmosphere. The longer N_2O remains in the soil, the higher the probability it is further reduced to N_2 by denitrifying bacteria. In wet soils and in soils with a large N_2O production in the sub soil, initial production of N_2O in the soil may be much larger than the ultimate N_2O flux towards the atmosphere. Figure 1 shows the concept of N_2O production in and emission from soils and is a visualization of the "hole-in-the-pipe" model of Firestone and Davidson (1989). This figure also indicates that soils may act as sink of N_2O; the magnitude of this sink is still unknown.
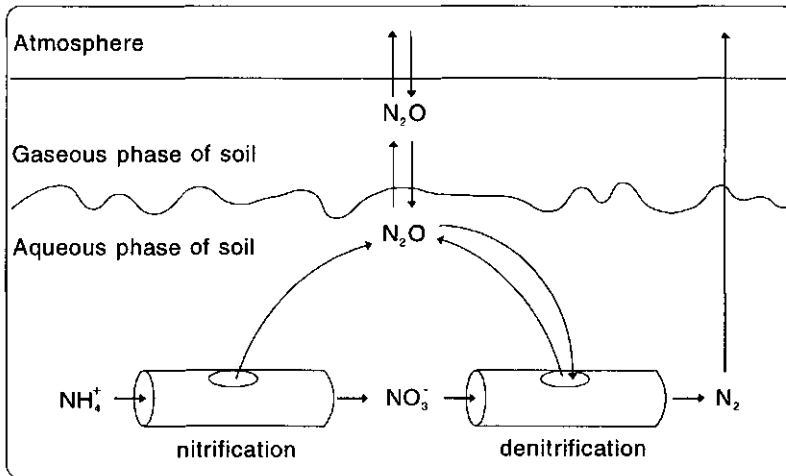

Figure 1. Three levels of regulation of N_2O emission from soils: (i) the rates of nitrification and denitrification (amount of N transformed in the pipe); (ii) the ratios of end products (the size of the holes in the pipes); and (iii) diffusion and consumption of N gases prior to escape from the soil to the atmosphere (Firestone and Davidson, 1989; Davidson, 1991).

Because of the many factors that may control N_2O emission, temporal and spatial variability of N_2O emissions from soils are often found to be large (Ambus and Christensen, 1994; Blackmer *et al.*, 1982; Folorunso and Rolston, 1984; Groffman, 1991; Webster and Dowdell, 1982). This large spatial and temporal variability strongly hampers the quantification of N_2O emission from soils.

Nitrogen plays a key role in the production and emission of N_2O from soils. The N inputs to intensively managed grasslands of dairy farming systems are large and, therefore, these grasslands represent a potentially large N_2O source.

The N cycle of dairy farming systems

The N cycle of dairy farming systems is complex, because it involves the contribution of plants, soils and animals (Figure 2). Moreover, N is present as rather immobile organic compounds, as water-soluble inorganic compounds like NH_4^+, NO_3^-, and NO_2^-, and as highly mobile and volatile compounds like ammonia (NH_3), N_2O and N_2.

The major N input into dairy farming systems occurs via N fertilizer and animal feeds. A large part of the total N input into dairy farming systems is not recovered into the major products milk and meat and is probably lost into the environment (Aarts *et al.*, 1992; Jarvis, 1993; Korevaar, 1992). Losses of N from dairy farming systems may occur via NH_3 volatilization, NO_3^- leaching, and denitrification (Figure 2). A large part of these N losses from dairy farming systems occurs from the intensively managed grasslands.

Intensively managed grasslands in the Netherlands

In recent decades, dairy farming systems in the Netherlands have been strongly intensified, mainly due to increased inputs of nutrients via fertilizers and purchased feeds (Table 2). At present, in total about 1 million ha of land is under permanent grassland, representing 25 percent of the total area of the Netherlands and more than half of the total area of agricultural land (Anonymous, 1995a). The permanent grasslands are mainly used for grazing and for forage production. About 50% of the permanent grasslands in the Netherlands are found on sandy soils, 25% on peat soils, and 25% on clayey soils (Anonymous, 1995a; Steur *et al*, 1985). Grasslands on peat soils have a large N and C turnover and shallow groundwater levels, which may promote production of N_2O.

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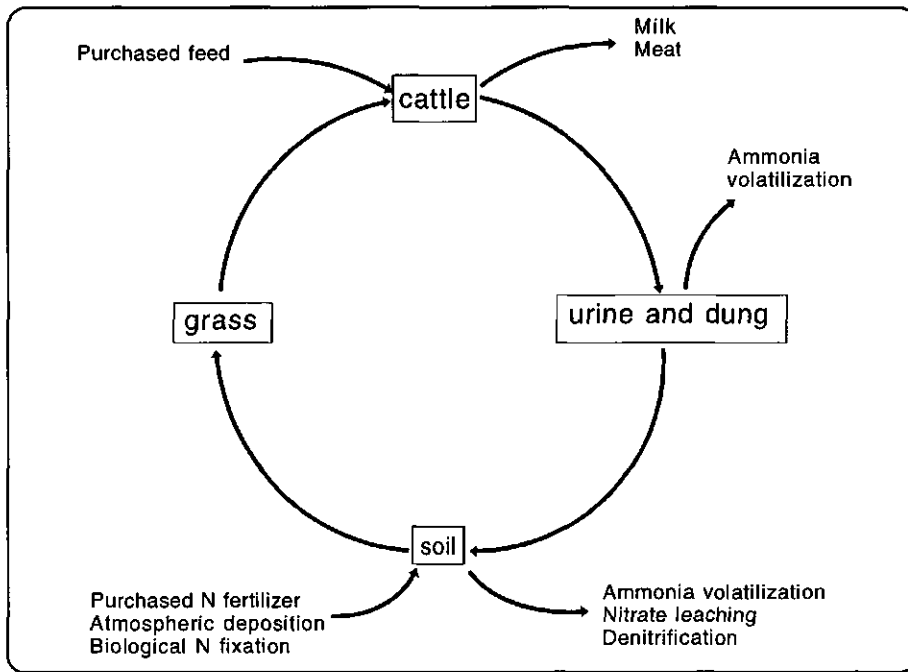
Figure 2. Major N flows on dairy farming systems.

Aims of this thesis

The major aims of the study presented in this thesis are:
i) To quantify N_2O emission from intensively managed grasslands in the Netherlands. It may be suggested that N_2O emission from intensively managed grasslands in the Netherlands is large, because of the large N inputs via animal excreta and N fertilizer, the generally shallow groundwater levels, and the large contents of mineralizable C in grassland soils. Moreover, a large part of the grasslands in the Netherlands are situated on peat soils, which are potentially large sources of N_2O. Emission of N_2O from intensively managed grasslands in the Netherlands is poorly quantified yet, because in-situ field measurements of N_2O emission from these grasslands are scarce.
ii) To increase the insight into the factors controlling N_2O emission from intensively managed grasslands on a field scale. More knowledge of the factors controlling N_2O emissions from grassland soils is necessary to develop options to reduce these

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emissions. Moreover, relationships between N_2O emisison and controlling factors can be used to develop models that predict N_2O emission from soils.

iii) To explore the possibilities to reduce N_2O emission from intensively managed grasslands. Measures are needed to at least alleviate the increasing concentration of atmospheric N_2O.

Table 2. Characteristics of dairy farming systems in the Netherlands in the period 1965 to 1993. Figures are derived from Van Burg *et al.* (1980), Van der Meer (1991), Nutrient Management Institute (unpublished results) and Anonymous (1995a).

	1965	1980	1985	1993
Total grassland area, km^2	13,070	11,980	11,640	10,640
Number of dairy farms	161,950	67,167	57,995	40,525
Number of dairy cows (x 1000)	1,723	2,356	2,367	1,747
Milk production, kg cow^{-1} yr^{-1}	4,200	5,080	5,371	6,325
N fertilizer[1], kg N ha^{-1} yr^{-1}	150	285	315	275
Concentrates, kg cow^{-1} yr^{-1}	650	2,120	2,250	2,215
Manure/slurry production, Tg yr^{-1}	26	65	72	58

[1]calcium ammonium nitrate (CAN) is/was by far the most used N fertilizer

Set-up

The focus of the study was on field measurements, because the interactions between grassland management, soil, plants, and weather conditions strongly control the N_2O emission from soils. Therefore, most reliable estimates of N_2O emission from grasslands are obtained under field conditions.

The major part of this thesis consists of monitoring studies, in which N_2O fluxes were measured weekly during two years on four grassland sites in the Netherlands, with three management types. The monitoring studies were carried out on three Regional Research Farms (ROC's) of the national Research Station for Cattle, Sheep and Horse Husbandry (PR). The grassland sites were situated on a sandy soil, clay soil and peat soils with different groundwater levels. Two peat soils were included in the study, because they represent potentially large N_2O sources and because literature data on N_2O emission from grasslands on peat soils are still very scarce.

The grassland management treatments in the monitoring study were on each

site: unfertilized and mown, N fertilized and mown, N fertilized and grazed. By chosing these treatments the effects of N fertilizer application and grazing on N_2O emission could be quantified.

Methodology

Fluxes of N_2O were measured in the field using a closed flux chamber method. The closed flux chamber method involves placing a closed box, typically $< 1 \ m^2$, over the soil surface, after which the flux is calculated from the change in N_2O concentration in the headspace of the box. This is an easy-to-handle and robust measuring system. Moreover, the chamber method is sensitive (detection limit for N_2O flux generally $< 20 \ \mu g \ N \ m^{-2} \ hr^{-1}$) and provides an easy opportunity to quantify fluxes in small-scale factorial experiments with replicates. A disadvantage associated with the use of closed chambers is that the conditions within the chamber may be disturbed due to closing of the chamber, which may affect the flux of N_2O (Mosier, 1989). Moreover, measurements using flux chambers are strongly hampered by the large spatial variability of N_2O fluxes from soils. Therefore a large number of chambers is generally required to obtain an accurate estimate of the average field flux (Folorunso and Rolston, 1984).

The disadvantages of the flux chamber method have lead to the development of micro-meteorological methods, in which the average N_2O flux over a large soil area, typically 10 to 100 ha is measured and which do not disturb the soil-plant-atmosphere environment of the measurement area (e.g. Fowler and Duyzer, 1989). Disadvantages of micrometeorological methods for N_2O flux measurements are the requirement of specialized expertise, sensitive and expensive equipment, the relatively high detection limit for N_2O flux (generally $> 50 \ \mu g \ N \ m^{-2} \ hr^{-1}$), the requirement of extensive homogeneous areas with minimum air turbulence and constant atmospheric conditions during the measurement.

The major reasons to use a closed flux chamber method in the study described in this thesis are:

(i) a closed flux chamber method has a relatively low detection limit for N_2O flux;

(ii) closed flux chambers are simple to construct, cheap, and can be well used in long-term studies under field conditions;

(iii) closed flux chambers are very suitable for experimental designs in which treatments are compared, e.g. fertilizer treatments and grassland management type, using statistical designs with replicates;

(iv) sampling of the soil within the chamber after flux measurements allows an assessment of the major soil variables controlling the N_2O flux.

Outline of this thesis

This thesis is a compilation of several articles, published in or submitted to various international scientific journals[1]. Results of the monitoring studies in which N_2O fluxes were measured weekly during two years on four grasslands sites in the Netherlands, with three management types each, are presented in Chapters 2, 3, and 4. In Chapter 2 a description is given of the closed flux chamber method and of the problems associated with the calculations of fluxes from chamber measurements. Chapter 3 deals with the effects of soil type, N fertilizer application and grazing on N_2O fluxes during the growing season. Chapter 4 focuses on seasonal and inter-annual variations of N_2O fluxes from the different grassland sites and management types.

In Chapter 5, the major soil variables controlling spatial variability of N_2O fluxes from managed grassland on peat soil are examined and a simple empirical model to estimate N_2O fluxes from peat soils is presented and tested. This chapter includes also a comparison of fluxes measured with flux chambers and a micro-meteorological technique. A study on the spatial variability of N_2O fluxes from managed grasslands on a clay soil is presented in Chapter 6. In Chapter 7 the effects of type and amount of N fertilizer on N_2O fluxes are evaluated. Chapter 8 deals with total N_2O emissions from dairy farming systems with different nutrient management, using a whole farm approach. Finally, in Chapter 9 the main findings of this thesis are discussed and integrated.

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[1] In this thesis, the terms 'N_2O flux', 'N_2O loss', and 'N_2O emission' are used. Different terminology is used in the different chapters/journal articles to meet the wishes of the corresponding editorial boards. All three terms indicate the same process; i.e. the flow of N_2O from the soil towards the atmosphere.

CHAPTER 2

Nitrous oxide fluxes from grassland in the Netherlands: I. Statistical analysis of flux chamber measurements

Nitrous oxide fluxes from grassland in the Netherlands: I. Statistical analysis of flux chamber measurements

Summary

Accurate estimates of total nitrous oxide (N_2O) losses from grasslands derived from flux chamber measurements are hampered by the large spatial and temporal variability of N_2O fluxes from these sites. In this study, four methods for the calculation of mean N_2O fluxes (n=6) on total N_2O losses are compared, namely the arithmetic mean, the geometric mean, the lognormal mean and the mean derived from Finney's method. Mean fluxes were calculated from weekly flux measurements on grassland at four contrasting sites in the Netherlands with three management treatments each. Total losses were calculated by interpolation of the mean fluxes and integration over time. Spatial variation of N_2O fluxes was large. The geometric mean was generally much smaller, up to a factor of 7, than the arithmetic mean. The lognormal mean was much larger, up to a factor of 11, than the arithmetic mean, possibly because this estimator is biased for small sample size. Arithmetic means and Finney's method were generally in reasonable agreement. The order in estimated N_2O loss increased in the order geometric mean < arithmetic mean ≤ Finney's mean < lognormal mean. Because of the small sample size (n=6), the uncertainty about the precise frequency distribution, the sensitivity of estimators based on logtransformed data, and the problems associated with negative fluxes, the arithmetic mean was preferred as the most appropiate estimator. Evidently, the choice of an estimator of the mean can have great effects on the estimation of total N_2O losses.

Introduction

Soil is suggested to be the major global source of nitrous oxide (N_2O) (Bouwman, 1995). Spatial and temporal variations in N_2O fluxes from soil are large. This is because the variables controlling the production of N_2O in soil during the microbiological denitrification and nitrification also vary in space and time (Firestone and Davidson, 1989). The variables include temperature and the contents of mineral nitrogen (N), mineralizable carbon (C), oxygen and moisture.

Flux chamber techniques are the most used techniques for measuring N_2O fluxes from soil to atmosphere (Mosier, 1989), and in them, too, variation of N_2O fluxes is

often found to be large (Ambus and Christensen, 1994; Folorunso and Rolston, 1984). Increasing the number of replicates may decrease the estimation variance, but is not usually feasible for lack of time. Micrometeorological methods have the advantage that they integrate fluxes from a large area (Fowler and Duyzer, 1989). However, they are rather expensive, need large uniform areas, and are less suitable for comparing experimental treatments, e.g. fertilizer applications. For these reasons flux chamber techniques seem to be a reasonable compromise for field studies.

Flux measurements of N_2O using flux chambers often approximate a lognormal distribution. In reviews of Aitchison and Brown (1966), Koch and Link (1970) and Parkin *et al.* (1988), various estimators of the mean of lognormal distributions are given. Accurate calculations of total N_2O losses from soil are important for accurate estimates of global N_2O budgets, and also for the development of policies to diminish N_2O losses. The global N_2O budget is still unbalanced (Bouwman, 1995), and there is an urgent need for more accurate estimates of the N_2O sources. Therefore, possible differences in mean N_2O fluxes due to the choice of different estimators have to be considered when dealing with total N_2O losses.

In this paper, the effects of the method of calculating mean N_2O fluxes on total N_2O losses from soil is discussed. Mean fluxes were calculated from weekly flux measurements on grassland at four contrasting sites in the Netherlands with three management treatments each. Effects of soil type, grassland management and weather on N_2O fluxes are discussed in a companion paper (Velthof and Oenema, 1995b).

Materials and methods

Experimental set up
A detailed description of the experimental site and set up is given by Velthof and Oenema (1995b). Briefly, N_2O fluxes were measured on managed grassland at four contrasting sites in the Netherlands, a clay soil near Lelystad, a sand soil near Heino, and two peat soils near Zegveld, from March to November 1992. There were three grassland management treatments on each site, namely mowing without N fertilizer application, mowing in combination with N fertilizer application and predominantly grazing in combination with N fertilizer application. The experiments were laid out as randomized blocks, in three replicates. Fertilizer N was applied as calcium ammonium nitrate (CAN) in six or seven dressings.

Monitoring of N_2O fluxes

Fluxes were measured using vented closed flux chambers (Mosier, 1989). Flux chambers, PVC cylinders with an internal diameter of 20 cm and height of 15 cm, were inserted 3 cm into the soil using a knife, about 30 minutes before flux measurements started. All chambers were vented with a tube with an internal diameter of 0.3 cm and length of 20 cm, and were insulated with an aluminium foil cover to prevent pressure and temperature fluctuations in the flux chamber. Concentration of N_2O in the headspace was determined in the field at 0, 10, 20 and 30 minutes after closing the flux chamber, using a photo-acoustic spectroscopic infra-red gas analyzer of Brüel and Kjær. The analyzer was directly attached to six flux chambers via a multipoint sampler in a closed system (Figure 1), using polytetrafluorethylene tubes with an internal diameter of 0.3 cm and length of 400 cm. Gas samples were taken and analyzed for N_2O automatically every 90 s after the air in the headspace was pumped around for 20 s at a flow rate of 30 ml s^{-1}. Both gas analyzer and multipoint sampler were controlled using a portable computer, which also functioned as a data logger (Figure 1).
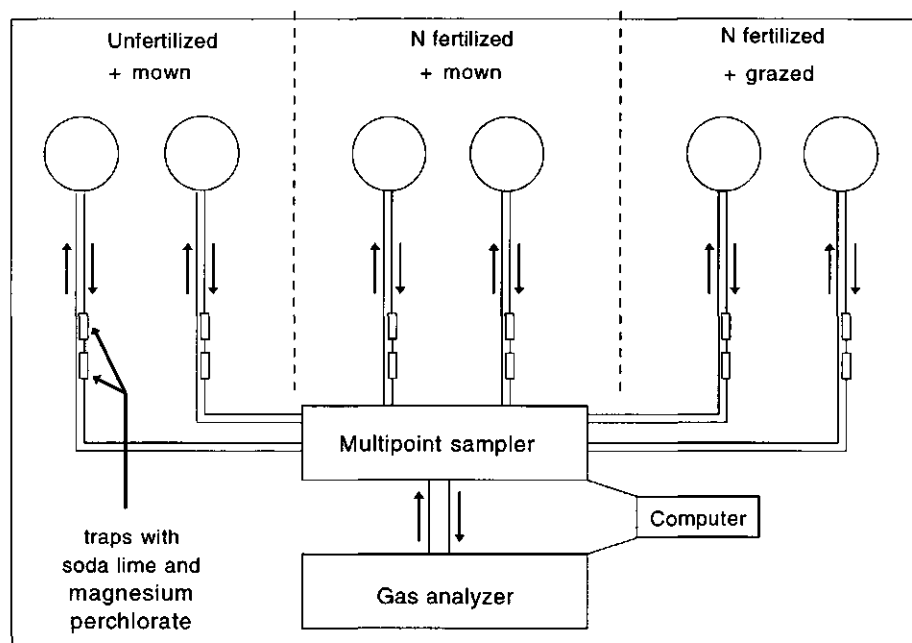

Figure 1. Schematic set-up of N_2O flux measurements. Six flux chambers were directly attached in a closed system to a multipoint sampler and photo-acoustic spectroscopic infra-red gas analyzer. Two flux chambers were placed in each plot, about 1 m apart.

The gas analyzer was fitted with optical filters to measure selectively concentrations of N_2O, carbon dioxide (CO_2) and water vapour (Velthof and Oenema, 1993). Concentration of N_2O was compensated for interferences of CO_2 and water vapour. Traps of soda lime and magnesium perchlorate were placed in the air stream to the gas analyzer to reduce variations in the concentration of CO_2 and water vapour respectively (Figure 1). The accuracy of the gas analyzer was about 5 % in the range of 300-5000 µl N_2O m^{-3} under field conditions. The measured N_2O concentrations in the headspace were corrected for the amount of N_2O which was pumped from one flux chamber into the next flux chamber. This amount was equal to the internal volumes of the multipoint sampler, gas analyzer and connecting tubes times the N_2O concentration. This internal volume was about 2.5 % of the headspace volume of the flux chamber. Fluxes of N_2O were calculated from the course of N_2O concentration in the headspace in time, using linear regression analysis.

All three treatments were measured simultaneously in duplicate (Figure 1). The three replicates (blocks) were measured sequentially, so that six flux measurements were carried out per treatment. The flux chambers were placed on the plots in stratified random design. All flux measurements at one site were carried out within three hours, usually between 9.00 and 12.00 a.m. Generally, fluxes were measured once per week. Incidentally, measurements of spatial variation of N_2O fluxes were made using 48 flux chambers within 4 hours using two gas analyzers.

Calculation of mean fluxes and total losses
The N_2O flux measurements were carried out in six replicates, a sample size too small adequately to determine the frequency distribution. In the literature it has been shown that frequency distributions of N_2O fluxes are generally positively skewed and better approximated by lognormal than normal distribution (e.g Ambus and Christensen, 1994; Folorunso and Rolston, 1984). Four methods were applied to estimate the sample mean of the six replicate fluxes, namely the arithmetic mean, the geometric mean, the lognormal mean and Finney's method.

The arithmetic mean is the common method to estimate the mean of populations which have a symmetric distribution, such as normally distributed populations, and it is the most used estimator of mean N_2O fluxes (e.g. Ryden, 1983). It is an unbiased estimator of the population mean, regardless of the form of the underlying distribution, but it is less efficient for skewed populations than for symmetric ones.

The geometric mean is the antilogarithm of the mean of logtransformed data. For lognormally distributed populations, the geometric mean is close to the sample median.

The geometric mean of a sample is a biased estimate of the population mean. The geometric mean or median have been used in N_2O-studies by e.g. Arah *et al.* (1991) and Skiba *et al.* (1993).

The lognormal mean is the geometric mean adjusted for the variance of the distribution (Aitchison and Brown, 1966). It is biased for sample size < 100 (Parkin *et al.*, 1988). The lognormal mean has been applied in studies dealing with spatial variability of nitrification, denitrification and mineral N contents in soils by e.g. Folorunso and Rolston (1984), Parkin *et al.* (1985), White *et al.* (1987), and Bramley and White (1991).

A minimum variance unbiased estimator of the mean of lognormally distributed populations was given by Finney (1941) and is described in detail by Aitchison and Brown (1966). Parkin *et al.* (1988) have recommended Finney's estimator as best estimator for samples of lognormal distributions and it has been used in recent N_2O-studies, e.g. Ambus and Christensen (1994), Clayton *et al.* (1994) and Hansen and Bakken (1993). However, Finney's method is not robust and may result in biased estimates when used for non-lognormal or contaminated lognormal distributions, especially for sample size < 40 (Koch and Link, 1970; Myers and Pepin, 1990).

Three of the four estimators are based on logtransformation. A part of the calculated fluxes were negative, but close to 0. Adding a positive value to all data to obtain positive values only does not solve this problem. Due to the transformations, the added value also changes, and thus cannot be readily substracted after the transformation. A reasonable alternative is to set all values below a certain value at a certain positive value. This is justified by the fact that negative fluxes were small and imprecise. For a comparison of the four methods, all single fluxes less than 3 µg N m^{-2} hr^{-1}, including the negative fluxes, were quite arbitrarily set at 2 µg N m^{-2} hr^{-1}. To assess the effect of this procedure, mean N_2O fluxes were also calculated with the four methods, after setting all fluxes less than 3 µg N m^{-2} hr^{-1} at 1 µg N m^{-2} hr^{-1} and at 3 µg N m^{-2} hr^{-1}.

Total N_2O loss was calculated for each treatment from the time course of the mean N_2O flux (n=6), by linearly interpolating the mean N_2O fluxes and integrating the area using the trapezoidal method (France and Thornley, 1984). This procedure was carried out for all four estimators of mean.

Results

Single N₂O fluxes

The determination coefficient R^2, derived from linear regression analysis of the N_2O concentration in the headspace in time, increased with increasing flux magnitude (Figure 2). In Table 1, frequency tabulations are given of all single N_2O fluxes measured per treatment per site, during the whole experiment. For all sites and treatments, many fluxes were fairly small, i.e. less than 25 µg N m^{-2} hr^{-1}, relatively few fluxes were large. Fluxes larger than 100 µg N m^{-2} hr^{-1} were found more often on fertilized and grazed than on unfertilized grasslands and more often on the peat soils than on the sand and clay soils. For all treatments negative fluxes were found (Table 1). These negative fluxes were close to 0, ranging from 0 to -19 µg N m^{-2} hr^{-1}, and imprecise (Figure 2).
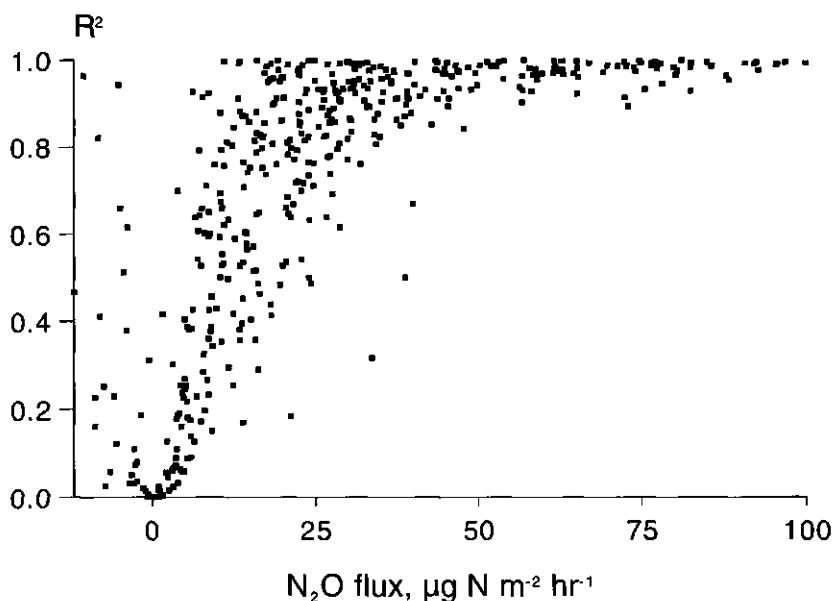
Figure 2. Relationship between calculated N_2O flux and the determination coefficient R^2, for all fluxes less than 100 µg N m^{-2} hr^{-1} of the sandy soil near Heino. Flux of N_2O was calculated using linear regression analysis of N_2O concentration in the headspace and time. Concentration of N_2O was measured four times, with intervals of 10 minutes. Values of R^2 of fluxes > 100 µg N m^{-2} hr^{-1} were > 0.99, generally.

Table 1. Frequency tabulations of all N_2O fluxes measured at the four sites during the experimental period. Fluxes of N_2O are expressed in μg N_2O-N m^{-2} hr^{-1}.

Treatment	Number of N_2O fluxes						
	< 0	0-25	25-50	50-100	100-500	> 500	Total
Sand							
Unfertilized-mown	22	111	45	10	1	0	189
N fertilized-mown	8	86	47	28	19	3	191
N fertilized-grazed	7	41	33	38	62	11	192
Clay							
Unfertilized-mown	42	112	23	13	3	0	193
N fertilized-mown	28	85	22	13	21	8	177
N fertilized-grazed	27	75	26	15	23	15	181
Peat I							
Unfertilized-mown	12	78	38	26	11	0	165
N fertilized-mown	9	40	26	35	41	14	165
N fertilized-grazed	4	43	32	33	34	17	164
Peat II							
Unfertilized-mown	11	47	41	40	64	33	236[a]
N fertilized-mown	5	21	21	14	44	24	129[a]
N fertilized-grazed	6	14	12	19	50	27	128[a]

[a] the mown and grazed treatment were not fertilized for the first cut; all fluxes measured till the second cut are from unfertilized grassland.

Mean N_2O flux per measurement time

Measurements of N_2O fluxes using 48 flux chambers indicated that the frequency distributions of N_2O fluxes were positively skewed (e.g. Figure 3), and better approximated by lognormal than normal distribution. The routine measurements of N_2O fluxes using six flux chambers indicated similar patterns, because the arithmetic mean was generally much larger than the geometric mean, by up to 7-fold (Figure 4). The arithmetic mean was much smaller than the lognormal mean, by a factor of 11 (Figure 4). The ratio between the mean derived from Finney's method and the arithmetic mean ranged from 0.6 to 2.5 and was on average 1.0.

The effects of setting fluxes less than 3 μg N m^{-2} hr^{-1} at 1, 2 or 3 μg N m^{-2} hr^{-1}

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were larger for the three estimators based on logtransformation than for the arithmetic mean (not shown). Effects were most significant for the lognormal mean. In some cases, the calculated lognormal mean of the six fluxes was even larger than the single fluxes. Generally, using the lognormal mean, setting the fluxes at 1 µg N m^{-2} hr^{-1} resulted in larger mean fluxes than setting fluxes at 3 µg N m^{-2} hr^{-1}.
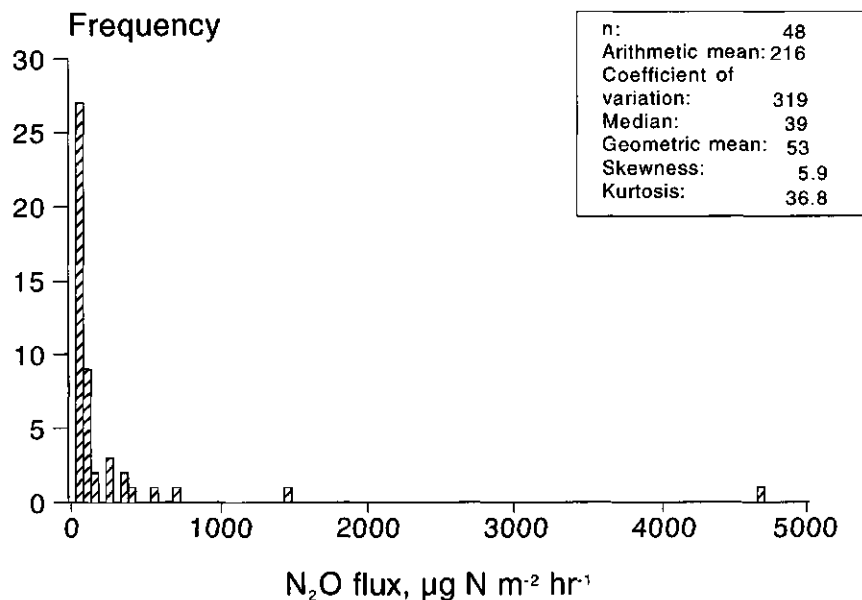
Figure 3. Frequency distribution of N$_2$O-fluxes, from 48 flux measurements carried out on grazed grassland on peat soil II, in September 1992.

Total N$_2$O losses during the experimental period
Peak fluxes were generally found after N fertilizer application and grazing, except during dry weather (Velthof and Oenema, 1995b). The increase of N$_2$O flux due to N application and the effects of grazing lasted one to three weeks, generally. Week-to-week variations were much smaller on unfertilized and mown swards than on fertilized and grazed swards, except for swards on the peat soil II (Velthof and Oenema, 1995b).

The estimate of total N$_2$O loss was smallest when derived from the geometric mean and the largest when derived from the lognormal mean (Table 2). The total N$_2$O losses calculated from arithmetic means and means derived from Finney's method were generally in good agreement. The results indicate that setting all fluxes less than 3 µg

N m^{-2} hr^{-1} at 2 µg N m^{-2} hr^{-1} did not affect or only slightly affected the estimation of total N$_2$O losses from arithmetic means (Table 2). This was also the case for the geometric mean and Finney's method, but the effect was much larger for the lognormal mean (not shown).

Figure 4. Relationship between arithmetic means and geometric means, arithmetic means and lognormal means and arithmetic means and means derived from Finney's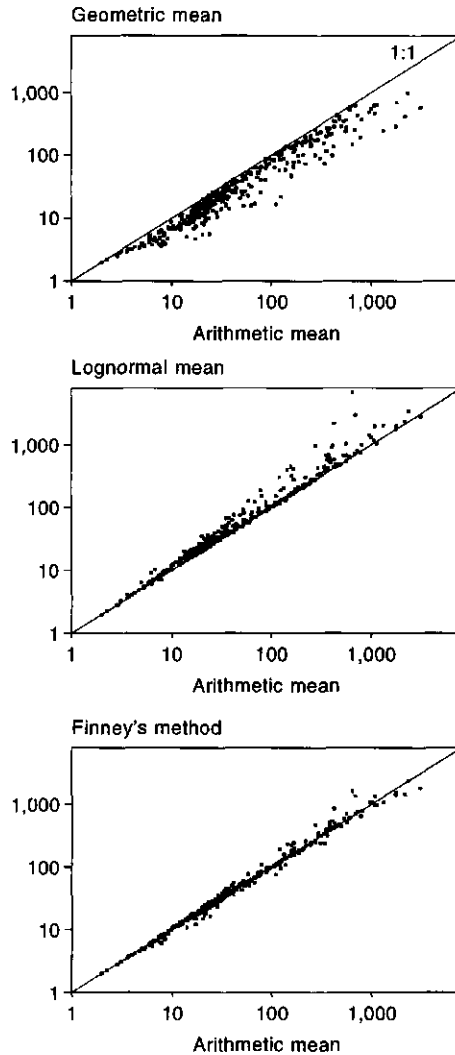 method. All means were calculated from six replicate N$_2$O fluxes and are expressed in µg N m^{-2} hr^{-1}. Note logarithmic scales.

Discussion

The calculation of total N_2O losses from soils using a flux chamber technique may be split into three parts, namely the measurement and calculation of single N_2O fluxes, the calculation of the mean flux from replicate flux measurements at one time, and the calculation of the total N_2O loss from the time course of the mean N_2O flux.

Single N_2O fluxes

For N_2O fluxes larger than about 25 µg N m^{-2} hr^{-1} the increase of N_2O concentration in the headspace was generally linear (Figure 2). This agrees with the results of other studies (e.g. Matthias *et al.*, 1980), in which also a linear increase of the N_2O concentration in the headspace was found. Apparently, the diffusion rate of N_2O from the soil to the headspace atmosphere was not significantly influenced by the increasing N_2O concentration in the headspace and no correction for a decreasing N_2O diffusion rate had to be applied, as suggested by e.g. Hutchinson and Mosier (1981). Therefore, all fluxes were calculated using linear regression analysis.

Table 1 shows that many fluxes were small, i.e. less than 25 µg N m^{-2} hr^{-1}. This confirms the findings of other studies on managed grassland, namely a fairly small background flux with relatively few large N_2O fluxes, mostly after rain, N fertilizer application and grazing (Christensen, 1983; Ryden, 1983). These small N_2O fluxes were measured inaccurately (Figure 2). Better accuracy for small fluxes could have been obtained by increasing the closure time of the flux chamber and decreasing the ratio headspace volume to soil area. Such measures may, however, contribute to a greater disturbance of the micro climate in the headspace, which is unwanted because it may affect N_2O flux. Accuracy could also have been improved by more accurate measurement of N_2O concentration or by increasing the number of the measurements. Both of these measures require better facilities and more time, and are therefore not easily applicable. It may also be questioned whether an increased accuracy of small fluxes would have contributed much to accuracy of the estimated total N_2O loss. Our calculations indicate that the few large fluxes (fluxes > 100 µg N m^{-2} hr^{-1}) contributed more strongly to the estimated total N_2O loss than the larger number of small fluxes, except to some extent for unfertilized grasslands. For these reasons, we decided not to attempt to increase the accuracy of measurement of the small fluxes.

Negative fluxes suggest adsorption of N_2O from the atmosphere, though they may be caused by experimental error (Figure 2). Ryden (1983) suggested that the grassland soil may absorb N_2O from the atmosphere during dry periods when grass growth

suffers from shortage of N. Absorption of N_2O by the soil is a sink of atmospheric N_2O, but its contribution to the global N_2O budget is still uncertain (Bouwman, 1995).

Table 2. Calculated total N_2O losses during the experimental period, using the four estimators of the mean.

Treatment	Total N_2O losses in kg N ha^{-1}				
	Arithmetic mean		Geometric mean[b]	Lognormal mean[b]	Finney's method[b]
	All values[a]	Positive values[b]			
Sand					
Unfertilized + mown	1.0	1.0	0.8	1.2	1.1
N fertilized + mown	2.7	2.7	2.1	3.0	2.8
N fertilized + grazed	7.1	7.1	4.3	9.0	7.1
Clay					
Unfertilized + mown	0.8	0.9	0.6	1.0	0.9
N fertilized + mown	4.7	4.8	3.1	5.8	4.8
N fertilized + grazed	10.7	10.7	4.4	25.8	11.3
Peat I					
Unfertilized + mown	2.0	2.0	1.4	2.6	2.2
N fertilized + mown	8.2	8.2	5.6	10.2	8.6
N fertilized + grazed	12.1	12.2	6.9	19.3	13.3
Peat II					
Unfertilized + mown	11.0	11.1	5.0	13.1	10.7
N fertilized + mown	17.2	17.2	9.6	21.9	17.7
N fertilized + grazed	32.3	32.3	12.8	38.3	27.7

[a] including negative values

[b] all values < 3 μg N m^{-2} hr^{-1} were set at 2 μg N m^{-2} hr^{-1}

Mean N_2O flux per measurement time

The estimators of the mean had a large effect on mean N_2O fluxes per measurement time (Figure 4) and total N_2O losses (Table 2). Mean fluxes and total losses calculated from the arithmetic mean and the mean of Finney's method were in reasonable agreement, but geometric and lognormal means greatly differed from the arithmetic mean and the mean of Finney's method (Figure 4 and Table 2). The question that

arises is, what is the most appropriate estimator of the mean flux in this study? Criteria that are important in choosing the most appropriate estimator are that the estimator should be unbiased, efficient, and robust.

The frequency distribution of the N_2O fluxes provides the first argument, generally. In this study, fluxes were determined from six replicate measurements, a sample size too small to determine the frequency distribution. The large difference between arithmetic mean and geometric mean (Figure 4), and the measurements using 48 flux chambers suggest that the distributions were positively skewed. It is questionable, however, to state that the distribution of N_2O fluxes were always approximately lognormal during the experiment. Frequency distribution of N_2O fluxes from soils may change during a year because of changes in moisture and mineral N contents of the soil and temperature, as also pointed out by Tiedje *et al.* (1989). Obviously, the exact frequency distributions of the N_2O fluxes at each measurement time, the extent of skewness of the distribution and possible changes of the distribution in time are uncertain. The arithmetic mean is unbiased, regardless of the form of the distribution, whereas the lognormal mean and Finney's method may be biased when applied to non-lognormal distributions. The geometric mean is a biased estimator of the mean of lognormal distributions.

Another important argument in the choice of an estimator arises from the occurrence of negative fluxes. When using the arithmetic mean negative fluxes can be included. When using the geometric mean, lognormal mean and the mean of Finney's method, the negative fluxes can not be included in the calculations because all three estimators are based on logtransformed N_2O fluxes. Setting negative fluxes at a certain positive value strongly affected lognormal mean and, to a lesser extent, also the mean of Finney's method. Our results indicate that a small change in the value of one of the six replicate measurements may greatly affect the mean of estimators based on logtransformed values, suggesting low robustness of these estimators. The arithmetic mean was not or only slightly affected by a small changes in one of the six replicates, indicating that the arithmetic mean was robust.

Myers and Pepin (1990) reported that the arithmetic mean is more robust than Finney's method and recommended the arithmetic mean in stead of Finney's method in cases that it is uncertain that the data follow lognormal distribution. This indicates that because of the uncertainty about the exact distributions Finney's method is less suitable than the arithmetic mean as estimator of the mean flux per measurement time in the present study.

In conclusion, because of the small sample size, the uncertainty about the frequency

distribution at each measurement time, the sensitivity of the estimators based on logtransformed data and the problems associated with negative fluxes, the arithmetic mean seems to be the most straightforward and robust estimator in this study. We therefore prefer this estimator for the calculation of mean N_2O fluxes per measurement time.

Total N_2O losses during the experimental period

Total N_2O losses were calculated by linear interpolation of the mean fluxes per measurement time and integration over time, assuming that the results of flux measurements carried out during morning were representative for day and night. Several papers report distinct diurnal variations in N_2O flux from soils, due to diurnal variations in temperature and moisture contents in the soil (e.g. Christensen, 1983; Conrad _et al._, 1983). Minimum fluxes were observed during early morning, and maximum fluxes during the afternoon in these studies. Assuming diurnal patterns with small fluxes during early morning and large fluxes during the afternoon, it is reasonably to suggest that the mean N_2O flux derived from flux measurements carried out between 9.00 and 12.00 a.m., as in the present study, is representative for the mean flux over that day.

Fertilizer N application and grazing greatly increased N_2O fluxes for one to three weeks, when soils were sufficiently wet. This suggests that flux measurements during the first weeks after fertilizer application and grazing are essential for reliable estimation of total N_2O losses. Daily measurements indicate that the increase in N_2O flux following application of N fertilizer and urine may vary greatly, both in terms of flux magnitude and duration (e.g. Velthof and Oenema, 1993). A model pattern of the time course of N_2O flux after fertilizer application and grazing cannot be readily inferred because of the complexity of temporal variability in the major factors controlling N_2O production in soil. Obviously, daily measurements would provide a more accurate total N_2O loss than weekly measurements, but we did not have the resources to make them, as in most of this type of monitoring studies. Weekly measurements seem to give reasonably accurate estimates for intensively managed grasslands receiving frequent N fertilizer applications, when viewed over a whole growing season or several years. The weekly measurements will be continued for two years on all treatments and sites, and additional daily measurements, simultaneous measurements with micrometeorological methods in combination with modelling might provide a check on the accuracy of the total N_2O loss from grassland as calculated from weekly measurements using six replicates. Because of the unpredictable time

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course of N_2O fluxes, linear interpolation of the weekly flux seems to be the most straightforward procedure for the calculation of N_2O losses at this moment.

Acknowledgements

CHAPTER 3

Nitrous oxide fluxes from grassland in the Netherlands: II. Effects of soil type, nitrogen fertilizer application and grazing

Nitrous oxide fluxes from grassland in the Netherlands: II. Effects of soil type, nitrogen fertilizer application and grazing

Summary

Intensively managed grasslands are potentially a large source of nitrous oxide (N_2O) in the Netherlands because of the large nitrogen (N) input and the fairly wet soil conditions. To quantify the effects of soil type, N fertilizer application and grazing on total N_2O losses from grassland, fluxes of N_2O were measured weekly from unfertilized and mown, N fertilized and mown, and N fertilized and predominantly grazed grassland on a sand soil, a clay soil, and two peat soils during the growing season of 1992. Total N_2O losses from unfertilized grassland were 2.5 to 13.5 times more from the peat soils than from the sand and clay soils. Application of calcium ammonium nitrate fertilizer significantly increased N_2O flux on all sites, especially when the soil was wet. The percentage of fertilizer N applied lost to the atmosphere as N_2O during the season, ranged from 0.5 on the sand soil to 3.9 on one of the peat soils. Total N_2O losses were 1.5 to 2.5 times more from grazed grassland than from mown grassland, probably because of the extra N input from urine and dung. From 1.0 to 7.7% of the calculated total amount of N excreted in urine and dung was emitted as N_2O on grazed grassland. The large N_2O losses measured from the peat soils combined with the large proportion of grassland on peat in the Netherlands, mean that these grasslands contribute significantly to the total emission from the country.

Introduction

Nitrous oxide (N_2O) is a trace gas that possibly contributes to the depletion of stratospheric ozone (Crutzen, 1970) and to global warming (Wang et al., 1976). Soil is a major source of N_2O, where it is produced during microbiological nitrification and denitrification, controlled primarily by the availability of mineral nitrogen (N), oxygen (O_2) and, in case of denitrification, also mineralizable carbon (C) (Firestone and Davidson, 1989).

Soil type may affect the N_2O emission, but the relation between soil type and N_2O flux is difficult to predict because of the various chemical and physical soil properties that directly and indirectly control N_2O fluxes. In general, larger N_2O fluxes may be expected from clayey soils than from sandy soils, because they are wetter and partially

anaerobic from time to time. In addition, large fluxes are expected from peat soils, because they contain much organic C. Large N_2O losses were found on peat soils in the USA by Duxbury *et al.* (1982).

In the Netherlands, intensively managed grassland is a potentially large source of N_2O, because grassland covers 30% of the total surface area, the N input is large and many soils have a high groundwater table and are wet therefore. In such intensively managed grassland, there is a large cycling of C and N due to the effects of fertilizer and manure application and the effects of grazing animals.

Results of field studies elsewhere indicate that losses of N_2O from ammonium nitrate fertilizers applied in several dressings to mown grassland are about 1 to 2% of the amount of N applied (McTaggart *et al.*, 1994; Ryden, 1983). Patches of urine in grazed grasslands are also a significant source of N_2O (e.g. De Klein and Van Logtestijn, 1994), predominantly because these patches contain much mineral N and also easily mineralizable organic C. At the end of the season up to 40% of the total surface area of intensively managed grasslands with about 5 grazing cycles may be affected by urine and about 4% by dung (Lantinga *et al.*, 1987). As a consequence, the soil contains more available N and C in grazed grasslands than in mown grasslands.

A comparison of the integral effects of grazing versus mowing on N_2O flux from grassland on various soil types and during a whole growing season has not been carried out, thus far. In the monitoring study described here, N_2O fluxes from grazed and mown grasslands were measured weekly during the growing season of 1992 on a sand soil, clay soil and two peat soils in the Netherlands. Two peat soils were included in this study because i) more than 25% of the grassland area in the Netherlands is located on peat soils and ii) peat soils are expected to be large emitters of N_2O. The two sites on peat soil differ in mean groundwater level (GWL) and in organic N and C contents. The major factors controlling N_2O fluxes from the soil are assessed using the data on fluxes, soil, and weather. Special attention is given to the relations between N_2O fluxes and denitrification potentials (DNP) and organic C mineralization potentials (CMP) of the soils. We describe the methodology of the estimation of mean fluxes and total N_2O losses in Part I (Velthof and Oenema, 1995a). Here, the emphasis is given on the effects of soil type and grassland management on N_2O fluxes and losses, based on the mean fluxes.

Materials and methods

Experimental sites

Fluxes of N_2O were measured from March to November 1992 at four grassland sites (Figure 1): a sand soil near Heino (52°26'N 6°14'E), a calcareous clay soil near Lelystad (52°30'N 5°30'E), and two peat soils near Zegveld (52°08'N 4°48'E). Peat soil I had a mean GWL of 40 cm below soil surface during the experimental period, and peat soil II had a mean GWL of 55 cm. Both peat soils were clayey peats originating from reeds and sedges. Contents of total N, total C and clay, and the pH of the 0-20 cm layers, and the bulk density of the 0-30 cm layers are given for all soils in Table 1. Soil classification (FAO) and total amounts of rainfall during the experiment are also given in Table 1. Perennial ryegrass (*Lolium perenne* L.) was the dominant grass species in all swards.

Figure 1. Map of the Netherlands showing the experimental sites.

Table 1. Soil properties of the 0-20 cm layers and total rainfall during the experimental period, for each site.

Property	Site			
	Sand	Clay	Peat I	Peat II
Total N, g kg^{-1}	2.5	2.4	16.3	18.6
Total C, g kg^{-1}	30	27	156	223
pH-KCl	5.5	7.2	5.0	4.7
Clay content ($\leq$ 2 µm), g kg^{-1}	51	295	284	287
Dry bulk density[a], kg dm^{-3}	1.35	1.30	0.52	0.45
Soil classification (FAO)	Fimic Anthrosol	Calcaric Fluvisol	Terric Histosol	Terric Histosol
Total rainfall, mm	520	570	540	540

[a] of the 0-30 cm layer

Treatments

At each site the experiment was designed with complete randomized blocks, with three treatments in three replicates. The treatments were mown grassland without N fertilizer applications, mown and N fertilized grassland and predominantly grazed and N fertilized grassland. The plots on which N_2O fluxes were measured were 2.5 m x 20 m. Each grazed plot was part of a grazed grassland area of 20 m x 20 m. Fertilizer N was applied as calcium ammonium nitrate (CAN), in six or seven dressings (Table 2). The economic optimum application rates of N fertilizer were assessed using an interactive fertilization system based on a combination of modelling and measuring soil mineral N and N uptake (Wouters and Vellinga, 1994). Fertilizer N was applied three days after mowing or grazing. The application rates for the grazed grasslands were equal to those of the mown grasslands (Table 2). The stocking density was adjusted in such a way that the dairy cattle could graze on clay and peat soils in about one day and on the sand soil in about two days, when herbage yield was about 1700 kg dry matter ha^{-1}. The predominantly grazed grasslands were mown once, at the end of the regrowth after the second grazing. Total N input by urine and dung of the grazing cattle was calculated using standard procedures and data of the amount, type and N contents of the feed consumed by the cows, the number of grazing days and the production of milk (Bussink, 1994).

Table 2. Fertilizer N application rates (kg N ha^{-1}) for all sites.

Site	Cut number/grazing cycle							
	1	2	3	4	5	6	7	Total
Sand	46	61	85	32	10	32	47	313
Clay	67	58	85	24	8	35	-	277
Peat I	28	61	73	15	34	55	-	266
Peat II	0	40	53	0	4	16	48	161

Measurement of N$_2$O fluxes and soil variables

Vented closed flux chambers and a photo-acoustic infra-red gas analyzer and multipoint sampler directly attached to the chambers were used to measure N$_2$O fluxes in the field. A detailed description of procedures for the measurement and calculation of the N$_2$O fluxes is given in Part I (Velthof and Oenema, 1995a).

