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Field Measurements of NO and NO_2 Emissions from Fertilized and Unfertilized Soils

F. SLEMR and W. SEILER
Max-Planck-Institut für Chemie, Saarstrasse 23, D-6500 Mainz, F.R. Germany

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Abstract. Field measurements of NO and NO_2 emissions from soils have been performed in Finthen near Mainz (F.R.G.) and in Utrera near Seville (Spain). The applied method employed a flow box coupled with a chemiluminescent NO_x detector allowing the determination of minimum flux rates of 2 μg N m^{-2} h^{-1} for NO and 3 μg m^{-2} h^{-1} for NO_2.

The NO and NO_2 flux rates were found to be strongly dependent on soil surface temperatures and showed strong daily variations with maximum values during the early afternoon and minimum values during the early morning. Between the daily variation patterns of NO and NO_2, there was a time lag of about 2 h which seem to be due to the different physico-chemical properties of NO and NO_2. The apparent activation energy of NO emission calculated from the Arrhenius equation ranged between 44 and 103 kJ per mole. The NO and NO_2 emission rates were positively correlated with soil moisture in the upper soil layer.

The measurements carried out in August in Finthen clearly indicate the establishment of NO and NO_2 equilibrium mixing ratios which appeared to be on the order of 20 ppbv for NO and 10 ppbv for NO_2. The soil acted as a net sink for ambient air NO and NO_2 mixing ratios higher than the equilibrium values and a net source for NO and NO_2 mixing ratios lower than the equilibrium values. This behaviour as well as the observation of equilibrium mixing ratios clearly indicate that NO and NO_2 are formed and destroyed concurrently in the soil.

Average flux rates measured on bare unfertilized soils were about 10 μg N m^{-2} h^{-1} for NO_2 and 8 μg N m^{-2} h^{-1} for NO. The NO and NO_2 flux rates were significantly reduced on plant covered soil plots. In some cases, the flux rates of both gases became negative indicating that the vegetation may act as a sink for atmospheric NO and NO_2.

Application of mineral fertilizers increased the NO and NO_2 emission rates. Highest emission rates were observed for urea followed by NH_4Cl, NH_4NO_3 and $NaNO_3$. The fertilizer loss rates ranged from 0.1% for $NaNO_3$ to 5.4% for urea. Vegetation cover substantially reduced the fertilizer loss rate.

The total NO_x emission from soil is estimated to be 11 Tg N yr^{-1}. This figure is an upper limit and includes the emission of 7 Tg N yr^{-1} from natural unfertilized soils, 2 Tg N yr^{-1} from fertilized soils as well as 2 Tg N yr^{-1} from animal excreta. Despite its speculative character, this estimation indicates that NO_x emission by soil is important for tropospheric chemistry especially in remote areas where the NO_x production by other sources is comparatively small.

Key words. NO, NO_2, soil, decomposition, production, global budget, mineral fertilizer.

1. Introduction

Nitrogen oxides play a key role in the atmospheric photochemistry (Crutzen, 1981). Nitrogen monoxide and nitrogen dioxide act as catalysts in various reaction chains and thereby strongly influence the concentration and distribution of tropospheric O_3 and OH radicals. Consequently, they have a strong impact on the distribution and abundance of many carbon, sulphur and halogen compounds in the atmosphere. Thus, knowledge of

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the atmospheric cycle of nitrogen oxides is of primary importance for an understanding of atmospheric chemistry.

Nitrogen monoxide and nitrogen dioxide are emitted into the atmosphere by a number of anthropogenic processes. such as combustion of fossil fuels and biomass burning. In addition, NO and NO_2 are formed by lightning, atmospheric conversion of ammonia, and by biological processes in soils. The global NO_x source strength ($NO_x = NO + NO_2$) has been estimated repeatedly by several authors with figures varying between 20 and 80 Tg N yr^{-1} (Böttger *et al.*, 1980; Ehhalt and Drummond, 1982; Hahn and Crutzen, 1982; Crutzen, 1983; Logan, 1983). In all these estimates, the source strength of NO and NO_2 from soil is the most uncertain.

It is known from laboratory experiments that NO and NO_2 are formed by biological processes. Nitrogen monoxide has been proved to be an obligatory intermediate in the denitrification process (John and Hollocher, 1977; Firestone *et al.*, 1979). More recently, Lipschultz *et al.* (1981) reported that NO is also produced by soil nitrifying bacteria (*Nitrosomas europaea*) and McKenney *et al.* (1982) found the NO production from anaerobic denitrification in soil to be significant. In addition to the biological NO and NO_2 formation, both gases may also be produced by the chemical decomposition of nitrite (Nelson and Bremner, 1970; Smith and Chalk, 1979, 1980a, 1980b) which is known to be an intermediate of denitrification and nitrification (Payne, 1981; Bremner and Blackmer, 1981). Although all these measurements have been performed in the laboratory and may not be applicable to natural conditions, they clearly indicate that soil may provide a significant source of the global NO and NO_2 budget.

Field measurements of the NO_x emission processes are very rare. The first data were published by Makarov (1969) who found a mean NO_2 emission rate of 0.01 g N m^{-2} $week^{-1}$ from a nonfertilized soil over the entire vegetation period. In addition, his experiments with mineral fertilizers showed that 0.2% of the applied nitrogen was lost as NO_2 to the atmosphere demonstrating that the increased application of mineral fertilizer may have an effect on the atmospheric NO_x budget. Kim (1973) found NO_2 emission rates of about 0.02 g N m^{-2} $week^{-1}$ on the forest soil in July 1971. In contrast, the NO_2 emissions measured in May and June were below the detection limit of his technique. The possible emission of NO could not be observed since both authors used wet chemical absorption techniques insensitive to NO (Cheng and Bremner, 1965). The only data on NO emission were reported by Galbally and Roy (1978) who found values on the order of 0.1 g N m^{-2} yr^{-1} from nonfertilized grazed and ungrazed grassland. All these data clearly show that NO_x is actually formed in soils under natural conditions and is emitted into the atmosphere. However, the present data base on the NO_x flux rates at the soil/atmosphere interface is too limited to derive a reliable estimate of the global NO_x emissions from soils.

