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Sect 4 # 3

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Emission of nitric oxide from arable land

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ABSTRACT

The flux of NO between arable land and atmosphere has been measured with a chamber technique. The net flux from the soil to the atmosphere varied from less than 0.1 up to 62 ng NO–N m^{-2} s^{-1} for a fertilized area (200 kg N ha^{-1} as calcium nitrate) and up to 17 ng NO–N m^{-2} s^{-1} for an unfertilized area. The emission was high in the summer when the temperature was high and the soil was dry and decreased to low values when the soil surface was thoroughly wetted by rain. Previously reported findings of equilibrium concentrations of NO (compensation point) have been verified. These concentrations ranged from 2 to more than 75 ppbv. At the rural site where the measurements were made, the atmospheric NO concentration was always below this compensation point and there was consequently a net emission of NO from the soil. Nitrogen gases, measured as the difference between NO and NO_x (including NO_2 and possibly also HNO_3 and PAN), were found to be absorbed on soil and vegetation. The absorption of NO_2 was generally smaller than the emission of NO.

The areal variability within an area of 100 m^2 was found to be moderate with a standard deviation of 25%, somewhat higher on recently fertilized soil (between 50 and 80%). The temperature dependence of NO emission could be described with an activation energy of 65 to 83 kJ mol^{-1} (Q_{10} between 2.7 and 3.6). A more rapid increase of production than that predicted by the temperature increase was observed in morning hours. This is tentatively explained to be caused by nutrient dynamics in the soil.

The yearly emission is estimated to be about 0.6 kg NO–N ha^{-1} and 0.2 kg NO–N ha^{-1} for the fertilized and unfertilized areas, respectively. During the vegetation period, NO emission from highly fertilized areas might be of some importance when compared with anthropogenic emission from combustion within Sweden.

1. Introduction

From the atmospheric chemist's point of view, emission of NO from soil is a source of odd nitrogen for the atmosphere that has to be added to other more well-known sources when estimating atmospheric N budgets. For the soil system, NO emissions represent a loss of N. Our knowledge about the chemical and biological processes leading to NO losses is poor, although it is known that NO can be produced both during nitrification (Lipschultz et al., 1981), and denitrification (Firestone et al., 1979; McKenney et al., 1982). Lipschultz et al. (1981) found that nitrifying bacteria (*Nitrosomonas europaea*) produced NO and N_2O in molar ratios ranging from 2.8 to 7.8 at 0.5% O_2. The ratio decreased as the oxygen concentration increased to give a value of about 1.1 at 20% O_2. These authors also showed that the NO production was insignificant when the respiratory system of the bacteria was inhibited by $HgCl_2$. Studying a Brookstone clay column undergoing anaerobic denitrification, McKenney et al. (1982) reported production of NO and N_2O in molar ratios ranging from 2.0 to 2.5.

NO can also be produced by chemical decomposition of NO_2^-. In the measurements by McKenney et al. (1982) it was found that up to 45% of the NO produced during denitrification came from decomposition of NO_2^-. Since no laboratory experiment has been conducted so far at conditions which closely simulate those in the field,

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there is an obvious need to verify findings by field experiments. It is of particular importance to estimate the magnitude of the flux and its variation in time and space as a function of identifiable environmental variables.

To our knowledge, only three papers have reported on field measurements of NO_x emissions from soils. Kim (1973) measured emission from soil beneath three stands of vegetation (pine, oak and sod). A plastic hood containing petri dishes with a solution of sodium hydroxide to absorb NO_2 was placed on the ground. The average values for the stands of pine, oak and sod were 0.21, 0.12 and 0.19 kg NO_2 ha^{-1} $week^{-1}$, respectively (corresponding to 10.6, 6.0 and 9.6 ng NO_2–N m^{-2} s^{-1}). Galbally and Roy (1978) measured emissions of NO_x from grazed and ungrazed areas using a chamber technique. A box was placed on the ground and the increase in concentration during the first few minutes was followed. The average emission of NO for ungrazed and grazed pastures was observed to be 1.6 and 3.5 ng NO–N m^{-2} s^{-1}, respectively. In later measurements on grazed pasture NO emission ranging from 1 to 50 ng NO–N m^{-2} s^{-1} were found (Galbally and Roy, 1981).

The measurements of NO/NO_x emission presented below, form part of an integrated research effort to study the biogeochemical nitrogen cycle of arable land. Efforts have been made to measure simultaneously emissions of N_2O, NO, NO_x and NH_3 from several plots with different treatment. In this paper we will mainly deal with the NO measurements and in a later paper compare the fluxes of several gaseous N compounds to and from the field. For a detailed description of the project with its many subprojects, including the results from measurements of NO_x emissions during 1981, the reader is referred to Rosswall (1982).

2. Experimental site

The measurements were performed in an agricultural field at Kjettslinge, approximately 40 km north of Uppsala, Sweden (Steen et al., 1984). The main part of the experimental field consists of four cropping systems:

1. Barley with no addition of N fertilizer (hereafter called B0);
2. Barley with an annual addition of 120 kg N ha^{-1} (calcium nitrate) (B 120);
3. Grass ley with an annual addition of 200 kg N ha^{-1} (calcium nitrate) (GR 200);
4. Lucerne with no addition of N fertilizer (LU).

Each cropping system has four replicates, each plot measuring 40 × 14 m. The soil consists of three distinct layers:

(i) top soil (plough layer), a sandy loam (mean thickness 27 cm);
(ii) a fine sand layer (very varying thickness, from 0 to 50 cm, mean 15 cm);
(iii) a clay layer.

The top soil consists of 15–20% clay, 4% carbon and has a pH of 6.0–6.5. As a median for the top soil of the four cropping systems during the growing season, the NH_4^+–N and NO_3^-–N contents was about 7.5 and 6.7 kg N ha^{-1}, respectively. The NO_2^- concentration was less than 0.05 kg N ha^{-1}.

