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THE PRODUCTION OF ATMOSPHERIC NO_x AND N_2O FROM A FERTILIZED AGRICULTURAL SOIL

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Abstract—The source strength of atmospheric trace gases from rural or remote locations must be quantified in order to assess the effect of such inputs on the background tropospheric chemistry. To assess the importance of biological production of NO_x and N_2O from fertilized agricultural soil, enclosure techniques have been used to determine the emission fluxes of NO_x and N_2O at a site in Southern Ontario, Canada. NO_x fluxes on the unfertilized soil range from 1.5 to 41.6 $\mu g(NO)\ m^{-2}\ h^{-1}$. The corresponding N_2O fluxes are 0–61.8 $\mu g(N_2O)\ m^{-2}\ h^{-1}$. For the most highly fertilized soil NO_x fluxes range from 3.1 to 583 $\mu g(NO)\ m^{-2}\ h^{-1}$ and the N_2O fluxes from 0 to 446 $\mu g(N_2O)\ m^{-2}\ h^{-1}$. The fluxes increase linearly with fertilizer application, with 11% of the nitrogen in the fertilizer converted to NO_x and 5% to N_2O. The emission rates were studied as functions of the soil parameters temperature, moisture, ammonium, nitrate and pH, to attempt to understand better the production mechanisms, although a model for the process could not be developed. In rural areas away from transportation corridors the increased NO_x emission from fertilized soil may dominate local oxidant production but is not significant on the Province-wide scale.

Key word index: Flux chamber, NO_x emissions, N_2O emissions, fertilizer loss, soil, agriculture, oxidants.

1. INTRODUCTION

The oxides of nitrogen are important species in the cycling of nitrogen through the atmosphere and are involved in both radiative and chemical processes.

Nitrous oxide (N_2O) is important in climate control as it is a greenhouse gas absorbing in two bands where the atmosphere and Earth emit, namely at 7.78 μm and 17.0 μm. Its present concentration of slightly over 300 ppbv contributes ~1 K to the greenhouse warmed mean surface temperature (Kuhn, 1985). Since N_2O has a long tropospheric lifetime (150 years) it can diffuse into the stratosphere where, through reaction with excited oxygen atoms, it produces nitric oxide (NO). Reaction with the nitric oxide so produced is the major removal process for ozone in the stratosphere (WMO, 1985). The concentration of N_2O has been observed to be increasing at about 0.2% per year (WMO, 1985). This can be expected to result in an increase in surface temperature via greenhouse warming and a decrease in stratospheric ozone by increasing the rate of odd nitrogen catalysed ozone destruction.

The nitrogen oxides NO and NO_2 (collectively known as NO_x) control the oxidative capacity of the troposphere. At high concentrations the photolysis of NO_2 results in the net production of ozone which in turn produces hydroxyl radicals which are believed to initiate most atmospheric oxidation processes. However, at low NO_x levels the reaction of NO with oxidants can lead to the net destruction of ozone (Chameides *et al.*, 1987). The threshold for ozone production is an NO concentration between 10 and 30 pptv. The post industrial revolution increase in ozone (Volz and Kley, 1988) has been attributed to man's input of NO_x to the atmosphere. This increase can produce deleterious effects on human and vegetative health. It will also contribute to greenhouse warming (Ramanathan *et al.*, 1985).

Prior to the industrial revolution the atmospheric concentr[illegible]on of these gases over land masses was likely dominated by biological processes. The onset of industrialization certainly increased the NO_x production to the point where today fossil fuel combustion is the major NO_x source (NAS, 1984). The N_2O situation is not as clear. Direct production from combustion is generally thought to be small but production from biomass burning may be significant. Since combustion sources are generally localized, biological production of N_2O and NO_x is still significant away from major urban and industrial centres. However, biological production does not mean pre-industrial production. Man is having an indirect effect on the nitrogen budget by chemical conversion of atmospheric nitrogen into ammonium nitrate, the bulk of which is used as fertilizer. Any of this nitrogen released into the atmosphere as NO_x or N_2O represents a significant incremental source of these trace gases. This could be especially important in the rural areas of the western world where there is a high usage of inorganic fertilizer.