The DNP is defined as the maximum rate at which nitrate (NO$_3^-$) will be reduced under anaerobic conditions without addition of exogenous reductant (Focht, 1978) and CMP is defined as the rate at which organic C is mineralized under aerobic conditions. The DNP and CMP were determined once, in the 0-5, 5-10, 10-20, 20-40 and 40-60 cm layers of the four soils using procedures similar to those of Bijay-Singh *et al.* (1988) and Burford and Bremner (1975). The DNP was determined at 20 °C from the linear increase of the N$_2$O concentration in the headspace of 1-ℓ bottles, during incubation of 100 g field moist soil to which KNO$_3$ was added (100 mg NO$_3^-$-N kg^{-1} soil), in a N$_2$ atmosphere containing 5% acetylene (C$_2$H$_2$). The CMP was calculated from the linear increase of the concentration of carbon dioxide (CO$_2$) in the headspace of 1-ℓ bottles during aerobic incubation at 20 °C of 100 g field moist soil samples. The DNP and CMP were determined using a photo-acoustic infra-red gas analyzer for analysis of N$_2$O and CO$_2$ concentration.

Soil water content of the 0-30 cm layers was determined gravimetrically once per week by drying at 105 °C for 24 hours. Soil temperature was measured at a depth of 5 cm. Total soil mineral N (NH$_4^+$-N + NO$_3^-$-N) contents of the 0-30 layer were also determined weekly on each treatment, in 4 replicates. Each sample was composed of 15 cores (diameter 3 cm) from one plot. Mineral N content was analyzed after extraction of 50 ml field moist soil in 100 ml of 1 M NaCl solution, using standard

auto-analyzer techniques. Mean GWL was calculated from weekly readings of water level in 12 perforated pipes (internal diameter 4 cm) per site. The amount of rainfall was measured daily.

Mean water-filled pore space (WFPS) of the 0-30 cm soil layers was calculated to compare the moisture status of the different soils (Davidson, 1991). Standard procedures were used to calculate the density of the solid phase ρ_s, the porosity ϕ, and WFPS.

Statistical analysis

For each site, the significance of the difference between N_2O fluxes from the treatments was assessed by analysis of variance (ANOVA) and Least Significance Difference (LSD) test at 5% significance level. Variance was analyzed for each measurement time separately, with treatment as source of variation. All fluxes were transformed to natural logarithms to obtain stable variance. In case one or more of the 18 fluxes per measurement time (three treatments times six replicates) was negative (Velthof and Oenema, 1995a), a value was added to all 18 fluxes to obtain only positive values with 2.0 as minimum.

For each site, multiple linear regression analyses were carried out using the following model:

$$F = \alpha + \beta N + \gamma W + \delta W^2 + \varepsilon T,$$

in which F is the N_2O flux in $\mu g\ N\ m^{-2}\ hr^{-1}$ transformed to natural logarithm, N is the mineral N content of the 0-30 cm layer in kg N ha^{-1}, W is WFPS of the 0-30 cm layer in % and T is temperature at 5 cm depth in °C. The variable W^2 was included, because the relationship between WFPS and N_2O flux as suggested by Davidson (1991), can be fitted with a quadratic function. All treatments were included in the regression analyses. On pooled data of all sites, multiple linear regression analysis was carried out, using the following model:

$$F = \alpha + \beta N + \gamma W + \delta W^2 + \varepsilon T + \zeta D$$

in which D is the denitrification potential of the 0-10 cm layer in kg N ha^{-1} day^{-1}, assuming that the DNP of the 0-10 cm layer was a major factor causing the differences in N_2O fluxes between the soils. All statistical analyses were carried out using Genstat 5 (Genstat 5 Committee, 1987).

Results

DNP and CMP

For all soils, both DNP and CMP strongly decreased with increasing depth (Table 3). The largest difference was between the 0-5 and 5-10 cm layers. The DNP of the peat soils was much larger than those of the sand and clay soils. The DNP of the 0-5 cm layer was larger for the clay soil than for the sand soil, but the DNP of the deeper layers of these soils were in the same range. The CMP of the sand soil was less than that of the other soils. For all sites DNP and CMP were correlated. However, the relation between DNP and CMP was specific to individual sites, i.e. at equal CMP, DNP was about twice as much on the peat soils than on the sand and clay soil.

Table 3. Denitrification potentials (DNP) and organic C mineralization potentials (CMP) of the 0-5, 5-10, 10-20, 20-40 and 40-60 cm layers of the soils.

Layer cm	DNP, mg N kg^{-1} dry soil day^{-1}				CMP, mg C kg^{-1} dry soil day^{-1}			
	Sand	Clay	Peat I	Peat II	Sand	Clay	Peat I	Peat II
0-5	19	30	103	87	85	161	216	191
5-10	8	6	30	37	38	69	63	77
10-20	3	4	13	12	20	40	25	26
20-40	4	2	12	4	14	29	37	32
40-60	0	1	13	5	0	22	43	20

N_2O fluxes

Fluxes of N_2O from unfertilized grassland on the sand and clay soils and peat soil I were small, less than 0.1 mg N m^{-2} hr^{-1}. By contrast, fluxes from the unfertilized treatment on peat soil II were high, up to 1.7 mg N m^{-2} hr^{-1} in April. Mineral N contents in the top 30 cm of the soil of unfertilized grassland were generally less than 35 kg N ha^{-1} in the sand and clay soils and peat soil I. Mineral N contents in unfertilized peat soil II were in the range of 30 to 50 kg N ha^{-1}.

Application of N fertilizer increased both mineral N contents and N_2O fluxes (Figures 2 and 3). There was no clear relation between magnitude of N_2O flux and the amount of fertilizer applied. The increase of N_2O flux after application of N fertilizer lasted 1-2 weeks generally. A total of seven out of 34 weekly measured fluxes on the

Figure 2. Time course of N₂O fluxes, mineral N contents and WFPS of the 0-30 cm soil layer, soil temperature at 5 cm depth and GWL for the sand soil and the clay soil. Thick arrows indicate time of N application and grazing and dotted arrows time of grazing without N application.
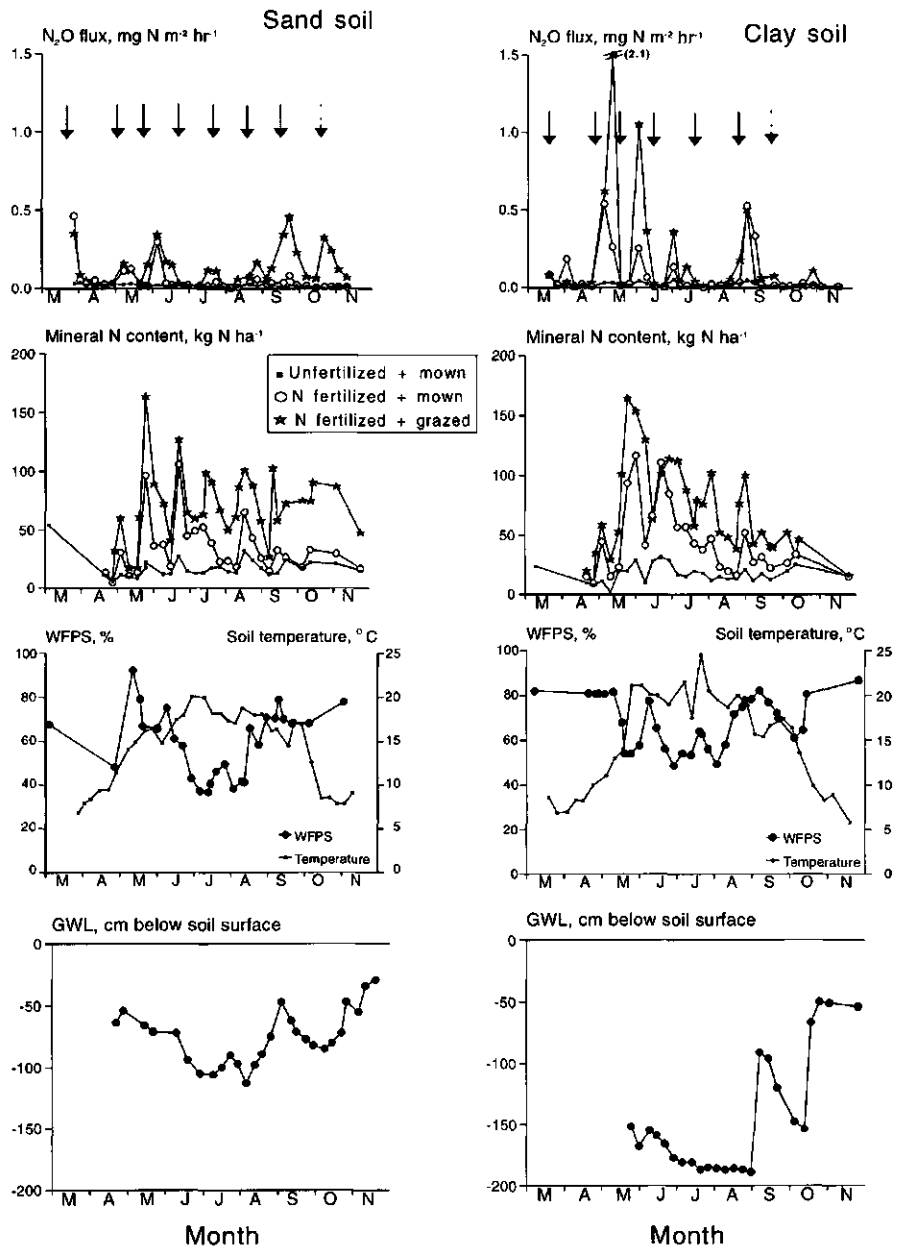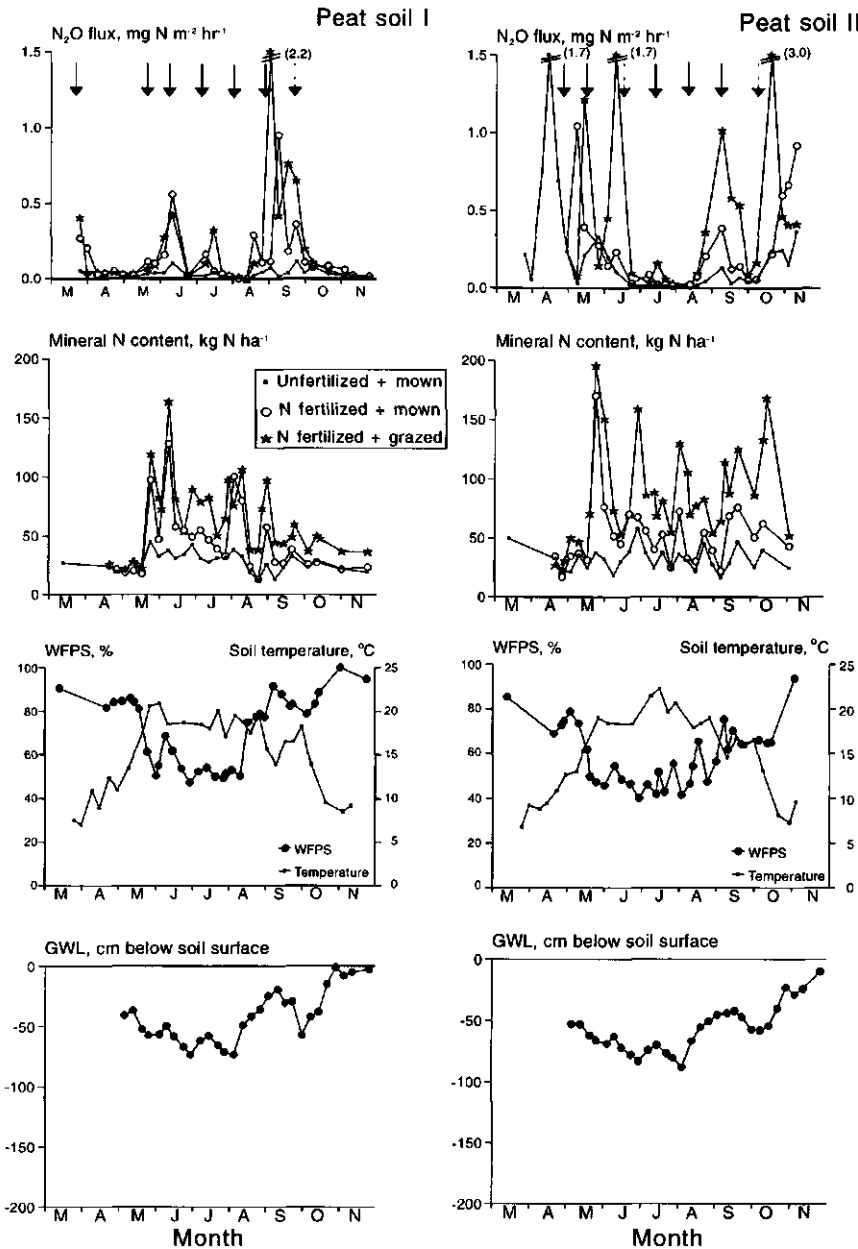
Figure 3. Time course of N_2O fluxes, mineral N contents and WFPS of the 0-30 cm soil layer, soil temperature at 5 cm depth and GWL for the peat soil I and the peat soil II. Thick arrows indicate time of N application and grazing and dotted arrows time of grazing without N application.

sand soil, eight out of 32 on the clay soil, nine out of 30 on peat soil I, and six out of 21 weekly measured fluxes on peat soil II were significantly larger on N fertilized and mown grassland than on unfertilized and mown grassland.

Both, soil mineral N contents and fluxes of N_2O were much larger on N fertilized and grazed grassland than on N fertilized and mown grassland (Figures 2 and 3). Fluxes were significantly larger from grazed grassland than from mown grassland in 18 out of the 28 weekly measurements after the first grazing on the sand soil, five out of the 27 on the clay soil, one out of the 23 on peat I and six out of the 21 on peat soil II.

The largest fluxes occurred when the soil was wet and the WFPS exceeded about 70%. Fluxes were smallest during the dry and warm period in June and July when WFPS of the 0-30 cm layer was less than 50%, for all sites. The GWL was much higher in the peat soils than in the sand and clay soils (Figures 2 and 3). In wet late-summer and autumn, WFPS and GWL increased strongly at all sites. Peat soil I was waterlogged in November.

The percentage of variance in N_2O flux accounted for ranged from 28% for all sites to 41% for peat soil II (Table 4). Mineral N contents and WFPS showed a significant effect in all regression models. Temperature was only a significant variable in the models for the sand soil and both peat soils.

Table 4. Results of multiple linear regression analyses. Models presented are models with highest values for R^2_{adj} including only significant independent variables.

Site	n	Model	R^2_{adj}
Sand	68	F = - 1.0 + 0.015N + 0.04W + 0.09T	0.34
Clay	63	F = -10.4 + 0.028N + 0.30W - 0.0016W^2	0.31
Peat I	73	F = -10.8 + 0.017N + 0.24W - 0.0011W^2 + 0.20T	0.36
Peat II	60	F = 3.0 + 0.018N + 0.04W - 0.10T	0.41
All	264	F = - 3.2 + 0.020N + 0.13W - 0.0007W^2 + 0.027D	0.28

Total N_2O losses

The order of total N_2O loss during the growing season was sand soil < clay soil < peat soil I < peat soil II for almost all treatments (Figure 4). Total N_2O losses were 1.5 to 6 times larger on N fertilized grasslands than on unfertilized grasslands and were 1.5 to 2.5 times larger on grazed grasslands than on mown grasslands.

Due to the differences in herbage yield, herbage N content (not shown) and

grazing days, the amount of N excreted via urine and dung on the grassland differed strongly between the sites, ranging from 195 kg N ha^{-1} for peat soil II to 430 kg N ha^{-1} for the sand soil (Table 5). The amount of N excreted via urine was about 3 times that via dung. The N fertilizer-derived N_2O losses ranged from 1.7 kg N ha^{-1} for the sand soil to 6.2 kg N ha^{-1} for both peat soils, or 0.5 to 3.9 when expressed in % of N applied as CAN (Table 6). The grazing-derived N_2O losses were larger than the N fertilizer-derived N_2O losses, except for peat soil I (Table 6).

Total N_2O loss, kg N ha^{-1}
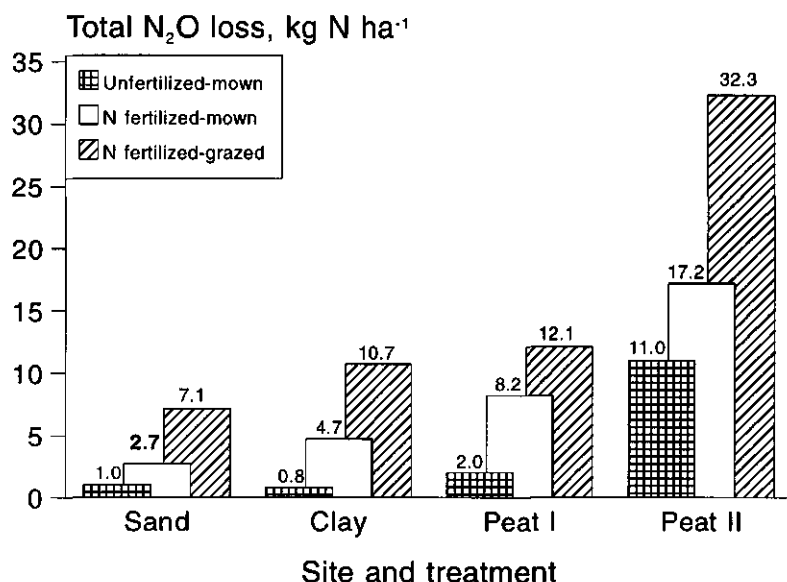
Figure 4. Total N_2O losses during the experimental period March-November 1992, for all sites and treatments.

At all sites, the total N_2O loss increased with increasing N input via N fertilizer, dung and urine (Figure 5). Remarkably, total N_2O losses from grazed grassland on sand soil, the treatment with the highest N inputs via N fertilizer, urine and dung, were lower than total N_2O losses from unfertilized grassland on peat soil II, with no N input via fertilizer, urine and dung.

Discussion

Soil type and N_2O fluxes and losses
The decrease in DNP and CMP with increasing soil depth is related to the distribution

of easily mineralizable organic C in grassland soils. The relation between CMP and DNP was not the same for all soils, suggesting that other factors than CMP controlled DNP in this study. This is in contrast with studies of Bijay-Singh *et al.* (1988) and Burford and Bremner (1975), who found a relation between DNP and CMP applicable for all the soil they studied. Differences in the presence and activity of bacterial populations may have contributed to the differences between the soils.

Table 5. Number of cow grazing days and calculated amounts of N excreted via dung and urine on the grazed grassland, for all sites and the whole growing season.

Site	Number of cow grazing days	Total excreted N, kg N ha^{-1}		
		Urine	Dung	Total
Sand	783	320	110	430
Clay	497	210	70	280
Peat I	475	185	70	255
Peat II	362	145	50	195

There was only a weak relationship between DNP or CMP and total N_2O losses from unfertilized and mown grassland. Results of the regression analyses indicate that DNP was a significant variable (Table 4), but the percentage accounted for was low. Yet, DNP and CMP, and total N_2O losses from unfertilized grassland were much larger on the peat soils than on the sand and clay soils, but there were remarkable differences between the two peat soils. Differences between the peat soils must be attributed to differences in GWL and actual mineralization rates. The larger mineral N content in the top 30 cm (Figure 3) and the smaller economically optimum N application rate (Table 2) both suggest that actual mineralization rates were larger on peat soil II than on peat soil I. Lowering the GWL of peat soils has been shown to greatly increase N mineralization rates (Williams and Wheatley, 1988) and N_2O emission (Martikainen *et al.*, 1993). Results of the present study also suggest that small differences in GWL (Figure 3) may contribute to large differences in N_2O emission. It must be noted, however, that possible differences in other soil variables may also have contributed. Peat soil I and peat soil II lie 1 km apart and have been managed differently, prior to this experiment.

Generally largest fluxes were found in the range of 60-80% WFPS, which is in

agreement with Davidson (1991), who suggested that the relation between WFPS and N_2O flux has an optimum. In three out of the five models of Table 4 (WFPS)^2 was a significant variable.

Table 6. N fertilizer-derived[*] and grazing-derived[**] N_2O losses in kg N ha^{-1} and in % of N applied as CAN or N excreted via dung and urine.

Site	N fertilizer-derived N_2O loss		Grazing-derived N_2O loss	
	kg N ha^{-1}	% of N applied	kg N ha^{-1}	% of N excreted
Sand	1.7	0.5	4.4	1.0
Clay	3.9	1.4	6.0	2.1
Peat I	6.2	2.3	3.9	1.5
Peat II	6.2	3.9	15.1	7.7

[*] losses from fertilized and mown grassland minus losses from unfertilized and mown grassland
[**] losses from fertilized and grazed grassland minus losses from fertilized and mown grassland

The large differences in total N_2O loss between the two peat soils was due in part to the large differences in N_2O fluxes in spring and autumn. During these periods, WFPS of peat soil II was lower (<80%) than that of peat soil I (>80%). Perhaps, N_2O was a more important end product of denitrification for the peat soil II than for the peat soil I.

Effect of N fertilizer application on N_2O fluxes and losses
At all sites, application of N fertilizer increased N_2O fluxes, generally for a maximum of two weeks. The flux patterns depicted in Figures 2 and 3 are typical for N_2O fluxes from grasslands fertilized in several N dressings (McTaggart *et al.*, 1994; Ryden, 1983). This pattern is due mainly to fluctuations in mineral N content in the soil (Figures 2 and 3), caused by fertilizer application, a rapid N uptake by grass roots and possibly microbial biomass, and losses by leaching, denitrification and volatilization. In all regression models (Table 4), mineral N content was a highly significant variable.

The N fertilizer-derived N_2O losses of the sand (0.5%) and clay soil (1.4%) are in the range of those reported in literature (Bouwman, 1995). The fertilizer-derived N_2O losses from the peat soils (2.3 and 3.9%) are large in comparison to those reported

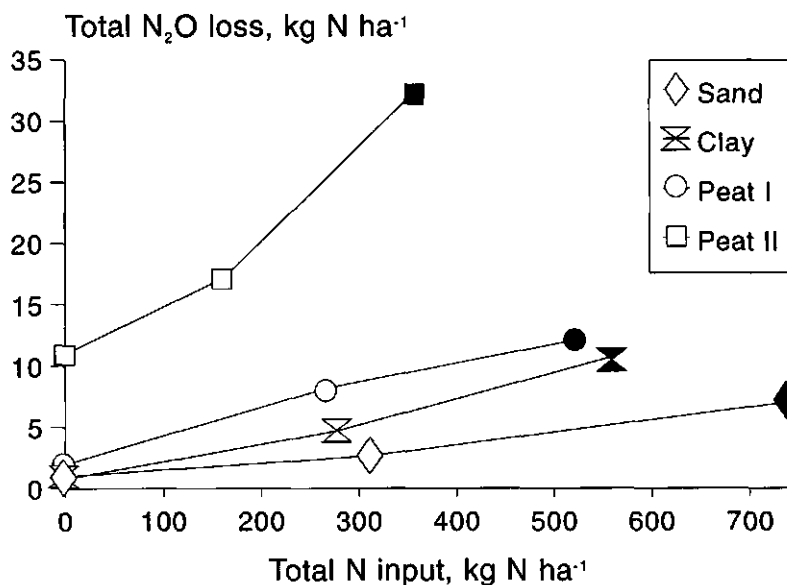in literature. This indicates that intensively managed grassland on peat soils is a large N_2O source.

Figure 5. Relationship between total N_2O loss during the experimental period and N input via N fertilizer, urine and dung, for all sites. Open symbols represent mown treatments and closed symbols represent grazed treatments.

Effect of grazing on N_2O fluxes and losses

Because the fertilizer applications were equal for the grazed and mown swards, the differences in N_2O fluxes and losses between the mown and grazed treatments (Figures 2, 3, 4 and 5) have to be attributed to the effects of the grazing animal, *i.e.* the N input via urine and dung and compaction of the soil by treading. The effect of excretal N is also shown by the increased soil mineral N contents of the grazed swards relative to those of the mown swards (Figures 2 and 3).

Dung and urine patches are significant sources of N_2O, because they contain much mineral N and mineralizable N and C. Denitrification losses from dung-affected and urine-affected areas have been shown to be large during wet conditions in autumn (Ryden, 1986). Production of N_2O in urine patchess may be enhanced due to inhibitory effects of high ammonia (NH_3) concentrations on nitrification leading to nitrite (NO_2) accumulation (Monaghan and Barraclough, 1992). In soils, NO_2 can be biologically and

chemically denitrified into N_2O (Firestone and Davidson, 1989). Moreover, grazing cows compact the soil by treading, thereby decreasing O_2 diffusivity in the soil, which may result in an increased denitrification rate and N_2O production. The large grazing-derived N_2O losses in comparison to the fertilizer-derived N_2O losses (Table 6) suggests that these mechanisms may have played a role in grazed grassland.

For the sand and clay soils and peat soil II, the grazing-derived N_2O losses, expressed in percentage of the N input via urine and dung, were roughly a factor 2 larger than the fertilizer-derived N_2O losses, expressed as percentage of the N input via N fertilizer. This difference may be the result of the stimulating effects of compaction of the soil and of dung and urine on N_2O flux from the grazed soil. In addition, the much larger total N input of grazed grassland compared to mown grassland is likewise important, because N_2O becomes a more important end product of denitrification when NO_3^- concentrations increase (Firestone and Davidson, 1989). For the peat soil I, grazing-derived N_2O loss was somewhat smaller than fertilizer-derived N_2O loss, in terms of % of the N input. The exact reason for this finding is yet unknown.

In conclusion, this study shows that both grassland management and soil type are major factors controlling N_2O losses from grassland. The strong increase of N_2O losses due to grazing shows that the effect of grazing has to be considered in N_2O budget calculations. The large N_2O losses from the peat soils, combined with the fact that more than 25% of the grassland area in the Netherlands is situated on peat soils, indicate that grasslands on peat soils are a major source of N_2O in the Netherlands.

Acknowledgements

CHAPTER 4

Seasonal variations in nitrous oxide losses from managed grasslands in the Netherlands

Seasonal variations in nitrous oxide losses from managed grasslands in the Netherlands

Summary

Seasonal and interannual variations in nitrous oxide (N_2O) losses from agricultural soils hamper the accurate quantification of the N_2O source strength of these soils. This study focuses on a quantification of seasonal and interannual variations in N_2O losses from managed grasslands. Special attention was paid to N_2O losses during the growing season and off-season as affected by grassland management. Fluxes of N_2O from grasslands with three different types of management and on four different soil types in the Netherlands were measured weekly during two consecutive years, using flux chambers. There were distinct seasonal patterns in N_2O losses, with large losses during spring, summer, and autumn but relatively small losses during the winter. These seasonal variations were related to fertilizer N application, grazing and weather conditions. Measurements of N_2O concentrations in soil profiles showed that a rise in groundwater level was accompanied by increased N_2O concentrations in the soil. Disregarding off-season losses would underestimate total annual losses by up to 20%, being largest for unfertilized grassland and smallest for N fertilized grazed grassland. Total annual N_2O losses ranged from 0.5 to 12.9 kg N ha^{-1} yr^{-1} for unfertilized grasslands to 7.3 to 42.0 kg N ha^{-1} yr^{-1} for N fertilized grazed grasslands. Despite the considerable interannual variations in N_2O losses, this study indicates that the results of measurements carried out in one year have predictive power for estimating N_2O losses in other years.

Introduction

There is still considerable uncertainty in the global nitrous oxide (N_2O) budget (Bouwman, 1995). Agricultural soils are suggested to be a major source of nitrous oxide (Bouwman, 1995), but quantification of its importance is hampered by the huge temporal and spatial variations in the flux (e.g. Clayton *et al.*, 1994; Conrad *et al.*, 1983; Webster and Dowdell, 1982). To overcome the uncertainties related with temporal variability, continuous measurements are needed throughout the whole year. In practice, most measurements are discontinuous and focus on the growing season (e.g. Conrad *et al.*, 1983; Ryden, 1983). The off-season period is neglected

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as being of minor importance. However, a study of Bouwman (1995) suggests, in part, that the off-season cannot be neglected when assessing total emissions and fertilizer-derived N_2O losses.

Distinct seasonal patterns of N_2O losses from grassland have been observed, caused by weather conditions and grassland management (e.g. McTaggart *et al*, 1994; Webster and Dowdell, 1982). Generally, losses are much higher during the growing season (spring, summer and autumn) than during the off-season (winter). The off-season losses from grassland are likely to be related to weather conditions and residual effects of fertilizer N and excretal N from grazing cattle, but little is known about these effects.

Improved knowledge of seasonal and interannual variations of N_2O losses from managed grasslands will improve the reliability of estimates of N_2O losses from grasslands. It can also help to set up strategies for field measurements in which N_2O losses are quantified. This study focuses on the relative importance of off-season N_2O losses as a function of previous grassland management. We hypothesize that N_2O losses in the off-season is strongly related to residual effects of fertilizer N and grazing in the previous growing season, and that N_2O loss in the off-season increases in the following order: unfertilized mown grassland < N fertilized mown grassland < N fertilized grazed grassland. We expect that groundwater level has a large effect on N_2O losses, because for example a shallow groundwater level will limit mineralization, nitrification and, thereby, denitrification rates, and it will also decrease the N_2O/N_2 ratio in denitrification (e.g. Martikainen *et al.*, 1993). To be able to detect its effect, groundwater level was recorded together with N_2O concentrations in the soil profiles, and N_2O surface fluxes.

Results of weekly flux measurements for two consecutive years on four sites with three management strategies each, were used to calculate the effects of seasons, years, fertilizer N application and grazing on the size of the N_2O losses.

Materials and methods

Experimental set-up
A detailed description of the sites and experimental set up is given by Velthof and Oenema (1995a and b). Briefly, N_2O fluxes were measured on intensively managed grasslands at four contrasting sites: a sand soil in Heino (FAO classification: Fimic Anthrosol), a clay soil in Lelystad (Calcaric Fluvisol) and two peat soils in Zegveld (Terric Histosols), during the period March 1992 to March 1994. Major differences

between the two peat soils was the difference in groundwater level (Table 1).

All grasslands had *Lolium perenne* swards and had been intensively managed for more than 10 years before the study was started. There were three grassland management treatments on each site, namely mowing without N fertilizer application, mowing with N fertilizer application and predominantly grazing with N fertilizer application. At each site the experiment was designed with complete randomized blocks, with the three management treatments in three replicates. Amounts of fertilizer N were assessed by using an interactive fertilization system aiming at economically optimum amounts, with equal portions on the mown and grazed swards (Vellinga *et al.*, 1996). Fertilizer N was applied as calcium ammonium nitrate (CAN) in six or seven dressings per year. Total fertilizer N application rates ranged from 161 kg N ha^{-1} for peat soil II in 1992 to 464 kg N ha^{-1} for peat soil I in 1993.

Grazing started at a target herbage yield of 1700 kg dry matter ha^{-1}. Stocking density was adjusted in such a way that the dairy cows were able to graze the sward for one to two days. Total N input via urine and dung excreted by the grazing cattle was calculated using standard calculation procedures (Bussink, 1994).

Fluxes and losses of N$_2$O

Fluxes of N$_2$O were measured in six replicates on a weekly basis using circular vented closed flux chambers with an internal diameter of 20 cm and a height of 15 cm, as described in detail by Velthof and Oenema (1995a). Concentrations of N$_2$O in the headspace of each flux chamber were determined *in situ* four times, with 10 minutes intervals, using a photo-acoustic spectroscopic infra-red gas analyzer of Brüel & Kjær, directly attached to the chambers. The relative standard deviation of replicate N$_2$O analyses with the gas analyzer was about 5% in the range of 300-1000 μl N$_2$O m^{-3} under field conditions. Flux of N$_2$O was calculated from the linear increase in N$_2$O concentration in the headspace of the chambers. All flux measurements at one site were carried out within 3 hours, usually between 9.00 and 12.00 hours. Mean fluxes (n=6) were calculated as arithmetic means (Velthof and Oenema, 1995a). Total N$_2$O losses were estimated by interpolation of the mean fluxes and integration of the area of the curve.

There are a number of possible limitations associated with closed flux chamber techniques when used for the quantification of total N$_2$O losses from soils, as discussed for example by Mosier (1989). A discussion of the advantages and possible methodological problems of the present flux chamber technique is given by

Velthof and Oenema (1995a). To be able to quantify total N_2O losses of three different management treatments at four different grassland sites during a period of two years, weekly flux measurements using flux chambers in six replicates per treatment was the maximum we could achieve.

Table 1. Seasonal variations in rainfall, soil temperature at 5 cm depth, groundwater level (GWL) and N input via N fertilizer and via urine and dung, for March-May (spring), June-August (summer), September-November (autumn) and December-February (winter) of both years.

Site and treatment	1992-1993				1993-1994			
	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter
Total rainfall, mm								
Sand	201	239	244	184	135	293	309	258
Clay	183	259	329	222	113	267	313	238
Peat I and II	146	257	272	145	102	281	256	255
Range in soil temperature, °C								
Sand	6.9-16.4	14.8-20.1	7.9-17.3	1.2-6.0	3.0-17.9	14.6-17.8	0.4-15.5	2.8-6.0
Clay	6.9-21.1	17.5-24.5	5.8-17.4	0.9-5.2	0.8-17.1	14.3-22.2	0.5-14.9	1.7-5.1
Peat I	7.0-20.6	17.1-20.9	8.5-18.3	0.6-7.6	2.8-15.2	14.3-17.9	2.6-16.1	0.6-6.0
Peat II	6.8-15.3	17.9-22.3	7.3-16.7	0.6-7.9	1.2-17.7	14.9-19.1	0.6-17.7	0.2-7.0
Range in GWL, cm								
Sand	49-71	75-122	8-86	10-65	45-80	24-95	20-49	0-62
Clay	152-169	155-189	54-154	47-58	93-99	60-90	57-69	26-83
Peat I	37-57	36-73	1-57	5-18	38-58	19-61	6-37	2-19
Peat II	53-66	56-88	10-58	16-34	48-67	37-74	13-57	2-40
N input[a], kg N ha^{-1}								
Sand	192 (136)	74 (147)	47 (147)	0 (0)	239 (112)	136 (121)	49 (69)	0 (0)
Clay	210 (135)	67 (102)	0 (43)	0 (0)	251 (93)	187 (157)	0 (43)	0 (0)
Peat I	89 (34)	123 (152)	55 (68)	0 (0)	230 (89)	234 (130)	0 (30)	0 (0)
Peat II	93 (68)	20 (76)	48 (50)	0 (0)	160 (77)	123 (86)	40 (58)	0 (0)

[a] total N input via N fertilizer for N fertilized grasslands. In parentheses: total N input via dung and urine, for grazed grasslands.

Concentration of N_2O in the soil, weather conditions and soil variables
Concentrations of N_2O in the soil atmosphere were measured at 5 depths (0-10, 10-20, 20-30, 30-40 and 40-50 cm) in N fertilized mown grassland on the sand soil

and on peat soil I, using sampling probes constructed of perforated PVC pipes of 7.5 cm internal diameter and 50 cm length. Each pipe consisted of 5 isolated compartments of 10 cm length and a volume of 0.44 L. The concentration of N_2O in each compartment was measured via two tygon tubes directly attached to the inlet and outlet of a photo-acoustic spectroscopic infra-red gas analyzer. The sample probes remained at the same place during the experimental period. Measurements were carried out weekly between August 1992 and July 1993, except in periods with high groundwater levels.

Mean soil temperature at 5 cm depth was determined weekly (during flux measurements) and rainfall was recorded daily, at all sites. Mean groundwater level was calculated weekly from water level readings in 12 perforated pipes (I.D. 4 cm) per site. Soil mineral N (NH_4^+-N + NO_3^--N) contents of the 0-30 cm layer of each treatment were determined weekly in 4 replicates during the growing season and about monthly during winter. Each sample was composed of 15 cores (diameter 3 cm) per plot. In the first year of the experiment 50 ml field moist soil was extracted in 100 ml of 1 M NaCl solution. In the second year, 10 g dry soil (24 hours drying at 40°C) was extracted in 100 ml 0.01 M $CaCl_2$ (Vellinga *et al.*, 1996). In the extracts, NH_4^+ and NO_3^- were analyzed using standard auto-analyzer techniques (Houba, *et al.*, 1989).

Results

Seasonal variations in weather conditions, groundwater levels and nitrogen input
Both years had similar patterns of rainfall, with a dry spring and a wet summer and autumn (Table 1). Winter was dry in 1992-1993. Highest soil temperatures at 5 cm depth were found in summer and ranged from 20 to 25 °C (Table 1). Both winter periods were relatively genial; there were no long periods of frost and the soil temperatures at 5 cm depth exceeded 0 °C at all occasions. However, the uppermost few cm of the soil were frozen sometimes during flux measurements. The median groundwater water level during the whole experimental period was 61 cm for the sand soil, 73 cm for the clay soil, 30 cm for peat soil I and 48 cm for peat soil II.

For all sites, groundwater levels were highest during autumn and winter, in both years (Table 1). Peat soil I was often nearly flooded during autumn and winter. Application of N fertilizer was concentrated in spring and summer (Table 1). The N input via dung and urine from grazing dairy cattle was largest in spring and summer (Table 1).

Concentration of N_2O in the soil

Typical N_2O concentration profiles of the N fertilized mown treatment of the sand soil and peat soil I are presented in Figure 1. Generally, concentrations increased with increasing soil depth. Concentrations were more than an order of magnitude higher in the peat soil than in the sand soil.

Effects of a rising groundwater level on N_2O concentrations in the sand soil are illustrated in Figures 1A to 1E, for the period 6 October to 23 November 1992. The rise in groundwater level between 14 and 27 October from 78 cm to 45 cm below soil surface coincided with an increase in N_2O concentration, at all depths. The strong increase in groundwater level in the second half of November markedly increased N_2O concentrations in the 0-10 cm layer (Figure 1E). This increase was accompanied with a strong increase in surface N_2O flux (not shown). The latest application of N fertilizer was 10 September, and soil temperature at 5 cm depth remained similar, 8-12 °C, between 6 October and 23 November, suggesting that N fertilizer application and changes in soil temperature were not involved in the changes in N_2O concentrations.

Variations in N_2O concentrations in peat soil I during the period 22 June to 26 July 1993 (Figures 1F to 1J) suggest that the 20-30 cm soil layer contained a major N_2O source. After N fertilizer application on 9 July and just before the rapid rise in groundwater level, N_2O concentration in the 20-30 cm layer increased from less than 20 to more than 200 µl l^{-1}. Apparently, optimum conditions for N_2O production were created in this layer where the descending NO_3^- front met the rising anaerobic front, during periods with heavy rainfall and rising groundwater levels. The rapid rise in groundwater level in the second half of July was accompanied by a strong increase in N_2O concentrations in the 0-20 cm soil layer (Figure 1J) and in surface N_2O flux (not shown).

Flux of N_2O tended to increase with increasing N_2O concentration in the 0-10 cm layer (Figure 2). The determination coefficient (R^2) between log transformed N_2O concentration in the 0-10 cm layer and log transformed surface N_2O flux was 23% for the sand soil (n=33) and 45% for the peat soil (n=25).

Seasonal variations in N_2O losses and soil mineral N contents

On all sites, N_2O fluxes from unfertilized mown grassland were generally smaller in the off-season (winter) than in the growing season (spring, summer, autumn) (Figure 3). Losses of N_2O from the sand soil, clay soil and peat soil I were ≤ 0.2 kg N ha^{-1} during winter; those from peat soil II amounted to 1.6 and 0.8 kg N ha^{-1} in
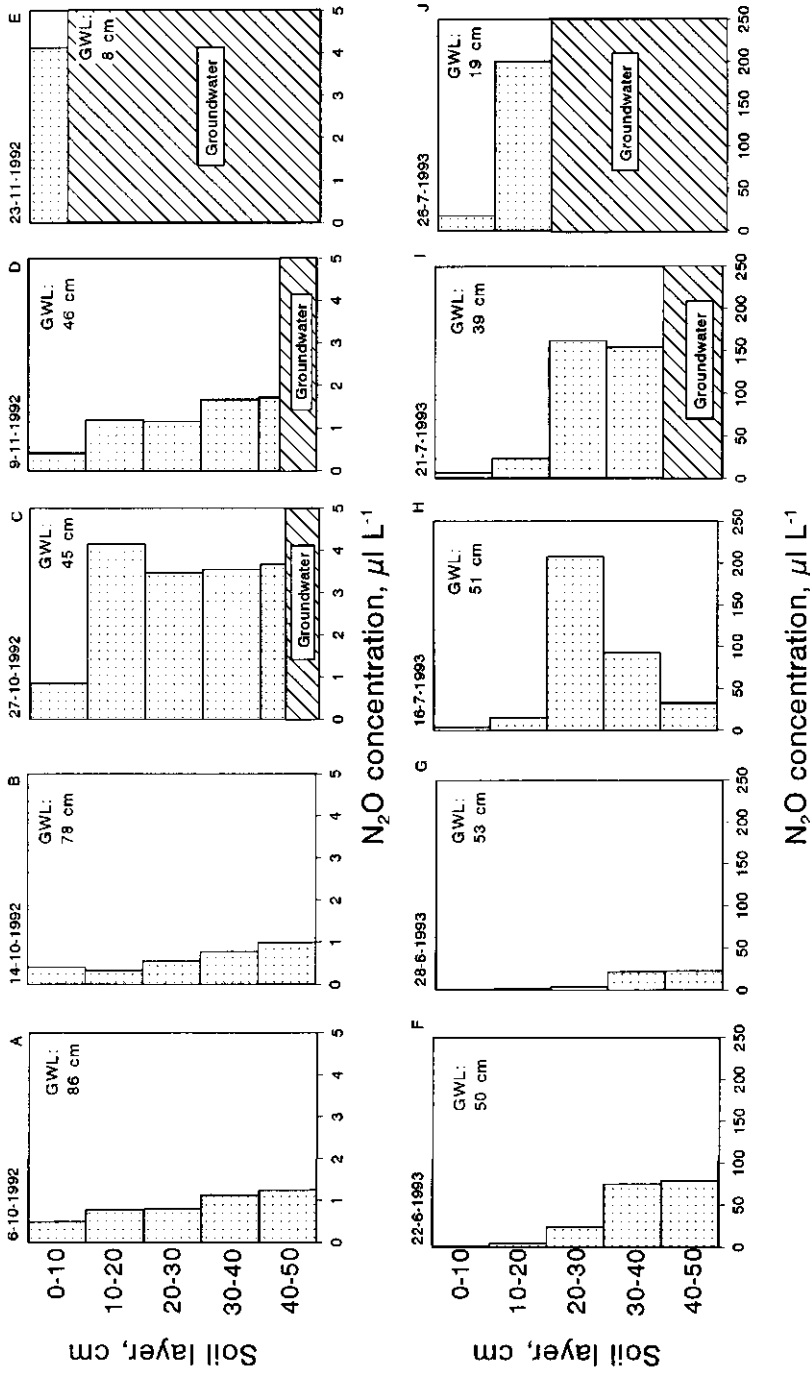
Figure 1. Typical N_2O concentration profiles in the soil of N fertilized mown grassland showing the effect of groundwater level (GWL) rise on N_2O concentrations. In Figures A to E, concentration profiles in the sand soil and in Figures F to J, concentration profiles in peat soil I. Note differences in scales of X-axes in the upper and lower graphs.

the first and second winter, respectively (Table 2). Significant fluxes were measured on peat soil II at times that the surface of the soil was frozen, suggesting that the subsoil was a source of N_2O. Mineral N contents in the top 30 cm of unfertilized mown grasslands showed seasonal patterns, with generally higher contents during the growing season than during winter (Figure 3). Mineral N contents were much higher in peat soil II than in the other soils (Figure 3).

Seasonal patterns in N_2O losses and mineral N contents were much more distinct for N fertilized than for unfertilized grasslands (Figure 4 and Table 2). Losses of N_2O were much larger in the growing season than in the off-season. Peak fluxes after N fertilizer application lasted 1-3 weeks, after which fluxes generally decreased to levels close to those of unfertilized grassland. Small fluxes were found during dry periods in summer and during winter. In winter, losses from N fertilized mown grasslands were similar to or slightly larger than those from unfertilized mown grasslands (Table 2).
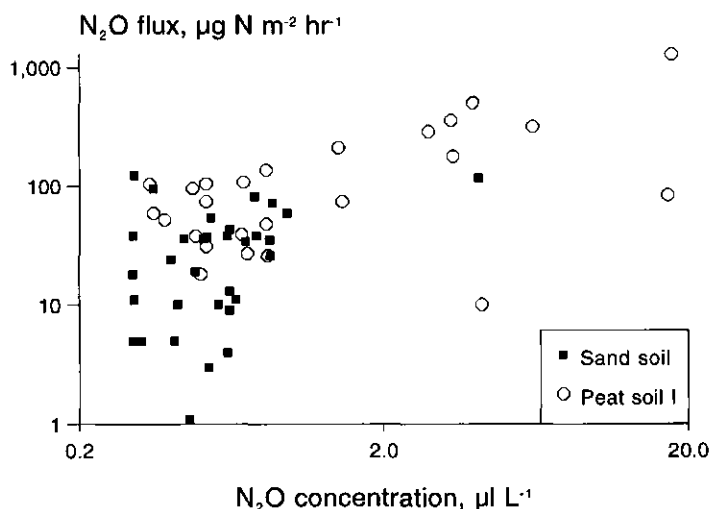
Figure 2. Relationship between N_2O concentration in the 0-10 cm soil layer and surface N_2O flux, for N fertilized mown grassland on the sand soil and peat soil I. Note logarithmic scales.

Fluxes and total losses of N_2O were much larger from grazed grasslands than from mown grasslands (Figure 4 and Table 2). Differences were most pronounced during summer and autumn, except for the clay soil where largest losses occurred during spring. During winter, fluxes from grazed grassland were similar to or

slightly larger than those from mown grassland.

Soil mineral N concentrations in grazed grasslands were high in the growing season but decreased in autumn and winter to a level similar to or slightly higher than those of mown grasslands (Table 3 and Figure 4). Mineral N contents in autumn were in the order: unfertilized mown < N fertilized mown < N fertilized grazed grasslands for all sites and both years (Table 3).

Table 2. Seasonal averaged losses of N_2O in kg N ha^{-1} and, in parentheses, as percentage of the total annual loss, for March-May (spring), June-August (summer), September-November (autumn) and December-February (winter) of both years.

Site and treatment	1992-1993				1993-1994			
	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter
Unfertilized-mown								
Sand	0.4 (33)	0.3 (25)	0.3 (25)	0.2 (17)	0.3 (30)	0.5 (50)	0.1 (10)	0.1 (10)
Clay	0.3 (30)	0.3 (30)	0.2 (20)	0.2 (20)	0.2 (40)	0.3 (60)	0.0 (0)	0.0 (0)
Peat I	0.4 (19)	0.7 (33)	0.8 (38)	0.2 (10)	0.5 (28)	0.9 (50)	0.4 (22)	0.0 (0)
Peat II	7.3 (57)	1.0 (8)	3.0 (23)	1.6 (12)	0.9 (21)	1.0 (24)	1.5 (36)	0.8 (19)
N fertilized-mown								
Sand	1.0 (32)	1.0 (32)	0.9 (29)	0.2 (6)	0.8 (12)	4.3 (65)	1.3 (20)	0.2 (3)
Clay	2.2 (44)	1.2 (24)	1.3 (26)	0.3 (6)	2.0 (77)	0.6 (23)	0.0 (0)	0.0 (0)
Peat I	1.1 (14)	3.0 (38)	3.7 (46)	0.2 (2)	1.2 (12)	6.8 (71)	1.5 (16)	0.1 (1)
Peat II	9.4 (47)	2.1 (10)	6.7 (33)	2.0 (10)	3.0 (19)	2.5 (16)	8.5 (53)	1.9 (12)
N fertilized-grazed								
Sand	1.3 (18)	2.1 (29)	3.5 (48)	0.4 (5)	3.1 (23)	8.3 (63)	1.7 (13)	0.1 (1)
Clay	5.9 (56)	3.2 (30)	1.2 (11)	0.3 (3)	14.4 (89)	1.2 (7)	0.5 (3)	0.0 (0)
Peat I	0.9 (8)	4.6 (39)	6.1 (51)	0.3 (2)	1.8 (10)	11.8 (68)	3.7 (21)	0.0 (0)
Peat II	9.4 (26)	7.1 (20)	15.4 (43)	4.1 (11)	2.6 (6)	11.4 (28)	25.2 (61)	1.8 (4)

Total annual N_2O losses and interannual variations

Annual losses from the sand soil, clay soil and peat soil I ranged from 0.5-2.1 kg N ha^{-1} yr^{-1} for unfertilized mown grassland to 7.3-17.3 kg N ha^{-1} yr^{-1} for N fertilized grazed grassland (Table 4). Annual losses from peat soil II were much larger, ranging from 4.2-12.9 kg N ha^{-1} for unfertilized mown grassland to 36.0-41.0 kg N ha^{-1} for N fertilized grazed grassland, despite the fact that N input was much lower than on the other sites (Table 4).