To provide a better data base, we have performed field measurements of the NO_x flux from fertilized and unfertilized soils into the atmosphere. Measurements were carried out on two different types of soils in two different climatic zones. NO and NO_2 fluxes obtained on bare and plant covered soils are reported and discussed. The data n understanding

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show that the production of NO_x in soils plays an important role in the atmospheric NO_x cycle.

2. Methodology

Measurements of the NO and NO_2 flux rates at the soil/atmosphere interface have been performed using the flow box method described in detail by Slemr *et al.* (1984). Figure 1 shows the schematic of the experimental set-up consisting of the flow box, a pump and the NO_x detector. The flow box (length = 40 cm, width = 22.5 cm, height = 20 cm) was set on a stainless steel frame which was inserted 20 cm deep into the soil to prevent exchange of the enclosed and free atmosphere. The interception between the box and the frame was sealed with boiled distilled water. The pump provided a constant flow of ambient air through the box with flow rates of up to 45 l (STP) min^{-1}. Pressure differences between the box and the atmosphere causing a convective flux of NO and NO_2 from the soil into the box were avoided by supplying the box with a large inlet opening (i.d. = 50 mm). The opening was shielded by a glass plate fixed about 20 mm in front of the inlet to minimize the influence of changing wind speed and direction on the pressure inside the box and consequently a convective NO and NO_2 flux at the soil/atmosphere interface.

The flux P of NO or NO_2 at the soil/atmosphere interface expressed in $\mu g\ N\ m^{-2}\ h^{-1}$ was determined from the mass balance of the box by

$$P = \frac{V \times N}{A \times M} (m_0 - m_1)$$

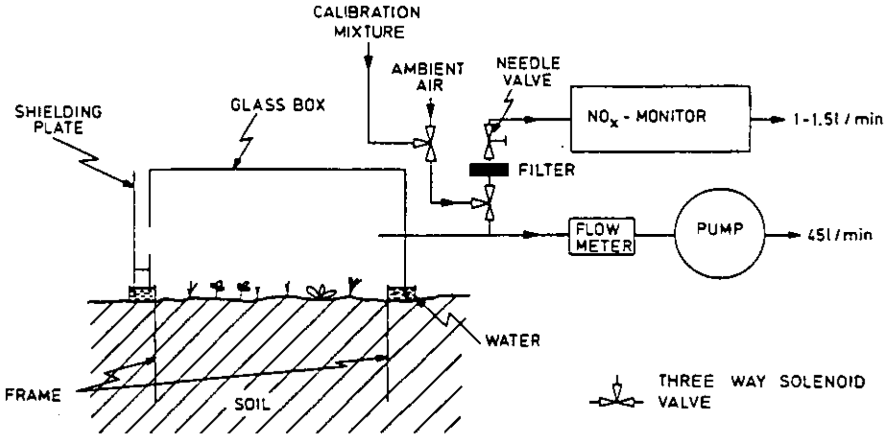

Fig. 1. Schematic of the experimental set-up used for the measurements of the NO and NO_2 flux rates at the soil/atmosphere interface.

where V is the mass flow rate of ambient air through the box in l (STP) h^{-1}, A is the soil surface area enclosed by the box (about 0.075 m^2), N is the atomic weight of nitrogen, M is the molar volume, m_0 is the NO or NO_2 mixing ratio (ppbv) at the inlet of the box (ambient air) and m_1 is the NO or NO_2 mixing ratio (ppbv) at the outlet of the box. The NO and NO_2 mixing ratios at the inlet and outlet of the box were measured with a commercial chemiluminescent detector (Thermo-Electron 14 B) modified according to Delany *et al.* (1982). The detection limit of the NO_x detector was 100 pptv and the accuracy at typical mixing ratios of NO and NO_2 of less than a few ppbv were in the range of ±4%. NO_2 was determined by conversion of NO_x into NO by a molybdenum converter heated to 400°C and subtracting the original NO signal of the air stream. Since the molybdenum converter reduces not only NO_2 but also HNO_3, PAN, N_2O_5, alkyl nitrites and alkyl nitrates (Winer *et al.*, 1974; Delany *et al.*, 1982), the difference between the NO_x and NO signals may not only be due to NO_2 but may also include other nitrogen compounds. There is evidence that the nitrogen compounds listed do not contribute significantly to the total odd nitrogen in soil air so that the difference between NO_x and NO may be almost exclusively due to NO_2. Therefore, we will denote the measured difference between NO_x and NO as NO_2. The NO_x detector was repeatedly calibrated using a standard of 1 ppmv in N_2 provided by Messer Griesheim (Frankfurt, Germany).

The NO_x instrument was installed in a small trailer located next to the experimental field and connected with the box using Teflon-tubes (about 5 m long, inside diameter = 4 mm). Absorption or desorption processes in the tube were not observed. The lower detection limit of the NO and NO_2 flux rates were determined to be 2 $\mu g\ m^{-2}\ h^{-1}$ and 3 $\mu g\ m^{-2}\ h^{-1}$, respectively. The whole system was operated automatically providing a data point for the NO and NO_2 flux rates once every 6 min.

The soil moisture was determined by a standard gravimetric method on samples taken from the uppermost 5 cm soil layer. The values are given in percent of wet weight. Soil surface temperatures were measured at a depth of 10 mm using mercury thermometers or thermocouples. In Utrera, the method recommended by Taylor and Jackson (1965) was applied for the measurement of the soil temperature. This method uses a thermocouple attached to the 100 x 100 mm large, 1.5 mm thick copper plate covered by a soil layer of 10 mm. Soil moisture and temperature were both measured in a separate plot which was treated the same way as the plots measured.

Nitrous oxide fluxes were measured concurrently by an automatically operating semicontinuous closed-static method described by Conrad *et al.* (1983). The soil was covered for at most 1 h and subsequently exposed to natural conditions for several hours before beginning a new experiment.

Each experimental station consisted of several plots. The frames surrounding the plots were inserted into the soil about a week before starting the experiment and remained in the soil during the whole measuring period. Prior to fertilization, the NO and NO_2 fluxes were determined on all plots, and only plots showing comparable fluxes were taken for further measurements. Each plot was covered by the glass box only during the measurement period required (12 min) in order to obtain two consecutive data points for the NO and NO_2 flux rates. During the rest of the time, the plots remained uncovered and exposed to natural environmental conditions.

