

NITROUS OXIDE EMISSIONS

END OF PROJECT REPORT

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Authors

B. Hyde¹, M. Ryan¹, M. Hawkins², J. Connolly², O. T. Carton¹

¹ Johnstown Castle Research Centre, Wexford

² Department of Statistics, University College Dublin, Belfield, Dublin 4

Johnstown Castle Research Centre Wexford

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SUMMARY

Nitrous oxide (N_2O) is one of the three most important greenhouse gases (GHG). Nitrous oxide emissions currently account for approximately one third of GHG emissions from agriculture in Ireland. Emissions of N_2O arise naturally from soil sources and from the application of nitrogen (N) in the form of N fertilizers and N in dung and urine deposition by grazing animals at pasture.

Nitrous oxide emission measurements were conducted at three different scales. Firstly, a large-scale field experiment was undertaken to compare emission rates from a pasture receiving three different rates of N fertilizer application and to identify the effects of controlling variables over a two-year period. Variation in emission rates was large both within and between years.

Two contrasting climatic years were identified. The cooler and wetter conditions in year 1 gave rise to considerably lower emission levels than the warmer and drier year 2. However, in both years, peak emissions were associated with fertilizer N applications coincident with rainfall events in the summer months.

A small-plot study was conducted to identify the individual and combined effects of fertilizer, dung and urine applications to grassland. Treatment effects were however, difficult to obtain due to the overriding effects of environmental variables.

Thirdly, through the use of a small-scale mini-lysimeter study, the diurnal nature of N_2O emission rates was identified for two distinct periods during the year. The occurrence of a diurnal pattern has important implications for the identification of a measurement period during the day which is representative of the true daily flux.

The research presented aims to identify the nature and magnitude of N_2O emissions and the factors which affect emission rates from a grassland in Ireland. Further work is required to integrate the effects of different soil types and contrasting climatic regimes across soil types on N_2O emissions.

1.1 Introduction

Gaseous nitrogen (N) emissions to the environment occur in all biological systems whether natural or agricultural. Ultimately the fate of all N contained within these systems is that it is denitrified and returned to the atmosphere to maintain a balance within the global N cycle. Transmission of N from agricultural production to the atmosphere is a result of excesses present in mobile pools in the soil, reaction to particular combinations of biological activities and environmental conditions. The routes which N takes, and the quantities involved, are the result of these interacting factors and competition between the processes involved which remove or transform ammonium (NH_4^+) and/or nitrate (NO_3^-). As a result of the varying processes which occur, the system is “leaky” and N is readily lost to the wider environment. The concern here is denitrification as it pertains to the loss of nitrous oxide (N_2O) to the atmosphere. Denitrification is the biological reduction of NO_3^- under anaerobic conditions by facultative aerobes with the ability to reduce NO_3^- to nitrite (NO_2^-) by NO_3^- reductase, NO_2^- to N_2O by NO_2^- reductase and N_2O to dinitrogen (N_2) by N_2O reductase (Knowles, 1982).

Nitrous oxide is of considerable environmental importance as it indirectly, through the formation of nitric oxide (NO), depletes the stratospheric ozone (Cicerone, 1987), enhances the formation of acid rain (HNO_3) (Tanner, 1990) and contributes to the greenhouse effect (Lashof and Ahuja, 1990). Most studies globally, have identified soils as the major source (Bouwman, 1994).

Nitrous oxide is one of the three most important Greenhouse Gases (GHG), the other two being carbon dioxide (CO_2) and methane (CH_4). It is a radiatively active atmospheric trace gas, currently accounting for 2 – 4% of total Global Warming Potential (GWP) (Watson *et al.*, 1992), although a more recent estimate proposes a figure of 15% (Iserman, 1994). Its concentration in the atmosphere has increased from 275 ppb in the pre-industrial era to 312 ppb at present with an annual increase of 0.2 to 0.3% (Prather *et al.*, 1995). Although its atmospheric concentration is much smaller than that of CO_2 (365ppm), its GWP is 310 times that of the latter over a 100-year time horizon with an atmospheric lifetime of approximately 130 years (IPCC, 1995).

The emission of N_2O from soil generally represents a very small fraction of the annual input of N cycling within unmanaged or farmed soils. In Western Europe, emissions of N_2O from extensively managed, unfertilized and mown grasslands are in the range of 0.2 to 1.5 kg N ha^{-1} year⁻¹, but from fertilized and grazed grasslands,

are in the range of 10 to 20 kg N ha⁻¹ year⁻¹ (Velthof and Oenema, 1997; McTaggart *et al.*, 1994).

Studies of N₂O emissions from soils are met with the complexities of microbial processes and a multitude of physical and chemical factors, which affect them. The most important factors governing N₂O emissions from soil are soil mineral N content, soil moisture content and soil temperature.

Even though a large amount of information has been generated in relation to N₂O emission rates, causative factors and methods available for mitigation, globally, there is very little country-specific information available for Ireland. Currently, in the absence of this, the calculation of Ireland's N₂O emission inventory is based on emission factors published by the IPCC (IPCC, 1997). These factors are used to derive an estimate of N₂O losses from N inputs as fertilizer and from unmanaged manures (i.e., excretal N deposited on pasture). Currently the emission factors used for IPCC inventory reporting of direct emissions from fertilizer N and N deposited by grazing animals are 1.25% (0.25 - 2.25) and 2% (0.5 - 3), respectively. However, research has indicated that the use of "default" values may result in an unreliable estimate of national emission inventories.

Nitrous oxide emission measurements were conducted at three different scales to provide a detailed insight into N₂O emissions from a grassland site. Firstly, a large - scale field experiment was conducted to compare N₂O emissions from grazed pasture receiving three rates of N fertilizer and rotationally grazed by cattle. Secondly, a small-plot experiment was carried out to assess the contribution of dung and urine patches to N₂O emissions from agricultural soils. Thirdly, a mini-lysimeter experiment was developed to enable frequent monitoring of N₂O emissions from soil and to provide an indication of the diurnal variability of N₂O emission rates.

1.2 Nitrous oxide emissions from a grazed pasture receiving 3 levels of fertilizer N application

1.2.1 Materials and methods

This trial was conducted, from November 2001 to November 2003, in the “Tower Field” at Johnstown Castle Research Centre, Wexford, mean annual rainfall and temperature, 1014 mm and 10°C, respectively. The soil in the “Tower Field” is predominantly an imperfectly drained gley of loam over clay loam texture derived from Irish Sea Till (Gardiner and Ryan, 1964; S. Diamond, pers comm.). The experimental site is under an established (> 10 years) and uniform ryegrass (*L. perenne*) sward. Three N fertilizer levels, 0, 225 and 390 kg N ha⁻¹ yr⁻¹ were used in a randomised block design with three replicates. Fertilizer-N was applied as urea (46% N) for the first two applications in spring with CAN (27.5% N) applied in the remaining applications during the summer months (June – September). Rotational grazing was practiced using steers (300 – 350 kg lw at turnout in spring).

For each grazing interval, the N deposited by grazing animals in dung and urine, was calculated, based on annual nutrient production levels (Department of Agriculture Food and Rural Development, 2000). The N deposited was subsequently added to total N fertilizer application on each treatment for the calculation of percentage N₂O losses.

