

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

G.L. VELTHOF^{1*}, J.G. KOOPS¹, J.H. DUYZER² AND O. OENEMA¹

¹ NMI, Department of Soil Science and Plant Nutrition, Wageningen Agricultural University, P.O. Box 8005, NL 6700 EC Wageningen, The Netherlands

² TNO, Institute of Environmental Sciences, P.O. Box 6011, NL 2600 JA Delft, The Netherlands

* Corresponding author (fax: +31-317-483766; e-mail: gerard.velthof@nmi.benp.wau.nl)

Received 2 July 1996; accepted 13 October 1996

Abstract

Three measurement campaigns were carried out to answer questions related to the factors controlling variations in nitrous oxide (N₂O) 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 N₂O fluxes from intensively managed grassland on peat soils. Fluxes of N₂O 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 (NO₃) and ammonium (NH₄⁺) in the top soil and the water-filled pore space (WFPS) explained 37–77% of the variance in N₂O flux. Spatial variability of N₂O 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 N₂O 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 N₂O fluxes from similar sites.

Keywords: denitrification, empirical model, flux chamber technique, flux gradient technique, grassland, nitrous oxide, peat soil

Introduction

Total annual N₂O emissions from soils can be quantified by field measurements of N₂O fluxes, but due to the very large spatial and temporal variability in these fluxes,

intensive sampling is required (e.g. Ambus & Christensen, 1995; Flessa *et al.*, 1995; Velthof *et al.*, 1996a, b). Estimates of N₂O emissions can also be obtained using models. Mechanistic models that simulate the basic processes involved in N₂O 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 N₂O (eg. 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 N₂O fluxes at a certain site are mainly related to variations in moisture content and in the amounts of nitrate (NO₃⁻) and ammonium (NH₄⁺) 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 N₂O fluxes from intensively managed grassland on peat soils in the Netherlands. Cultivated peat soils are a major source of N₂O (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 N₂O 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 N₂O fluxes from managed grassland on peat soil and which can be easily manipulated by grassland management. In soil, N₂O 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 N₂O flux at the field scale are contents of moisture, NO₃⁻, NH₄⁺ and mineralizable C. It is suggested that microsites contents of these variables do better explain N₂O 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 cm²), from which two 9 cm² soil cores from the top soil were taken for analyses of soil variables. We considered the top soil as most important in the control of N₂O 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 the sub soil (Velthof & Oenema, 1995b), (ii) contents of mineral N in this layer are generally much higher than in the sub soil, 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 N₂O production during nitrification and denitrification. To provide more insight into the microbial processes involved in the production of N₂O 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 & 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 & Kjær photo-acoustic spectroscopic infra-red gas analyzers and multi-sampler, as described in detail by Velthof & 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 N₂O fluxes. In September, 48 flux chambers were placed at 1 m intervals in a grid of 4×12; in November, 42 flux chambers were placed at 1 m intervals in a grid of 6×7. These sampling schemes were chosen to assess the random variation of N₂O fluxes from the grazed grassland. It was expected that the random variation of N₂O 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, N₂O fluxes were measured continuously during a period of two days to compare the results of the flux chamber 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 N₂O 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 N₂O 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 7% 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 $\mu g N m^{-2} hr^{-1}$ 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 (Anonymous, 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 log-normal 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 & 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 & 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).