For determination of the fertilizer loss rates, the plots were treated with fertilizer dissolved in 0.5 l distilled water. The control plots were also irrigated with the same amount of distilled water. The amount of mineral fertilizer applied corresponded to an application rate of 100 kg N ha^{-1}. The fertilizer loss rates were calculated by

$$L = \frac{P_F - P_C}{R} \times 100\,(\%)$$

where P_F and P_C are the flux rates observed at the fertilized and control plot, respectively, integrated over the entire measuring period and R is the amount of fertilizer nitrogen.

3. Field Stations

The measurements were performed in Finthen near Mainz in July and August 1982 and at the BASF experimental station in Utrera near Seville, Spain in September and October 1982. Relevant details on the soils studied are listed in Table I.

Table I. Characteristics of soil

Location	Soil type	pH (0.1 N KCl)	$CaCO_3$ (% wJ)	org. C (% wJ)	Size fractions (%)		
					Clay (2 μm)	Silt (2–20 μm)	Sand (20–2000 μm)
Finthen, Mainz	loess	7.4	2.0	0.8	20	21	59
Utrera, Seville	loamy sand	7.4	–	0.5	7	4	89

In Finthen, the experiments were carried out on a meadow which had never been used for agricultural purposes and had always remained unfertilized. The grass was cut twice a year. For measurements on bare soil, part of the meadow was ploughed one week before starting the experiments. The ploughing depth was about 30 cm. Measurements were performed on seven plots with two plots in the meadow and five in the ploughed area. One of the plots in the meadow was fertilized with NH_4Cl whereas the other remained undisturbed, acting as control. Two of the five plots with bare soil remained unfertilized, the others were fertilized with $NaNO_3$, NH_4NO_3 and NH_4Cl, respectively. Measurements were performed discontinuously between 8 a.m. and 6 p.m. During this period, 1 to 3 individual flux rates per plot and day were obtained. The experimental field in Utrera consisted of nine plots, six of which were used for measurements of NO_x fluxes and the rest for measurements of the N_2O emission rates. All plots were without vegetation cover. From the six plots used for the NO_x measurements, one remained unfertilized, two were fertilized with NH_4NO_3 and three were fertilized with $NaNO_3$, NH_4Cl and urea, respectively. The N_2O measurements were carried out on one unfertilized plot and on two plots fertilized with NH_4NO_3 and urea, respectively. All plots were fertilized on 9 September and irrigated on 16 and 20 September (precipitation rate of 7 mm each), on 24 September (3.5 mm) and on 1 October (10 mm). In addition, 10 mm of rain fell on 25 September. The NO and NO_x flux rates were determined 5 to 8 times per day and plot. The frequency of the measurements on urea treated plots was doubled to ensure more detailed information on the NO_x flux rate. The data were obtained between 6 a.m. and 11 p.m. thus covering two-thirds of the day and including the periods with minimum and maximum daily temperatures of surface soil.

The experimental station in Utrera is used in conjunction with agricultural experiments with fertilizers and insecticides and the history of each field has been carefully recorded for many years. The field selected for our experiments was used for cultivation of field beans in 1980 and for soy beans in 1981. The soy beans were ploughed under in September 1981. Since that time, the field has not been used for cultivation purposes. The field was harrowed on 2 September 1982, one week before starting our experiments. In the course of the last two years, the field was fertilized several times: on 11 November 1980 with 26 kg N ha^{-1}; on 30 April 1981 with 75 kg N ha^{-1}; on 4 June 1981 with 65 kg N ha^{-1} (all applied as NH_4NO_3) and on 8 November 1981 with 120 kg P ha^{-1}, and 240 kg N ha^{-1}. Insecticides have not been applied since June 1981.

4. Results

Table II summarizes the NO/NO_2 flux rates measured at 16 individual plots located within the experimental field in Utrera covering an area of 10 m^2. Data show significant

Table II. NO and NO_2 flux rates from different plots in Utrera on 7 September 1982

Plot number	Local time	Soil temperature (°C)	NO flux (μg N m^{-2} h^{-1})	NO_2 flux (μg N m^{-2} h^{-1})
1	11.50	35,4	10	4
2	12.02	36,4	8	21
3	12.14	37,0	12	19
4	12.28	38,6	12	18
5	12.40	40,5	17	17
6	12.52	42,1	18	16
7	13.04	45,1	30	28
8	14.10	50,5	3	44
9	14.22	50.5	44	62
10	14.34	52,0	372	877
11	15.20	53,2	732	1397
12	15.32	53,2	27	23
13	15.44	53,4	27	23
14	15.56	53,4	16	25
15	16.08	53,2	22	37
16	16.20	53,2	14	4

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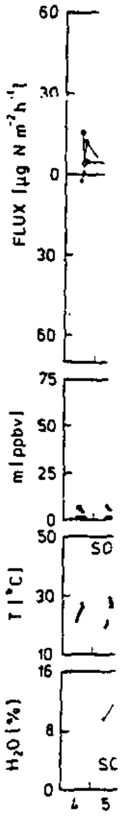

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spatial variation of the NO/NO_2 flux rates with values of 8-732 μg NO–N m^{-2} h^{-1} and 4–1397 μg NO_2–N m^{-2} h^{-1}. Measurements were carried out on a single day at different times so that part of the variations may be due to changes of soil temperature or soil moisture, etc. which have a significant influence on the absolute figure of the individual NO/NO_2 flux rates. The extremely high NO/NO_2 fluxes from plot No. 10 and 11, however, indicate that 'hot spots' with higher production of NO and NO_2 and thus high flux rates of NO and NO_2 from the soil into the atmosphere may exist. The observed spatial variation of NO and NO_2 flux rates may be explained by the soil inhomogeneity, e.g., of the distribution of organic soil matter.