Nitrous oxide emissions were measured using the closed chamber technique (Smith *et al.*, 1995). This involves placing a collection chamber over the soil surface for the period of measurement (1 hour), thereby enclosing an area of the atmosphere adjacent to the soil surface. The chambers, 11.3 cm dia and 15 cm high, were inserted 2 cm deep into the soil to provide a seal from the atmosphere and an effective volume of air above the soil within the chamber headspace of 1303 cm³. A total of eight chambers was used per replicate plot (i.e., 72 chambers per measurement day).

After insertion, the chambers were left in place for 1 hour after which a sample of the chamber headspace was withdrawn through a rubber septum using a 10 ml polypropylene syringe fitted with a hypodermic needle. A sample of the headspace was then immediately transferred into a pre-evacuated vial for storage and analysis within 6 hours. The N₂O concentration in each sample was analysed using a gas chromatograph (Varian CP 3800 GC) fitted with an electron capture detector.

In addition to N₂O emission measurements, a system of soil moisture and temperature probes, under datalogger control, was installed in the experimental area. Three replicate soil moisture probes were installed in each experimental plot to monitor the volumetric soil moisture status of the top 150 mm of the soil profile. Soil temperature was monitored at 50 mm depth. Additionally, rainfall data and soil temperature data, at 100 mm and 300 mm, were obtained from the Johnstown Castle meteorological station.

1.2.2 Results and Discussion

The emission from the unfertilized plots (0 N) was consistently low, with values, on average, less than 20 µg N₂O – N m⁻² h⁻¹ recorded. Emissions from the treated plots (225 & 390 kg N ha⁻¹) were concentrated in relatively short periods (1–2 weeks) following grazing intervals and fertilizer N applications, with marked differences between treatments and the relative patterns and magnitudes of emission rates at different times of the year and between years. The higher emission rates were associated with N fertilizer applications in the summer months in conjunction with rainfall events and increasing soil temperatures.

The emission patterns depicted (Figure 1.1) are typical of those from grazed grasslands fertilized in several N applications. This pattern occurs as a direct result of fluctuations in soil mineral N content, caused by grazing, fertilizer applications, N uptake by the grass sward and possibly microbial biomass and N losses through leaching, denitrification and volatilisation.

Cumulative N₂O emission totals were greater in year 2 than in year 1. In year 1 the mean cumulative N₂O release from the control plots (0 N) was 4.21 ± 0.79 kg N₂O – N ha⁻¹ compared with 6.45 ± 1.95 and 12.55 ± 3.61 kg N₂O – N ha⁻¹, in the 225 and 390 kg N ha⁻¹ treatments, respectively. In year 2 the mean cumulative N₂O release from the 0N plots was 4.66 ± 0.55 kg N₂O – N ha⁻¹ compared with 18.51 ± 2.91 and 28.93 ± 4.86 kg N₂O – N ha⁻¹ in the 225 and 390 kg N ha⁻¹ treatments, respectively.

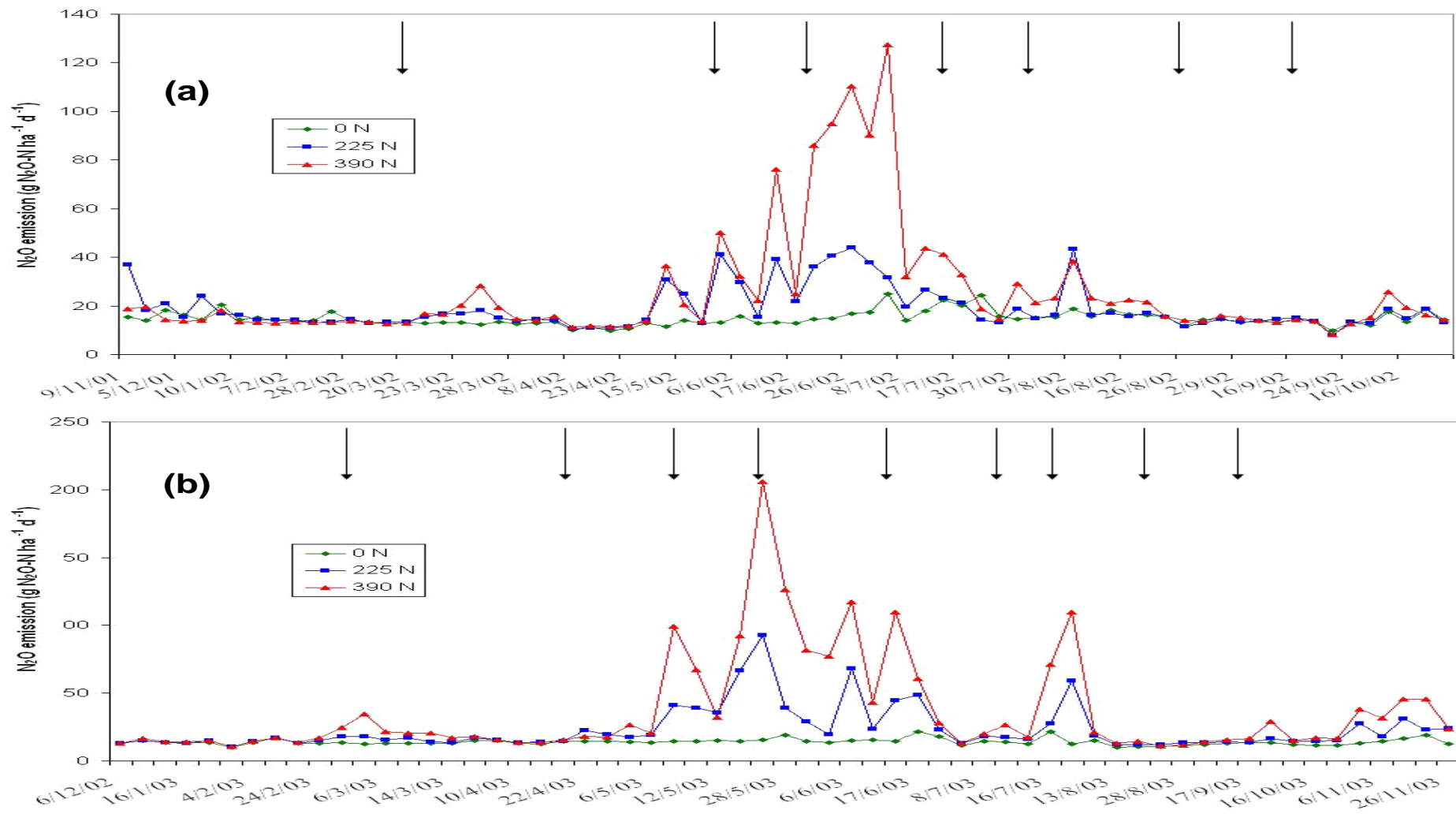


Figure 1.1: Pattern of N₂O emission rates in year 1 (a) and year 2 (b). Fertilizer N applications are indicated by the arrows.

Cumulative and percentage losses were calculated for each fertilized treatment after subtraction of cumulative losses from the control (0 N) treatment for each N fertilizer application and grazing interval (Table 1.1) and for each of the two years of the study (Table 1.2).

