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Nitrous oxide production and denitrification in Scottish arable soils

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SUMMARY

Nitrous oxide (N_2O) emissions and concentrations in the soil atmosphere were measured at a number of sites of differing soil type in south-east Scotland between 1985 and 1988. Concentrations followed log-normal distributions and were significantly affected by soil type, tillage treatment, and nitrate application rate. The shape of the profiles suggested significant consumption in the upper 5 cm, making calculations of emission rates using Fick's Law unsatisfactory. Emission rates measured using closed flux chambers were at least one order of magnitude smaller from heavier-textured arable soils than from lighter ones.

Denitrification fluxes measured by field application of the acetylene inhibition technique were lowest in a clay loam, and highest in an alluvial sandy loam; this was attributed to a failure to achieve a satisfactory distribution of acetylene in the heavier soil. Denitrification rates in soil cores generally exceeded measured surface fluxes; incubation at decreased oxygen concentrations typical of those measured in the field produced a further significant increase. Core incubation should be used as an alternative to *in situ* field measurement only if the oxygen concentration in the incubation vessels is adjusted to mimic that in the field; otherwise denitrification rates may be significantly underestimated.

INTRODUCTION

There is a need to quantify the emission of N_2O from soils because of its contribution to the greenhouse effect (Bouwman, 1990) and its role in the destruction of stratospheric ozone (Crutzen, 1981). Denitrification in poorly aerated soils is a major source of N_2O (Bouwman, 1990). Quite apart from its effects on the atmosphere, denitrification results in a diminution of the pool of soil-N available to the plant or for leaching. Soil structure, texture and water content, and the concentration and form of mineral-N are all significant factors: denitrification occurs when nitrate is present in anaerobic microsites, which develop wherever the microbial demand for O_2 exceeds the diffusion-mediated supply (Arah & Smith, 1989). This may occur where O_2 diffusion is impeded by water, either at the centres of soil aggregates (Smith, 1980) or in saturated regions within a structureless soil (Arah, 1988), or wherever the local O_2 demand is exceptionally high (Parkin, 1987). Losses can be considerable (Ryden *et al.*, 1978; Egginton & Smith, 1986b; Myrold, 1988). Between 1985 and 1988 we investigated N_2O production and denitrification in several arable soils in south-east Scotland. This followed an earlier study in grassland soils (Egginton & Smith, 1986a,b).

Production and emission of N_2O do not necessarily occur in step; N_2O produced at depth can be reduced to molecular nitrogen (N_2) on its way up the soil profile, especially when diffusion is slow. Concentrations recorded at depth reflect the outcome of a competition between N_2O reduction and escape. Here we report measured N_2O concentration profiles and surface fluxes measured using

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closed chambers. Fluxes estimated from Fick's Law are compared with those measured at the surface.

We proposed to monitor denitrification rates in the field using a modification of the standard acetylene inhibition technique (Ryden *et al.*, 1979a,b; Ryden & Dawson, 1982). In response to problems that became apparent as the work progressed, in 1986 we supplemented the field method with a core incubation technique similar to that described by Aulakh *et al.* (1984) and Ryden *et al.* (1987). Our results are presented in this paper, together with a critical review of the measurement techniques employed.

EXPERIMENTAL SITES AND METHODS

Field sites

Four sites were employed, all on the Edinburgh School of Agriculture's land at the Bush Estate near Penicuik, 13 km south of Edinburgh. Meteorological data were obtained from the Bush Estate weather station. Site characteristics are listed in Table 1.

Table 1. Description of experimental sites

Site	Bush House	Croft Field	Glencorse Mains	South Road	South Road
Map reference	NT246633	NT246652	NT236627	NT262633	NT262633
Date	1986	1988	1987–1988	1985–1988	1985–1988
Soil series	Darvel	[a]Alluvium	Winton	Macmerry	Winton
Topsoil texture	SL	SL	CL	L	CL
sand (%)	66.5	59.9	43.0	49.5	47.5
silt (%)	23.7	28.1	33.0	35.2	35.3
clay (%)	9.8	12.0	24.0	15.2	17.4
Organic matter (%)	3.3	4.6	4.8–6.0	4.4	3.3
pH	5.9	6.0	6.2–6.7	6.6	6.5
Crop	spring barley	none	spring barley	winter barley	winter barley

[a]Unclassified alluvial deposit

Bush House. This experimental plot was divided into eight sub-plots, half of which were compacted by tractor wheels after sowing to investigate the effect on aeration and denitrification. Fertilizer was applied as ammonium nitrate at two rates (100 kg N ha^{-1} and 160 kg N ha^{-1}).

Croft Field. This site is located on the School of Agriculture's Boghall Farm. Equipment was installed on an area of bare unfertilized soil adjacent to a potato crop. Fertilizer was later applied as calcium nitrate at 0 kg N ha^{-1} and 100 kg N ha^{-1}.

Glencorse Mains. This site is divided into hydrologically isolated plots (Redman *et al.*, 1989; Vinten *et al.*, 1991). Fertilizer was applied as ammonium nitrate to duplicate plots at rates of 0, 75 and 150 kg N ha^{-1}, and there was an additional treatment involving incorporation of 300 kg N ha^{-1} as organic N from a leguminous green manure (forage peas) in September 1987.

South Road. This is the site of a long-term tillage experiment with two main blocks (Pidgeon, 1980; Smith *et al.*, 1984, 1988; Ball *et al.*, 1988, 1989). One block is located predominantly on the Macmerry soil series, the other is a Winton/Macmerry complex. Investigations on the latter block were located on areas of Winton soil. During the period of this study the crop was winter barley. Most of the work reported here took place on plots under two tillage treatments (long-term direct-drilling and conventional ploughing) and two spring N-application rates, which we termed Low N and High N. All plots received 60 kg N ha^{-1} at the end of October and 50 kg N ha^{-1} in mid-March; in early April the Low N plots received an additional 100 kg N ha^{-1} and the High N plots received 175 kg N ha^{-1}. Fertilizer was applied as ammonium nitrate.

Measurement of N_2O concentration profiles

Probes were constructed to allow sampling of the soil atmosphere. Consisting of cylindrical sintered bronze chambers some 10 cm^3 in capacity attached to 3 mm (outside diameter) copper tubes equipped with taps at the soil surface, these probes were smaller and cheaper than those employed in previous studies (Dowdell *et al.*, 1972; Egginton & Smith, 1986a), they caused less disturbance to the soil, and they more closely approximated to the volume of real pores. Gas samples taken in 1 cm^3 glass syringes, which were found to be satisfactorily airtight when greased, were analysed within 24 h of sampling by gas chromatography. A Philips PU4500 instrument equipped with a Porapak Q column and an electron capture detector (ECD) was used for measuring N_2O. Concentrations of O_2, CO_2 and acetylene were measured using a thermal conductivity detector (TCD) after separation on parallel columns of Porapak Q and molecular sieve 5A (Smith & Arah, 1990); an automated sample injector based on a 2 × 20-port rotary valve permitted the unattended analysis of up to 40 samples.

