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FLUXES OF NITRIC AND NITROUS OXIDES FROM AGRICULTURAL SOILS IN A COOL TEMPERATE CLIMATE

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Abstract—Fluxes of NO and N₂O from sandy loam soils cropped with winter wheat and a clay loam soil under ryegrass, with and without the addition of NH₄NO₃ fertilizer, were measured using static and dynamic chamber methods. Nitric oxide fluxes ranged from −0.3 (deposition) to 6.9 (emission) ng NO-N m⁻² s⁻¹. The corresponding N₂O flux ranged from 0 to 91 (emission) ng N₂O-N m⁻² s⁻¹. The NO flux was temperature dependent. Activation energies ranged from 40 to 81 kJ mol⁻¹. Nitric oxide and N₂O fluxes increased linearly with soil available nitrogen (NH₄⁺+NO₃⁻). Emissions of NO and N₂O were not detectable from unfertilized ryegrass plots. Instead, nitric oxide was absorbed by the soil and vegetation at a maximum rate of 0.31 ng NO-N m⁻² s⁻¹. The aeration state of the soil controlled the relative rates of NO and N₂O emission. Nitric oxide was the major gas emitted from well aerated soils, conditions that favour nitrification. The NO/N₂O emission ratio was >100 for the coarse-textured sandy loam soil and the clay loam soil only during low rainfall periods. Nitrous oxide was the major gas emitted from less aerated soils, conditions that allowed denitrification to occur. The NO/N₂O emission ratio was <0.001 for the clay loam soil when rainfall was high and soils were wet. Extrapolation to the U.K. situation showed that agricultural land may account for 2–6% of the total annual NO emission and for 16–64% of the total annual N₂O emission in the U.K.

Key word index: Static and dynamic chambers, NO emission, NO deposition, N₂O emission, NO/N₂O emission ratio, nitrification, denitrification, soil nitrogen, sandy loam soil, clay loam soil.

INTRODUCTION

Emissions of oxides of nitrogen as nitric oxide (NO) and nitrous oxide (N₂O) from soils are currently attracting interest as sources of important reactants for tropospheric and stratospheric nitrogen chemistry (Crutzen, 1983). Nitric oxide plays a central role in the production of photochemical oxidants and following oxidation to nitric acid contributes to acid deposition in Europe and North America (Logan, 1983; Rothe and Rood, 1986). In industrial regions fossil-fuel combustion provides the main source of atmospheric nitric oxides (NOₓ) (DoE, 1990), but in rural areas, NO produced biologically in soil may provide a significant source of atmospheric NOₓ (Watson et al., 1990). Emissions of nitrous oxide play an important role in the chemistry of the stratosphere and in the longwave exchange of radiation between the Earth's surface and the atmosphere as an infrared absorber (Crutzen, 1981; Warneke, 1988). Nitrous oxide accounts for approximately 5% of the total greenhouse effect (Bouwman, 1990). Its concentration in the troposphere is increasing currently at a rate of 0.2% per year. Soils are the dominant source of N₂O (Watson et al., 1990). Some industrial processes, for example, nylon production, are also important sources for atmospheric N₂O (Thiemens and Trogler, 1991). Biomass and fossil-fuel burning, however, have recently been shown to contribute less than 10% of the global atmospheric N₂O budget (Cofer et al., 1991).

In soils, nitrification, the oxidation of ammonia of nitrate (Bremner and Blackmer, 1981) and denitrification, the anaerobic reduction of nitrate to gaseous forms of N (Payne, 1981), are responsible for most of the NO and N₂O produced. Nitrification is believed to be the main source of biological NOₓ (Anderson and Levine, 1986), Nitrous oxide is a product of both nitrification and denitrification. Nitrification is believed to be the dominant source until soils become very wet (Poth and Focht, 1985). Nitrous oxide produced during nitrification has a greater possibility of being lost from the soil than when produced during denitrification. Under aerobic soil conditions that favour nitrification, soil pores are generally open and allow diffusion of gaseous products to the atmosphere, whereas in conditions that favour denitrification diffusion is impeded and further transformations, eg. N₂O to N₂, may occur (Byrnes et al., 1990). Soil emission rates of NO or N₂O have been studied in a variety of environments (e.g. Sahrawat and Keeney, 1986; Anderson et al., 1988). Only on a few occasions, however, were both gases measured simultaneously (Johansson and Granat, 1984; Slemr et al., 1984; Anderson et al., 1988; Shepherd et al., 1991). The purpose of this project was to investigate emissions of NO and N₂O from agricultural soils and factors controlling the NO/N₂O emission ratio in cool
temperate climates. Here we report field measurements of NO and N,O emission from two contrasting soil types: a heavy clay loam sown with ryegrass and two sandy loam soils sown with winter wheat.

