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Nitrous oxide emissions from fertilised grassland:
A 2-year study of the effects of N fertiliser form and environmental conditions

Abstract The aim was to investigate the effects of different N fertilisers on nitrous oxide (N_2O) flux from agricultural grassland, with a view to suggesting fertiliser practices least likely to cause substantial N_2O emissions, and to assess the influence of soil and environmental factors on the emissions. Replicate plots on a clay loam grassland were fertilised with ammonium sulphate (AS), urea (U), calcium nitrate (CN), ammonium nitrate (AN), or cattle slurry supplemented with AN on three occasions in each of 2 years. Frequent measurements were made of N_2O flux and soil and environmental variables. The loss of N_2O-N as a percentage of N fertiliser applied was highest from the supplemented slurry (SS) treatment and U, and lowest from AS. The temporal pattern of losses was different for the different fertilisers and between years. Losses from U were lower than those from AN and CN in the spring, but higher in the summer. The high summer fluxes were associated with high water-filled pore space (WFPS) values. Fluxes also rose steeply with temperature where WFPS or mineral N values were not limiting. Total annual loss was higher in the 2nd year, probably because of the rainfall pattern: the percentage losses were 2.2, 1.4, 1.2, 1.1 and 0.4 from SS, U, AN, CN and AS, respectively. Application of U in the spring and AN twice in the summer in the 2nd year gave an average emission factor of 0.8% – lower than from application of either individual fertiliser. We suggest that similar varied fertilisation practices, modified according to soil and crop type and climatic conditions, might be employed to minimise N_2O emissions from agricultural land.

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Introduction

Nitrous oxide (N_2O) emissions from agricultural soils are of concern because they signify a decrease in N availability to crops and because they contribute to global warming and the destruction of the ozone layer (Crutzen 1981). Emissions can occur by nitrification and/or denitrification if N is applied as an NH_4^+-forming fertiliser, but only by denitrification if it is applied solely as NO_3^-. Both processes are strongly influenced by soil temperature, moisture, pH and soluble organic matter availability (Bouwman 1990). Nitrification is favoured by aerobic soil conditions and N may be lost as nitric oxide (NO) as well as N_2O. Denitrification is favoured by anaerobic conditions, but increased anaerobicity may lead to enhanced reduction of N_2O to N_2 and thus to decreased N_2O emissions. Although NO is an intermediate in the reduction sequence leading to N_2O, little appears to be emitted, from temperate soils at least, in conditions favouring denitrification (Skiba et al. 1992).

Although both Eichner (1990) and Bouwman (1994) found difficulty in comparing different studies, their reviews suggest that emissions are higher from anhydrous ammonia (AA) and organic-mineral N combinations than from other fertilisers. Few studies have made simultaneous direct comparisons of a wide range of fertiliser types.

High emissions have been reported for agricultural grassland in moist temperate environments (e.g. Webster and Dowdell 1982; Christensen 1983; Ryden 1983; Clayton et al. 1994; Velthof and Oenema 1995). The aim of the field trial described in this paper was to investigate the effects of different N fertilisers on N_2O flux from agricultural grassland cut for conservation, with a view to suggesting fertiliser practices least likely to cause substantial N_2O losses, and to assess the influence of soil and environmental factors on flux.

Table 1 Timing of fertiliser applications in 1992 and 1993

Fertiliser	Dates of fertilisation					
	1992	1992	1992	1993	1993	1993
Ammonium sulphate (AS)	29 April	8 June	10 August	2 April	9 June	4 August
Urea (U)	29 April	8 June	10 August	2 April	9 June	4 August
Calcium nitrate (CN)	29 April	8 June	10 August	2 April	9 June	4 August
Ammonium nitrate (AN)	29 April	8 June	10 August	2 April	9 June	4 August
Urea,	–	–	–	2 April	–	–
then ammonium nitrate				–	9 June	4 August
Slurry/AN (SS)	9 April/ 16 April	23 June/ 24 June	18 August	5 April/ 7 April	10 June/ 9 June	4 August

Field site and methods

Field site

The field trial was conducted at Glencorse Mains, Penicuik, about 10 km south of Edinburgh (lat. 55°53′ N, long. 3°26′ W, grid ref. NT238628, elevation 210 m). The soil was an imperfectly draining gleysol (FAO-UNESCO classification) with a clay loam texture (15% coarse sand, 19% fine sand, 37% silt, 22% clay), a mean pH of 5.5 and an organic matter content of 5.5%. The field had been under an arable rotation prior to 1980, then cropped with winter barley (1980–1984), and perennial ryegrass (*Lolium perenne* L.), 1986–1991, when it was ploughed and reseeded with the same species (cv. Talbot). The plots were part of a study of compaction treatments, and had received no tractor traffic.