Concentration gradients were determined by sampling the soil atmosphere at depth (usually 5, 20 and 40 cm). A separate series of experiments was performed to determine the gaseous diffusion constants of intact soil cores at various moisture tensions (Ball *et al.*, 1981). These data were employed to calculate N_2O fluxes using Fick's Law.

Flux chambers for measurement of gaseous emissions

Closed chambers were employed for the present study. The larger the chamber the more representative is the area it covers; we made our chambers as large as possible subject to the constraints of portability. Sixteen chambers, 70 cm square, were constructed in two parts: a sheet steel frame 15 cm deep permanently installed to a depth of about 5 cm, and a lid which could be clamped onto the frame to form an airtight seal. Flanged extension sections ('chimneys') some 30 cm high could be inserted between the lid and the frame to accommodate the crop as it grew. Each lid was equipped with a sampling port and a flexible plastic window to transmit atmospheric pressure fluctuations to the soil (Hutchinson & Mosier, 1981). No account was taken of the possible effects of heating of the soil, since the chamber lid was usually in position for no more than a few hours. Samples for gas chromatographic analysis were extracted at regular intervals (usually 0, 30, 60 and 120 min) after closure of the lid. N_2O flux was calculated from the initial rate at which the concentration in the chamber increased.

Addition of acetylene

Outer frames, 1 m square, were installed around the 70 cm square flux chambers. To these frames could be attached transparent perspex canopies tall enough (40 cm) to accommodate the crop throughout most of the growing season. Acetylene was passed through the canopies at a rate sufficient to maintain a concentration above the microplots of approximately 20% by volume. Diffusion of acetylene into the soil was monitored by gas sampling at depths of 5, 20 and 40 cm. Sampling probes were installed in the guard area between the inner and the outer frames. The combined acetylene addition/flux chamber apparatus is illustrated in Fig. 1.

Core incubation

Sixteen 1.5-dm^3 resealable Kilner-type preserving jars were equipped with gas sampling ports and tested for air-tightness. Intact cores, some 3.5 cm in diameter, taken from 0–10 cm and 10–20 cm were incubated, five per jar, for a period of 24 h at the mean temperature recorded in the field over the previous few days. The enclosed atmosphere contained 10% acetylene by volume. At the end of the incubation period duplicate 1 cm^3 gas samples were withdrawn by syringe for N_2O analysis by gas chromatography. For comparison with measured surface fluxes, core denitrification rates were scaled up on an areal basis. We assumed an active layer of 20 cm, taking no account of processes below this depth; our measurements represent lower limits to the field denitrification flux. In the majority of cases no attempt was made to control the O_2 concentration in the incubation vessels,

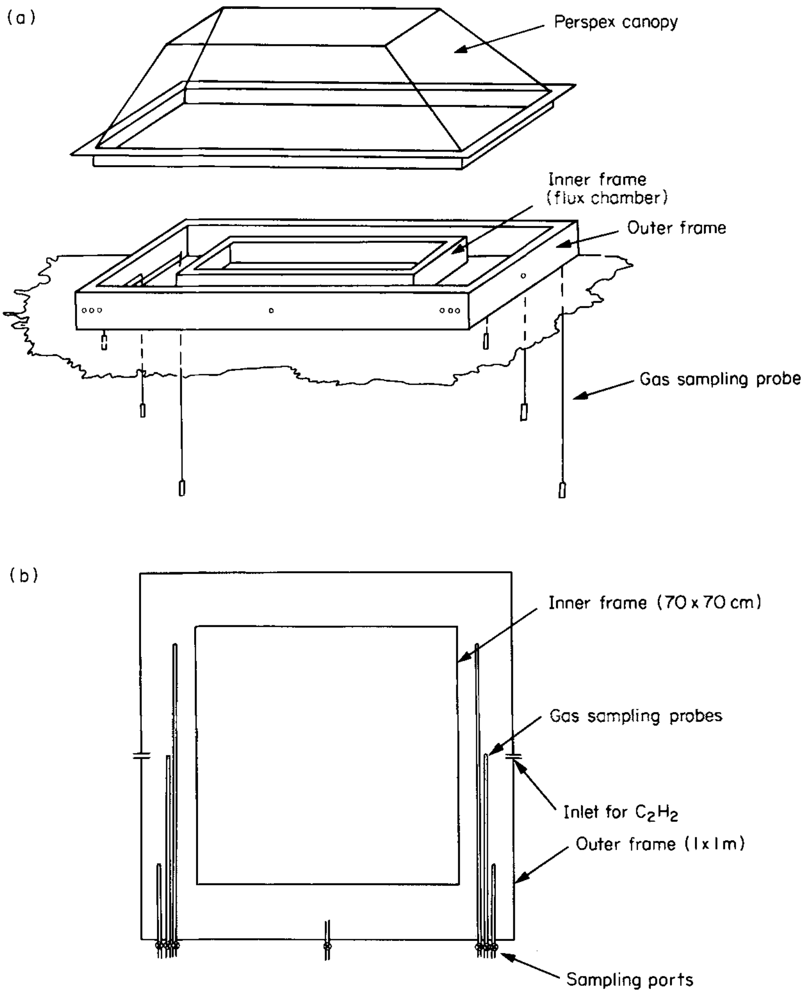

Fig. 1. Apparatus for field application of acetylene and measurement of gaseous emissions from soil: (a) 'exploded' view showing perspex canopy for covering soil and crop during application of acetylene; (b) plan view showing location of gas sampling probes in guard area between frames.

which remained close to atmospheric throughout. However, in an exploratory investigation conducted on soils from the South Road and Croft Field sites, the O_2 concentration in the vessels was manipulated by flushing with standard O_2/N_2 mixtures to cover the range of O_2 concentrations (3–21%) encountered at coring depth in the field.