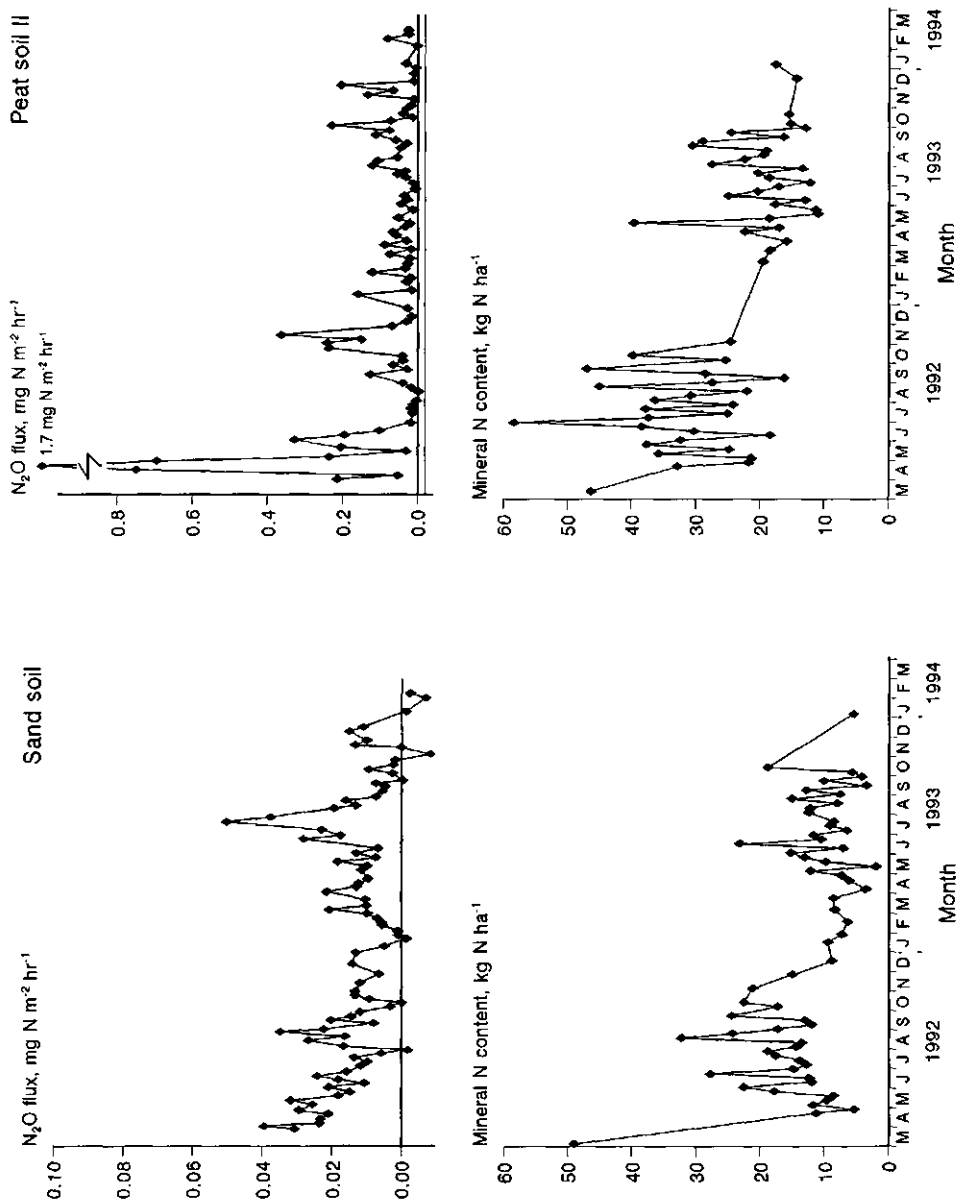**Figure 3.** Time course of N_2O fluxes and mineral N contents for unfertilized mown grassland on two contrasting sites, i.e. the sand soil and peat soil II. Note differences in scale of the Y-axes of the upper graphs.
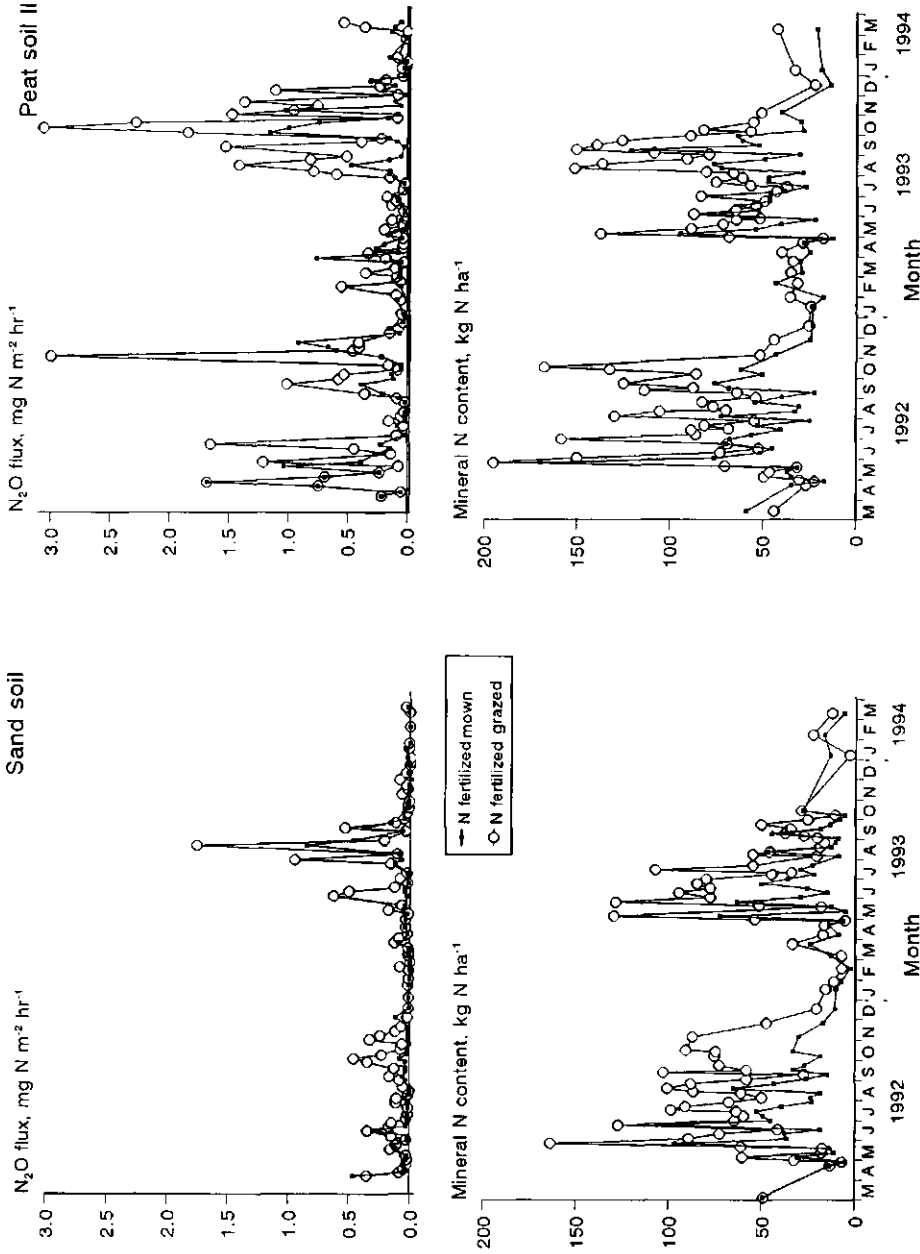
Figure 4. Time course of N_2O fluxes and mineral N contents for N fertilized mown and N fertilized grazed grassland on two contrasting sites, i.e. the sand soil and peat soil II.

Losses of N_2O from unfertilized mown grasslands were larger in the first year than in the second year at all sites (Table 4). By contrast, losses from grazed grassland were larger in the second year than in the first year, for all sites. Results for N fertilized mown grassland were intermediate; two sites showed larger losses in the first year and two in the second year.

The percentage of fertilizer N lost as N_2O on N fertilized mown grassland, averaged over the two years, ranged from about 1% for the sand and clay soils to 3.9% for peat soil II (Table 4). For the clay soil and both peat soils, the percentage of fertilizer N lost as N_2O was larger in the first than the second year. The percentage of dung and urine N emitted as N_2O was larger than the percentage of fertilizer N emitted as N_2O, and was larger in the second than in the first year, for all sites.

Table 3. Mineral N contents in kg N ha^{-1} in grasslands in the middle of October and in the middle of December in both years, for all sites and treatments.

Site	Treatment	1992		1993	
		October	December	October	December
Sand	Unfertilized-mown	22	9	19	6
	N fertilized-mown	33	11	28	14
	N fertilized-grazed	75	21	29	3
Clay	Unfertilized-mown	25	10	6	10
	N fertilized-mown	34	13	13	14
	N fertilized-grazed	33	12	28	26
Peat I	Unfertilized-mown	30	9	20	15
	N fertilized-mown	28	11	26	24
	N fertilized-grazed	50	21	34	32
Peat II	Unfertilized-mown	40	-	15	14
	N fertilized-mown	62	23	30	14
	N fertilized-grazed	133	26	56	23

Discussion

Variations in N_2O concentration in the soil

Temporal variations in N_2O concentrations in soils have been attributed to N fertilizer applications (Webster and Dowdell, 1982), changes in oxygen concentration in the soil (Egginton and Smith, 1986a) and rainfall (Goodroad and Keeney, 1985). The present study suggests that changes in N_2O concentration profiles were related, in part, to changes in groundwater level. A rise in groundwater level is accompanied by a displacement of soil air and a decrease in soil gas diffusivity. These changes will contribute to decreased O_2 concentration in the soil, increased denitrification activity and, possibly, increased N_2O production during nitrification. This in turn may contribute to increased N_2O concentrations in the soil (Figure 1) and to increased N_2O fluxes from the soil (Figure 2).
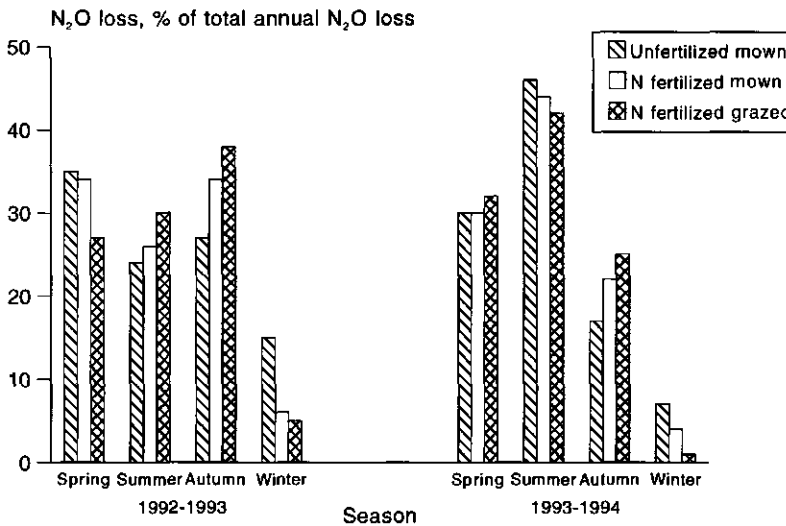
Figure 5. Relative N_2O losses in spring, summer, autumn, and winter in both years, in percentage of the total annual N_2O loss. Averages of all sites.

Concentration of N_2O in the soil and surface N_2O flux were weakly correlated (Figure 2). This confirms the results of other studies (e.g. Benckiser, 1994; Clayton *et al.*, 1994; Goodroad and Keeney, 1985). The weak correlation may be due to (i) a delay between N_2O production in the soil and emission from the soil surface, (ii)

absorption and/or dissolution of N_2O in the soil (water), and (iii) rapid production of N_2O near the soil surface with rapid diffusion of N_2O out of the soil. Another factor may be the large spatial variability of N_2O fluxes (Velthof and Oenema, 1995a).

Generally, N_2O concentration increased with increasing soil depth. Similar steady-state concentration profiles were also found by Benckiser (1994). They demonstrate, in part, the importance of N_2O production in the subsoil. The topsoil is generally the most active site for N_2O production, especially after N fertilizer application (e.g. Clayton et al., 1994). This is because N fertilizer application directly increases NO_3^- and NH_4^+ contents in the top soil and potential nitrification (MacDuff and White, 1985) and denitrification rates (Velthof and Oenema, 1995b) are much larger in the topsoil than in the subsoil of grasslands. However, due to higher moisture and lower oxygen contents in the subsoil N_2O production can be much larger in the subsoil than in the topsoil, especially in peat soils with significant denitrification potential in the subsoils (Velthof and Oenema, 1995b).

Seasonal variations in N_2O losses
Seasonal variations in N_2O losses are mainly the result of variations in weather conditions and grassland management. Temperature and rainfall control rates of carbon (C) and nitrogen (N) mineralization (MacDuff and White, 1985), denitrification (Keeney et al., 1979) and nitrification (MacDuff and White, 1985), N uptake by the grass, groundwater level and gas diffusivity in soils. Besides application of N fertilizer and grazing, other management measures may also affect N_2O losses, e.g. tractor wheels compact the soil during e.g. mowing and harvesting, which may enhance N_2O losses (Hansen and Bakken, 1993). Mowing itself may also increase N_2O flux (Beck and Christensen, 1987). After mowing, roots may release carbon compounds. Moreover, evapotranspiration and NO_3^- uptake by the sward may be decreased. All these temporaly changes after mowing may enhance denitrification activity in the soil. In addition, irrigation, adjustment of groundwater level, liming and application of phosphate and other nutrients and chemicals may affect seasonal fluctuations in N_2O losses (Granli and Bøckman, 1994).

The seasonal patterns in mineral N contents of the unfertilized mown grassland (Figure 3) are probably related to seasonal patterns in N mineralization rate, with highest rates during the growing season and lowest rate during the off-season (Gill et al., 1995). Similar seasonal patterns were found for N_2O losses (Figures 3 and 4 and Table 4). The much larger losses from peat soil II during winter, 0.8-1.6 kg N

Table 4. Total annual N$_2$O losses and N input via fertilizer, urine and dung, for all sites and treatments and both years.

Site	Treatment	March 1992-March 1993			March 1993-March 1994			Annual average		
		N input kg N ha^{-1}	N$_2$O loss kg N ha^{-1}	% of N-input[a]	N input kg N ha^{-1}	N$_2$O loss kg N ha^{-1}	% of N-input	N input kg N ha^{-1}	N$_2$O loss kg N ha^{-1}	% of N-input
Sand	Unfertilized-mown	0	1.2	-	0	1.0	-	0	1.1	-
	N fertilized-mown	313	3.1	0.6	426	6.6	1.3	370	4.9	1.0
	N fertilized-grazed	753	7.3	0.8 (1.0)	727	13.2	1.7 (2.2)	735	10.3	1.2 (1.5)
Clay	Unfertilized-mown	0	1.0	-	0	0.5	-	0	0.8	-
	N fertilized-mown	277	5.0	1.4	437	2.6	0.5	357	3.8	0.9
	N fertilized-grazed	557	10.6	1.7 (2.0)	730	16.1	2.1 (4.6)	644	13.4	2.0 (3.3)
Peat I	Unfertilized-mown	0	2.1	-	0	1.8	-	0	2.0	-
	N fertilized-mown	266	8.0	2.2	464	9.6	1.7	365	8.8	1.9
	N fertilized-grazed	521	11.9	1.9 (1.5)	712	17.3	2.2 (3.1)	617	14.6	2.1 (2.3)
Peat II	Unfertilized-mown	0	12.9	-	0	4.2	-	0	8.6	-
	N fertilized-mown	161	20.2	4.5	323	15.9	3.6	242	18.1	3.9
	N fertilized-grazed	356	36.0	6.5 (8.1)	544	41.0	6.8 (11.4)	450	38.5	6.7 (9.8)

[a]expressed as:

(N$_2$O loss from N fertilized mown grassland-N$_2$O loss from unfertilized mown grassland)/(amount of applied fertilizer N)

In parentheses: percentage of dung and urine N emitted as N$_2$O expressed as:

(N$_2$O loss from N fertilized grazed grassland-N$_2$O loss from N fertilized mown grassland)/(amount of emitted dung and urine N)

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ha^{-1}, than from the other soils may have been due to higher mineralization rates and higher mineral N contents during winter in peat soil II than in the other soils. In grazed grasslands, much N is accumulated in the soils via deposition of urine and dung from grazing cattle (Figure 4). This N is vulnerable to loss via ammonia volatilization (Bussink, 1994), leaching (Ryden *et al.*, 1984) and denitrification (Watson *et al.*, 1992; Kirkham and Wilkins, 1993). The results of the present study showed that total N$_2$O losses were larger from grazed grasslands than from mown grasslands in spring, summer and autumn (Tables 2 and 4). In autumn, absolute and relative losses generally increased in the order unfertilized mown < N fertilized mown < N fertilized grazed grassland. This order reflects the differences in the built up of mineral N in the soil between different treatments (Figure 4 and Table 3).

The small differences in N$_2$O loss between the treatments in the winter (Table 2) did not confirm our hypothesis that N$_2$O loss in the off-season increases in the order: unfertilized mown grassland < N fertilized mown grassland < N fertilized grazed grassland. At the end of the autumn, soil mineral N contents in the top soil had decreased to relatively low levels in all treatments (Figure 4 and Table 3), probably because of leaching and denitrification after the heavy rainfall and groundwater level rise. As a consequence, residual effects of fertilizer N and N from dung and urine on N$_2$O losses were very small.

Relative N$_2$O losses in the off-season were in the order unfertilized mown > N fertilized mown > N fertilized grazed grassland (Figure 5). These results clearly indicate that disregarding off-season losses underestimates the total from unfertilized mown grassland to a greater extent than those from N fertilized mown and grazed grasslands.

Differences in seasonal N$_2$O losses between soil types were large. Relatively large losses occurred on the clay soil in spring (Table 2). By contrast, peat soil I exhibited relatively small losses in spring. So far, we have no clear explanation for these phenomena, but differences in rainfall patterns and groundwater level (Table 1) are probably involved.

Interannual variations in N$_2$O losses

The larger N$_2$O losses from the unfertilized grasslands in the first year than in the second year of the experiment (Table 2 and Figure 6), have to be attributed, in part, to the intensive grassland management in the year before the experiment started, with N applications via mineral N fertilizer in the range of 250-350 kg N ha^{-1} and 4 to 6 grazing cycles per year. This is supported indirectly by the higher mineral N

contents in the unfertilized soil in the first year than in the second year (Figure 3).

Interannual variations in N_2O losses from N fertilized grasslands are confounded with interannual variations in e.g. N fertilizer application. The economically optimum fertilizer N input was considerably larger in the second year than in the first year (Table 4). This may have contributed to larger N_2O losses. Whilst many factors may have contributed to interannual variations, there is a fairly good linear relationship between N_2O losses in 1992-1993 and 1993-1994 (Figure 6). This suggests that results of flux measurements carried out in one year have predictive power for estimating losses in other years.
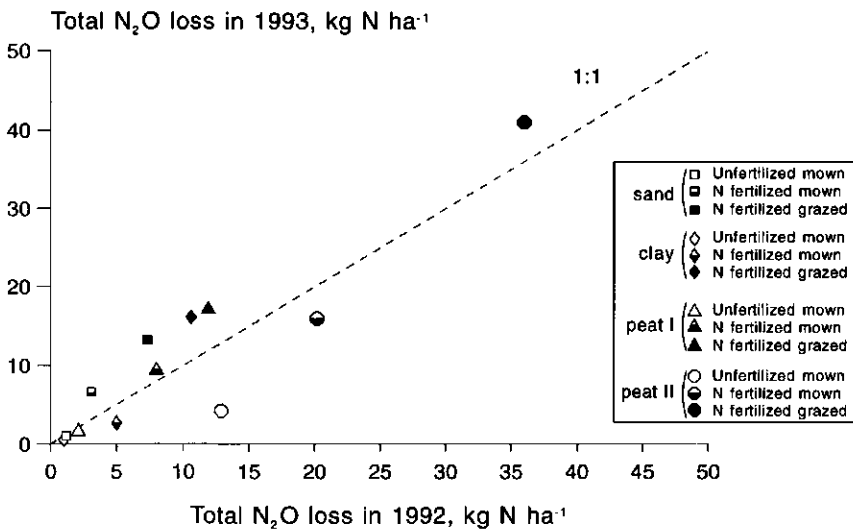

Figure 6. Total N_2O losses in 1992 (March 1992-February 1993) versus total N_2O loss in 1993 (March 1993-February 1994) for the four sites.

Total annual N_2O losses
Using data from studies with a coverage of one year on cropped fields and ungrazed grasslands on mineral soils, Bouwman (1995) estimated total annual N_2O losses from agricultural land with the equation: N_2O loss $= 1 + 0.0125(N$ application), in which N_2O loss and N application rate are given in kg N ha^{-1} yr^{-1}. The mean total N_2O loss for unfertilized and mown grassland on the sand and clay soils was 0.9 kg N ha^{-1} yr^{-1} and on average 0.95% of the fertilizer N applied was

lost as N_2O on these soils (Table 4; n=4). These results for mown grassland on sand and clay soils reasonably fit the regression equation of Bouwman (1995). Results for mown grassland on peat soils and all grazed grassland do not agree with the equation of Bouwman (1995).

The mean total N_2O loss from unfertilized mown grasslands on peat soils was 5.3 kg N ha^{-1} yr^{-1} and on average 3.0% of the fertilizer N applied to the peat soils was lost as N_2O (Table 4; n=4). Hence, the average N_2O loss from mown and fertilized grasslands on peat soils is: N_2O loss = 5.3 + 0.03(N application), in which N_2O loss and N application rate are given in kg N ha^{-1} yr^{-1}. The differences between the peat soils were large and most probably related to differences in GWL, denitrification potential and contents of mineralizable carbon (Velthof and Oenema, 1995b).

N_2O loss from grazed grassland, kg N ha^{-1} yr^{-1}

Y = 3.4 + 1.8X: R^2 = 0.80

N_2O loss from mown grassland, kg N ha^{-1} yr^{-1}
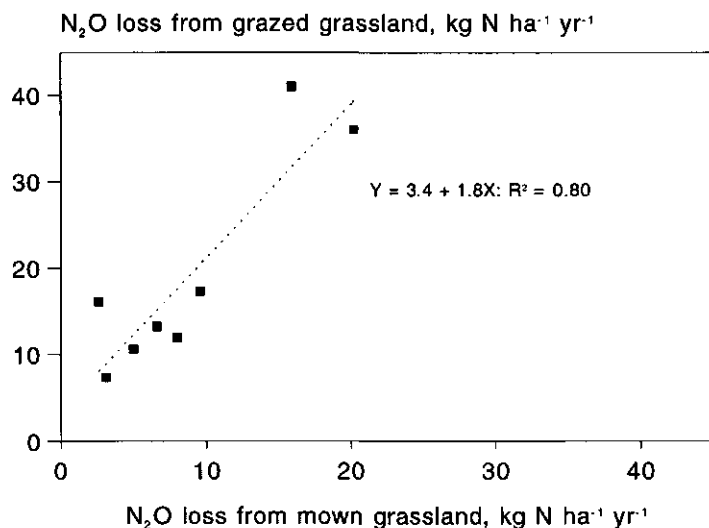
Figure 7. Relationship between N_2O loss from N fertilized and mown grassland and that from N fertilized and grazed grassland. Results for all sites and both years. Amount of applied N fertilizer was equal for mown and grazed grasslands.

The relationship between N_2O losses from mown grassland and those from grazed grassland on all soils in the present study was (Figure 7): N_2O loss grazed grassland = 3.4 + 1.8(N_2O loss mown grassland). The much larger N_2O losses from

grazed than from mown grasslands indicate that N_2O budget calculations for grasslands must include the effects of grazing and N cycling via urine and dung (Bouwman, 1995).

The equations to estimate N_2O losses from managed grasslands on peat soils and from grazed grasslands may be considered as a rough approximation of N_2O losses from these grasslands. Their applicability to other peat soils and grazed grasslands are still unknown. More N_2O monitoring studies on grassland are needed to check and improve the equations for grassland on peat soils and for grazed grasslands.

Conclusions

Seasonal variations in N_2O losses from managed grasslands in the Netherlands were large and were related to fertilizer N application, grazing, weather conditions and changes in groundwater level. On all soils, largest N_2O losses occurred during the growing season. In late-autumn, losses of N_2O tended to increase in the order unfertilized mown < N fertilized mown < N fertilized grazed grassland, which reflected the built-up of mineral N in the soils. In winter the differences in both N_2O losses and mineral N contents were small between the management treatments. Disregarding off-season losses would underestimate total annual losses by up to 20%, total losses being largest for unfertilized mown grassland and the smallest for N fertilized grazed grassland. Off-season losses from grassland on peat soil II were much larger than those from the other soils. This indicates that disregarding off-season N_2O losses will underestimate total annual losses from various sites in a different way.

Despite the considerable interannual variations in N_2O losses, this study indicates that the results of measurements carried out in one year have predictive power for estimating N_2O losses in other years. The interannual variations in N_2O losses in the present study and in studies of Webster and Dowdell (1982) and McTaggart _et al._ (1994) points to the present uncertainties in the estimates of total N_2O losses from agricultural land. Unless we are able to relate variations in N_2O losses between years to differences in N input, groundwater level, and weather conditions, errors in the estimates will remain, due to spatial and temporal variations. However, the effects of this random variation on the global budget calculations will attenuate if the number of monitoring studies increase.

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Acknowledgements

CHAPTER 5

Prediction of nitrous oxide fluxes from managed grassland on peat soil using a simple empirical model

Prediction of nitrous oxide fluxes from managed grassland on peat soil using a simple empirical model

Summary

Three measurement campaigns were carried out to answer questions related to the factors controlling variations in nitrous oxide (N_2O) fluxes from intensively managed grassland on peat soil, comparison of flux measurements with a closed flux chamber method and a flux gradient technique and the development and testing of a simple empirical model for the estimation of N_2O fluxes from intensively managed grassland on peat soils. Fluxes of N_2O were measured with 42-48 flux chambers and ranged from less than 0.01 to 6.66 mg N m^{-2} hr^{-1}. Fluxes were significantly correlated with denitrification activity (R^2 = 0.34-0.56). Contents of nitrate (NO_3^-) and ammonium (NH_4^+) in the top soil and the water-filled pore space (WFPS) explained 37-77% of the variance in N_2O flux. Spatial variability of N_2O fluxes was large with coefficients of variation ranging from 101 to 320%. Spatial variability was suggested to be related to distribution of mineral N fertilizer and cattle slurry, urine and dung patches and variations in groundwater level within the field. Average field fluxes obtained with the closed flux chamber method were about a factor 10 larger than those with the flux gradient technique on one measurement day but were similar on two other measurement days. The results of the measurement campaigns were used to derive a simple empirical model including total mineral N content and WFPS. This model was tested using an independent data set, i.e. the results of a monitoring study of two years carried out on two other grassland sites on peat soil. The model reasonably predicted magnitude of and temporal variations in N_2O fluxes. It is suggested that a simple empirical model which requires only easily obtainable data such as mineral N content and moisture content, in combination with a few days lasting measurement campaigns, may be a valuable tool to predict N_2O fluxes from similar sites.

Introduction

Total annual N_2O emissions from soils can be quantified by field measurements of N_2O fluxes, but due to the very large spatial and temporal variability in these fluxes, intensive sampling is required (e.g. Ambus and Christensen, 1995; Flessa *et al.*, 1995; Velthof *et al.*, 1996a, b). Estimates of N_2O emissions can also be obtained using

models. Mechanistic models that simulate the basic processes involved in N_2O emissions (e.g. Bril *et al.*, 1994; Grant *et al.*, 1993a, b) are generally complex and moreover need a large number of input data. Therefore, mechanistic models are not easily applicable to a field scale (Rolston, 1990). Empirical or regression models and combinations of mechanistic/empirical models are rather simple and may provide reasonable estimates of fluxes and total emission of N_2O (e.g. Clayton *et al.*, 1994 and Parton *et al.*, 1988), but these models are site specific by definition.

It is a generally held view that variations in N_2O fluxes at a certain site are mainly related to variations in moisture content and in the amounts of nitrate (NO_3^-) and ammonium (NH_4^+) in the soil (e.g. Clayton *et al.*, 1994; Mosier *et al.*, 1983) and to a lesser extent by temperature and mineralizable carbon (C). These soil variables can be readily obtained and a number of studies have indeed provided regression models. Simple empirical models, derived at one site, have rarely been applied at other sites to test the validity. The present study focuses on the development and subsequent testing of a simple empirical model for the estimation of N_2O fluxes from intensively managed grassland on peat soils in the Netherlands. Cultivated peat soils are a major source of N_2O (Anonymous, 1996), due to the large amounts of mineralizable N and C and the shallow groundwater levels. The model in the present study is based on the results of three measurement campaigns carried out on managed grassland. Fluxes of N_2O were measured using a large number of flux chambers and a flux gradient technique and were related to a number of soil variables. The study was designed to answer three questions.

The first question deals with the major factors controlling N_2O fluxes from managed grassland on peat soil and which can be easily manipulated by grassland management. In soil, N_2O is produced during two different processes, i.e. nitrification and denitrification. Both processes are controlled by complex interactions of biological, chemical and physical factors. Generally, the major soil variables controlling N_2O flux at the field scale are contents of moisture, NO_3^-, NH_4^+ and mineralizable C. It is suggested that microsites contents of these variables do better explain N_2O fluxes than concentrations in bulk samples (e.g. Clayton *et al.*, 1994). Therefore, the size of the flux chambers and the size of the soil samples are crucial for the assessment of relationships between fluxes and soil variables in the field. We used relatively small flux chambers (300 cm^2), from which two 9 cm^2 soil cores from the top soil were taken for analyses of soil variables. We considered the top soil layer as most important in the control of N_2O flux from peat soils, because (i) both denitrification potential and contents of mineralizable C in the top soil of peat soils are much larger than in the

subsoil (Velthof and Oenema, 1995b), (ii) contents of mineral N in this layer are generally much higher than in the subsoil, due to applications of mineral N fertilizer and cattle slurry and deposition of urine and dung during grazing, and (iii) soil moisture and oxygen concentrations in this layer respond rapidly to changes in weather conditions and these conditions promote N_2O production during nitrification and denitrification. To provide more insight into the microbial processes involved in the production of N_2O in managed grassland on peat soils, denitrification activity in the top soil was determined after the N_2O flux measurement.

The second question deals with spatial variability of N_2O fluxes from managed grassland on peat soils and the comparison of the flux chamber method with the flux gradient technique. A better knowledge of the spatial patterns of N_2O fluxes and the factors controlling these patterns may improve strategies for N_2O flux measurements. Micrometeorological methods, like the flux gradient technique, are less hampered by spatial variability of N_2O fluxes than a flux chamber method and may obtain a more precise estimation of the average field N_2O flux. However, micrometeorological methods are more difficult to operate than flux chambers, require large uniform soil areas, have a relatively large detection limit for N_2O flux and, therefore, can be less widely applied than flux chamber methods. We expected that diurnal variations in N_2O flux were most pronounced in the flux gradient data due to diurnal changes in atmospheric turbulence. Therefore, N_2O fluxes were continuously measured using both methods during a period of two days.

The third question deals with the applicability of a simple empirical model for N_2O flux from managed grassland on peat soil at other sites. A simple empirical model based on the results of three 1-day measurement campaigns was tested using an independent data set, i.e. the results of a monitoring study of two years carried out on two other grassland sites on peat soil (Velthof and Oenema, 1995a, b; Velthof _et al._, 1996a).

Materials and methods

Experimental sites
Measurements were carried out in 1993 on an intensively managed grassland measuring 270 by 50 m in Zegveld in the Netherlands (site 1). The peat soil was classified as Terric Histosol (FAO classification). Organic matter content of the 0-5 cm soil layer was 50.6%, pH(KCl) 4.9 and clay content was 20.1%. The grassland was surrounded by ditches. At one side the average water level in the ditches was kept at

40 cm and at the other side 60 cm below the soil surface. Nitrogen application was 244 kg N ha^{-1}, both as mineral N fertilizer (140 kg N ha^{-1} in 6 dressings in the period March-July) and cattle slurry (104 kg N ha^{-1} in 4 dressings in the period February-August using trailing feet). Grassland was grazed with dairy cows in April (3 days), May (4 days), July (7 days), August (5 days), September (5 days) and October (2 days). Herbage was mown once, on 2 June.

The empirical model was tested at two other grassland sites (sites 2 and 3) on peat soil in Zegveld surrounded by ditches. Organic matter content of the 0-5 cm soil layer was 39.9% and 50.6%, pH(KCl) was 4.9 and 4.7, and clay content was 15.3% and 19.1%, at site 2 and site 3, respectively. The water level in all ditches surrounding site 2 was kept at -40 cm and at site 3 at -60 cm. Fertilizer N applications were in the same range as on site 1 (Velthof *et al.*, 1996a).

Closed flux chamber method
Measurements with flux chambers were carried out at site 1 on 22-24 June, 23 September and 9 November 1993. Fluxes were measured using closed circular PVC flux chambers (diameter 20 cm, height 15 cm) directly attached to Brüel and Kjær photo-acoustic spectroscopic infra-red gasanalyzers and multi-sampler, as described in detail by Velthof and Oenema (1995a). Fluxes in 6 to 12 flux chambers were measured simultaneously.

In June, 48 flux chambers were placed in a row over the width of the plot between the two ditches with different water level and perpendicular to the direction in which cattle slurry and N fertilizer had been applied. The distance between the chambers was 90 cm from the centre of each flux chamber. This sampling scheme was chosen to assess the possible effects of application of cattle slurry and fertilizer N and groundwater level on the spatial variability of N_2O fluxes. In September, 48 flux chambers were placed at 1 m intervals in a grid of 4 x 12; in November, 42 flux chambers were placed at 1 m intervals in a grid of 6 x 7. These sampling schemes were chosen to assess the random variation of N_2O fluxes from the grazed grassland. It was expected that the random variation of N_2O fluxes was large at the end of the growing season, due to the heterogeneous distribution of urine and dung and due to treading during the grazing periods earlier in the season.

In June, N_2O fluxes were measured continuously during a period of two days to compare the results of the flux chambers method with results of a flux gradient technique. The 48 flux chambers (four series of 12 flux chambers) were sampled once every 4 hours, in total 11 times during two days. In September and November,

measurements were carried out during the afternoon.

Flux gradient system

Measurements with a flux gradient technique were carried out on 22-24 June and 9 November 1993. A detailed description of the experimental set up and N_2O analyses are given by Duyzer (1995). Briefly, air was drawn from various heights above the soil surface (0.25-7.5 m) via teflon tubing connected with mass flow controllers and airtight pumps into 12 L aluminum coated airtight bags. During sampling, bags were stored in aluminum cases at the tower base. It was assumed that the samples were taken at the appropriate temperature. In June, samples were taken from 0.35 m and 7.5 m above the soil surface. In November, samples were taken from 4 heights (0.25, 0.60, 2.00 and 4.15 m above the soil surface), to improve sensitivity.

Bags were analyzed in the laboratory using ECD detection after gas chromatographic separation (Chrompack CP9001 system). To improve the sensitivity of the method 50 repetitive samples were taken from each bag. The repeatability of this method was 3.6%. Using a robust method described by the Analytical Methods Committee (Anonymous, 1989) outliers were traced and rejected. Typical 95 % confidence intervals of the value of Δc (difference in N_2O concentration) after outlier rejection were in the order of 0.5 ppb. This leads to a detection limit of approximately 0.06 mg N $m^{-2} hr^{-1}$ during day time and 0.02 mg N $m^{-2} hr^{-1}$ at night .

Denitrification activity, soil variables and weather conditions

Denitrification activity in the soil in the flux chambers was determined immediately after the last N_2O flux measurement. Denitrification activity was determined from the amount of N_2O evolved from two soil cores (diameter 4.7 cm) of the 0-20 cm soil layer, incubated for 24 hrs in an atmosphere with 5% acetylene at in situ soil temperature (Koops _et al._, 1996a). After denitrification measurement, the soil samples were analysed for moisture, by drying at 105 °C for 24 hours, and NO_3^- and NH_4^+, after extraction of 10 g dry soil (24 hours at 40°C) in 100 ml 0.01 _M_ $CaCl_2$ (Houba _et al._, 1989). To be able to compare soil moisture status at the three sites, all moisture contents were transformed into water-filled pore space (WFPS). Bulk density of the soil cores was measured in September and November. Contents of water soluble C was measured with a Dissolved Organic Carbon Analyzer in the samples of November, after extraction of 10 g dry soil in 100 ml water. During the flux measurements, soil and air temperatures, amounts of rainfall and groundwater levels were recorded.

Statistical analyses

Multiple regression analyses were carried out for each period with the logtransformed N_2O flux in μg N m^{-2} hr^{-1} as dependent variable and the logtransformed NO_3^- and NH_4^+ contents in kg N ha^{-1}, WFPS and $WFPS^2$ as independent variables. $WFPS^2$ was included, because it has been suggested that the relation between N_2O flux and WFPS has an optimum (Davidson, 1991). The models for September and November also included bulk density in kg dm^{-3}, and the model for November included also water soluble C in mg C kg^{-1}.

All regression analyses were carried out using stepwise multiple regression techniques in Genstat 5.0 (Genstat 5 Committee, 1987). Distributions of N_2O fluxes and logtransformed N_2O fluxes (n=48) were tested for normality using Shapiro-Wilk's W Test at $\alpha=0.05$. Because most distributions were not approximated by both normal and lognormal distribution we used the arithmetic mean as the estimator of the mean N_2O flux, because it is a robust estimator of the mean (Velthof and Oenema, 1995a).

Testing of the model

A regression model of the pooled data of the present study was tested against independent data: results of a monitoring study carried out between March 1992 and March 1994 on two other grasslands on peat soil in Zegveld (Velthof and Oenema, 1995a, b; Velthof *et al.*, 1996a). This model included logtransformed total mineral N content (NH_4^+-N + NO_3^--N) in kg N ha^{-1}, WFPS, and $WFPS^2$. Contents of NH_4^+ and NO_3^- were not included separately in this model, because only data on total mineral N contents were available for the monitoring study.

In the monitoring study, N_2O fluxes were measured weekly in six replicates on unfertilized-mown, N fertilized-mown and N fertilized-grazed grasslands on both soils. Soil mineral N and soil water contents of the 0-30 cm soil layer of all treatments were determined in 4 replicates weekly during the growing season and monthly in the winter. The results of the 0-30 cm layer were multiplied by 2/3 to correct for the difference in length of the soil cores taken in the flux chambers (0-20 cm). There was a fair correlation between N concentration in the 0-20 cm and 0-30 cm soil layers (data not shown). All analytical methods used in the monitoring study were similar to those described for the present study. The regression model was tested with the means per measurement time of mineral N content (n=4), WFPS (n=4) and N_2O flux (n=6), of all treatments of the monitoring study.

Results

Flux chamber measurements in June

There was a marked relationship between N_2O flux and NO_3^- content (Figure 1A). Flux of N_2O and NO_3^- content were low at the borders of the field and large in the middle of the field. Fluxes were largest on the part of the field with highest groundwater levels and highest WFPS (Figure 1B). Observations in the field indicated that chambers with largest fluxes and highest NO_3^- contents generally contained largest amounts of cattle slurry. Contents of NH_4^+ were much lower than NO_3^- contents and the range in NH_4^+ content was small in comparison to that of NO_3^- (Table 1). WFPS decreased from one side to the other side of the field (Figure 1B), with a minimum of 0.45 and maximum of 0.85. Groundwater level also decreased from one side to the other side of the plot, from 41 cm to 66 cm below soil surface (Figure 1B). A multiple regression model with logtransformed NO_3^- content and WFPS as the independent variables explained 77% of the variance in logtransformed N_2O flux (Table 2). Logtransformed N_2O flux was also significantly correlated with logtransformed denitrification rate ($R^2 = 0.34$). Denitrification rates were generally (much) larger than N_2O fluxes (Figure 2). The ratio N_2O flux/denitrification rate ranged from 0.01 to 3.23 and was on average 0.40 (Table 1). There was a tendency that this ratio increased with increasing mineral N content (not shown).

Flux chamber measurements in September and November

The spatial variability in N_2O flux, denitrification rate, contents of NH_4^+ and NO_3^-, WFPS and bulk density was large and had a patchy pattern (Table 1 and Figure 3). Soil was wet in both September and November: the average WFPS was 0.92. Mean N_2O flux obtained by chamber measurements was similar in September (0.22 mg N m^{-2} hr^{-1}) and November (0.26 mg N m^{-2} hr^{-1}). The best regression models for September and November included contents of NO_3^- and NH_4^+ and explained 54 and 37% of the variance in N_2O flux, respectively (Table 2). Logtransformed denitrification rates and logtransformed N_2O fluxes were significantly correlated (Figure 2), with R^2 of 0.54 in September and 0.56 in November. In both September and November, denitrification rates were mostly larger than the N_2O fluxes (Figure 2). The average ratio of N_2O flux/denitrification rate was 0.14 (Table 1).
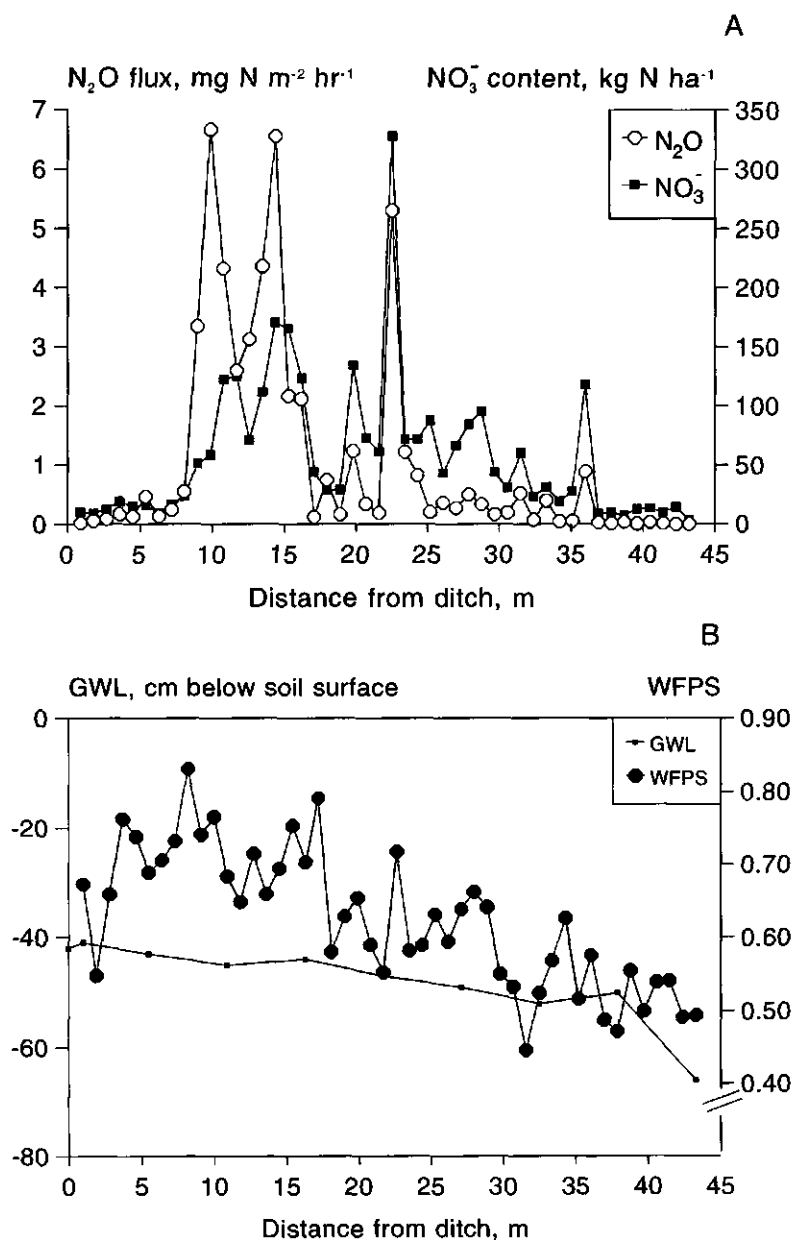
Figure 1. Spatial variability of N_2O flux and NO_3^- content in Figure A and groundwater level (GWL) and water-filled pore space (WFPS) in Figure B, in grassland on a peat soil in June 1993.

Table 1. Mean and range of N_2O fluxes, denitrification rates, soil properties, soil temperature and groundwater level, for all measurement days.

Variable	24 June[*]		23 September		9 November	
	mean	range	mean	range	mean	range
N_2O flux, mg N m^{-2} hr^{-1}						
Chambers	1.07	<0.01-6.66	0.22	<0.01-4.62	0.26	<0.01-1.28
Flux gradient	0.89	0.59-1.38	n.d.[**]		0.15	0.1-0.5
Denitrification, mg N m^{-2} hr^{-1}	2.54	0.75-6.69	1.10	0.27-10.0	1.31	0.43-5.13
Ratio N_2O flux/denitrification rate	0.40	0.01-3.23	0.14	0.01-1.17	0.14	0.01-0.37
Mineral N content, kg N ha^{-1}						
NO_3^-	58	4-328	7	1-70	9	1-29
NH_4^+	20	13-32	10	5-47	15	6-131
Total	78	21-351	17	7-101	24	8-141
Water-filled pore space	0.62	0.45-0.85	0.91	0.77-1.00	0.92	0.74-1.00
Bulk density, kg dm^{-3}	n.d.		0.43	0.33-0.49	0.45	0.37-0.93
Water-soluble C, g C kg^{-1}	n.d.		n.d.		0.63	0.20-1.00
Soil temperature, °C	14.4	13.6-15.6	14.8	14.7-14.9	7.7	6.9-8.0
Groundwater level, cm	49	41-66	37	33-42	47	43-50

[*] fluxes of N_2O and temperature of the last measurement period of 4 hours on 24 June
[**] not determined

Table 2. Best multiple regression models with logtransformed N_2O flux in µg N m^{-2} hr^{-1} as dependent variable, for the three periods and for the pooled data. Models only include significant ($\alpha=0.05$) independent variables.

Period	Model[*]	n	R^2_{adj}
June	$\ln(N_2O) = -4.2 + 1.5\ln(NO_3^-) + 7.2WFPS$	48	0.77
Sept.	$\ln(N_2O) = -2.2 + 0.5\ln(NO_3^-) + 2.4\ln(NH_4^+)$	48	0.54
Nov.	$\ln(N_2O) = 1.5 + 0.7\ln(NO_3^-) + 0.8\ln(NH_4^+)$	42	0.37
Total	$\ln(N_2O) = -11.9 + 2.0\ln(NO_3^-+NH_4^+) + 20.7WFPS - 10.5WFPS^2$	138	0.64

[*]contents of NO_3^- and NH_4^+ in kg N ha^{-1}

Comparison of the flux chamber and the flux gradient measurements

In June, the average flux of the 48 flux chambers decreased from 2.3 mg N m^{-2} hr^{-1}, for the first measurement to 1.1 mg N m^{-2} hr^{-1}, for the last measurement (Figure 4). Fluxes derived from gradient measurements were continuously well above the detection limit (Figure 4). In the morning of the 24th an inverse gradient was observed. This may be related to rapid changes of the conditions in the boundary layer just after sunrise. Around this time there was also some rainfall. Since no good explanation is available for this result it should be interpreted with care. During the first day the flux estimates by the gradient method were a factor 10 smaller than the estimates of the chamber measurements. The results obtained during the second day showed a much better agreement. Both flux chamber and gradient measurements showed no clear diurnal fluctuations in N_2O flux, as found for air and soil temperatures (Figure 4).
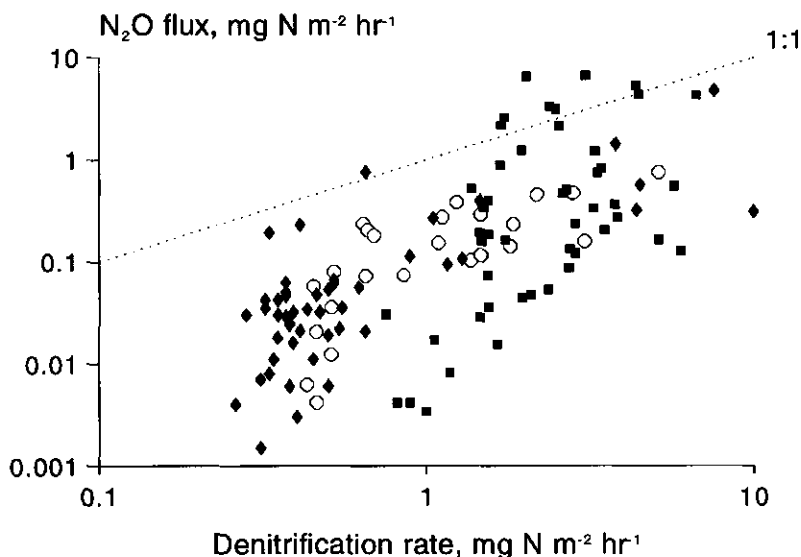
Figure 2. Logtransformed N_2O flux versus logtransformed denitrification rate, for June (■), September (◆) and November (○).