Three replicates of six (in 1992) or seven (in 1993) treatments were laid out in a randomised block design. Each plot measured 2.4×14 m. Treatments were as given in Table 1. All fertilisers, except slurry, were in granular or crystalline form and were surface applied by hand at a rate of 120 kg N ha^{-1} per application. The mineral fertiliser addition of 360 kg N ha^{-1} was slightly greater than the 300 kg N ha^{-1} year^{-1} used locally for silage production with a similar fertilisation/cutting regime. For the slurry treatments, the slurry was pumped from a tanker via a curtained dribble bar. The April and June applications in each year were accompanied by application of 60 and 50 kg N ha^{-1} as AN, respectively; in the late summer only slurry was applied. Slurry-derived NH$_4^+$-N amounted to 50–60 kg ha^{-1} per application (Douglas et al. 1994).

In 1993, one treatment involved fertilising with U in the spring, and with AN in the early and mid-summer, to see whether the total N$_2$O emissions would be lower than from repeated applications of each individual fertiliser.

Grass was cut and removed for silage 3 times each year, at the ends of May and July, and in late September (1992) or early October (1993). The mean total annual DM production was 11.2 and 12.6 t ha^{-1} in 1992 and 1993, respectively.

N$_2$O flux measurement

N$_2$O fluxes were measured using 40-cm-diameter closed chambers (area 0.126 m^2) (Clayton et al. 1994; Smith et al. 1995). Sampling was carried out daily for a week immediately after fertilisation, twice weekly for another month, then weekly or fortnightly. In all, fluxes were measured on 112 occasions on the plots treated with mineral fertiliser, and on 98 occasions on the slurry-treated plots, over the 2-year period. To minimise diurnal variation in the flux pattern, sampling was always carried out between 9.30 a.m. and 12.30 p.m. On each sampling occasion, duplicate air samples (1–5 ml) were taken 70 or 75 min after closing the chamber. The samples, in airtight greased glass syringes, were returned to the laboratory for N$_2$O analysis on the same day, by electron-capture gas chromatography.

An automated computer-controlled sample injector based on two 16-port solenoid valves and a sample loop connected to the gas chromatograph (Arah et al. 1994) permitted the unattended analysis of 32 samples. N$_2$O standards (ambient, i.e. 0.31 ppm, 1, 10 and 100 ppm) were analysed on each occasion. Peak areas were determined with an electronic integrator, and the data were downloaded directly to a computer for calculation of N$_2$O concentrations according to the calibration standards.

The chambers remained in the soil, but open to the atmosphere, throughout the field trial, except during grass cutting and fertiliser application. They were moved to new positions between years 1 and 2 of the study.

Soil sampling and analysis

Soil samples (0–10 cm depth in 1992; 0–10 and 10–20 cm in 1993) were taken from triplicate plots, using a 3-cm-diameter gauge auger, normally on alternate N$_2$O-sampling occasions, and bulked. In all, there were 62 samplings over the 2 years. Nitrate-N, NH$_4^+$-N and (in 1993 only) NO$_2^-$-N were measured by continuous flow colorimetric analysis of 1 *M* KCl extracts of the field-moist soil using a soil:solution ratio of 15 g:50 ml. Soil pH was determined on suspensions of 10 ml fresh soil in 25 ml water. Soil water content was measured gravimetrically, after drying at 105 °C, and the corresponding volumetric water content and water-filled pore space calculated from measurements of bulk density and total porosity.

Air temperature and soil temperature at 10 cm were measured on each sampling occasion using a digital thermometer. Rainfall data were obtained from a local Meteorological Office station (in the same field).

Calculation of fluxes

Since N$_2$O fluxes tended towards a log-normal distribution, means (daily and cumulative) were calculated from the six replicate chambers in each treatment, using the uniformly minimum variance unbiased estimator method of Finney referred to by Parkin et al. (1988). Cumulative fluxes were calculated by interpolation between measured daily fluxes. Relationships between flux and soil variables were investigated by standard linear regression analysis and visualised using the SigmaPlot Mesh Plot facility (Jandel Scientific 1994).

Results

Nitrous oxide emissions from the unfertilised plots were consistently low throughout the experiment: always less than 5 g ha^{-1} day^{-1} (mean of six replicate chambers). Emissions from the treated plots were concentrated in relatively short periods (about 3 weeks) following each fertiliser application, and there were marked differences between the relative magnitudes of emissions from different fertilisers at different times of year (Fig. 1). The highest

Table 2 Cumulative N_2O-N losses from various fertiliser types after three fertiliser applications and the final silage cuts in 1992 and 1993

Fertiliser	1992						1993					
	g N_2O-N ha^{-1}					N_2O-N as % of N applied	g N_2O-N ha^{-1}					N_2O-N as % of N applied
	After fertiliser application in:			From Oct to Mar	Total		After fertiliser application in:			From Oct to Mar	Total	
	April	June	August				April	June	August			
AS	146±31	55±14	298±116	201±28	690±128	0.2	450±74	573±110	121±20	146±40	1280±150	0.4
Urea	73±39	516±92	2230±230	204±83	3010±230	0.8	1030±170	3530±500	552±133	92±27	5210±550	1.4
CN	839±212	80±25	685±231	78±32	1630±270	0.5	2620±410	1200±120	115±16	76±35	4010±490	1.1
AN	634±91	129±95	711±170	116±84	1500±170	0.4	2190±340	1490±110	468±128	100±24	4230±340	1.2
U/AN/AN	–	–	–	–	–	–	707±79	1860±350	309±62	48±25	2940±340	0.8
Slurry[a]	(83±44)[b]	137±49	89±20	237±144	(480±101)[b]	(0.2)[b]	2150±250	4060±300	127±23	59±38	6390±220	2.2
None	−6±6	−20±13	−15±10	70±22	42±56	[c]	92±42	74±9	36±14	49±20	260±55	[c]