RESULTS AND DISCUSSION

N_2O concentrations

Concentrations of N_2O in 1 cm^3 gas samples taken from duplicate sampling probes installed at depths of 5, 20 and 40 cm in 16 experimental plots at the South Road site were determined at intervals between 24 May 1985 and 21 August 1986. The probes were removed so that the crop could be harvested at the end of July 1985, and re-installed after sowing the next crop in October. Measured concentrations showed a highly skewed, approximately log-normal distribution; such a distribution was also observed by Egginton & Smith (1986a). Separate four-way analyses of variance were performed on the log-transformed concentrations recorded at each depth in order to

Table 2. Analysis of variance of log-transformed N_2O concentrations

Depth (cm)	Source of variation	Degrees of freedom	Sum of squares	Variance ratio
5	Date	25	147.3	29.4**
	Soil	1	1.7	8.4**
	Tillage	1	1.0	4.9*
	Nitrate	1	—	—
	Date.Soil	25	14.5	2.9**
	Soil.Tillage	1	1.1	5.3*
	Date.Soil.Tillage	25	7.7	1.5*
	Residual	648	129.9	
	Total	830	327.0	
20	Date	25	367.9	34.9**
	Soil	1	2.9	6.9**
	Tillage	1	19.3	45.8**
	Nitrate	1	0.2	0.5
	Date.Soil	25	30.7	2.9**
	Date.Tillage	25	24.5	2.3**
	Date.Nitrate	25	18.4	1.7*
	Tillage.Nitrate	1	3.0	7.1**
	Date.Soil.Tillage	25	18.7	1.8*
	Residual	649	273.4	
	Total	831	776.7	
40	Date	25	301.6	23.9**
	Soil	1	—	—
	Tillage	1	3.0	5.9*
	Nitrate	1	0.7	1.5
	Date.Tillage	25	37.7	3.0**
	Tillage.Nitrate	1	12.5	24.8**
	Date.Soil.Tillage	25	19.6	1.6*
	Residual	649	327.7	
	Total	831	753.7	

*Probability of arising by chance less than 0.05; **probability of arising by chance less than 0.01.

determine the relative significance of the effects of sampling date (Date), soil type (Soil), nitrate application rate (Nitrate) and tillage treatment (Tillage). Results are summarized in Table 2.

Soil type had a highly significant effect ($P<0.01$), tillage treatment was significant ($P<0.05$), and the rate of nitrate application had no significant effect on the N_2O concentration at 5 cm. There was a highly significant interaction between Date and Soil (an effect of soil type which altered with time), and significant interactions between Soil and Tillage (an effect of the tillage treatment differing between the two soil types) and between Date, Soil and Tillage (the same, but varying with time). Fig. 2a shows the N_2O concentration at 5 cm as a function of sampling occasion for the four soil/tillage combinations in the 1986 growing season, during which most of the trends visible elsewhere were best represented. Each point represents the geometric mean (appropriate for a log-normally distributed variable) of eight individual measurements. It is apparent that in all cases

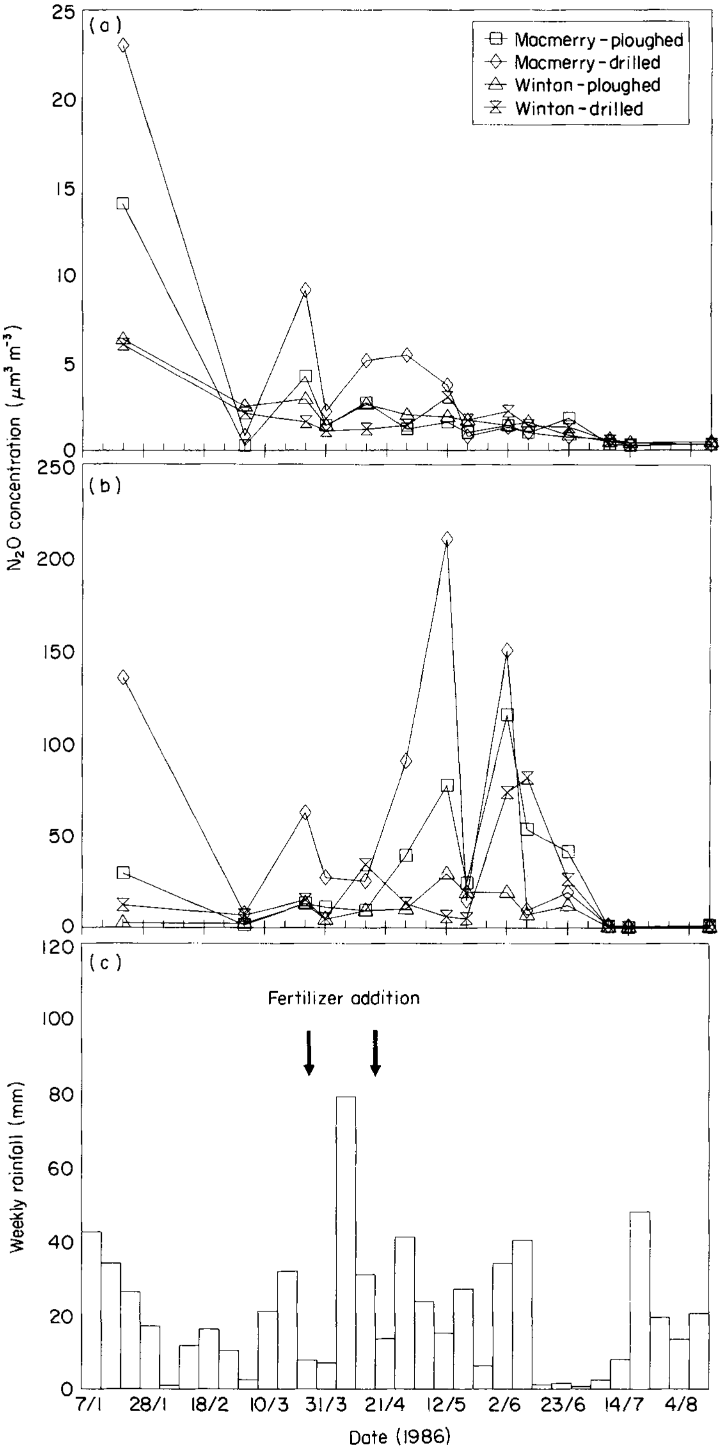

Fig. 2. N_2O concentrations recorded in soil atmosphere, South Road, 1986: (a) 5 cm depth; (b) 20 cm depth; (c) weekly precipitation.

there was a fall from high concentrations between January and March, a transient increase between March and April possibly in response to the application on 18 March of 50 kg N ha^{-1} of nitrate to all plots, and a more gradual increase followed by a fairly steady decline after the final application of fertilizer on 9 April. The highest concentrations were found in the direct-drilled plots on the Macmerry soil, and the lowest generally on the direct-drilled Winton. Ploughing decreased the N_2O concentrations recorded at 5 cm in the Macmerry soil and increased it in the Winton.

N_2O concentrations at 20 cm (Fig. 2b) were highly significantly affected by sampling occasion, soil type, and tillage treatment. There were also highly significant interactive effects between Date and Soil, Date and Tillage, Tillage and Nitrate, and significant interactions between Date and Nitrate and between Date, Soil and Tillage. Fig. 2b shows the same general trends of rise and decline as Fig. 2a, with the addition of a second transitory increase in N_2O concentration in June. This second summer peak was not reflected in the concentrations recorded at 5 cm, perhaps because the surface soil by this time may have been too dry to restrict the escape of N_2O to the atmosphere. Concentrations at 20 cm were, in general, about an order of magnitude greater than those recorded at 5 cm, reflecting the greater rate of N_2O production at depth and the increased difficulty it has in escaping. Concentrations in the Macmerry soil tended to be higher than those in the Winton, and concentrations in the direct-drilled plots generally exceeded those in the corresponding ploughed ones, in contrast to what was observed at 5 cm.