The flux gradient measurements in November were severely troubled by shifts in the wind direction that necessitated reinstalments of the meteorological equipment. Possibly as a result of the shifts in wind direction the results obtained by the gradient method were variable. Only five 90 minute average flux estimates were obtained. The average flux amounted to 0.15 mg N m^{-2} hr^{-1}, ranging from the detection limit of

around 0.1 mg N m^{-2} hr^{-1} to a maximum of 0.5 mg N m^{-2} hr^{-1} (Table 1). These results agreed quite well with the observations using the flux chamber method.
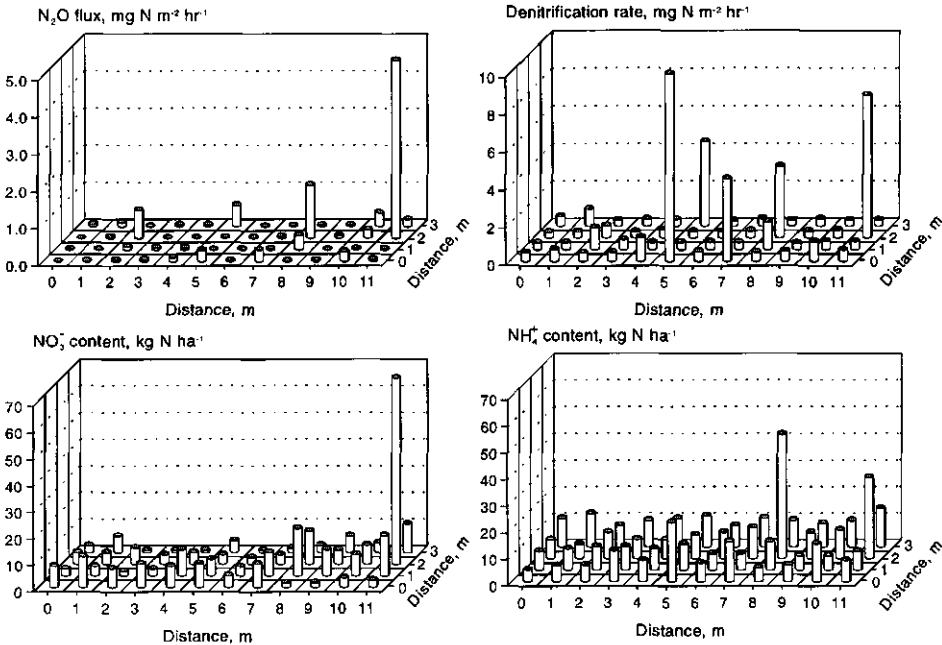
Figure 3. Spatial variability of N$_2$O flux, denitrification rate and contents of NO$_3^-$ and NH$_4^+$ in grassland on a peat soil in September 1993.

Testing the empirical model

Mineral N content and WFPS were the major factors controlling N$_2$O fluxes from the peat soil. The best model of the pooled data of the three experiments included total mineral N contents, WFPS and WFPS^2 and explained 64% of the variance in N$_2$O flux (Table 2). This model reasonably predicted N$_2$O fluxes from the monitoring study, especially for site 3 (Figure 5). For site 2, the model systematically overestimated the N$_2$O flux at measured fluxes smaller than about 25 µg N m^{-2} hr^{-1}. The model reasonably simulated the temporal behaviour of N$_2$O fluxes, with the largest fluxes during the growing season, associated with N fertilizer application and grazing, and the smallest fluxes during winter (Figure 6). For site 2, 45% of the predicted N$_2$O fluxes fell within the standard deviation of the measured flux (n=6), 2% of the fluxes fell below and 55% of the fluxes fell above the standard deviation of the measured flux.

79

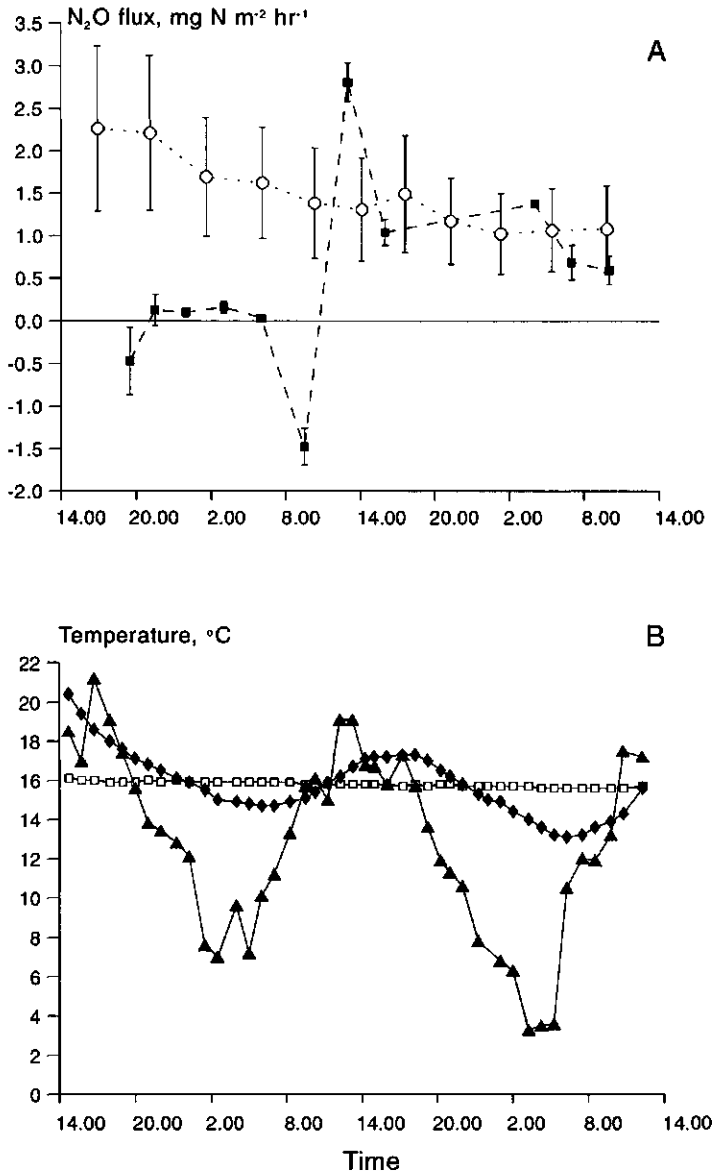**Figure 4.** Results of N$_2$O flux measurements on grassland on peat soil during 22-24 June 1993. A. Time course of N$_2$O fluxes (and 95% confidence intervals) derived from a flux chamber method (O) and a flux gradient technique (■). B. Time course of the atmospheric temperature (▲), soil temperature at 5 cm depth (♦) and soil temperature at 30 cm depth (□).

For site 3, 50% of the predicted fluxes fell within the standard deviation of the measured flux, 16% were smaller and 34% were larger.

Total annual N_2O emissions based on the fluxes derived from the simple empirical model reasonably agreed with those based on the measured fluxes (Figure 7). For site 2, total annual N_2O emissions derived from the modeled fluxes were somewhat larger than those derived from the measured fluxes (Figure 7). For site 3, the opposite was found: the modeled fluxes resulted in a somewhat smaller total annual N_2O emission than the measured fluxes.

Discussion

The study was designed to answer questions, related to (i) the factors controlling N_2O fluxes from peat soil, (ii) spatial variability of N_2O fluxes and comparison of flux measurement methods and (iii) testing of a simple empirical model for N_2O fluxes from peat soils.

Controlling factors
Multiple regression models including NO_3^- and NH_4^+ contents and WFPS explained 37 to 77% of the variance in N_2O flux, indicating that these were major factors controlling the N_2O flux. The relatively large percentage of the variance in N_2O flux accounted for by these variables suggests that the chosen combination of flux chamber size and soil sampling strategy was adopted sufficient to study the controlling factors of N_2O flux.

In June, the flux of N_2O was strongly related to the NO_3^- content and WFPS (Figure 1 and Table 2). September and November models only included contents of NO_3^- and NH_4^+. The fluxes of N_2O and denitrification rates were both much larger in June than in September and November. This coincided with much higher contents of NO_3^-, much smaller WFPS and a higher ratio N_2O flux/denitrification rate in June than in September and November (Table 1). Generally, high NO_3^- contents and moderate WFPS increase relative production of N_2O during denitrification (e.g. Davidson, 1991). The higher denitrification rate in June than in September and November may have been due to the higher NO_3^- content. The results suggest that the relatively low WFPS in June did not hamper denitrification activity. In September and November, fluxes of N_2O were similar. Also denitrification rates and contents of NO_3^- and NH_4^+, bulk density, and WFPS were similar in September and November (Table 1). Apparently, the lower temperature in November than in September did not reduce N_2O flux and denitrification activity.
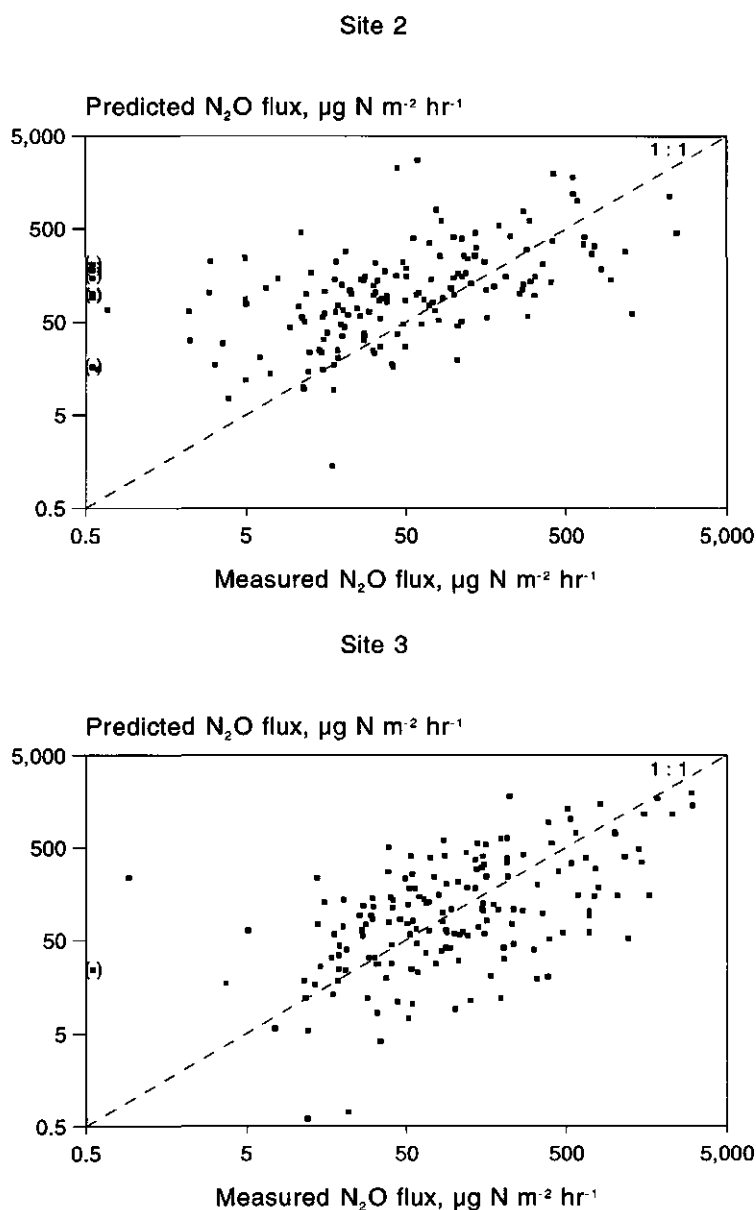
Site 2

Site 3

Figure 5. Measured N_2O flux (mean of 6 replicates) in the monitoring study versus predicted N_2O flux using the empirical model derived in the present study, for site 2 and site 3. Note logarithmic scales. Points in parentheses indicate that the mean measured N_2O flux was negative.

Denitrification was significantly related to the N_2O flux, for all periods (Figure 2). Denitrification rate was generally (much) larger than the N_2O flux (Table 1 and Figure 2). This indicates that N_2 was the major end product during denitrification. The addition of acetylene to the soil during the denitrification measurement inhibits the nitrification activity and thus N_2O production during nitrification. Ratios of N_2O flux/denitrification rate higher than 1 indicate that nitrification was a major source of N_2O. Kester *et al.* (1996) and Koops *et al.* (1996b) also showed that nitrification may be a significant source of N_2O in managed grasslands on peat soils. The large variation in the ratio N_2O flux/denitrification rate, ranging from < 0.01 to 3.23 indicates that estimation of denitrification rate on the basis of measured N_2O fluxes and a fixed ratio N_2O flux/denitrification rate is not feasible for grasslands on peat soil. The N_2O flux/denitrification rate tended to increase with increasing mineral N contents, but no clear relationship between soil variables and this ratio could be established.
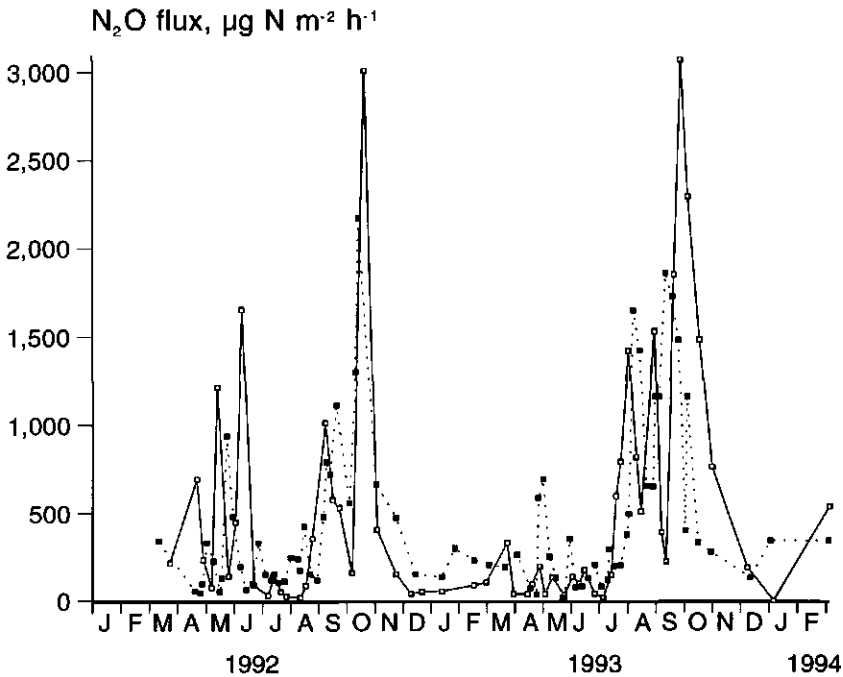

Figure 6. Time course of measured (□) and modeled (■) N_2O fluxes during March 1992 to March 1994, for N-fertilized and grazed grassland on site 3.

Spatial variability

In all three periods, the spatial variability of N_2O fluxes was large. The coefficients of variation of the mean flux were 163% in June, 320% in September and 101% in November. Similar coefficients of variation are also found for N_2O fluxes from grasslands on mineral soils (e.g. Ambus and Christensen, 1994; Velthof *et al.*, 1996b) suggesting that the presence of large amounts of organic C in the peat soil did not decrease spatial variability of N_2O flux.

The significant relationship between the N_2O flux and WFPS (Table 2) and the relationship between groundwater level and WFPS (Figure 1), indicate that differences in groundwater level attributed to the observed spatial variability in the N_2O flux in June. Velthof *et al.* (1996a) pointed out that groundwater level may be an important factor controlling N_2O flux from managed grasslands in the Netherlands. The distribution of NO_3^- in the plot in June with high contents in the middle and low contents at the borders (Figure 1) was probably related to heterogeneous distribution of cattle slurry with trailing feet. Observations in the field indicated that the flux chambers with the highest NO_3^- contents and the highest N₂O fluxes contained largest amounts of slurry. The low NO_3^- contents at the borders of the field were due to the fact that the borders were not supplied with cattle slurry and fertilizer, because farmers generally do not apply fertilizers near ditches.

The patchy distribution of NO_3^-, NH_4^+, N_2O flux and denitrification rate in September (Figure 3) and November (not shown) were probably related to the uneven distribution of urine and/or dung patches. The average size of urine and dung patches from dairy cattle are typically less than 1 m^2 (e.g. Afzal and Adams, 1992).

Comparison of the flux chamber and the flux gradient measurements

During the first 24-h measurements in June, the fluxes obtained with the flux chamber method were much larger than those with the flux gradient technique (Figure 4). We do not have a clear explanation for this large difference between the methods. Fluxes obtained with both methods were similar during the second 24-h measurements in June and during the measurements in November. Because of the narrow fields and rapidly changing wind directions flux gradient techniques require frequent adjustments of the positions of the masts. The reinstalment of the masts is necessary because the N_2O fluxes from adjacent grassland fields may largely differ from the grassland field on which measurements are made, e.g. because of different grassland management.

Neither measurement technique detected clear diurnal variations in N_2O flux (Figure 1). We expected a stronger diurnal pattern with the flux gradient technique than

with flux chambers, due to diurnal variations in atmospheric turbulence. Apparently, changes in atmospheric turbulence did not largely affect N_2O fluxes. In several studies using flux chambers, distinct diurnal variations in N_2O flux have been observed, attributed to diurnal variations in soil temperature and moisture (e.g. Christensen, 1983; Denmead *et al.*, 1979). The results of the chamber measurements in the present study suggests that the site of N_2O production in the soil was not significantly affected by diurnal variations in moisture content and temperature.
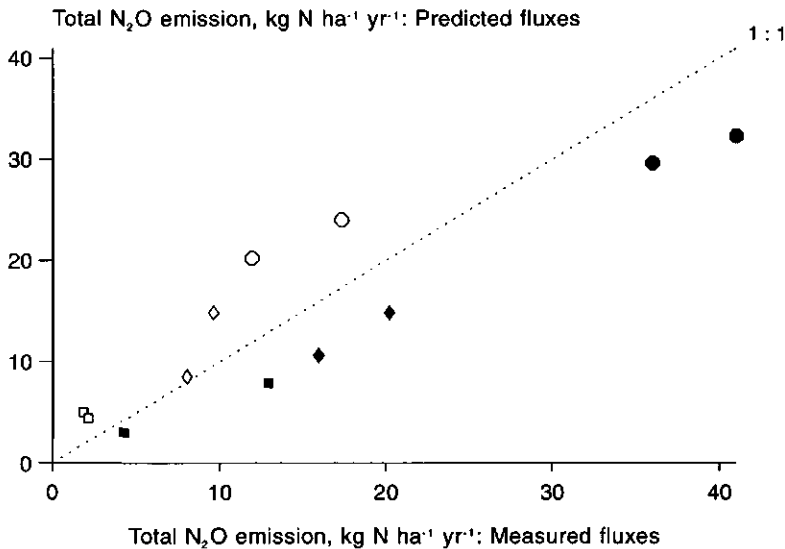
Figure 7. Estimated total annual N_2O emissions based on N_2O fluxes measured in the monitoring study versus those based on the fluxes derived from the empirical model.
□ = unfertilized-mown on site 2, ◊ = N fertilized-mown on site 2, ○ = N fertilized-grazed on site 2, ■ = unfertilized-mown on site 3, ◆ = N fertilized-mown on site 3, and ● = N fertilized-grazed on site 3.

Matthias *et al.* (1993) and Mosier and Hutchinson (1981) obtained similar N_2O fluxes with closed chambers and micrometeorological methods, when flux was relatively large and atmospheric conditions stable. In a study on grassland in which different chamber and micrometeorological methods were compared (Smith *et al.*, 1994), mean N_2O fluxes derived from chamber measurements were about a factor two larger than the N_2O flux derived from micrometeorological methods. This was

attributed either to spatial variability of the fluxes, with chambers located in regions of relatively greater source strength or to factors associated with the methods, like for example possible disturbance of the soil and atmosphere in the chambers and possible effects of spatial variability on the measurement with micrometeorological methods. Similar factors may have played a role in the differences between the chamber method and the flux gradient technique as found in the present study, and especially during the first measurement day in June.

Testing of the model

Reasonably correlations between N_2O fluxes and soil variables were found in this study (Table 2) and by e.g. Clayton *et al.* (1994) and Mosier *et al.* (1983). By contrast, very weak correlations between N_2O fluxes and soil variables were found by e.g. Folorunso and Rolston (1985) and Velthof *et al.* (1996b). Obviously, the soil variables in bulked samples did not represent the interactions of factors in soil microsites controlling N_2O production in these studies.

The model derived in the present study was tested using the results of the independent data set of the monitoring study. Spatial variability of the measured fluxes in this monitoring study was large on both site 2 and site 3 (Velthof and Oenema, 1995a), with typical coefficients of variation of the mean flux (n=6) between 50 and 300%. Temporal variations in N_2O fluxes were also significant (Velthof *et al.*, 1996a). Taking the spatial and temporal variability of the measured fluxes in the monitoring study into account, the simple empirical model reasonably predicted the magnitude of the N_2O fluxes, the temporal variations of the fluxes, and total annual N_2O emissions from site 2 and site 3 (Figures 5, 6 and 7).

Results were better for site 3 than for site 2, especially for the smaller fluxes. Site 2 had lower organic C content, a higher bulk density and a lower porosity than sites 1 and 3. These differences in the top soils were due to top soil remediation by application of town waste on site 2 in the beginning of this century. The applicability of the model was thus better for the soil which was most similar to the soil from which the model was derived. The model systematically overestimated the small fluxes on site 2. Most of these fluxes were obtained during winter, when soil was generally completely saturated with water and WFPS was larger than 0.95. Site 3 was less wet during winter, and winter fluxes were predicted reasonably by the model. Clearly, the model poorly predicted N_2O fluxes during prolonged wet periods during winter. A factor which may have played a role in this is the temperature. Temperature was not a variable in the model, by which a possible limitation of N_2O production during

winter by low temperature could not be predicted. The three experimental periods during which the model was derived were carried at soil temperature at 5 cm of 7.7 to 14.8 °C, which is higher than the soil temperatures generally found in winter in the Netherlands.

The empirical model derived in the present study reasonably predicted N_2O fluxes from managed grasslands on peat soil sites. This model for peat soils overestimated the fluxes of N_2O when applied to managed grassland on sand and clay soils (results not shown), indicating that such a simple empirical model will be applicable only for similar vegetations, crops and soil types. The availability of C is probably a major factor causing differences between soils in N_2O flux. To obtain a more widely applicable model for N_2O fluxes, a mechanistic or a mechanistic-empirical approach should be chosen (e.g. Bril *et al.*, 1994; Grant *et al.*, 1993a, b). These types of models are mostly coupled to larger mechanistic models in which, for example, water flows, C and N transformations and gas transport are described. They generally require a large amount of input data to characterize soil, crop and climate conditions and are therefore difficult to apply on a field scale. The results of the present study suggest that a simple empirical model which requires only easily obtainable data as mineral N content and WFPS, in combination with a few days lasting measurement campaigns, may be a valuable tool to predict N_2O fluxes from similar sites.

Acknowledgements

CHAPTER 6

Spatial variability of nitrous oxide fluxes in mown and grazed grasslands on a poorly drained clay soil

Spatial variability of nitrous oxide fluxes in mown and grazed grasslands on a poorly drained clay soil

Summary

Fluxes of nitrous oxide (N_2O) were measured in mown and intensively-grazed plots on a slightly-sloping, poorly-drained clay soil, using 144 flux chambers on four consecutive days. We tested the hypotheses that (i) spatial variability of N_2O fluxes is larger in grazed than in mown grassland and (ii) spatial dependency is larger in mown than in grazed grassland. Distributions were approximately log-normal. Fluxes from grazed grassland were larger than those from mown grassland. Multiple linear regression analyses showed weak relationships between N_2O flux and moisture, NH_4^+, NO_3^-, and C contents, with less than 15% of the variance in N_2O flux accounted for. Spatial variability was large both on a relatively small scale (less than 6 m) and on a larger scale (10-100 m) and was larger on mown grassland than on grazed grassland. Geostatistics showed that N_2O fluxes were spatially dependent for a lag distance less than 6 m on mown grassland. On grazed grassland fluxes were spatially independent on a scale of < 6 m. The large spatial variability of N_2O fluxes suggests that even measurement techniques that integrate N_2O fluxes over a large area may be hampered by the large spatial variability of N_2O fluxes.

Introduction

Grazing animals affect the chemical, biological and physical properties of grassland soils, through excretion of urine and dung, and treading. Urine and dung contain mineral N and mineralizable C. Moreover, soil organic C may be solubilized by the high pH of urine (Monaghan and Barraclough, 1993). Hence, uneven distribution of animal excreta leads to large and heterogeneously distributed amounts of mineralizable N and C in grassland soil (e.g. White *et al.*, 1987).

Mineral N and mineralizable C largely control nitrous oxide (N_2O) production in soils (e.g. Davidson, 1991). In addition, the high NH_3 concentrations in urine patches may lead to accumulation of nitrite (NO_2^-) during nitrification, which may enhance N_2O production (Chalk and Smith, 1983). Treading by grazing animals compacts the soil (Naeth *et al.*, 1990), which limits diffusion of O_2 and promotes denitrification (Douglas

and Crawford, 1993). The combined effects of dung, urine and treading on grazed grassland lead to larger N_2O fluxes than from comparable mown grasslands (Carran *et al.*, 1995; Velthof and Oenema, 1995b). The distribution of dung, urine and treading in grazed grassland is random, except where grazing animals tend to congregate, i.e. in camping areas. Camping is minimal, however, in intensively managed open fields with a high stocking rate. Hence, grazed grassland is expected to show large random variability in N_2O fluxes, associated with high substrate levels and restricted diffusivity locally caused by dung and urine and by treading, respectively. We hypothesize that the random spatial variability of N_2O fluxes is larger in intensively-grazed than in mown grassland.

A slightly-sloping, poorly-drained ungrazed grassland is expected to show a low-level spatial dependence (coherent variation) in N_2O fluxes, related to microtopography and coherent variability in especially moisture content. Our second hypothesis is that N_2O fluxes are spatially dependent to a greater extent in mown-only than in intensively-grazed grassland on a slightly-sloping, poorly drained soil. Hence, our first hypothesis states that the random noise of N_2O fluxes is larger in grazed than in mown grassland and the second hypothesis states that the pattern of the N_2O fluxes is less coherent on grazed than on mown grassland.

We tested the two hypotheses on (sheep) grazed and mown grasslands. A rapid-flux chamber technique was used to measure N_2O fluxes from grazed and mown plots in Devon UK. The flux chambers covered 300 cm^2 of soil. We considered this size of flux chamber to be suitable for assessing the effect of grazing on N_2O fluxes, because sheep dung and urine patches, and soil compaction by sheep affect soil areas less than 100 cm^2. Results were analyzed using geostatistical techniques.

Materials and methods

Experimental site and weather conditions
Measurements were carried out on 0.8 ha subplots of a 30 ha, slightly-sloping long-term grassland sward on a poorly-drained soil in North Wyke, Devon, UK, during 20-23 September 1994. The soil was a clay loam of the Halstow series (gleyic cambisol) in which the top soil is typically wet from late autumn until spring. Average precipitation at the site is 1035 mm of which two-thirds fall between October and March. Average bulk density of the 0-10 cm soil layer was 1.08 kg dm^{-3} (n=64).

The soil was wet during the measurement period (there had been 118 mm rainfall during the preceeding 19 days). No significant rainfall occurred during the

measurement period, except for a total of 5 mm of rainfall in the night of 20 to 21 September. There were relatively small fluctuations, between 12-16 °C, of soil temperature at 5 cm depth during day time (Figure 1).
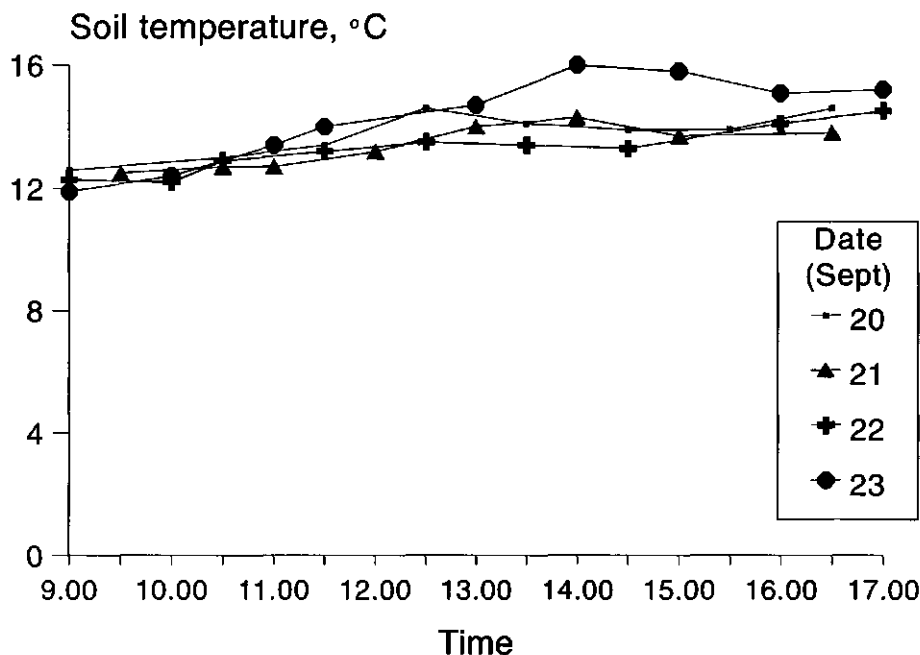
Figure 1. Time course of soil temperature at 5 cm depth, for all measurement days.

Experimental set-up and N₂O flux measurements

Two plots each of 80x96m on the flattest part of the field were delineated, one of which was mown and the other grazed. Each plot was divided into eight square subplots of equal size (Figure 2). The mown plot was mown on 18 September 1994 and grass was removed early on 19 September. Grazing with 150, 6-month old lambs started on 15 September and was continued throughout the experiment: the high number was chosen to reduce camping. Due to this high number and the wet soil conditions, the sward was smothered and water and/or urine filled hoof-holes were visible. Both plots received 125 kg N ha^{-1} as ammonium nitrate early on 19 September. The objective for both systems was to provide large potential substrates for N_2O generation under wet soil conditions.

Fluxes of N_2O were measured using vented closed flux chambers. Within each subplot, 3x6 grids of 18 flux chambers 1 m apart were placed at random. For each day's measurements there were eight grids, one in each subplot: four of the grids were oriented North-South, four East-West. Flux chambers, PVC cylinders (20 cm internal diameter and 15 cm high and sharp edges) were inserted 2 cm into the soil 30 min before flux was measured. Each chamber had a removable lid which could be sealed. Each day, 144 flux measurements were made between 09.00 h and 17.00 h. Fluxes from mown grassland were determined on 20 and 23 September and fluxes from grazed grassland on 21 and 22 September.

Changes in the concentrations of N_2O in the headspace of the flux chambers were determined in the field, using a photo-acoustic infra-red gas analyzer and a multipoint sampler (Velthof and Oenema, 1995a). Measurements of N_2O concentrations every 10 minutes showed that fluxes were large, i.e. greater than 100 µg N m^{-2} h^{-1}, and that N_2O concentration increased linearly with time (Figure 3), which agreed with earlier experiments in which large N_2O fluxes were shown (Velthof and Oenema, 1995a). In order to be able to measure 144 fluxes between 09.00 h and 17.00 h, we decided to measure the N_2O concentration only once per chamber, 30 to 45 min after closing the chamber. Flux of N_2O was then calculated assuming an initial background N_2O concentration of 310 µl m^{-3} and a linear increase in N_2O concentration in the headspace after closing the chamber.

Additional soil measurements

Soil from all 144 flux chambers on the mown plot on 20 September and from the grazed plot on 22 September, was sampled and analyzed for contents of moisture, NH_4^+ and NO_3^-. Three samples of the 0-10 cm soil layer in each chamber were taken using a 2.0 cm corer, immediately after N_2O flux had been measured. Moisture contents were determined in sub-samples of 100 g field moist soil after drying at 105 °C for 24 h. Other sub-samples of 100 g moist soil were extracted with 200 ml 1 M KCl, within 2 h after sampling. The KCl extracts were frozen prior to analysis for NH_4^+ and NO_3^- contents using standard auto-analyzer techniques.

Carbon mineralization potential (CMP) was determined in soil samples taken in all 144 flux chambers on the grazed plot on 22 September. CMP was estimated from CO_2 evolution during aerobic incubation of 40 g moist soil in 500 ml bottles at 20°C, using the method of Burford and Bremner (1975), with minor modifications. Concentration of CO_2 was measured with a photoacoustic infra-red gas analyzer.
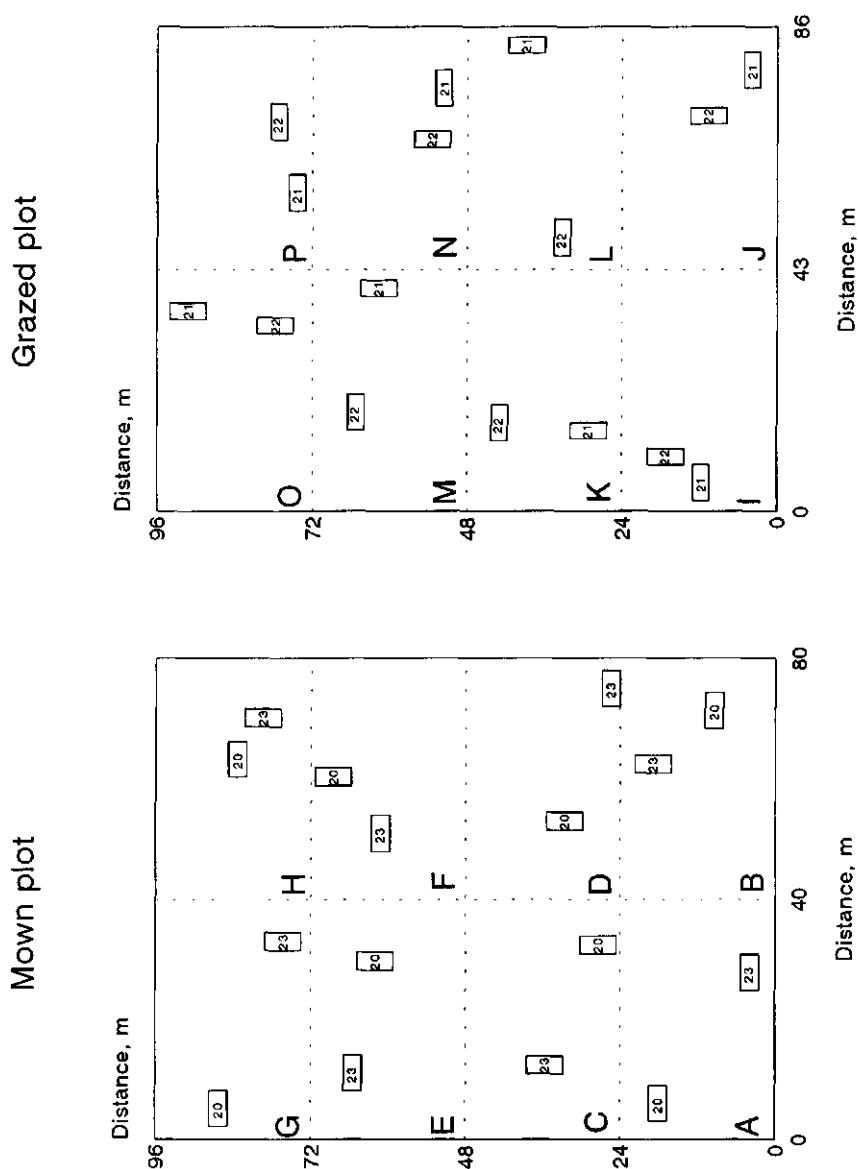
Figure 2. Map showing the location of the flux chambers on the mown and grazed plot, for all days. Each plot was divided in 8 subplots giving in total 16 sub plots: A to P. On each subplot, a 3x6 grid of 18 flux chambers with an in between distance of 1 m was placed at random. The squares indicate the place on the subplots where the grids of 3x6 flux chambers were placed, for all days. The number in the squares indicate the day in September.

Statistical and geostatistical analyses

For each day, the frequency distributions of untransformed and log-transformed N_2O fluxes, moisture, NH_4^+, NO_3^-, mineral N contents and CMP (n=144) were tested for normality using the Lilliefors Test for Normality (Lilliefors, 1967). Differences between the subplots in N_2O flux and soil variables were determined by analysis of variance (ANOVA) and least significant difference (LSD) test ($\alpha=0.05$). Simple and multiple linear regression analyses ($\alpha=0.05$) were carried out with log-transformed N_2O flux as dependent variable and combinations of the soil variables as independent variables. ANOVA and linear regression analyses were carried out using Genstat 5 (Genstat 5 Committee, 1987).

The effect of the number of samples on the precision of the estimated mean flux was assessed assuming that the data were spatially independent and using the equation $N = (t^2s^2)/d^2$ (e.g. Snedecor and Cochran, 1989), where N is the number of samples required, t is the value of Student's t for a chosen probability α, s^2 is the estimated 'true' variance and d the tolerable deviation of the sample mean from the 'true' mean. The sample number N was estimated for various deviations of the sample mean from the 'true' mean of log-transformed N_2O fluxes ($\alpha=0.05$). For each day, the 'true' mean and variance were set at the mean and variance of the 144 log-transformed fluxes. Back-transformations were carried out using an uniformly minimum variance unbiased estimator of the mean (UMVUE-mean) of log-normal distributions (e.g. Parkin and Robinson, 1992).

Spatial variability of N_2O fluxes and soil variables were analyzed using geostatistics (e.g. Webster, 1985). The degree of spatial dependence between samples can measured by calculating the semivariance $\gamma(h)$. The semivariance was estimated by

$$\hat{\gamma}(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z(x_i) - Z(x_i+h)]^2$$

where $N(h)$ is the number of pairs of observations separated by lag distance h and $Z(x_i)$ and $Z(x_i+h)$ represent the value of property Z at two positions separated by h (e.g. Webster, 1985). The spatial variability was modelled with a variogram, in which the semivariance is plotted against the lag distance between the sample points. Variograms were calculated for the log-transformed data for N_2O fluxes, NH_4^+, NO_3^- and mineral N contents and untransformed data for moisture contents and CMP from each day, with a maximum lag distance of 6 m (the maximum distance between the flux chambers

within each subplot). There was no evidence that spatial dependence differed between the different grid alignments: spatial variability was assessed using isotropic variograms. Linear, spherical and exponential functions were fitted, using least square estimation SAS procedures (SAS Institute, 1985).
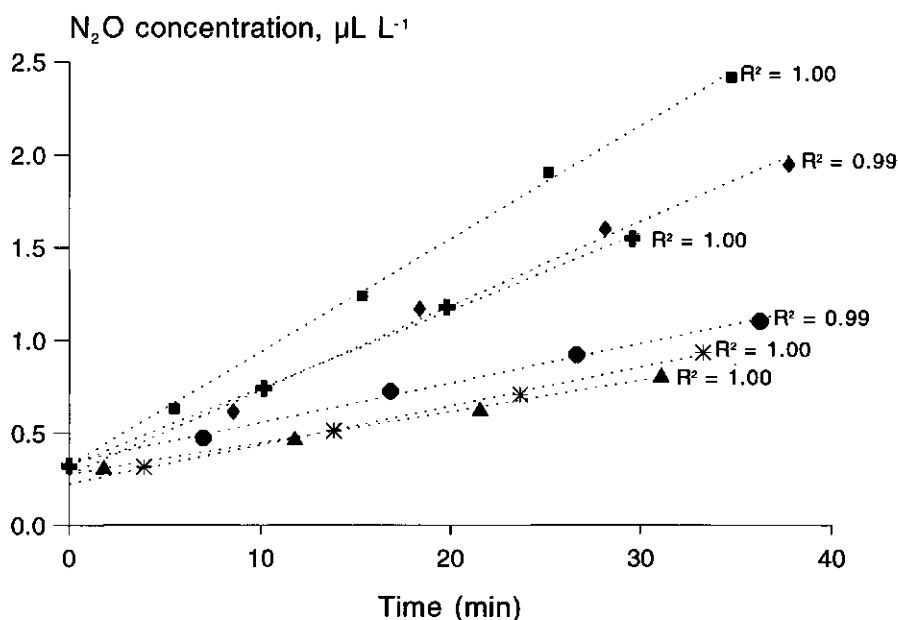
Figure 3. Examples of time course of changes in N_2O concentration in the headspace of six flux chambers, measured every 10 min. Chambers were closed at t=0. Lines were fitted using linear regression analysis.

Results

N_2O fluxes
Flux of N_2O increased quickly after N application (Table 1), suggesting that the surface layer was the main site of N_2O production. Mean N_2O flux from subplot G on mown grassland was relatively constant on 22 and 23 September; small variations in mean flux appeared to be related to differences in soil temperature (Table 1).

The spatial variability of fluxes was large, both within the subplots (less than 6 m distance between flux chambers) and between the subplots (10 to 100 m distance between the subplots) (Table 2). Coefficients of variation of N_2O flux ranged from 46

97

to 273% within the subplots and mean N_2O flux of the subplots ranged from 0.39 to 12.76 mg N m^{-2} h^{-1}. Fluxes from grazed grassland were substantially larger than from mown grassland (Table 2).

Coefficients of variation of 18 replicate fluxes were generally smaller on grazed grassland than on mown grassland (Table 2). The larger arithmetic means than medians (Table 2) indicate that the frequency distributions of the 18 fluxes from each subplot were positively skewed (Table 2). Distributions of the 144 fluxes from each measurement day were also positively skewed (Figure 4) and approximated log-normal distributions (α=0.1). Mean flux from grazed grassland, calculated as UMVUE mean, was 5.68 mg N m^{-2} h^{-1} on 21 September and 6.46 mg N m^{-2} h^{-1} on 22 September and values for mown grassland were 4.81 and 1.22 mg N m^{-2} h^{-1} on 20 and 23 September, respectively (Figure 4). For both the grazed and mown plots, the ranking in mean flux per subplot was similar on both days (Table 2).

To obtain a mean within 50% of the 'true' mean (α=0.05), 7 to 30 N_2O flux measurements were required (Figure 5). An increased precision to within 10% of the 'true' mean, required 375 to 1240 flux measurements. More flux measurements were required for mown than for grazed grassland to obtain a defined precision of the estimated mean N_2O flux.

Table 1. Temporal variability of N_2O fluxes from mown grassland, just after N application on 19 September and during 3 to 4 days after N application.

19 September		22 and 23 September		
Time, min after N application at 11.00 h	Flux[*] (mg N m^{-2} h^{-1})	Date + time	Flux[**] (mg N m^{-2} h^{-1})	Soil temperature °C
30-50	0.04 ± 0.01	22 Sept., 17.00 h	1.59 ± 0.53	14.5
50-70	0.05 ± 0.01	23 Sept., 9.00 h	1.38 ± 0.34	11.9
70-90	0.08 ± 0.01	23 Sept., 17.00 h	1.80 ± 0.43	15.2
90-110	0.10 ± 0.02			
110-130	0.12 ± 0.02			
130-150	0.13 ± 0.02			

[*]mean ± standard error (n=6); subplot C
[**]mean ± standard error (n=18); subplot G

Table 2. Summary statistics of the N_2O fluxes (mg N m^{-2} h^{-1}) per subplot (n=18).

Plot + date	Subplot[a]		Arithmetic mean	sd.	Cv., %	Minimum	Median	Maximum
Mown	G	d	6.85	4.97	73	0.96	5.87	20.87
20 Sept	D	cd	5.40	4.32	80	0.12	4.83	12.71
	A	bc	4.29	5.05	118	0.00	1.82	17.31
	C	ab	1.47	2.33	159	0.06	0.52	8.77
	F	a	1.11	1.23	110	0.00	0.63	4.72
	B	a	0.63	0.75	118	0.00	0.57	3.04
	H	a	0.55	0.61	110	0.00	0.31	2.15
	E	a	0.43	0.35	79	0.02	0.36	1.27
Grazed	O	d	12.76	9.26	73	0.59	10.81	40.23
21 Sept	I	bc	5.48	4.53	83	1.46	4.62	17.91
	K	c	5.14	2.36	46	1.51	5.12	9.99
	M	bc	4.85	3.72	77	0.38	4.37	15.38
	J	abc	4.27	3.71	87	0.11	3.96	15.53
	P	ab	4.05	3.70	91	0.32	2.98	12.02
	N	a	2.42	2.21	92	0.30	1.73	9.20
	L	a	2.07	1.89	91	0.27	1.43	6.62
Grazed	I	e	10.29	5.98	58	0.36	8.55	26.49
22 Sept	O	de	7.05	4.02	57	1.84	6.36	15.96
	J	bcd	6.80	7.51	110	0.16	4.18	25.39
	M	cd	5.89	3.84	65	0.02	6.00	11.80
	N	cde	5.30	2.68	51	0.38	5.06	10.24
	P	bc	3.71	2.44	66	0.92	3.42	9.87
	K	ab	3.58	4.64	129	0.15	2.11	18.00
	L	a	1.65	1.11	68	0.40	1.38	4.78
Mown	D	c	2.40	2.34	98	0.48	1.51	9.71
23 Sept	C	bc	1.74	1.31	75	0.11	1.70	4.92
	G	bc	1.38	1.44	104	0.05	0.89	5.25
	H	a	1.23	3.36	273	0.05	0.20	14.40
	E	b	1.07	0.83	77	0.04	0.76	3.03
	B	a	0.42	0.44	105	0.03	0.22	1.54
	A	a	0.40	0.40	102	0.02	0.32	1.74
	F	a	0.39	0.54	140	0.05	0.19	2.18

[a] Subplots are given in capitals and are presented in descending order of mean flux. Difference in small letter denote significant difference in flux, using LSD test on log-transformed fluxes (α=0.05). Letters are only valid for comparison of subplots of one measurement day, not for comparison between the four days.
Chronological order of measurement on 20 Sept.: D-H-F-C-E-G-B-A, on 21 Sept.: K-P-M-L-N-J-O-I, on 22 Sept.: M-I-J-L-N-K-O-P, and on 23 Sept.: G-H-B-E-D-C-A-F

Soil variables

Significant differences between subplots were found for both measurement days and for all soil variables (Table 3). Within the subplots, the range in moisture contents and CMP were small, with coefficents of variation of the 18 replicates being less than 15% (data not shown). Despite the heavy N application, the range in NH_4^+, NO_3^- and total mineral N contents was large in both mown and grazed grasslands. Contents of NH_4^+, NO_3^- and total mineral N were higher in mown grassland on 20 September than in grazed grassland on 22 September (Table 3). The ratio NH_4^+ to NO_3^- ranged from 0.1 to 4.4 (on average 0.9) on mown grassland and from 0.10 to 47.7 (on average 2.2) on grazed grassland. On both days, moisture contents ranged ranged from 21-38% (wt/wt), and were on average 31.4% which corresponds with an average water-filled pore space of 85% (ranging from 50 to > 100%).

On mown grassland, the frequency distributions of moisture, NH_4^+ and mineral N contents were approximately log-normal (α=0.1). Distributions of NO_3^- contents did not follow normal or log-normal distributions (α=0.1). On grazed grassland, distributions of moisture contents and CMP were approximately normal and those of NH_4^+, NO_3^- and total mineral N contents approximately log-normal (α=0.1).

Multiple linear regression analyses showed that variance in N_2O fluxes was poorly explained by the soil variables. For mown grassland on 20 September, the best regression model with log-transformed N_2O flux as dependent variable included moisture content and log-transformed NO_3^- content (R_{adj}^2 = 0.13). The best model for grazed grassland, only included log-transformed NH_4^+ content (R_{adj}^2 = 0.12). There were also weak correlations between the means of the fluxes and soil variables per subplot.