There have been several studies of the emission rates of these trace gases in the laboratory and in the field. Johansson and Galbally (1984), Levine *et al.* (1984) and McKenney *et al.* (1984), have carried out laboratory studies on the aerobic nitrification and anaerobic

denitrification processes capable of producing NO_x and N_2O. Field measurements of NO_x emissions have been undertaken by Anderson and Levine (1987), Galbally and Roy (1978), Johansson (1984), Johansson and Granat (1984), Parrish *et al.* (1987), Slemr and Seiler (1984) and Williams *et al.* (1987). Field measurements of N_2O emissions have been made by Anderson and Levine (1987, 1988), Bremner *et al.* (1980), Cates and Keeney (1987), Duxbury *et al.* (1982), McKenney *et al.* (1980), Mosier and Hutchinson (1982) and Slemr *et al.* (1984).

The purpose of this work is to focus on the importance of agricultural fertilizer as a source of atmospheric nitrogen species. This was done by measuring the fluxes of NO_x and N_2O from an agricultural soil under controlled fertilizer applications.

2. EXPERIMENTAL

2.1. *Site*

Emission fluxes of NO_x and N_2O were measured from an experimental field at Agriculture Canada's Harrow Research Station in South Western Ontario, between 19 April and 29 September 1988. The soil was a grey brown Fox fine sandy loam with an approximate composition of 78% sand, 9% silt and 13% clay. The organic matter content was between 1.5% and 2%. The field has been under continuous cultivation for about 100 years. The four plots used in this study have been treated identically for the last 19 years except for the amount of fertilizer each received. Ammonium nitrate fertilizer has been applied to each of the four plots for each of these 19 years as follows: the first, no fertilizer; the second, 100 kg ha^{-1}; the third, 200 kg ha^{-1}; and the fourth, 300 kg ha^{-1}. Note that the fertilizer was 33% NH_4NO_3 and the remainder was crushed limestone filler. For convenience these plots will be referred to as Plots 0, 100, 200 and 300, respectively. Although the field was sown with beans, all measurements were made on bare soil. This was done to separate the soil emission process from the plant uptake of nitrogen. The latter process has been studied separately and there are many estimates of deposition velocities and surface resistances (McRae and Russell, 1984). As a result the fluxes determined here may well overestimate the net emission of nitrogen in cases where there is significant plant uptake of atmospheric nitrogen in the plant canopy.

2.2. *Methodology*

Emission fluxes were measured using enclosure techniques. For N_2O a static chamber was used and the increase in the N_2O concentration in the headspace used to determine the flux. As NO_x is more reactive, a dynamic chamber was used. In this, clean air was passed through the chamber and the NO_x concentration in the air leaving the chamber was used to determine the flux.

The N_2O flux chambers were aluminium cylinders, 25 cm high and 17 cm in diameter, with removable plexiglass lids. Two cylinders per plot were placed approximately 5 cm into the soil at the start of experiment and left in place, where possible, to minimize the perturbation to the soil. For a measurement the lid, which contained a stirrer and a syringe needle, was placed onto the cylinder. A 25 ml sample of the headspace gas was withdrawn immediately by piercing a rubber septum of a pre-evacuated tube with the needle on the lid. Similar samples were taken at regular intervals over the next hour. In all but the largest emission measurements, the increase in N_2O concentration in this period was generally less than a 25% increase on the ambient level which gave good precision in the flux determination but which was not expected to influence the emission process. The needle was left open to the atmosphere to ensure there was no pressure gradient between the chamber and the ambient atmosphere. The samples were analysed for N_2O within 36 h with an HP5880A series Gas Chromatograph using a Porapac Q column and a Nickel 63 electron capture detector. A least squares fit of the N_2O concentration against time was converted to an emission flux from a knowledge of the headspace volume and the cross-sectional area of the chamber. Initially up to eight samples per hour were taken but as confidence in the technique grew this was reduced to five. Measurements were usually made between 10 a.m. and 6 p.m. and in this time it was possible to make one N_2O flux determination at each of two canisters on each of the four plots, for a total of eight flux determinations per day.