3. Instruments and methods

We have used a "chamber" technique, similar to that used by Galbally and Roy (1978). A box is placed on the ground and the air is mixed with a fan to reduce the transfer resistance between soil and atmosphere. The flux is calculated either from measured changes in concentration in an air stream passing through the chamber at steady state (open system), or from the gradual increase in concentration, in an almost closed chamber (later referred to as closed system). This appears to be the only practically possible method, as methods using a micrometeorological approach are invalidated by the structure of the experimental field which consists of several small plots of different treatment.

Cylindrical chambers of three different sizes have been used. The volume of the chambers was 5, 30 and 110 litres and the covered area 0.03, 0.20 and 0.20 m^2, respectively. Generally the smaller chambers were used during measurements in the open system and the large one (110 litres) for measurements in the closed system. The chambers had a sharp bottom edge and were inserted a few centimetres into the soil to prevent movement of air into or out of the chamber. The chambers were teflon-lined and the air was well stirred with a paddle (30 cm diameter, approximately 250 rpm) driven by an external motor (80 W) mounted on

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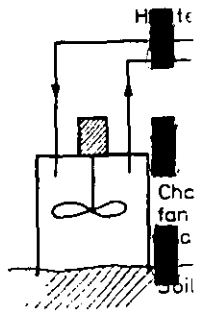


Fig. 1. Schemat d

the top of the chamber. In the open system ambient air was pumped to the chamber and the concentration of NO, NO_x and O_3 was measured (Fig. 1). The majority of the air was then pumped from the chamber to the analytical instruments. The sampling and delivery tubes were teflon (about 15 m long), and in order to avoid condensation of water they were heated and insulated. Absorption in tubes and pumps was small and without consequence for the flux determinations. When measurements were made in the open system, the residence time could be varied between 2 and 25 minutes. Deliberate leaks ensured that the pressure difference between chamber and atmosphere was small, in fact it was below detection, less than 0.2 mm H_2O measured with a tilting water manometer. In the "closed" system, throughflow was limited to that required for the gas analysers (about 1.5 l min^{-1}). The air in the chamber was then replaced by outside air through the leaks. The NO concentration gradually built up and usually reached an equilibrium value in about 30 minutes. In this system both NO and O_3 were measured.

The NO analyser was a Thermo Electron series 14 modified according to Delany et al. (1982). The sensitivity of the instrument was ±0.2 ppbv. A change in the NO concentration in the chamber of 0.2 ppbv during 10 minutes (closed system) corresponds to an NO emission of 0.1 ng NO–N m^{-2} s^{-1}. The NO_x concentration was determined after conversion to NO in a heated molybdenum converter. Not only NO_2 but also substances like HNO_2, HNO_3, alkyl nitrites, alkyl nitrates and PAN (peroxylacetyl nitrate) are known to be converted to NO by this treatment (Winer et al., 1974). NO calibration was performed using a cylinder containing 1.02 ± 0.05 ppmv NO in N_2. A permeation tube system was used for NO_2 calibration. O_3 was measured with a continuous chemiluminescent analyser.

The analyses of N_2O and CO_2 were made with GC and infrared absorption respectively and performed by Leif Klemendtsson and Bo Svensson, Swedish University of Agricultural Sciences, Uppsala. The NH_3 determinations mentioned in this report were made by collection of oxalic acid impregnated pyrex tubes for subsequent chemical analysis (Ferm, 1979). These analyses were made by M. Ferm, Swedish Water and Air Pollution Research Institute, Gothenburg.

4. Results and discussion

4.1 *Chamber technique*

The air in the chamber was mixed with a moving "paddle". This makes the chamber air homogenous and facilitates the measurements. Air turbulence above the soil (occurring both naturally and in the chamber) can significantly increase the exchange of gases between soil and atmosphere (Kimball and Lemon, 1971). The maximum windspeed in the chamber was less than 2 m s^{-1}. In a set of measurements of NO emission on the same area with the air in the chamber unstirred, it was found that the emission then decreased to between 30 and 70% of the flux in the stirred chamber.

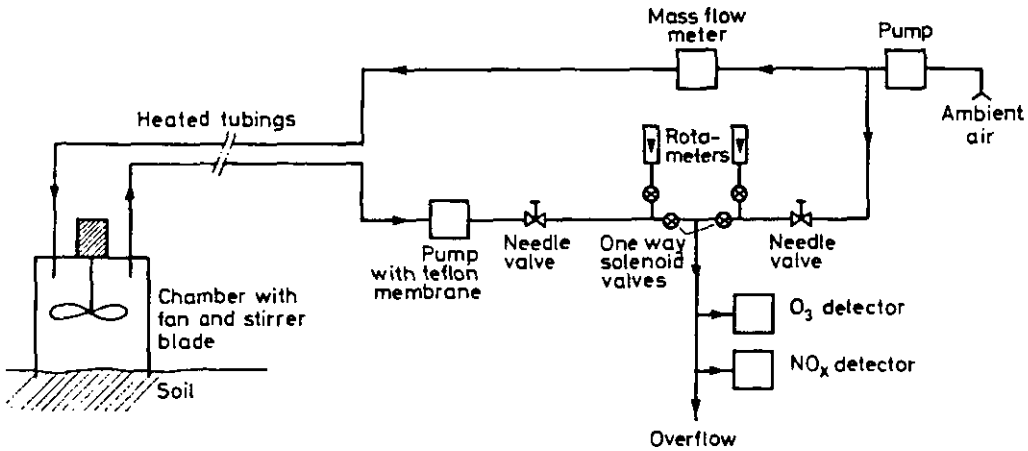


Fig. 1. Schematic diagram of the sampling system.

Comparison of measurements of the NO emission using the open and closed system is shown in Table 1. The measurements were made over the same area, at similar times, and the chamber stirring was identical. We attribute the smaller emission rates in the open system to increased concentration of NO in the chamber and disturbance of the natural environment in the soil. We believe that for these measurements, the closed system is the most reliable, with the chamber covering the soil for only 2 to 10 minutes depending on the emission rate. With this technique it is possible to compare the emission rate from several areas in a very short time.