Geostatistical analysis
Variograms of N_2O fluxes from mown grassland on 20 and 23 September established the presence of spatial dependency for a lag distance of less than 6 m (Figure 6). The variogram for 20 September was fitted best with a linear model, that on 23 September with a spherical model with a range of 5.5 m (Figure 6). This range is not precisely determined, because there were no measurement points greater than 5.4 m. A "nugget" effect (i.e. non-zero variance as h tends to 0; Webster, 1985) of approximately 1 (μg N m^{-2} h^{-1})^2 was shown. The variograms of mown grassland showed larger variance on 20 September than on 23 September. In contrast, variograms of N_2O fluxes from grazed grassland on 21 and 22 September revealed no clear spatial dependency on either measurement days and were similar on both occasions and followed a "nugget"
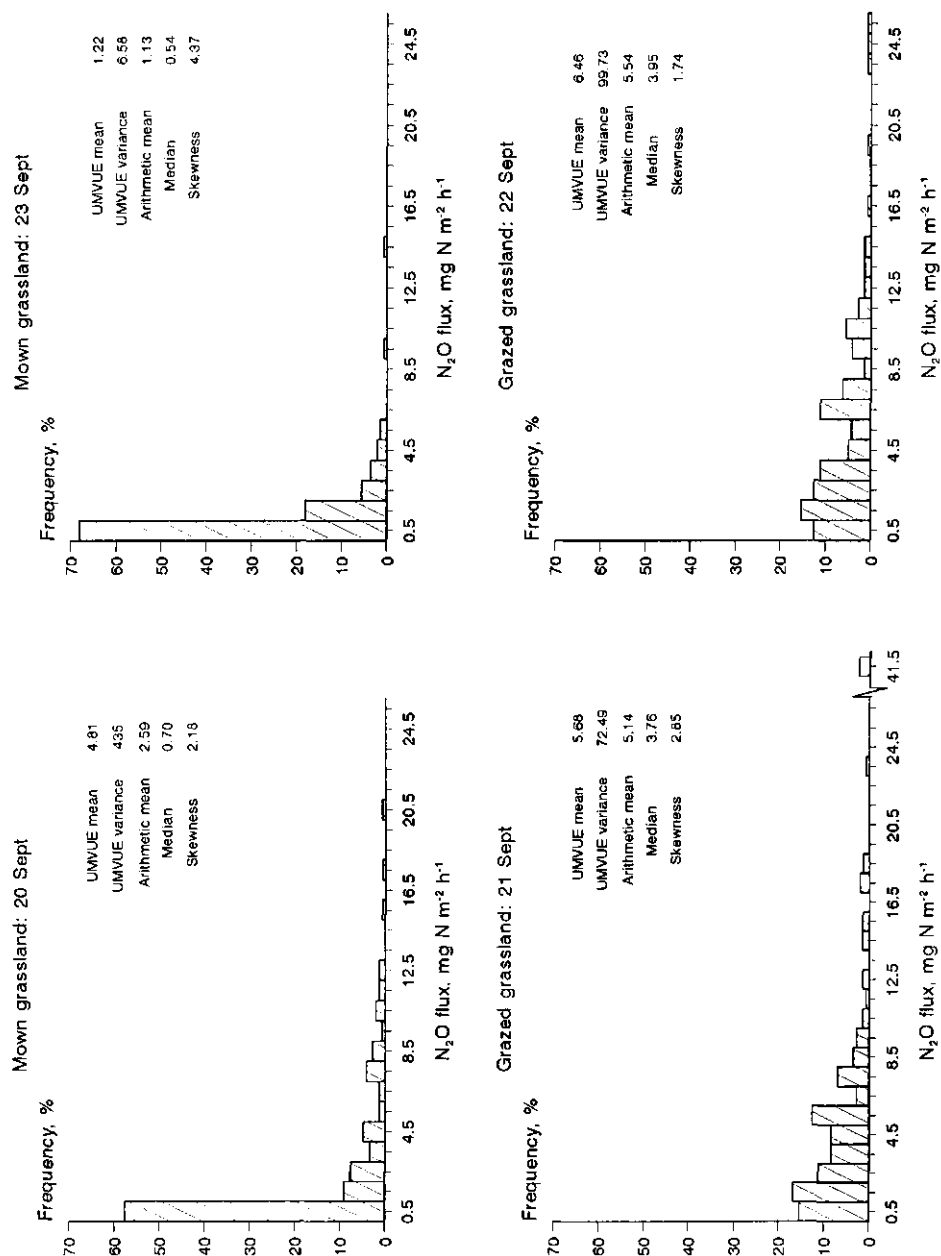
Figure 4. Frequency distributions of N_2O fluxes (n=144), for all measurement days.
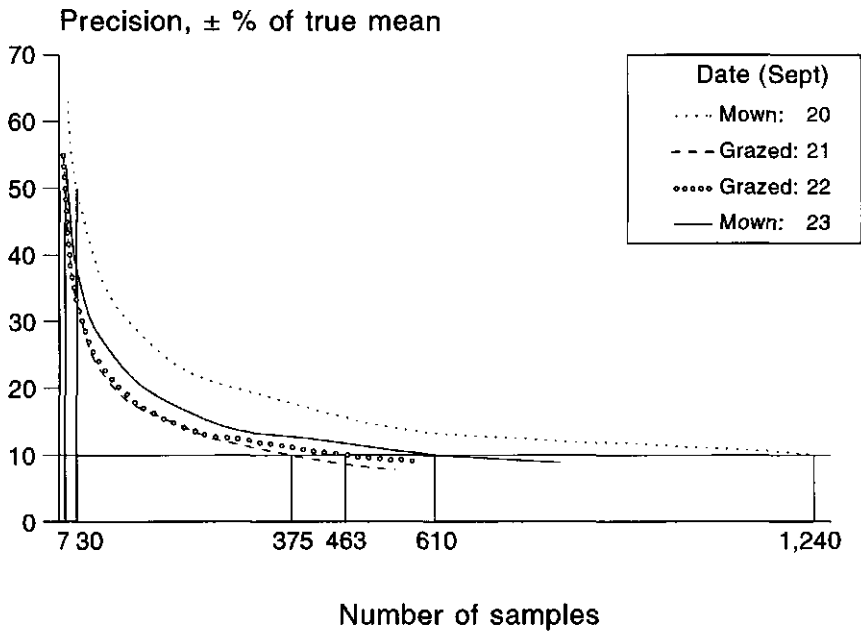
Figure 5. Relationship between the number of samples and the degree of precision of estimated mean N_2O flux ($\alpha=0.05$).

model type (Figure 6). Semivariance was smaller on grazed than on mown grassland. Variograms of moisture, NH_4^+, NO_3^-, total mineral N contents and CMP showed weak spatial dependence, with R^2 values for linear fits being less than 0.45 (data not shown).

Discussion

Temporal variability of N_2O fluxes
Measurements of N_2O fluxes were made between 09.00 h and 17.00 h, each day and we assumed that N_2O flux during this period did not vary much. The few data available suggested that day time variations in fluxes were relatively small, except on 19 September immediately after N fertilizer application (Table 1). The main measurements started one day after N application. The absence of substantial rainfall and the slight variations in soil temperature during the measurement days (Figure 1) will have contributed to only small temporal fluctuations of N_2O fluxes.

Table 3. Mean moisture content in % (w/w), NH_4^+ content in mg N kg^{-1}, NO_3^- content in mg N kg^{-1}, total mineral N content (Nmintot) in mg N kg^{-1} and CMP in mg C kg^{-1} day^{-1}, for the mown plot on 20 September and the grazed plot on 22 September (see Figure 2).

Plot+date	Subplot	Moisture[a]	NH_4^+[a]	NO_3^-[a]	Nmintot[a]	CMP[a]
Mown	A	30.4 b	48 bc	57 c	105 c	ND
20 Sept.	B	31.5 c	50 bc	59 bc	108 c	ND
	C	30.8 bc	33 ab	35 ab	57 ab	ND
	D	34.8 e	50 c	62 c	111 c	ND
	E	30.9 bc	43 bc	52 bc	90 bc	ND
	F	30.1 ab	24 a	28 a	53 a	ND
	G	32.7 d	32 ab	29 a	61 a	ND
	H	29.1 a	78 c	83 c	161 c	ND
	Overall mean	31.3	45	51	93	
	Overall sd.	2.3	46	43	85	
	Overall Cv., %	7.3	102	84	91	
	Overall range	27-38	2-239	1-253	3-492	
Grazed	I	30.6 ab	63 d	39 d	102 c	66 b
22 Sept.	J	31.9 bc	31 c	30 cd	61 b	64 ab
	K	31.6 bc	35 abc	7 a	42 a	77 c
	L	30.8 ab	21 a	29 cd	51 ab	60 a
	M	30.9 ab	27 bc	11 b	38 ab	74 c
	N	32.9 cd	28 abc	18 bc	46 ab	76 c
	O	29.8 a	30 c	19 c	49 ab	73 c
	P	33.6 d	27 ab	29 cd	56 ab	78 c
	Overall mean	31.5	33	23	55	71
	Overall sd.	2.6	30	20	44	10
	Overall Cv., %	8.3	91	87	80	14
	Overall range	21-38	2-224	2-124	5-349	46-95

[a] Arithmetic mean; difference in letter denote significant difference between subplots using LSD test (α=0.05). Prior to LSD test, NH_4^+, NO_3^- and Nmintot contents were log-transformed. Letters are only valid for comparison of subplots of each measurement day, not for comparision between the two days.

Relationship between N_2O fluxes and soil variables

Flux measurements on mown and grazed grassland were not carried out on the same days, and so a real comparison is difficult to make. Our results suggested that fluxes were larger from grazed grasslands than from mown grasslands (Table 2), which is also

found in a study of Velthof and Oenema (1995b).

There would have been a number of differences between the swards in the contents of and competition for mineral N. The grazed sward would have had greater potential for removal by uptake than the mown sward, but would have received large returns of NH_4^+ via urine and dung in the first instance. More total mineral N was present under mowing on 20 September than under grazing on 22 September, but the ratios NH_4^+ to NO_3^- were greater with grazing. The range in water-filled pore space of 50 to 100% suggests that both nitrification and denitrification may have been N_2O sources (Davidson, 1991). On grazed grassland, the regression model that explained the most of the variance in N_2O flux contained only NH_4^+ contents, and on mown grassland the best regression model contained both moisture and NO_3^- contents. These models may suggest that nitrification was a significant N_2O source on grazed grassland and denitrification on mown grassland. It must be noted however, that these models explained only less than 15% of the variance in N_2O flux.

Also in many other studies a poor relationships between N_2O fluxes and soil variables have been found (e.g. Jarvis *et al.*, 1994). The determination of the soil variables in bulk samples probably does not represent accurately the integrated effect of interactions of factors in soil microsites controlling N_2O production.

Spatial variability of N_2O fluxes
The large differences in N_2O fluxes between and within the subplots on both grazed and mown grasslands, indicate that spatial variability was large over a relatively small scale (i.e. less than 6 m distance between the flux chambers) and larger scale (10 to 100 m between the subplots).

It was hypothesized that spatial variability of N_2O fluxes would be larger on grazed grassland than on mown grassland, because of the uneven distribution of urine and dung and effects of treading. Surprisingly, coefficients of variation of the fluxes within the subplots (Table 2) and semivariance (Figure 6) were larger on mown than on grazed grassland. This suggests that the intensive grazing regime buffered changes with respect to N_2O production. The poor relationship between the soil variables and N_2O fluxes did not permit identification of possible differences in the causes of spatial variability between the grasslands. We speculate that the high stocking rate caused an 'unnaturally' uniform distribution of mineralizable C in the grazed grassland, which may have decreased spatial variability of denitrification-derived N_2O fluxes on grazed grassland.
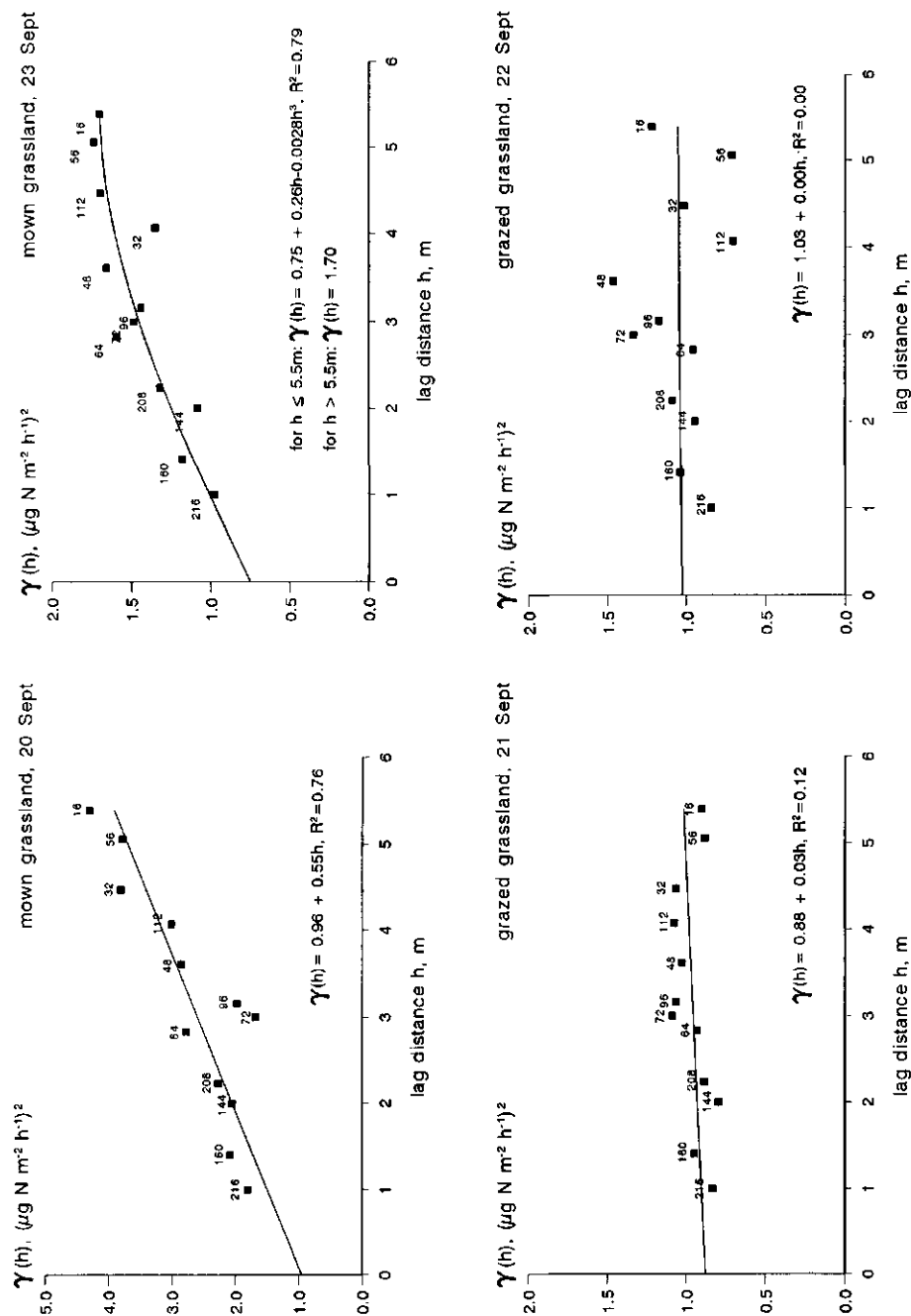
Figure 6. Variograms of log-transformed N_2O fluxes for all measurement days. The numbers in the figures indicate the number of data pairs.

Despite the heavy N application of 125 kg N per ha, the range in contents of NH_4^+, NO_3^- and total mineral N was large on both grasslands (Table 3), suggesting that variability in mineral N contents may also have contributed to the spatial variability of N_2O fluxes.

Spatial dependency of N_2O fluxes

The presence of spatial dependency of N_2O fluxes on mown grassland and the absence of spatial dependency of N_2O fluxes on grazed grassland, agree with our second hypothesis. Variograms of soil variables (not shown) showed no clear differences between mown and grazed grasslands and do not explain the observed differences in spatial dependency of N_2O fluxes. There was some evidence that topography played a role in the differences in fluxes between the subplots on mown grassland, with relatively large fluxes on low parts of the field (e.g subplot G) and relatively small fluxes on high parts of the field (e.g. subplots B, F and H). On grazed grassland, there were no indications that (micro)topography affected N_2O fluxes. Van Kessel *et al.* (1993) suggested that topography influenced denitrification rate and N_2O fluxes, because it affects hydrology and soil processes.

The nugget effect in the variograms was about 2 µg N m^{-2} h^{-1} on the untransformed scale, which is below the detection limit of the flux measurement technique (Velthof and Oenema, 1995a). The size of the nugget effect is caused by measurement error and microvariability, which cannot be detected at the scale of sampling (Webster, 1985). The nugget effect in our study was probably due to measurement error, with which microvariability played only a minor role. Variations in N_2O fluxes and denitrification rates at distance less than 1 m have been reported by Parkin *et al.* (1987), Robertson *et al.* (1988) and Ambus and Christensen (1994), indicating that soil microsites play an important role in determining N_2O release.

The presence of spatial dependency of N_2O fluxes from mown grassland suggests that the in-between distance of the flux chambers should be more than 6 m to obtain spatial independent and random samples.

Number of flux measurements

A large number of flux chambers was required to obtain a high precision of the mean N_2O flux. Similar results were found by Folorunso and Rolston (1984). Because of the many assumptions made for this type of analysis, the estimates of required numbers must be interpreted with caution. However, such calculations indicate clearly that precise estimation of the mean N_2O flux of a field requires many chambers. The larger

number of flux measurements required for mown grassland than for grazed grassland to obtain a defined precision was due to the larger spatial variability of N_2O fluxes from mown than from grazed grasslands. Increasing the size of the flux chamber and the emitting surface may increase the precision of the estimated mean flux, because it may decrease the spatial variability involved (Ambus *et al.*, 1993).

Knowledge of variograms for soil variables prior to sampling, can considerably reduce sampling effort required to obtain an estimate of the mean with a certain precision, using kriging (McBratney and Webster, 1983). Because of the complexity of factors controlling N_2O fluxes and the strong temporal variations it seems unlikely that general applicable variograms of N_2O fluxes from managed grassland can be obtained.

The large spatial variability of N_2O fluxes in our study suggests that even measurement techniques that integrate N_2O fluxes over a large area (>1 m^2), such as micrometeorological methods and megachambers, may be hampered by the large spatial variability of N_2O fluxes.

Acknowledgements

CHAPTER 7

Effects of type and amount of applied nitrogen fertilizer on nitrous oxide fluxes from intensively managed grassland

Effects of type and amount of applied nitrogen fertilizer on nitrous oxide fluxes from intensively managed grassland

Summary

Five field experiments and one greenhouse experiment were carried out to assess the effects of nitrogen (N) fertilizer type and the amount of applied N fertilizer on nitrous oxide (N_2O) emission from grassland. During cold and dry conditions in early spring, emission of N_2O from both ammonium (NH_4^+) and nitrate (NO_3^-) containing fertilizers applied to a clay soil were relatively small, i.e. less than 0.1% of the N applied. Emission of N_2O and total denitrification losses from NO_3^- containing fertilizers were large after application to a poorly drained sand soil during a wet spring. A total of 5-12% and 8-14% of the applied N was lost as N_2O and via denitrification, respectively. Emissions of N_2O and total denitrification losses from NH_4^+ fertilizers and cattle slurry were less than 2% of the N applied. Addition of the nitrification inhibitor dicyandiamide (DCD) reduced N_2O fluxes from ammonium sulphate (AS). However, the effect of DCD to reduce total N_2O emission from AS was much smaller than the effect of using NH_4^+ fertilizer instead of NO_3^- fertilizer, during wet conditions. The greenhouse study showed that a high groundwater level favors production of N_2O from NO_3^- fertilizers but not from NH_4^+ fertilizers. Increasing calcium ammonium nitrate (CAN) application increased the emitted N_2O on grassland from 0.6% of the fertilizer application rate for a dressing of 50 kg N ha^{-1} to 3.1% for a dressing of 300 kg N ha^{-1}. In another experiment, N_2O emission increased proportionally with increasing N rate. The results indicate that there is scope for reducing N_2O emission from grasslands by choosing the N fertilizer type depending on the soil moisture status. Avoiding excessive N application rates may also minimize N_2O emission from intensively managed grasslands.

Introduction

Nitrous oxide (N_2O) is produced in soils through the microbiological processes of nitrification and denitrification (Firestone and Davidson, 1989). The rates of these processes and the rate of N_2O production are dependent on the amounts of ammonium (NH_4^+) and nitrate (NO_3^-) in the soil, as well as other factors. In agricultural soils, there are several sources of NH_4^+ and NO_3^-, including fertilizers, animal wastes, atmospheric

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deposition, and mineralization of soil organic matter. For NO_3^- containing nitrogen (N) fertilizers, denitrification is initially the only possible direct source of N_2O, whereas both nitrification and denitrification can be involved in the production and emission of N_2O from NH_4^+ containing fertilizers.

A review of field studies by Bouwman (1995) indicates that on average the effect of N fertilizer type on N_2O fluxes is small from agricultural soils. However, in some studies (e.g. McTaggart *et al.*, 1994) larger fluxes have been found from NO_3^- fertilizers than from NH_4^+ fertilizers, whilst in other studies the opposite has been found, particularly from anhydrous ammonia applications, which emitted up to 5% of the amount of fertilizer-N as N_2O (eg. Breitenbeck and Bremner, 1986). The discrepancies between studies suggest that site specific conditions control the N_2O emission from NO_3^- and NH_4^+ fertilizers. Soil moisture status and temperature are probably key factors because they affect the relative rates of nitrification, denitrification, N_2O production and N_2O consumption (Firestone and Davidson, 1989). Temperature may also affect the relative uptake rate of NH_4^+ and NO_3^- by the sward, thereby possibly indirectly affecting N_2O emission. For example, Watson (1986) showed a preferential uptake of NH_4^+-N over NO_3^--N by ryegrass under cold early spring conditions.

We explored the possibilities for reducing N_2O emission from intensively managed grassland in temperate areas by manipulating the type and the amount of N fertilizer and by the use of a nitrification inhibitor. Soil incubation studies under controlled conditions may provide a good insight in the effects of N type and N rate on N_2O emission from soil (e.g. Bremner and Blackmer, 1978). However, we focused on field and greenhouse experiments on grass, because the soil-root-plant interface may have a tremendous effect on local N, carbon and oxygen availabilities and thereby on N_2O emission (Beck and Christensen, 1987; Smith and Tiedje, 1979).

On intensively managed grasslands a total N application of 200 to 400 kg N ha^{-1} per year is split in 4 to 7 dressings in decreasing amounts, generally. We hypothesized that fewer heavy dressings result in a larger N_2O emission than more frequent lighter dressings. With the lighter dressings, the mineral N content of the soil is lower throughout the growing season (Prins, 1980).

Materials and methods

Three field experiments and one greenhouse experiment were carried out to assess the effects of common N fertilizers on N_2O emission (experiments 1, 2, 3 and 4) and two field experiments (experiments 5 and 6) were carried out to assess the effect of the

amount of N fertilizer application on N_2O emission (Table 1). Three experiments (1, 2 and 5) involved springtime conditions, two with summertime conditions (experiments 3 and 4) and one covered the whole growing season (experiment 6). Soil properties are given in Table 2. In all experiments, fluxes were measured during the daytime, sometime in the period between 9.00 and 13.00 h. Soil temperature at 5 cm depth, rainfall and soil moisture content were determined at regular intervals.

Table 1. Overview of experiments.

Exp.	Location	Soil	Period	Treatments[*]	Design
1	Wageningen	riverine clay	March 1993	Control AS, CN, CAN, UR: 80 kg N ha^{-1}	randomized blocks in 4 replicates
2	Bennekom	poorly drained sand	March - April 1994	Control AS, AS+DCD, CN, CAN, UR: 80 kg N ha^{-1} Cattle slurry surface-applied: 15 m^3 ha^{-1} [**] Cattle slurry sod injected: 15 m^3 ha^{-1} [**]	randomized blocks in 4 replicates
3	Bennekom	poorly drained sand	June - July 1994	Control AS, AS+DCD, CN, CAN, UR: 80 kg N ha^{-1} Cattle slurry surface-applied: 15 m^3 ha^{-1} [**] Cattle slurry sod injected: 15 m^3 ha^{-1} [**]	randomized blocks in 4 replicates
4	Greenhouse	sand	July-Sept. 1994	Two groundwater depths: 15 and 30 cm Control AS, CN: 80 kg N ha^{-1}	split-plot in 3 replicates
5	Bennekom	poorly drained sand	April-May 1994	CAN: 0, 50, 100, 150, 200, 300 kg N ha^{-1} applied in one dressing	randomized blocks in 4 replicates
6	Lelystad	calcareous clay	March-1993	CAN: 0, 220, 440, 660, 880 kg N ha^{-1} split in 7 dressings	randomized in 6 replicates

[*] AS: ammonium sulphate, AS+DCD: ammonium sulphate + nitrification inhibitor DCD, CN: calcium nitrate, CAN: calcium ammonium nitrate, UR: urea
[**] Mineral N application rate was about 45 kg N ha^{-1}

Experiment 1
Experiment 1 was to assess the effect of N fertilizer type on N_2O emission from

grassland in early spring. There were four fertilizer treatments and a control (Table 1). Fluxes of N_2O were measured 19 times during 3.5 weeks, following fertilizer applications on 3 March 1993. Fluxes were measured using the flux chamber technique described in detail by Velthof and Oenema (1995a). Briefly, fluxes were measured using circular PVC flux chambers with an internal diameter of 20 cm and a height of 15 cm. Concentration of N_2O in the headspace was determined in the field at 0, 10, 20 and 30 minutes after closing the flux chamber, using a photo-acoustic spectroscopic infra-red gas analyzer of Brüel & Kjær. The analyzer was directly attached to six flux chambers via a multipoint sampler in a closed system via tubes. Gas samples were taken and analyzed for N_2O automatically every 90 s after the air in the headspace was pumped around for 20 s. The accuracy of the gas analyzer was about 5 % in the range of 300-5000 µl N_2O m^{-3} under field conditions.

Table 2. General properties of the three soils.

Property	Riverine clay Wageningen[*]	Poorly drained sand Bennekom[*]	Calcareous clay Lelystad[**]
Total N, g kg^{-1}	3.7	1.8	2.4
Total C, g kg^{-1}	47	27	27
pH-KCl	5.2	4.8	7.2
Clay content ($\leq$ 2 µm), g kg^{-1}	250	50	295

[*] 0-10 cm layer
[**] 0-20 cm layer

Experiments 2 and 3
The effects of type of N fertilizer and cattle slurry on N_2O emission from grassland in spring and summer was assessed in experiments 2 and 3, respectively. The identical experiments 2 and 3 were carried out on a poorly drained sand soil in Bennekom in March-April and June-July 1994, respectively (Table 1). In one treatment the nitrification inhibitor dicyandiamide (DCD) was mixed with AS. Application rate of DCD (67% N) was 20 kg N ha^{-1}. Total application rate of the AS+DCD mixture was 80 kg N ha^{-1}.

The cattle slurry was either surface-applied or injected, to study the effect of application method on N_2O emission. Fresh cattle slurry, obtained from a local farm, was injected with a sod-injector to a depth of 5 cm at a rate of 15 m^3 ha^{-1}, which was

equal to a mineral N application rate of about 45 kg N ha^{-1}. Rectangular PVC chambers (width of 30 cm, length of 42 cm and height of 23 cm) were inserted 3 cm into the soil to cover two bands of injected slurry (distance between the slurry bands was 20 cm). The flux chambers have removable lids. Fluxes of N_2O were measured 20 times during 4 weeks in experiment 2 and 22 times during 4.5 weeks in experiment 3, using the system described for experiment 1.

Denitrification rates were measured in duplicate using the acetylene inhibition technique (e.g. Ryden and Dawson, 1982). Denitrification rate was calculated from the amount of N_2O evolved from four undisturbed soil cores of the 0-10 cm soil layer (diameter 4.7 cm), incubated in 3 L incubation containers in an atmosphere with 5% acetylene. The containers were placed in holes in the soil to carry out incubation at soil temperature. The concentration of N_2O in the headspace of the containers was measured after 24 hours using the photo-acoustic infra-red gas analyzer. After the denitrification measurements in experiment 2, the soil cores were dried at 40°C and ground. The concentrations of NO_3^- and NH_4^+ were measured by extraction of 10 g dry soil in 100 ml 0.01 M $CaCl_2$ and analysis by standard auto-analyzer techniques (Houba et al., 1989).

Experiment 4
Groundwater levels in grassland soils in the Netherlands are often shallow (i.e. within one meter from the soil surface), and are being adjusted to some extent by controlling the water level in ditches surrounding these grasslands. The interaction effect between N fertilizer type and groundwater level on the N_2O emission was examined in a greenhouse experiment. Undisturbed soil cores with an intact sward were taken to a depth of 30 cm from the Bennekom site, using stainless steel columns (internal diameter 20 cm and height 30 cm) with sharp edges. The main factor of the split-plot experiment in three replicates was groundwater level (Table 1). The columns were randomly placed in containers with groundwater levels at 15 and 30 cm below the soil surface. These depths to the groundwater are often observed at the Bennekom site, in the spring and autumn (e.g. Figure 1). The experiment had two fertilizer treatments, AS and CN at a rate of 80 kg N ha^{-1}, and a control treatment. To simulate rainfall, 2 mm water was added on top of the column, three times a week.

Fluxes of N_2O were measured for almost two months, using the flux chamber technique described for experiment 1. The chambers had a collar of insulation foam and were put over the columns with soil. In total 39 flux measurements were carried out.

Experiment 5

The effect of the amount of N on N_2O emission from grassland in spring was assessed in experiment 5. Fluxes of N_2O were measured after application of calcium ammonium nitrate (CAN: NH_4NO_3 + $CaCO_3$ + $MgCO_3$; 27% N, 6% CaO, 4% MgO) in one dressing of 0, 50, 100, 150, 200 and 300 kg N ha^{-1} on 18 April (Table 1). The study was carried out on the same field as experiments 2 and 3. Fluxes were measured as described for experiment 1. During the first 18 days, flux measurement was carried out daily, except on days 7 and 13. In the period thereafter, the N_2O flux was measured every 2 to 4 days.

Experiment 6

The effect of the amount of N applied on N_2O fluxes from mown grassland during a whole growing season was assessed in experiment 6. Fluxes of N_2O were measured weekly in six replicates from grassland on a calcareous clay soil in the polder close to Lelystad. CAN was applied at 5 rates; 0, 0.5, 1, 1.5 and 2 times the recommended application rate for each dressing, based on an interactive fer~lization system (Vellinga *et al.*, 1996). This recommended rate amounted 440 kg N ha^{-1} for the whole growing season, split in seven dressings: 85, 75, 92, 50, 38, 53, and 47 kg N ha^{-1}, following each mowing and harvesting. The measurement technique was the same as in experiment 1. Flux was measured 29 times between March and November 1993.

Calculations and statistical analyses

Fluxes of N_2O were calculated from the course of the N_2O concentration in the headspace in time, using linear regression analysis. Total N_2O emission was calculated from the time course of the arithmetic mean N_2O flux, by linearly interpolating the mean N_2O fluxes and integrating the area using the trapezoidal method (Velthof and Oenema, 1995a). Statistical differences between the treatments were assessed by Analysis of Variance (ANOVA) and Least Square Difference (LSD) Test ($\alpha=0.05$), using the statistical package Genstat 5.0 (Genstat 5 Committee, 1987). Prior to the statistical analyses, fluxes of N_2O were log-transformed to stabilize variance.

Results

Experiment 1

Application of both NH_4^+ and NO_3^- fertilizers increased the N_2O flux from grassland on the clay soil in early spring (data not shown). However, fluxes were low, less than 0.1

mg N m^{-2} hr^{-1}, and there were no significant differences in N$_2$O flux between the mineral N fertilizers. Total emissions during the experimental period were less than 0.1% of the N applied as mineral N fertilizer (Table 3). These small emission were probably due to the cold (mean soil temperature 3.5 °C) and dry (< .3 mm rainfall) conditions during the first half of the experimental period.

Experiment 2

During the first three days, the groundwater depth in the poorly drained sandy soil rose from about 40 cm to 5 cm below the surface, following heavy rainfall (Figure 1). A temporary drop in the groundwater depth between days 2 and 6 was followed by a rapid rise to about 5 cm below the soil surface again after heavy rainfall. Soil temperatures during the experimental period were below 10 °C (Figure 1).

The fluxes of N$_2$O and the rates of denitrification from the different fertilizers peaked after 2-3 days after N fertilizer application (Figures 2A and 2C). Fluxes were much larger from CN and CAN than from AS. Fluxes from cattle slurry and urea were low, and similar to those from AS (data not shown). The patterns of N$_2$O fluxes and denitrification rates were related to NO$_3^-$ contents and not to NH$_4^+$ contents in the soil (Figures 2B and 2D). About 3 to 4 weeks after N application, mineral N contents of the fertilized grasslands were similar to the unfertilized, and N$_2$O fluxes and denitrification rates were low.

Total N$_2$O emission from CN and CAN were relatively large, i.e. 5.2% of the N applied (Table 3). More than 10% of the N applied as CAN and CN was lost by denitrification (Table 3). By contrast, emission of N$_2$O from the NH$_4^+$ fertilizers were < 0.2% of the N applied, and total N losses via denitrification < 1.1%.

Experiment 3

The groundwater depth in the poorly drained sandy soil rose from about 80 cm to 10 cm following heavy rainfalls during the first week after N fertilizer application (Figure 1). The soil temperature increased from about 13 °C during the first week to more than 20 °C during the last days of the experiment (Figure 1).

The fluxes of N$_2$O and the rates of denitrification were much larger from CN and CAN than from AS and cattle slurry (Figures 3A, B and C). The fluxes of N$_2$O from CN and CAN were similar to denitrification rates in terms of N loss (Figures 3B and 3C), indicating that N$_2$O was by far the major end product of denitrification. Fluxes of N$_2$O were sometimes higher than the denitrification rates, despite the fact that the data indicate that the N$_2$O orginated predominantly from denitrification. The higher N$_2$O

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fluxes compared to denitrification rates are probably due to the facts that i) spatial variability of both processes was large and that ii) the measurement of N_2O fluxes and denitrification rates were carried out on different plots.
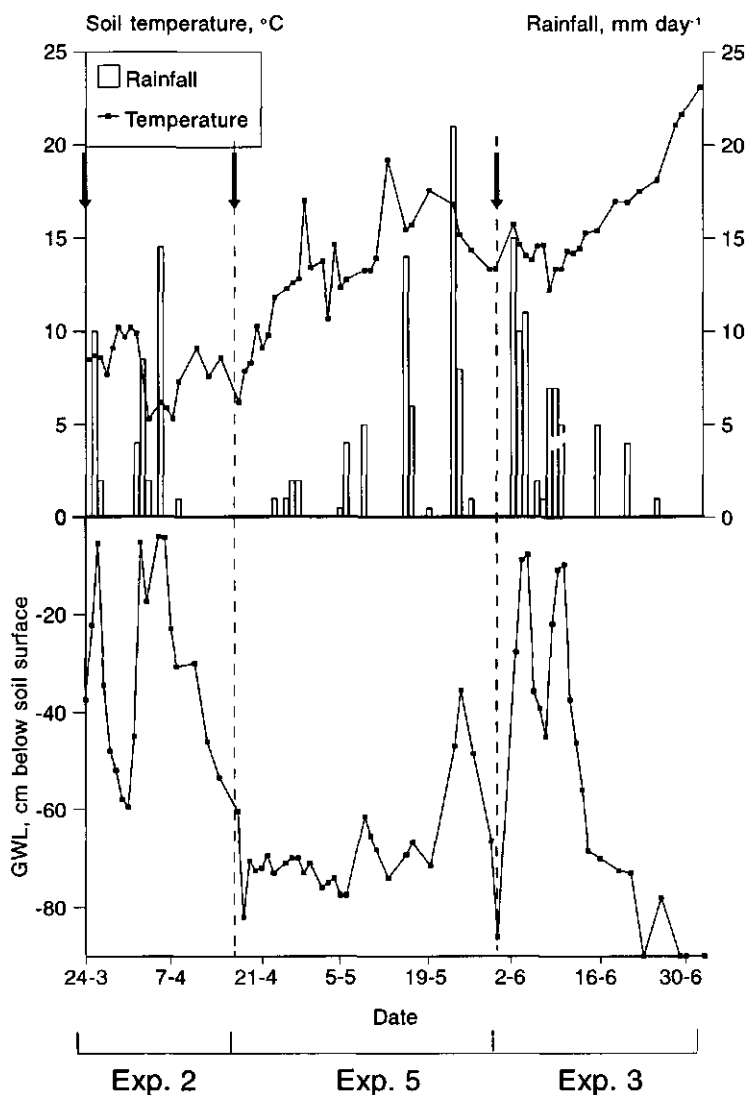

Figure 1. Soil temperature at 5 cm depth, rainfall and groundwater level (GWL) in the poorly drained sand soil in Bennekom in spring of 1994. Arrows indicate the time of N application in the experiments 2, 3, and 5.

Table 3. Emissions of N_2O, denitrifcation losses (Deni), total rainfall and mean soil temperature at 5 cm depth, for experiments 1, 2 and 3.

N source[*]	Experiment 1[**]	Experiment 2[**]		Experiment 3[**]	
	N_2O	N_2O	Deni	N_2O	Deni
	% of mineral N applied[***]				
CAN	<0.1a	5.2c	14.1b	8.3d	8.3b
CN	<0.1a	5.2c	12.4b	12.0d	10.5b
AS	<0.1a	0.2b	0.6a	1.0c	0.0a
AS + DCD	-	<0.1a	0.2a	0.1b	0.0a
Urea	<0.1a	<0.1a	1.1a	0.7c	1.9a
Cattle slurry, surface-applied	-	<0.1a	0.4a	<0.1a	0.4a
Cattle slurry, injected	-	0.1ab	0.0a	<0.1a	0.0a
Total rainfall, mm	13	42		68	
Mean soil temperature, °C	6.0	8.2		16.0	

* N fertilizers were applied at a rate of 80 kg N ha^{-1}, slurries at a rate of 15 m^{-3} ha^{-1} (about 45 kg mineral N ha^{-1}).
**Different letters in each column denote statistically significant differences between treatments (α=0.05).
*** Fertilizer-derived N_2O flux in % of the N applied =
(N_2O-N fertilized grassland - N_2O-N unfertilized grassland)/(amount of N applied) x 100

The N_2O peak fluxes from AS, AS+DCD and cattle slurry occurred during the first three days (Figure 3A), and coincided with the rainfall events and the concomitant rise in groundwater depth (Figure 1). These peak fluxes were probably related to denitrification activity and gas displacement by the rising water. Between days 3 and 25, fluxes were larger from AS than from AS+DCD, cattle slurry and the control.

The total N_2O emission from the CN and CAN treatments were very large; 8.3% of the N applied as CAN and 12.0% of the N applied as CN escaped as N_2O (Table 3). The emissions of N_2O-N and the N losses by denitrification were similar (Table 3). The emissions of N_2O from AS, AS + DCD, urea and the slurries were less than 1.0% of the amount of fertilizer N, and emissions from AS+DCD were significantly less than those from AS.

Experiment 4

The greenhouse experiment on the interaction effect between N fertilizer type and groundwater depth was carried out under warm conditions, with the soil temperature at 5 cm ranging from 20 to 27 °C. Grass growth was restricted during the experiment, probably because of the high soil temperatures. Fluxes from CN were larger when the groundwater depth was at 15 cm than when it was at 30 cm (data not shown). In contrast, fluxes from AS were larger for a groundwater level of 30 cm than for a level of 15 cm (data not shown). Peak fluxes of 9.8 mg N m^{-2} hr^{-1} occurred at one day after CN application and peak fluxes of 0.3 mg N m^{-2} hr^{-1} occurred 9 days after AS application (data not shown). The duration of fertilizer-derived N_2O flux was much longer for the groundwater level of 30 cm than for the groundwater level of 15 cm, for both AS and CN (Table 4). The order in the total N_2O emission was: no fertilizer < AS < CN, for both groundwater levels (Table 4).

Experiment 5

The amount of the fertilizer applied affected both the flux magnitude and duration, i.e. the heavier the N application, the larger the peak flux and the longer the duration of the flux (Figures 4A and B). Fluxes of N_2O increased after rainfall, especially for the heavier N application rates (Figures 1 and 4). A peak flux was found for the unusually heavy dressing of 300 kg N ha^{-1} five weeks after N application at 18 April, during a relatively wet and warm period (Figures 1 and 4).

Total N_2O emission increased with an increase in the amount of N application (Figure 5A). The percentage of the N applied which was lost as N_2O increased from 0.6% for a dressing of 50 kg N ha^{-1} to 3.1% for 300 kg N ha^{-1}.

Experiment 6

Generally, the fluxes from the clay soil were relatively small (i.e. less than 0.1 mg N m^{-2} hr^{-1}) during the growing season for all N application rates, except after the third N application when peak N_2O fluxes up to 1.5 mg N m^{-2} hr^{-1} were measured (not shown). Total N_2O emission during the growing season increased from 0.5 to 4.7 kg N ha^{-1}, when total N application rate increased from 0 to 880 kg N ha^{-1} (Figure 5B). The percentage of N emitted as N_2O was relatively small; 0.4% for a total application rate of 220 kg N ha^{-1} and 0.5% for application rates of 440, 660 and 880 kg N ha^{-1} (Figure 5B).
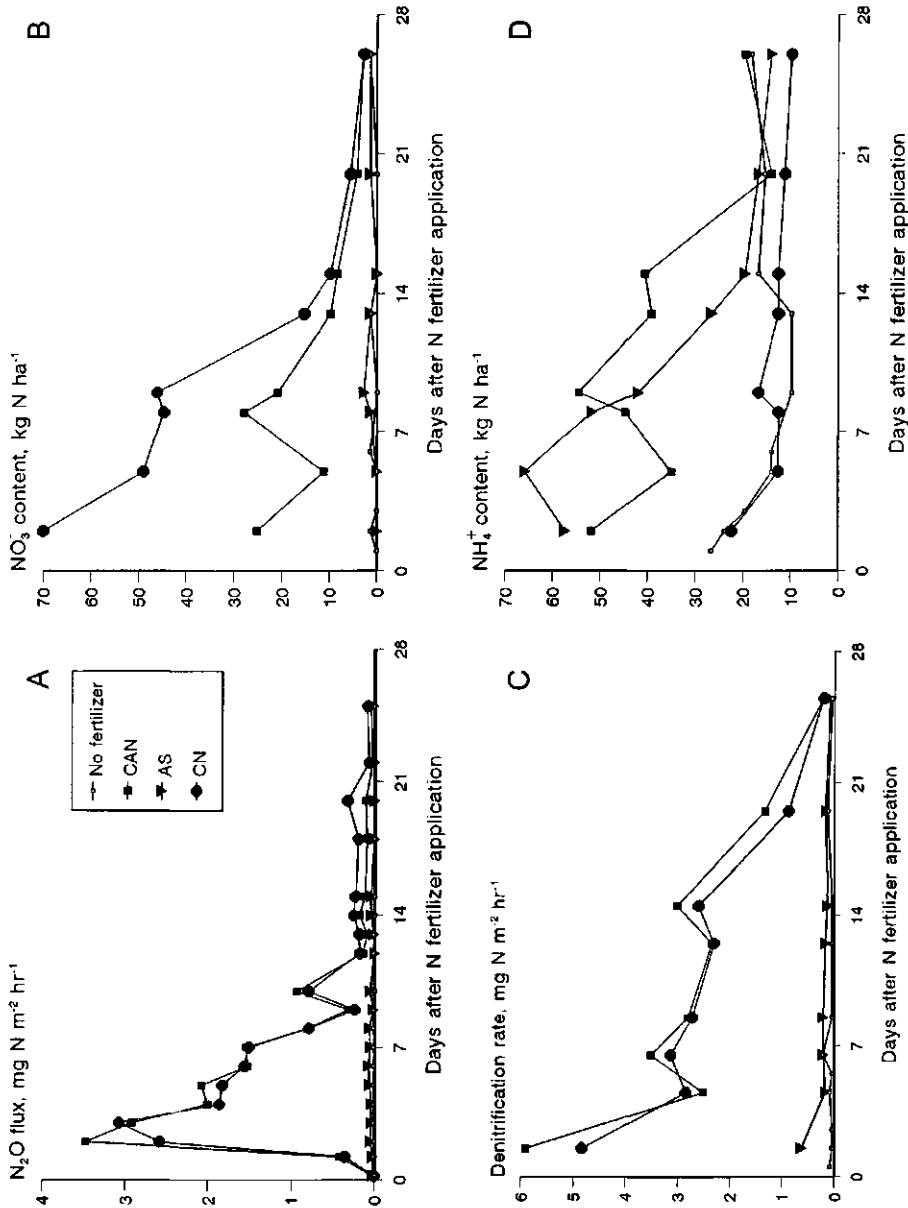
Figure 2. Rate of N_2O flux (A), NO_3^- content (B), denitrification rate (C) and NH_4^+ content (D) for unfertilized and N fertilized grassland (experiment 2).

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A

N$_2$O flux, mg N m^{-2} hr^{-1}

Legend:
- No N fertilizer
- AS
- AS + DCD
- Cattle slurry

Days after N fertilizer application

B

N$_2$O flux, mg N m^{-2} hr^{-1}

Legend:
- CAN
- CN

Days after N fertilizer application

C

Denitrification rate, mg N m^{-2} hr^{-1}

Legend:
- No fertilizer
- CAN
- AS
- CN

Days after N fertilizer application

Figure 3. Rates of N$_2$O flux from control and NH$_4^+$ fertilizers (A) and from NO$_3^-$ fertilizers (B) and denitrification rates (C) (experiment 3). Note differences in scale of Y-axes.

Discussion

Effect of fertilizer type on N_2O flux

The relatively small N_2O emission from the clay soil in early spring (experiment 1) suggests that the cold and dry soil conditions did not favor N_2O production. By contrast, the extremely large N_2O fluxes in the first 8 days from CN and CAN (experiments 2 and 3) indicate that the wet conditions favoured N_2O emission from the poorly drained sandy soil. The much larger N_2O emission from the NO_3^- fertilizers than from the NH_4^+ fertilizers indicates that denitrification was by far the major source of N_2O during wet condit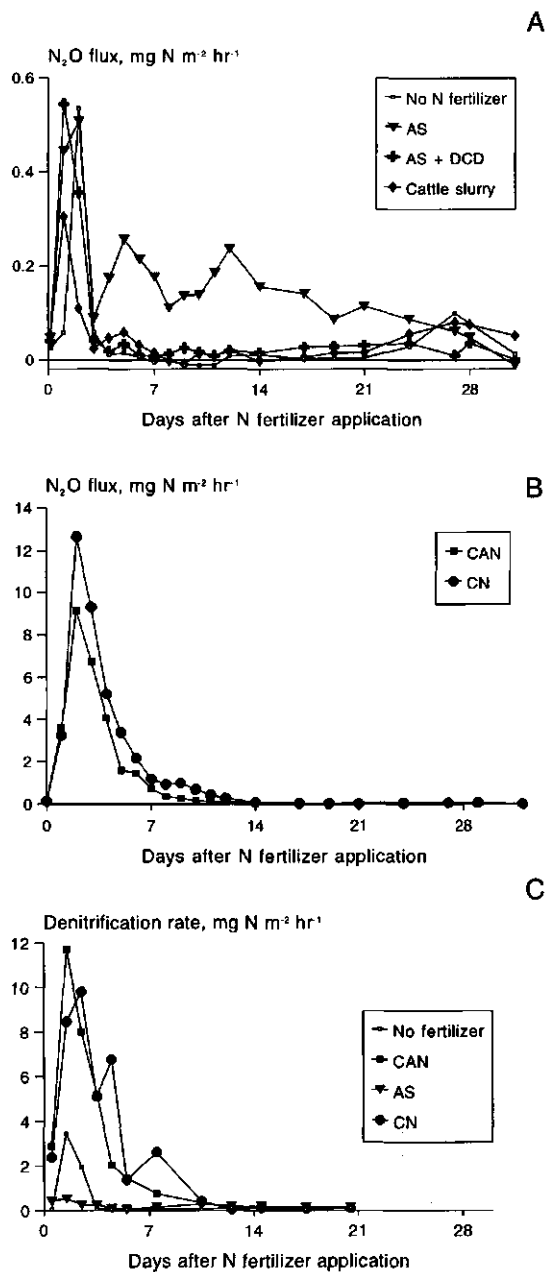ions in the poorly drained sand soil (experiments 2 and 3). This was confirmed by the denitrification rates which were much higher for the NO_3^- fertilizers than for the NH_4^+ fertilizers (Figures 2 and 3 and Table 3). The denitrification rates for the NH_4^+ fertilizers may have been slightly underestimated in case denitrification rate was dependent on the release of NO_3^- from nitrification of fertilizer NH_4^+. This is so because acetylene also inhibits nitrification (e.g. Aulakh *et al.*, 1984). However, the low NO_3^- concentrations and the high NH_4^+ concentrations in the NH_4^+ treated soil (Figure 2), indicate that nitrification was slow anyway, due to the wet conditions in the field. Generally, NO_3^- concentrations are much higher than NH_4^+ concentrations in grassland soils in the Netherlands.

The lower emission from AS+DCD than from AS indicates that the nitrification inhibitor reduced N_2O fluxes from NH_4^+ fertilizers, as also indicated by e.g. McTaggart *et al.* (1994) and Skiba *et al.* (1993). However, the effect of DCD to reduce the total N_2O emission from AS was much smaller than the effect of using NH_4^+ fertilizer instead of NO_3^- fertilizer (Table 3). Groundwater fluctuations had a tremendous effect on N_2O flux from fertilizers, and especially from NO_3^- sources (Experiment 4).

McTaggart *et al.* (1994) found a much larger emission from urea than from AS, suggesting that hydrolysis of urea and associated pH increase stimulated N_2O production. Probably, ammonia inhibits the oxidation of nitrite (NO_2^-) to NO_3^- by *Nitrobacter*, resulting in NO_2^- accumulation and enhanced N_2O production. This is supported by the much higher N_2O fluxes from anhydrous ammonia than from other N fertilizers (e.g. Breitenbeck and Bremner, 1986). In contrast, similar N_2O emission from urea and AS were found in experiments 1, 2 and 3 (Table 3). We suggest that the cold conditions in experiment 1 and the very wet conditions in experiments 2 and 3 reduced the increase in soil pH due to urea hydrolysis, causing emission from urea and AS to be similar.