The NO_x flux measurements apparatus is shown in Fig. 1. The system is designed around the chamber which is a 27ℓ plexiglass cube open at the bottom and lined on all five sides with FEP Type L fluorocarbon film. A stainless steel fan was used to circulate the air within the chamber. This chamber was sealed to a stainless steel frame set approximately 5 cm into the ground. Two frames were set into each plot and left undisturbed throughout most of the measurement period. The chamber was placed on one of these frames when a measurement was taken. Ambient air was scrubbed of NO_x and ozone using activated charcoal and pumped into the chamber at a rate of 4.0–4.5 ℓ min^{-1}, thus the residence time for air in the chamber (τ) was 6–7 min. Approximately

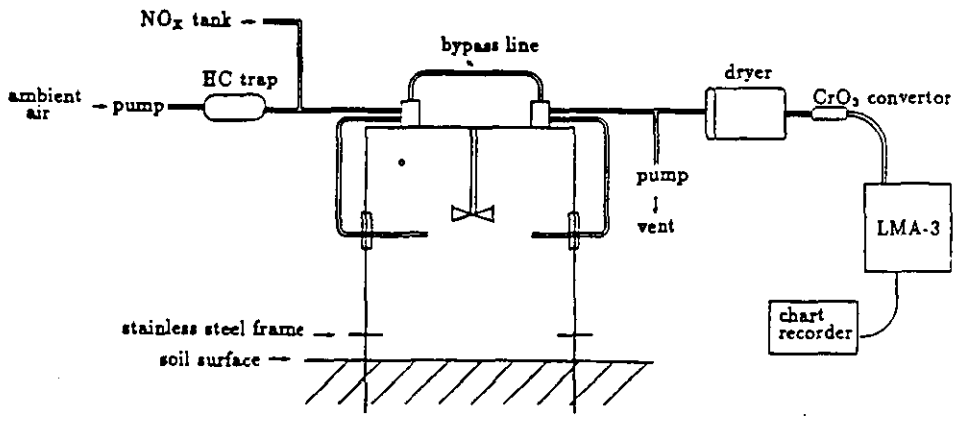

Fig. 1. Dynamic chamber equipment used for the field measurement of NO_x emission fluxes.

$2\,\ell\,min^{-1}$ of the air leaving the chamber was analysed for NO_x using an LMA-3 commercial NO_2 analyser preceded by a CrO_3 based NO to NO_2 converter (Drummond *et al.*, 1989). After approximately 10–20 min the NO_x concentration reached a steady level and the NO_x flux was determined from the total mass of NO in the chamber (m), and the area of soil exposed (A) using

$$NO_x\,\text{flux} = m\,\tau^{-1}A^{-1}.$$

The time the soil was covered was kept as short as possible to minimize the perturbations of the chamber on the soil and was never more than 45 min. Pressure gradients between the chamber and ambient air were prevented by a 0.2 cm hole in the chamber and on sunny days heating of the chamber was minimized by shading with an umbrella. In this way the air temperature inside the chamber was kept within a degree or two of the ambient temperature, and because of the short time the chamber was in place the soil temperature was not measurably different inside or outside of the chamber.

Prior to this experiment the chamber had been evaluated in the laboratory, and on both grass and bare soil sites on the grounds of York University. By placing a Teflon sheet on the bottom of the chamber and adding ambient concentrations of NO and NO_2 it was found that above $-10°C$ the walls of the chamber did not absorb either NO or NO_2, below this temperature NO_2 absorption was observed. Zero air was used to improve the precision of the measurement by removing the fluctuating ambient NO_x levels and to prevent ozone oxidation of the emitted NO to the more readily deposited NO_2. Flux determinations were found to independent of the residence times (τ) between 3.5 and 13 min. This is consistent with the inert nature of the chamber and the lack of uptake of the emitted gases. In general, the concentrations of NO_x measured in the chamber were between 1 and 40 ppbv.

On several occasions the NO to NO_2 converter was removed so the NO_2 flux could be determined. It was always less than 2% of the total NO_x flux showing the emitted gas to be NO. On a typical field day NO_x fluxes were determined two or three times for each of the eight frames.

In conjunction with each emission flux measurement a number of supporting measurements were made. Soil temperature was measured with a mercury thermometer inserted 2 cm into the soil. Moisture, nitrate, ammonium and pH were measured in soil samples taken from next to the chambers. The soil moisture was determined gravimetrically by the weight loss on drying at 105°C for 24 h. Ammonium was measured by extracting the soil with 0.05 M K_2SO_4 and quantified using an Orion ammonium electrode (Orion, 1987). Nitrate was extracted in a similar manner and also measured as ammonium following reduction by $TiCl_3$ (Orion, 1987). Soil pH was determined by extracting the soil with de-ionized water and measuring the pH of the extract with a pH electrode.