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

MODELLING NITROUS OXIDE FLUXES FROM GRASSLAND ON PEAT SOIL

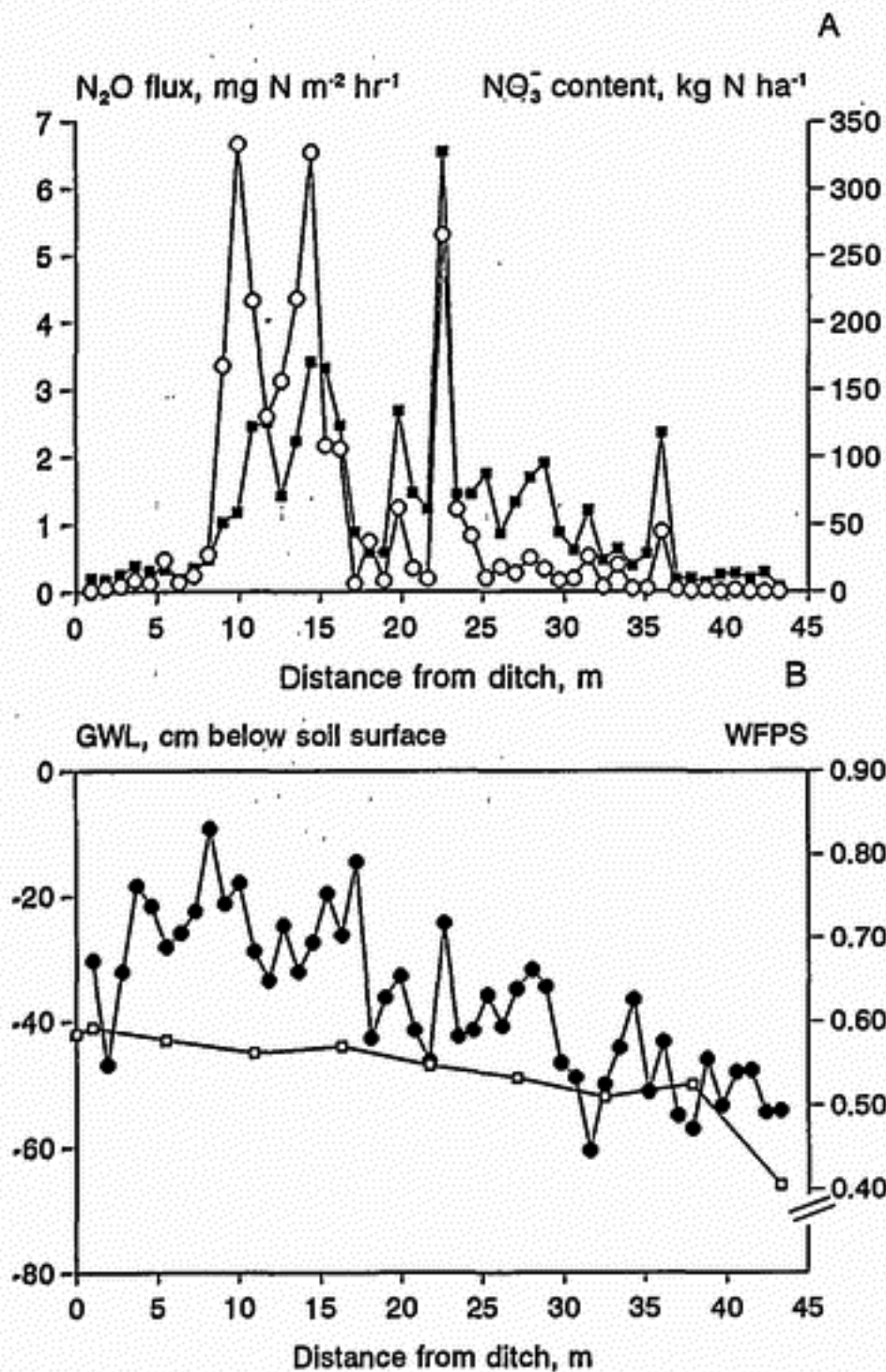


Figure 1. Spatial variability of N_2O flux (○) and NO_3^- content (■) in Figure A and groundwater level (GWL: □) and water-filled pore space (WFPS: ●) in Figure B, in grassland on a peat soil in June 1993.

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).

Table 2. Best multiple regression models with logtransformed N_2O flux in $\mu g N m^{-2} hr^{-1}$ 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 $kg N ha^{-1}$

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).