Similar comparisons of fluxes of N_2O derived from measurements with closed and open systems were performed by Denmead (1979). In his system the chamber covered the soil for approximately 3 hours and was removed for 34 minutes between each measurement. The fluxes as observed from measurements in the closed system were about 30% higher than the fluxes measured in the open system, and thus, were similar to our results for NO. However, Denmead explains this difference by disturbance of the N_2O concentration profile in the soil when the closed system was used and insufficient time for the soil profile to readjust between the measurements. Therefore, he concluded that the closed system overestimated the flux.

4.2 *Production of NO—existence of an equilibrium concentration (compensation point)*

Fig. 2 shows the increase in NO concentration in the closed chamber, immediately after chamber installation. The increase in concentration during the first few minutes is used to estimate the flux of NO from the undisturbed soil. After 10 to 30 minutes, depending on the emission rate, a steady state is reached. This behaviour can be simulated by an expression of the type:

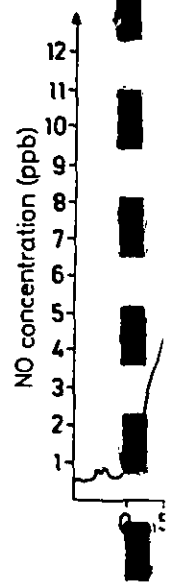
$$c = c^* (1 - e^{-kt})$$

where c^* is an equilibrium concentration in the chamber and k a parameter which depends both on the transfer resistance in soil and air and on losses in the chamber due to withdrawal of air and absorption on the chamber walls. This expression is easily derived from an assumption of an equilibrium concentration in the soil. The same expression can also be obtained from other hypotheses on production and consumption of NO in the soil. The relation is useful when discussing influence of dilution and absorption on the change in NO concentration in the chamber. In our experiments

Table 1. *Comparisons of measurements using the open and closed systems on the same area (times in parentheses correspond to the time when measurements in the open system were started)*

Date	Time	Plot	System used Open = O Closed = C	Soil surface temp. (°C)	Residence time in chamber (min)	Emission rate (ng NO–N $m^{-2} s^{-1}$)	Ratio of emission rate Closed system / Open system
Apr. 22	20^{02}	LU	C	6.5	—	2.68	1.5
	21^{40} (20^{10})		O	4.9	21	1.84	
Apr. 23	19^{02}	LU	C	9.7	—	5.50	2.0
	20^{40} (19^{10})		O	9.5	21	2.80	
Apr. 28*	8^{14}	LU	C	6.3	—	1.17	1.0
	7^{47} (19^{10})†		O	6.1	1.8	1.13	
July 1	9^{28}	GR 200	C	11.7	—	2.13	1.6
	10^{18} (9^{40})		O	12.7	8.2	1.36	
July 1	10^{50}	GR 200	C	13.0	—	2.83	2.1
	11^{33} (11^{02})		O	14.2	22	1.36	2.3
	11^{47}		C	14.5	—	3.19	

* Different chambers were used. 110 and 5 l in the closed and open system respectively.
† The measurements in the open system were started on April 27.
GR = grass ley; LU = lucerne.



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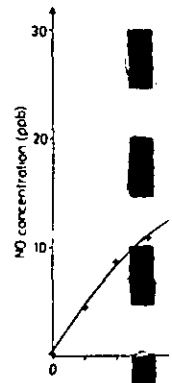

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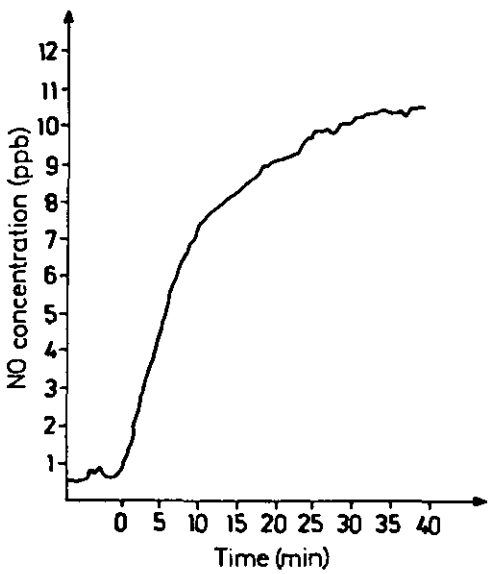


Fig. 2. Example of a typical measurement of NO emission rate (closed system) showing the increase in NO concentration in the chamber air when the chamber is placed on the soil surface (=0 minutes).

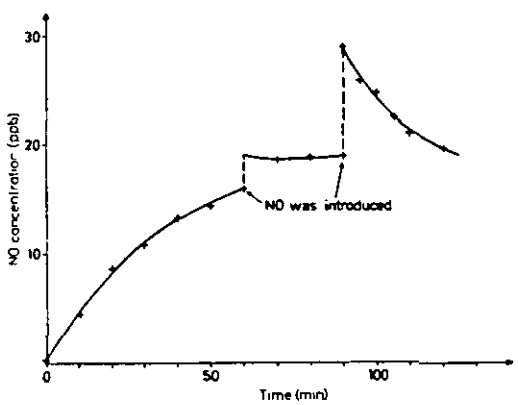


Fig. 3. NO concentration in the chamber air (closed system). NO was introduced by a rapid injection from a cylinder. Curves fitted by hand.

the rate constant k varied between 0.02 and 0.09 min^{-1}. Of this, 0.014 min^{-1} is accounted for by withdrawal of air for the O_3 and NO_x detectors.

In an experiment shown in Fig. 3, the NO concentration in the chamber was increased above the equilibrium concentration by rapid injection of NO. The concentration of NO decreased to reach equilibrium concentration. The rate of removal of NO corresponded in this particular case to k = 0·07 min^{-1}. Thus, the withdrawal of air can in some cases affect the measured equilibrium concentration to some degree, but is, in most cases, of little importance compared to other removal mechanisms.

There are several possible explanations for the decrease in net emission of NO during an experiment.