AS ammonium sulphate, *CN* calcium nitrate, *AN* ammonium nitrate, *U/AN/AN* urea/ammonium nitrate/ammonium nitrate

[a] The slurry applications were supplemented with ammonium nitrate in April and June each year

[b] N_2O fluxes were not measured immediately after the April 1992 slurry application, so the total loss for that period is not known
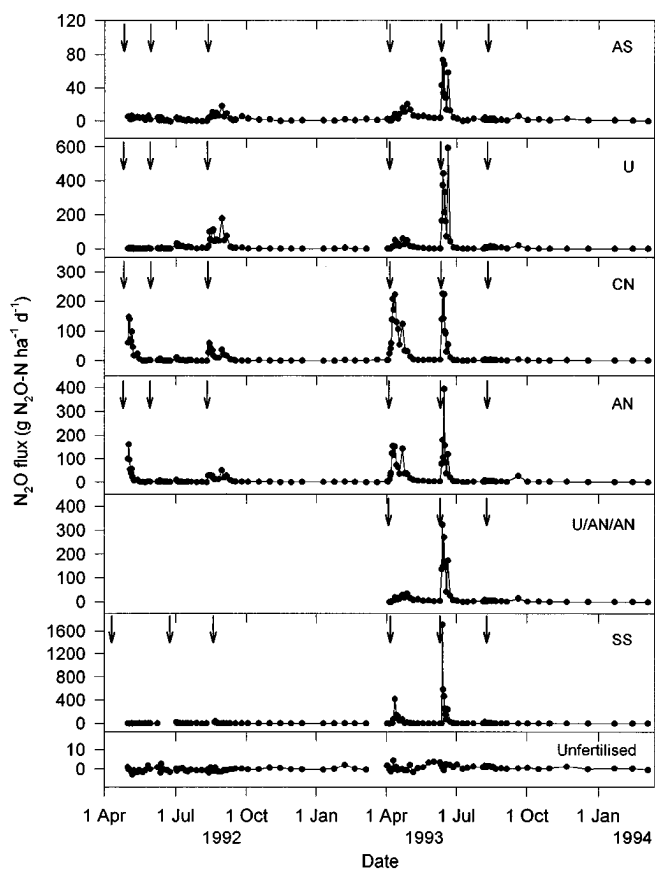
[c] Not applicable

Fig. 1 N_2O fluxes from plots fertilised with different N fertilisers, and from unfertilised control plots, April 1992 to March 1994. Note different scales on *y*-axes. *Arrows* indicate fertiliser application. The slurry applications were supplemented with ammonium nitrate in April and June each year

rate measured on any one day was nearly 1800 g N_2O-N ha^{-1} day^{-1} from the SS plots. Small negative fluxes were observed occasionally, generally towards the end of each fertiliser period, in all treatments.

The total N_2O emissions from all treatments where comparisons were possible were greater in 1993–1994 than 1992–1993 (Table 2), with the differences being significant at $P<0.01$ for U, CN and AN, and at $P<0.05$ for AS. Total N_2O losses in each year ranged from 0.2 to >2% of the fertiliser N applied. Urea caused the greatest total emissions in 1992–1993, which were significantly ($P<0.01$) greater than the next highest emissions, from CN and AN. In 1993–1994 the emissions from urea were second highest, after those from the SS treatment (the difference here was not quite significant at the 5% level: $P = 0.063$), but they were not significantly different from those from AN. The total emissions from U were five- to six-fold greater than from AS, which caused the lowest emissions. Emissions from CN and AN were similar to each other and, in 1992–1993, intermediate between those from AS and U (Table 2).

The highest total emissions from U occurred in August 1992 and June 1993, whereas the losses from CN and AN were generally greater after the April applications (Table 2). Most of the emissions from the slurry treatment in 1993 occurred after the April and June applications, when AN was also applied. The 1992–1993 flux measurements were not begun immediately after the April fertilisation; it is probable that the total N_2O-N loss was much greater than shown. Although the total amount of N applied to the slurry plots in April and June was similar to that applied to the AN-only plots, the maximum fluxes from the former were higher, as was the 1993–1994 total N_2O emission; the difference in total emission was significant at $P<0.01$. The response of flux to N application was rapid in both cases (Fig. 2). Emissions from slurry alone (the August applications) were still at least four-fold those from the unfertilised plots, and 30–100% of the emissions from the August applications of AS.