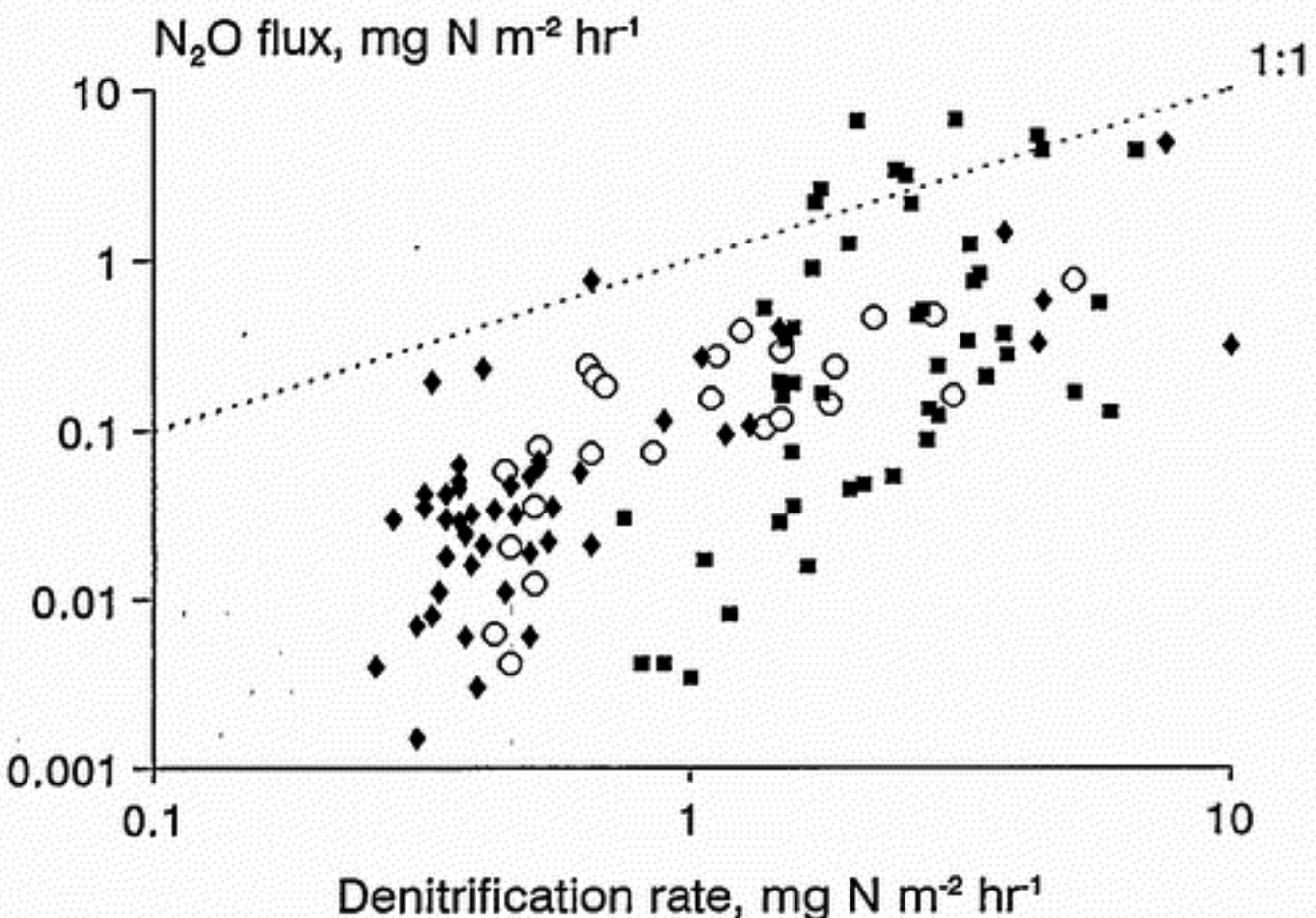


Figure 2. Logtransformed N_2O flux versus logtransformed denitrification rate, for June (■), September (◆) and November (○).

MODELLING NITROUS OXIDE FLUXES FROM GRASSLAND ON PEAT SOIL

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 N₂O flux, as found for air and soil temperatures (Figure 4).

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.

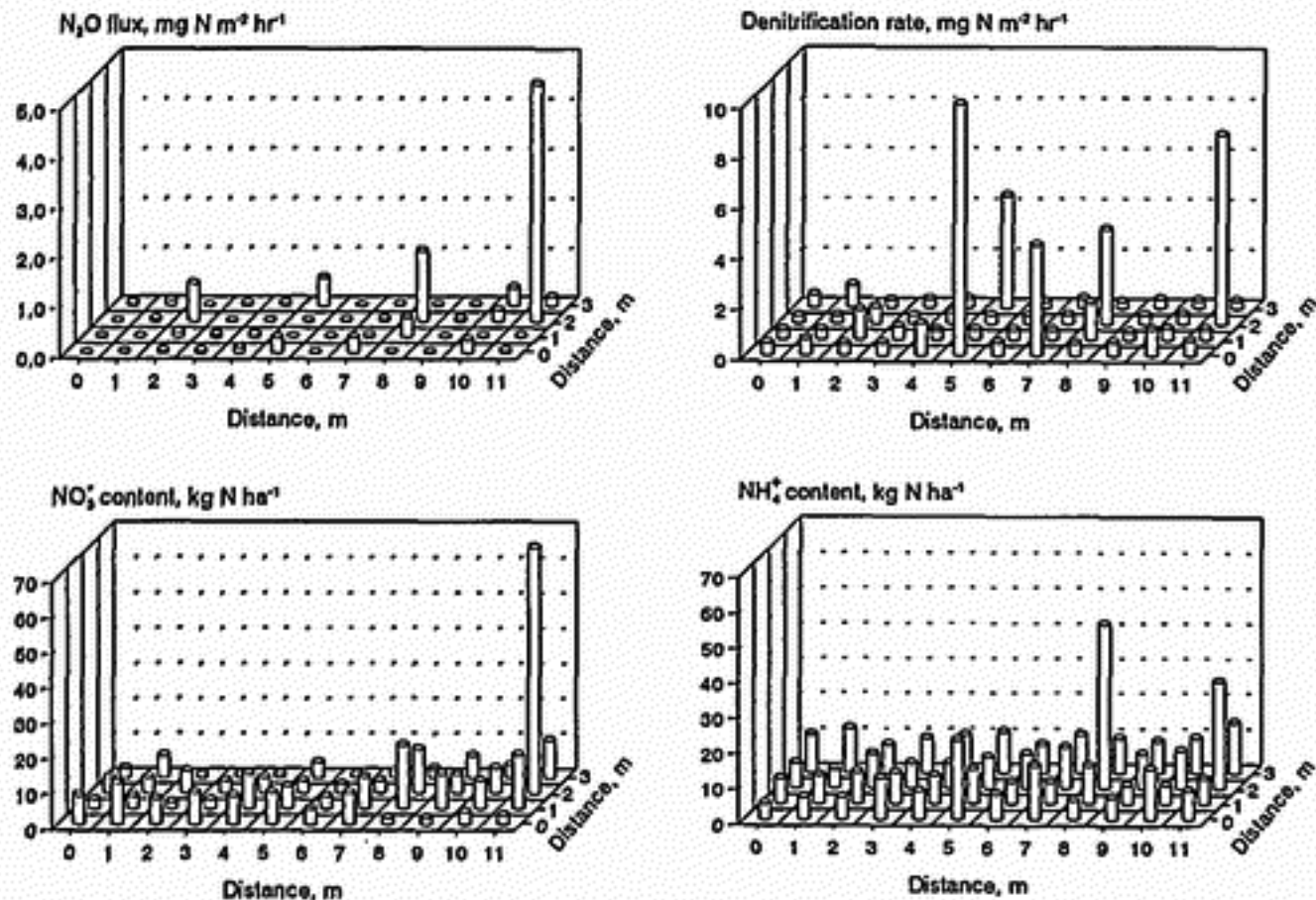


Figure 3. Spatial variability of N₂O flux, denitrification rate and contents of NO₃⁻ and NH₄⁺ in grassland on a peat soil in September 1993.