1. There is an equilibrium NO concentration in the soil and the driving force for NO emission decreases as NO concentration in the chamber increases.
2. The production of NO in the soil is counteracted by a deposition which increases as NO concentration in the chamber increases.
3. Losses of NO due to uncontrolled exchange with the atmosphere and/or absorption of NO on the chamber walls.

We can exclude the last explanation based on measurements of changes in NO concentration in the chamber when this was placed on a teflon film instead of on the ground. Experimental data satisfy both the first and second hypothesis.

Neither the flux estimates nor the magnitude of the equilibrium concentrations were affected by O_3 as the O_3 concentration in the chamber air decreased to less than 2 ppbv immediately after the chamber was installed over the soil.

From measurements under different conditions (temperature, soil, moisture, vegetation cover and NO_3^- content) equilibrium concentrations ranging from 2 to more than 75 ppbv were observed. The concentrations in the ambient air were generally less than 1 ppbv and consequently there was always an upward flux of NO. The existence of an equilibrium concentration for NO was first reported by Galbally and Roy (1978). In later measurements on a grazed pasture, equilibrium concentrations ranging from 3 to 150 ppbv were observed (Galbally, pers. comm.).

Efforts to compare the fluxes of NO, N_2O and CO_2 and NH_3 have been made. The measurements of the concentrations of these gases were made simultaneously in the same chamber. N_2O, CO_2 and NO were measured using the closed system and it was found that an equilibrium concentration was established, not only for NO but also for the two other gases. Results from the measurements are shown in Fig. 4. Both the equilibrium concentration and the flux of N_2O were almost two orders of magnitude higher than that for NO. It

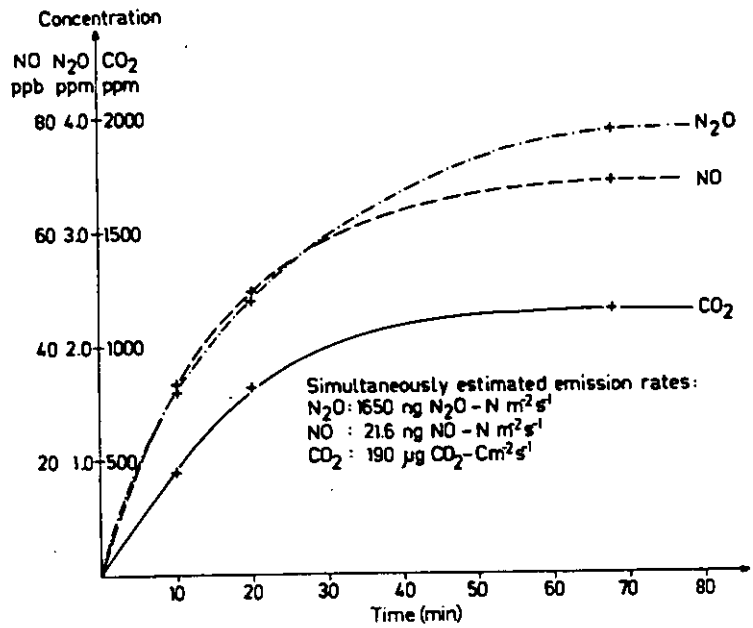


Fig. 4. Simultaneous measurements of the concentration of NO, N_2O and CO_2 in the same chamber (closed system).

Table 2. *Comparison of NO and NH_3 emissions in the same chamber during the same period using an open system (April 1982)*

Day and time		Emission (ng N m^{-2} s^{-1}) of		Range of soil temp.
from–to	Plot	NO*	NH_3	(°C)
20 20^{40}–21 08^{30}	LU	0.84	1.53	−0.1–+3.9
21 11^{20}–21 13^{20}	LU	1.76	9.5	7.0–10.0
21 21^{00}–22 09^{00}	LU	0.96	0.57	0.1–3.9
22 13^{15}–22 15^{40}	LU	2.30	3.5	10.5–11.2
22 20^{40}–23 08^{40}	LU	1.7	0.78	1.2–5.9
23 11^{40}–23 12^{30}	B 120†	0.61	1.23	5.6–6.8
23 13^{30}–23 14^{35}	GR 200†	0.22	0.84	8.8–9.0
23 20^{40}–27 11^{50}	LU	2.98	2.52	3.0–12.2

* Average of hourly data.
† Fertilized in May 1981.
LU = lucerne; B = barley; GR = grass ley.

should be pointed out that this measurement was made on an area recently fertilized with NO_3^- and glucose.

Similar conditions apply for the measurements of NH_3. Table 2 shows simultaneous measurements of NH_3 and NO emissions using the open system. The NH_3 concentration in the chamber was actually an equilibrium concentration indicating that the actual emission is higher (Ferm, pers. comm.). A direct comparison with NH_3 emission is therefore uncertain, but indicates that the fluxes were always in the same order of magnitude. As each measurement of the NH_3 concentration took at least one hour, it was not possible to use the closed system for the NH_3 measurements.

4.3 *Emission and deposition of NO_2*

On several occasions, NO_x was measured in addition to NO. The concentration difference between NO_x and NO indicates the presence of

NO_2 and, possibly, also some other nitrogen-containing trace gases (see discussion under Instruments and methods), and we will in this section denote the difference between NO_x and NO as NO_2. All measurements of the flux of NO_2 were made using the open system. With this method it is important to remove O_3 in the air entering the chamber in order to know if NO_2 is emitted from the soil or just formed as a product of the oxidation (with O_3) of NO. This was done on some occasions by putting an active carbon filter on the air intake and results from these measurements are shown in Table 3.

When NO_2 in the air entering the chamber was high (>2 ppbv) there was an uptake of NO_2 in the chamber. On occasions when the concentration was low, measurements indicate that there might be an emission of NO_2 of less than 10% of the NO emission.