SITE DESCRIPTION

Nitric oxide and N,O fluxes were measured on two types of lowland agricultural soil between April and July 1990:

1. A heavy clay loam soil sown with ryegrass, at Glencorse Mains Farm, 8 miles south of Edinburgh (grid ref. NT 239629).
2. Two sandy loam soils cultivated with winter wheat, at Drylawhill (grid ref. NT 581786) and Howmuir (grid ref. NT 615767), both in East Lothian, 25 miles southeast of Edinburgh.

Glencorse Mains

This was a grassland site where the response of ryegrass to fertilizer application and compaction by agricultural traffic was being studied (Douglas and Crawford, 1992). The soil at Glencorse Mains was an imperfectly drained clay loam of the Winton series (Ragg and Futty, 1967). The pH (CaCl₂) was 4.9. Earlier work by Arah et al. (1991) had shown that denitrification rates were large at this site. The experimental plots employed in this study were those representing the most contrasting soil conditions, both in terms of N availability and likely soil aeration:

(a) plots that received an initial spring application of 150 kg N ha⁻¹ as ammonium nitrate and a similar application following cutting and removal of the crop for silage in June,
(b) plots that had not received any nitrogen fertilizer for the last 3 years.

Drylawhill and Howmuir

These sites were both on commercial farms sown with winter wheat. The soil at Drylawhill was mapped as the Kilmarnock series and at Howmuir as the Winton series. Both soils, however, were of much coarser texture (sandy loam) than the classification of these series would suggest (Ragg and Futty, 1967). The pH (CaCl₂) of the soil was 4.8 and 5.3, respectively. Both fields received three applications of N fertilizer in spring. At Drylawhill a total of 200 kg N ha⁻¹ (as NH₄NO₃) was applied and at Howmuir a total of 150 kg N ha⁻¹ (as nitrochalk, NH₄NO₃+CaCO₃). Flux measurements were made in parallel with measurements of NO, NO₂, O₃ and SO₂ by micrometeorological techniques by colleagues from the Institute of Terrestrial Ecology and the University of Manchester, Institute of Science and Technology. Nitric oxide and N,O fluxes were measured using the open chamber technique approximately 1 week (Drylawhill) and 7 weeks (Howmuir) after the last application of fertilizer. The crop height made use of the closed-chamber method impractical.

EXPERIMENTAL PROCEDURE

Fluxes of NO, NO₂ and N,O from the soil surface were measured using an open-chamber technique. A perspex chamber (Fig. 1) with a ground area of 0.9 m² and a height of 0.72 m was attached to a stainless steel frame, which was inserted into the soil to a depth of at least 30 mm, to prevent...

Fig. 1. A schematic diagram of the flowthrough chamber for NO and N,O flux measurements.
air leaking into and out of the chamber at its sides. Charcoal-filtered air was pushed through the chamber by a speed adjustable fan (800-3750 rpm), allowing flow rates through the chamber to be varied between 50 and 150 litres min\(^{-1}\). The charcoal filter removed \(O_3\) from the ambient air. This was necessary to eliminate reactions between \(O_3\) and NO within the chamber. Ambient NO and \(N_2O\) concentrations were not affected by the charcoal filter. Ozone concentrations in the chamber were monitored continuously and did not exceed concentrations of 2 ppb. Losses of NO, \(N_2O\), and \(O_3\) to the chamber walls were minimal. This was tested by filling the sealed chamber with high concentrations of \(O_3\) or \(NO_2\) (>100 ppb) and then monitoring the decay of the gases. The deposition velocities to the chamber surfaces calculated for \(O_3\) and \(NO_2\) were \(8.3 \times 10^{-6}\) and \(4.1 \times 10^{-7}\) m s\(^{-1}\), respectively. The air inside the chamber was stirred by a second fan. Adequate mixing was provided by a tubular baffle made from a thin aluminium sheet. Concentrations of NO, \(N_2O\), \(O_3\) and O\(_3\) were measured at the air inlet and the air outlet of the chamber. For \(NO\), \(N_2O\), \(O_3\), air was pumped through PTFE tubing at a rate of 700 ml min\(^{-1}\) into a NO-NO\(_2\)-NO\(_{x}\) chemiluminescence analyzer (Thermo Environmental Instruments, Model 42) and at a rate of 2l min\(^{-1}\) into a dual channel UV photometric ozone analyzer (Analytical Automation, Model 427). The chemiluminescence analyzer had a detection limit of 0.3 ppb and a precision of 0.15 ppb for NO. Previous work showed that for very polluted conditions a maximum error of 10% for NO was introduced by conversion of NO\(_2\) to NO. Calibration was performed by diluting 10.3 ppm NO in nitrogen by gas-phase titration using an Environics 5100 calibrator. Inlet and outlet air was sampled at 3-min intervals using a solenoid valve under the control of a data logger (Campbell Scientific, Model 21X). Measurements during the first 2 min were discarded as purge time. Measurements during the third minute were stored by the data logger.