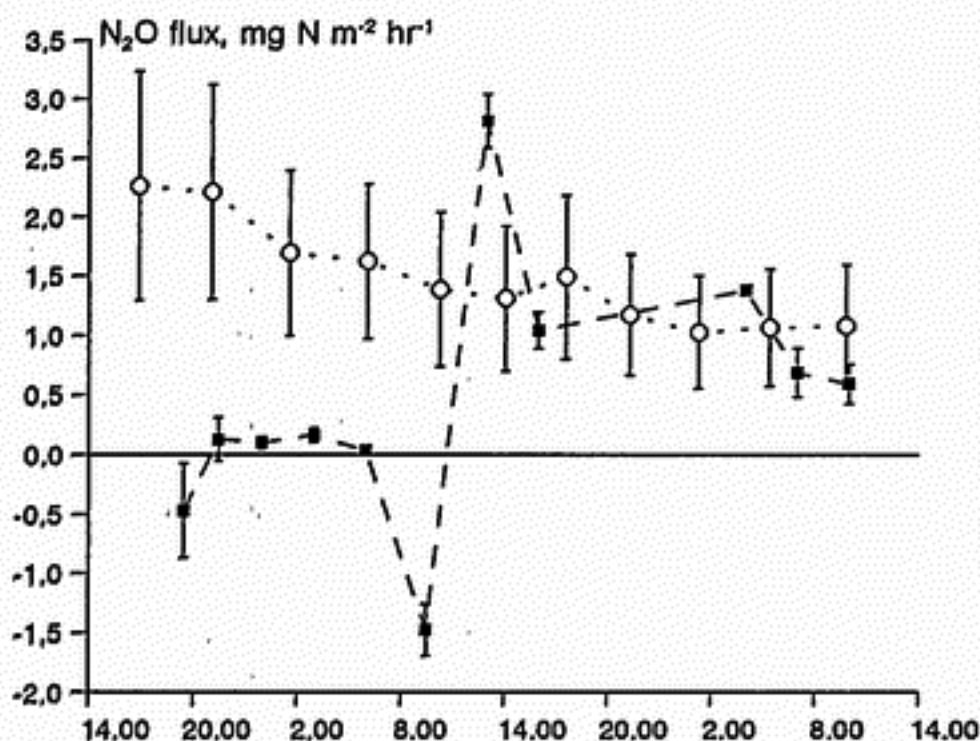
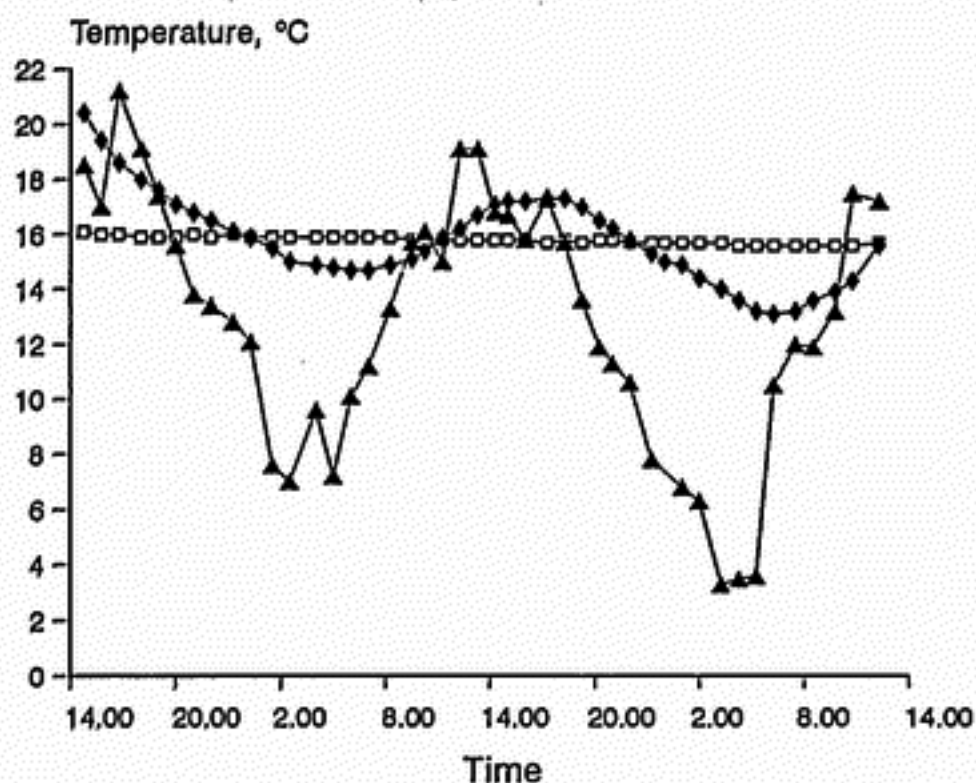


Figure 4. Results of N₂O flux measurements on grassland on peat soil during 22–24 June 1993. Upper Figure. Time course of N₂O fluxes (and 95% confidence intervals) derived from a flux chamber method (○) and a flux gradient technique (■).