Concentrations at 40 cm (not shown) were generally slightly higher than those recorded at 20 cm, and remained elevated for longer; there was a third peak at the end of June which was not observed at 20 cm. There was, as at 5 cm and 20 cm, a highly significant effect of Date, and a significant Tillage effect. Interactive effects between Date and Tillage and between Tillage and Nitrate were also highly significant. Soil type, however, had no discernible effect.

N_2O fluxes

Fick's Law calculations. Diffusion coefficients measured at a moisture tension of 6 kPa are presented as dimensionless diffusion coefficients (diffusion coefficients measured in the soil divided by that in free air) in Table 3. Diffusion coefficients in the Macmerry and Winton soils are not particularly sensitive functions of moisture tension around field capacity, and moisture contents at South Road tend to be close to field capacity throughout most of the growing season (B. C. Ball, personal communication). The values in Table 3 represent average values for the whole season; they were employed to calculate N_2O fluxes from the Fick's Law relationship:

$$J(z,t) = D(z,t)\delta C(z,t)/\delta z \tag{1}$$

where z is the depth, t is the time, $J(z,t)$ is the flux per unit surface area, $D(z,t)$ is the diffusion coefficient and $C(z,t)$ is the concentration of the diffusing substance. The bulk concentration $C(z,t)$ is proportional to the concentration $C_p(z,t)$ measured in the sampling probes, assuming that these are representative of the air-filled pores in the soil:

$$C(z,t) = \varepsilon(z,t)C_p(z,t) \tag{2}$$

where $\varepsilon(z,t)$ is the air-filled porosity of the soil.

Calculated N_2O fluxes between 20 and 5 cm were integrated by linear interpolation to obtain total N_2O losses during the 1986 growing season. The 20–5 cm, rather than the surface (5–0 cm), fluxes were employed because the diffusion coefficients reported in Table 3 refer to cores taken from depths of 10–15 cm. Losses from the Macmerry soil amounted to some 6 to 7 kg N ha^{-1}, and by the end of the season less had been lost from the direct-drilled than from the ploughed plots; losses from the Winton soil were insignificant. At first sight, these results are somewhat surprising: it was expected from previous studies on the recovery of ^{15}N-labelled fertilizer (Smith *et al.*, 1984) that denitrification would be more significant in the Winton than in the Macmerry soil, and more important in the direct-drilled than in the ploughed plots. However, (i) calculated fluxes depend on the values of $D(z,t)$ and $\varepsilon(z,t)$ used in the calculation, and these could not be measured at the same time as the concentration profiles, and (ii) high denitrification fluxes need not entail high N_2O fluxes. When analogous calculations were performed using the 5–0 cm concentration gradient data the apparent losses amounted to no more than half of those above, suggesting that N_2O consumption occurred in the upper few cm of the field.

Fick's Law has been used to calculate field N_2O fluxes by Rolston *et al.* (1976), Mosier & Hutchinson (1981) and Egginton & Smith (1986a), amongst others. The necessary equipment is relatively cheap, and there is very little disruption to the soil in the course of an investigation (serious disruption occurs only when the probes are installed). Fluxes at depth may be estimated from concentration profiles; the depth of the most significant zone of N_2O production may thus be determined (Goodroad & Keeney, 1985), offering some insight into the mechanics of denitrification.

Table 3. Diffusion coefficients and air-filled porosities at South Road (23 May 1986); moisture tension 6 kPa

Soil	Tillage	Diffusion coefficient, D/D_0	Air-filled porosity, ε
Macmerry	Ploughed	0.0541	0.232
Macmerry	Direct-drilled	0.0254	0.187
Winton	Ploughed	0.0182	0.115
Winton	Direct-drilled	0.0086	0.122

From Ball *et al.* (1989).

Table 4. Measured surface N_2O flux at South Road, 1–8 July 1985

	N_2O flux (g N ha^{-1} d^{-1})			
	Plough		Direct-drill	
Soil	Low N	High N	Low N	High N
Macmerry	1.1 (2.5)	1.6 (2.5)	1.6 (−0.5)	1.6 (−0.5)
Winton	1.1 (0.1)	0.5 (0.1)	1.1 (−1.5)	1.1 (−1.5)

Figures in parentheses are calculated Fick's Law fluxes between 20 and 5 cm.

The method is not entirely appropriate, however, for the determination of fluxes through a heterogeneous medium (such as an aggregated soil) of a substance (such as N_2O) that is both produced and consumed in discrete microsites. In such a medium, coherent variation occurs on scales smaller than the minimum practicable distances (about 5 cm) between sampling points, and the relationship between measured concentration (C_p) and bulk concentration (C) is unlikely to be as simple as that in Equation (2). The evidence cited above for consumption of N_2O near the soil surface at the South Road site suggests that Fick's Law calculation is an unsatisfactory method of estimating fluxes in these soils. The method is likely to be more successful in more physically homogeneous soils. It is intended to test this hypothesis at the Croft Field and Bush House sites. The method ideally calls for the simultaneous measurement of diffusion coefficients, air-filled porosities and concentration gradients in the field: a technique for the field measurement of gaseous diffusion coefficients has been evaluated by Jellick & Schnabel (1986), but it has yet to be widely adopted.

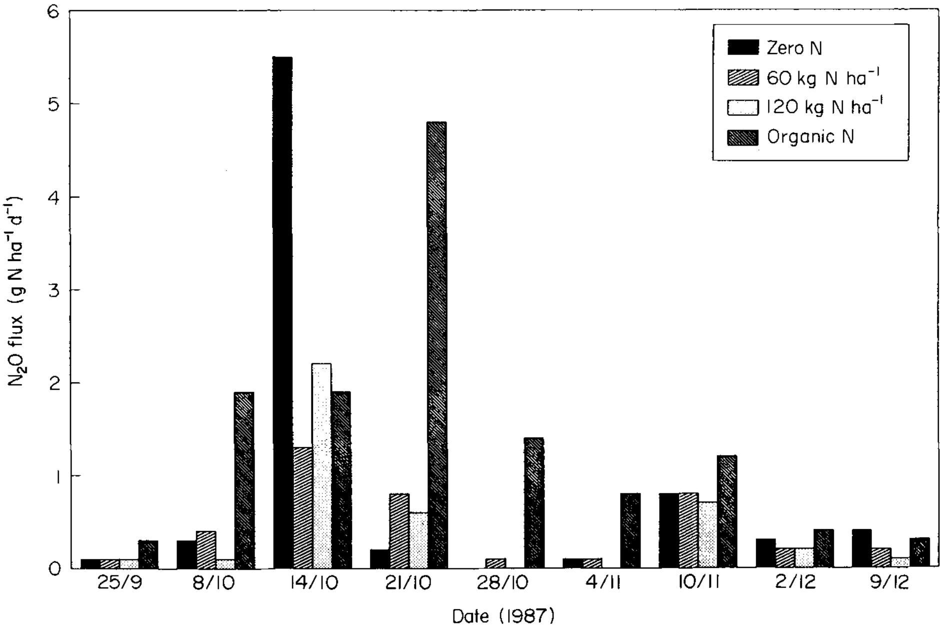

Fig. 3. Surface N_2O flux measured using closed chambers, Glencorse Mains, autumn 1987.