In addition, the NO and NO_2 fluxes show significant temporal variations. Typical examples are given in Figures 2, 3a and 3b for NO and NO_2 measurements carried out in Finthen and Utrera on nonfertilized soils and in Figures 7a and 7b for NO and NO_2

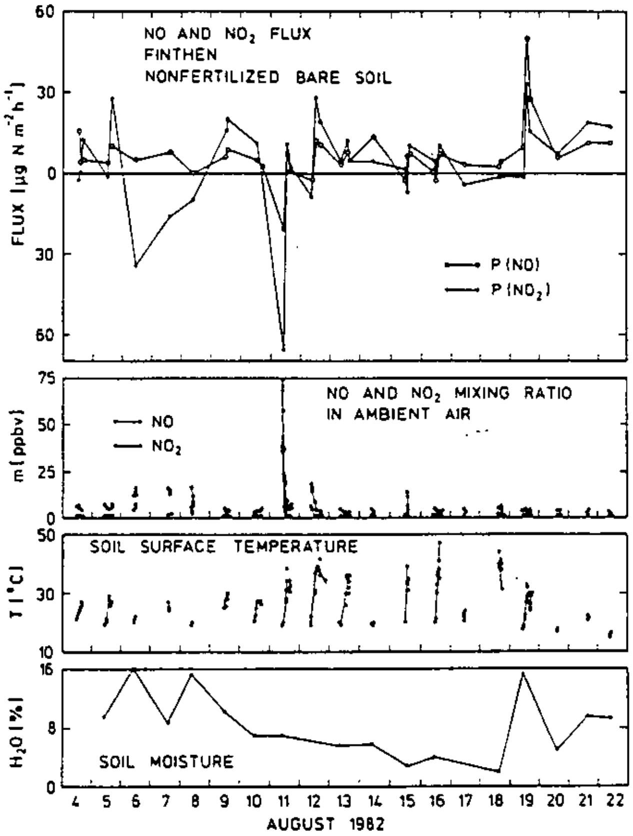

Fig. 2. Temporal variation of the NO and NO_2 flux rates measured in Finthen on nonfertilized soils without vegetation. Lower part of the figure shows the temporal variation of NO and NO_2 mixing ratios in ambient air as well as the variation of soil surface temperature and soil moisture.

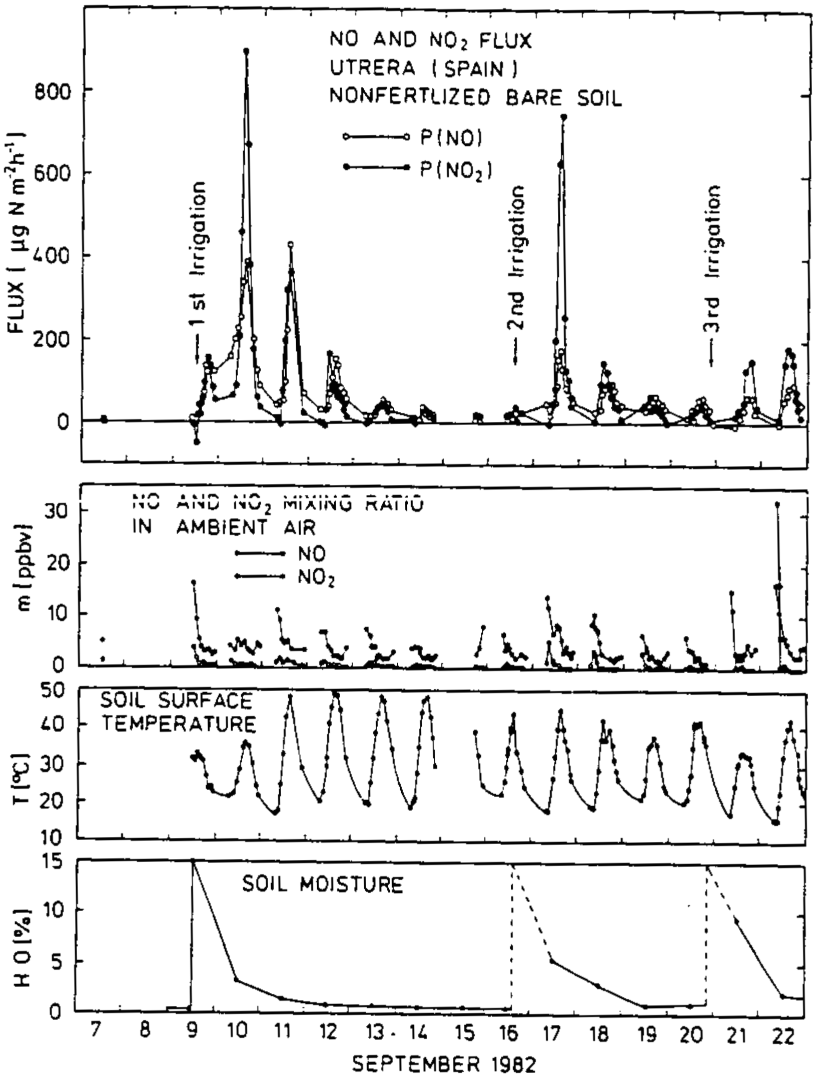

Fig. 3a. Variation of the NO and NO_2 flux rates measured in Utrera on nonfertilized soils without vegetation. The lower part of the figure shows the temporal variation of NO and NO_2 mixing ratios in ambient air as well as the variation of soil surface temperature and soil moisture.

measurements in Utrera on fertilized soils. In Finthen, the flux rates ranged between −21 and 51 μg N m^{-2} h^{-1} for NO and −66 and 33 μg N m^{-2} h^{-1} for NO_2. The corresponding figures for unfertilized soils in Utrera were −8 to 385 μg N m^{-2} h^{-1} for NO and −54 to 893 μg N m^{-2} h^{-1} for NO_2.

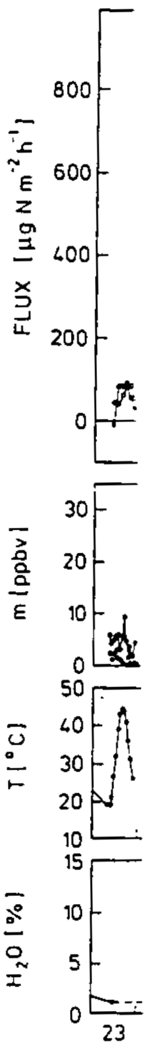

Fig. 3b. Continuation

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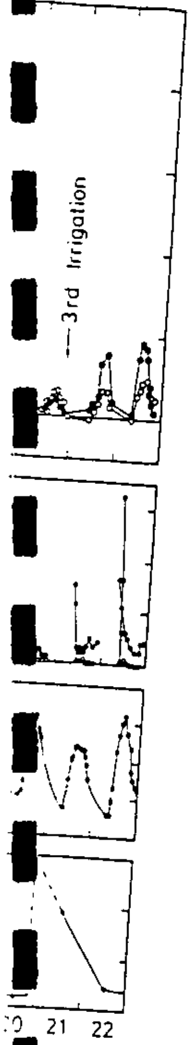