The results from 1992–1993 suggested that there was scope for minimising N_2O emissions by varying the fertiliser according to the season; hence the 1993–1994 test of U followed by two applications of AN. The emissions
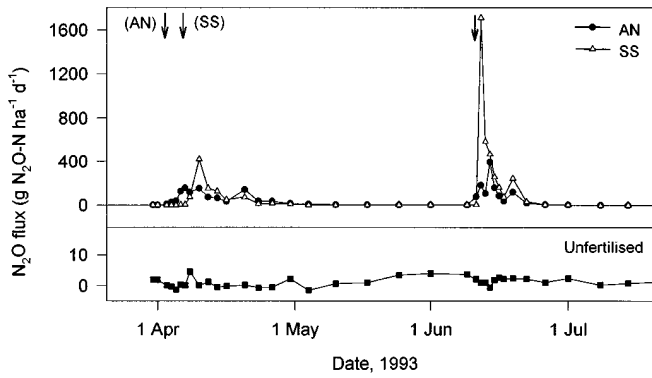
Fig. 2 N₂O fluxes from plots fertilised with AN or SS, and from unfertilised control plots, in April and June 1993. *Arrows* indicate fertiliser application. Note different scales on *y*-axes
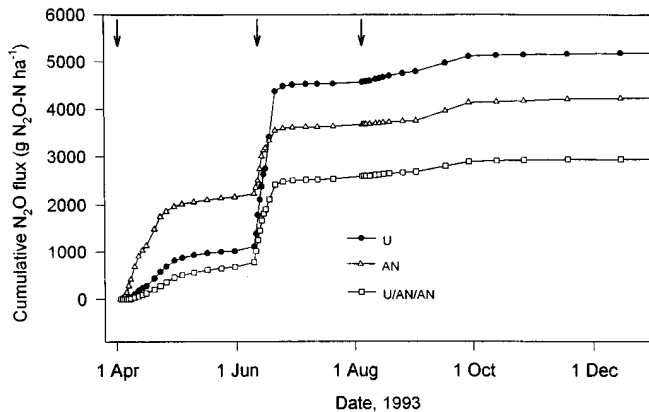

Fig. 3 Cumulative N₂O-N loss from plots fertilised consistently with urea or ammonium nitrate, or sequentially with urea then ammonium nitrate. *Arrows* indicate fertiliser application

Fig. 4 N₂O loss occurring within 7 and 21 days of fertiliser application, as a proportion of the total lost during each measurement period, in two successive seasons. Total period lengths for all but the slurry treatments were 39, 62, 52, 67, 55 and 56 days for the applications in April, June and August 1992 and April, June and August 1993, respectively. The periods were 55 and 44, 63, 54 and 56 days for the slurry applications in June and August 1992, April, June and August 1993. [a] U/AN/AN not applied in 1992, [b] measurements for the April 1992 application of slurry were not complete

from this sequence were about 25% lower than those from repeated AN applications and 40% lower (significant at $P<0.01$) than from repeated U applications, but still $2\frac{1}{2}$ times greater (significant at $P<0.001$) than from AS. The plot of cumulative fluxes (Fig. 3) emphasises why applying U instead of AN in the spring, followed by AN instead of U in the summer, reduced the total N₂O emissions.

Figure 4 shows that a greater proportion of the total loss from the nitrate fertilisers occurred within a week of fertilisation than did so from AS and U, except under the driest conditions, e.g. June 1992. Most of the total N₂O emissions during each period following nitrate fertilisation occurred within 3 weeks of fertilisation; this was true also for the emissions from AS and U after the June 1993 application, when the environmental conditions were warm and wet.

Rainfall occurred more evenly in 1992–1993 than in 1993–1994, except for a dry period in the early summer of 1992 which coincided with high soil temperatures (Fig. 5). The pHs of the plots varied between fertiliser treatments; the AS plots had the lowest pH (mean 5.3, SE 0.04), the CN plots the highest (mean 6.3, SE 0.05), both being sig-
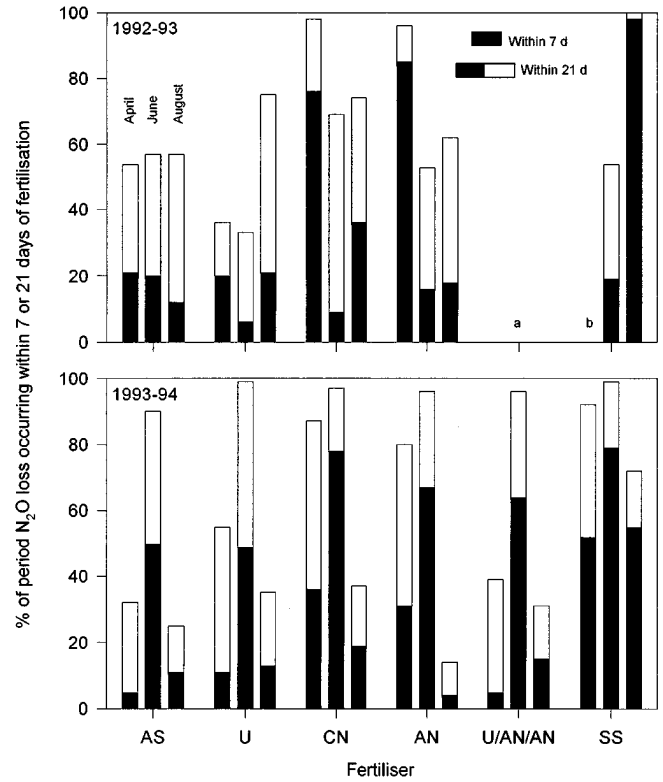
nificantly different ($P<0.01$) from the pH of the unfertilised control and other treatment plots.