Table 1.1: Percentage N₂O loss ((kg N₂O-N emitted/ kg N applied) × 100) for each fertilizer application (mean of three replicates per treatment).								
Year 1					Year 2			
Treatment					Treatment			
225 N		390 N			225 N		390 N	
Application	N applied	% loss	N applied	% loss	N applied	% loss	N applied	% loss
1	59	1.61	102	1.35	35	0.36	60	0.78
2	59	1.27	102	3.94	30	0.61	50	0.77
3	19	1.21	32	3.10	25	17.78	45	21.15
4	19	0.36	32	0.45	25	6.30	45	9.94
5	19	0.88	32	1.91	23	4.83	40	1.67
6	19	0.10	32	0.10	23	13.60	40	7.40
7	19	0.10	28	0.50	23	0.30	40	0.35
8	N/A	N/A	N/A	N/A	23	0.10	40	0.17
9	N/A	N/A	N/A	N/A	18	0.14	30	0.70

Table 1.2: Cumulative annual (kg N₂O -N ha⁻¹) and percentage loss ((kg N₂O-N emitted/ kg N applied) × 100) for each year.			
Treatment	Total N input * kg N ha⁻¹	Total N₂O - N evolved (kg)	Emission factor** (% N evolved)
Year 1			
225	310	2.24	0.72
390	429	8.34	1.80
Year 2			
225	303	13.85	4.56
390	493	24.27	4.92

* Total N input = N fertilizer + N from dung and urine deposition

** % loss = (kg N₂O - N loss per kg N applied) × 100

Two climatologically contrasting years are evident in this study. The initiation of the study in November 2001 was followed by a relatively dry period in which the total rainfall for November and December was 50% below average for the same period over the last 35 years (Figure 1.2). In sharp contrast, 2002 was the wettest year on record at Johnstown Castle: total rainfall for the year (1400 mm) was 140% of

annual average (1014.8 mm). Total rainfall in 2003 was 1019.7 mm, which is similar to average yearly rainfall.

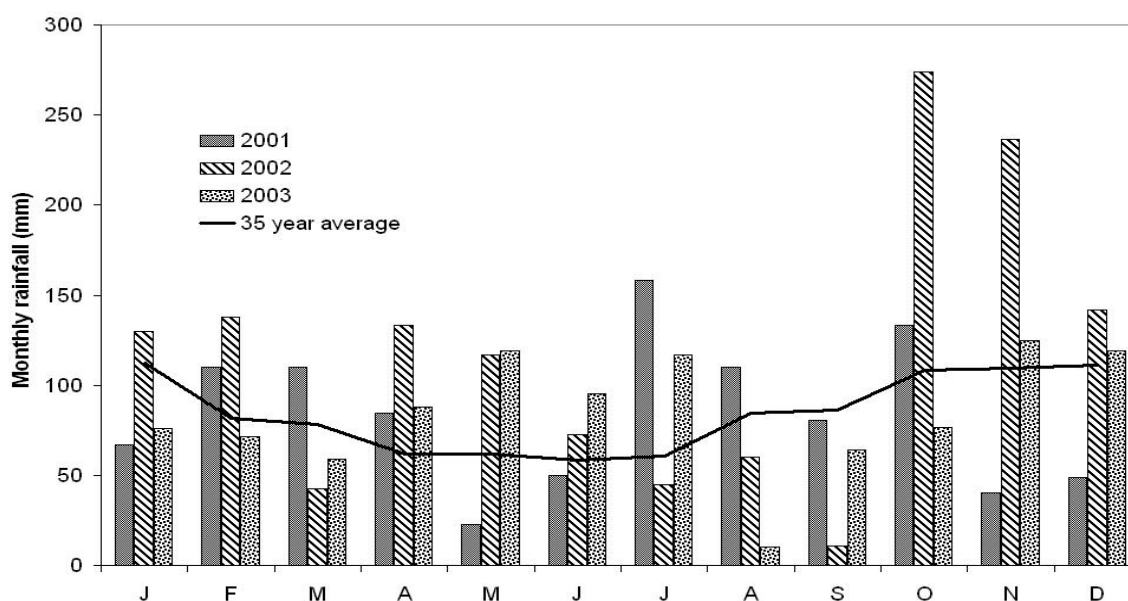


Figure 1.2: Rainfall distribution in 2001, 2002 and 2003 – Johnstown Castle meteorological station data.

The cooler and wetter conditions in year 1 gave rise to considerably lower emissions than the warmer and drier year 2. Indeed the higher than average rainfall in 2002 compared with 2003 is evidence that short-term vagaries in weather can have a dominating influence on total annual emissions as suggested by Dobbie *et al.* (1999).

Annual calculated N₂O - N losses for year 1 (Table 1.2) are within the range of values used for inventory reporting purposes for N-fertilized grasslands under IPCC calculation procedures (IPCC, 1997). In contrast, calculated emission factors for year 2 (Table 1.2) are substantially higher. This is in agreement with Fowler *et al.* (1997) who, in a compilation of some studies of N₂O emissions from grassland soils, observed that the fractional loss of N₂O from fertilizer and excretal N inputs to grasslands is substantially higher than the 1.25% used by the IPCC (IPCC, 1997). In addition, the values observed agree with those found by Velthof and Oenema (1997) and McTaggart *et al.* (1994) who observed that N₂O emission totals from grazed and fertilized grasslands were generally in the range of 10 to 20 kg N ha⁻¹ yr⁻¹.

1.3 Nitrous oxide emissions from dung and urine application to grassland

1.3.1 Materials and methods

The experiment was undertaken between May and November, 2003 on a site that had been previously developed to monitor N flows on cut grassland under a range of managements and N fertilizer inputs on small plots (15 m²) (R. Schulte, pers comm.) in the “Tower Field” at Johnstown Castle. The soil type is as described in section 1.2.1.

Dung and urine were collected from a grazing herd in the large-scale field experiment, described in section 1.3, and stored at 4°C prior to analysis and application to the experimental area. Representative sub-samples of both dung and urine were analyzed for N content (Table 1.3).

Table 1.3: Nitrogen contents of dung and urine used.				
Excreta	N content (mg N kg⁻¹)	N content %*	N content as % D W +	Moisture content as % F W
Dung	5248	0.41	3.15	87
Urine	675	0.68	N/A	100

* calculations are on a w/w basis for dung and w/v basis for urine

+ D W = Dry weight

Based on the results of N content analysis (Table 1.3), treatment applications to the experimental plots were equivalent to 0.75 kg of dung (2312.5 kg N ha⁻¹) on a fresh weight basis and 1.25 L of urine (479.5 kg N ha⁻¹), which are representative of typical cattle excreta deposition rates, on a mass per unit area basis (Lantinga *et al.*, 1987). Inorganic fertilizer, as CAN, was applied at a rate equivalent to 90 kg N ha⁻¹, either alone or in combination with dung and/or urine.

Eight treatments were imposed with three replicates of each treatment. The treatments were distributed in a factorial design, each separated by approximately 50 cm. The treatments imposed were as follows:

1. 0 N control
2. Dung only
3. Urine only
6. Fertilizer only
5. Urine + dung
6. Dung + fertilizer
7. Urine + fertilizer
8. Fertilizer + urine + dung

Permanent steel collars (30 cm dia), 5 cm deep were inserted 3 cm into the soil, leaving 2 cm above the soil surface, approximately two weeks before the allocation of treatments to the experimental area. Steel chambers (30 cm dia, 33 cm high) were attached to the permanently installed steel collars during measurement periods using tyre inner tubes to act as a seal. Once attached, the chambers were left in place for 1-hour and a sample of the emitted gas was withdrawn as discussed in section 1.3.1.