For \(N_2O\) analysis, air was pumped from the chamber inlet and outlet via nylon tubing (6 mm o.d.) through a series of traps at a flow rate of around 150 ml min\(^{-1}\). Perspex pre-columns (350 mm long, 24 mm i.d.) were filled with anhydrous CaSO\(_4\) and soda lime (35 g of each, both self-indicating) to remove \(H_2O\) and \(CO_2\), respectively, from the air stream. Nitrous oxide was adsorbed onto molecular sieves \(5A\) (8-12 mesh) (27 g) held in a separate perspex column (420 mm long, 19 mm internal diameter) which was connected to the pre-column via plastic tubing. The traps were assembled vertically. Molecular sieves were usually replaced after 2-8 h. For overnight measurements two molecular sieve traps were installed in series. Used molecular sieve was stored in gastight glass vials until analysis. Trapped \(N_2O\) was released with distilled \(H_2O\) (50 ml) in 500 ml conical flasks (Rydin et al., 1978). After 15 h equilibration the \(N_2O\) concentration in the head space of the flasks was measured by gas chromatography (Pyre Unicam 104 gas chromatograph fitted with a Tracer 92\(^{15}\)N detector).

Nitrous oxide fluxes were also measured using the closed-chamber technique. A shallow perspex chamber (height 150 mm, volume 0.19 m\(^3\)) with slightly inwardly sloping sides was used. The surface area and the method of attachment to a frame were the same as for the large chamber described above. Gas samples were taken from the sealed chamber at time intervals until a concentration difference between enclosed and ambient air could be measured (usually after 30-120 min). Glass syringes (1 ml) fitted with three-way taps were used for sampling and storage (not more than 3 h) until analysis by gas chromatography.

In the open-chamber system, fluxes \((F)\) of NO and \(N_2O\) were calculated from the concentration differences between inlet \((C_i)\) and outlet air \((C_o)\) (ng m\(^{-2}\)), the flow rate of air through the chamber \((J)\) (m\(^2\) s\(^{-1}\)), and the surface area covered by the chamber \((A)\) (m\(^2\)).

With a flow rate of 50 litres min\(^{-1}\) the minimal detectable NO flux was 0.1 ng N m\(^{-2}\) s\(^{-1}\) and the \(N_2O\) flux (by trapping onto molecular sieve) was 9 ng N m\(^{-2}\) s\(^{-1}\).

For the closed-chamber design \(N_2O\) fluxes were calculated from the concentration differences between the chamber air \((C)\) and ambient air \((C_o)\) (μg m\(^{-3}\)), chamber volume \((V)\) (m\(^3\)), the time for which the chamber was sealed \((t)\) (s) and the surface area covered by the chamber \((A)\) (m\(^2\)).

\[
F = \frac{(C_o - C)J}{A} \quad (1)
\]

\[
F = \frac{(C_o - C)V}{At} \quad (2)
\]

For \(t=60\) min the minimal detectable \(N_2O\) emission was 3 ng N m\(^{-2}\) s\(^{-1}\).

Soil temperature at 30 mm depth inside the chamber and chamber air temperature were measured using chromel-alumel thermocouples. Average temperatures for 3-min time intervals were stored by the data logger.

Soil samples (top 100 mm) were taken every time fluxes were measured. They were analysed for moisture content (weight loss on drying), pH (CaCl\(_2\)) and available \(NH_4^+\) and \(NO_3^-\) (15 g soil extracted with 50 ml 1M KCl) (Crooke and Simpson, 1971; Henrikson and Selmer-Olsen, 1970).

**RESULTS AND DISCUSSION**

**NO emissions and diurnal variations**

Nitric oxide was both emitted from the soil and deposited to it. Deposition was only observed when the soil available nitrogen concentrations were low (<8 mg kg\(^{-1}\) \(NH_4^+\); <1.2 mg kg\(^{-1}\) \(NO_3^-\)) (Table 1). At Drylawhill and Howmuir the NO flux was measured by the chamber method (Table 1) and a micrometeorological approach (Hargreaves et al., 1992). With the chambers the NO flux was measured on four 0.96 m\(^2\) plots near the edge of the field. The micrometeorological approach integrated the NO flux of a 300-1000 m\(^2\) uniform area. Nitric oxide fluxes measured by these two methods were in good agreement. At Drylawhill, NO fluxes measured using the chamber, ranged from 4.7 to 18.6 ng NO-N m\(^{-2}\) s\(^{-1}\) (median 6.91). Using the micrometeorological approach, a NO emission rate of 22 ng NO-N m\(^{-2}\) s\(^{-1}\) was calculated for 12 May 1990. At Howmuir using the chambers, the NO flux ranged from 0.91 to 4.8 ng NO-N m\(^{-2}\) s\(^{-1}\) (median 1.5). The NO flux calculated by the micrometeorological method was 3 ng NO-N m\(^{-2}\) s\(^{-1}\) for 24 June 1990.