A

B

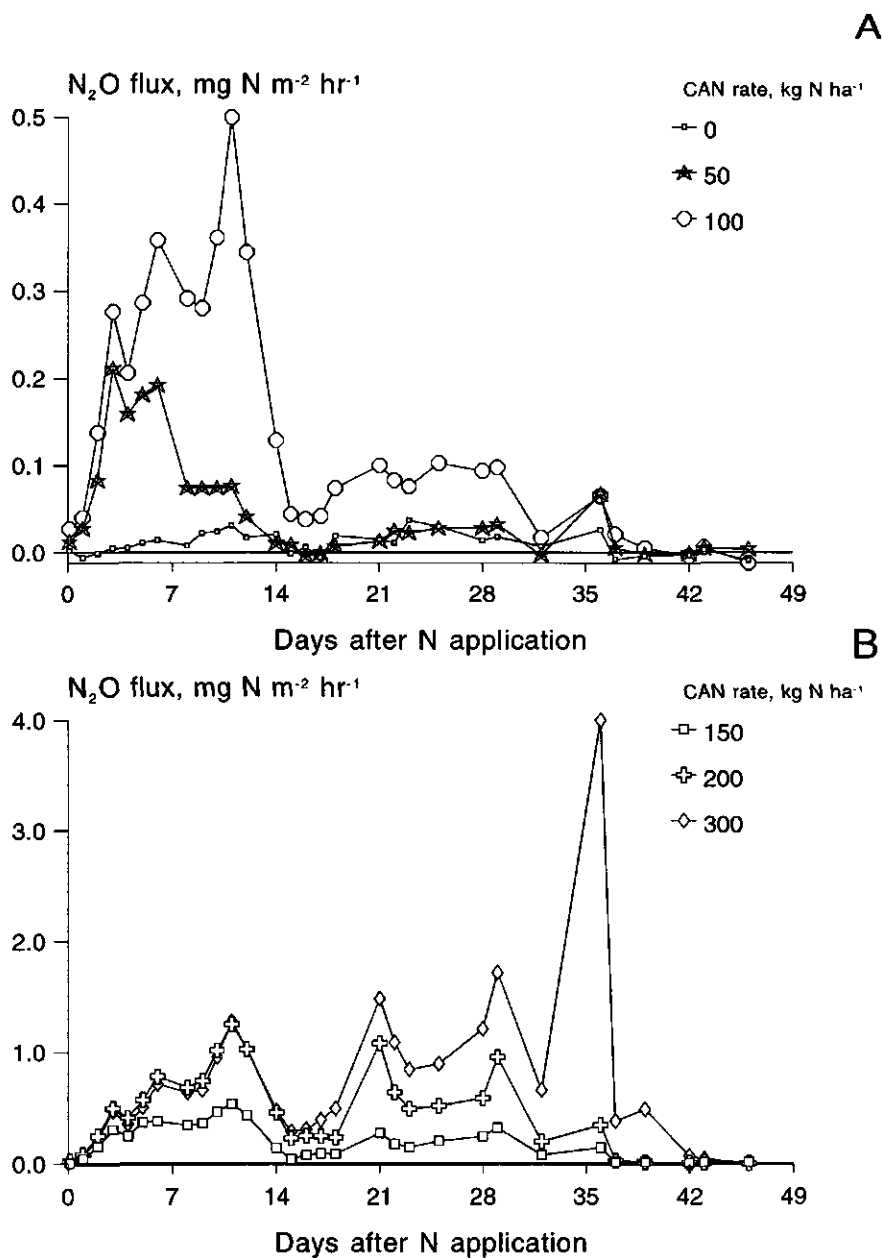**Figure 4.** Rates of N_2O flux after application of CAN to grassland at rates of 0, 50 and 100 kg N ha^{-1} (A) and 150, 200 and 300 kg N ha^{-1} (B) (experiment 5). Note differences in scale of Y-axes.
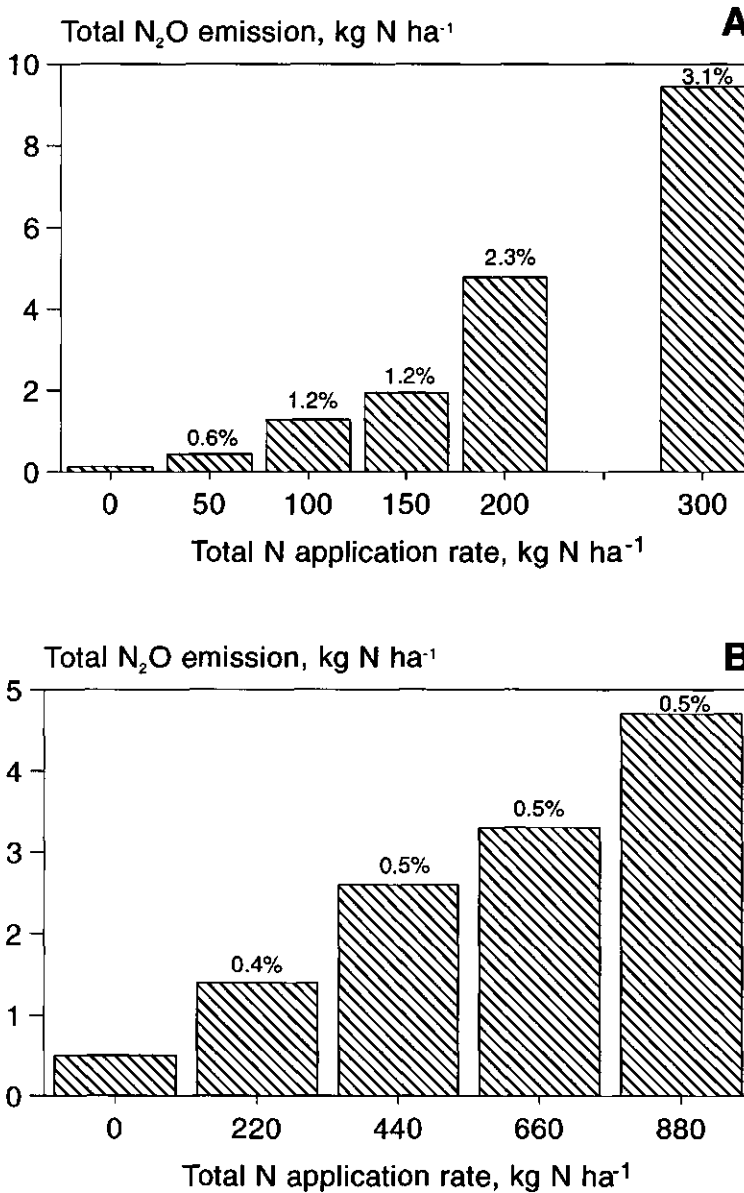
Figure 5. Relationship between total N application rate and total N_2O emission from grassland. (A: experiment 5 and B: experiment 6). Percentages indicate the percentage of applied fertilizer N emitted as N_2O.

Experiments 1-4 indicate that the use of NH_4^+ fertilizer instead of NO_3^- fertilizers may greatly reduce N_2O emission and denitrification losses from grasslands during wet conditions. Similar results were found by McTaggart *et al.* (1994) for N_2O emission and by Jordan (1989) and Ryden (1984) for denitrification losses from intensively managed grasslands. Peak N_2O fluxes and denitrification rates are generally found during the first few days after N application, when mineral N content is highest (eg. Figures 2 and 3). Thereafter, mineral N content in the soil strongly decreases due to the rapid N uptake by the sward. This indicates that there is scope for reducing N_2O emissions from intensively managed grasslands by choosing the N fertilizer type depending on the soil moisture status in combination with the expected rainfall and evapotranspiration during the next few days. Such a fertilization strategy should take into account also other effects of fertilizer type, like the effects on mineral composition of the grass, ammonia volatilization, soil acidification and botanical compostion of the sward (e.g. Van Burg *et al.*, 1982).

Fluxes of N_2O from cattle slurry

Fluxes of N_2O from cattle slurry were small and were not affected by the application method. As pointed out before, the much larger emissions from the NO_3^- fertilizers than from the NH_4^+ fertilizers, including cattle slurry, were due to the very wet conditions which favoured denitrification. The lower application rate of mineral N via the cattle slurries (about 45 kg N ha^{-1}) than via the mineral N fertilizers (80 kg N ha^{-1}) may have contributed to the lower N_2O emissions from the cattle slurries than from the NH_4^+ fertilizers (Table 3 and Figure 3). Egginton and Smith (1986a) and Velthof and Oenema (1993) also found much lower N_2O emission from slurry than from ammonium nitrate (AN) or CAN. By contrast, N_2O emission from slurry treated grassland were larger than from AN treated grassland in the study by Christensen (1983). Granli and Bøckman (1994) suggested that emission of N_2O is larger from organic manures than from mineral N fertilizers after application to soils in which the availability of organic C is limiting the denitrification rate and that the opposite is shown for soils in which organic C does not limit the denitrification rate. The much larger emission from AN and CAN than from the cattle slurry in the present study suggests that availability of organic C was not limiting the denitrification rate in the grassland soil.

Present laws in the Netherlands, require farmers to use slurry application techniques that minimize NH_3 volatilization, like sod-injection, deep-injection, and trailing-feet (Huijsmans *et al.*, 1996). These techniques differ in the way in which

slurry is in contact with soil and also differ in the ease with which N from the slurry can be taken up by the grass roots. The present study shows no clear effect of slurry application technique on N_2O emission. However, both experiments were carried out under extremely wet conditions. Further studies are needed to assess the effects of application technique on N_2O emission from slurry.

Table 4. Emission of N_2O related to fertilizer type and depth to groundwater table for the greenhouse experiment (experiment 4).

Fertilizer	Depth to groundwater, cm	Duration of fertilized-derived flux, days[*]	Total N_2O emission[**]	
			kg N ha^{-1}	% of N applied
Control	15	-	0.35a	-
	30	-	0.17a	-
AS	15	21	1.09b	0.9
	30	48	1.30b	1.4
CN	15	11	9.39d	11.3
	30	40	5.03c	6.1

[*] number of days in the 60-day period that N_2O flux from the fertilized treatments was significantly ($\alpha=0.05$) larger than the N_2O flux from the control treatment.
[**] Different letters denote statistically significant differences between treatments ($\alpha=0.05$).

Effect of application rate of N fertilizer on the N_2O flux

The pattern of N_2O flux after application of CAN in amounts of 0 to 300 kg N ha^{-1} in experiment 5 is related to interactions of the amount of N application, N uptake by the sward and soil moisture (Figures 1 and 4). Applications of more than about 100 kg N ha^{-1} likely exceeded the uptake capacity of the sward, by which mineral N contents of the top soil remained high for 3 to 5 weeks. By contrast, the flux of N_2O remained small from day 14 onwards when N application did not exceed 100 kg N ha^{-1}. Obviously, the fertilizer N applied at a low rate was taken up rapidly by the sward, keeping the mineral N contents in the soil low.

The relationship between N application and total N_2O emission had an exponential shape (Figure 5A), confirming our hypothesis that one heavy application may result in much larger N_2O emissions than split dressings of an equal total N application. The

results of this experiment substantiate those of Ryden (1983) showing that increasing the N application rate increases the percentage of fertilizer N emitted as N_2O. Similar results were found by Garret *et al.* (1992) for denitrification losses from grasslands. However, the results of experiment 6 do not show this effect (Figure 5B). A factor which may have contributed to the apparently linear relationship between N input and N_2O emission is the high N uptake capacity of this particular sward and the large apparent recovery of fertilizer N at this site, even at N application rates up to 700 kg N ha^{-1} yr^{-1} (e.g. Deenen and Lantinga, 1991). Another factor that may have contributed to the relatively small N_2O emission at high N application rates at this site is the apparent immobilization of fertilizer N into the soil organic matter pool. The organic matter content of this recently reclaimed soil is increasing and up to 245 kg N ha^{-1} per year can accumulate in the soil organic matter pool (Hassink and Neeteson, 1991).

Conclusions

The results of these studies and those of McTaggart *et al.* (1994), Jordan (1989) and Ryden (1984) indicate that there is scope for reducing N_2O emission and denitrification losses from grasslands using a fertilization strategy in which the choice of N fertilizer type is dependent on the soil moisture status in combination with the expected rainfall and evapotranspiration during the next few days. Moreover, the present study also indicates that preventing excess N applications and splitting of N applications may minimize N_2O emission from intensively managed grasslands. Hence, further refinement of N fertilizer recommendations may result in a progressive reduction of N_2O emission from grassland.

Acknowledgements

CHAPTER 8

Nitrous oxide emission from dairy farming systems in the Netherlands

Nitrous oxide emission from dairy farming systems in the Netherlands

Summary

A large part of the nitrogen (N) input in dairy farming systems in the Netherlands is lost from the system via N leaching and volatilization of gaseous N compounds, including the greenhouse gas nitrous oxide (N_2O). The aim of the present study was to quantify N_2O emission from dairy farming systems in the Netherlands, using a whole-farm approach. A total of 14 N_2O sources was identified and emission factors were derived for each of these using literature. Figures are presented for the amounts of N_2O produced per kg herbage N produced (ranging from 4 to 89 g N_2O-N kg^{-1} herbage N), depending on soil type and grassland management. Using Monte Carlo simulations, variations in mean total N_2O emissions from the different sources were calculated for three model dairy farming systems differing in nutrient management. These different farming systems were chosen to assess the effect of improved nutrient management on total N_2O emission. The total direct N_2O emissions ranged from 15.4 $\pm$ 9.4 kg N_2O-N ha^{-1} yr^{-1} for the average dairy farming system in the eighties to 5.3 $\pm$ 2.6 kg N_2O-N ha^{-1} yr^{-1} for a prototype of an economically feasible farming system with acceptable nutrient emissions. Leaching-derived, grazing-derived and fertilizer-derived N_2O emissions were the major N_2O sources on dairy farming systems. The total direct N_2O emissions accounted for 3.2 to 4.6% of the N surplus on the dairy farming systems, suggesting that only a small amount of N was lost as N_2O. Total N_2O emissions from dairy farming systems in the Netherlands were estimated at 13.7 $\pm$ 5.1 Gg N yr^{-1}, which is about 35% of the estimated total N_2O emission in the Netherlands. It is concluded that improvement of nutrient management of dairy farming systems will significantly decrease the N_2O emissions from these systems, and thus the total N_2O emission in the Netherlands.

Introduction

Dairy farming is the dominant land use system in the Netherlands. A total of 1.02×10^6 ha of land is under permanent grassland and 0.23×10^6 ha under forage maize, which together amounts to more than 30 percent of the total area of the Netherlands (Anonymous, 1995a). The permanent grasslands are used for grazing and forage

production. Both grassland and maize are intensively managed to allow high yields of good quality forage. These high yields are obtained among others by the application of plant nutrients via animal slurry and fertilizers.

The reverse side of the intensification of the dairy farming systems shows up in the large surplus of nitrogen (N) on budgets of these farming systems (Korevaar, 1992). On average, about 80% of the N input on dairy farming systems in the Netherlands is not recovered in animal products. Part of this N may be incorporated in soil organic matter, but the major part of this excess N is lost from the system via nitrate (NO_3^-) leaching, and volatilization of ammonia (NH_3), dinitrogen (N_2), nitrogen oxides (NO_x) and nitrous oxide (N_2O). Nitrous oxide is a trace gas involved in both the enhanced greenhouse effect and the destruction of stratospheric ozone and is produced during oxidation-reduction reactions of nitrogenous compounds (Houghton *et al.*, 1996). Major N_2O sources are denitrification and nitrification in soil and a few studies have been carried out to quantify the N_2O emission from grassland soils (e.g. Egginton and Smith, 1986a); Mc Taggart *et al.*, 1994; Velthof *et al.*, 1996a). Other possible sources of N_2O on dairy farming systems are generally assumed to be unimportant. There are many interactions within the complex N-cycle of dairy farming systems. It is well known that changing the nutrient management may affect the N flows at many different places (e.g. Aarts *et al.*, 1992) and also the N_2O leakages from the N cycle. This complicates a straightforward quantification of the effect of nutrient management on N_2O emission from dairy farming systems.

The aim of the present study was i) to identify the major sources of N_2O production in dairy farming systems, and ii) to quantify the N_2O emission from dairy farming systems in the Netherlands, using a whole-farm approach. We chose for a whole-farm approach to be able to quantify all possible sources of N_2O on dairy farming systems. Emission factors were derived from literature for the different N_2O sources and the possible variations in total mean N_2O emission were calculated using Monte Carlo simulations for three model dairy farming systems, largely differing in nutrient management. These different farming systems were chosen to assess the effects of nutrient management on total N_2O emission.

Description of farms

Emissions of N_2O were calculated for three model dairy farming systems on sandy soil in the Netherlands, namely i) the average farm in the eighties, mentioned as Farm '80, ii) farm Kloosterboer, and iii) the experimental model farm De Marke. These dairy

systems were chosen because they strongly differed in nutrient management and because the major N flows of these systems are well described, based on measurements and modeling. Data on land use, milk production and the major N flows for the three dairy farming systems are presented in Table 1.

Table 1. Some key properties of the three dairy farming systems.

Property		Farm '80	Kloosterboer	De Marke	Relative standard deviation[2]
Area	grassland, ha	22	20	31	
	maize, ha	3	12	18	
	fodder-beet, ha	0	0	6	
Milk production, kg ha^{-1} yr^{-1}		13195	12760	11724	
N flows and pools[1], kg N ha^{-1} yr^{-1}					
	Purchased N fertilizer	330	156	53	5%
	Purchased concentrates	136	90	82	5%
	Purchased roughage	42	0	2	5%
	Produced cattle slurry	198	232	209	25%
	Soil applied cattle slurry	120	206	185	15%
	N excreted during grazing	191	167	52	25%
	Biological N fixation	4	4	12	15%
	Nitrate leaching	200	130	50	100%
	Ammonia volatilization	109	38	24	50%
	Silage-nitrate	8	5	5	15%
	N surplus	477	249	141	

[1]Assumptions

- Farm '80 and farm Kloosterboer: Biological N fixation: 4 kg N ha^{-1}

- Farm '80: Aarts *et al.* (1992) presented total N emission by leaching and denitrification. It is assumed that 70% of this N was leached and 30% was denitrified, based on leaching-denitrification ratios for a moderately drained sandy loam given by Scholefield *et al.* (1991).

- Farm Kloosterboer: Amount of N leached was calculated from: N surplus = NH_3 emission + denitrification emission + leaching emission + other emission, assuming that 70% of the total amount of N lost by leaching + denitrification was lost by leaching (Scholefield *et al.*, 1991) and that 'other emission' accounted for 10% of the N surplus. Emission of NH_3 was derived from Den Boer *et al.* (1990).

[2]Relative standard deviations used in the Monte Carlo calculations

Data for Farm '80 were based on nutrient budgets of groups of specialist dairy farms on sandy soil during 1983-1986 (Aarts *et al.*, 1992). The farm Kloosterboer has introduced a package of measures in 1988 to reduce nutrient emissions to the environment. These measures included expanded storage capacity of slurry, injection of slurry on grassland in spring and summer, no autumn and winter applications of slurry, application of N fertilizer and slurry strictly according to current recommendations, and restricted grazing. We calculated N_2O budgets for 1991/1992 using data derived from Den Boer *et al.* (1990), Den Boer (1993) and Nutrient Management Institute (NMI, unpublished results). The experimental farm De Marke started in 1992, with the aim to develop a prototype of an economically feasible farming system with acceptable nutrient emissions. Measures include those taken at Kloosterboer, but are more stringent. Much attention is given to the nutrition of the cattle, to obtain a high production of milk per cow and a high efficiency of utilization of ingested N. The N_2O budget was calculated for 1993/1994 using data presented by Aarts *et al.* (1994).

Flows of N and sources of N_2O

The major N flows and pools in dairy farming systems are presented in Figure 1. There is a rapid cycling of N in this system. Input of N is via N fertilizer, purchased roughage and concentrates, biological N fixation, and atmospheric deposition. Output is via milk, meat and N emissions. Accumulation of N may (temporarily) occur in the soil, slurry storage basins and in roughage and silage.

The magnitudes of the major N flows on the three dairy farms were derived from the pertinent literature (Table 1). Standard deviations were assigned to the mean magnitude of the N flows based on additional literature and best guess values: the larger the variability or uncertainty in the N flow the larger the standard deviation (Table 1).

Emissions of N_2O from the dairy farming system occur from the top soil, the sub soil, cattle, slurry storage units, and sites where fuel is burned. When the site of N_2O production is inside the dairy farming system sources are mentioned as direct sources of N_2O. Sources of N_2O outside the dairy farming system are mentioned as indirect sources, e.g. N_2O that is emitted during the production of the purchased N fertilizer, roughage and concentrates. We included these three indirect N_2O sources in the calculations, because the management of the farming system strongly affects the magnitude of these sources. Other possible indirect N_2O sources were not considered.
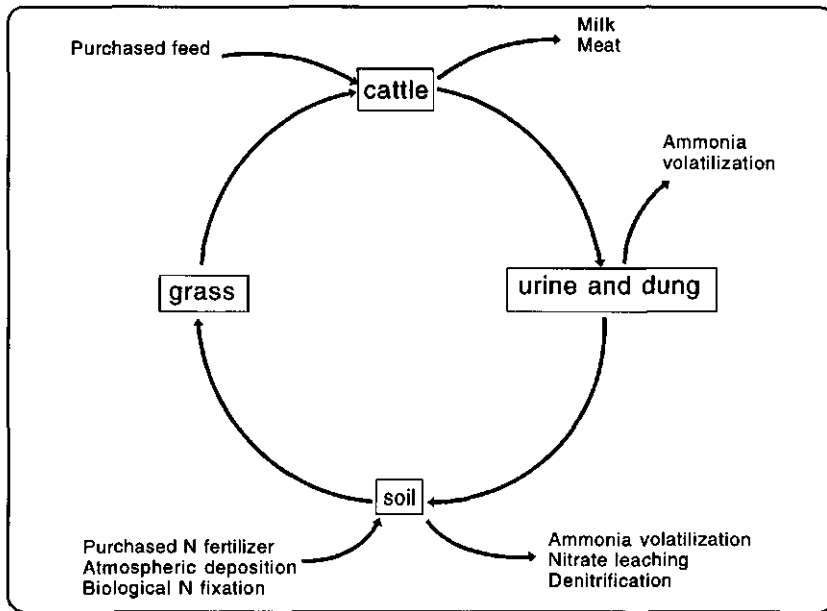
Figure 1. Schematic presentation of the major N flows in the N cycle in dairy farming systems. Essential all pools and flows are capable of releasing N_2O.

Emission factors of N_2O

A mean N_2O emission factor was assigned to each source, based on literature data or a best guess if literature data were not available. The emissions factors are expressed in g N_2O-N per kg N, assuming assuming a linear relationship between the N flow and N_2O production. Emission factors are generally applied in N_2O budget studies (Kroeze, 1994; Houghton *et al.*, 1996). Because the N_2O production is highly stochastic by nature, the variability in N_2O emissions is large both in time and space (e.g. Velthof *et al.*, 1996a, b). Consequently, the mean emission factors have a large standard deviation or in case of best guess values there is a large uncertainty. We assigned a 'standard deviation' to all mean emission factors based on literature data and best guess values. The direct and indirect sources are shortly described and N_2O emission factors are given for both mineral and peat soils. A summary of the emission factors is given in Table 2.

Background N_2O emission from soils

Unfertilized and mown-only grasslands produce N_2O during nitrification and/or denitrification of N released during mineralization of soil organic N and from atmospheric N deposition. In the calculations we estimate the background N_2O flux for sand and clay soils at 900 ± 300 g N_2O-N ha^{-1} yr^{-1} and for peat soils at 5300 ± 5200 g N_2O-N ha^{-1} yr^{-1}, based on the results of a N_2O monitoring study on grasslands of two years on sand, clay and peat soils (Velthof *et al.*, 1996a).

Table 2. Emission factors used in the calculations: mean $\pm$ standard deviation.

Source of N_2O	Mineral soils	Peat soils
Direct		
Soil, background, g N_2O-N ha^{-1} yr^{-1}	900 ± 300	5300 ± 5200
Soil, N fertilizer, g N_2O-N kg^{-1} fertilizer N	10 ± 5	30 ± 13
Soil, cattle slurry, g N_2O-N kg^{-1} slurry N		
Surface-applied	3 ± 3	6 ± 6
Application with low NH_3 emission	5 ± 5	10 ± 10
Grazing, g N_2O-N kg^{-1} excreted N	25 ± 15	60 ± 46
Biological N fixation, g N_2O-N kg^{-1} fixed N	5 ± 5	5 ± 5
Leaching, g N_2O-N kg^{-1} leached N	25 ± 25	25 ± 25
Housing and slurry storage, g N_2O-N kg^{-1} slurry N	0.05 ± 0.05	0.05 ± 0.05
Ammonia volatilization, g N_2O-N kg^{-1} NH_3-N	5 ± 5	5 ± 5
Rumen, g N_2O-N kg^{-1} consumed N	0.05 ± 0.05	0.05 ± 0.05
Silage, g N_2O-N kg^{-1} NO_3^--N	15 ± 10	15 ± 10
Energy use, g N_2O-N GJ^{-1}	1 ± 1	1 ± 1
Indirect		
Purchased N fertilizer, g N_2O-N kg^{-1} fertilizer N	5 ± 5	5 ± 5
Purchased roughage, g N_2O-N kg^{-1} roughage N	20 ± 10	20 ± 10
Purchased concentrates, g N_2O-N kg^{-1} concentrate N	10 ± 5	10 ± 5

Fertilizer-derived N_2O emission from soils

The fertilizer-derived N_2O emissions (the amount of applied N fertilizer that is lost as N_2O) for grassland fertilized with calcium ammonium nitrate (CAN) were set at 10 ± 5 g N_2O-N kg^{-1} N for mineral soils and at 30 ± 13 g N_2O-N kg^{-1} N for peat soils, based on the study of Velthof *et al.* (1996a). For arable land, we also use 10 ± 5 g N_2O-N kg^{-1} N as emission factor for fertilizer-derived N_2O emission on mineral soils.

There is evidence that N_2O emissions are larger from NO_3^- containing fertilizers than from fertilizers only containing NH_4^+, especially during wet conditions (McTaggart *et al.*, 1994; Velthof *et al.*, 1997). We will not distinguish between the different N fertilizers, because CAN is by far the major N fertilizer on grassland in the Netherlands (Anonymous, 1995b).

Slurry-derived N_2O emissions from soils

In studies of Egginton and Smith (1986a), Velthof and Oenema (1993), and Velthof *et al.* (1997) N_2O emissions from grassland were much smaller after application of cattle slurry than of CAN or ammonium nitrate (AN). The difference ranges from a factor of 5 up to more than 1000. Slurry application technique may also affect N_2O emissions from grassland, because it affects NH_3 emissions and the site of N_2O production in the soil. For mineral soils, we estimate the average slurry-derived N_2O emission (the amount of the total slurry N applied lost as N_2O) at 3 ± 3 g N_2O-N kg^{-1} N for surface-applied slurry and 5 ± 5 g N_2O-N kg^{-1} N for slurry applied with a technique that minimizes NH_3 emissions. Emission factors for peat soils were set at twice those of mineral soils (Table 2).

Grazing-derived N_2O emission from soils

Emissions of N_2O were much larger from N fertilized and grazed grasslands than from N fertilized and mown grasslands (Velthof *et al.*, 1996a). On average, 25 ± 15 g N_2O-N kg^{-1} N excreted as urine and dung during grazing was lost as N_2O on the mineral soils and 60 ± 46 g N_2O-N kg^{-1} N on peat soils.

Biological nitrogen fixation

Studies of Ruz-Jerez *et al.* (1994) in New Zealand and Garret *et al.* (1992) in Northern Ireland suggest smaller denitrification and N_2O emissions from grass-clover than from N fertilized grassland. We assume the N_2O emission derived from biological nitrogen fixation is 5 ± 5 g N_2O- N kg^{-1} N fixed.

Leaching of N

Considerable amounts of N may be lost from intensively managed grasslands via NO_3^- leaching (Ryden *et al.*, 1984). This leached NO_3^- may be denitrified in the subsoil or may be drained to surface water, where it will be denitrified for the greater part in the long term. The amount of N_2O that is produced from leached NO_3^- is unknown and is difficult to predict (Mosier, 1994). We adopt the N_2O emission factor for N leaching

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derived by the Intergovernmental Panel on Climate Change (IPCC), i.e. 25 g N_2O-N kg^{-1} leached N, which includes N_2O that is produced from leached NO_3^- and directly leached N_2O (Anonymous, 1996). Due to the many uncertainties we use a large relative standard deviation of 100%: 25 ± 25 g N_2O-N kg^{-1} leached N.

Emission of N_2O in housing and during the storage of slurry

Measurements in housing indicated that N_2O fluxes from fresh cow urine applied to a stable floor were less than 5 μg N m^{-2} hr^{-1}, during two hours after application (Velthof, unpublished results). Therefore, we assume that N_2O emissions directly from the stable floor are negligible. Cattle slurry produced in cubicle houses in autumn and winter is stored below the stable floor or in a separate slurry pit. Emissions of N_2O from cattle slurry stored for up to 6 months were less than 0.05 mg N kg^{-1} slurry N day^{-1} (Oenema and Velthof, 1993 and Oenema *et al.*, 1993). The small N_2O emissions were attributed to the absence of NO_3^- in the anoxic slurry. Total emissions of N_2O in housing and during the slurry storage were set at 0.05 ± 0.05 g N_2O-N kg^{-1} slurry N.

Ammonia volatilization

Nitrogen lost from dairy farming systems via NH_3 volatilization may ultimately return to the atmosphere as N_2 and N_2O after nitrification and denitrification. The greater part of the volatilized NH_3 will deposit elsewhere. The impact of this NH_3 on N_2O emissions has not been addressed explicitly yet (Mosier, 1994). A fraction of the NH_3 will be deposited on grassland and than will contribute to the background N_2O emissions from soils. We assume that the amount of N_2O produced from NH_3 is lower than the fertilizer-derived N_2O emission: 5 ± 5 g N_2O-N kg^{-1} NH_3-N.

Silage production

With N application rates less than 400 kg N ha^{-1} yr^{-1}, NO_3^- contents of grass cut at silage stage (2500-4000 kg dry matter ha^{-1}) are typically less than 8 g kg^{-1} herbage dry matter (Prins, 1983). If total annual N application is higher and/or grass is cut in a younger stage, NO_3^- contents may be in the range of 8 to 15 g N kg^{-1}. Ensiled grass is stored under anoxic conditions and under these conditions NO_3^- in the ensiled herbage is reduced. Within a few hours after ensiling, the reduction of NO_3^- starts, with N_2O as one of the possible end products (Spoelstra, 1985). In a study of Ataku (1982), referred by Spoelstra (1985), 0.9-2% of ^{15}N-NO_3^- added to grass was recovered as N_2O. We used as emission factor 15 ± 10 g N_2O-N kg^{-1} NO_3^--N in silage.

Rumen of cattle

Kaspar and Tiedje (1981) showed in a study under controlled conditions that trace amounts of N_2O were produced during dissimilatory reduction of nitrite (NO_2^-) to NH_4^+ in the rumen. We assume that the amounts of N_2O emitted directly by the cattle are small: 0.05 ± 0.05 g N_2O-N kg^{-1} consumed N.

Energy use

The N_2O emission from gas fired power plants in the Netherlands was estimated at 0.1-0.4 mg N_2O-N MJ^{-1} (Spoelstra, 1995). Emission of N_2O for personal cars with engine type diesel was estimated at 6.4 mg N km^{-1} (Baas and Rijkeboer, 1995). Assuming that this factor is also applicable for agricultural machinery and assuming a usage of 0.1 liter diesel km^{-1} we calculate an emission factor of 64 mg N_2O-N l^{-1} diesel or 1.4 mg N_2O-N MJ^{-1}, taking 44.5 MJ l^{-1} as average energetic value for diesel (Van Dasselaar and Pothoven, 1994). We used one uniform emission factor for energy use on dairy farms: 1.0 ± 1.0 mg N_2O-N MJ^{-1}, from both the uses of electricity and diesel. The energy use was set at 6 ± 0.5 MJ kg^{-1} milk produced for dairy farms in the eighties and 5 ± 0.5 MJ kg^{-1} milk produced for dairy farms with improved nutrient management (Van Dasselaar and Pothoven, 1994).

Indirect source: production of mineral fertilizer

The catalytic oxidation of NH_3 to nitric oxide (NO) is a key step in the production of NO_3^- containing mineral fertilizers (France and Thompson, 1993). During this process N_2O may be formed. Estimates of N_2O emission factors for nitric acid production range from 4-27 g N_2O-N per kg HNO_3-N produced, with the lower values for modern fertilizer plants (Granli and Bøckman, 1994; De Soete, 1993; France and Thompson, 1993). We use an emission factor of 5 ± 5 g N_2O-N kg^{-1} N produced as CAN, that contains NO_3^--N and NH_4^+-N in equal amounts.

Indirect source: purchased feeds

The production of purchased concentrates and feeds is accompanied by emissions of N_2O, directly from the soils and, indirectly at the fertilizer plant if N fertilizer is used. As pointed out by Granli and Bøckman (1994), almost no figures are presented in literature about the N_2O emission expressed as the amount of N_2O-N emitted per unit crop production. We calculated the N_2O emission per kg herbage dry matter and herbage N for different soil types and management types, using the data on N_2O emission of Velthof *et al.* (1996a) and those on herbage dry matter and N yields of

Vellinga *et al.* (1996). These studies were carried out on the same experimental plots and during the same period. Emissions of N_2O per kg herbage dry matter and herbage N increased by application of N fertilizer and by grazing and were larger for the peat soils than for the mineral soils (Table 3). We estimated N_2O emission during the production of roughage and concentrates using these results.

Table 3. Application rate of CAN fertilizer and N_2O emission in g N kg^{-1} dry matter (DM) produced and in g N kg^{-1} herbage N, for four soils and three types of grassland management. Averages of March 1992 - March 1994. Data of DM and N yields are from Vellinga *et al.* (1996). Data of N_2O emissions are from Velthof *et al.* (1996a).

Soil	Treatment	Application rate kg N ha^{-1}	N_2O emission[*] g N kg^{-1} DM		g N kg^{-1} herbage N	
Sand	Unfertilized-mown	0	0.18	(0.18)	7	(7)
	N fertilized-mown	370	0.35	(0.49)	12	(16)
	N fertilized-grazed	370	0.73	(0.87)	21	(25)
Clay	Unfertilized-mown	0	0.10	(0.10)	4	(4)
	N fertilized-mown	357	0.27	(0.39)	8	(11)
	N fertilized-grazed	357	0.94	(1.07)	27	(31)
Peat I	Unfertilized-mown	0	0.33	(0.33)	11	(11)
	N fertilized-mown	365	0.73	(0.88)	20	(24)
	N fertilized-grazed	365	1.22	(1.37)	33	(37)
Peat II	Unfertilized-mown	0	0.97	(0.97)	32	(32)
	N fertilized-mown	242	1.53	(1.63)	44	(47)
	N fertilized-grazed	242	3.22	(3.31)	89	(91)

[*] in parentheses N_2O emissions including the N_2O emissions during the production of the used N fertilizer, assuming that 5 g N_2O-N is lost per kg produced CAN-N.

Purchased roughage mainly consists of grass and maize products. Based on the N_2O emissions from N fertilized and mown grasslands on mineral and peat soils (Table 3), we assume an emission factor of 20 ± 10 g N_2O-N kg^{-1} roughage N, which includes both the N_2O emission directly from the soil and the N_2O emission during the production of the required N fertilizer. Purchased concentrates may consist of many

products, partly grown in the Netherlands and partly grown abroad, e.g. in the tropics. On average, the N input is smaller to crops from which concentrates are produced than to crops from which roughage is produced. We use an emission factor of 10 ± 5 g N_2O-N kg^{-1} concentrate N.

Calculations

Calculations of N_2O emissions were carried out using a simple spreadsheet model. Monte Carlo simulations were used to calculate the effects of variations and uncertainties in N flows and pools (Table 1) and N_2O emissions factors (Table 2) on the total N_2O emissions at farm level. Monte Carlo simulations (2000 iterations) were carried out with the computer program @RISK (Anonymous, 1995c). It was assumed that all N sources on the dairy farming systems were normally distributed. Because of the high variability of N_2O emissions in time and space it was assumed that N_2O emissions were lognormally distributed.

Emissions of N_2O from the three dairy farming systems

There were large differences in direct and indirect N_2O emissions among the three farming systems on sandy soils (Table 4). Direct N_2O emissions ranged from 15.4 ± 9.4 kg N_2O-N ha^{-1} yr^{-1} on Farm '80 to 5.3 ± 2.6 kg N_2O-N ha^{-1} yr^{-1} on De Marke. The large standard deviations show that there is a considerable uncertainty in the estimated total mean N_2O emissions. The direct N_2O emissions accounted for 3.2, 4.6 and 3.7% of the N surplus on Farm '80, Kloosterboer and De Marke, respectively. Clearly, emissions of N_2O are only a minor N loss from dairy farming systems.

On all farms, N leaching accounted for about 25% of the total N_2O emission (i.e., direct + indirect emission). The relative standard deviation of the estimated leaching-derived N_2O emission was very large (170-180%), due to the large uncertainties in both the emission factors for leaching-derived N_2O emission and the amounts of leached N. Grazing was also an important N_2O source, accounting for 25% of the total N_2O emission. A third major source of N_2O was N fertilizer use. The sum of the direct and indirect N_2O emission from N fertilizer amounted to 13 to 26%. All other N_2O sources were relatively small in comparison to the leaching-, grazing- and N fertilizer-derived N_2O emissions.

Effects of management measures

The differences in N_2O emission among the three farming systems were due to the differences in nutrient management (Table 4). Largest differences were shown for leaching-derived, grazing-derived and N fertilizer-derived N_2O emissions. Nitrate leaching strongly decreased in the order Farm '80 > Kloosterboer > De Marke (Table 1). Nitrate leaching is affected by (a combination of) many management measures, including restricted grazing, proper slurry application, adjusted N application and a lower N content in urine due to changes in the nutrition of the cattle. The results of Table 4 show that measures taken to reduce NO_3^- leaching may also considerably reduce N_2O emission. The improved nutrient management implied smaller amounts of required N fertilizer (Table 1) and, by that, also smaller N fertilizer-derived N_2O

Table 4. Direct and indirect emissions of N_2O in kg N ha^{-1} yr^{-1} (mean ± standard deviation) for the three farming systems.

Source	Farm '80	Kloosterboer	De Marke
Direct			
Soil-background	0.9 ± 0.3	0.9 ± 0.3	0.9 ± 0.3
Soil-N fertilizer	3.3 ± 1.7	1.6 ± 0.8	0.5 ± 0.3
Soil-cattle slurry	0.6 ± 0.7	1.0 ± 1.1	1.0 ± 1.0
Grazing	4.8 ± 3.2	4.2 ± 2.8	1.3 ± 0.9
Biological N fixation	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
Leaching	5.2 ± 8.6	3.4 ± 6.1	1.3 ± 2.2
Housing and slurry storage	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
Ammonia volatilization	0.3 ± 0.4	0.2 ± 0.2	0.1 ± 0.1
Rumen	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
Silage	0.1 ± 0.1	0.1 ± 0.0	0.1 ± 0.1
Energy use	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
Total direct sources	15.4 ± 9.4	11.5 ± 6.8	5.3 ± 2.6
Indirect			
Purchased N fertilizer	1.6 ± 1.5	0.8 ± 0.7	0.3 ± 0.2
Purchased roughage	0.8 ± 0.4	0.0 ± 0.0	0.0 ± 0.0
Purchased concentrates	1.4 ± 0.7	0.9 ± 0.4	0.8 ± 0.4
Total indirect sources	3.8 ± 1.7	1.7 ± 0.9	1.1 ± 0.5
Total direct + indirect sources	19.2 ± 9.6	13.1 ± 6.9	6.4 ± 2.6

emission. Restricted grazing will decrease the amount of N deposited to the soil as urine and dung and increase the amount of slurry N collected in housing. The slurry is subsequently applied to the soil and when applied properly, the emission factor for slurry N is much lower than that for grazing-derived N (Table 2).

On Kloosterboer and De Marke measures were taken to reduce NH_3 volatilization from housing, slurry storage units and grassland. Reduction of NH_3 volatilization leaves more N in the slurry, so that less N fertilizer has to be purchased. Taking the differences in emission factors between N fertilizer and slurry into account (Table 2) and the difference in effectivity of the N from slurry and N fertilizer, we calculate that a reduction of the NH_3 volatilization from dairy farming systems with 1 kg N ha^{-1} yr^{-1} results in a reduction of the N_2O emission with 7.5 g N ha^{-1} yr^{-1} from these systems.

Effects of soil cultivation and changes in land use on N_2O emissions were not accounted for in this study. On De Marke 56% of the total area was used for grassland and 44% for fodder beets and maize (Table 1). Only 29% of the total area was permanent grassland. The other 27% was in rotation with fodder beet and maize. After ploughing out grassland, large amounts of N are mineralized (e.g. Whitehead _et al._, 1990). These amounts frequently exceed the capacity of the subsequent crop to take up. Consequently, significant quantities may be lost via leaching and via N_2O emission. Quantitative information on the fate on short-term ley's is lacking, however.

Total N_2O emissions from dairy farming systems in the Netherlands

Total direct N_2O emissions from dairy farming systems in the Netherlands were calculated for 1994 using the N_2O-emission factors derived in the present study and data of dairy farming systems in the Netherlands (see footnote of Table 5). Total N_2O emissions from dairy farming systems in the Netherlands were 13.7 ± 5.1 Gg N_2O-N yr^{-1}, from which 8.0 ± 4.3 Gg N_2O-N yr^{-1} was derived from mineral soils and 5.7 ± 3.5 Gg N_2O-N yr^{-1} from peat soils (Table 5). This indicates the importance of dairy farming systems on peat soils as N_2O source in the Netherlands. Largest N_2O sources are grazing-derived, fertilizer-derived and, in case of mineral soils, leaching-derived N_2O emissions. Background N_2O emissions from grasslands on peat soils are also a considerable source of N_2O, accounting for about 10% of the total N_2O emissions from dairy farming systems in the Netherlands.

Kroeze (1994) estimated the total N_2O emission towards the atmosphere in the Netherlands from agriculture, energy generation, industry and traffic at 37.1 Gg N yr^{-1}. Total N_2O emission from agriculture was estimated at 16.9 Gg N yr^{-1}. Our data thus

suggests that dairy farming systems are a major source of N_2O in the Netherlands. About 35% of the total amount of N_2O emitted into the atmosphere originates from dairy farming systems. Clearly, a significant reduction in N_2O emission from dairy farming systems due to improved nutrient management may not only reduce N_2O emission from these systems but will also contribute to a significant reduction of the total N_2O emissions in the Netherlands.

Table 5. Total direct emissions of N_2O from dairy farming systems in the Netherlands in 1994, in Gg N_2O-N yr^{-1}. For each source the mean ± standard deviation is presented, based on Monte Carlo simulation (2000 iterations) using the emission factors ± standard deviations presented in Table 2 and data derived from literature (see footnotes 1-8). Standard deviations for data derived from literature were based on best guess and are given as footnote 9.

Source	Minerals soils	Peat soils	Total
Soil-background[1]	0.8 ± 0.5	1.3 ± 0.3	2.1 ± 1.8
Soil-N fertilizer[2]	2.4 ± 1.2	2.0 ± 0.8	4.4 ± 1.5
Soil-cattle slurry[3]	0.7 ± 0.7	0.4 ± 1.1	1.0 ± 0.8
Grazing[3]	2.2 ± 2.9	1.8 ± 2.8	3.9 ± 4.1
Biological N fixation[4]	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
Leaching[5]	1.6 ± 2.7	0.1 ± 0.7	1.7 ± 2.8
Housing and slurry storage[3]	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
Ammonia volatilization[6]	0.3 ± 0.4	0.1 ± 0.1	0.4 ± 0.4
Rumen	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
Silage[7]	0.1 ± 0.1	0.0 ± 0.0	0.1 ± 0.0
Energy use[8]	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
Total	8.0 ± 4.3	5.7 ± 3.5	13.7 ± 5.1

[1]Anonymous (1995a) and Steur *et al.* (1985). Assumes that all maize and fodder crops are grown on mineral soils.
[2]Anonymous (1995b). Mean N fertilizer application rate was 280 kg N ha^{-1}, for all soils.
[3]Anonymous (1995a). Assuming a total N content of 5 g N kg^{-1} slurry (= dung + urine).
[4]Assuming 4 kg fixed N ha^{-1} on mineral soils and 0 kg N ha^{-1} on peat soils.
[5]Assuming 75 kg N ha^{-1} yr^{-1} leached NO_3^- on mineral soils and 10 kg N ha^{-1} yr^{-1} on peat soils
[6]Meeuwissen (1993)
[7]Anonymous (1995a). Assuming a dry matter content of grass silage of 33% and of maize silage of 60% and a NO_3^- content in grass silage of 2 g N kg^{-1} and in maize silage of 5 in g N kg^{-1} dry matter.
[8]Anonymous (1995a).
[9] Relative standard deviations: 5% for grassland area, 10% for N fertilizer, 25% for cattle slurry N, 25% for N excreted during grazing, 15% for fixed N, 25% for slurry N in housing and storage unit, 100% for leached N, 15% for silage N, 50% for volatilized N and 15% for energy use.

Acknowledgements

CHAPTER 9

General discussion

General discussion

Major aims and major findings

The major aims of the study presented in this thesis were
i)   to quantify N_2O emission from intensively managed grasslands in the Netherlands,
ii) to increase the insight into the factors controlling the N_2O emission from intensively managed grasslands, and
iii) to explore the possibilities to reduce N_2O emission from intensively managed grasslands.

The major findings of this thesis are:
-   Emissions of N_2O from unfertilized and mown grasslands were on average 0.9 kg N ha^{-1} yr^{-1} for mineral soils and 5.3 kg N ha^{-1} yr^{-1} for peat soils.
-   Over a two-year period, on average 1.0% of the N applied as calcium ammonium nitrate (CAN) was emitted as N_2O from mineral soils and 3.0% from peat soils.
-   During very wet conditions emission of N_2O from NO_3^- fertilizers was much larger than from than from NH_4^+ fertilizers.
-   Over a two-year period, on average 2.4% of the N excreted as urine and dung from grazing cattle was emitted as N_2O from the clay soil, the sandy soil and the peat soil with the relatively high groundwater level. This was 9.8% for the peat soil with the relatively low groundwater level.
-   Total N_2O emission from dairy farming systems in the Netherlands was estimated at 13.7 ± 5.1 Gg N yr^{-1}.
-   Spatial variability of N_2O fluxes from grasslands was high and mostly related to the high spatial variability of soil mineral N contents. Distributions of N_2O fluxes were positively skewed.
-   Temporal variability of N_2O fluxes was large and mainly related to i) temporal variations in soil mineral N content due to N fertilizer application and grazing and to ii) temporal variations in soil moisture content due to rainfall and fluctuations in groundwater level.
-   A simple empirical model reasonably predicted magnitude and temporal variations in N_2O fluxes from peat soil.

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- The most important management factors controlling the N_2O emission from intensively managed grassland are N fertilizer application, grazing, and drainage.
- Improved nutrient management may significantly decrease the N_2O emission from dairy farming systems. Emission of N_2O accounted for 3-5% of the N surplus on whole dairy farming systems.

In this chapter the major results of the study of this thesis are synthesized and discussed and some future perspectives are given. Special attention is paid to the uncertainties in the quantification of N_2O emission using closed flux chambers.

Quantification of N_2O emission

Intensively managed grasslands
Total emissions of N_2O from soils in a certain region or country are usually estimated with emissions factors, which express the flux in g N_2O-N per kg N applied or per ha (Kroeze, 1994; Houghton *et al.*, 1996). These emission factors are mostly derived from field experiments. Bouwman (1995) suggested that it is necessary to measure N_2O fluxes for at least one year to account for all fertilized-derived N_2O emissions from agricultural soils and to arrive at accurate emission factors.

Thus far, only a few studies have been carried out in which N_2O fluxes were measured for 1 year or more on intensively managed grasslands (Egginton and Smith, 1986a, b; Heinemeyer *et al.*, 1996, and McTaggart *et al.*, 1994). Egginton and Smith (1986a, b) found N_2O emissions in the range of 0.4 to 3.2 kg N ha^{-1} yr^{-1} for unfertilized and mown grassland on mineral soil, which reasonably agree with the background emissions of 0.5 to 1.2 kg N ha^{-1} yr^{-1} found for the mineral soils in the present study (Chapter 4). Literature data suggest that the fertilizer-derived N_2O emissions from CAN or ammonium nitrate (AN) are in the range of 1 to 1.4 % of the N applied (Egginton and Smith, 1986a, b, Heinemeyer *et al.*, 1996, and McTaggart *et al.*, 1994). This is in close agreement with the 1.0% of the N applied as CAN emitted as N_2O as found in our study (Chapter 4).

Long-term studies on the N_2O emission from unfertilized natural and managed grasslands on peat soils show N_2O emissions ranging from less than 5 up to 100 kg N_2O-N ha^{-1} yr^{-1} (Augustin and Merbach, 1996; Duxbury *et al.*, 1982; Nykänen *et al.*, 1995). In the present study, emission of N_2O from unfertilized grassland on peat

soils was 1.8 to 12.9 kg N ha^{-1} yr^{-1}. Annual N$_2$O emissions from grassland supplied with 0 to 480 kg CAN-N ha^{-1} yr^{-1} on a shallow drained peat soil in Germany ranged from 5.3 to 14.0 kg N ha^{-1} yr^{-1} (Augustin and Merbach, 1996). Assuming that N$_2$O emission was smallest on unfertilized grasland and largest on grassland supplied with 480 kg N ha^{-1} yr^{-1}, a N fertilizer-derived N$_2$O emission of 1.8% can be calculated. This figure agrees with the N fertilizer-derived N$_2$O emission from the peat soil with the high mean groundwater level in the present study (Chapter 4). Clearly, the much larger background N$_2$O emissions and N fertilizer-derived N$_2$O emissions from the peat soils than from the mineral soils indicate that different emission factors for peat soils than for mineral soils must be used in N$_2$O budget calculations.

Thus far, the integral effects of grazing on N$_2$O fluxes, i.e. the combined effects of urine and dung patches and treading, have not been studied in long-term field studies. The monitoring studies presented in this thesis are the first studies in which N$_2$O emission from grazed grassland is compared with that from mown-only grassland. The grazing-derived N$_2$O emissions ranged from 1.0% to 11.4% of the N excreted during grazing and were much larger than the N fertilizer-derived emissions (Chapter 4). The large grazing-derived emissions in this study and published data on the large emission from single urine and dung patches (Allen _et al._, 1996; De Klein and Logtestijn, 1994; Flessa _et al._, 1996; Monaghan and Barraclough, 1993; Sherlock and Goh, 1983; Yamulki and Jarvis, 1996) clearly indicate that the effect of grazing should be considered in N$_2$O budget calculations.

Dairy farming systems in the Netherlands
The total N$_2$O emission from dairy farming systems in the Netherlands in 1994 was estimated at 13.7 ± 5.1 Gg N$_2$O N yr^{-1} (Chapter 8). Kroeze (1994) estimated the total N$_2$O emission towards the atmosphere in the Netherlands at 37.1 Gg N yr^{-1}, including agriculture, energy generation, industry and traffic. The estimates of the emissions of N$_2$O from grasslands on mineral soils and peat soils in the study of Kroeze (1994) were based on the results of the present study (Chapters 2, 3 and 4). It is therefore a reasonable estimate that dairy farming systems account for about 35% of the total N$_2$O emission in the Netherlands.