Table 5. Measured surface N_2O flux at Croft Field in autumn 1988

	N_2O (g N ha^{-1} d^{-1})	
Date	Zero N	100 kg N ha^{-1}
25/8	0.5	
29/8	1.1	
30/8	0.2	
1/9	1.4	
7/9	224	
13/9	0.5	
3/10	1.6	8
10/10	18.7	85
18/10	5.4	167
25/10	17.1	89
1/11	2.7	143

Flux-chamber measurements. N_2O fluxes from the soil surface were measured at South Road using closed chambers at intervals during 1985. Results from early July, the only occasion on which the fluxes were measurable, are presented in Table 4, together with the 20–5 cm Fick's Law fluxes calculated for the same dates. The resolution of these measurements is approximately 0.6 g N ha^{-1} d^{-1}. There was little relationship between measured and calculated fluxes, although the numbers were at least all of the same order of magnitude. No flux exceeded 1.6 g N ha^{-1} d^{-1}. It is apparent from the high concentrations recorded at depth that there was significant production of N_2O in these plots; the fact that it was not observed emerging from the soil surface strongly suggests that it was further reduced to N_2 before it could escape.

Table 6. Surface denitrification flux at South Road in spring 1985

	Denitrification flux (g N ha^{-1} d^{-1})			
	Macmerry		Winton	
Date	Normal plough	Direct-drill	Normal plough	Direct-drill
24/4	1.3	1.3		4.0
3/6			1.4	5.4
21/6			3.4	2.7
24/6	3.4	2.7		
1/7	2.8	3.9		
7/7			4.1	4.4

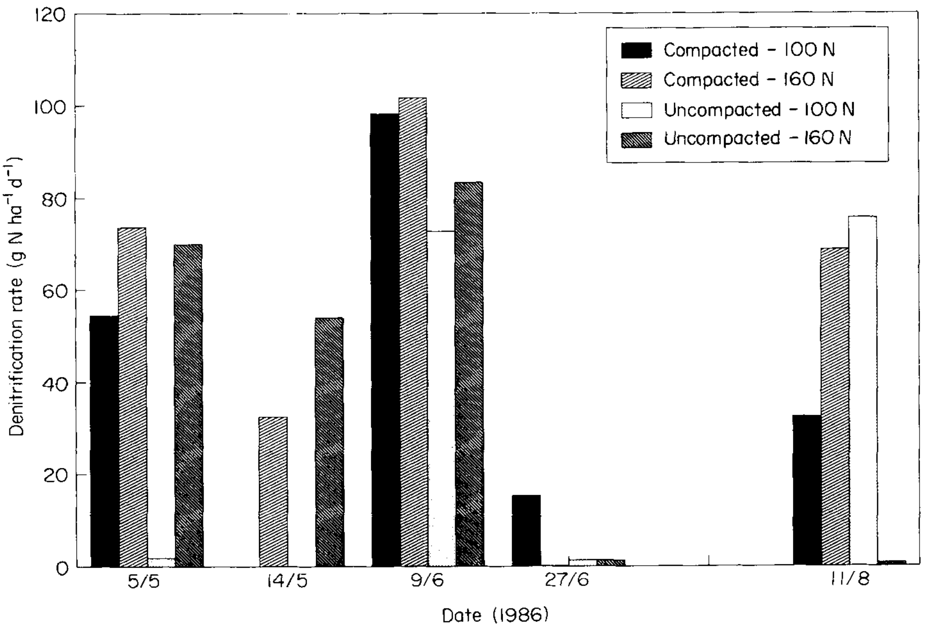

Fig. 4. Surface denitrification flux measured using acetylene inhibition, Bush House, 1986.

Fig. 3 shows the geometric means of duplicate N_2O surface flux measurements made at the Glencorse Mains site following removal of the crop in autumn 1987. These fluxes are marginally greater than those recorded in early summer 1985 at South Road, and except on one occasion are greatest from the green-manured (organic N) plots. Nitrate concentrations at the start of the measurement period ranged from 1.0 to 1.5 μg N g^{-1} soil, with no significant difference between treatments; moisture contents were also similar. Flux differences were probably attributable to different concentrations of oxidizable organic matter in the various treatment areas, and also perhaps to enhanced nitrification in the organic N plots.

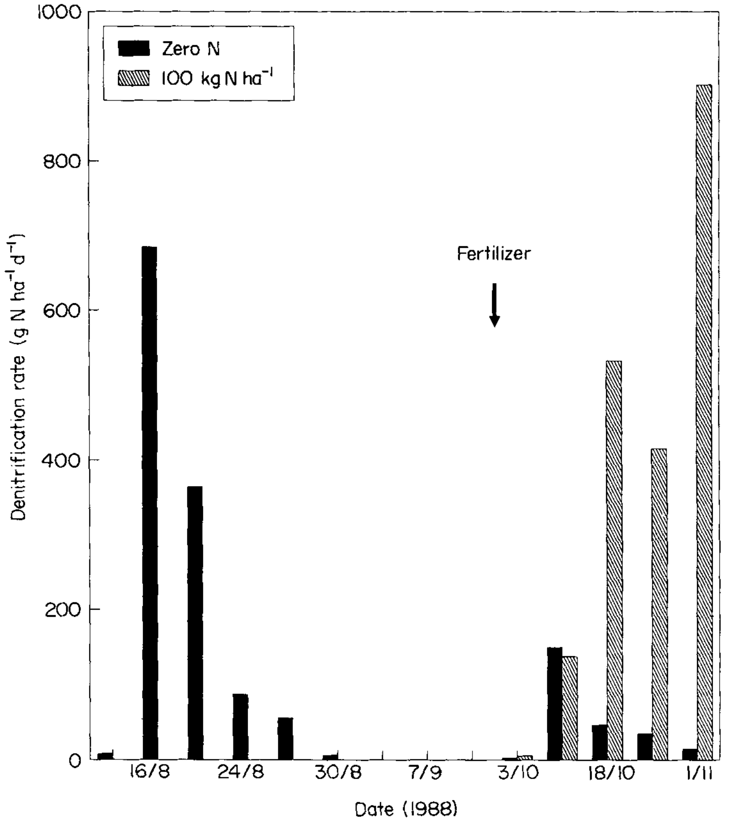

Fig. 5. Surface denitrification flux measured using acetylene inhibition, Croft Field, 1988.