A significant correlation between NO emission rate and soil surface temperature (at 3 cm depth) \((r^2 = 0.74, df=179)\) and air temperature \((r^2 = 0.76, df=179)\) was observed. Figure 2 shows a typical diurnal variation of NO emission with changes in soil and air temperature. Plots of the logarithm of the NO emission rate against the inverse absolute soil temperature were linear (Fig. 3). From the slope the activation energy for NO emission was calculated (Table 2). Variations were random, no systematic relationship with crop type or season was observed. Activation energies of similar magnitude were observed by Stiem and Seiler (1984).
<table>
<thead>
<tr>
<th>Crop, location</th>
<th>Date</th>
<th>NO flux*</th>
<th>N₂O flux*</th>
<th>Soil available N↓</th>
<th>Soil temperature</th>
<th>Soil moisture†</th>
<th>Rainfall (mm)</th>
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<tr>
<td></td>
<td></td>
<td>Median</td>
<td>Median</td>
<td>NH₄⁺ (mg kg⁻¹)</td>
<td>(°C)</td>
<td>(%) dry wt</td>
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<td>Winter wheat:</td>
<td></td>
<td>(ng N m⁻² s⁻¹)</td>
<td>(ng N m⁻¹ s⁻¹)</td>
<td></td>
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<td>Drylawhill</td>
<td>10–12 May</td>
<td>6.91</td>
<td>0.34</td>
<td>28.2</td>
<td>0.85</td>
<td>9</td>
<td>13</td>
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<td>Howmuir</td>
<td>20–26 June</td>
<td>1.50</td>
<td>0.31</td>
<td>0</td>
<td>12</td>
<td>36.2</td>
<td>4.3</td>
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<td>Glencorse Mains</td>
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<td>61</td>
<td>0.26</td>
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<td></td>
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<td>1.04</td>
<td>0.01</td>
<td>1.77</td>
<td>5</td>
<td>7.2</td>
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<td>14–June</td>
<td>4.55</td>
<td>0.05</td>
<td>0.01</td>
<td>1.74</td>
<td>4</td>
<td>59.2</td>
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<td>4–5 July</td>
<td>0.005</td>
<td>0.11</td>
<td>0.48</td>
<td>10.0</td>
<td>4</td>
<td>2.6</td>
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<tr>
<td>Glencorse Mains</td>
<td>21–23 April</td>
<td>-0.14</td>
<td>0.51</td>
<td>0</td>
<td>0</td>
<td>7</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>7 June</td>
<td>-0.31</td>
<td>0.16</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>15 June</td>
<td>-0.14</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>5–6 July</td>
<td>-0.14</td>
<td>0.33</td>
<td>1.73</td>
<td>5.2</td>
<td>3</td>
<td>13.9</td>
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</table>

*Median and geometric standard deviation (sg) for periods when NO and N₂O were measured simultaneously. n = number of molecular sieve traps used for N₂O analysis. For NO the median flux for that period was taken. n > 70. Positive numbers = emission, negative numbers = deposition.
†Mean of 4 replica for Drylawhill and Howmuir, mean of 2 replica for Glencorse.
‡n > 70.
§Cumulative rainfall: 2 days before and day of enclosing the plot.
NO and \( N_2O \) in agricultural soils

Fig. 2. Diurnal variations in the NO and \( N_2O \) flux from a fertilized clay loam soil cropped with ryegrass at Glencorse Mains, 14–15 June 1990. ■ NO flux, ○ \( N_2O \) flux, ▼ soil temperature, □ air temperature inside the chamber (n = 5 for every data point).

Fig. 3. Temperature dependence of the NO emission from a fertilized clay loam cropped with ryegrass at Glencorse Mains, 14–15 June 1990.

\((E_a = 44–103 \text{ kJ mol}^{-1})\) and Johansson and Granat (1984) \((E_a = 65–83 \text{ kJ mol}^{-1})\).