1.3.2 Results and discussion

Nitrous oxide emissions from the control plots were low, with fluxes ranging from 97 to 160 $\mu\text{g N}_2\text{O} - \text{N m}^{-2} \text{h}^{-1}$ during the experimental period. Dung only, urine only and fertilizer only treatments exhibited much higher emission rates reaching peak levels 6 days after application. The range of emission values recorded for these treatments over the experimental period was 113 to 736 $\mu\text{g N}_2\text{O} - \text{N m}^{-2} \text{h}^{-1}$, 112 to 1,209 $\mu\text{g N}_2\text{O} - \text{N m}^{-2} \text{h}^{-1}$ and 112 to 3,490 $\mu\text{g N}_2\text{O} - \text{N m}^{-2} \text{h}^{-1}$, with mean coefficients of variation (CV) of 49.8% (0.3 – 99.1%), 47.0% (0.3 – 93.7%) and 31.0% (0.4 – 61.7%), respectively. The highest emission levels were recorded in the urine + fertilizer treatment (Figure 1.3).

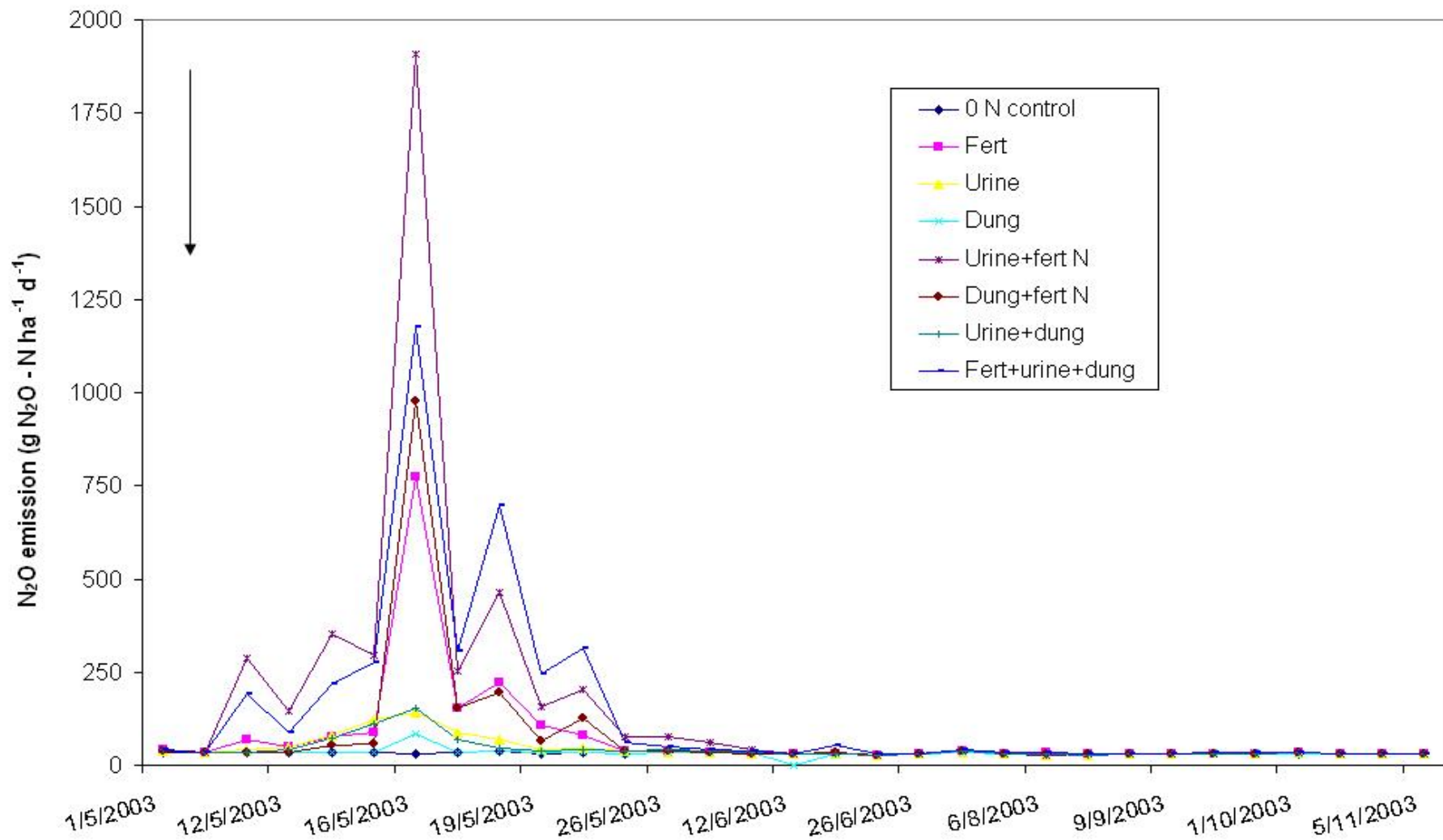


Figure 1.3: Time course of N₂O emission rates. Treatment application date is shown by the arrow.

Nitrous oxide emissions ranged from 109 to 12,256 $\mu\text{g N}_2\text{O} - \text{N m}^{-2} \text{h}^{-1}$, 112 to 3,704 $\mu\text{g N}_2\text{O} - \text{N m}^{-2} \text{h}^{-1}$, 113 to 826 $\mu\text{g N}_2\text{O} - \text{N m}^{-2} \text{h}^{-1}$ and 115 to 6,113 $\mu\text{g N}_2\text{O} - \text{N m}^{-2} \text{h}^{-1}$, from the urine + fertilizer, dung + fertilizer, urine + dung and fertilizer + urine + dung treatments with mean CV of 53.8% (0.2 – 107%), 29.7% (0.9 – 58.6%), 16.2% (0.6 – 31.7%) and 34.9% (0.7 – 69.1%), respectively.

The average daily soil temperature at 100 mm and 300 mm below the soil surface over the course of the study was 14°C with ranges of 4.2 - 20.1°C and 6.6 - 20.5°C, respectively. A total of 58.8 mm rainfall occurred in the 10 days prior to treatment application with a total of 115 mm rain within 30 days after application.

The observed, almost instantaneous peak in N_2O emission rates (within 6 days) across all treatments would appear to be a direct result of increased soil moisture status as a result of rainfall after treatment application, in addition to increasing soil temperatures creating conditions conducive to large losses of N_2O through denitrification. Similar environmental factor-driven N_2O emission peaks were found by Allen *et al.* (1996) in a study aimed at examining the effects of animal excreta on N_2O emission rate over a range of soil types.

Mean observed cumulative emission totals from applied treatments minus those measured from control (0 N) plots over the full period of investigation and the percentage loss (kg $\text{N}_2\text{O} - \text{N}$ per kg N applied) are shown in (Table 1.4).