In one experiment the concentration of NO_2 in the air entering the chamber was increased by addition of NO_2 from a permeation tube (April 22 at 3.05 p.m. in Table 3). Then the flux of NO_2 changed sign, from emission to uptake in the chamber. As the concentrations of NO_2 at the site of measurements were low, there was almost always a net production of NO_x in the chamber. In earlier measurements of NO_x emissions (reported in Rosswall, 1982), the flux of NO_2 was up to 50% of the NO flux. Later measurements of the concentration of O_3 at the inlet and outlet of the chamber have shown that oxidation of NO to NO_2 by O_3 might explain these high productions of NO_2 in the chamber. These results should be compared with those reported by Galbally and Roy (1978) who found NO_2 fluxes which were less than 3% of the NO flux on grazed and ungrazed pastures.

4.4 *Areal variability*

When the chamber was placed on exactly the same area several times in succession and removed for short periods (1–2 minutes) in between, the estimated rate varied slightly with a standard deviation of between 9 and 16% of the mean value. Fig. 5.1 shows the results from three measurements on the same place, within about 15 minutes, on both lucerne and grass ley. The emission rate has been normalized by division by the median value in each set of observations. These measurements indicate the expected precision of a point measure. When the emission rate was measured a few metres apart (close in time) the variation was higher—see Figs 5.2–5.5. Furthermore, the variation in the fertilized areas (GR 200 and B 120) was significantly higher than in the non-fertilized areas. This areal variation may be explained by an inhomogeneous distribution of both nutrients and microbiological activity. In the case of a recently fertilized area, the uneven distribution of fertilizer pellets certainly adds to the variability in NO emission rates. As an example, the emission from recently fertilized grass ley (Fig. 5.2b) varied from 4.5 to 62 ng NO–N m^{-2} s^{-1} within an area of 14 × 8 metres.

Areal variability in NO emission on grazed pasture in Australia gave a factor of 35 on an area of 300 m^2 (Galbally, pers. comm.). It is possible that the comparatively low spatial variability observed at Kjettslinge is due to more homogenous soil conditions than is the case with the grazed pasture in Australia.

Much larger areal variability has been found for N_2O production in the Kjettslinge soil (Klemendtsson, pers. comm.). N_2O emission is determined by taking soil cores of 10 cm diameter and measuring the production in the laboratory under standardized conditions. One reason for the larger variability in estimated N_2O emission could, therefore, be the smaller area used for the measurements, but other factors might also be of importance. Large areal variability for N_2O emissions has earlier been reported in the literature. Thus, Bremner and Blackmer (1980) found that N_2O emission rates from a "seemingly uniform area" of 100 m^2 varied from values corresponding to between 48 and 457 ng N_2O–N m^{-2} s^{-1} with a standard deviation of about 50%.

4.5. *Temperature dependence*

Fig. 6 shows the diurnal variation of the NO emission rate on all four treatments together with soil surface temperature (at about 3 cm depth). A plot of the logarithm of the net NO emission rate versus the inverse of absolute temperature is shown in Fig. 7. This figure indicates an interesting anomaly, in that the emission rate increases more rapidly than could be predicted from the increase in soil temperature during the morning hours (dashed arrows in Fig. 7). One possible explanation is that the roots of the plants exude organic substances during these morning hours just as the sun rises and when the soil has not yet been warmed up

Table 3. *Simultaneous measurements of NO and NO_2* using the open system*

Plot	Date	Time	Concentrations (ppbv) NO Inlet	NO Outlet	NO_2† Inlet	NO_2† Outlet	Flux (ng N m^{-2} s^{-1}) NO	Flux (ng N m^{-2} s^{-1}) NO_2	Temp. (°C) soil surface
LU	Apr. 21	11^{19}	0.72	7.1	3.7	1.9	1.5	−0.43	10.3
		11^{50}	1.0	8.0	3.3	2.1	1.7	−0.31	11.5
		12^{20}	0.8	8.4	3.9	2.5	1.8	−0.33	12.0
		13^{20}	1.1	8.9	4.9	2.5	1.9	−0.58	10.0
LU	Apr. 22‡	13^{35}	0.72	10.6	1.2	2.1	2.4	0.23	10.8
		14^{00}	0.60	11.0	1.3	1.8	2.5	0.11	10.5
		14^{40}	0.60	11.8	1.6	2.5	2.7	0.21	11.0
		15^{05}§	2.7	12.1	4.0	2.2	2.3	−0.44	11.0
		15^{40}§	1.9	12.7	4.2	2.2	2.6	−0.43	11.2
LU	Apr. 22‡	21^{40}	0.4	7.9	1.2	1.6	1.8	0.10	4.9
		22^{40}	0.2	8.2	1.3	1.3	1.9	0.03	4.0
		23^{40}	0.4	8.2	1.2	1.5	1.9	0.07	3.2
		00^{40}	0.3	8.2	1.3	1.5	1.9	0.05	2.8
		01^{40}	0.2	7.9	1.2	1.3	1.8	0.02	2.3
		02^{40}	0.2	7.2	1.1	1.3	1.7	0.05	2.0
		03^{40}	0.4	6.7	1.0	1.3	1.5	0.07	1.8
		04^{40}	0.3	6.3	1.1	1.4	1.5	0.07	1.5
		05^{40}	0.4	6.4	1.0	1.3	1.5	0.07	1.2
		06^{40}	0.5	7.0	1.2	1.4	1.6	0.05	2.0
		07^{40}	0.6	7.1	1.2	1.7	1.6	0.12	2.5
		08^{40}	0.7	7.9	1.3	1.7	1.7	0.10	4.1
B 120	Apr. 23‡	11^{20}	0.84	2.5	1.7	2.2	0.64	0.12	5.6
		12^{02}	0.72	2.5	1.8	2.0	0.61	0.06	6.0
		12^{50}	0.60	2.4	1.8	2.0	0.58	0.05	6.8
LU	Apr. 23	20^{40}	1.4	12.8	5.6	2.6	2.8	−0.72	9.5
		21^{40}	1.2	13.0	5.8	2.7	2.9	−0.74	9.0
		22^{40}	1.6	13.0	5.5	2.7	2.8	−0.67	8.2
		23^{40}	1.2	12.3	6.7	2.9	2.7	−0.91	8.0
		00^{40}	1.2	12.4	5.4	2.8	2.7	−0.62	7.8
		01^{40}	1.2	12.2	4.6	2.8	2.7	−0.43	7.6
		03^{40}	1.0	12.1	4.2	2.7	2.7	−0.36	7.1
		05^{40}	0.84	12.5	4.0	2.6	2.8	−0.33	6.9
		07^{40}	1.5	13.1	3.9	2.5	2.8	−0.33	6.8
		09^{40}	1.1	13.3	4.5	2.7	3.0	−0.45	7.0
		11^{40}	0.54	11.5	2.7	2.9	2.7	−0.05	7.8
		13^{40}	0.60	12.7	2.5	2.9	2.9	0.10	9.1
		15^{40}	0.48	10.3	2.3	3.2	2.4	0.22	10.0
		17^{40}	0.60	12.4	2.3	3.2	2.9	0.22	10.9
		19^{40}	0.42	12.8	2.3	3.1	3.0	0.19	10.5
LU	Apr. 27	19^{10}	0.5	3.0	3.3	4.1	2.1	0.67	10.8
		20^{10}	0.7	3.2	4.6	3.6	2.1	−0.84	9.4
		21^{10}	0.8	3.1	5.8	4.4	1.9	−1.2	8.6
		22^{10}	0.5	2.6	3.1	2.9	1.8	−0.17	8.1
		23^{10}	0.5	2.6	3.4	2.8	1.8	−0.50	7.2
		00^{10}	0.6	2.8	4.2	2.7	1.8	−1.3	7.2
		01^{10}	0.6	2.7	3.7	2.4	1.8	−1.1	6.3
		02^{10}	0.5	2.6	3.3	2.4	1.8	−0.76	6.1
		03^{10}	0.5	2.5	3.0	2.3	1.7	−0.59	6.0
		04^{10}	0.5	2.4	3.2	2.3	1.6	−0.76	6.0
		05^{10}	0.6	2.6	3.2	2.1	1.7	−0.92	5.8
		06^{10}	0.7	2.8	4.0	2.3	1.8	−1.4	5.8
		07^{10}	0.9	3.0	4.8	2.6	1.8	−1.8	6.0