N_2O flux measurements made on the alluvial soil at Croft Field in autumn 1988 are shown in Table 5. Once again, these are geometric means of duplicate measurements. Nitrate concentrations in the unfertilized plots averaged 6.4 µg N g^{-1} soil over the course of the investigation, with a peak of 9.4 µg N g^{-1} coinciding with the exceptionally high flux of 225 g N ha^{-1} d^{-1} recorded on 7 September. The gravimetric moisture content on this date was also high, at 25.3%. Fluxes from the fertilized plots, to which 100 kg N ha^{-1} was added as calcium nitrate at the beginning of October, were almost two orders of magnitude greater than those recorded on the heavier soils at South Road and Glencorse Mains.

Both 'closed' and 'open' chambers for flux measurement have their protagonists. Matthias *et al.* (1980) favoured the closed chamber (used in our work) on account of its simplicity and its relatively low cost, as did Hutchison & Mosier (1981), provided that a vent is included to allow transmission of pressure fluctuations to the atmosphere inside the chamber and an alteration (to allow for the accumulation of N_2O) is made in the equation for calculating flux. Ryden *et al.* (1978) and Denmead (1979) preferred open chambers in which N_2O is not allowed to accumulate. Jury *et al.* (1982) concluded, after mathematical simulation of the processes involved in both open- and closed-chamber techniques, that 'in many cases, neither measurement relates well to the N_2O production rate' because diffusion through the soil is so slow. They suggested that it might be necessary to monitor the soil for several weeks to trap all the products of a single transient denitrification event at depth. The log-normal spatial distribution of N_2O flux expected in most soils (Folorunso & Rolston, 1984) calls for considerable replication in any experiment designed to evaluate field emission rates with any degree of confidence. Where resources are limited the simpler and cheaper closed-chamber method seems preferable.

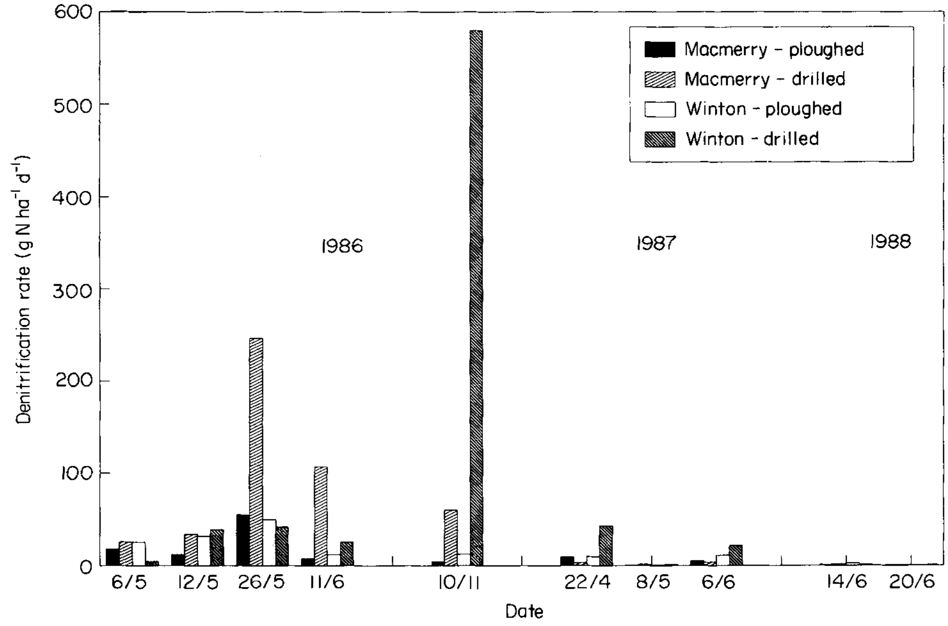

Fig. 6. Denitrification flux measured by core incubation, South Road, 1986–88.

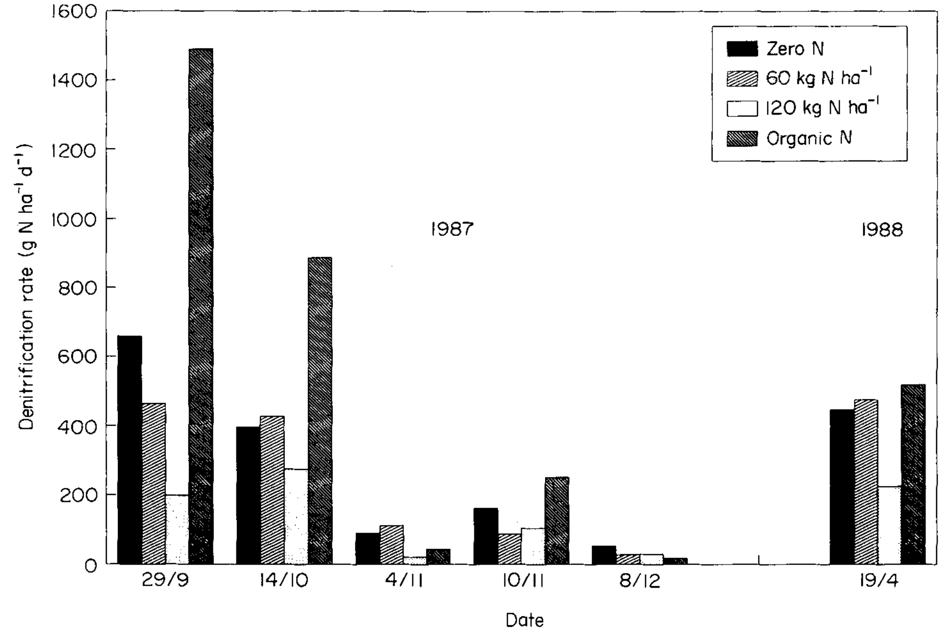

Fig. 7. Denitrification flux measured by core incubation, Glencorse Mains, 1987–88.