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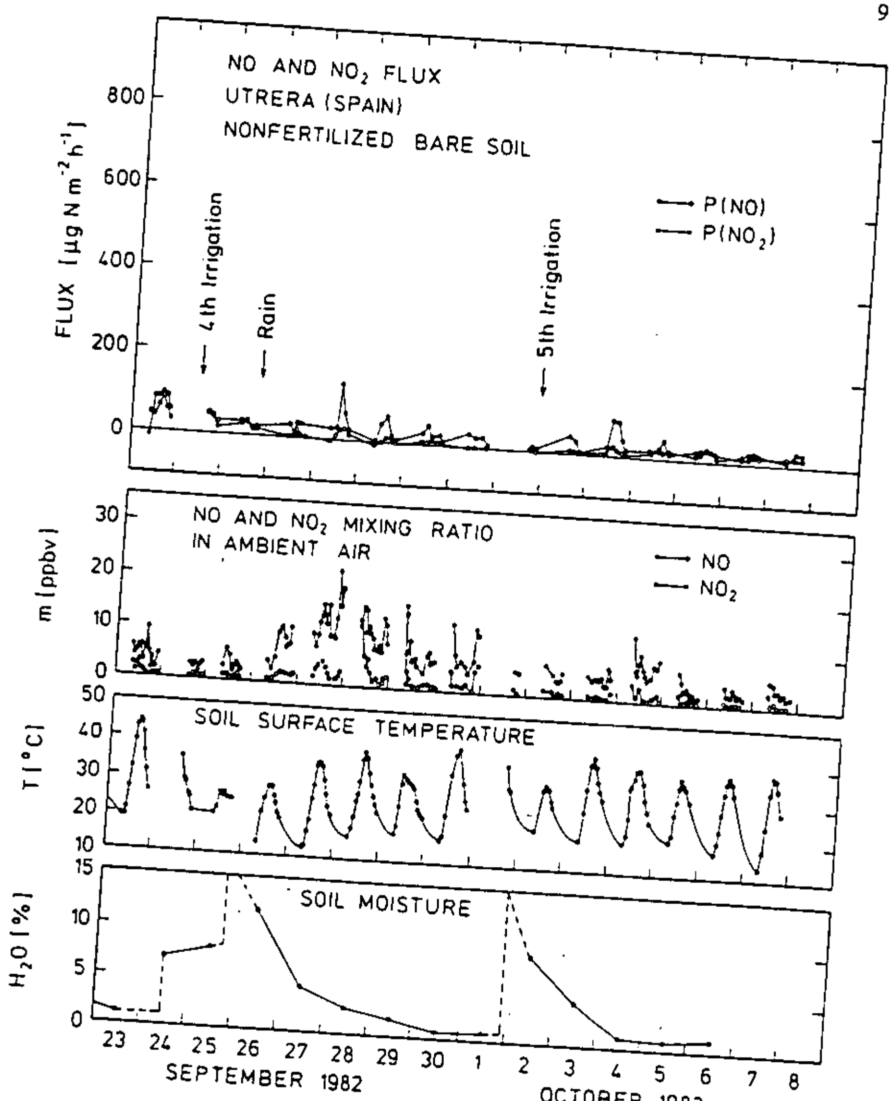

Fig. 3b. Continuation of Figure 3a.

In fertilized soils, maximum NO and NO$_2$ mixing ratios even reached values of 8000 and 6000 μg N m^{-2} h^{-1}, respectively. Negative flux rates, which means uptake of NO and NO$_2$ by soil, were always accompanied by high NO and NO$_2$ mixing ratios in ambient air. An excellent example is provided by the data observed in Finthen on 1 August. On this day, the NO and NO_2 mixing ratios in air reached values larger than 40 ppb and the fluxes of NO and NO_2 were -20 and -66 μg N m^{-2} h^{-1}, respectively.

In contrast, the soil is always a source of NO and NO_2 at very low NO and NO_2 mixing ratios. The compensation point or equilibrium mixing ratios, i.e., the mixing ratio at which the NO and NO_2 destruction equals the NO and NO_2 production is in the order of 20 ppbv for NO and 10 ppbv for NO_2 under the conditions existing in Finthen during August 1982. The absolute values of the equilibrium mixing ratios are dependent on several parameters, such as soil temperature, moisture, and organic carbon content and, therefore, should show large variations between the individual type of soil and climate.

The dependency of the size and direction of the NO and NO_2 fluxes at the soil surface on the NO and NO_2 mixing ratios in ambient air as well as the existence of equilibrium NO and NO_2 mixing ratios clearly indicate that NO and NO_2 are produced and destroyed concurrently in the soil or at the soil surface. Consequently, the measured NO and NO_2 flux rates represent net fluxes. Equilibrium mixing ratios have already been reported for other trace gases such as CO, H_2 and N_2O (Seiler, 1978; Seiler and Conrad, 1981).

The NO and NO_2 flux rates showed pronounced daily variations both on unfertilized and fertilized plots (see, e.g., Figures 3a, 3b, 4, 6a, 6b). The NO flux rates were positively correlated with the soil temperature with maximum values at about 7 a.m. The apparent activation energy calculated from the Arrhenius equation ranged between 44 and 103 kJ per mole. Interestingly, the NO_2 flux rates from soil did not correlate with soil temperature but correlate with the solar radiation. Maximum NO_2 flux rates were observed at 1 p.m. at minimum zenith angle (European summer time) and thus were about 2 h ahead of the maximum NO flux rates. This phase shift indicates that NO and NO_2 are

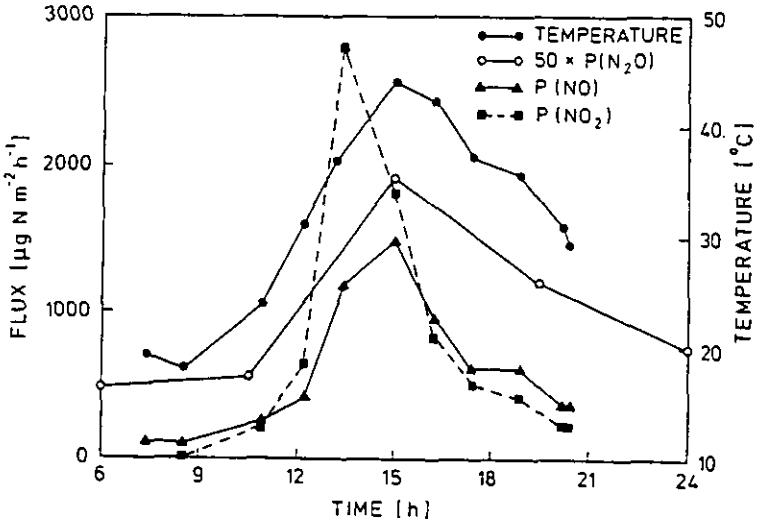

Fig. 4. Daily variation of the NO, NO_2 and N_2O flux rates and the soil surface temperature measured in Utrera.