3. RESULTS AND DISCUSSION

3.1. *Flux and soil parameter measurements*

Figures 2 and 3 show the soil ammonium and nitrate plotted against the day of the measurement. Prior to the fertilizer application on day 116, the levels on the fertilized plots are low indicating that little if any of the previous year's nutrients remain. The exceedingly low values on days 113 and 115 are due to the field being ploughed and the nutrient poor soil from below being brought to the surface. Since the fertilizer is applied as granules, it takes several days for the nutrient levels to rise after the application of the fertilizer. The soil ammonium appears to peak some 20–30 days after the fertilizer is applied. Only Plot 300 retains any significant amount of the applied ammonium past day 180. This may be due to a lower soil pH which may have either inhibited the microbial nitrification or plant growth and the subsequent uptake of ammonium. The nitrate appears to peak about 80 days after application, this is due in part to the continued production from ammonium. A striking feature of Figs 2 and 3, which to some extent masks the gross features, is the nutrient decrease for days 159 and 160. Prior to these measurements the field was irrigated with 2.5–5 cm of water. This exceeded the field capacity of the soil and so leached the nutrients from the upper level to the lower soil levels. The subsequent increase is due to the movement of nutrient rich water from below being brought to the surface by capillary action as the soil dried. The effect is less pronounced with ammonium as it has a higher exchange capacity

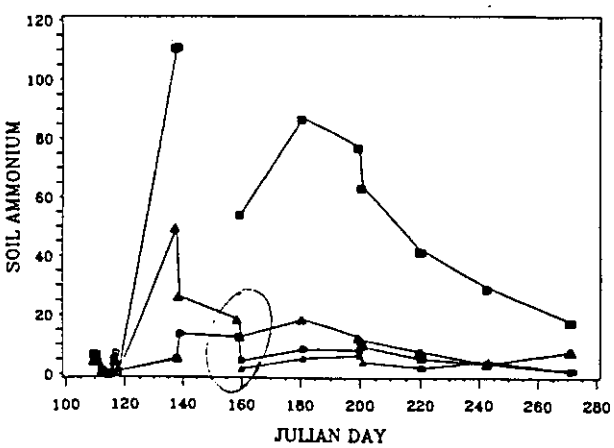

Fig. 2. Soil ammonium, in ppm, vs date for Plot 0 (open triangles), Plot 100 (open squares), Plot 200 (filled triangles) and Plot 300 (filled squares).

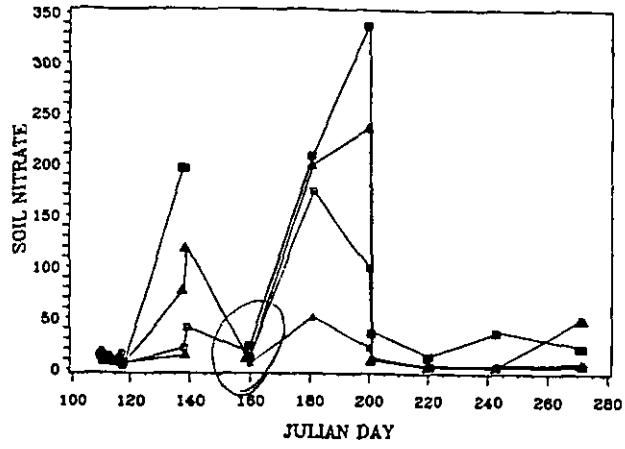

Fig. 3. Soil nitrate, in ppm, vs date for Plot 0 (open triangles), Plot 100 (open squares), Plot 200 (filled triangles) and Plot 300 (filled squares).

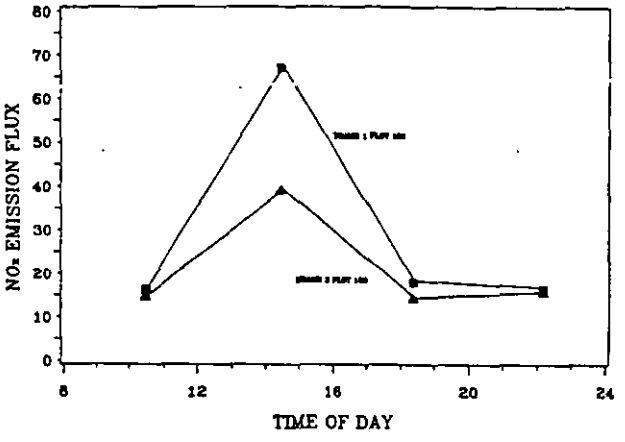

Fig. 4. Diurnal variation of the emission flux of NO_x from two frames on Plot 100 on day 243.

so is less easily leached from the soil. The maximum in the Plot 0 soil nitrate at day 180 could be due to the movement of nitrate rich water from one of the adjacent fertilized plots or to nitrogen fixation by the bean crop. The nutrient levels drop as the growing season progresses although heavy rain during the night of day 200 gives rise to an accentuated rate of removal between days 200 and 201.