Table 1.4: Summary of cumulative N_2O-N emission totals and calculated percentage loss for fertilizer, urine and dung application.		
Treatment	Treatment induced emission *	% loss**
Fertilizer	1.95	2.0 (1.38 – 2.83)
Urine	0.54	0.11 (0.06 – 0.22)
Dung	0.20	0.01 (0.01 – 0.13)

* Expressed as kg $\text{N}_2\text{O} - \text{N ha}^{-1}$ (minus cumulative emission totals from the control)

** Percentage loss as kg $\text{N}_2\text{O} - \text{N}$ per kg N applied

Treatment-induced peak and cumulative emission totals are ranked in the order of treatment from the highest to the lowest as follows: urine + fertilizer > fertilizer + urine + dung > dung + fertilizer > fertilizer only > urine only \approx urine + dung > dung only > control.

The fractional loss of 2% of fertilizer N is within the range used in the IPCC guidelines (IPCC, 1997) of 1.25 % (0.25 – 2.25%) for inventory reporting purposes. Fractional losses from both urine and dung are at the lower end of the range of values reported in the literature.

The application of approximately 480 kg N ha⁻¹ in the form of urine in this study is well in excess of immediate plant requirements. In urine patches the hydrolysis of its main constituent, urea by urease enzymes to NH₄⁺ is usually completed within one day (Ball and Ryden, 1984) thereby providing a substrate for nitrification and subsequent denitrification to proceed. Heavy rainfall before and after urine application with added moisture content in urine may have increased soil moisture content to above field capacity where the N₂O produced is reduced to N₂, allowing the full denitrification sequence to proceed (de Klein and van Logtestijn, 1996). In addition, the application of urine with fertilizer N in the combined fertilizer + urine treatment, which gave rise to the highest emission levels, suggests that the urine acted as a further source of moisture in addition to that from rainfall and as a source of readily available carbon compounds.

In contrast to the work of Yamulki *et al.* (1998), who found that emission rates from dung patches generally peaked within 40 days after application and the work of Flessa *et al.* (1996) who found peak emission rates 10 days after application, emission rates from dung application in this study remained at consistently low levels throughout the course of the study. Indeed the presence of dung in the fertilizer + urine + dung treatment when compared with that of fertilizer + urine had the net effect of reducing emission rates. This may be explained by the presence of the dung patch on the soil surface restricting the diffusion of N₂O into the atmosphere (Granli and Bøckman, 1994).

1.4 An examination of the diurnal variation in N₂O emission rates

1.4.1 Materials and methods

Large soil cores were taken by driving polyvinylchloride (PVC) piping (150 mm i.d. and 100 mm deep) into the soil in the “Foals House” field at Johnstown Castle. The soil is of the same classification as that used previously in sections 1.2 and 1.3.

Six replicate cores were taken and transported to a wire-mesh-enclosed area adjacent to the laboratory which was built on the site of an old glasshouse. Here the cores were placed in PVC couplers (150 mm i.d. and 145 mm deep) attached to the above piping which had been filled to a depth of 7.5 cm with washed garden gravel and sealed at the bottom with a PVC stop-end. For simplicity, the assembled cores are referred to as “mini-lysimeters”.

The study was undertaken once in spring and once in summer of 2003. In each experimental period, two N treatments were imposed with 3 replicates of each treatment at rates equivalent to 100 kg N ha⁻¹ and 150 kg N ha⁻¹ applied as ammonium nitrate (AN).

Nitrous oxide emission rates were measured using the static closed chamber technique. Up-turned PVC couplers with a stop-end fitted, made of the same material as those used in the construction of the mini lysimeters, were used as chambers to monitor N₂O emission rates. The effective volume of air above the soil surface enclosed within the chambers was 2032 cm³.

The chambers were deployed for a 1-hour period after which a sample of the atmosphere within the chamber was withdrawn through a septum following the methodology presented in section 1.2.1. After a headspace sample had been taken, the chambers were removed for one hour after which they were placed on the mini-lysimeters for a further one hour and the process repeated for up to 50 hours in each experiment.

1.4.2 Results

Experiment 1 - spring 2003

Nitrogen fertilizer as AN was applied on 16/3/03, 3 d before the initiation of continuous measurement at the rates indicated. Emission rates were subsequently monitored on a 2-hourly basis thereafter for a period of 52 hours.

The data presented show a clear diurnal pattern in the rates of N₂O emission with a similar pattern found in both N treatments (Figure 1.4). However, N₂O emission rates are markedly out of phase with both soil and air temperature (Figure 1.4). Daily minimum and maximum emission rates occurred at 1200 h and 2000 h, respectively, on day 1 (1000 h 19/3/2003 to 1000 h 20/3/2003) and at 1200 h and 2200 h, respectively, on day 2 (1000 h 20/3/2003 to 1000 h 21/3/2003) (Figure 1.4).

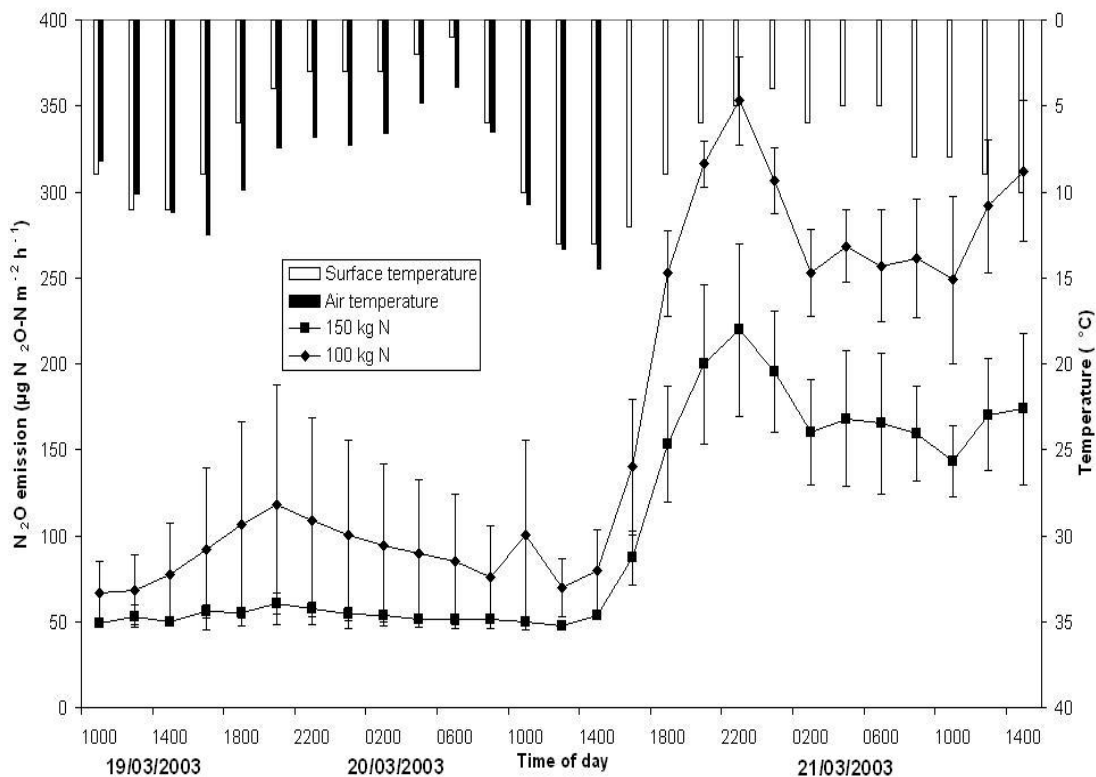


Figure 1.4: Nitrous oxide emission rates in experiment 1 (means \pm standard deviation; n=3).