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very likely produced by different processes. Possible NO_2 production by chemical conversion of NO in the presence of O_3 appears to be insignificant in view of the large phase shift (2 h) between the NO and NO_2 flux rates and the positive correlation between NO_2 flux rates and solar irradiation. This argument is in agreement with the observation of high NO_2 flux rates in the absence of O_3 in the flow box. Thus, we believe that NO_2 is also produced by biological or abiological processes in the soil. Because of the correlation between NO_2 flux rates and irradiation, the processes are active in the uppermost soil layers or at the soil surface. The time lag between NO flux rates and irradiation, on the other hand, indicates that NO formation occurs at depths deeper than 1 cm. It is worth mentioning that the N_2O flux from soil also exhibited a diurnal pattern (Slemr *et al.*, 1984) which agrees very well with the NO flux rates but is out of phase if compared with the NO_2 flux rates (Figure 4).

The NO and NO_2 flux rates were strongly dependent on the soil moisture. At soil moistures below 1%, the NO flux rates in unfertilized soils (on the order of 8–44 μg N m^{-2} h^{-1}) increased by a factor of about 10 after the soil moisture had been increased by artificial irrigation to values of about 15% (Figure 3a). Similarly, the amplitude of the daily NO flux rate variations increased dramatically after irrigation and declined with decreasing soil moisture. After 6 days, the soil moisture reached the 1% level and the NO flux rates approached the values initially measured before irrigation. Repeated artificial irrigation indicated that the effect of increasing soil moisture on the NO flux decreased with increasing number of irrigations and was no longer observed after the fourth irrigation (Figure 3b). There was generally a delay of approximately one day between irrigation and maximum NO flux which may be due to the fact that the soil pores in the uppermost soil layers were filled with water during irrigation so that the diffusivity within the uppermost soil layer and thus the exchange rate between soil and atmosphere were reduced. A similar but more pronounced relationship was observed between the NO_2 flux rates and soil moisture, with values of about 20 μg N m^{-2} h^{-1} at low soil moistures and up to 900 μg N m^{-2} h^{-1} after irrigation. Nitrogen dioxide fluxes also appear to respond much more rapidly to the change of the soil moisture than the NO flux which again supports the assumption that NO and NO_2 production occur at different depths with the NO_2 production at the uppermost soil layers. Similar dependence of the NO and NO_2 flux rates on soil moisture has also been observed on fertilized soils (Figures 6, 7).

The influence of vegetation on the NO and NO_2 fluxes from the soil into the atmosphere is illustrated in Figure 5. The measurements were carried out in Finthen in August 1982 on a soil plot with bare soil and a soil plot covered by dense grass vegetation. Both plots were fertilized with ammonium chloride at a rate of approximately 100 kg N ha^{-1}. Measurements on these two plots were performed within time intervals of 30 to 40 min for which the meteorological conditions can be assumed to be constant. Nevertheless, the NO flux rates obtained at these two plots show significant differences with low NO flux rates from grass covered soils. Even larger differences are observed for the NO_2 flux rate. In this case, the NO_2 sometimes showed negative values on plant covered soils which means uptake of NO_2 and emission rates up to 1500 μg N m^{-2} h^{-1} from unvegetated

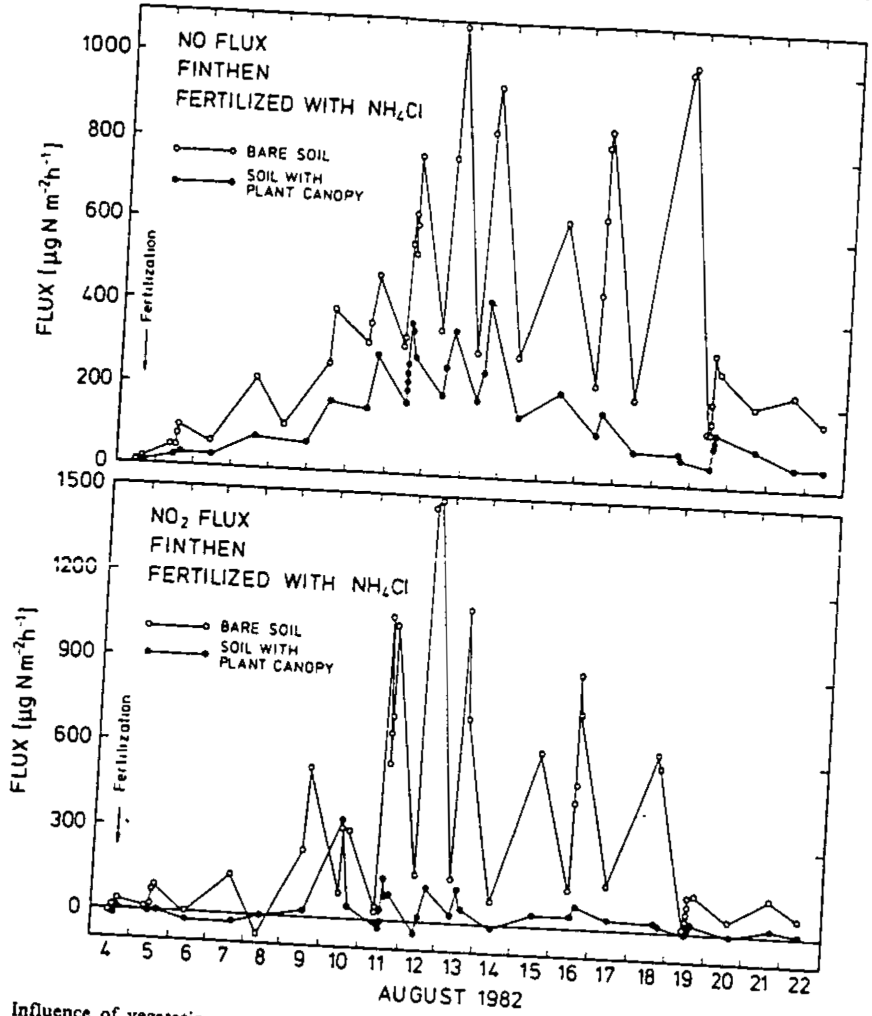

Fig. 5. Influence of vegetation cover on the flux rates of NO and NO_2. Data were obtained from measurements in Finthen on soil plots fertilized with NH_4Cl.

soil. The reduction of NO and NO_2 fluxes by vegetation may reflect the reduction of mean soil temperature from 26.2 to 23.8°C due to the shading of the soil surface by vegetation. The reduction might also result from the different content of organic soil matter and from an actual uptake of NO and particularly NO_2 at the leaf surface.