As expected, soil NO_3^- and NH_4^+ contents increased on fertilisation and then declined rapidly. The amounts in the 10–20 cm soil layer were small: about one-tenth or less of those in the 0–10 cm layer. NO_2^- was not detectable on most measurement occasions. Concentrations up to about 1 kg NO_2^--N ha^{-1} were observed in the 0–10 cm layer transiently after fertilisation with CN, AN and SS; a delayed but longer-lasting post-fertilisation NO_2^- elevation was seen with AS. Concentrations in the 10–20 cm layer were detectable only after fertilisation with CN and AN, and were no higher than about 0.3 kg NO_2^--N ha^{-1}.

Discussion

The N₂O fluxes reported here, both the rates and the percentage of N applied, are generally comparable with those reported in other studies. The largest fluxes were from the supplemented slurry applications in 1993–1994, in keeping with the data in Bouwman's (1994) review, which showed organic/organic-mineral mixtures $\cong$ anhydrous ammonia
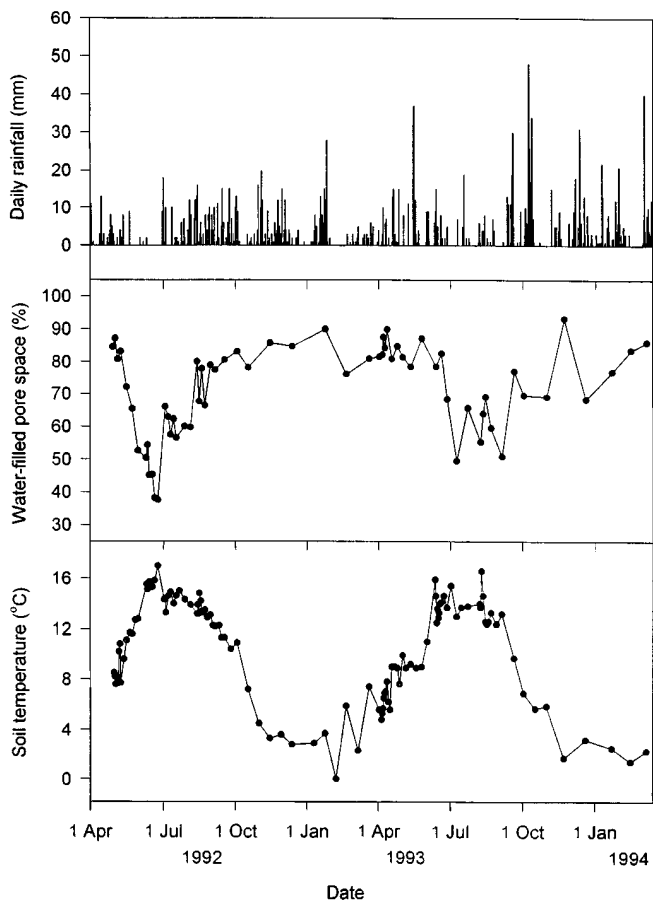
Fig. 5 Rainfall and soil WFPS and temperature at the field site through the two study years

(AA) > AN $\cong$ NO_3^--based > U $\cong$ NH_4^+-based, from a range of sites. Our data show: SS $\geqslant$ U $\geqslant$ AN $\cong$ CN > AS. However, the relatively large fluxes from U were unexpected, as the approximate order of emissions presented by Eichner (1990) for grassland was: AN > AA > NO_3^--based > U.

Comparisons between studies are difficult because the behaviour of different fertilisers depends on soil and crop type as well as environmental conditions. For example, Breitenbeck et al. (1980) found greater emissions from AS and U than from CN, but conditions were such that nitrification was favoured. In our study, in conditions favourable to both denitrification and nitrification, fluxes from CN were higher than those from AS ($P<0.01$). Christensen (1983) saw higher losses from slurry than from AN, but Hansen et al. (1993) saw the reverse, although denitrification was the cause in both studies. Differences in the environment were probably responsible for the difference.

The patterns of N_2O emission in 1992–1993 and 1993–1994 were strikingly different. Although the relative N_2O fluxes after the April applications were fairly similar in the two years, the fluxes after the June and August applications showed marked variation. This was probably due to the rainfall pattern, even though total rainfall in both seasons was very similar. This reinforces the need for long-term studies, to avoid misleading generalisations.

June 1992 was very dry, and N_2O fluxes did not increase until after rainfall in early July, but even then they were small. August 1992 was wetter, and fluxes increased immediately after fertilisation. In 1993 the situation was reversed: the higher fluxes after the June application compared with those after the August application were probably due to the soil being much wetter when the fertiliser was applied in June.