Denitrification rates

Flux-chamber measurements. N_2O fluxes recorded following acetylene treatment at South Road are presented (geometric means of duplicate measurements) in Table 6. Soil type, tillage treatment and fertilizer application rate produced no significant effects, and on no occasion did the rate exceed

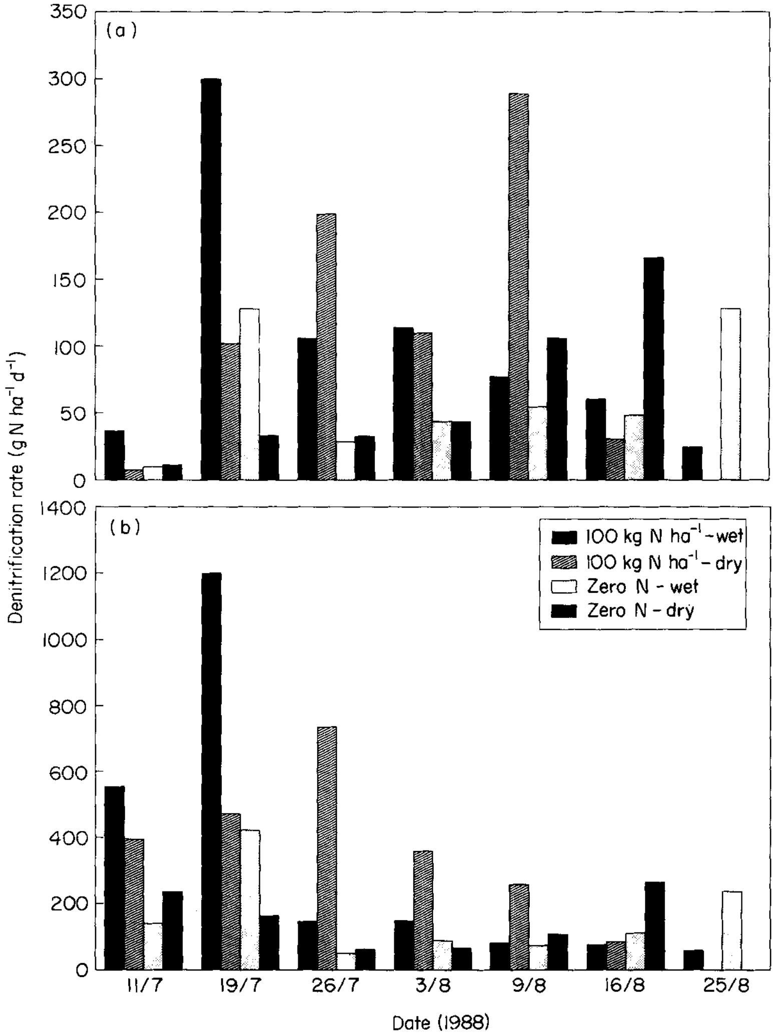

Fig. 8. Denitrification flux measured by core incubation, South Road, Winton soil, summer 1988: (a) cores incubated at atmospheric oxygen concentration; (b) cores incubated at decreased oxygen concentrations (3–12% by volume).

5.5 g N ha^{-1} d^{-1}. This was somewhat surprising in view of the nature of the soils at this site (an imperfectly-drained loam and a poorly-drained clay loam) in which leaching was unlikely to have been a very important cause of N loss; in a parallel study (Smith *et al.*, 1988) very low recoveries of ^{15}N-labelled nitrate fertilizer by the barley crop were measured (12–51% in 1985, and only 8–24% in 1986). The probable explanation of these small recorded fluxes is a failure to inhibit N_2O reduction. Sampling and analysis of the soil atmosphere beneath the chambers in spring 1985 showed that inhibitory concentrations (0.1% by volume) of acetylene were not obtained at 20 cm until some 9 h had elapsed. Moreover, these were not necessarily representative of those in the soil as a whole; if it takes 9 h for acetylene to diffuse through the large pores, then it is likely to take even longer for it to diffuse through the smaller (and possibly saturated) pores within denitrifying aggregates. A period of acetylene treatment of at least 12 h is indicated. In addition to possible effects on the soil microflora, this poses several practical problems: the crop can be damaged; small portable acetylene cylinders run out in a matter of hours; it is difficult to transport larger cylinders to the field and

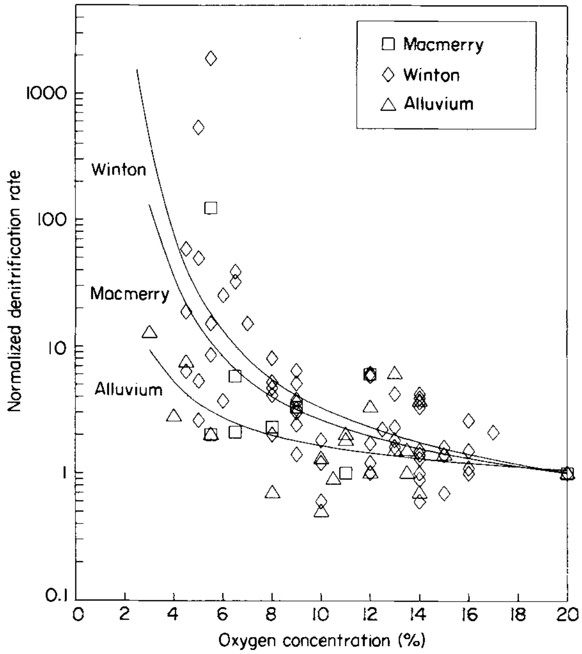

Fig. 9. Relationship between oxygen concentration in incubation vessel and measured denitrification rate, South Road and Croft Field, 1988.

unwise to leave them overnight in a site accessible to the public. A further problem is that if acetylene diffusion down through the soil is a slow process, then so will be the diffusion of N_2O up from depth.

The Darvel soil at Bush House is sandier, stonier, and less aggregated than the two South Road soils. We established early in April 1986 that acetylene diffusion was much more rapid at this site. N_2O fluxes following a period (between 1 h and 3 h) of treatment with acetylene are presented in Fig. 4. There was no consistent pattern to these fluxes, except that they were generally 10 to 20 times greater than those recorded at South Road.

Geometric means of duplicate measurements of denitrification flux made on the alluvial soil at Croft Field in autumn 1988 are shown in Fig. 5. This soil, intermediate in texture between those at South Road and the Darvel soil at Bush House, permitted relatively rapid diffusion of acetylene down the profile. Measured rates were considerably higher than those in the sandier soil, and more than two orders of magnitude greater than those obtained at South Road.

Acetylene is usually added in the field by radial diffusion from vertical supply tubes installed around the edge of the flux chamber (e.g. Ryden & Dawson, 1982). However, where the area to be treated is as large as 70 cm square, this method offers no advantage over addition by downward diffusion from a reservoir at the soil surface. In either case the maximum distance between the supply and the target area of interest is about 30 cm (assuming that denitrification is largely confined to the upper horizons of the soil). Addition of acetylene by downward diffusion has the potential to achieve more uniform concentrations in the soil under the reservoir because the entire surface is exposed to the gas. The soil is not physically disturbed; some damage to the crop is unavoidable, but it may be minimized by increasing the number of replicate plots and treating each one infrequently. Moreover, with no vertical supply tubes inserted into the soil there is no possibility that these may act as O_2 sources, altering the aeration of the soil under the chamber, or as preferred routes for the escape of N_2O. We therefore added acetylene by downward diffusion. Our data show that this appeared to be a satisfactory method in the more permeable Bush House and Croft Field soils, but at South Road it failed to work. In view of the low diffusion coefficients and air-filled porosities reported in Table 3, there is no reason to suppose that addition by lateral diffusion would have been any more successful—for some soil conditions no satisfactory method exists.