When the NO flux was less than 0.15 ng NO–N m\(^{-2}\) s\(^{-1}\) at Glencorse Mains and less than 2 ng NO–N m\(^{-2}\) s\(^{-1}\) at Howmuir, a reversal of the normal diurnal variation was observed. More NO was emitted into the atmosphere at night than during the day, and on plots where NO was deposited, the rate of deposition was less at night (Fig. 4). Plants absorb small amounts of NO (Hill, 1971), and Slemr and Seiler (1984), for instance, found that for an unfertilized soil the rate of NO emission into the atmosphere was lower from vegetated plots than from bare soil. During the day, when leaf stomata are open, more NO is absorbed than at night (Bennett and Hill, 1975). When soil emissions of NO are very small, absorption of NO by vegetation will certainly become noticeable, as shown in Fig. 4. The likely reason for the switch in diurnal variations being observed at higher NO emission rates at Howmuir than at Glencorse Mains is that at Howmuir the crop height (65 cm), and therefore the volume of the crop enclosed, were much greater than at the other sites, resulting in greater absorption.

Rates of NO emission averaged over the 1 to 7 days of the measurement period ranged from 0.005 to 6.9 ng NO–N m\(^{-2}\) s\(^{-1}\) (Table 1). Median values were quoted as the distribution was approximately lognormal. Our results agree with some of the lower NO emission rates quoted, for example with a grazed pasture in Australia (1.5–7.3 ng NO–N m\(^{-2}\) s\(^{-1}\)) (Galbally and Roy, 1978), wheat fields in Colorado, U.S.A. (0.8–5.0 ng NO–N m\(^{-2}\) s\(^{-1}\)) (Anderson and Levine, 1987) and the average NO emission rate from a barley crop near Glasgow, U.K., measured over the period April–July 1985 (5 ng NO–N m\(^{-2}\) s\(^{-1}\)) (DoE, 1990). The rates of NO emission reported here, however, were small compared to mean annual NO emission rates for fertilized cultivated land in temperate climates (3.5–39 ng NO–N m\(^{-2}\) s\(^{-1}\)) (Bouwman, 1990), and much smaller than the rates very recently reported for fertilized fallow soil in the warmer environment of southern Ontario (Shepherd et al., 1991).
NO\textsubscript{3} fluxes

Nitrogen dioxide was mainly deposited, as shown for Glencorse Mains in Table 3. Loss of NO\textsubscript{2} to the chamber walls was minimal (see above) and could not account for the negative NO\textsubscript{3} fluxes observed. The results are in agreement with the literature (Fowler et al., 1991). Stomata are the major sink for NO\textsubscript{2} and consequently diurnal variations in NO\textsubscript{2} deposition have been observed, with maximum deposition rates occurring during the day (Hargreaves et al., 1991). In contrast, we observed a small inverse diurnal variation in the NO\textsubscript{2} flux on 14–15 June 1990, where NO\textsubscript{2} was emitted during the day and deposited at night (Fig. 2). Much larger rates of NO\textsubscript{2} emission for an unfertilized bare soil, averaging 2.8 ng NO\textsubscript{2}-N m\textsuperscript{-2}s\textsuperscript{-1} were observed by Slemr and Seiler (1984). We are not aware of any biological processes responsible for this NO\textsubscript{2} production in the soil.

\textit{N}_2\textit{O} measurements with closed- and open-chamber systems

The flow rate of air (> 50 l min\textsuperscript{-1}) through the open chamber was too high to measure differences directly between the N\textsubscript{2}O concentrations in the air streams entering and leaving the chamber. The N\textsubscript{2}O from these streams at the chamber inlet and outlet was therefore concentrated by absorption onto molecular sieve (Ryden et al., 1978). The trapping efficiency of

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Table 2. Relationship between NO emission and soil temperature at 30 mm depth (\(T_s\)). The activation energy (\(E_a\)) for NO production was calculated from the Arrhenius equation: \(\ln \text{NO emission} = \ln A - E_a / RT\).

<table>
<thead>
<tr>
<th>Crop, location</th>
<th>Date</th>
<th>Correlation coefficient ((r^2))</th>
<th>Degrees of freedom</th>
<th>Activation energy ((kJ/mol)^{-1})</th>
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<tr>
<td>Winter wheat:</td>
<td></td>
<td></td>
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<tr>
<td>Drylawhill plot 2</td>
<td>11 May</td>
<td>0.787</td>
<td>5</td>
<td>40.1</td>
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<tr>
<td>plot 3</td>
<td>11–12 May</td>
<td>0.832</td>
<td>11</td>
<td>64.8</td>
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<tr>
<td>plot 4</td>
<td>13 May</td>
<td>0.319</td>
<td>13</td>
<td>71.5</td>
</tr>
<tr>
<td>Howmuir plot 4</td>
<td>20 June</td>
<td>0.306</td>
<td>19</td>
<td>72.8</td>
</tr>
<tr>
<td>Ryegrass fertilized:</td>
<td></td>
<td></td>
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<tr>
<td>Glencorse plot 1</td>
<td>18–19 April</td>
<td>0.566</td>
<td>26</td>
<td>59.5</td>
</tr>
<tr>
<td>Mains plot 1</td>
<td>14 June</td>
<td>0.835</td>
<td>3</td>
<td>43.2</td>
</tr>
<tr>
<td>plot 2</td>
<td>14–15 June</td>
<td>0.659</td>
<td>17</td>
<td>81</td>
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</table>