Lower Figure. Time course of the atmospheric temperature (▲), soil temperature at 5 cm depth (◆) and soil temperature at 30 cm depth (□).

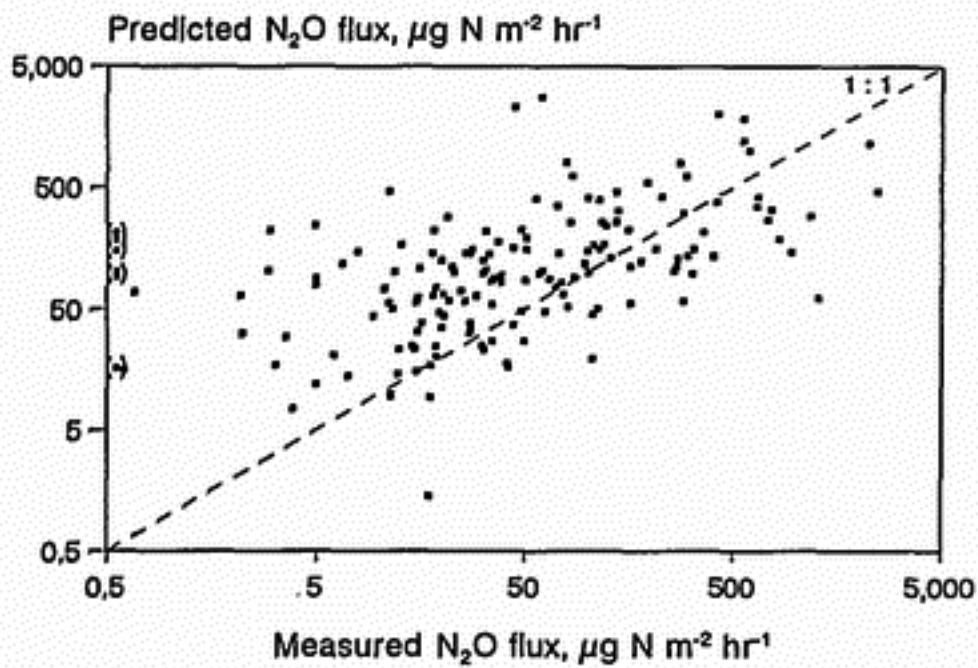


Testing the empirical model

Mineral N content and WFPS were the major factors controlling N₂O fluxes from the peat soil. The best model of the pooled data of the three experiments included total mineral N contents, WFPS and WFPS² and explained 64% of the variance in N₂O flux (Table 2). This model reasonably predicted N₂O fluxes from the monitoring

MODELLING NITROUS OXIDE FLUXES FROM GRASSLAND ON PEAT SOIL

Site 2



Site 3

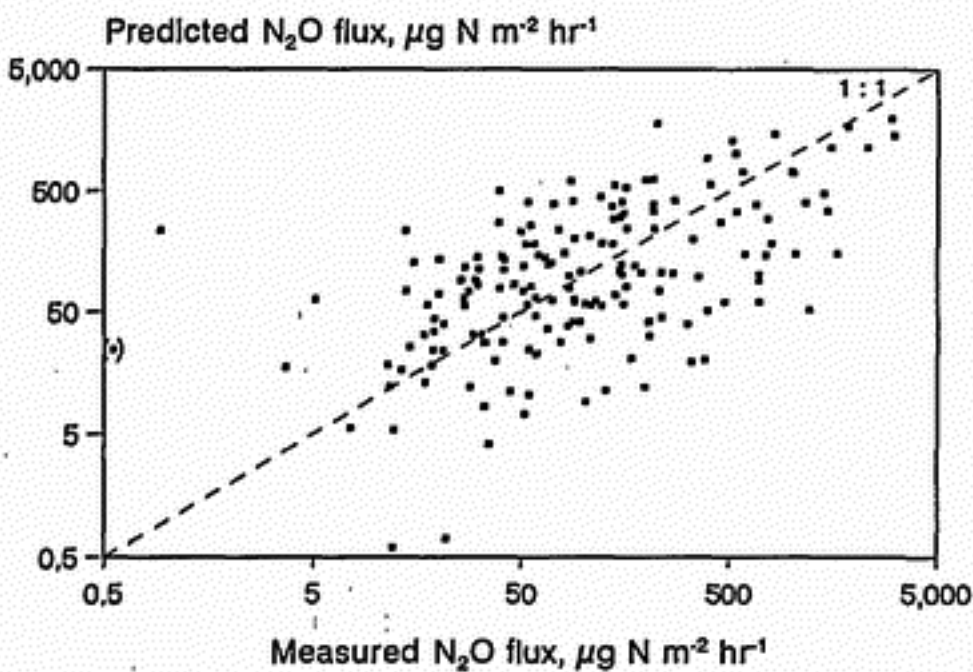


Figure 5. Measured N_2O flux (mean of 6 replicates) in the monitoring study versus predicted N_2O flux using the empirical model derived in the present study, for site 2 and site 3. Note logarithmic scales. Points in parentheses indicate that the mean measured N_2O flux was negative.