In contrast, maximum soil surface and air temperatures of 12.5°C and 11°C occurred at 1600 h and 1400 h, respectively, in day 1, while maximum soil surface temperatures

of 14.5°C occurred at 1400 h in day 2 (Figure 1.4). No data are available for air temperature after 1400 h on day 2 due to an electrical fault.

Maximum emission rates on day 1 were 1.68 and 1.25-fold higher than the minima for the 100 kg N ha⁻¹ and 150 kg N ha⁻¹ treatments, respectively. On day 2, maximum emission rates were 5.6 and 4.6-fold higher, respectively, than the minima (Figure 1.4).

The effect of soil temperature on emission rates of N₂O was not clear, which may be due to the overriding effects of soil mineral N and soil moisture content and the fact that maximum emission rates occurred at night-time when soil surface temperatures were at their lowest. Correlations were weak and negative ($r = -0.108$ and $r = -0.088$ for the 100 and 150 kg N ha⁻¹ treatments, respectively) and non-significant at the 5% significance level. Diurnal variation in emission rates followed an almost identical pattern in both N treatments (Figure 1.4), although, emission rates were significantly different from each other ($P < 0.001$).

Experiment 2 - summer 2003

Nitrogen fertilizer, as AN, was applied on 29/6/2003, 2 days before the initiation of intensive measurements at the N treatment rates indicated. As before, emission measurements were conducted on a 2-hourly basis thereafter for a period of 50 hours.

The data shows a clearly defined pattern of N₂O emissions with a similar pattern in both N treatments (Figure 1.5). The emission rates are markedly out of phase with soil temperature although less so than was found in experiment 1, with a time-lag of four hours evident between maximum soil temperature and maximum N₂O emission rates (Figure 1.5). Daily minimum and maximum fluxes occurred at 0300 h and 1500 h, respectively, on day 1 (1100 h 1/7/2003 to 1100 h 2/7/2003) and at 0900 h and 1700 h, respectively, on day 2 (1100 h 2/7/2003 to 1100 h 3/7/2003). Maximum soil surface temperature (20°C) and air temperatures (18.4°C), occurred at 1700 h, on day 1 with maximum temperatures of 24.0°C and 21.4°C, respectively, at 1500 h on day 2.

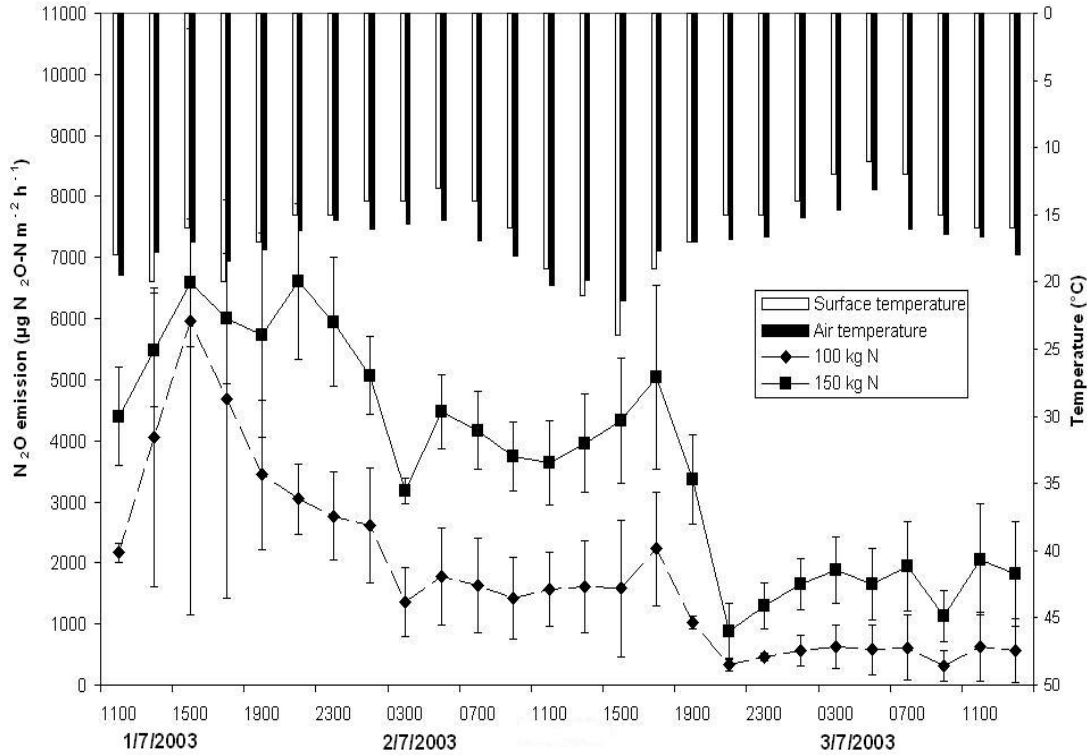


Figure 1.5: Nitrous oxide emission rates in experiment 2 (means \pm standard deviation; $n=3$).

Maximum emission rates on day 1 were 7.1 and 2.2-fold higher than the minima at 100 and 150 kg N ha⁻¹, respectively. In day 2, the maximum emission rates were 11.4 and 7.6-fold higher than the minima at 100 and 150 kg N ha⁻¹, respectively.

Correlations between N₂O emission rates and soil surface temperature were positive and significant ($r = 0.36$, $P < 0.1$ for the 100 kg N ha⁻¹ and $r = 0.41$, $P < 0.05$ for the 150 kg N ha⁻¹ treatments, respectively). No significant correlation was found between N₂O emission rates and air temperature. As established in experiment 1, highly significant ($P < 0.001$) differences existed between N application rates. In addition, highly significant differences were found between measurement times.

1.4.3 Discussion

Clear diurnal patterns in N₂O emission rates were observed both in the spring and summer. The difference in the emission rates found between the spring and summer studies indicate that temperature is a controlling variable on N₂O emissions. Maximum N₂O emission rates in the spring occurred in late evening/night time with minimum

rates observed at midday, whereas in the summer maximum emission rates were observed in early to late afternoon with minimum emission rates observed in the early morning.

In spring, weak and negative correlations were observed between N₂O emission rates and soil temperature, similar to the results of Blackmer *et al.* (1982). In experiment 1, based on a single emission measurement conducted between 0900h and 1200 h (time of emission measurement in the majority of studies found in the literature), and subsequent extrapolation by multiplication to a daily emission rate would only account for approximately 86% of the daily emission on day 1 and 34% of the daily emission on day 2. In experiment 2, 83% of the total emission on day 1 would be accounted for, however, it would have led to an over-estimation of approximately 163% of the total emission on day 2.

The diurnal variations in N₂O emission rates observed in this study confirm the difficulties in assessing daily emission rates based on a single time measurement which is often the only logistically feasible approach in large-scale field experiments.