The influence of mineral fertilizer application on the NO and NO_2 flux rates has been studied in Finthen and Utrera. Measurements were carried out only on those plots which showed similar NO and NO_2 flux rates prior to fertilization. The results of fertilization using NH_4Cl at a rate of 100 kg N ha^{-1} on a planted and unplanted plot in Finthen are

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Table III. Integrated

Plot	Fertili
bare	none
bare	none
bare	$NaNO_3$
bare	NH_4NO
bare	NH_4Cl
grass	none
grass	NH_4Cl

shown in Figure 5. The NO flux rates from the fertilized plot increased after fertilization to maximum values of 1100 μg N m^{-2} h^{-1} on 12 August and then declined approaching the initial values after 16 to 20 days. Similar time patterns with maximum values of almost 1500 μg N m^{-2} h^{-1} were observed for the NO_2 flux rates. In the same period, the NO and NO_2 flux rates from the unfertilized plot shown in Figure 2 did not exceed 51 and 33 μg N m^{-2} h^{-1}, respectively. The variations of NO and NO_2 fluxes are partially due to variations of the soil temperature and the strong fluctuations of the NO and NO_2 mixing ratios in ambient air typical for air masses near a big city. Heavy rainfall on the 19 August (Figure 2) caused an increase in the NO and NO_2 flux rates although it was not of great significance when compared with the overall variation of the NO and NO_2 flux rates after fertilization.

Somewhat different results were obtained from the experiments carried out on hot dry soil in Utrera, Spain. Under these conditions, the NO and NO_2 fluxes increased much more rapidly with time, reaching first maximum values 1 to 2 days after fertilization and approaching the original values after 5 days (see Figures 6 and 7). Moreover, additional irrigation without fertilizer caused another increase of the NO and NO_2 flux rates from the soil (Figures 6a, 7a). Surprisingly, the highest flux rates of NO and NO_2 were found after the first repeated irrigation when fertilized with $NaNO_3$, NH_4NO_3 and NH_4Cl. When using urea as fertilizer, the maximum flux rates did not occur until the second irrigation (see Figure 7a). After four irrigation cycles – which means after 8 October – the NO and NO_2 fluxes were no longer elevated compared to the unfertilized soils. The delay of the NO/NO_2 maximum for urea fertilization may be explained by the fact that urea must first be converted into ammonia NH_3 (Mulvaney and Bremner, 1981) before nitrification can take place.

The total fluxes of NO and NO_2 integrated over the entire observation period in Finthen and Utrera are summarized in Tables III and IV, respectively. Table IV also includes the flux rates of N_2O measured simultaneously and reported by Slemr *et al.* (1984). It is obvious from these tables that the NO and NO_2 flux rates are strongly dependent on the type of mineral fertilizer. Relatively low flux rates were observed on soil plots fertilized with $NaNO_3$ where the NO and NO_2 emission integrated over the observation period in Utrera reached values of 39 and 37 mg N m^{-2}, respectively which

Table III. Integrated NO and NO_x emission rates measured in Finthen between 4 and 22 August 1982

Plot	Fertilizer	$\Sigma P(NO)$ (mg N m^{-2}) 18 day	$\Sigma P(NO_x)$ (mg N m^{-2})	% applied fertilizer nitrogen loss as		
				NO	NO_2	Total
bare	none	2.57 *	0.46 *	–	–	–
bare	none	3.52 *	0.09 *	–	–	–
bare	$NaNO_3$	6.49	7.48	0.04	0.07	0.11
bare	NH_4NO_3	66.07	64.15	0.63	0.64	1.27
bare	NH_4Cl	154.91	118.64	1.52	1.18	2.70
grass	none	−0.72 *	−6.23 *	–	–	–
grass	NH_4Cl	55.04	6.18	0.56	0.13	0.69