study, especially for site 3 (Figure 5). For site 2, the model systematically overestimated the N_2O flux for measured fluxes smaller than about $25 \mu\text{g N m}^{-2} \text{hr}^{-1}$. The model reasonably simulated the temporal behaviour of N_2O fluxes, with the largest fluxes during the growing season, associated with N fertilizer application and graz-

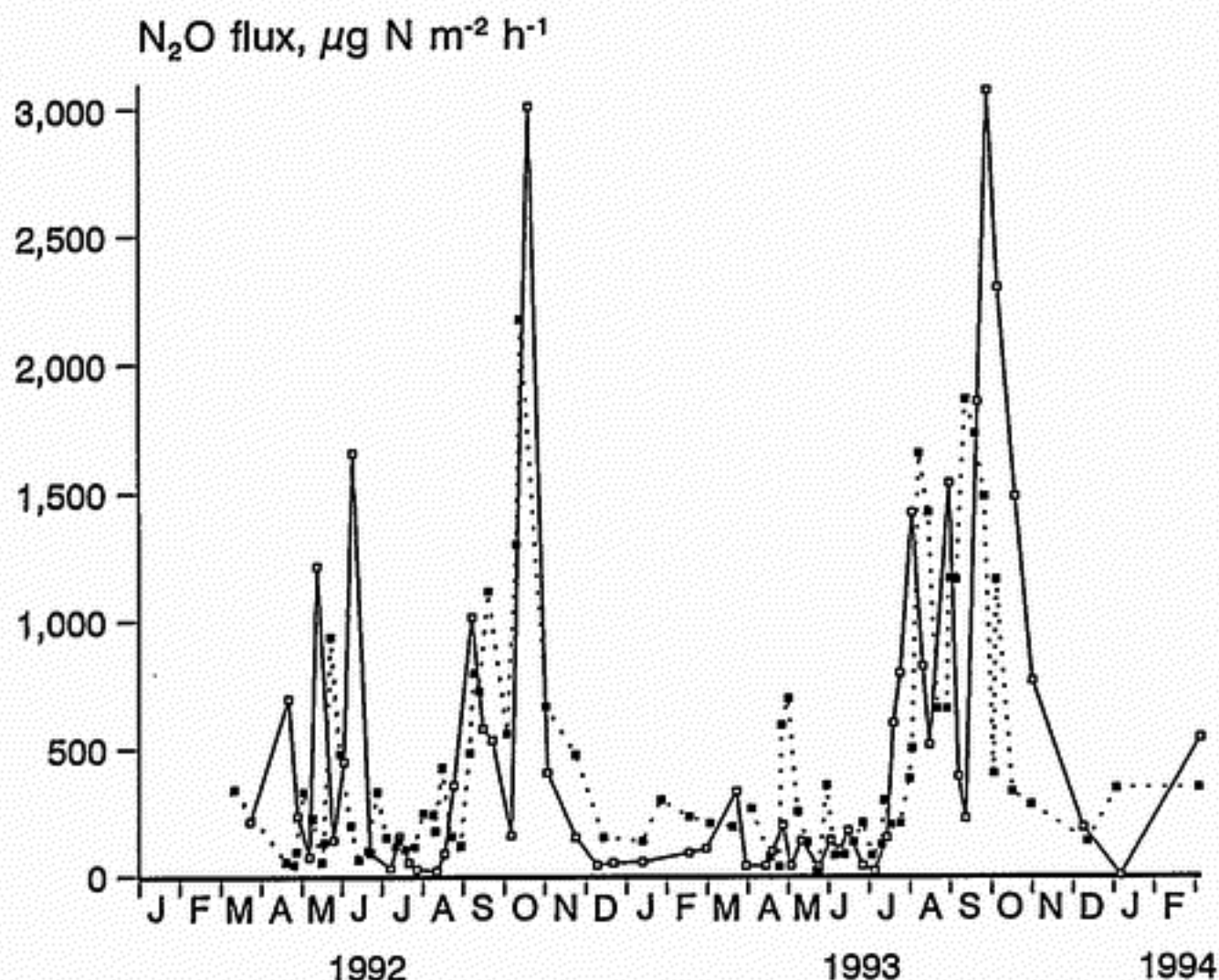


Figure 6. Time course of measured (□) and modeled (■) N_2O fluxes during March 1992 to March 1994, for N-fertilized and grazed grassland on site 3.

ing, and the smallest fluxes during winter (Figure 6). For site 2, 45% of the predicted N_2O 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. 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