Warmth and wetness tend to promote both nitrification and denitrification, and therefore N_2O loss, although nitrification declines if the soil becomes too anaerobic. Although increased wetness and temperature lead to an increase in the nitrification product ratio (N_2O/NO_3^-) and a decrease in the denitrification product ratio (N_2O/N_2), the net effect is generally an increase in N_2O because the total product increases (Granli and Bøckman 1994). However, at very high values of water-filled pore space (WFPS), reduction of N_2O to N_2 can result in a reduced N_2O flux (Focht 1978). This is discussed further below. The positive effect of increasing temperature on the nitrification product ratio may partly account for the higher summer/spring flux ratios for AS and U than for CN and AN in both study years. Similarly, the summer/spring ratios for AN were slightly higher than those for CN, probably because of the nitrification contribution.

The denitrification product ratio is affected also by the NO_3^- concentration, increasing at higher NO_3^- concentrations because NO_3^- inhibits the conversion of N_2O to N_2 (Granli and Bøckman 1994). If the high soil NO_3^- concentrations after nitrate application are followed by a rapid decrease due to plant uptake and denitrification, the N_2O/N_2 ratio may fall sharply, which could partly explain why such a high proportion of the total N_2O emission from AN and CN in each period was emitted within 1–3 weeks of fertiliser application compared with that from the NH_4^+-forming fertilisers (Fig. 4).

We analysed by linear regression the temporal relationships between flux and soil moisture (expressed as WFPS), soil temperature and soil NO_3^-, NH_4^+, and total mineral N for the individual fertiliser treatments, using data from the whole experimental period. The correlation coefficients for the complete data sets for the 2-year period April 1992 to March 1994 and for the periods encompassing most of the emissions (April to September) were generally low ($r^2 \leqslant 0.28$), with the exception of the slurry treatment (SS), where the correlations with soil mineral N concentration were much higher (Table 3). However, for certain combinations of temperature and WFPS, fluxes increased steeply with increasing temperature. This can be seen in Fig. 6, which contains mesh plots of flux versus temperature and WFPS for four of the fertiliser treatments used in this study.

When data from the winter (October to March) period were excluded from the analyses, the correlation coefficients for the flux-WFPS relationships improved. This is understandable; the winter data include many occasions when high WFPS is associated with low mineral N and/or low temperatures, which give rise to low fluxes, thus weakening any correlation of high flux with high WFPS.
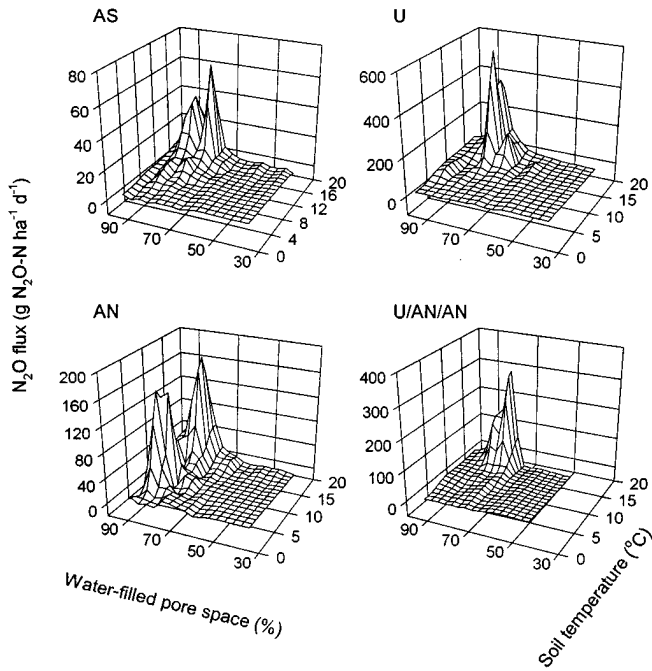
Fig. 6 Mesh plots of the relationship between N₂O flux, soil temperature and WFPS for four fertiliser treatments based on measurements over the whole experimental period. Abbreviations as in Table 1
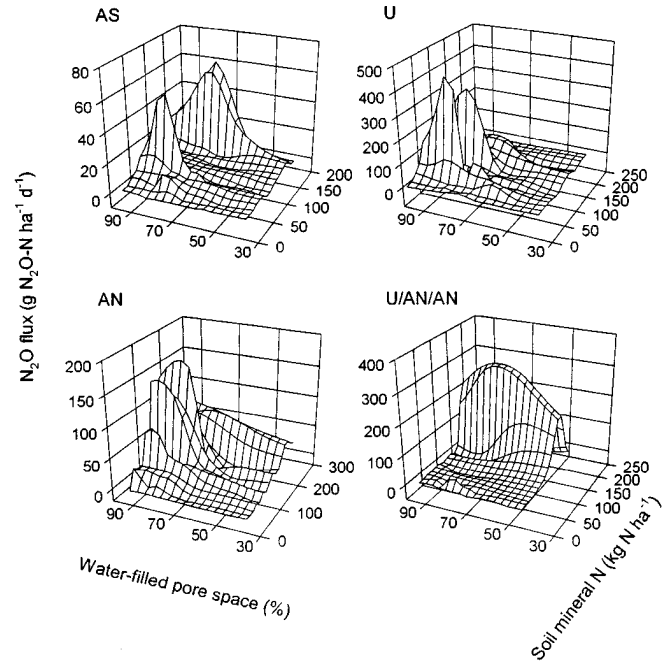
Fig. 7 Mesh plots of the relationship between N₂O flux, soil mineral N and WFPS for four fertiliser treatments, based on measurements over the whole experimental period. Abbreviations as in Table 1