Core incubations. The core incubation technique was employed to measure denitrification rates at south Road at intervals during 1986, 1987 and 1988. Only the High N (285 kg N ha^{-1}) plots were examined. No attempt was made to duplicate in the incubation vessels the O_2 regime of the field; thus the results presented in Fig. 6 represent lower limits to the true denitrification rates. Denitrification rates in cores taken from the direct-drilled plots were consistently higher than those in cores taken from the ploughed plots; all were around an order of magnitude greater than the surface fluxes recorded above. It is difficult to account for the exceptionally high rate (580 g N ha^{-1} d^{-1}) recorded in the direct-drilled Winton plots in November 1986; such apparently inexplicable variation, presumably caused by the chance conjunction of a number of interactive controlling variables, is typical of denitrification.

Denitrification fluxes from cores taken from the Glencorse Mains site in autumn 1987, and on one occasion in 1988, are presented in Fig. 7. Rates were high immediately following removal of the crop in September, especially so in the organic N plots, to which 300 kg N ha^{-1} had been added as a green manure. Again, the O_2 concentration in the incubation vessels was atmospheric (approximately 21% by volume), so these measurements represent lower limits to the true flux.

In summer 1988 we investigated the effects of decreasing the O_2 concentrations in the incubation vessels to reproduce those measured in the field. We set up a small-scale experiment in the guard area on the Winton soil at South Road: two microplots received 100 kg N ha^{-1} as ammonium nitrate on 5 July; one of these and one of the unfertilized microplots were saturated with water (50 mm) on 11 July. We carried out parallel incubations at atmospheric and at decreased O_2 concentrations. The decreased O_2 concentrations we employed were intended to be representative of those obtaining in the field at the time of the incubation; in practice this was difficult to achieve, because of the essentially unrepresentative nature of any gas sampling probe, because of the enormous spatial variability of O_2 concentrations measured in the field, and because of constraints on analysis time. Thus, our adopted procedure was to incubate the cores at a range of O_2 concentrations typical of those we had observed over the preceding weeks (these were occasionally as low as 3% by volume). Results are shown in Fig. 8. Core denitrification rates in the fertilized plots were significantly higher than those in the unfertilized ones, and the peak occurred sooner and did not last as long in the plot we watered to saturation (labelled Wet in Fig. 8). This was so both for those cores incubated at atmospheric O_2 (Fig. 8a) and for those incubated at decreased O_2 concentrations (Fig. 8b). Rates in the latter, presumably closer to the rates in the field, were roughly four times greater than those in the former.

We also incubated cores from the Macmerry and alluvial soils at decreased O_2 concentrations. Acetylene was present at a concentration of 10% in all incubation vessels. Denitrification rates in cores incubated at atmospheric O_2 concentrations ranged from 0 to 500 g N ha^{-1} d^{-1}; those in cores incubated at decreased O_2 ranged from 0 to 1700 g N ha^{-1} d^{-1}. Results are presented in Fig. 9, in which the denitrification rate measured at decreased O_2 concentrations is normalized (by dividing it by that measured at atmospheric O_2) in an attempt to isolate the effect of O_2. Decreasing the concentration in the incubation vessel had a major impact on the denitrification rate of the incubated cores; the rate increased sharply as external O_2 concentrated decreased. The magnitude of this effect differed from soil to soil, being greatest in the most coarsely structured. The shape of the curves in Fig. 9 is similar to that obtained by Parkin & Tiedje (1984) using a continuous flow incubation technique, although the concentrations at which the denitrification rate rises sharply are different. This is probably due partly to the technique (cores incubated in a static atmosphere are more likely to develop anaerobic microsites even in a comparatively well-aerated matrix than cores incubated in a continuous flow system) and partly to the structures of the different soils employed.

CONCLUSIONS

Soil type, tillage treatment, and nitrate application rate were statistically significant influences on the concentrations of N_2O measured in the soil at South Road in 1985 and 1986. These concentrations were log-normally distributed. Fick's Law calculations indicated N_2O fluxes from the Macmerry (loam) plots 10 to 100 times greater than those from the Winton soil (clay loam), whereas no significant difference was observed between the measured surface emission rates from the two soils. This discrepancy is probably attributable to a combination of factors: the use of inappropriate diffusion coefficients and air-filled porosities in the Fick's Law calculations; and the consumption of N_2O in anaerobic microsites in the upper 5 cm of the soil. Although Fick's Law is not a satisfactory basis for calculating surface fluxes of N_2O from aggregated soils, concentration profiles are of interest in their own right because they indicate zones of N_2O production and consumption.

Measurements of rates of emission of any gas from the soil surface are bedevilled by the problem of spatial variability. Where resources are limited, refinement should be sacrificed in the interest of replication; the simplest and fastest measurement technique (a large closed chamber) is the best. N_2O fluxes measured using 0.49 m^2 flux chambers showed great spatial and temporal variations. At South Road (loam and clay loam) in spring 1985 the maximum observed flux was 2.5 g N ha^{-1} d^{-1}; at the Glencorse Mains site (clay loam) in autumn 1987 it was 5.5 g N ha^{-1} d^{-1}; fluxes from the Croft Field site (sandy loam) in autumn 1988 reached 225 g N ha^{-1} d^{-1}. N_2O fluxes from the heavier-textured arable soils were lower than those from the lighter ones, by at least one order of magnitude. This may be attributable to increased reduction of N_2O to N_2 in the heavier soils.

There is no universally satisfactory method for measuring denitrification. Field application of the acetylene inhibition technique depends on achieving an acetylene concentration greater than 0.1% by volume throughout the soil under study; this is not always possible, and should always be checked. At South Road (loam and clay loam) in spring 1985 the maximum observed denitrification flux was 5.5 g N ha^{-1} d^{-1}, at the Bush House site (sandy loam) in 1986 it was 100 g N ha^{-1} d^{-1}; fluxes from the Croft Field site (sandy loam) in autumn 1988 reached 900 g N ha^{-1} d^{-1}. Measured fluxes from the heavier-textured arable soils were at least a factor of ten lower than those from the lighter ones. This may be attributable to a failure of the measurement technique (non-penetration of acetylene throughout the profile) in the heavier soils.

Denitrification rates in soil cores taken from South Road and incubated at atmospheric O_2 concentrations exceeded those measured at the surface, presumably because of more complete acetylene penetration. Incubation at decreased O_2 concentrations (typical of those measured in the soil) produced a further significant increase, suggesting that core incubation is a satisfactory alternative to field methods only where the O_2 concentration in the incubation vessel is adjusted to that obtaining in the field.

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