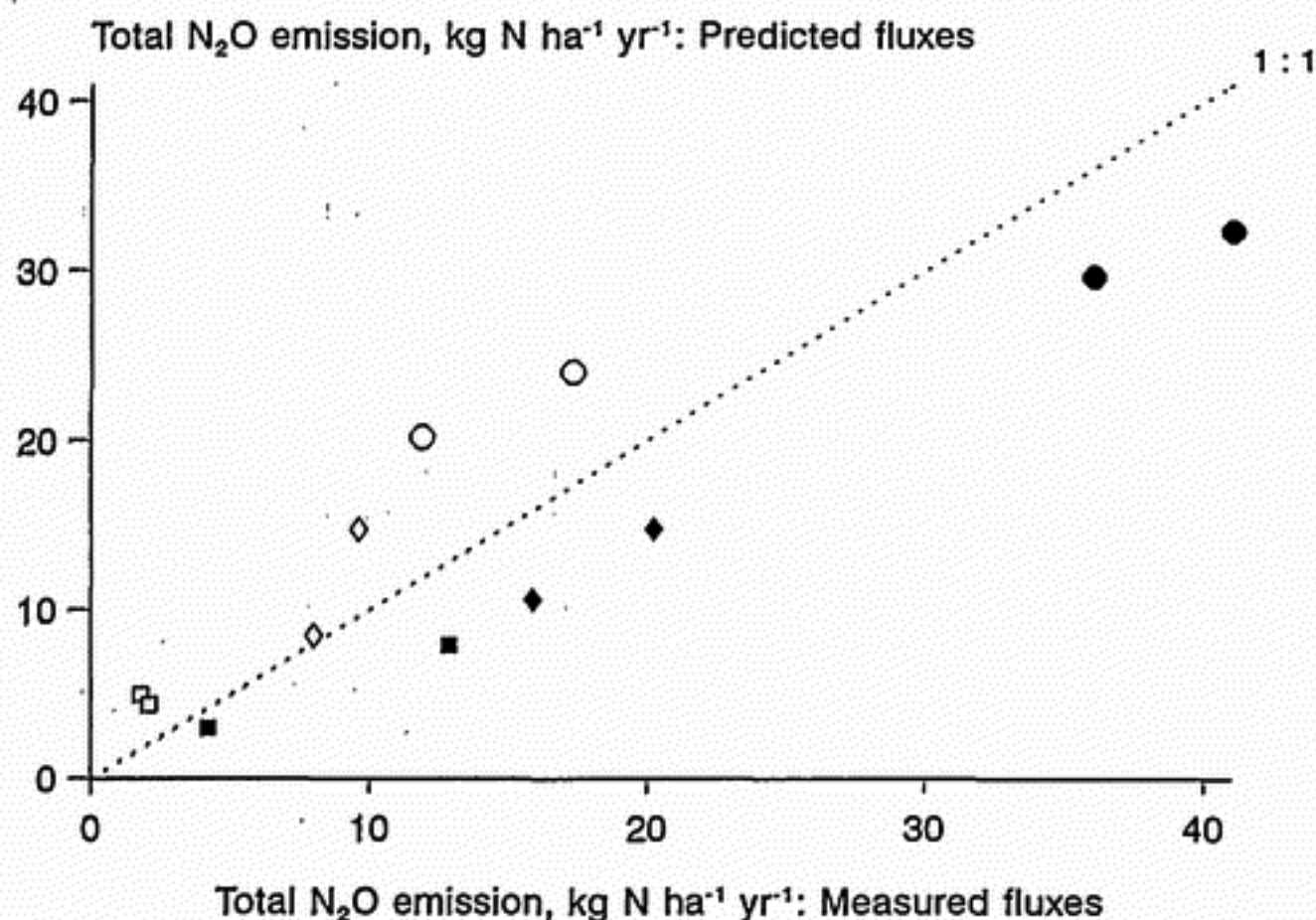


Figure 7. Estimated total annual N₂O emissions based on N₂O fluxes measured in the monitoring study versus those based on the fluxes derived from the empirical model.

□ = 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.

flux measurement methods and (iii) testing of a simple empirical model for N₂O fluxes from peat soils.

Controlling factors

Multiple regression models including contents of NO₃⁻ and NH₄⁺ and WFPS explained 37 to 77% of the variance in N₂O flux, indicating that these were major factors controlling the N₂O flux. The relatively large percentage of the variance in N₂O 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 N₂O flux.

In June, the flux of N₂O was strongly related to the NO₃⁻ content and WFPS (Figure 1 and Table 2). September and November models only included contents of NO₃⁻ and NH₄⁺. The fluxes of N₂O and denitrification rates were both much larger in June than in September and November. This coincided with much higher contents of NO₃⁻, much smaller WFPS and a higher ratio N₂O flux/denitrification rate in June than in September and November (Table 1). Generally, high NO₃⁻ contents and moderate WFPS increase relative production of N₂O 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.

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.* (submitted) 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. In the present study, the N_2O flux/denitrification rate tended to increase with increasing mineral N contents, but no clear relationship between the soil variables and this ratio could be established.

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 & 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 N_2O 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 m² (e.g. Afzal & 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 N₂O 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 N₂O 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 N₂O fluxes. In several studies using flux chambers, distinct diurnal variations in N₂O 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 N₂O production in the soil was not significantly affected by diurnal variations in moisture content and temperature.