Figure 4 shows a typical day of NO_x emission measurements. Four measurements were made on each of the two frames over a 10-h period. The variations in soil moisture and temperature are shown in Fig. 5. The first point to note is that there is substantial NO_x emission 2 h after sunset, showing that the process producing the NO_x is not sunlight dependent. The night-time emissions are lower than the midday values but are the same as the morning values where the soil temperature was comparable. It appears therefore that the diurnal variation in NO_x emission is a consequence of temperature variations. The other major feature is the variation in emission rate within what is expected to be a homogeneous plot. For example, there is almost a factor of two difference in some of the simultaneous NO_x emission measurements. The two frames were only 2.5 m apart and no closer than 3 m to the boundary of the plot. Since the field has been so carefully tended there is no reason to predict any variation between the sites. We must conclude that in spite of man's attempt to homogenize the soil there is a great deal of variation within it. This degree of variation has been seen elsewhere but never under such controlled conditions.

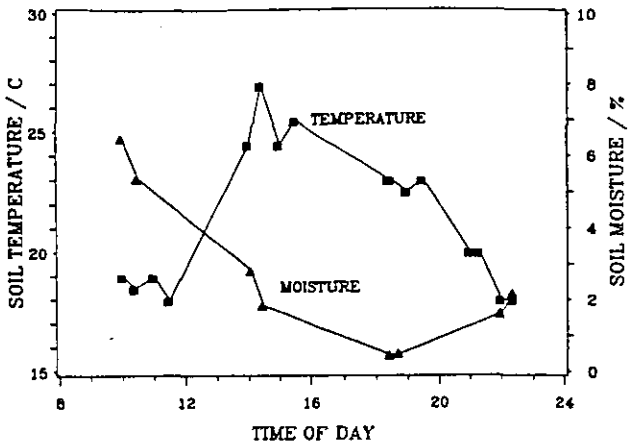

Fig. 5. Soil temperature (squares) and soil moisture (triangles) for Plot 100 on the same day as for Fig. 4.

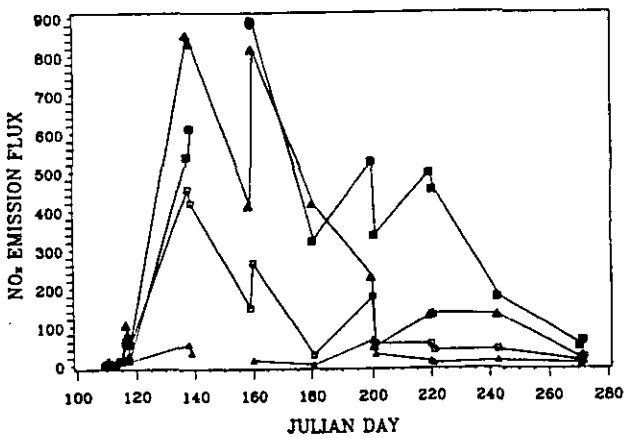

Fig. 6. NO_x emission flux in $\mu g(NO)\,m^{-2}\,h^{-1}$ vs date for Plot 0 (open triangles), Plot 100 (open squares), Plot 200 (filled triangles) and Plot 300 (filled squares).

This variation makes it difficult to make detailed measurements on the soil. A large number of measurements are needed to determine trends and true averages.

Figures 6 and 7 show the fluxes of NO_x and N_2O determined during this study. Each point is the average of measurements from both frames on each plot. The emission flux measurements showed huge variations throughout the measurement period. For Plot 0 the NO_x emission ranged from 1.5 to 41.6 $\mu g(NO)\,m^{-2}\,h^{-1}$ whereas for Plot 300 the range was from 3.1 to 583 $\mu g(NO)\,m^{-2}\,h^{-1}$. A similar variation was noted for N_2O where the flux for Plot 0 ranged from 0 to 61.8 $\mu g(N_2O)\,m^{-2}\,h^{-1}$ and for Plot 300 from 0 to 446 $\mu g(N_2O)\,m^{-2}\,h^{-1}$. There is a clear seasonal cycle in the emission fluxes which seem to follow the nutrient levels, but there are marked day-to-day variations.