Fig. 4. Diurnal variations in the NO deposition rate from an unfertilized ryegrass plot on clay loam soil at Glencorse Mains, 22–23 April 1990. ■ NO flux, ● soil temperature \(n=5\) for every data point.
NO and N₂O in agricultural soils

Table 3. NO₂ flux at Glencorse Mains

<table>
<thead>
<tr>
<th>Date</th>
<th>ng NO₂-N m⁻² s⁻¹</th>
<th>Range</th>
<th>n†</th>
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<td>Fertilized plots:</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>18-20 April</td>
<td>-0.09</td>
<td>-1.05+0.47</td>
<td>705</td>
</tr>
<tr>
<td>5-6 June</td>
<td>-0.08</td>
<td>-0.45+0.21</td>
<td>242</td>
</tr>
<tr>
<td>14-15 June</td>
<td>-0.04</td>
<td>-0.79+1.09</td>
<td>217</td>
</tr>
<tr>
<td>4-5 July</td>
<td>-0.59</td>
<td>-1.85+0.05</td>
<td>254</td>
</tr>
<tr>
<td>Unfertilized plots:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21-23 April</td>
<td>-0.24</td>
<td>-2.00+0.66</td>
<td>998</td>
</tr>
<tr>
<td>7 June</td>
<td>+0.00</td>
<td>-0.45+0.41</td>
<td>168</td>
</tr>
<tr>
<td>15 June</td>
<td>+0.10</td>
<td>-1.32+0.90</td>
<td>40</td>
</tr>
<tr>
<td>5-6 July</td>
<td>-0.11</td>
<td>-1.49+0.35</td>
<td>209</td>
</tr>
</tbody>
</table>

* Mean flux measured at 3-min intervals for x hours. Positive values = emission, negative values = deposition.
† Number of flux measurements carried out.

Table 4. Comparison of open- and closed-chamber methods for measuring N₂O fluxes at Glencorse Mains

<table>
<thead>
<tr>
<th>Date of measurement</th>
<th>Open chamber*</th>
<th>Closed chamber†</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Median</td>
<td>sg</td>
</tr>
<tr>
<td>18-19 April</td>
<td>91</td>
<td>0.2</td>
</tr>
<tr>
<td>5-6 June</td>
<td>0.01</td>
<td>1.72</td>
</tr>
<tr>
<td>14-15 June</td>
<td>0.01</td>
<td>1.74</td>
</tr>
<tr>
<td>4-5 July</td>
<td>58</td>
<td>0.48</td>
</tr>
</tbody>
</table>

* Consecutive traps from two plots.
† Triplicate or duplicate air samples taken approx. 60 min after sealing the chamber from two plots.

In addition, N₂O was measured by the closed-chamber technique at Glencorse Mains. Closed chambers are usually shallow to allow an increase in N₂O concentration to measurable levels in the shortest possible time, and this was true for our design (150 mm high). The closed chamber was therefore only suitable for the short ryegrass crop at Glencorse Mains. Nitrous oxide emissions measured by open and closed chambers here were in good agreement, in spite of a 24-h time delay between open- and closed-chamber measurements on the same plot (Table 4). Only in July were differences between open and closed chambers significant (p=0.03). Technical problems with the gas chromatograph when air samples from the closed chambers were taken in July may have resulted in inaccurate N₂O emission rates. The N₂O emission rates measured by trapping in July were in good agreement with simultaneous closed-chamber measurements from plots at Glencorse Mains by Arab et al. (1992) (60.8 ng N₂O-N m⁻² s⁻¹ on 4 July).

Rates of N₂O emissions averaged over the 1 to 7 days of the measurement period ranged from below the limit of detection (3) to 91 ng N₂O-N m⁻² s⁻¹ (Table 1). These results are at the lower end of the range in Bouwman's (1990) review of data for published studies on fertilized fields (0.6-520 ng N₂O-N m⁻² s⁻¹).

Although variations in N₂O emission rates with soil temperature were not observed this may have been due to the fact that insufficient N₂O flux measurements were made. For N₂O evolution by microbial nitrification and denitrification, activation energies ranging from 28 to 166 kJ mol⁻¹ have been reported (Conrad et al., 1983). These values compare with the activation energies calculated for NO emissions.