1.5 Modelling the effects of soil moisture and soil temperature on nitrous oxide emissions

Based on the research conducted in the large-scale field experiment, described in section 1.3, detailed statistical analysis was undertaken to identify the effects of soil moisture and soil temperature on N₂O emission rates. On this basis a model was developed to enable simulations and scenario analysis to be undertaken. The goal of the statistical analysis is to estimate a regression equation based on the experimental data that relates N₂O emission rates to soil moisture and temperature.

1.5.1 Simulation and scenario analysis

Using daily soil temperature data from the Meteorological Office and soil moisture status values (Schulte *et al.*, in prep), daily emission rates were predicted for the period January 1, 1994, to December 31, 2001, inclusive. The basic premise of the scenarios is that N fertilizer is applied once per month from February to September. Five annual application rates were simulated: 0, 170, 210, 350 and 390 kg N ha⁻¹ yr⁻¹ for a grazing season of moderate length with a stocking rate of 2.3 L.U. ha⁻¹ following Teagasc guidelines (Coulter, 2004). The simulated scenarios are:

1. **Frequent:** Fertilizer applied on the first day of each month of application season.
2. **Frequent Low:** Fertilizer applied on the day (in first week of the application month – the application “window”) that soil moisture content is at a weekly low.
3. **Frequent High:** Fertilizer is applied on the day in the application window that soil moisture content is at a weekly high.
4. **Infrequent:** Fertilizer applied on first day of every second month of application season – i.e. applications occur on the first day of April, June and August.
5. **Frequent Temp Moisture:** As for simulation 1 but with shifted values of soil temperature and soil moisture relative to their levels in simulation 1.

Results of scenario 1 (**Frequent**) suggest that there is non-negligible inter-annual variability in N₂O emissions. Annual emission totals (kg N₂O-N ha⁻¹ yr⁻¹) are presented for each of the 5 annual N fertilizer application rates described above (Table 1.4). As shown, the CV (%) of annual emission totals increases with the rate of fertilizer N applied.

Table 1.4: Annual N₂O emissions (kg N₂O-N ha⁻¹ yr⁻¹) for scenario 1 (Frequent).					
Year	Annual N fertilizer application (kg N ha⁻¹ yr⁻¹)				
	0	170	210	350	390
1994	10	12	13	15	16
1995	10	13	13	18	19
1996	10	10	10	10	10
1997	11	11	12	13	14
1998	11	12	13	15	16
1999	10	11	11	12	13
2000	11	11	11	11	11
2001	10	10	10	10	11
MEAN	10	11	12	13	14
CV (%)	3	10	12	21	24

Comparing scenarios 2 and 3 (i.e., **Frequent low** and **Frequent high**), the negligible difference in annual emission totals between application regimes on the wettest days, and those on the driest days of the application window, suggests that guidelines to

restrict N fertilizer applications in a like manner will not significantly reduce N₂O emissions (Tables 1.5 and 1.6).

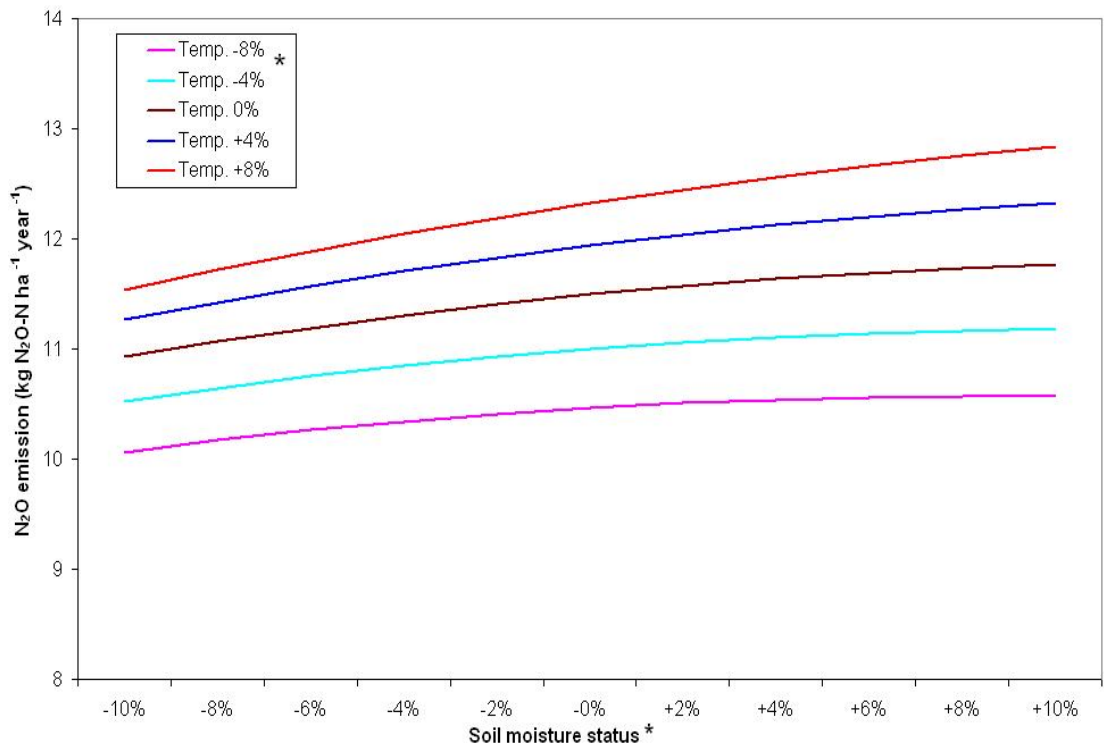
Table 1.5: Annual N₂O emission (kg N₂O-N ha⁻¹ yr⁻¹) for scenario 2 (Frequent low).					
Year	Annual N fertilizer application (kg N ha⁻¹ yr⁻¹)				
	0	170	210	350	390
1994	10	12	13	15	16
1995	10	13	14	18	20
1996	10	10	10	10	10
1997	11	11	12	13	13
1998	11	12	12	14	15
1999	10	11	11	12	12
2000	11	11	11	11	11
2001	10	10	10	10	11
MEAN	10	11	12	13	14
CV (%)	3	10	12	22	25

Table 1.6: Annual N₂O emission (kg N₂O-N ha⁻¹ yr⁻¹) for scenario 3 (Frequent high).					
Year	Annual N fertilizer application (kg N ha⁻¹ yr⁻¹)				
	0	170	210	350	390
1994	11	12	13	16	18
1995	11	13	14	20	22
1996	10	10	10	10	10
1997	11	12	12	14	15
1998	11	13	13	16	17
1999	11	11	12	13	14
2000	11	11	11	11	12
2001	10	10	10	11	12
MEAN	11	12	12	14	15
CV (%)	3	11	13	23	27

The result of the **Infrequent** applications simulation (Scenario 4), suggests that the effect of increasing the number of applications varies systematically with annual application rate (Table 1.7). Comparing Tables 1.4 and 1.7 we conclude that predicted emission levels are reduced by reducing the number of applications for the lower annual application rates, and are increased at the higher application rates.