Table 3 Correlation coefficients (r^2) for relationships between N₂O fluxes and environmental variables during the period from April 1992 to March 1994

Fertiliser	Variable						
	Soil temp.	Soil NH$_4^+$	Soil NO$_3^-$	Mineral N		WFPS	
				Total period	April–Sept. 1992+1993	Total period	April–Sept. 1992+1993
AS	0.04	0.07	<0.01	0.07	0.04	0.04	0.08
Urea	0.06	0.01	0.04	0.02	0.01	0.02	0.06
CN	<0.01	0.16	0.07	0.08	0.05	0.11	0.22
AN	<0.01	0.22	0.27	0.26	0.21	0.13	0.28
Slurry	0.03	0.56	0.60	0.61	0.62	0.03	0.09
None	<0.01	<0.01	0.05	<0.01	<0.01	0.01	<0.01

Fertiliser abbreviations as in Tables 1 and 2; *WFPS* water-filled pore space

There are many other reasons why regression analysis may fail to show strong correlations, and many other workers have been similarly disappointed (e.g. Shepherd et al. 1991). On a warm wet day there may be low soil mineral N and therefore little flux, and on a warm dry day there may be high N and high temperature but low WFPS, and again little flux, so relatively poor correlation is inevitable. The existence of threshold levels of soil factors for nitrification or denitrification activity was recognised by Ryden (1983) and Goulding et al. (1993), and has been observed by other workers, e.g. de Klein and van Lotestijn (1996).

There is much evidence that flux peaks are associated with rainfall events (Mosier et al. 1981, 1991; Clayton et al. 1994), whether or not soil moisture is already above

the threshold level. However, soil moisture conditions prior to fertiliser application may also be important. Soils subjected to a brief wetting may develop nitrifying but not denitrifying activity; the latter may develop only after a longer wetting (Højberg et al. 1996; Dendooven et al. 1996). Such effects may help to explain the differences between the fluxes in August 1992 and June 1993; WFPS was similar at fertilisation but had been very different over the previous few days.

Figures 6 and 7 (which contains mesh plots of the N₂O flux versus soil mineral N content and WFPS) show that normally the WFPS must be above about 65% for substantial N₂O emission to occur at this site, although some emissions may occur at lower WFPS when soil mineral N is very high (Fig. 7). This threshold at 65% is similar to

those reported by other workers for the occurrence of denitrification in similar soil types, as summarised by de Klein and van Lotestijn (1996). The response of the N_2O flux to rainfall in June 1992 is a good example of a threshold being reached; the flux beforehand was almost zero despite the high temperature and high soil mineral N. Figure 7 also shows that there is probably a low threshold for mineral N concentration, but that the highest fluxes tend to occur at high N concentrations. This is particularly true for the U/AN/AN sequence.

At very high values of WFPS, above 90%, there was evidence of a decrease in the N_2O flux. In these conditions the dominant factor is likely to be the reduction in gas diffusivity in the soil, inhibiting the escape of N_2O and enhancing the probability of its reduction to N_2. The trend visible here in Figs. 6 and 7 is compatible with the work of Focht (1978), who found comparable reductions in soil profile N_2O concentrations at very low soil water tensions, which correspond to high WFPS values. Figure 6 indicates that for AN, the WFPS threshold for the decline in N_2O emissions was lower in warmer summer conditions than in the cool spring. This suggests that increased soil respiration at the higher temperatures, with a concomitant increase in the size of anaerobic zones present (Tiedje et al. 1984), is also a factor contributing to the reduction of N_2O to N_2.

Figure 6 shows the peaking of the AN fluxes within two temperature ranges corresponding to the spring and summer applications; CN fluxes (not shown) followed a similar pattern. In contrast, AS and U produced most of the N_2O emissions in the higher temperature range, for reasons partly explained above. Although temperature thresholds for N_2O emission have been identified (Ryden 1983; Goulding et al. 1993), soil mineral N was in any case too low for significant N_2O emission to occur during the winter in this study. Application of U in the spring and AN in the summer eliminated the lower temperature emission peak seen in the AN graph and reduced the size of the higher temperature peak compared with that in the U graph, confirming the effectiveness of this strategy.

We are in the process of undertaking a more detailed analysis of the dataset to identify better the determinants of the temporal flux variation.

Our observation of occasional small negative fluxes in the intervals between fertiliser applications is consistent with the findings of Ryden (1981). There is still very little known about the extent to which soils act as a sink for N_2O (Granli and Bøckman 1994).