The emissions from the fertilized plots rose above that of Plot 0 simultaneously with the increase in soil nitrate and ammonium between days 116 and 138. The emissions appear to peak around day 160, about 40 days after the application of the fertilizer.

The N_2O emission dropped back to the Plot 0 level by day 180. This is not consistent with the soil nitrate measurements which are still high from days 180 to 200. There is some correlation with ammonium in the time scale for removal, but on Plot 300 there is little emission late in the season, even in the presence of elevated ammonium. A plot of emission flux against soil nutrients (ammonium and nitrate) gave no further insight into the process.

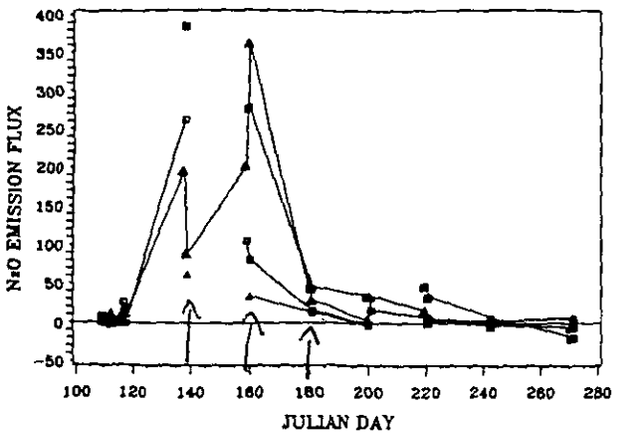

Fig. 7. N_2O emission flux in $\mu g\ (N_2O)\ m^{-2}\ h^{-1}$ vs date for Plot 0 (open triangles), Plot 100 (open squares), Plot 200 (filled triangles) and Plot 300 (filled squares).

The NO_x emissions persisted throughout the growing season with discernible emissions past day 240, 120 days after fertilizer application. This behaviour appears to correlate better with soil ammonium than nitrate, especially in the response to the irrigation on day 159 and the persistence of NO_x emissions on Plot 300. This would suggest that the NO_x is a product of biological nitrification consistent with the observations of Anderson and Levine (1987). However this correlation does not hold up to detailed analysis. Again a plot of emission against soil nutrients gave no additional information.

Although the emissions seem most closely related to the nutrient levels, the day to day variation is substantial and must be related to the more variable parameters of temperature and soil moisture, along with agricultural practice. The variability of the emissions between days 110 and 118 are largely due to the soil being ploughed three times so that most of the microbes, which live in the top 2–3 cm of soil, were buried about 15–20cm. The microbe population then took several days to regenerate in the surface layer. There is little variation in either N_2O or NO_x emissions between days 138 and 139 consistent with similar temperatures and no rain on those days. The major discrepancy occurred for the NO_x emission on days 159 and 160. As noted above heavy irrigation lowered the nutrients on these days. NO_x fluxes were measured for all four plots on day 160 but only for plots 100 and 200 on day 159. These two measurements show a substantial decrease in NO_x emission but it had returned to apparently more typical levels by the next day. In this case the drying of the field, and the associated movement of nutrients, appears to dominate the NO_x emissions. Plot 200 showed an increased N_2O emission on day 160 but otherwise the effect of the irrigation was minimal for N_2O. By the next measurement on day 180 the N_2O emissions had dropped to pre-fertilization levels and little day to day variation was observed subsequently. The NO_x levels at day 180 appear depressed by the hot dry conditions but recover by day 200. They are suppressed again by rain that night. There is some evidence for a small increase in N_2O emission on day 200 due to the moister soil conditions. The NO_x emission had recovered again by day 220 and showed a steady decrease to the end of the growing season.

3.2. *Comparison with previous studies*

As with previous studies, particularly those on agricultural soils, a wide range of emission fluxes were obtained with the values for the most fertilized plot among the highest reported.

Tables 1 and 2 present the results of NO_x and N_2O flux measurements on fertilized agricultural soils. While the values reported here are somewhat higher than most they are not remarkably so. The measurements were made on research soil subjected to abnormally high fertilizer applications, so higher emissions would be expected from these fields than those under regular cultivation. It must also be remembered that these measurements were made on bare soil and may overestimate the actual net nitrogen emission to the atmosphere.

3.3. *Discussion of the flux variation*

Examination of these data shows, as have a number of studies, that the emissions are dependent on soil nutrients (ammonium and nitrate), temperature, soil moisture and agricultural practice. We now describe our attempts to quantify these dependencies to obtain a model for the emission flux in terms of the readily measureable soil parameters.