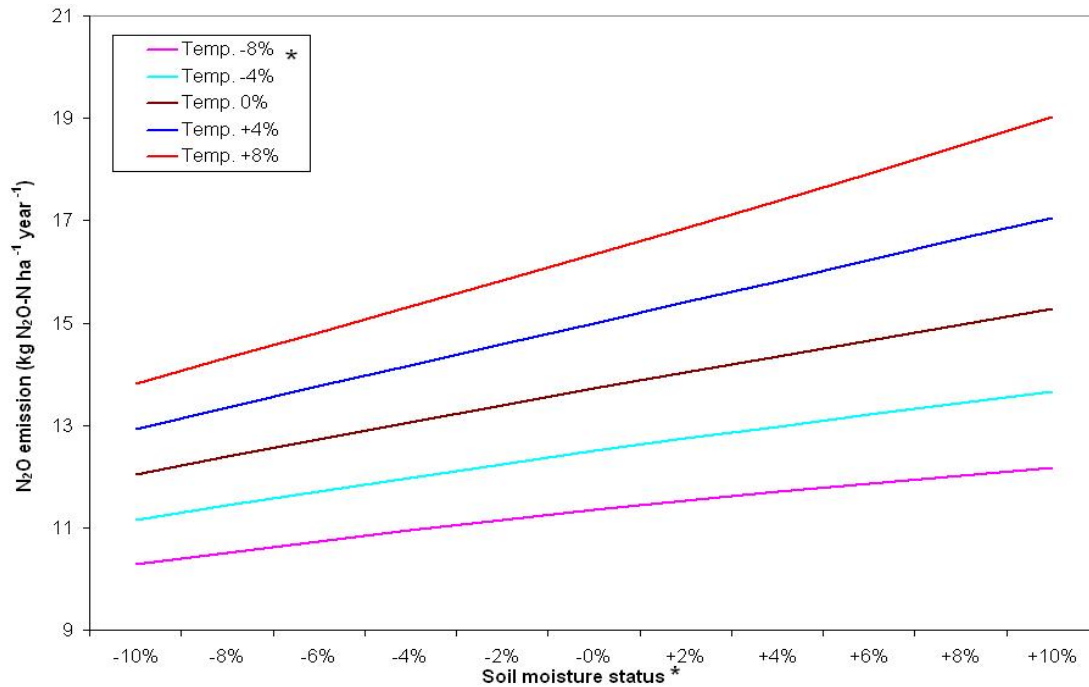
Table 1.7: Annual N₂O emission (kg N₂O-N ha⁻¹ yr⁻¹) for scenario 4 (Infrequent).					
Year	Annual N fertilizer application (kg N ha⁻¹ yr⁻¹)				
	0	170	210	350	390
1994	9	11	12	18	21
1995	9	11	13	21	25
1996	9	8	8	8	8
1997	9	9	10	12	13
1998	10	11	11	16	18
1999	9	9	9	11	12
2000	10	9	9	11	12
2001	9	8	8	9	9
MEAN	9	10	10	13	15
CV (%)	4	12	17	35	40

Simulation 5 explores the effect of changing climatic variables on N₂O emissions. By repeating simulation 1 at adjusted soil moisture status and soil temperature values and at different annual rates of fertilizer N application, differential responses to changing climatic variables for different N application rates can be investigated (Figures 1.6 and 1.7). This simulation was conducted for annual N application rates of 210 and 390 kg N ha⁻¹ year⁻¹ only.



*Where a Percentage change in soil moisture status and temperature values. e.g., “soil moisture status + 4%” denotes an increase in soil moisture by 4% from the original values used in simulation 1. Similarly, “soil moisture status - 4%” denotes a decrease in soil moisture by 4% from the original values used in simulation 1.

Figure 3.6: Mean annual emission totals (1994-2001) for adjusted levels of soil temperature and moisture status and annual fertilizer N rate of 210 kg N ha⁻¹ yr⁻¹.



*Where a Percentage change in soil moisture status and temperature values. e.g., “soil moisture status + 4%” denotes an increase in soil moisture by 4% from the original values used in simulation 1. Similarly, “soil moisture status - 4%” denotes a decrease in soil moisture by 4% from the original values used in simulation 1.

Figure 3.7: Mean annual emission totals (1994-2001) for adjusted levels of soil temperature and moisture status and annual fertilizer N rate of 390 kg N ha⁻¹ yr⁻¹.

1.6 Overall discussion, conclusions and recommendations

The emission of N₂O from grazed fertilized grassland follows an irregular pattern throughout the year which is dependent on N application rate, grazing management practices, seasonal variations in soil temperature and soil moisture status. There is

high inter-annual variability in N₂O emissions which has implications for emission rates that have been estimated from short (one-year) studies. Prolonged studies are therefore necessary. As a consequence, further work is required to identify the contribution of grazing and fertilizer N applications to grassland on a range of soil types. This would lead to more reliable estimates of N₂O emission rates for inclusion in national inventories.

The relative contributions of dung and urine deposition on grazed pastures and their interaction with fertilizer application regimes and soil and environmental variables needs to be examined for distinct periods during the grazing season to provide more robust estimates of emission rates from fertilized and grazed grassland. The seasonally variable interactions found in other studies on the effects of excretal returns on N₂O emission rates also needs to be determined for a range of soil types.

The diurnal variation in N₂O emission rates poses the problem of establishing a measurement time during the day which is representative of the true daily flux. Nitrous oxide emission rates show both diurnal and seasonal variation. Emission measurements should ideally be carried out over several periods within a 24-hour day and or for several 24 hour periods, several times in the course of a year, where this is logistically feasible.

The negligible difference in annual emission totals between N applications on the wettest days, and those on the driest days of the application “window”, in scenario analysis, suggests that guidelines to farmers to restrict their applications in a like manner would not lead to a reduction in emission levels. However, simulations were performed with this in mind. In practice, farmers apply fertilizer N before rainfall, therefore future work could be conducted in identifying a strategy more in line with rainfall levels rather than on a soil moisture basis.

Current N fertilizer application advice favours frequent applications to match plant or crop needs. Scenario analysis of the “twice as much applied half as often” approach is further evidence to support this approach. However, where soil temperature and soil moisture regimes are not conducive to large N₂O emission (i.e. cool dry soil), the applied N will not promote higher than background emission levels.

The soil type used in the studies presented is classified as an imperfectly drained gley of loam over clay loam texture derived from Irish Sea Till (Gardiner and Ryan, 1964; S.

Diamond, pers comm) which is representative of the wetter third of lowland soils in Ireland (S. Diamond, pers comm.). Because of its imperfect drainage, heavy texture and weak structure, this soil is mainly used for grassland (Gardiner and Radford, 1980). However, in this study and others it has been established that inherent soil properties strongly influence the magnitude of N₂O formation and subsequent emission (Hénault *et al.*, 1998; Arah *et al.*, 1991). In general, larger N₂O fluxes can be expected from clayey soils than from sandy soils because they are wetter and partially anaerobic from time to time. In addition, larger fluxes are expected from peat soils, because they contain large quantities of organic C. Hénault *et al.* (1998) suggest that soil type and regional climatic fluctuations can have a greater impact on N₂O emissions than parameters such as crop type, fertilizer type and rate of application.

Additionally, in a lysimeter experiment aimed at measuring N₂O emissions from five soil types (Hyde *et al.*, 2004) which range from the seriously impeded, through to moderately well drained to a very well drained soil, the authors found that the effect of soil type appears to be as great as the effect of fertilizer application with higher emissions associated with the seriously impeded soils.

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