Slurry usually contains most of its N as NH_4^+. Urea and uric acid may also be present (Granli and Bøckman 1994). Slurry application increases the supply of organic C to the soil (Christensen 1983) and provides additional moisture, both of which favour N_2O emissions especially through denitrification. Most of the "extra" N_2O flux from the SS treatment compared with that from AN only occurred after the June 1993 application (Fig. 2, Table 2). Although overall there was no detectable increase in WFPS in the slurry-treated plots relative to the others, the slurry application in June 1993 closely followed rather than preceded

(as on the other occasions) the spreading of the AN supplement, and this may, by acting as an irrigation event, have provoked the exceptionally high flux by causing more rapid dissolution of the fertiliser granules. Combinations of slurry and AN are common in agricultural practice, and further work is in progress on procedures to minimise the resulting emissions.

The very large difference between the emissions from U and AS, both of them nitrifiable fertilisers, is probably best accounted for by pH effects. The U appears to have been rapidly hydrolysed to NH_4^+, and is likely to have caused alkalinisation (Yadvinder-Singh and Beauchamp 1988). The mean pH in the U plots was approximately 6.0, slightly higher than the control plots, and the pH close to the U granules is likely to have been higher. In contrast, the mean soil pH of the AS plots was only approximately 5.3. Low pH has been shown previously to inhibit nitrification and the production of N_2O (Goodroad and Keeney 1984), and support for this is provided by the low soil nitrate concentrations in the AS plots, reported in the accompanying paper (McTaggart et al. 1997). Conversely, Christianson et al. (1979) have suggested that high N_2O fluxes from U may arise because the high pH values near hydrolysing granules lead to NO_2^- accumulation. Our study failed to show accumulation, but if it were restricted to areas immediately surrounding U granules it may not have been detectable. Also, the NO_2^- concentrations measured in our study may have been underestimates since extraction procedures of the type we used may allow transformation of much NO_2^- to NO_3^- (Stevens and Loughlin 1995).

The relatively high pH in the CN treatments was probably the result of the liming effect of calcium and root anion exchange associated with NO_3^- uptake (Granli and Bøckman 1994). Although there is some evidence that denitrification increases with increasing pH up to neutral or slightly alkaline conditions, above pH 5–6 the denitrification product ratio falls. This might partly explain why the emissions from CN were no higher than those from AN despite the slightly higher pH.

In summary, our data show that N_2O emissions from N fertilisers may vary substantially within and between seasons. They indicate that, at least at similar sites, emissions are likely to be higher from AN and CN than from U in the spring, if conditions are cool and wet, and vice versa in the summer, if warm and wet. Emissions from SS applications may be high in spring and summer, and will be aggravated if the slurry is applied soon after the mineral fertiliser. Emissions from grassland fertilised with AS will probably be lower than when other fertilisers are used, particularly if a low pH is maintained. An alternative to using AS may be to vary the fertiliser type according to the time of year, and the associated environmental conditions, as was done with the U/AN/AN sequence, which produced lower fluxes than those from repeated applications of either individual fertiliser. The total annual emission was 2940 g N_2O-N ha^{-1} (Table 2), not significantly different from the hypothetical emission calculated by adding the emission from the U-only plots for April to June 1993 to that from the AN-only plots for the rest of the

year (3088 g N_2O-N ha^{-1}). This suggests that the type of fertiliser used in one period had little or no impact on the flux during the following period, and thus cumulative fluxes may be calculated for other hypothetical sequences with some confidence. For the sequence AS/CN/CN, the data in Table 2 indicate a total annual emission for 1993–1994 of 1841 g N_2O-N ha^{-1}, less than that observed for the CN-only plot just for the April to June period. In future work it is intended to model current emissions from grassland on the UK and European scales, based on the present pattern of fertiliser use, and potential emissions from alternative fertiliser practices.

Procedures which maximise N-use efficiency are generally those which minimise losses to the environment. Wilson et al. (1994) have utilised a similar approach to that used in this work with the U/AN/AN sequence to optimise N uptake by rice at different developmental stages. It is obviously important that future trials of different fertiliser regimes involve assessment of crop growth and other environmental impacts such as nitrate leaching, before a particular regime is adopted. The regime should be modified according to soil and crop type, and to variation in climatic conditions.

The annual N_2O fluxes observed in this study ranged from 0.2 to 2.2% of the N applied. These values match the mean value of 1.25 ± 1.0% calculated from published data for experiments of at least 1 year's duration (Bouwman 1994; Bouwman et al. 1995), on which the current IPCC assessment for global emissions from fertilised land is based (Cole et al. 1996). Our observation of higher fluxes from a combination of slurry and mineral fertiliser than from the latter alone, and the level of emissions from our unfertilised control plots, is also in accord with the findings of Bouwman's (1994) review, although our control values were in the lower part of the range he cited. In general, this study provides additional support for the IPCC assessment, which recognises much more clearly than an earlier assessment (Watson et al. 1990) that globally significant emissions occur from fertilised land.

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