Plot	N… m… s
1. LU GR 200	b
2. GR 200	a b
3. LU	b c
4. B 120	a b a
5. B 0	a b

Fig. 5. NO emission va… at different places w… fertilized grass ley; B…

* Might also include a…

† The absolute value… signal.

‡ Periods when O…

§ Addition of NO_2 to …

LU = lucerne; B = ba…

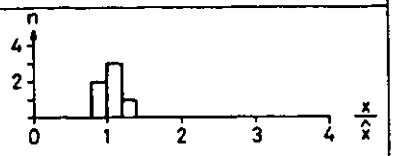
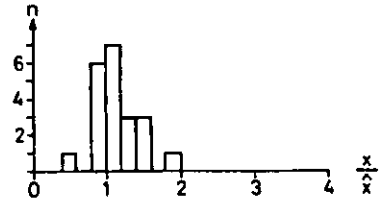
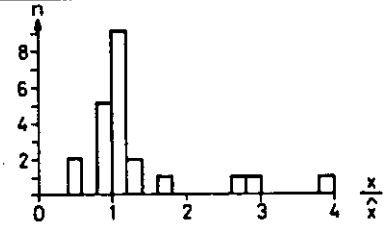
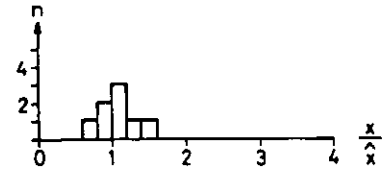
Plot	Number of measurements (n)	NO emission (mean value) ($ng\,N\,m^{-2}\,s^{-1}$)	Standard deviation (% of mean)	Frequency distribution (normalized to median value, $\hat{x}$)
1. LU GR 200	a 3	1.4	9	
	b 3	0.38	16	
2. GR 200	a 3	0.45	60	
	b 6	23.5	89	
3. LU	a 5	2.0	33	
	b 7	1.9	20	
	c 4	0.37	30	
	d 5	3.1	18	
4. B 120	a 8	1.6	66	
	b 4	0.38	68	
	c 5	1.9	29	
	d 5	35.3	26	
5. B 0	a 5	12.0	21	
	b 3	2.3	26	

Fig. 5. NO emission variability. Set 1: Consecutive measurements at exactly the same place. Sets 2–5: Measurements at different places within the plot. Within each subset (i.e., 2a, 2b, etc.) measurements were close in time. GR 200: fertilized grass ley; B 0: unfertilized barley; B 120: fertilized barley; LU: lucerne.

* Might also include alkyl-nitrates, -nitrites, HNO_2, HNO_3 and PAN (peroxyacetylnitrate).

† The absolute values of the concentrations of NO_2 might be 0.5 ppbv too high due to offset of the NO_2 zero signal.

‡ Periods when O_3 was removed from the air entering the chamber.

§ Addition of NO_2 to the air entering the chamber.

LU = lucerne; B = barley.

(Rosswall, *personal communication*). These compounds can then be utilized by the denitrifying bacteria which will start to reduce NO_3^- and, subsequently, NO will be produced more rapidly than the soil temperature will predict. This explanation is consistent with the fact that this phenomenon is most obvious in the fertilized soils where the NO_3^- content is higher. Measurements of NO emission in Australia on grazed pastures did not show any temperature dependence (0 to 25 °C) (Galbally, personal communication). This fact indicates that different processes are involved in the production of NO at the two experimental fields.