Prather _et al._ (1995) estimated the total global N$_2$O source strength at 10 to 17 Tg N yr^{-1}, from which 3.7 to 7.7 Tg N yr^{-1} is derived from anthropogenic activities, including agriculture (Chapter 1; Table 1). Combining these and our data, we estimate that dairy farming systems in the Netherlands account for about 0.1% of

the total global N_2O source or about 0.3% of the global anthropogenic N_2O sources.

Factors controlling N_2O emission from intensively managed grasslands

Figure 1 presents the major factors controlling N_2O emission from intensively managed grasslands at the scale of an individual grassland field. The factors are grouped into three interacting categories, i.e. climate, grassland management and soil conditions.
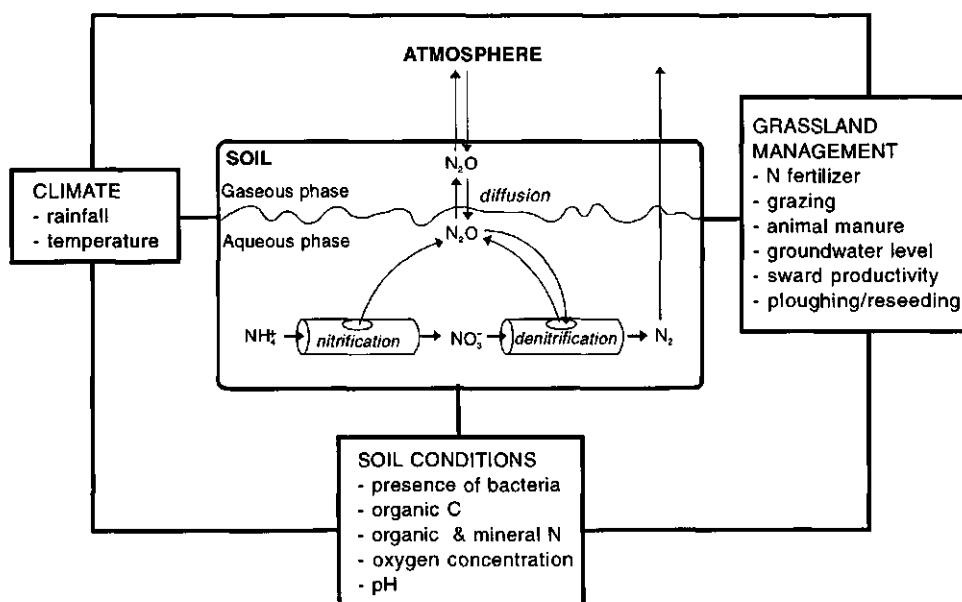

Figure 1. Major factors controlling N_2O emission from grassland soils. The inner part of the figure shows the *hole in the pipe model* of Firestone and Davidson (1989). There are three levels of microbial regulation of N_2O emission from soils: (i) the rates of nitrification and denitrification (amount of N transformed in the pipe); (ii) the ratios of end products (the size of the holes in the pipes); and (iii) diffusion and consumption of N gases prior to escape from the soil to the atmosphere. These microbial regulations are influenced by climate, soil conditions and grassland management.

Climate

Both rainfall and temperature are major factors controlling N_2O fluxes from soils. They affect the activity of many biological processes in the soil, including mineralization (e.g. Stanford *et al.*, 1973), nitrification (e.g. Goodroad and Keeney, 1984), denitrification (e.g. Keeney *et al.*, 1979), and the rate of N uptake by the roots (e.g. Watson, 1986). Moreover, they also affect gas diffusivity in the soil (e.g. Benckiser, 1994).

In the present studies the stimulating effects of rainfall on N_2O fluxes have been clearly demonstrated; largest fluxes were found during wet soil conditions (Chapters 3, 4, 6, and 7). However, a quantification of the effects of rainfall in terms of increase in N_2O flux per unit rainfall could not be derived properly due to the many interacting soil and climate factors.

Temperature and N_2O flux were not or only weakly correlated (Chapters 3 and 5), probably because temperature is mostly negatively correlated with soil moisture and because a possible effect of temperature on N_2O flux was interrelated with grassland management. Highest temperatures are found during the growing season when both application of N fertilizer and grazing strongly affect N_2O fluxes.

Grassland management

Nitrogen fertilizer

Fluxes of N_2O typically increased after N fertilizer application, reaching a maximum within a few days and then gradually decreased in 1 to 4 weeks to levels similar to unfertilized grassland (Chapters 3, 4, and 7). A similar pattern was found for mineral N contents in the soil, indicating the key role of mineral N in the emission of N_2O from grassland soil.

CAN is the common N fertilizer for grassland in the Netherlands (Anonymous, 1995a) and was also used in the monitoring studies (Chapters 2, 3, and 4). Results in Chapter 7, show that under wet conditions the type of N fertilizer largely affects the N_2O flux, with much larger N_2O fluxes from NO_3^- fertilizers than from NH_4^+ fertilizers.

Emissions of N_2O from cattle slurry were smaller than from CAN under wet conditions (Chapter 7). Possible long-term effects of cattle slurry application on N_2O fluxes were not assessed and, therefore, accurate emission factors for cattle slurry cannot be presented here.

Grazing

Grazing affects the emission of N_2O in three ways, i.e. via i) urine patches, ii) dung patches, and iii) treading and trampling. Both urine and dung patches are considerable sources of N_2O, which has been attributed to the high contents of ammoniacal N and mineralizable C compounds in these patches (Allen *et al.*, 1996; De Klein and Logtestijn, 1994; Flessa *et al.*, 1996; Monaghan and Barraclough, 1993; Sherlock and Goh, 1983; Yamulki and Jarvis, 1996). No studies have been published yet that address the effects of treading and trampling on N_2O emission. Treading and trampling by grazing animals may compact the soil (e.g. Naeth *et al.*, 1990; Warren *et al.*, 1986). Soil compaction retards water infiltration and gas diffusion, leading to decreased oxygen (O_2) concentrations in the soil (Hansen and Bakken, 1993) and to an increased production of N_2O (Hansen and Bakken, 1993 and Douglas and Crawford, 1993). Effects of treading and trampling on N_2O emission are probably largest when urine and dung affected areas are compacted, because then conditions are created with high contents of mineral N and mineralizable C, in combination with low concentration of O_2. Urine-filled hoof holes may be major sites of N_2O production in grazed grasslands. Evidently, there is a need for quantifying the effect of treading and trampling on N_2O emission from grazed grassland.

Groundwater level

Groundwater level in grasslands in the Netherlands can be adjusted to some extent by drainage and by controlling the water level in the ditches surrounding these grasslands. Therefore, groundwater level is categorized in this study as a grassland management option.

Kliewer and Gilliam (1995) showed that N_2O emission increased with increasing groundwater level in a mineral soil. In our study, high groundwater levels promoted N_2O emission from sandy soils (Chapters 4 and 7). By contrast, emission of N_2O from the peat soil with the relatively low groundwater level were much larger than from the peat soil with the relatively high groundwater level (Chapters 3 and 4). Similar results for peat soils were found by Augustin and Merbach (1996).

Groundwater levels in the sandy soils fluctuated strongly during certain periods. In Chapter 7, groundwater levels increased with more than 50 cm within a few days (Figure 1 in Chapter 7). Such conditions may promote N_2O emission, because i) soil air with high N_2O concentrations may be driven out of the soil due

to the rising water, and because ii) short periods of drying and wetting of soils promote both N_2O production during nitrification and denitrification and also emission of N_2O from the soil towards the atmosphere. Fluctuations of the mean groundwater levels in the peat soils were relatively smaller and periods of high groundwater levels lasted much longer than in the sandy soils. Figure 2 presents a hypothetical relationship between groundwater level and N_2O emission for soils with a relatively constant groundwater level. When groundwater level is near the soil surface for prolonged periods, the soil becomes strictly anaerobic and N_2O production from nitrification and denitrification is small (e.g. Davidson, 1991). Moreover, diffusion of N_2O is also small in wet soils, increasing the probability on reduction of N_2O into N_2. Highest N_2O emission is found for a groundwater level at which the soil moisture content in the top soil is optimal for N_2O production and emission. When groundwater level is deep, moisture content in the top soil decreases and thereby also the N_2O production. In the field, effects of groundwater level on N_2O emission are strongly interrelated with rainfall and irrigation and the potential capillary rise of groundwater in the soil. The differences in N_2O emissions between the two peat soils with different groundwater levels (Chapters 3 and 4) are most likely related to the effects of groundwater level as postulated in Figure 2.

Sward productivity
All factors that affect the productivity of the sward, e.g. sod quality, mowing frequency, and application of phosphorus and other nutrients, may indirectly affect N_2O emission. A low productivity of the sward generally coincides with suboptimal uptake of soil mineral N, thereby increasing the chance on N_2O emission. Another management factor that may affect N_2O emission, is ploughing and/or reseeding of the sward. Ploughing increases the mineralization of organic C and N, especially in old permanent grassland, which may result in significantly increased N_2O emission.

Soil conditions
In soils, N_2O is produced by nitrifying and denitrifying bacteria. The presence of bacteria that nitrify and denitrify is a prequisite for production of N_2O in the soil. No microbiological assays were made in this thesis and, therefore, it is unknown whether differences in bacteria populations contributed to the differences in N_2O emission between the soils. All soils had been used for more than 10 years as intensively managed permanent grasslands. It can be assumed that due to the regular addition of N fertilizer, cattle slurry, urine and dung to the soil and the

accumulation of organic matter in these permanent grasslands, many types of bacteria involved in N transformations were present in these soils.

Denitrification potentials and C mineralization rates were much larger in the peat soils than in the sandy and clay soils, both in the top and sub soil (Chapter 3). The availability of mineralizable C is probably one the major soil factors causing the large differences in N_2O emission between the peat and mineral soils (Chapters 3 and 4). Mineral N contents in the top soil of unfertilized grassland were higher in the peat soils than in the mineral soils (Chapters 3 and 4), most probably because of differences in N mineralization rates. Differences in mineral N contents and N mineralization rates may also have contributed to the differences between mineral and peat soils. There were no or only small differences in mineral N contents between the different soils when N fertilized and grazed (Chapters 3 and 4).
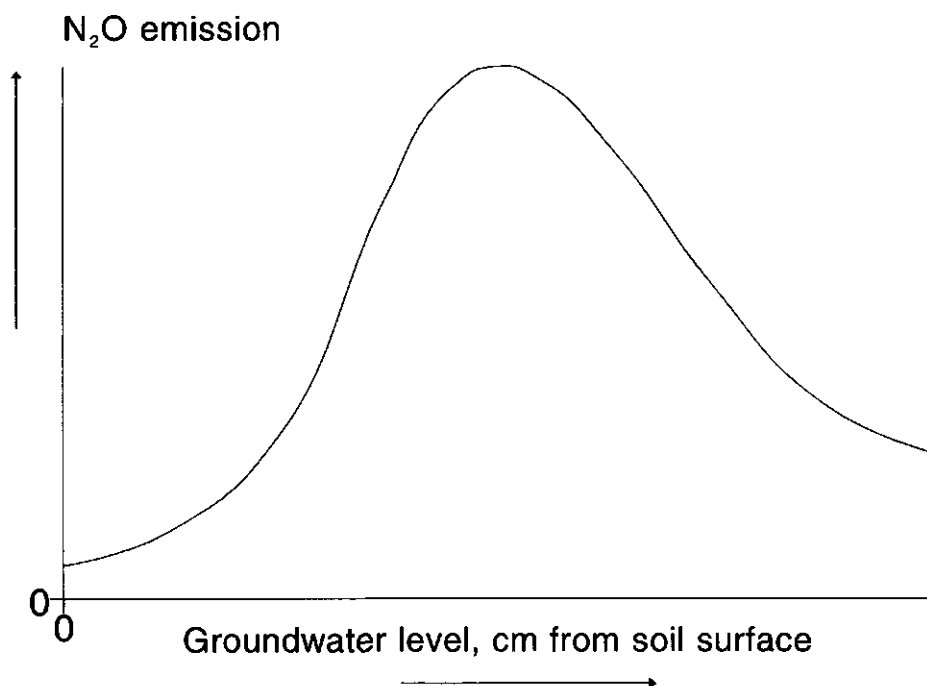

Figure 2. Hypothetical relationship between mean groundwater level (more or less kept at a constant level) and N_2O emission from the soil surface. The shape of the curves may vary somewhat with soil type and conditions.

Oxygen strongly controls nitrification and denitrification activity in the soil and also the relative production of N_2O during these processes. The oxygen concentration in soil is affected by soil moisture content, porosity and biological oxygen consumption. Moisture content in soil is controlled by rainfall, irrigation, groundwater level, moisture retention capacity of the soil and the removal of water by drainage and evapotranspiraton. The water-filled pore space (WFPS) is a measure for the fraction of water in the soil pores and can be used to compare the soil moisture or aeration status of different soils. Davidson (1991) indicated that the the maximal production of N_2O occurs when the WFPS is between 60 and 80%. We found that WFPS strongly fluctuated during the year, but was on average smallest in the sandy soil and largest in the peat soil with the high groundwater level (Chapter 3). Hence, WFPS is a major controlling factor and may have contributed to the large difference in N_2O emission between the two peat soils.

The pH of the soil may affect both the nitrification and denitrification activity as well as the relative N_2O production during these processes. Generally, the emission of N_2O increases when soil pH decreases. The pH-KCl of the four soils in the monitoring studies were 7.2 for the clay, 5.5 for the sandy, 5.0 for the peat soil with the relatively high groundwater level and 4.7 for the peat soil with the relatively low groundwater level (Chapters 3 and 4). Apparently, the mean N_2O emission was inversely related to the pH of the different soils. However, no assessment was made whether these differences in pH played a role in the differences in N_2O emissions from the four soils.

Uncertainties in the quantification of N_2O emission using flux chambers

A flux chamber method was used to quantify the N_2O emission from grasslands. There are several possible sources of error and bias in the quantification of N_2O fluxes from soils using flux chambers (e.g. Hutchinson and Livingston, 1993), associated with (i) the sampling strategy in the field, (ii) the sampling strategy in time, (iii) a possible disturbance of the conditions in the chamber, (iv) the calculation of the flux from the change in the N_2O concentration in the headspace of the chamber, (v) the calculation of the mean field flux from replicate measurements, and (vi) the calculation of total N_2O emission from a field during a certain period (Figure 3).

i). Sampling strategy in the field

More than 100 flux measurements were necessary to obtain a precise estimation of the mean field N_2O flux from a clay soil (Chapter 6). This was due to the large spatial variability of the fluxes. Similar results were found by Folorunso and Rolston (1984). The estimates of the mean field N_2O flux from grasslands in the monitoring studies (Chapters 2, 3, and 4) had a large standard error, due to the relatively small number of replicates (n=6). However, statistical analysis indicated that a number of only 4 to 6 replicates was sufficient to obtain statistically significant ($\alpha=0.05$) differences between N_2O fluxes of different fertilizer or management treatments (Chapters 3 and 7).
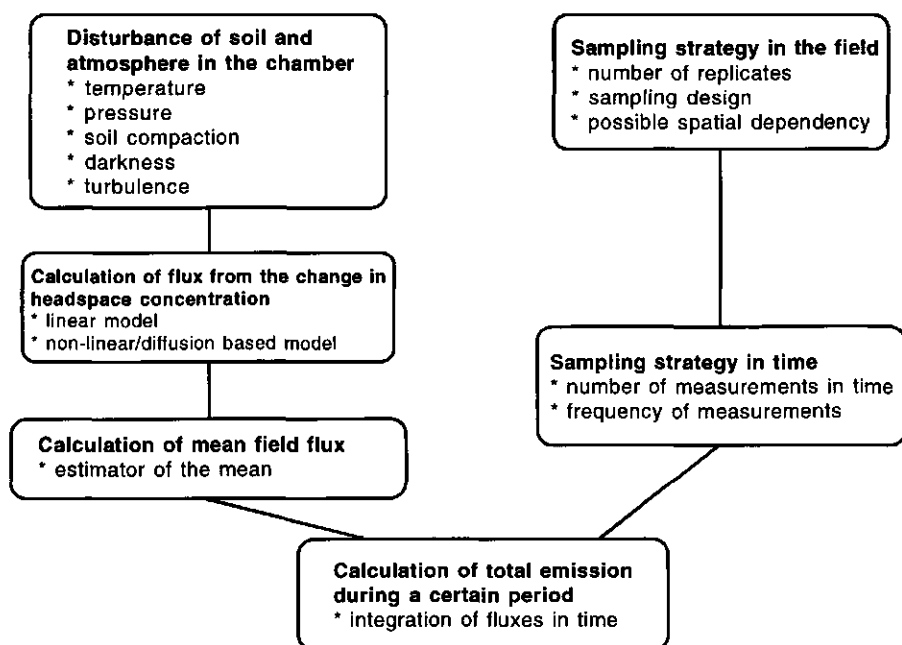
Figure 3. Summary of possible sources of error and bias in the quantification of total N_2O emission from soils using flux chambers.

The geostatistical analyses in Chapter 6 showed a spatial dependency of N_2O fluxes on N fertilized and mown grassland on clay soil, for a distance of less than 6 m. A possible spatial dependency of the fluxes should be considered when setting-up field measurements using flux chambers. To diminish the probability on dependent samples, a randomized or stratified randomized sampling scheme should be used.

The experiments in this thesis in which treatments were compared were designed in randomized blocks (Chapters 3, 4, and 7).

ii). Sampling strategy in time

The number and frequency of flux measurements was dependent on the aim of the experiment and the available time. Continuous measurements during two days and nights were made when flux measurements using flux chambers were compared with those using the flux gradient technique (Chapter 5). To study the effects of N fertilizer type and application rate on N_2O emission, daily measurements were made when significant N fertilizer-derived fluxes were expected, i.e. during the first 1-3 weeks after N application (Chapter 7). After this period, fluxes were measured less frequently. In the monitoring studies, weekly measurements were carried out for two years (Chapters 2, 3, and 4). We did not choose for an event-oriented measurement strategy, i.e. a large number of measurements during periods of large fluxes (e.g. after N fertilizer application) and a small number of measurements during periods of small fluxes (e.g. during winter and dry periods in summer), because such a strategy may result in biased estimates of the total annual emission. When annual emission estimates have to be made it is also important to quantify the duration of periods with small fluxes and the magnitude of these small fluxes. The occassionally high fluxes from grassland during the end of autumn and during winter (Chapter 4) indicate that flux measurements throughout the year are needed to obtain reliable estimates of total annual emissions.

The continuous flux measurements in Chapter 5 showed no significant diurnal variations in N_2O fluxes. By contrast, Christensen (1983) and Conrad et al. (1983) found clear diurnal patterns of N_2O fluxes, with smallest fluxes during the night and early morning and highest fluxes during the afternoon. Flux measurements were generally carried out between 9.00h and 12.00h in the morning (Chapters 2, 3, 4, and 7), assuming that the mean N_2O flux in this period was representative for the mean flux over the whole day. This measurement strategy may have been a possible source of bias. However, continuous measurements during one whole day were not achievable as a standard procedure.

iii). Disturbance of the soil and atmosphere

The placement of the chambers on grassland may disturb the conditions within the chamber, e.g. by soil compaction, damaging roots of the grass, and changes in temperature and pressure in the chamber. All these factors may affect N_2O flux, but

can be minimized by using an appropiate chamber design, by a relatively short measurement time, and by a reasonable user care (Hutchinson and Livingston, 1993). In the present study, several measures were taken to minimize possible perturbations of the physical and biological conditions within the chamber, including the use of small flux chambers (diameter 20 cm) with sharp edges that could be gently inserted into the soil, the insulation and venting of the chambers, and a restricted closure time of only 30 minutes. The relation between the N_2O concentration in the headspace and the closure time of the chamber (n=4) was linear (Chapters 2 and 6), indicating that the N_2O flux from soil did not change significantly during the measurements.

iv). Calculation of the flux from the change in the headspace concentration
In many studies (e.g. Matthias *et al.*, 1980) the flux was calculated using a linear model. In other studies (Hutchinson and Mosier, 1981; Jury *et al.*, 1982) a diffusion-based flux model was used to calculate the flux, because of a non-linear relationship between time and N_2O concentration in the headspace. Calculations of Healy *et al.* (1996) pointed out that gas fluxes within a flux chamber are smaller than outside the chamber, because the soil gas concentration gradient decreases in the vertical and increases in the radial direction, and because the diffusion rate in the chamber is slow relative to turbulent mixing outside the chamber. Application of a linear model to non-linear chamber concentration data represent a potentially serious source of measurement bias (Anthony *et al.*, 1995; Healy *et al.*, 1996). However, the relation between the closure time and N_2O concentration (n=4; 10 minutes intervals) in the present study was much better described by a linear model than a non-linear model (Chapters 2 and 6). The relatively short measurement time, insertion of the flux chamber into the soil, and the mixing of the atmosphere in the headspace of the chamber by the photoacoustic analyzer (Chapter 2) may have reduced possible errors as pointed out by Healy *et al.* (1996).

v). Calculation of the mean field flux
The choice of the estimator of the mean may largely affect the calculated mean field flux, when a relative small number of samples is available (Chapter 2; Parkin and Robinson, 1992). Frequency distributions of 42 to 48 fluxes from peat soil did neither follow normal nor lognormal distributions (Chapter 4). Frequency distributions of 144 N_2O fluxes from a clay soil were lognormally distributed on all four measurement days (Chapter 6). Apparently, a large number, i.e. > 100, of flux

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measurements is needed to obtain a proper lognormal frequency distribution. When it is uncertain whether the distribution follows a lognormal pattern and/or when part of the measured fluxes are negative, the robust arithmetic mean is a more appropiate estimator of the mean than sensitive estimators based on logtransformed data, such as the geometric mean, lognormal mean, or Finney's or UMVUE mean (Chapter 2).

When looking at literature data, one would suggest that differences in N_2O emission between flux chamber studies using different estimators of the mean are not only related to site-specific factors (e.g. soil conditions, climate, management), but also to the choice of the estimator of the mean. Evidently, the use of appropiate estimators of the mean in N_2O studies that make use of replicate flux chamber measurements is necessary to compare and integrate these studies and to obtain an accurate estimate of the global N_2O budget.

vi). Calculation of total emission during a certain period
Frequently, the temporal variability of N_2O fluxes was large and shown at different time scales: within a day (Chapter 5), within a week (Chapter 7), within a season (Chapters 3 and 4), between seasons (Chapter 4) and between years (Chapter 4). The most accurate estimate of the total N_2O emission is obtained when fluxes are measured continuously over a prolonged period, i.e. several years, using automatic flux chambers directly attached to a gas chromotograph or gas analyzer (e.g. Loftfield *et al.*, 1992). However, such a measurement device was not achievable in this 2-yr lasting monitoring study on four locations with three management types in six replicates. The measuring device as used in the present study was simple but robust. It never failed for longer than one day, and therefore remained constant and stabile during the whole measuring period.

The increase in N_2O flux following application of N fertilizer and grazing may vary greatly, both in terms of flux magnitude and duration (Chapters 3, 4, and 7). A model pattern of the time course of N_2O flux after fertilizer application and grazing could not be inferred readily because of the complexity and interactions between the major factors controlling N_2O production in soil. Linear interpolation of the measured fluxes was therefore chosen as a straightforward procedure for the calculation of total N_2O emission during a certain period.

Options to mitigate N$_2$O emission from intensively managed grasslands

There are several management options to mitigate N$_2$O emission from intensively managed grasslands and whole dairy farming systems. In Figure 4 these options are categorized into three groups: N fertilizer, cattle, and soil.
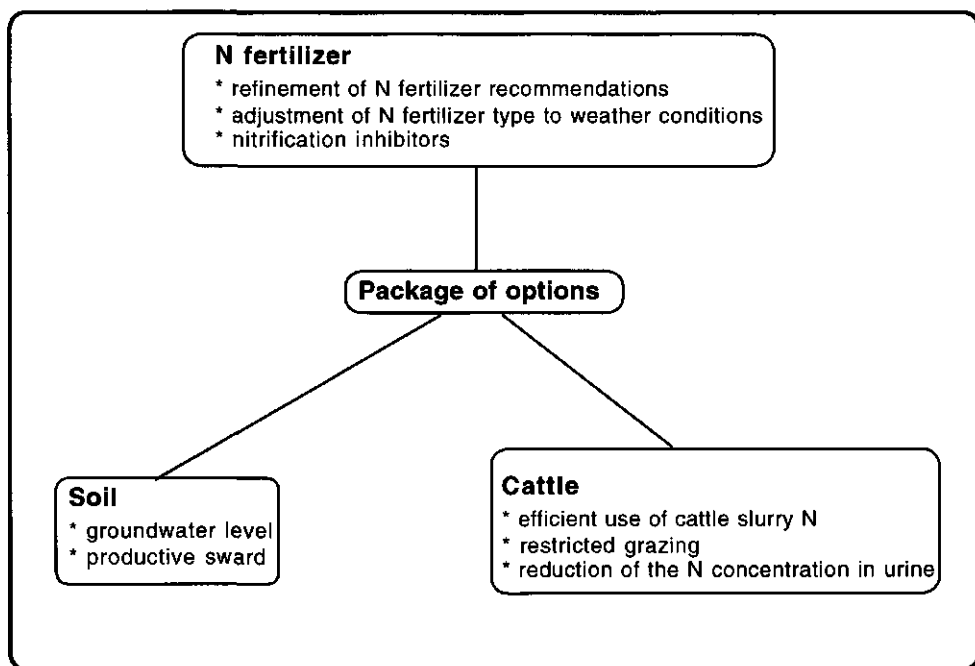

Figure 4. Packages of management options for the mitigation of N$_2$O emissions from intensively managed grassland that deal with N fertilizers, soil conditions and cattle.

N fertilizer

Refinement of N fertilizer recommendations
Highest N$_2$O fluxes from mown grasslands were found when mineral N contents in the soil were highest (Chapters 3, 4, and 7). Results in Chapter 7 showed that the N$_2$O emission rate increased near exponentially with increasing N fertilizer application rate. Preventing high soil mineral N contents for a prolonged period is a proper measure to reduce N$_2$O emissions from grasslands. Hence, a further

refinement of N fertilizer recommendations may result in a reduction of the N_2O emission from grassland.

Adjustment of N fertilizer type to weather conditions

During wet conditions, N_2O fluxes from grasslands were much larger from NO_3^- containing N fertilizers than from N fertilizers containing only NH_4^+ (Chapter 7). A fertilization strategy in which the choice of N fertilizer is dependent on the soil moisture status in combination with the expected rainfall and evapotranspiration during the next days, may be a cheap and effective tool to mitigate N_2O emission from grasslands. Such a fertilization strategy should also take into account other effects of fertilizer type, like ammonia volatilization, soil acidification and effects on botanical composition of the sward (e.g. Van Burg _et al.,_ 1982).

Nitrification inhibitors

Results in Chapter 7 and studies in literature (e.g. Mosier _et al.,_ 1996) indicate that the use of nitrification inhibitors may reduce N_2O emission from NH_4^+ fertilizers. We found that the reduction of the N_2O emission caused by the addition of dicyandiamide (DCD) to ammonium sulphate (AS) was relatively small in comparison of using AS instead of CAN (Chapter 7). In the Netherlands, DCD is the only nitrification inhibitor widely tested in field experiments and allowed to be applied in practice. The potentials of the use of DCD to mitigate N_2O emissions from intensively managed grasslands in the Netherlands are probably small, because i) the inhibitory effect of DCD on nitrification has been shown to vary strongly, probably due to the variations in weather conditions (e.g. Van Enckevort, 1988), and because ii) DCD is relatively expensive.

Soil

Groundwater level

High and fluctuating groundwater levels promoted N_2O emission from sandy soils, when soil mineral N content was high (Chapters 4 and 7). Preventing high groundwater levels may be an option to reduce N_2O emissions from sandy soils. Emissions of N_2O from grasslands on peat soils (Chapters 3 and 4) indicate that maintaining the groundwater level at a high level (within 30 cm from the soil surface) gives much lower emissions of N_2O in comparison to mean groundwater level of 50 cm and deeper. It should be noted that such a high groundwater level in

managed grasslands has many disadvantages. It strongly favours denitrification losses of NO_3^- containing fertilizer and it hampers grazing and cultivation practices including mowing and application of fertilizer and slurry. The ultimate result may be a bad sod quality and a suboptimal forage production. Moreover, high groundwater levels may result in increased emission of methane (CH_4), an other important greenhouse gas. On the other hand, a low groundwater level in peat soils may result in an undesired shrinkage of the soil, due to enhanced mineralization of organic matter to CO_2, the most important greenhouse gas. Clearly, emission of N_2O from intensively managed grasslands on peat soil may be regulated to some extent by maintaining the groundwater level at a certain level. However, the effects of groundwater level on other factors must also be considered, because these factors may dramatically affect the productivity of the dairy farming system and the emission of other greenhouse gases.

Productive sward
All factors that affect the productivity and the N use of the sward, e.g. sod quality, mowing frequency, and application of plant nutrients, may indirectly affect N_2O emission. Soil mineral N contents are generally higher as the productivity and N uptake of the sward is lower. It has been indicated that the higher the mineral N contents and the longer the periods of elevated mineral N contents in the soil, the larger the risk on N_2O emission.

Cattle

Efficient use of cattle slurry N
Generally, cattle slurry is applied to grassland and forage land on the farm where it is collected. When the amount of applied slurry-N does not meet the required amount of N for herbage growth, the farmer applies N fertilizer, in the Netherlands generally as CAN. An increase in the N use efficiency of cattle slurry, by e.g. diminishing NH_3 volatilization, will decrease the amount of CAN required on the farm. Results in Chapter 7 and in literature (Egginton and Smith, 1986a; Velthof and Oenema, 1993) suggest that slurry-derived N_2O emission is smaller than CAN-derived N_2O emission. Thus, substitution of CAN by cattle slurry may result in a decrease in N_2O emission. Moreover, a decrease in NH_3 volatilization and NO_3^- leaching due to more efficient use of cattle slurry will decrease the N_2O emission derived from atmospheric NH_3 deposition and from leached NO_3^- (Chapter 8).

Restricted grazing
Grazing-derived emissions were much larger than N fertilizer-derived emissions, expressed in unit N_2O-N per unit N (Chapters 3 and 4). When grazing is restricted, the cattle will be stalled for a longer time and more urine and dung will be collected and stored as slurry. This slurry has to be applied as fertilizer to the grassland. Results in Chapters 3, 4, and 7 suggest that the N_2O emission expressed in unit N_2O-N per unit N, is much larger from dung and urine patches in grassland than from slurry which has been properly applied to soil. Thus, restricted grazing may be an option to mitigate N_2O emission from intensively managed grasslands. However, also other effects should be taken into account when switched to restricted grazing, like the need for harvesting more fodder, for larger slurry storage basins and for application equipment. Thereby, restricted grazing may result in an increased NH_3 volatilization (Bussink and Oenema, 1997).

Reduction of the N concentration in urine
The large N_2O emission from urine patches are associated with the high ammoniacal N concentrations in the urine-affected soil. A reduction of the N concentration in urine may reduce N_2O emissions from urine patches. Hence, all strategies that aim at reducing the total N intake of the animal but maintain the nutritional value of the animal feed will reduce the N excretion and thereby the N_2O emission per animal head. These strategies include supplemental feeding of low-N fodders, reduction of the amount of N fertilizer application, and postponed grazing to offer animals herbage with lower N contents.

Package of measures

Substantial reductions in N_2O emissions will be obtained when a combination of mitigation options is implemented. For a successful implementation, a thorough quantitative understanding of the N cycling processes on dairy farming systems with its many interactions between soil, plant, animals and animal excreta, is needed. Implementation of a measure to mitigate N_2O emissions may result in an increase of other unwanted emissions. As an example, the effects of restricted grazing on N_2O, CH_4, NH_3 emissions and NO_3^- leaching are briefly discussed. In a non-grazing system, urine and dung are collected as slurry in slurry storage basins. Emission of N_2O is much smaller from slurry which is stored and thereafter applied to soil than that from grazed grassland, per unit N (Oenema *et al.*, 1993; Oenema and Velthof,

1993; Chapters 4, 7, and 8). When slurry is collected and applied efficiently, less N fertilizer has to be applied and N fertilizer-derived N_2O emissions are then smaller. Thus, N_2O emission tends to be larger in a grazing system than in a non-grazing system. Restricted grazing will increase both NH_3 and CH_4 emissions, because emissions of NH_3 and CH_4 from stored and soil-applied slurry are much larger than from grazed grassland (Bussink and Oenema, 1997; Van den Pol-Van Dasselaar *et al.* 1997; De Wit, 1994). The additional amount of CAN required in the grazing system has only a slight effect on NH_3 emissions (Velthof *et al.*, 1990) and CH_4 emissions (Van den Pol-Van Dasselaar *et al.*, 1997) from soil, but will have a significant effect on indirect CO_2 emissions. Because large amounts of NO_3^- are leached from urine patches (Ryden *et al.*, 1984), restricted grazing results in reduced leaching of NO_3^-. Leaching of NO_3^- from grassland to which slurry is applied is much less than from grazed grassland, provided that slurry is applied according to fertilizer recommendations. Thus, restricted grazing may result in decreased emissions of N_2O and leaching of NO_3^- and in increased emissions of NH_3 and CH_4. Hence, the interactions between the emissions of N_2O and other greenhouse gases such as CO_2, CH_4 and NH_3 should be considered, as well as the interaction between N_2O emission and NO_3^- leaching.

Thus far, little attention has been given to quantify the effects of mitigation options on N_2O emission from intensively managed grasslands and whole dairy farming systems. The N_2O budget calculations for three dairy farming systems on sandy soil with different nutrient management clearly indicate that the potentials to reduce N_2O emission are large (Chapter 8).

Scope for reducing uncertainties in the N_2O budget

Many uncertainties exist in the N_2O budget. This section summarizes briefly the developments that may contribute to a further reduction of the uncertainties.

Measurement technique
At present, flux chambers methods are the most widely used to estimate N_2O fluxes from soils. Recent developments in flux chamber methods are automatic equipment by which N_2O fluxes can be measured continuously (e.g. Loftfied *et al.*, 1992), the use of large flux chambers or mega-chambers to integrate fluxes over a larger soil area (Galle *et al.*, 1994), direct measurement of the N_2O concentrations in the field

thereby avoiding storage and possible leakages of gas samples (e.g. Chapter 2), the use of geostatistical techniques to improve the insight into the spatial patterns of N_2O fluxes (e.g. Ambus and Christensen, 1994; Chapter 6), and a critical consideration of the mathematics to calculate the flux from the time-course of the N_2O concentration in the headspace (e.g. Anthony *et al.*, 1995; Healy *et al.*, 1996) and to calculate the mean flux from replicate samples (e.g. Parkin and Robinson, 1992; Chapter 3). All these developments may improve the accuracy of field N_2O emission estimates.

Micrometeorological techniques like the flux gradient and eddy correlation techniques have been strongly improved recently (e.g. Smith *et al.*, 1994) and can be applied to field studies. Field measurements in which flux chamber measurements are compared with micrometeorological methods (e.g. Smith *et al.*, 1994; Chapter 5) are needed to critically evaluate both techniques and, therefore, may contribute to the improvement of the accuracy of N_2O flux estimates.

Modelling
Models can be used to increase the understanding and to improve the quantification of N_2O emission from soils and to assess the factors controlling the N_2O emission. In only a limited number of studies, empirical, mechanistic or combinations of mechanistic and empirical models have been developed and used to estimate field fluxes of N_2O (e.g. Clayton *et al.*, 1994; Grant *et al.*, 1993a, b; Mosier *et al.*, 1983; Chapter 5). Field measurements are still needed to calibrate and/or validate these models. The data set of the present study will be used to calibrate and/or validate the model for N_2O emission from grassland that is being developed by Langeveld and Leffelaar (1996).

Sampling strategies
Uncertainties in the estimates for soil-derived N_2O emissions are not only due to the uncertainties in the measurements and understanding of N_2O emissions, but also in the upscaling of N_2O emissions. There are only a limited number of sites at which flux measurements have been carried out. Most N_2O-studies have been carried out in agro-ecological zones in Europe and the USA and, for example, in Africa and Asia almost no N_2O flux measurements have been carried out. The uncertainties in the N_2O budgets will reduce when N_2O flux measurements are carried out in agro-ecological zones where until now no flux measurements have been carried out.

Nitrous oxide sinks and sources in the atmosphere
There are not only uncertainties in the estimates of the N_2O emission from the surface of the earth towards the atmosphere, but also the atmospheric processes in which N_2O is involved are not yet fully understood. McElroy and Jones (1996) recently suggested that there may be a N_2O-source in the atmosphere. If this N_2O-source really exists, the present estimates of the N_2O emissions from the earth surface are overestimations.

The data presented in this thesis provide accurate emission factors for N fertilizer-derived and grazing-derived N_2O emissions from intensively managed grasslands in temperate regions. Moreover, they provide emission factors for intensively managed grasslands on peat soils. Therefore, the present work may assist in decreasing the uncertainties in the estimates of the N_2O budget of the Netherlands and of the global N_2O budget.

References

Aarts, H.F.M., E.E. Biewinga and H. Van Keulen (1992) Dairy farming systems based on efficient nutrient management. _Netherlands Journal of Agricultural Science_ 40: 285-299.

Aarts, H.F.M., M. Hack, G. Hilhorst, F. Mandersloot, A. Meijer, N. Middelkoop, C. de Vries and W. Zaalmink (1994) De Marke Interim balance 1992-1994. Report nr. 10. De Marke, Hengelo, 159 pp. (In Dutch).

Afzal, M. and W.A. Adams (1992) Heterogeneity of soil mineral nitrogen in pasture grazed by cattle. _Soil Science Society of America Journal_ 56: 1160-1166.

Aitchison, J. and J.A.C. Brown (1966) The Lognormal Distribution, with special reference to its uses in ecomomics. Cambridge University Press, London.

Allen, A.G., S.C. Jarvis and D.M. Headon (1996) Nitrous oxide emissions from soils due to inputs of nitrogen from excreta return by livestock on grazed grassland in the UK. _Soil Biology and Biochemistry_ 28: 297-307.

Ambus, P. and S. Christensen (1994) Measurement of N_2O emission from a fertilized grassland: An analysis of spatial variability. _Journal of Geophysical Research_ 99: 549-555.

Ambus, P. and S. Christensen (1995) Spatial and seasonal nitrous oxide and methane fluxes in Danish forest-, grassland-, and agroecosystems. _Journal of Environmental Quality_ 24: 993-1001.

Ambus, P., H. Clayton, J. R. M. Arah, K.A. Smith K. A. and S. Christensen (1993) Similar N_2O flux from soil measured with different chamber techniques. _Atmospheric Environment_ 27A: 121-123.

Anonymous (1989) Robust Statistics - How not to reject outliers Part 1. Basic Concepts and Part 2. Inter-laboratory trials. _Analyst_ 114: 1693-1702

Anonymous (1995a) Agricultural data 1995, LEI-CBS, Den Haag, 269 pp (In Dutch).

Anonymous (1995b) Trading results in agriculture (BUL), LEI-DLO, Den Haag (In Dutch).

Anonymous (1995c) @Risk, Risk Analysis and Simulation Add-In for Microsoft Excel or Lotus 1-2-3, Windows Version, Palisade Corporation, Newfield.

Anonymous (1996) Nitrous oxide and carbon dioxide in agriculture, OECD/IPCC/IEA phase II development of IPCC guidelines for national greenhouse gas inventory methodology. Workshop report, December 4-6 1995, OECD/IPCC/IEA, Geneva (in press).

Anthony, W.H., G.L. Hutchinson and G.P. Livingston (1995) Chamber measurement of soil-atmosphere gas exchange: linear vs. diffusion-based flux models. _Soil Science Society of America Journal_ 59: 1308-1310.

Arah, J.R.M., K.A. Smith, I.J. Crichton and H.S. Li (1991) Nitrous oxide production and denitrification in Scottish arable soils. _Journal of Soil Science_ 42: 351-367.

Ataku, K. (1982) The role of nitrate in silage fermentation and its significance. *Journal of the College of Dairying*, Ebetsu Hokkaido, Japan, 9: 209-213.

Augustin, J. and W. Merbach (1996) Factors controlling nitrous oxide and methane emission from minerotrophic fens in Northeast Germany. pp. 133-136. In: Transactions of the 9th Nitrogen Workshop, Braunschweig September 1996, Technische Universität Braunschweig.

Aulakh, M.S., D.A. Rennie and E.A. Paul (1984) Acetylene and N-serve effects upon N_2O emissions from NH_4^+ and NO_3^- treated soils under aerobic and anaerobic conditions. *Soil Biology and Biochemistry* 16: 351-356.

Baas, J. and R.C. Rijkeboer (1995) Investigations of the contribution of traffic to N_2O emissions both now and in the future. Poster Abstracts of International Conference on Climate Change Research: Evaluation and Policy Implications, Maastricht 6-9 December 1994, 243 pp.

Beck, H. and S. Christensen (1987) The effect of grass maturing and root decay on N_2O production in soil. *Plant and Soil* 103: 269-273.

Benckiser, G. (1994) Relationships between field-measured denitrification losses, CO_2 formation and diffusional constraints. *Soil Biology and Biochemistry* 26: 891-899.

Bijay-Singh, J.C. Ryden and D.C. Whitehead (1988) Some relationships between denitrification potential and fractions of organic carbon in air-dried and field-moist soils. *Soil Biology and Biochemistry* 20: 737-741.

Blackmer, A.M. and J.M. Bremner (1978) Inhibitory effect of nitrate on reduction of nitrous oxide to molecular nitrogen by soil microorganisms. *Soil Biology and Biochemistry* 10: 187-191.

Blackmer, A.M, J.M. Bremner and E.L. Schmidt (1980) Production of nitrous oxide by ammonia-oxidizing chemoautotrophic microorganisms in soil. *Applied Environmental Microbiology* 40: 1060-1066.

Blackmer, A.M., S.G. Robbins and J.M. Bremner (1982) Diurnal variability in rate of emission of nitrous oxide from soils. *Soil Science Society of America Journal* 46: 937-942.

Bouwman, A.F. (1995) Compilation of a global inventory of emissions of nitrous oxide. Doctoral Thesis, Wageningen Agricultural University, The Netherlands.

Bramley, R.G.V. and R.E. White (1991) An analysis of variability in the activity of nitrifiers in a soil under pasture, I. Spatially dependent variability and optimum sampling strategy. *Australian Journal of Soil Research* 29: 95-108.

Breitenbeck, G.A. and J.M. Bremner (1986) Effects of various nitrogen fertilizers on emission of nitrous oxide from soils. *Biology and Fertility of Soils* 2: 195-199.

Bremner, J.M. and A.M. Blackmer (1978) Nitrous oxide: emission from soils during nitrification of fertilizer nitrogen. *Science* 199: 295-296.

Bril J., H.G. Van Faassen and H. Klein Gunnewiek (1994) Modeling N_2O emission from grazed grassland. Report 24 of the DLO Research Institute for Agrobiology

and Soil Fertility (AB-DLO). AB-DLO, Haren, 45 pp.

Burford, J.R. and J.M. Bremner (1975) Relationships between the denitrification capacities of soils and total watersoluble and readily decomposable soil organic matter. _Soil Biology and Biochemistry_ 7: 389-394.

Bussink, D.W. (1994) Relationships between ammonia volatilization and nitrogen application rate, intake and excretion of herbage nitrogen by cattle on grazed swards. _Fertilizer Research_, 38: 111-121.

Bussink, D.W. and O. Oenema (1997) Ammonia volatilization from dairy farming systems in temperate areas; a review. _Nutrient Cycling in Agroecosystems_ (submitted).

Carran, R.A., P.W. Theobald and J.P Evans (1995) Emission of nitrous oxide from some grazed pasture soils in New Zealand. _Australian Journal of Soil Research_ 33: 341-352.

Chalk, P.M. and C.J. Smith (1983) Chemodenitrification. In: Gaseous losses of nitrogen from plant soil systems (eds J.R. Freney and J.R. Simpson), pp. 65-89. Martinus Nijhoff & Dr. W. Junk Publishers, The Hague.

Christensen, S. (1983) Nitrous oxide emission from a soil under permanent grass: seasonal and diurnal fluctuations as influenced by manuring and fertilization. _Soil Biology and Biochemistry_ 15: 531-536.

Clayton, H., J.R.M. Arah and K.A. Smith (1994) Measurement of nitrous oxide emissions from fertilized grassland using closed chambers. _Journal of Geophysical Research_ 99: 599-607.

Conrad, R., W. Seiler and G. Bunse (1983) Factors influencing the loss of fertilizer nitrogen into the atmosphere as N_2O. _Journal of Geophysical Research_ 88: 6708-6718.

Crutzen, P.J. (1970) The influence of nitrogen oxides on the atmospheric ozone content. _Quarterly Journal of the Royal Meteorological Society_ 96: 320-325.

Davidson, E.A. (1991) Fluxes of nitrous oxide and nitric oxide from terrestial ecosystems. In: Microbial production and consumption of greenhouse gases: methane, nitrogen oxides, and halomethanes (eds J.E. Rogers and W.B. Whitman), pp. 219-235. American Society for Microbiology, Washington D.C.

Deenen, P.J.A.G. and E.A. Lantinga (1991) Herbage and animal production responses to fertilizer nitrogen in perennial ryegrass swards. I. continuous grazing and cutting. _Netherlands Journal of Agricultural Science_ 41: 179-203.

De Klein, C.A.M. and R.S.P. Van Logtestijn (1994) Denitrification and N_2O emission from urine-affected grassland soil. _Plant and Soil_ 163: 235-242.

Den Boer, D.J., D.W. Bussink and W.H. Prins (1990) Measures to reduce emissions of nitrogen and other nutrients from dairy farms, with emphasis on ammonia emission. _Meststoffen 1990_ 3: 26-28.

Den Boer, D.J (1993) Reduction of mineral surplus on commercial dairy farms.

Meststoffen 1993: 19-24. (In Dutch).

Denmead, O.T., J.R. Freney and J.R. Simpson (1979) Studies of nitrous oxide emission from a grass sward. *Soil Science Society of America Journal* 43: 726-728.

De Soete, G.G, 1993. Nitrous oxide emissions from combustion. In: Methane and nitrous oxide, methods in national emissions inventories and options for control (ed. A.R. van Amstel), pp. 287-339. RIVM, Bilthoven.

De Wit, H. (1994) Methane fluxes from sandy grassland soils. An inventory on uptake and emission of methane in aerobic grassland soils in the Netherlands under different management regimes. Department of Soil Science and Plant Nutrition, Wageningen Agricultural University, Wageningen, 57 pp.

Douglas J. T. and C.E. Crawford (1993) The response of a ryegrass sward to wheel traffic and applied nitrogen. *Grass and Forage Science* 48: 91-100.

Duxbury, J.M., D.R. Bouldin, R.E. Terry and R.L. Tate (1982) Emissions of nitrous oxide from soils. *Nature* London, 298: 462-464.

Duyzer, J.H. (1995) Measurements of the atmospheric emission of N_2O from biogenic sources in general and by grassland ecosystems in particular. TNO report R95/213, TNO, Delft, 33 pp.

Egginton, G. M. and K.A. Smith (1986a) Nitrous oxide emission from a grassland soil fertilized with slurry and calcium nitrate. *Journal of Soil Science* 37: 59-67.

Egginton, G.M. and K.A. Smith (1986b) Losses of nitrogen by denitrification from a grassland soil fertilized with cattle slurry and calcium nitrate. *Journal of Soil Science* 37: 69-80.

Finney, D.J. (1941) On the distribution of a variate whose logarithm is normally distributed. *Journal of the Royal Statistical Society (Series B)* 7: 155-161.

Firestone, M.K. and E.A. Davidson (1989) Microbiological basis of NO and N_2O production and consumption in soil. In: Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere, Life Sciences Research Report 47 (eds M.O. Andreae and D.S. Schimel), pp. 7-21. John Wiley and Sons, Chichester.

Firestone, M.K., R.B. Firestone and J.M. Tiedje (1980) Nitrous oxide from soil denitrification: Factors controlling its biological production. *Science* 208: 749-751.

Flessa, H., P. Dörsch and F. Beese (1995) Seasonal variation of N_2O and CH_4 fluxes in differently managed arable soils in southern Germany. *Journal of Geophysical Research* 100: D11 23,115-23,124.

Flessa, H., P. Dörsch and F. Beese (1996) N_2O emissions from cattle excrements in pasture land - a global inventory-. In: Transactions of the 9th Nitrogen Workshop, Braunschweig September 1996, pp. 142-144. Technische Universität Braunschweig.

Focht, D.D. (1978) Methods for analysis of denitrification in soils. In: Nitrogen in the environment Vol 2 (eds D.R. Nielsen and J.G. MacDonald), pp. 433-490.

Academic Press, New York.

Folorunso, O.A. and D.E. Rolston (1984) Spatial variability of field-measured denitrification gas fluxes. *Soil Science Society of America Journal* 48: 1214-1219.

Fowler, D. and J.H. Duyzer (1989) Micrometeorological techniques for the measurement of trace gas exchange. In: Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere, Life Sciences Research Report 47 (eds M.O. Andreae and D.S. Schimel), pp. 189-207. John Wiley and Sons, Chichester.

France, G.D. and D.C. Thompson (1993) An overview of efficient manufacturing processes. The Fertiliser Society, Proceedings No. 337, 47 pp.