Matthias *et al.* (1993) and Mosier & Hutchinson (1981) obtained similar N₂O 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 N₂O fluxes derived from chamber measurements were about a factor two larger than the N₂O 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 N₂O 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 N₂O fluxes and soil variables were found by e.g. Folorunso & 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 N₂O 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 & 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

We thank Arie Brader (NMI), Romke Postma (NMI), and Henk Verhagen (TNO) for practical assistance and the staff of the experimental farm ROC Zegveld for providing and maintaining the experimental plot. Dr. M.L. Van Beusichem (WAU) and

P.J. Van Erp (NMI) are greatly acknowledged for critical reading of the manuscript. This study was financially supported by the the Dutch National Research Program on Global Air Pollution and Climate Change.

References

- Afzal, M. & W.A. Adams, 1992. Heterogeneity of soil mineral nitrogen in pasture grazed by cattle. *Soil Science Society of America Journal* 56: 1160–1166.
- Ambus, P. & S. Christensen, 1994. Measurement of N₂O emission from a fertilized grassland: An analysis of spatial variability. *Journal of Geophysical Research* 99: D8 16,549–16,555.
- Ambus, P. & S. Christensen, 1995. Spatial and seasonal nitrous oxide and methane fluxes in Danish forest-, grassland-, and agroecosystems. *Journal of Environmental Quality* 24: 993–1001.
- Anonymous, 1987. Genstat 5 reference manual. Oxford University Press, Oxford, 749 pp.
- Anonymous, 1989. Robust Statistics – How not to reject outliers Part 1. Basic Concepts and Part 2. Inter-laboratory trials. *Analyst* 114: 1693–1702.
- 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).
- Bril J., H.G. Van Faassen & H. Klein Gunnewiek, 1994. Modeling N₂O emission from grazed grassland. Report 24 of the DLO Research Institute for Agrobiolgy and Soil Fertility (AB-DLO). AB-DLO, Haren, 45 pp.
- 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 & K.A. Smith, 1994. Measurement of nitrous oxide emissions from fertilized grassland using closed chambers. *Journal of Geophysical Research* 99: D8 16,599–16,607.
- Davidson, E.A., 1991. Fluxes of nitrous oxide and nitric oxide from terrestrial ecosystems. In: J.E. Rogers & W.B. Whitman (Ed), *Microbial production and consumption of greenhouse gases: methane, nitrogen oxides, and halomethanes*. American Society for Microbiology, Washington D.C., pp. 219–235.
- Denmead, O.T., J.R. Freney & J.R. Simpson, 1979. Studies of nitrous oxide emission from a grass sward. *Soil Science Society of America Journal* 43: 726–728.
- Duyzer, J.H., 1995. Measurements of the atmospheric emission of N₂O from biogenic sources in general and by grassland ecosystems in particular. TNO report R95/213, TNO, Delft, 33 pp.
- Flessa, H., P. Dörsch & F. Beese, 1995. Seasonal variation of N₂O and CH₄ fluxes in differently managed arable soils in southern Germany. *Journal of Geophysical Research* 100: D11 23,115–23,124.
- Folorunso, O.A. & D.E. Rolston, 1985. Spatial and spectral relationships between field-measured denitrification gas fluxes and soil properties. *Soil Science Society of America Journal* 49: 1087–1093.
- Grant, R.F.M., M. Nyborg & W. Laidlaw, 1993a. Evolution of nitrous oxide from soil: I. Model development. *Soil Science* 156: 259–265.
- Grant, R.F.M., M. Nyborg & W. Laidlaw, 1993b. Evolution of nitrous oxide from soil: II. Experimental results and model testing. *Soil Science* 156: 266–277.
- Houba, V.J.G., I. Novozamsky & J.J. Van der Lee, 1989. Some aspects of determinations of nitrogen fractions in soil extracts, *VDLUFA-Schriftenreihe* 30: 305–312.
- Kester, R.A., M.E. Meijer, J.A. Libochant, W. De Boer & H.J. Laanbroek, submitted. The contribution of nitrification and denitrification to the NO and N₂O emission of an acid forest soil, a river sediment and a fertilized grassland soil. *Soil Biology and Biochemistry*.
- Koops, J.G., O. Oenema & 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 & O. Oenema, 1996b. Nitrogen loss from grassland on peat soils through nitrous oxide production. *Plant and Soil* (in press).
- Matthias, A.D., J.F. Artiola & S.A. Musil, 1993. Preliminary study of N₂O flux over irrigated bermudagrass in a desert environment. *Agricultural and Forest Meteorology* 64: 29–45.

- Mosier, A.R. & G.L. Hutchinson, 1981. Nitrous oxide emissions from cropped fields. *Journal of Environmental Quality* 10: 169-173.
- Mosier, A.R., W.J. Parton & G.L. Hutchinson, 1983. Modelling nitrous oxide evolution from cropped and native soils. *Environmental Biogeochemistry, Ecological Bulletin* (Stockholm) 35: 229-241.
- Parton, W.J., A.R. Mosier & D.S. Schimel, 1988. Rates and pathways of nitrous oxide production in a shortgrass steppe. *Biogeochemistry* 6: 45-58.
- Rolston, D.E., 1990. Modeling of denitrification: Approaches, successes and problems. *Mitteilungen der Deutschen Bodenkundlichen Gesellschaft* 60: 397-402.
- 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 & 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.
- Velthof, G.L. & 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. & 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 & 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 & 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.