From the slope in Fig. 7 the activation energy can be calculated and is given in Table 4 together

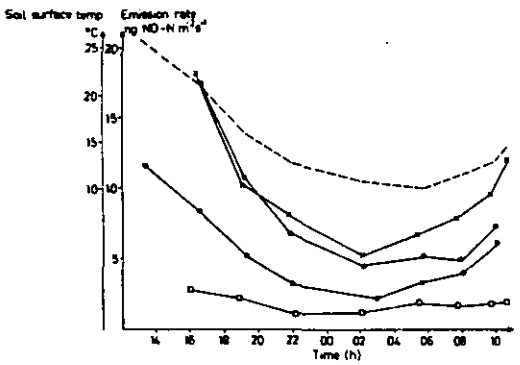


Fig. 6. Diurnal variation of NO emission rate on four cropping systems. Fertilized barley (×) and grass ley (○), unfertilized barley (★) and lucerne (□). Dashed line is soil surface temperature.

Table 4. *Activation energy and Q_{10} values for NO production (cf. Fig. 7). Q_{10} is the change of emission rate between 10 and 20 °C*

Plot	Activation energy (kJ mole^{-1})	Q_{10}
Barley (B 120)	83	3.6
Grass ley (GR 200)	83	3.6
Barley (B 0)	79	3.5
Lucerne (LU)	65	2.7

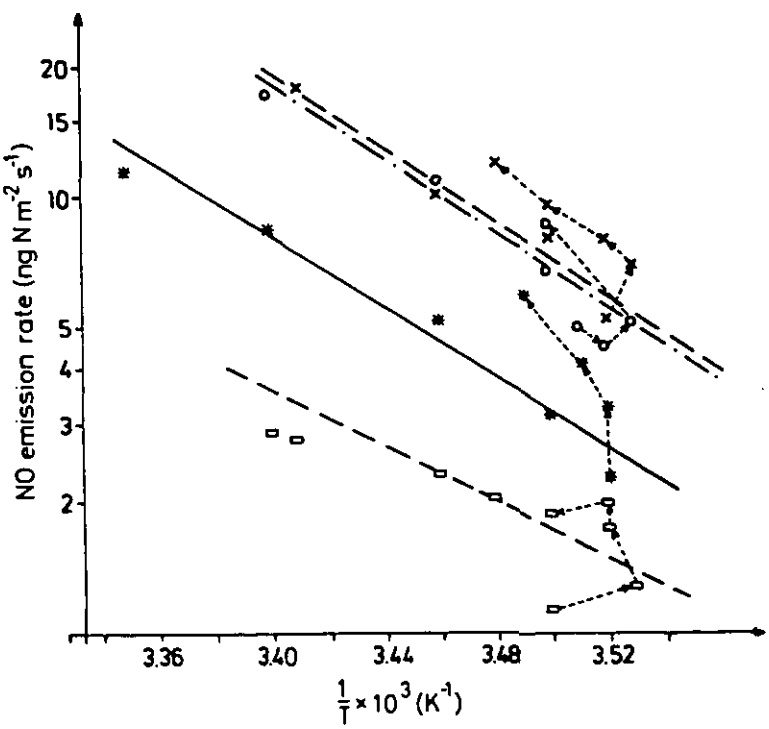


Fig. 7. Temperature dependence of NO emission rate (data from Fig. 6) on: fertilized barley (×), fertilized grass ley (○), unfertilized barley (★) and lucerne (□). Dashed arrows combine points in the morning hours in Fig. 6.

with Q_{10} values (cha e 10 and 20 °C). Thes al = 2.7–3.6) can be comp N_2O production in an ar the range 77–83 (McKenney et al., 1 0) found in a field investiga a grass-sword (Den ea temperature depend e during anaerobic conditi (McKenney et al., 1982).

4.6. *The effect of soi a.*

The many measureme Kjettslinge field hav sh lowest from thoro ly shown by the measurem events both in 1981 an watering of the soil c able to find a simple la rate of NO and soil m consideration of for inst ature). As an exampl h with regard to tempe tu to soil moisture conte weight loss or from ten was found. The fo wi indicate that the rela n soil water content far complex. After a m es period of drought, th N period of half a day. A decreased to low values rainfall.

4.7. *Production versus s*

There are sever i production occurs in e (the first few centimetres

1. The emission rate res surface temperat . much better relat n and chamber air te temperature at, say, 1
2. The NO emissio r. only enough wate s few centimetres of the
3. In one experime t soil was measure e soil was removed. Th

with Q_{10} values (changes in emission rate between 10 and 20 °C). These values (65–83 kJ mole^{-1}; Q_{10} = 2.7–3.6) can be compared with those found for N_2O production in an anaerobic soil which were in the range 77–83 kJ mole^{-1} (Q_{10} = 3.1–3.4) (McKenney et al., 1980), and Q_{10} = 2.8 which was found in a field investigation of N_2O emission from a grass-sword (Denmead et al., 1979). A strong temperature dependence of NO production in soil during anaerobic conditions has also been observed (McKenney et al., 1982).

4.6. *The effect of soil water content*

The many measurements of NO emission in the Kjettslinge field have shown that NO emission is lowest from thoroughly wetted soil. This was shown by the measurements before and after rain events both in 1981 and 1982 and after artificial watering of the soil. However, we have not been able to find a simple relation between the emission rate of NO and soil moisture content (with due consideration of for instance the effect of temperature). As an example, the emission was normalized with regard to temperature (to 20°) and compared to soil moisture content (obtained either from weight loss or from tensiometers), but no relation was found. The following measurements further indicate that the relation between NO emission and soil water content far from saturation is very complex. After a modest rain which came after a period of drought, the NO emission increased for a period of half a day. After that the NO emission decreased to low values in response to very heavy rainfall.

4.7. *Production versus soil depth*

There are several indications that the NO production occurs in the uppermost layer of the soil (the first few centimetres). These include:

1. The emission rate responded to rapid changes in surface temperature. For example, there was a much better relation between NO emission rate and chamber air temperature than with soil temperature at, say, 10 or 15 cm depth
2. The NO emission rate decreased, even when only enough water is added to moisten the upper few centimetres of the soil.
3. In one experiment, the NO emission from the soil was measured before and after 5 cm of top soil was removed. The NO emission immediately after removal was about one-fifth of the value before removal.
4. The calculation of the diffusion rate of NO in the soil suggests that an equilibrium concentration is already reached at a depth of only a few centimetres. The calculations are not very precise, and the results vary with the variations in compensation point and production rate from day to day. However, they indicate that only a very shallow layer is responsible for NO emission. This finding is of importance for the interpretation and parameterization of the flux in future experiments. Similar conditions may also occur for the production of N_2O, judging from vertical concentration gradients in the soil (Seiler and Conrad, 1981), although it appears to be generally believed that a layer of several tens of centimetres is responsible for the measured flux of N_2O from the soil.