France, J. and J.H.M. Thornley (1984) Mathematical models in agriculture, A quantitative approach to problems in agriculture and related sciences. Butterworths, London.

Galle, B, L. Klemedtsson and D.W.T. Griffith (1994) Application of an FTIR system for measurements of nitrous oxide fluxes using micrometeorological methods, an ultralarge chamber system, and convential field chambers. *Journal of Geophysical Research* 99 D8: 16,575-16,583.

Garrett, M.K., C.J. Watson, C. Jordan, R.W.J. Steen and R.V. Smith (1992) The nitrogen economy of grazed grassland. *Proceedings of the Fertiliser Society* No 326. The Fertiliser Society, Peterborough.

Genstat 5 Committee (1987) Genstat 5 reference manual. Oxford University Press, Oxford.

Gill, K., S.C. Jarvis and D.J. Hatch (1995) Mineralization of nitrogen in long-term pasture soils: effects of management. *Plant and Soil* 172: 153-162.

Goodroad, L.L. and D.R. Keeney (1984) Nitrous oxide production in aerobic soils under varying pH, temperature and water content. *Soil Biology and Biochemistry* 16: 39-43.

Goodroad, L.L. and D.R. Keeney (1985) Site of nitrous oxide production in field soils. *Biology and Fertility of Soils* 1: 3-7.

Granli, T. and O.C. Bøckman (1994) Nitrous oxide from agriculture. *Norwegian Journal of Agricultural Science*, Supplement 12, 128 pp.

Grant, R.F.M., M. Nyborg and W. Laidlaw (1993a) Evolution of nitrous oxide from soil: I. Model development. *Soil Science* 156: 259-265.

Grant, R.F.M., M. Nyborg and W. Laidlaw (1993b) Evolution of nitrous oxide from soil: II. Experimental results and model testing. *Soil Science* 156: 266-277.

Groffman, P.M. (1991) Ecology of nitrification and denitrification in soil evaluated at scales relevant to atmospheric chemistry. In: Microbial production and consumption of greenhouse gases: Methane, nitrogen oxides and halomethanes (eds J.E. Rogers and W.B. Whitman), pp. 201-217. American Society for Microbiology, Washinton, D.C.

Hansen, S. and L.R. Bakken (1993) N_2O, CO_2 and O_2 concentrations in soil air influenced by organic and inorganic fertilizers and soil compaction. *Norwegian Journal of Agricultural Sciences* 7: 1-10.

Hassink, J. and J.J. Neeteson (1991) Effect of grassland management on the amounts of soil organic N and C. *Netherlands Journal of Agricultural Science* 39: 225-236.

Healy, R.W., R.G. Striegl, T.F. Russel, G.L. Hutchinson and G.P. Livingston (1996) Numerical evaluation of static-chamber measurements of soil-atmosphere gas exchange: identification of physical processes. *Soil Science Society of America Journal* 60: 740-747.

Heinemeyer, O., M. Kücke, K. Kohrs, E. Schnug, J.C. Munch and E.A. Kaiser (1996) Nitrous oxide release from cultivated soils: Influence of different grass/clover ratios in fodder production. In: Transactions of the 9th Nitrogen Workshop, Braunschweig September 1996, pp. 495-497. Technische Universität Braunschweig.

Houba, V.J.G., I. Novozamsky and J.J. Van der Lee (1989) Some determinations of nitrogen fractions in soil extracts, *VDLUFA-Schriftenreihe* 30, 305-312.

Houghton, J.T., L.G. Meiro Filho, B.A. Callander, N. Harris, A. Kattenberg and K. Maskell (1996) Climate Change 1995: The Science of Climate Change. Contribution of Working Group I to the Second Assessment Report of the Intergovernmental Panel on Climate Change.

Huijsmans, J.F.M., J.M.G. Hol and D.W. Bussink (1996) Reduction of ammonia emission by new slurry application techniques. In: Proceedings of the International Conference on Nitrogen Emissions from Grasslands, Gaseous Transfers and their Interactions, IGER, North Wyke, Okehampton, May 1996 (in press).

Hutchinson, G.L. and G.P. Livingston (1993) Use of chamber systems to measure trace gas fluxes. In: Agricultural ecosystem effects on trace gases and global climate change, ASA Special Publication Number 55 (eds L.A. Harper, A.R. Mosier, J.M. Duxbury and D.E. Rolston), pp. 63-78, ASA, CSSA and SSSA, Madison.

Hutchinson, G.L. and A.R. Mosier (1981) Improved soil cover method for field measurement of nitrous oxide fluxes. *Soil Science Society of America Journal* 45: 311-316.

Jarvis, S.C. (1993) Nitrogen cycling and losses from dairy farms. *Soil Use and Management* 3: 99-105.

Jarvis S.C., D.J. Hatch, B.F. Pain and J.V. Klarenbeek (1994) Denitrification and the evolution of nitrous oxide after the application of cattle slurry to a peat soil. *Plant and Soil* 166: 231-241.

Jordan, C. (1989) The effect of fertiliser type and application rate on denitrification losses from cut grassland in Northern Ireland. *Fertilizer Research* 19: 45-55.

Jury, W.A., J. Letey and T. Collins (1982) Analysis of chamber methods used for measuring nitrous oxide production in the field. *Soil Science Society of America Journal* 46: 250-256.

Kaspar, H.F. and J.M. Tiedje (1981) Dissimilatory reduction of nitrate and nitrite in the bovine rumen: Nitrous oxide production and effect of acetylene. *Applied Environmental Microbiology* 41: 705-709.

Keeney, D.R., I.R. Fillery and G.P. Marx (1979) Effect of temperature on the gaseous nitrogen products of denitrification in a silt loam soil. *Soil Science Society of America Journal* 43: 1124-1128.

Kester, R.A., M.E. Meijer, J.A. Libochant, W. De Boer and H.J. Laanbroek (1996) The contribution of nitrification and denitrification to the NO and N_2O emission of an acid forest soil, a river sediment and a fertilized grassland soil. *Soil Biology and Biochemistry* (submitted)

Khalil, M.A.K. and R.A. Rasmussen (1992) The global sources of nitrous oxide. *Journal of Geophysical Research* 97: 14,651-14,660.

Kirkham, F. W. and R.J. Wilkins (1993) Seasonal fluctuations in the mineral nitrogen content of an undrained wetland peat soil following different rates of fertiliser nitrogen application. *Agriculture, Ecosystems and Environment* 43: 11-29.

Kliewer, B.A. and J.W. Gilliam (1995) Water table management effects on denitrification and nitrous oxide evolution. *Soil Science Society of America Journal* 59: 1694-1701.

Koch, G.S. and R.F. Link (1970) Statistical analysis of geological data, John Wiley and Sons, New York.

Koops, J.G., O. Oenema and M.L. Van Beusichem (1996a) Denitrification in the top and sub soil of grassland on peat soils. *Plant and Soil* 184: 1-10.

Koops, J.G., M.L. Van Beusichem and O. Oenema (1996b) Nitrogen loss from grassland on peat soils through nitrous oxide production. *Plant and Soil* (In press).

Korevaar, H. (1992) The nitrogen balance on intensive Dutch Dairy farms: a review. *Livestock Production Science* 31: 17-27.

Kroeze, C. (1994) Nitrous oxide (N_2O) emission inventory and options for control in The Netherlands. Report nr. 773001004, National Institute of Public Health and Environmental Protection, Bilthoven, 163 pp.

Langeveld, C.A. and P.A. Leffelaar (1996) Modelling nitrous oxide emission from soils: a tool for exploring emission reduction strategies. In: Climate Change Research: Evaluation and Policy Implications (eds S. Zwerver, R.S.A.R. van Rompaey, M.T.J. Kok and M.M. Berk), pp. 619-622. Elsevier Science B.V., Amsterdam.

Lantinga, E.A., J.A. Keuning, J. Groenwold and P.J.A.G. Deenen (1987) Distribution of excreted nitrogen by grazing cattle and its effects on sward quality, herbage

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production and utilization. In: Animal manures on grassland and fodder crops (eds H.G. Van der Meer *et al.*), pp. 103-117. Martinus Nijhoff Publishers, Dordrecht.

Lilliefors, H.W. (1967) On the Kolomogorov-Smirnov test for normality with mean and variance unknown. *Journal of the American Statistical Association* 62: 399-402.

Loftfield, N.S., R. Brumme and F. Beese (1992) Automated monitoring of nitrous oxide and carbon dioxide flux from forest soils. *Soil Science Society of America Journal* 56: 1147-1150.

MacDuff, J.H. and R.E. White (1985) Net mineralization and nitrification rates in a clay soil measured and predicted in permanent grassland from soil temperature and moisture content. *Plant and Soil* 86: 151-172.

Matthias, A.D., A.M. Blackmer and J.M. Bremner (1980) A simple chamber technique for field measurement of emissions of nitrous oxide from soils. *Journal of Environmental Quality* 9: 251-256.

Matthias, A.D., J.F. Artiola and S.A. Musil (1993) Preliminary study of N_2O flux over irrigated bermudagrass in a desert environment. *Agricultural and Forest Meteorology* 64: 29-45.

Martikainen, P.J., H. Nykänen, P. Crill and J. Silvola (1993) Effect of a lowered water table on nitrous oxide fluxes from northern peatlands, *Nature* London 366: 51-53.

McBratney, A.B. and R. Webster (1983) How many observations are needed for regional estimation of soil properties? *Soil Science* 135: 177-183.

McElroy, M.B. and D.B.A. Jones (1996) Evidence for an additional source of atmospheric N_2O. *Global Biogeochemical Cycles* 10, 651-659.

McTaggart, I., H. Clayton and K.A. Smith (1994) Nitrous oxide flux from fertilised grassland: strategies for reducing emissions. In: Non-CO_2 Greenhouse Gases Why and How to Control, (eds Van Ham, J. *et al.*), pp. 421-426. Kluwer Academic Publishers, Dordrecht.

Meeuwissen, P.C. (1993) Backgrounds of the evaluation ammonia policy. *Meststoffen 1993*: 28-33.

Monaghan, R.M. and D. Barraclough (1992) Some chemical and physical factors affecting the rate and dynamics of nitrification in urine-affected soil. *Plant and Soil* 143: 11-18.

Monaghan, R.M. and D. Barraclough (1993) Nitrous oxide and dinitrogen emissions from urine-affected soil under controlled conditions. *Plant and Soil* 151: 127-138.

Mosier, A.R. (1989) Chamber and isotope techniques. In: Exchange of trace gases between terrestrial ecosystems and the atmosphere (eds M.O. Andreae and D.S. Schimel), pp. 175-187. John Wiley and Sons, Chichester.

Mosier, A.R. (1994) Nitrous oxide emissions from agricultural soils. *Fertilizer Research* 37: 191-200.

Mosier, A.R. and G.L. Hutchinson (1981) Nitrous oxide emissions from cropped fields.

Journal of Environmental Quality 10: 169-173.

Mosier, A.R., W.J. Parton and G.L. Hutchinson (1983) Modelling nitrous oxide evolution from cropped and native soils. _Environmental Biogeochemistry, Ecological Bulletin_ (Stockholm) 35: 229-241.

Mosier, A.R., J.M. Duxbury, J.R. Freney, O. Heinemeyer and K. Minami (1996) Nitrous oxide emissions from agricultural fields: Assessment, measurement and mitigation. _Plant and Soil_ 181: 95-108.

Myers, R.A. and P. Pepin (1990) The robustness of lognormal-based estimators of abundance, _Biometrics_ 46: 1185-1192.

Naeth, M. A., D.J. Pluth, D.S. Chanasyk, A.W. Bailey and A.W. Fedkenheuer (1990) Soil compacting impacts of grazing in mixed prairie and fescue grassland ecosystems of Alberta. _Canadian Journal of Soil Science_ 70: 157-167.

Nykänen H., J. Alm, K. Lång, J. Silvola and P.J. Martikainen (1995) Emissions of CH_4, N_2O and CO_2 from a virgin fen and a fen drained for grassland in Finland. _Journal of Biogeography_ 22: 351-357.

Oenema, O. and G.L. Velthof (1993) Denitrification in nitric-acid-treated cattle slurry during storage. _Netherlands Journal of Agricultural Science_ 41: 63-80.

Oenema, O., G.L. Velthof and D.W. Bussink (1993) Emissions of ammonia, nitrous oxide and methane from cattle slurry. In: Biogeochemistry of Global Change, Radiatively Active Trace Gases (ed R.S. Oremland), pp. 419-433. Chapman & Hall, New York-London.

Parkin, T. B., J.L. Starr and J.J. Meisinger (1987) Influence of sample size on measurement of soil denitrification. _Soil Science Society of America Journal_ 51:, 1492-1501.

Parkin, T.B., J.J. Meisinger, S.T. Chester, J.L. Starr and J.A. Robinson (1988) Evaluation of statistical estimation methods for lognormally distributed variables. _Soil Science Society of America Journal_ 52: 323-329.

Parkin, T. B. and J.A. Robinson J. A. (1992) Analysis of lognormal data. _Advances in Soil Science_ 20: 193-235.

Parkin, T.B., A.J. Sextone and J.M. Tiedje (1985) Comparison of field denitrification rates determined by acetylene-based soil core and nitrogen-15 methods. _Soil Science Society of America Journal_ 49: 94-99.

Parton, W.J., A.R. Mosier and D.S. Schimel (1988) Rates and pathways of nitrous oxide production in a shortgrass steppe. _Biogeochemistry_ 6: 45-58.

Prather, M., R. Derwent, D. Ehhalt, P. Fraser, E. Sanhueza and X. Zhou (1995) Other trace gases and atmospheric chemistry. In: Climate Change 1994 (eds J.T. Houghton, L.G. Meira Filho, J. Bruce, H. Lee, B.A. Callander, E. Haites, N. Harris and K. Maskell, pp. 73-126, Cambridge University Press.

Prins, W.H. (1980) Changes in quantity of mineral nitrogen in three grassland soils as affected by intensity of nitrogen fertilization. _Fertilizer Research_ 1: 51-63.

Prins, W.H. (1983) Effect of a wide range of nitrogen applications on herbage nitrate content in long-term fertilizer trials on all-grass swards. *Fertilizer Research* 4: 101-113.

Robertson, G. P., M.A. Huston, F.C. Evans and J.M. Tiedje (1988) Spatial variability in a successional plant community: patterns of nitrogen availability. *Ecology* 69: 1517-1524.

Rolston, D.E. (1990) Modeling of denitrification: Approaches, successes and problems. *Mitteilungen der Deutschen Bodenkundlichen Gesellschaft* 60: 397-402.

Ruz-Jerez, B.E., R.E. White and P.R. Ball (1994) Long-term mesurement of denitrification in three contrasting pastures grazed by sheep. *Soil Biology and Biochemistry* 26: 29-39.

Ryden, J.C. (1983) Denitrification loss from a grassland soil in the field receiving different rates of nitrogen as ammonium nitrate. *Journal of Soil Science* 34: 355-365.

Ryden, J.C. (1984) The flow of nitrogen in grassland. *Proceedings of the Fertiliser Society* No 229 The Fertiliser Society, London.

Ryden, J.C. (1986) Gaseous losses of nitrogen from grassland. In: Nitrogen fluxes in intensive grassland systems, Developments in Plant and Soil Sciences, Volume 23 (eds H.G. van der Meer *et al.*), pp. 59-73. Martinus Nijhoff Publishers, Dordrecht.

Ryden, J.C. and K.P. Dawson (1982) Evaluation of the acetylene-inhibition technique for the measurement of denitrification in grassland soils. *Journal Science Food and Agriculture* 33: 1197-1206.

Ryden, J.C., P.R. Ball and E.A. Garwood (1984) Nitrate leaching from grassland. *Nature* 311: 50-53.

SAS Institute (1985) SAS User's Guide: Statistics. 5th ed. SAS Institute, Cary.

Scholefield, D., D.R. Lockyer, D.C. Whitehead and K.C. Tyson (1991) A model to predict transformations and emissions of nitrogen in UK pastures grazed by beef cattle. *Plant and Soil* 132: 165-177.

Sherlock, R.R. and K.M. Goh (1983) Initial emission of nitrous oxide from sheep urine applied to pasture soil. *Soil Biology and Biochemistry* 15, 615-617.

Skiba, U., K.A. Smith and D. Fowler (1993) Nitrification and denitrification as sources of nitric oxide and nitrous oxide in a sandy loam soil. *Soil Biology and Biochemistry* 25: 1527-1536.

Smith, K.A., H. Clayton, J.R.M. Arah, S. Christensen, P. Ambus, D. Fowler, K.J. Hargreaves, U. Skiba, G.W. Harris, F.G. Wienhold, L. Klemedtsson and B. Galle (1994) Micrometeorological and chamber methods for measurement of nitrous oxide fluxes between soils and the atmosphere: Overview and conclusions. *Journal of Geophysical Research* 99: D8 16,541-16,548.

Smith, M.S. and J.M. Tiedje (1979) The effects of roots on soil denitrification. *Soil Science Society of America Journal* 43: 951-955.

Snedecor G. W. and W.G. Cochran (1989) Statistical Methods, 8th Ed. Iowa. State University Press, Ames.

Spoelstra, S.F. (1985) Nitrate in silage. *Grass and Forage Science* 40: 1-11.

Spoelstra, H. (1995) N₂O emissions from combustion processes. In: Climate Change Research: Evaluation and Policy Implications (eds S. Zwerver, R.S.A.R. van Rompaey, M.T.J Kok and M.M. Berk), pp. 639-642. Elsevier, Amsterdam.

Stanford, G., M.H. Frere and D.H. Schwaninger (1973) Temperature coefficient of soil nitrogen mineralization. *Soil Science* 115: 321-323.

Steur, G.G.L., F. de Vries and C. van Wallenburg (1985) Soil map of the Netherlands 1 : 250.000. Stichting Bodemkartering Stiboka, Wageningen (In Dutch).

Tiedje, J.M., S. Simkins and P.M. Groffman (1989) Perspectives on measurement of denitrification in the field including recommended protocols for acetylene based methods. *Plant and Soil* 115: 261-284.

Van Burg, P.F.J., M.L. 't Hart and H. Thomas (1980) Nitrogen and grassland - past and present situation in the Netherlands. In: The role of nitrogen in intensive grassland production (eds W.H. Prins and G.H. Arnold), pp. 15 - 33. Centre for Agricultural Publishing and Documentation, Wageningen.

Van Burg, P.F.J., K. Dilz and W.H. Prins (1982) Agricultural value of various nitrogen fertilizers, results of research in the Netherlands and elsewhere in Europe. *Netherlands Nitrogen Technical Bulletin* 13. LBNM, The Hague.

Van Cleemput, O. and A.H. Samater (1996) Nitrite in soils: accumulation and role in the formation of gaseous N compounds. *Fertilizer Research* 45: 81-89.

Van Dasselaar, A. and R. Pothoven (1994) Energy use in agriculture in the Netherlands: Comparison of different fertilization strategies, NMI, Wageningen, 85 pp. (In Dutch).

Van den Pol-van Dasselaar, A., M.L. van Beusichem and O. Oenema (1997) Effects of grassland management on the emission of methane from intensively managed grasslands on peat soil. *Plant and Soil* (In press).

Van Enckevort, P.L.A. (1988) Nitrification inhibitors and nitrate leaching after application of animal manure IV. Summary of parts I, II and III and suggestions for further research. Institute for Soil Fertility Research, report 194 (In Dutch).

Van der Meer, H.G. (1991) Nitrogen budgets In: Efficiency and losses of nitrogen in grassland and maize land (ed H.G. Van der Meer) *Onderzoek inzake de mest- en ammoniakproblematiek in de veehouderij* 10, pp. 5-12 (In Dutch).

Van Kessel, C., D.J. Pennock and R.E. Farrell (1993) Seasonal variations in denitrification and nitrous oxide evolution at the landscape scale. *Soil Science Society of America Journal* 57: 988-995.

Vellinga Th. V., A.P. Wouters and R.G.M. Hofstede (1996) System of Adjusted Nitrogen Supply (SANS) for fertilization of grassland. In: Progress in nitrogen cycling studies. Proceedings of the 8th nitrogen workshop in Ghent, 5-8

September 1994. Developments in plant and soil sciences 68 (eds O. van Cleemput, G. Hofman and A. Vermoesen), pp. 381-385. Kluwer Academic Publishers, Dordrecht.

Velthof, G.L., O. Oenema, J. Postmus and W.H. Prins (1990) In-situ measurements of ammonia volatilization from urea and calcium ammonium nitrate applied to grassland. *Meststoffen 1/2 1990*: 41-45.

Velthof, G.L. and O. Oenema (1993) Nitrous oxide flux from nitric-acid-treated cattle slurry applied to grassland under semi-controlled conditions. *Netherlands Journal of Agricultural Science* 41: 81-94.

Velthof, G.L. and O. Oenema (1995a) Nitrous oxide fluxes from grassland in the Netherlands: I. Statistical analysis of flux chamber measurements. *European Journal of Soil Science* 46: 533-540.

Velthof, G.L. and O. Oenema (1995b) Nitrous oxide fluxes from grassland in the Netherlands: II. Effects of soil type, nitrogen fertilizer application and grazing. *European Journal of Soil Science* 46: 541-549.

Velthof, G.L., A.B. Brader and O. Oenema (1996a) Seasonal variations in nitrous oxide losses from managed grasslands in the Netherlands. *Plant and Soil* 181: 263-274

Velthof, G.L., S.C. Jarvis, A. Stein, A.G. Allen and O. Oenema (1996b) Spatial variability of nitrous oxide fluxes in mown and grazed grasslands on a poorly drained clay. *Soil Biology and Biochemistry* 28: 1215-1225.

Velthof, G.L., O. Oenema, R. Postma and M.L. Van Beusichem (1997) Effect of type and amount of applied nitrogen fertilizer on nitrous oxide fluxes from intensively managed grassland. *Nutrient Cycling in Agroecosystems* 46: 257-267.

Wang, W., Y. Lacis, T. Mo and J. Hansen (1976) Greenhouse effects due to man made perturbations of trace gases. *Science* 194: 685-690.

Warren, S.D., M.B. Nevill, W.H. Blackburn and N.E. Garza (1986) Soil response to trampling under intensive rotation grazing. *Soil Science Society of Amercia Journal* 50: 1336-1341.

Watson, C.J. (1986) Preferential uptake of ammonium nitrogen from soil by ryegrass under simulated spring conditions. *Journal of Agricultural Science Cambridge* 107: 171-177.

Watson, C. J., C. Jordan, P.J. Taggart, A.S. Laidlaw, M.K. Garret and R.W.J. Steen (1992) The leaky N-cycle on grazed grassland. In: Nitrate and Farming systems, Aspects of Applied Biology 30. (ed J.R. Archer *et al.*), pp. 215-222. Association of Applied Biologists, Warwick.

Webster, C.P. and R.J. Dowdell (1982) Nitrous oxide emission from permanent grass swards. *Journal of Science Food and Agriculture* 33: 227-230.

Webster, R. (1985) Quantitative spatial analysis of soil in the field. *Advances in Soil Science* 3: 1-70.

White, R.E., R.A. Haigh and J.H. Macduff (1987) Frequency distributions and spatially

dependent variability of ammonium and nitrate concentration in soil under grazed and ungrazed grassland. _Fertilizer Research_ 11: 193-208.

Whitehead, D.C., A.W. Bristow and D.R. Lockyer (1990) Organic matter and nitrogen in the unharvested fractions of grass swards in relation to the potential for nitrate leaching after ploughing. _Plant and Soil_ 123: 39-49.

Williams, B.L. and R.E. Wheatley (1988) Nitrogen mineralization and water-table height in oligotrophic deep peat. _Biology and Fertility of Soils_ 20: 141-147.

Wouters, A.P. and Th.V. Vellinga (1994) Development of System of Adjusted Nitrogen Supply (SANS) for grassland, Workshop Proceedings of the 15th General Meeting of the European Grassland Federation Wageningen, The Netherlands, 6-9 June 1994, Netherlands Society for Grassland and Fodder Crops, pp. 258-262.

Yamulki, S. and S.C. Jarvis (1996) Nitrous oxide emissions from excreta from simulated grazing pattern and fertilizer application to grassland. In: Proceedings international conference on Nitrogen emissions from grasslands, Gaseous transfers and their interactions, May 1996, IGER, North Wyke, Devon UK (in press).

Summary

Introduction

The concentration of nitrous oxide (N_2O) in the atmosphere is at present about 310 $\mu l \ m^{-3}$, and is increasing with about 0.25% per year. This increase is of concern, because N_2O is involved both in the enhanced greenhouse effect and the destruction of stratospheric ozone. The enhanced greenhouse effect may lead to an increase of the temperature on earth. Destruction of stratospheric ozone may result in an increased ultraviolet radiation of sunlight onto the earth, thereby increasing the risk on skin cancer. There are many uncertainties in the causes of the increase of the atmospheric N_2O. Possible sources and sinks of N_2O on earth and in the atmosphere are badly identified and weakly quantified. A good insight into the processes producing N_2O and an accurate quantification of the sources and sinks of N_2O are needed to set-up efficient strategies to diminish the increase in the atmospheric N_2O concentration.

The microbiological processes nitrification (oxidation of ammonium to nitrate) and denitrification (reduction of nitrate to the gaseous compounds N_2 and N_2O) in soil are probably the major sources of N_2O. Relatively largest amounts of N_2O are produced in soils when mineral nitrogen (N) content is high and O_2 concentration is low. Interactions between soil, plants, and weather conditions strongly control the N_2O emission from soils.

About 25% of the total area of the Netherlands is used as intensively managed grassland. The N input to these grasslands via animal manure, mineral N fertilizer and excretion of urine and dung during grazing is large. Because of the relatively large area and the large N input, intensively managed grasslands represent a potentially large source of N_2O in the Netherlands. The major aims of this study are to increase the insight into the major factors controlling N_2O emission from intensively managed grasslands, to quantify the N_2O emission from intensively managed grasslands in the Netherlands, and to explore the possibilities to reduce N_2O emission from these grasslands.

Set-up of the study

The study was part of the integrated project 'N$_2$O emissions from grassland'. The

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focus of the present study was predominantly on field measurements. The N_2O emission was measured in the field using flux chambers (enclosures of 300 cm^2 and 15 cm high, in which the N_2O emitted from the soil surface is collected). The concentration of N_2O in the headspace of the flux chambers was measured using a photo-acoustic infra-red gas analyzer (Chapter 2).

A major part of the work consisted of monitoring studies, in which N_2O fluxes were measured weekly during two years on four grassland sites in the Netherlands, each with three management types. The grassland sites were situated on a sandy soil in Heino, a clay soil in Lelystad and two peat soils with different groundwater level in Zegveld. On all sites, N_2O fluxes were measured weekly in six replicates during a 2-year period from unfertilized + mown, N fertilized + mown and N fertilized + grazed grasslands (Chapters 2, 3, and 4). The applied N fertilizer was calcium ammonium nitrate (CAN), the most commonly used N fertilizer in the Netherlands. Emission factors[1] of N_2O were derived from these monitoring studies, for grassland with different types of management and on different soil types. Other field experiments mainly focused on the controlling soil factors and the effects of type and application rate of N fertilizer on the N_2O emission from grassland (Chapters 5, 6, and 7).

Factors controlling N_2O emission from grasland

Climate
Rainfall and temperature affect biological and physical soil processes in soils, and are identified as major factors controlling N_2O emission from soils. The stimulating effects of rainfall on N_2O fluxes were clearly demonstrated; largest fluxes were found during wet soil conditions (Chapters 3, 4, and 7). Temperature and N_2O flux were weakly correlated (Chapters 3 and 5), probably because temperature is negatively correlated with soil moisture and because a possible effect of temperature on N_2O flux was interrelated with grassland management.

Grassland management
Fluxes of N_2O typically increased after N fertilizer application, reaching a

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[1]Emission factors represent the amounts of N_2O-N that is produced per ha or per kg N of fertilizer, cattle slurry, urine etc. Emission factors can be used to quantify N_2O emission on regional, national, or a global scale.

maximum within 2 to 5 days and then gradually decreased within 1 to 4 weeks to levels similar to unfertilized grassland (Chapters 3, 4, and 7). A similar pattern was found for mineral N contents in the soil following N fertilizer application, indicating the key role of mineral N as a source of N_2O from grassland soil. During wet conditions, emission of N_2O from nitrate fertilizers was much larger than from ammonium fertilizers (Chapter 7).

Emissions of N_2O from cattle slurry were smaller than from CAN under wet conditions, per unit N applied (Chapter 7). Possible long-term effects of cattle slurry application on N_2O fluxes were not assessed and, therefore, accurate emission factors for cattle slurry cannot be presented here.

Emission of N_2O was much larger from grazed grassland than from mown grassland (Chapters 3 and 4). Grazing affects the emission of N_2O in three distinct ways: via urine patches, via dung patches and via treading and trampling. Both urine and dung patches are considerable sources of N_2O, due to the high contents of mineral N and easily mineralizable organic carbon in these patches. Mineral N contents were higher in grazed than in mown grasslands (Chapters 3 and 4).

Soil factors
Contents of mineral N and moisture were major factors controlling the N_2O emission from grasslands (Chapters 3 and 4). Higher organic carbon contents contributed to the higher N_2O emissions from peat soils than from mineral soils. Under anaerobic conditions and in the presence of nitrate, the high organic carbon contents in the peat soils also resulted in a high denitrification activity (Chapter 3). Further, high groundwater levels in the peat soils also contributed to the high N_2O emission from the peat soils. High groundwater levels coincide with low O_2 concentrations in the soil, thus promoting conditions for N_2O production. The peat soil with the highest groundwater level was water-logged during 3 to 5 months per year (Chapters 3 and 4). Under these conditions, mineralization of organic carbon, nitrification, and N_2O production through denitrification are hampered. The difference in groundwater level was probably the major factor causing the large difference in N_2O emission between the two peat soils.

Quantification of N_2O emission

Intensively managed grasslands
Emission of N_2O from unfertilized and mown grasslands ranged from 0.5 to 1.2 kg

N per ha per year on mineral soils and from 1.8 to 12.9 kg N per ha per year on peat soils (Chapter 4). Application of CAN resulted in an increase of the N_2O emission. On average, 1.0% of the N applied on mineral soils and 3.0% on the peat soils was emitted as N_2O. The much larger N_2O emissions from the peat soils clearly indicate that different emission factors for peat soils and for mineral soils have to be used in N_2O budget calculations.

The grazing-derived N_2O emissions from the mineral soils and the peat soil with the relatively high groundwater level amounted on average 2.4% of the N excreted as urine and dung during grazing (Chapter 4). This was 9.8% for the peat soil with the relatively low groundwater level. These large emissions clearly indicate that the effect of grazing should be taken into account in N_2O budget calculations.

Dairy farming systems in the Netherlands
The field studies were focused on emission of N_2O from grassland (Chapters 2-7). There are also other possible sources of N_2O in dairy farming systems, such as housings, slurry storage basins, and fuel. Using model calculations, total N_2O emission was estimated, based on 14 possible sources of N_2O on dairy farming systems (Chapter 8). For these calculations, emission factors from our field studies and from different literature sources were derived.

The total emission of N_2O-N from dairy farming systems accounted for 3 to 5% of the N surplus on the farm level (the total N input via fertilizers, feed, etc. minus the total N output via milk and meat). The total N_2O emission from dairy farming systems in the Netherlands in 1994 was estimated at 13.7 ± 5.1 Gg N_2O-N yr^{-1}, from which 8.0 ± 4.3 Gg N_2O-N yr^{-1} was emitted from mineral soils and 5.7 ± 3.5 Gg N_2O-N yr^{-1} from peat soils (Chapter 8). According to these estimates, N_2O emission from dairy farming systems accounts for about 35% of the total N_2O emission in the Netherlands. This large percentage suggests that changes in N_2O emission from dairy farming systems will largely affect the total N_2O emission in the Netherlands.

Mitigation of N_2O-emission from grassland

N fertilizers
Considerable fluxes of N_2O were detected when the mineral N contents in the soil were high. Grassland management scenarios that aim at preventing high soil mineral

N contents for a prolonged period will lead to reduced N_2O emissions from grasslands. In this respect, a further refinement of N fertilizer recommendations will certainly result in a decrease of the N_2O emission from grassland.

During wet conditions, N_2O fluxes were much larger from nitrate-containing N fertilizer than from N fertilizers containing only ammonium. A fertilization strategy in which the choice of N fertilizer type is dependent on the soil moisture status in combination with the expected rainfall and evapotransipration during the next days, may be a cheap and effective tool to mitigate N_2O emission from grasslands. Nitrification inhibitors may further decrease N_2O emissions from ammonium-based fertilizers.

Grazing

When grazing is restricted, more slurry has to be collected in the housing and will be applied as fertilizer to grassland. The emission of N_2O per unit N applied as slurry is smaller than the grazing-derived N_2O emission. Therefore, restricted grazing may result in a decrease in N_2O emissions.

Drainage

The N_2O emission from the mineral soils was largest under wet conditions. Drainage of wet grasslands on mineral soils may, therefore, lead to a decrease in the N_2O emission. The lower N_2O emission from the peat soil with the relatively high groundwater level than from the peat soil with the relatively low groundwater level, suggests that peat soils with groundwater levels near the soil surface emit less N_2O than peat soils with deep groundwater levels.

Package of measures

The largest reduction in N_2O emission will be obtained when a combination of mitigation options is implemented. Factors controlling the compartmentation of N compounds between soil, plant, atmosphere, animal and excreta are very complex and seldom acting independently. Thorough quantitative understanding of the factors interacting in N cycling processes on dairy farming systems, including N_2O production/emission, is essential for a successful implementation. Moreover, the interactions between the emissions of N_2O and of other greenhouse gases should be considered as well. For example, increasing the groundwater level in peat soil may result in a lower N_2O emission, but in a higher emission of methane. Thus far, little attention has been given to the quantification of the effects of mitigation options on

N$_2$O emission from intensively managed grasslands and whole dairy farming systems. The model calculations in Chapter 8 indicate that N$_2$O emission from dairy farming systems may be considerably decreased by improved nutrient management.

Samenvatting

Inleiding

De concentratie van lachgas (N_2O) in de atmosfeer is thans ongeveer 310 µl m^{-3} en stijgt met ongeveer 0,25% per jaar. Deze stijging baart zorgen, omdat N_2O bijdraagt aan zowel het broeikaseffect als aan de afbraak van de ozonlaag in de stratosfeer. De versterking van het broeikaseffect leidt mogelijk tot een stijging van de temperatuur op aarde. Door de afbraak van ozon in de stratosfeer kan meer van het schadelijke ultraviolette zonlicht de aarde bereiken, waardoor onder andere het risico op huidkanker toeneemt. Er zijn nog veel onduidelijkheden over de oorzaken van de stijging van de atmosferische N_2O-concentratie. De mogelijke producerende en consumerende processen van N_2O op aarde zijn slechts globaal bekend en de grootte van de N_2O-fluxen is nog onvoldoende gekwantificeerd. Voor het opstellen van efficiënte maatregelen, om de stijging van de N_2O-concentratie in de atmosfeer te verminderen, is kennis van de processen waarin N_2O wordt geproduceerd of geconsumeerd én een goede kwantificering van deze processen noodzakelijk.

De microbiologische processen nitrificatie (omzetting van ammonium in nitraat) en denitrificatie (omzetting van nitraat in de gasvormige verbindingen N_2 en N_2O) in de bodem zijn waarschijnlijk de belangrijkste N_2O-bronnen. De hoeveelheid minerale stikstof (N) en het O_2-gehalte in de bodem spelen een sleutelrol bij de N_2O-productie tijdens deze processen. De productie is hoog bij een hoog gehalte aan minerale N en een laag O_2-gehalte. De N_2O-emissie wordt sterk bepaald door allerlei interacties tussen klimaat- en bodemfactoren.

Ongeveer 25% van het totale oppervlak van Nederland bestaat uit intensief beheerd grasland. De N-aanvoer naar deze graslanden via rundermest, kunstmest en via uitscheiding van urine en mest tijdens beweiding is groot. Het relatief grote oppervlak en de grote N-aanvoer maken de intensief beheerde graslanden in Nederland tot een mogelijk grote N_2O-bron. De belangrijkste doeleinden van deze studie waren het vergroten van de kennis over de factoren die de N_2O-emissie uit grasland bepalen, het kwantificeren van de N_2O-emissie uit intensief beheerd grasland in Nederland, en het bestuderen van de mogelijkheden om deze N_2O-emissie te verminderen.

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De opzet van het onderzoek

Het onderzoek maakte deel uit van een groot geïntegreerd project naar de N_2O-emissie uit grasland. De aandacht in de studie, die in dit proefschrift wordt beschreven, was vooral gericht op veldonderzoek. Voor het verkrijgen van de meest nauwkeurige schatting van de N_2O-emissie uit grasland zijn directe metingen van N_2O-emissies in het veld, gecombineerd met registratie van graslandbeheer, bodem- en klimaatfactoren nodig. In deze studie werd de N_2O-emissie in het veld gemeten met behulp van fluxkamers (afgesloten koepels van 300 cm^2 en 15 cm hoog, waarin de N_2O die uit de bodem ontwijkt wordt opgevangen). De N_2O-concentratie in de fluxkamers werd met een foto-akoestische infra-rood gasmonitor gemeten (Hoofdstuk 2).

Een belangrijk deel van het onderzoek bestond uit monitoringstudies op vier sterk verschillende graslandlocaties in Nederland: een zandgrond in Heino, een kalkrijke kleigrond in Lelystad en twee veengronden met verschillende grondwaterstand in Zegveld. Op elke locatie werd de N_2O-emissie uit onbemest + gemaaid, bemest + gemaaid en bemest + beweid grasland wekelijks in zesvoud gemeten gedurende twee jaren (Hoofdstukken 2, 3 en 4). Er was gekozen voor deze lange meetperiode om tot een nauwkeurige schatting te komen van de door bemesting en beweiding veroorzaakte N_2O-emissies. De N-bemesting vond plaats via kalkammonsalpeter (KAS), de meeste gebruikte N-kunstmest in Nederland. Uit de monitoringstudies werden N_2O-emissiefactoren[1] afgeleid voor grasland bij verschillende typen beheer en op verschillende bodemsoorten. Het overige veldonderzoek richtte zich voornamelijk op de rol van verschillende bodemfactoren (Hoofdstukken 5 en 6) en de effecten van verschillende meststoffen op de N_2O-emissie uit grasland (Hoofdstuk 7).

Factoren die de N_2O-emissie uit grasland bepalen

Klimaat
Regen en temperatuur beïnvloeden allerlei biologische en fysische processen in de

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[1] Een emissiefactor geeft de hoeveelheid N_2O-N aan die per ha of per kg N uit kunstmest, dierlijke mest, urine etc. wordt geproduceerd. Emissiefactoren worden gebruikt bij de kwantificering van de totale N_2O-emissie op regionaal, nationaal of mondiaal niveau.

bodem en daardoor ook de N_2O-emissie uit de bodem. Het effect van regen op de N_2O-emissie was duidelijk: de N_2O-emissie was het hoogst onder natte omstandigheden (Hoofdstukken 3, 4 en 7). Er werd geen duidelijk verband gevonden tussen de temperatuur en de N_2O-emissie. Een mogelijk temperatuurseffect op de N_2O-emissie werd waarschijnlijk gemaskeerd door de grote effecten van bemesting en beweiding op de N_2O-emissie. Daarnaast is de temperatuur vaak negatief gecorreleerd met het vochtgehalte; tijdens warme periodes is het vochtgehalte meestal laag en dus niet optimaal voor N_2O-productie.

Beheer van grasland

De emissie van N_2O nam na toediening van N-meststoffen sterk toe, bereikte binnen 2 tot 5 dagen een maximum en nam binnen 1 to 4 weken geleidelijk af tot een vergelijkbaar niveau als bij onbemest grasland (Hoofdstukken 3, 4 en 7). Een vergelijkbaar patroon werd gevonden bij de gehalten aan minerale N in de bodem, hetgeen aangeeft dat N een sleutelrol speelt bij de N_2O-emissie uit grasland. Emissies van N_2O onder natte omstandigheden waren veel hoger bij nitraathoudende meststoffen, inclusief KAS, dan bij ammoniumhoudende meststoffen (Hoofdstuk 7). Dit geeft aan dat denitrificatie een veel grotere N_2O-bron is tijdens natte omstandigheden dan nitrificatie.

De N_2O-emissie uit grasland na toediening van dunne rundermest was veel lager dan die na toediening van KAS per eenheid toegediende N tijdens natte omstandigheden. Een mogelijke effect van rundermest op de N_2O-emissie op langere termijn, veroorzaakt door mineralisatie van toegediende organische stof, is niet bestudeerd in deze studie. Deze kennis is wel noodzakelijk om tot een nauwkeurige schatting te komen van de door rundermest veroorzaakte N_2O-emissie.

De N_2O-emissie was veel hoger uit beweid grasland dan uit gemaaid grasland (Hoofdstukken 2, 3 en 6). In beweid grasland wordt de N_2O-emisssie sterk beïnvloed door (een combinatie van) drie factoren, namelijk i) urineplekken, ii) mestflatten en iii) betreding. In urineplekken en mestflatten wordt veel N_2O geproduceerd door de hoge gehalten aan minerale N en mineraliseerbare organische stof in deze plekken. De minerale N-gehalten in beweid grasland waren veel hoger dan in gemaaid grasland, vooral aan het eind van het groeiseizoen (Hoofdstukken 3 en 4).

Bodemfactoren

Minerale N en vocht waren belangrijke bodemfactoren die de N_2O-emissie uit

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grasland bepaalden (Hoofdstukken 3 en 4). Mineraliseerbare organische koolstof was een factor die bijdroeg aan de hogere N_2O-emissies uit veengronden dan uit minerale (zand- en klei-) gronden. De hoge gehalten aan mineraliseerbare organische koolstof in de veengronden leidden tot een hogere denitrificatieactiviteit onder zuurstofloze omstandigheden bij aanwezigheid van nitraat dan in minerale gronden (Hoofdstuk 3). Daarnaast werd de hoge N_2O-emissie uit de veengronden waarschijnlijk voor een deel veroorzaakt door de hoge grondwaterstand in deze gronden. Hoge grondwaterstanden leiden tot zuurstofarme omstandigheden, waardoor de productie van N_2O wordt bevorderd.

De veengrond met de hoogste grondwaterstand was gedurende 3 tot 5 maanden van het jaar volledig met water verzadigd (Hoofdstukken 3 en 4). Onder deze omstandigheden zijn de mineralisatie van organische koolstof, de nitrificatie en de N_2O-productie tijdens denitrificatie geremd. Dit is waarschijnlijk de oorzaak voor de lagere N_2O-emissies uit de veengrond met de hoge grondwaterstand vergeleken met die met de lagere grondwaterstand.

Kwantificering van de N_2O-emissie

Intensief beheerd grasland
De N_2O-emissie uit onbemest en gemaaid grasland varieerde van 0,5 tot 1,2 kg N per ha per jaar op de minerale gronden en van 1,8 tot 12,9 kg N per ha per jaar op de veengronden (Hoofdstuk 4). Bemesting met KAS verhoogde de N_2O-emissie. Op de minerale gronden werd 1,0% van de toegediende N geëmitteerd als N_2O (Hoofstuk 4). Op de veengronden was dit 3,0%. De hoge N_2O-emissie uit veengronden geeft aan dat de N_2O-emissie uit veengronden met een andere emissiefactor geschat moet worden dan de emissie uit minerale gronden.

Op de minerale gronden en de veengrond met de relatief hoge grondwaterstand werd 2,4% van de N, die als urine en mest was uitgescheiden tijdens beweiding, geëmitteerd als N_2O (Hoofdstuk 4). Dit was 9,8% op de veengrond met de relatief lage grondwaterstand. De hoge N_2O-emissie bij beweiding geeft aan dat de N_2O-emissie door beweiding niet mag worden verwaarloosd bij de kwantificering van de totale N_2O-emissie uit grasland.

Totale melkveehouderij in Nederland
Het veldonderzoek was gericht op de N_2O-emissie uit grasland (Hoofdstukken 2-7). In melkveehouderijen zijn nog andere N_2O-bronnen aanwezig, zoals de stal, de

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mestopslag en de verbranding van fossiele brandstoffen. In hoofdstuk 8 is met behulp van modelberekeningen de totale N_2O-emissie door de melkveehouderij in Nederland geschat. Hiertoe zijn veertien mogelijke N_2O-bronnen op melkveehouderijen geïdentificeerd. Er is in de modelberekeningen gebruik gemaakt van de emissiefactoren die uit het veldonderzoek en van zeer uiteenlopende literatuurgegevens zijn afgeleid.

De grootte van de totale N_2O-emissie uit melkveehouderijen vertegenwoordigde 3 tot 5% van het N-overschot op bedrijfsniveau (de N-aanvoer via kunstmest, kracht- en ruwvoer etc. minus de N-afvoer via melk en vlees). De totale N_2O-emissie door de melkveehouderij in Nederland werd geschat op 13,7 ± 5,1 Gg N_2O-N in 1994, waarvan 8,0 ± 4,3 Gg N_2O-N per jaar afkomstig was van melkveehouderijen op minerale gronden en 5,7 ± 3,5 Gg N_2O-N per jaar van bedrijven op veengronden (Hoofdstuk 8). De N_2O-emissie uit de melkveehouderij bedraagt ongeveer 35% van de totale N_2O-emissie in Nederland naar de atmosfeer. Veranderingen in de N_2O-emissie uit de melkveehouderij kunnen daarom mogelijk een groot effect hebben op de totale N_2O-emissie in Nederland.

Beperking van de N_2O-emissie uit grasland

Stikstofmeststoffen
Hoge N_2O-emissies traden op indien de minerale N-gehalten in de bodem hoog waren. Het voorkómen van hoge minerale N-gehalten in de bodem door het afstemmen van de N-bemesting op de N-behoefte van het gras is daarom een mogelijkheid om de N_2O-emissie uit grasland te beperken. Een verdere verfijning van het bemestingsadvies zal daarom leiden tot een vermindering van de N_2O-emissie uit grasland.

Nitraathoudende meststoffen veroorzaakten tijdens natte omstandigheden een veel hogere N_2O-emissie dan meststoffen die alleen ammonium bevatten. Een bemestingsstrategie waarin de keuze van het type meststof afhankelijk wordt gesteld van het vochtgehalte van de bodem en de verwachte neerslag en verdamping, is mogelijk een zeer effectieve maatregel om de N_2O-emissie uit grasland te verminderen. Het toedienen van nitrificatieremmers aan ammoniummeststoffen kan leiden tot een verdere vermindering van de N_2O-emissie.

Beweiding
Beperking van beweiding leidt tot een toeneming van de hoeveelheid rundermest

die in de stal wordt verzameld en aan het grasland wordt toegediend. De N_2O-emissie uit grasland waaraan rundermest is toegediend, is lager dan de N_2O-emissie uit beweid grasland, uitgedrukt in kg N_2O-N per kg toegediende of uitgescheiden N. Beperking van beweiding zal daarom leiden tot een vermindering van de N_2O-emissie.

Drainage

De N_2O-emissie uit minerale gronden was het hoogst tijdens natte perioden. Drainage van natte graslanden op deze gronden kan de N_2O-emissie beperken. In veengrond zal verhoging van de grondwaterstand tot nabij het maaiveld leiden tot een vermindering van de N_2O-emissie.

Combinatie van maatregelen

De grootste vermindering in N_2O-emissie zal worden verkregen indien een combinatie van maatregelen wordt toegepast. Bij het opzetten van combinaties van maatregelen is een goed inzicht in de vele interacties tussen de verschillende stofstromen op een melkveehouderij noodzakelijk. Een maatregel, die de emissie van een bepaalde verbinding vermindert, kan de emissie van een andere verbinding doen toenemen. Bijvoorbeeld, verhoging van de grondwaterstand in veengrond zal leiden tot een vermindering in de N_2O-emissie, maar tot een verhoging van de emissie van methaan, een ander belangrijk broeikasgas. Er is tot nu toe weinig aandacht besteed aan de effecten van maatregelen op de N_2O-emissie uit de melkveehouderij op bedrijfsniveau. Modelberekeningen uit hoofdstuk 8 laten zien dat door een verbeterd nutriëntenmanagement op melkveehouderijen, de N_2O-emissie aanzienlijk kan worden verminderd.

Curriculum vitae

Gerard (Gerardus Lambertus) Velthof werd geboren op 5 juli 1964 te Elsloo (L). In 1982 behaalde hij het VWO-diploma aan de scholengemeenschap Groenewald te Stein. Vervolgens begon hij de studie Bodemkunde aan de Landbouwuniversiteit te Wageningen. Zijn praktijktijd van een half jaar bracht hij door in Sri Lanka aan het FAO Fertilizer Project for Small Farmers in Peradeniya en aan het Iron Toxicity and Soil Fertility Project in Kandy. In 1988 rondde hij zijn studie af met de afstudeervakken Bodemvruchtbaarheid & Bemesting en Microbiologie.

In 1989 kwam hij in dienst als onderzoeker bij het toenmalige Nederlands Meststoffen Instituut (NMI), het huidige Nutriënten Management Instituut. In de periode 1989-1992 was hij gedetacheerd bij het Instituut voor Bodemvruchtbaarheid te Haren en sinds eind 1992 bij de vakgroep Bodemkunde en Plantenvoeding van de Landbouwuniversiteit te Wageningen. Tussen maart 1992 en maart 1995 werkte hij aan het project 'Effecten van stikstofbemesting en beweiding op de lachgasemissie uit grasland'. Het onderzoek dat in het kader van dit project werd verricht, heeft geleid tot dit proefschrift. Zijn huidige werkzaamheden bestaan uit onderzoek op het gebied van bemesting, nutriëntenmanagement en gasvormige stikstofverliezen, op zowel grasland als bouwland.