Table 1. NO_x emission fluxes from fertilized agricultural soils

Ground character	NO_x Flux $\mu g(NO)\ m^{-2}\ h^{-1}$	Reference
Corn field	20–860	Williams *et al.* (1988)
Wheat field	1.3–6.2	Williams *et al.* (1988)
Corn field	21–241	Anderson and Levine (1987)
Soy field	2.5–33.8	Anderson and Levine (1987)
Arable field	0.4–223	Johansson and Granat (1984)
Experimental field	1.5–583	This study

Table 2. N_2O emission fluxes from fertilized agricultural soils

Ground character	N_2O flux $\mu g(N_2O)\ m^{-2}\ h^{-1}$	Reference
Arable field	228–1712	Blackmer *et al.* (1982)
Arable field	34–367	Bremner *et al.* (1980)
Arable field	35–482	Anderson and Levine (1987)
Corn field	411–594	Cates and Keeney (1987)
Cropped field	868 (average)	Mosier and Hutchinson (1982)
Experimental field	0–446	This study

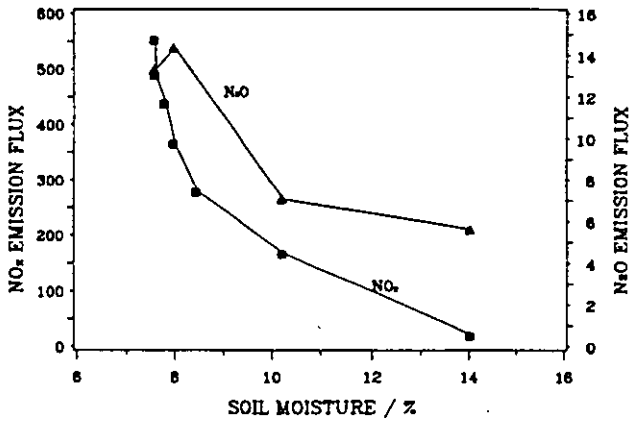

Fig. 8. NO_x (squares) and N_2O (triangles) emission fluxes in μg(NO or N_2O) $m^{-2}\ h^{-1}$ vs soil moisture (%) for Plot 200 on day 182.

An experiment to investigate the soil moisture dependence was performed on day 182 when 1.5–2.0 cm of water was applied. This brought the soil close to field capacity, about 14% soil moisture, but did not exceed it as on day 159. Measurements commenced immediately after the irrigation ceased. The NO_x emission flux was less than 5%, and the N_2O flux less than 20% of the previous day's values. As the soil dried the fluxes increased to values consistent with those obtained in the period before irrigation. The variation of the fluxes with soil moisture are given in Fig. 8. The steady increase in the NO_x emission rate with decreasing soil moisture is consistent with the depression of an aerobic process by the high water content of the soil. This is the same conclusion drawn in section 3.1 on the basis of the ammonium dependence of the emission flux. The N_2O emission appears to be limited by a physical process as evidenced by the sharp increase in flux below 10% soil moisture. Davidson and Firestone (1988) have shown that, for N_2O emission, diffusion through the soil pore spaces is important. Thus it appears likely that in this case the anaerobic production of N_2O continued even at the high soil moisture levels but the emission was physically controlled by the presence of water in the soil pores. This effect has been observed previously by several groups including Slemr and Seiler (1984) and Grundmann *et al.* (1988). The NO_x flux results were

found to be best fitted by a ln(flux) dependence on soil moisture, but a simple analytical expression for N_2O flux was not possible.

There is a wide temperature range from which a temperature dependence can be determined. The temperature dependence is best described by an activation energy type expression, i.e.

$$\ln(\text{flux}) = \ln(A) - E_a/RT_s.$$

Here A is a constant, T_s the soil temperature, R the gas constant and E_a the activation energy. However, when E_a was so determined it was found to be plot dependent. This was due, in part, to the simultaneous variation of soil nitrogen and temperature. The nutrients were greatest when the temperatures were the highest, thus we were fitting some nitrogen dependence as well. Restricting the determination of E_a to the latter half of the season where the nitrogen variation was small produced a more consistent result of 108 ± 20 kJ mol^{-1}. This is similar to the values of 65–83 kJ mol^{-1} obtained by Johansson and Granat (1984), 44–103 kJ mol^{-1} by Slemr and Seiler (1984) and 97 $\pm$ 11 kJ mol^{-1} by Williams *et al.* (1988).