Effect of soil moisture

Nitric oxide and N₂O fluxes were affected by changes in soil moisture contents following rainfall. NO emissions decreased with increasing rainfall (r² = 0.71 for 17 df at fertilized plots at Glencorse Mains; r² = 0.58 for 15 df at Howmuir) (Fig. 5). Correlations between NO emission and rainfall were better than between NO emission and the soil moisture content, averaged over the top 100 mm of the soil. The amount of rainfall received was only sufficient to change the soil moisture content of the top 30 mm (Table 1) and...
would not be accurately reflected by the bulk soil moisture content. The good correlation between NO emission and soil moisture content at the soil surface (indirectly measured by rainfall), suggests that NO production does occur close to the soil surface. At Glencorse Mains, NO was emitted most rapidly immediately after the second fertilizer application in June. The total rainfall in the 5 days before the flux measurement was less than 1 mm and the average air temperature was 12°C. As no rainfall was forecast for the days following fertilizer application, the plots were watered: 5/ m² were applied, equivalent to 5 mm of rain, which would have transferred the bulk of the fertilizer into the top few centimetres of the soil. The lack of rainfall and the relatively low soil moisture content (compared to the April figures) suggest that the surface layer of the soil was well aerated. Such soil conditions are necessary for nitrifiers to operate. The comparable NO flux in April was much lower (Table 1) and was associated with a larger total amount of rainfall (10.5 mm in the previous 5 days) and a higher soil moisture content. The average daily air temperature was 7.4°C and therefore the potential evaporation from the soil was considerably smaller. The soil was therefore likely to have been less well aerated than in June, which would favour denitrification. Johansson and Granat (1984) also observed a decrease in NO emission in response to heavy rainfall. For extremely dry soil conditions, however, wetting was shown to increase the NO flux between a factor of 2 to a factor of 20 (Galbally, 1989). This is a commonly observed feature of soil microbial processes (Alexander, 1977).

Nitrous oxide emissions increased with increasing rainfall and soil moisture content ($r^2 = 0.924$, df = 8) (Fig. 6). The dependence of N₂O emission on soil moisture is further illustrated by comparing the N₂O emission rate at Glencorse after the first and second fertilizer application (Table 1). N₂O was not emitted immediately after the second fertilizer application. The lack of rain ensured that the top soil layer was well aerated, thus preventing the development of anaerobic microsites where denitrification or production of N₂O by nitrification could have occurred. Movement of fertilizer into lower, less aerated, zones was also prevented. However, a high N₂O flux was observed when plots were resampled 3 weeks later, following sufficient rainfall to move some of the fertilizer to lower soil layers and reduce the aeration of the topsoil. This delayed N₂O emission was also observed by Arah et al. (1992) on other plots at the same site.

**Effect of fertilizer**

Nitric oxide and N₂O fluxes strongly depend on the concentration of soil-available NH₄⁺ and NO₃⁻. For NO a significant correlation with soil-available NH₄⁺ and NO₃⁻ was observed ($r^2 = 0.89$ for NH₄⁺, $r^2 = 0.86$ for NO₃⁻, df = 8), overriding other variables such as soil moisture content, soil temperature and soil type (Fig. 7, Table 1). At Glencorse Mains there was always a net uptake of NO by both unfertilized plots and by the fertilized plots when the soil NH₄⁺ concentration decreased to less than 8 μg N g⁻¹ soil⁻¹ and soil NO₃⁻ to less than 0.5 μg N g⁻¹ soil. Stomatal absorption of NO by plants (as discussed earlier) appeared to be the cause of the small daytime absorption of NO. Fertilized plots generally emit more NO than nonfertilized plots (Galbally, 1989; Williams...
Sandy loam soils have a high proportion of large pores and therefore tend to be well aerated, whereas in fine-textured soils such as a clay loam, regions of low O₂ potential, necessary for N₂O production, will occur more readily (Groppman and Tiedje, 1991). We found that, provided the available nitrogen concentration in the soil was sufficient to allow nitrification or denitrification to occur, after prolonged rainfall N₂O was emitted from the clay loam soils, but not from the sandy loam soil (compare Howmuir, 20–25 June, with Glencorse Mains, 4–5 July, Table 1). Smith and Arah (1990) also reported that on sandy loam soils high denitrification rates were less likely than on clay loam soils. For NO emission rates the results shown in Table 1 are less conclusive. Comparison of individual data points, rather than means, showed that after long dry periods NO emissions from the sandy loam were occasionally very high, ranging from 3.99 to 20.5 ng NO–N m⁻² s⁻¹ for Drylawhill, 10–12 May. Under similar dry conditions at Glencorse Mains, 14–15 June, NO emissions from the clay loam soil did not exceed 4.75 ng NO–N m⁻² s⁻¹. These results suggest that high rates of NO emission were associated with coarse-textured soils and high rates of N₂O emission with finer textured soils. Further work is necessary to substantiate these claims.