4.8. *Effect of vegetation*

We have also observed an interesting influence of vegetation on the emission rate. Fig. 8 shows the

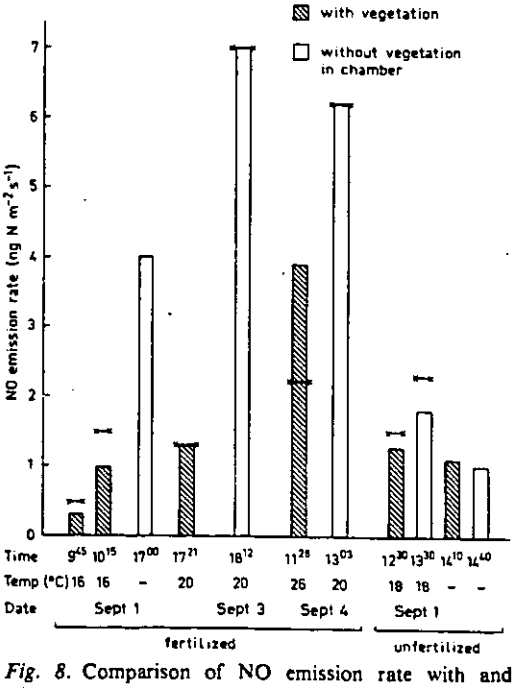


Fig. 8. Comparison of NO emission rate with and without vegetation (barley plants) in the chamber. The plants were cut before the measurements; from 60–80 cm to approx. 5 cm. ×—×, value if normalized to 20 °C according to the temperature dependence in Fig. 7.

flux of NO from the B 120 plot with and without vegetation, and B0 with and without vegetation normalized to the same temperature with the aid of the temperature dependence in Fig. 7. The results could be interpreted basically in two ways:

(i) that NO is deposited on vegetation;
(ii) that vegetation to some extent prevents the vertical mixing, and a higher NO concentration builds up near or slightly below the soil surface which, as we have discussed earlier, will give a reduced net emission rate of NO.

4.9. *Yearly losses to the atmosphere*

From present knowledge, we cannot give a very accurate estimate of the yearly emission of NO_x from the measured areas. Table 5 summarizes measurements made during 1982 and in September 1981. Although the time distribution is not very even, we think that they give a fairly good estimate of temporal variation during the vegetation period, with the highest emission rates in June and comparatively low in spring and autumn.

In order to obtain an approximate estimate of the emission for a whole year, we used the measurements so far available, considered emission rates during day and night and during periods with different soil temperatures, assumed zero emission during winter and calculated a weight average value for the year. We then arrived at an estimated emission of 0.6 kg N ha^{-1} a^{-1} from fertilized grass ley and 0.2 kg N ha^{-1} a^{-1} from unfertilized barley.

This can be compared with the yearly deposition of nitrogen compounds from the atmosphere. Wet deposition is measured in the area to be about 4 kg N ha^{-1} a^{-1} (1.7 kg NO_3^-–N ha^{-1} a^{-1}, 1.9 kg NH_4^+–N ha^{-1} a^{-1} and 0.7 kg organic N ha^{-1} a^{-1}). Dry deposition of particulate matter contributes less than 0.3 kg N ha^{-1} a^{-1} as estimated from particulate nitrate concentration, particle size distribution and a dry deposition velocity as a function of particle size. These deposition fluxes are typical for areas affected by the large anthropogenic emissions in Europe.

As a comparison, the average NO emission from

Table 5. *Summary of the measurements of NO emission (closed system) during 1982*

Plot	Month	Number of measurements	Range of emission rates (ng N m^{-2} s^{-1})	Soil temperature (range) (°C)
Barley	Apr.	5	0.29–2.99	4.9–6.1
(B0)	May	3	1.20–2.23	9.8–11.0
	June	40	0.46–17.0	10.7–25.5
	July	22	0.66–2.08	11.5–28.6
	Sept.*	4	1.0–1.8	18.0
Lucerne	Apr.	26	0.31–5.50	5.0–11.9
(LU)	May	2	0.82–1.95	nm
	June	14	1.03–4.1	10.7–21.8
Barley	Apr.	28	0.15–5.66	2.9–13.0
(B 120)	May†	8	0.96–4.38	7.3–10.7
	June	23	0.99–52.8	10.6–25.5
	July	1	3.24	13.9
	Sept.*	7	0.3–7.0	16–26
Grass ley	Apr.	6	0.1–1.29	7.2–10.1
(GR 200)	May†	1	0.45	10.0
	June‡	15	1.86–61.6	10.7–25
	July	3	1.36–3.19	11.7–14.5
	Sept.*	1	1.7	21.0

* Measurements performed in 1981.
† Fertilization 120 kg NO_3^-–N ha^{-1}.
‡ Fertilization 80 kg NO_3^-–N ha^{-1}.
nm = not measured.

grazed and ungrazed pastures in Australia was 3.5 and 1.6 ng N m^{-2} s^{-1} which corresponds numerically to 1.1 and 0.5 kg N ha^{-1} a^{-1}, respectively (Galbally and Roy, 1978).

We can conclude that the losses of NO from agricultural soils appear to be of little importance for the soil nitrogen budget. On the other hand, the emission might be an important source of atmospheric NO_x. For example, if our experimental site is representative for all Sweden's agricultural land, the emission during the growing season is about 10% of the emission from anthropogenic combustion sources within the country. Continuing investigations of processes leading to NO and NO_x emission from arable land (and other soils) are, therefore, of considerable interest both from the point of view of atmospheric chemistry and for a better understanding of soil nitrogen processes.

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