Using this dependence on moisture and temperature, and assuming a linear dependence of the flux rates on ammonium, nitrate and pH, we attempted to develop a model for the emission flux in terms of these parameters. The results of this exercise were disappointing. Within a single plot or for a limited time period the model was able to simulate the fluxes satisfactorally. However for the data set as a whole the model was unsatisfactory indicating this simple model to be incomplete. For example the soil moisture dependence appears to change with nutrient level. A multiple regression model cannot be used for this kind of non-linear system and we have insufficient data for a more detailed model. The relationships we have described apply well to the system as it was studied, but extrapolation to different moisture and nutrient conditions is not possible.

3.4. *Total* NO_x *and* N_2O *released*

By integrating the data in Figs 6 and 7 we can determine a total seasonal release of NO_x and N_2O. Figure 9 gives the total emission for each plot as a function of the applied fertilizer. There appears to be a simple linear relationship between the emission flux and the applied fertilizer. From these data an average of 5.3% of the nitrogen applied as fertilizer (NH_4 or NO_3) is released to the atmosphere as N_2O and 11% as NO_x.

As the area in which these measurements were made is a major population area, the anthropogenic emissions of NO_x are well quantified. Thus using the results of this study with anthropogenic emissions does allow the assessment of the importance of biological input into the atmosphere. For a 5×5 km^2 area centred on the city of Windsor, the annual anthropogenic NO_x emission is 732.8 tonnes (MOE, 1985). The average for the same area of agricultural land in southwestern Ontario, off the transit corridor, is only 15 tonnes. Assuming an equivalent of 150 kg ha^{-1} of NH_4NO_3 fertilizer is applied to the agricultural land in this area then the annual biogenic emission is 14.5 tonnes for the same 5×5 km^2 area. Thus in a rural area the biological emission is comparable to the anthropogenic emission.

On a province wide basis only 3.9% of Ontario is under cultivation for cereal, legume or vegetable production. Using the same assumptions, as above, yields an Ontario biological NO_x production of 14 kilotonnes per year. The comparable anthropogenic emissions are 329 kilotonnes for vehicular emissions, 178 kilotonnes from point sources and 78 kilotonnes from other sources (MOE, 1985). Thus on the larger scale anthropogenic NO_x emissions are dominant.

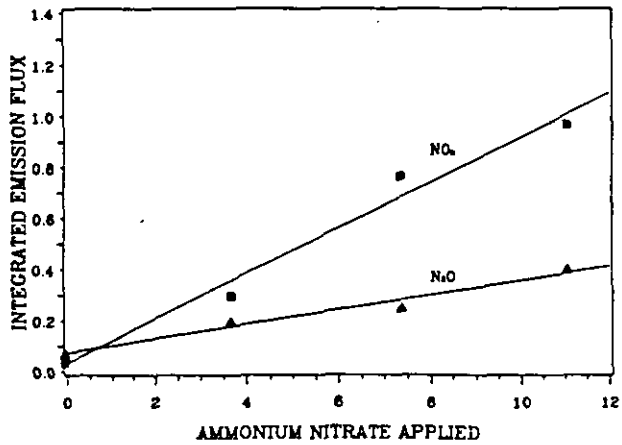

Fig. 9. Total seasonal emission of NO_x (squares) and N_2O (triangles) vs the amount of fertilizer applied (g ammonium nitrate m^{-2}).

This exercise shows how carefully these agricultural data must be used. Near a major urban centre the agricultural component is insignificant, as is the total provincial wide contribution. However, away from major anthropogenic centres and for cases where transport from such centres is small, the agricultural contribution is significant.

4. CONCLUSIONS

A study of the emissions of NO_x and N_2O from a field with controlled fertilizer applications has been performed. The fluxes of these gases to the atmosphere are strongly related to the nutrient levels, the moisture and the temperature within the soil. Attempts to develop a model for the fluxes in terms of these parameters were unsuccessful. Over the course of a full growing season approximately 11% of the nitrogen supplied to the field as ammonium nitrate fertilizer was converted to NO_x and 5% to N_2O. In rural areas away from major transportation routes the NO_x emission from fertilized soils may be comparable to the anthropogenic NO_x production and so may dominate the local oxidant chemistry. However, for the Province of Ontario as a whole the increased NO_x emission as a result of fertilizer usage is small.

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