**NO/N₂O emission ratio**

Laboratory studies have shown that for nitrifiers the NO/N₂O emission ratio was greater than unity, but for denitrifiers was less than unity, often around 0.01 (Lipschultz et al., 1981; Anderson and Levine, 1986). Direct extrapolation to the field situation may be difficult, as nitrification and denitrification are likely to take place simultaneously. Emission rates of the gases produced in the soil depend, amongst other factors, on the diffusivity of the soil. This work, however, suggests that, even for the more heterogeneous field situation, the molar NO/N₂O emission ratio may provide an indication of the main pathway involved in the observed NO and N₂O emission. The NO/N₂O emission ratios for the fertilized plots at Glencorse Mains, Howmuir and Drylawhill are presented in Table 5. The ratio varied widely from >100 (when only NO was emitted) to <0.001 (when only N₂O was emitted). Correlations between the NO/N₂O emission ratio and soil moisture content (r² = 0.48, df = 15), cumulative rainfall (r² = 0.34, df = 15) and soil texture (r² = 0.25, df = 15) were significant; those with soil-available N and soil temperature were not significant. NO/N₂O emission ratios greater than unity were observed for soil conditions that favour nitrification: the sandy loam soils at Drylawhill and Howmuir, and the clay loam soil immediately after the second fertilizer application. This was after a long period without rain, which allowed the soil to become drier and therefore better aerated, thus inhibiting the action of denitrifiers, while not becoming so dry as to inhibit aerobic microbial activity including nitrifie-

**Effect of soil physical properties**

In this study NO and N₂O emissions were measured from a clay loam soil and two sandy loam soils.
The lack of rain also ensured that the bulk of the applied fertilizer remained in the top few centimetres of the soil. Low NO/N$_2$O emission ratios typical for denitrifiers were only observed for the clay loam soil. At Drylawhill a NO/N$_2$O emission ratio of 0.1 was observed for plot 4. Considering the large concentration of soil-available NO$_3^-$, both nitrification and denitrification may have both been responsible for the observed NO and N$_2$O emissions.

### SPECULATION ON ANNUAL NO AND N$_2$O EMISSION RATES

An attempt was made to calculate annual rates of NO and N$_2$O emission for fertilized agricultural land in the U.K. Estimates were based on the assumption that NO was emitted at an average rate of 5-15 ng NO-N m$^{-2}$ s$^{-1}$ for 180 days per year. The lower value (5 ng NO-N m$^{-2}$ s$^{-1}$) was the average NO flux measured over a barley field in Scotland between April and July 1985 (DoE, 1990), and agrees with the larger rates of NO emission measured at Glencorse Mains (4.4 ng NO-N m$^{-2}$ s$^{-1}$) and Drylawhill (6.9 ng NO-N m$^{-2}$ s$^{-1}$) (Table 1). The lower NO emission rates observed in this study were not included, as the range observed here was already very low compared to values quoted elsewhere (Bouwman, 1990). The upper value (15 ng NO-N m$^{-2}$ s$^{-1}$) was the average annual rate of NO emission for fertilized cultivated land in temperate climates compiled by Bouwman (1990) as NO is a product of nitrification it is likely to be emitted for at least the period when conditions are warm enough for crop growth, i.e. of the order of 180 days. The production of N$_2$O requires a low oxygen tension, and therefore is much more variable in time and space. High rates of N$_2$O emission are generally confined to the first 2 to 3 weeks after fertilizer application (Ryden et al., 1981). Bolle (1986) estimated that for cultivated fields 0.5 to 2% of the added N fertilizer is released as N$_2$O. For Drylawhill and Glencorse Mains the N$_2$O emission accounted for 0.5-1% of the fertilizer added, assuming that the emission rates were maintained for 21 days at the median levels observed, i.e. 28.2 and 46.5 ng N m$^{-2}$ s$^{-1}$, respectively. This estimate is likely to be a conservative one, as N$_2$O flux measurements were not necessarily carried out when N$_2$O emission rates were largest.

Based on these assumptions we estimated that for fertilized crop and grassland in the U.K., the annual NO emission would be between 0.013 and 0.038 Tg NO-N and the annual N$_2$O emission would be between 0.008 and 0.031 Tg N$_2$O-N. In the U.K. fertilized agricultural land would account for 2-6% of the total annual NO$_x$ emission (0.6 Tg NO$_x$-N; DoE, 1990) and for 16-64% of the total annual N$_2$O emission (0.8 Tg N$_2$O-N for Europe; Prather, 1988).

### CONCLUSION

This study has shown that both NO and N$_2$O were emitted from agricultural soils cropped with winter wheat or ryegrass. Rates of NO emission ranged from 0.005 to 6.9 ng NO-N m$^{-2}$ s$^{-1}$ and rates of N$_2$O emission ranged from 0 to 91 ng N$_2$O-N m$^{-2}$ s$^{-1}$. Nitric oxide emissions increased with increasing soil...