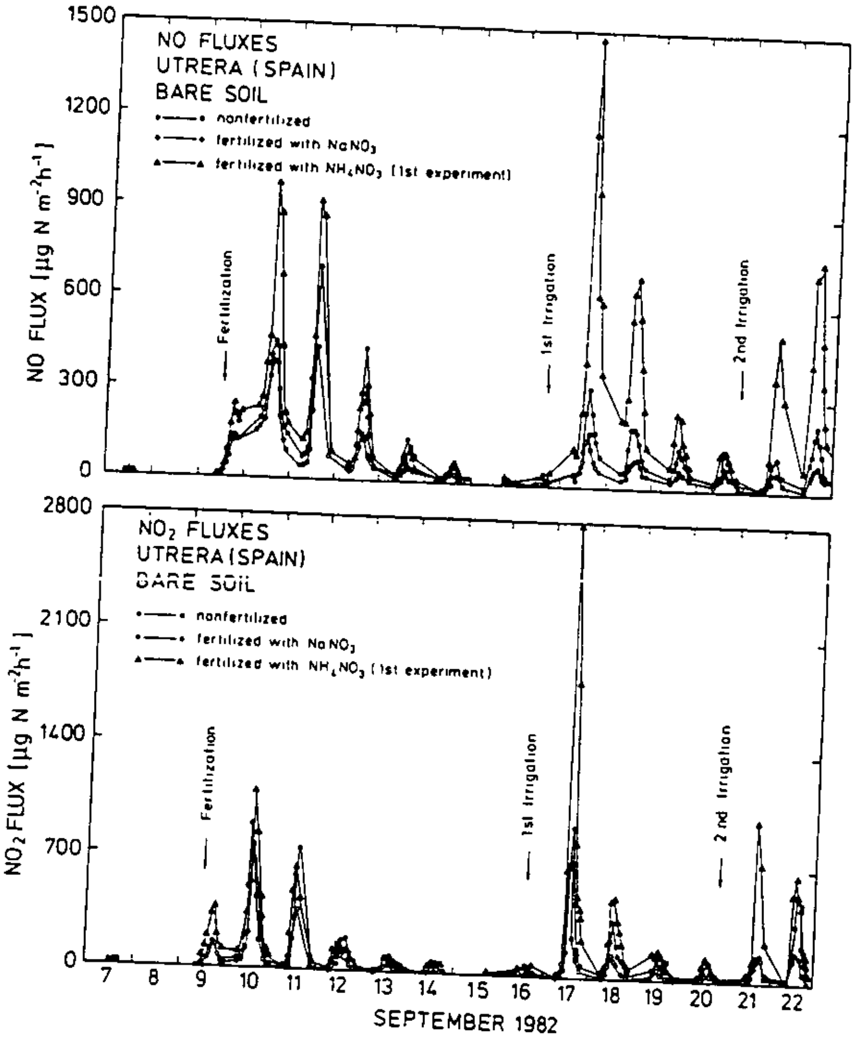

Fig. 6a. NO and NO$_2$ flux rates measured in Utrera on unfertilized soil plots and soil plots fertilized with NaNO$_3$ and NH$_4$NO$_3$. All Plots were artificially irrigated on 16 and 20 September with a precipitation rate of 7 mm H$_2$O.

are only slightly higher than the corresponding values of 24 and 23 mg N m^{-2} observed from unfertilized soil plots on the same field (Table IV). Considerably higher NO and NO$_2$ flux rates were found on plots fertilized with NH$_4$NO$_3$ and NH$_4$Cl with values of 100–150 mg N m^{-2} for NO and 80–83 mg N m^{-2} for NO$_2$. The highest emission rates, 350 mg N m^{-2} for NO and 240 mg N m^{-2} for NO$_2$ were observed from plots fertilized with urea exceeding the corresponding emission rates on unfertilized soils by more than

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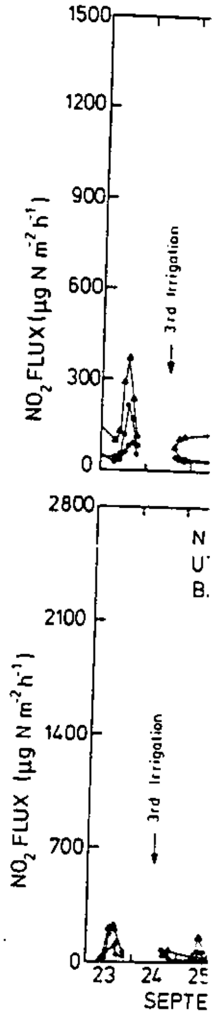

Fig. 6b. Continuation of Figu
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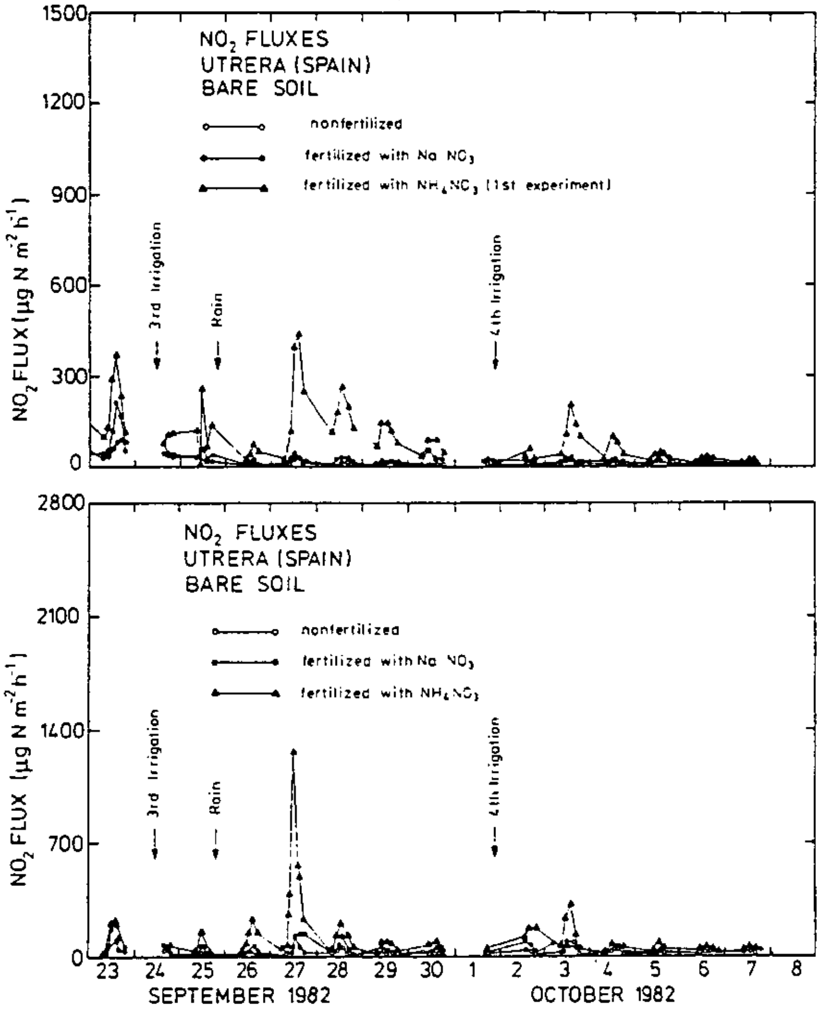

Fig. 6b. Continuation of Figure 6a. All plots were irrigated on 24 September and 1 October with a precipitation rate of 3.5 and 10 mm H$_2$O.

a factor of 10 (Table IV). A similar dependence of the NO and NO$_2$ emission on the type of mineral fertilizer has been found in Finthen. Interestingly, the absolute values of the integrated NO and NO$_2$ emission measured in Utrera and Finthen on soil plots fertilized with the individual types of mineral fertilizers agree reasonably well despite the large differences in soil moisture and temperature.

It is noteworthy that measurements of the N$_2$O emission from fertilized soils showed

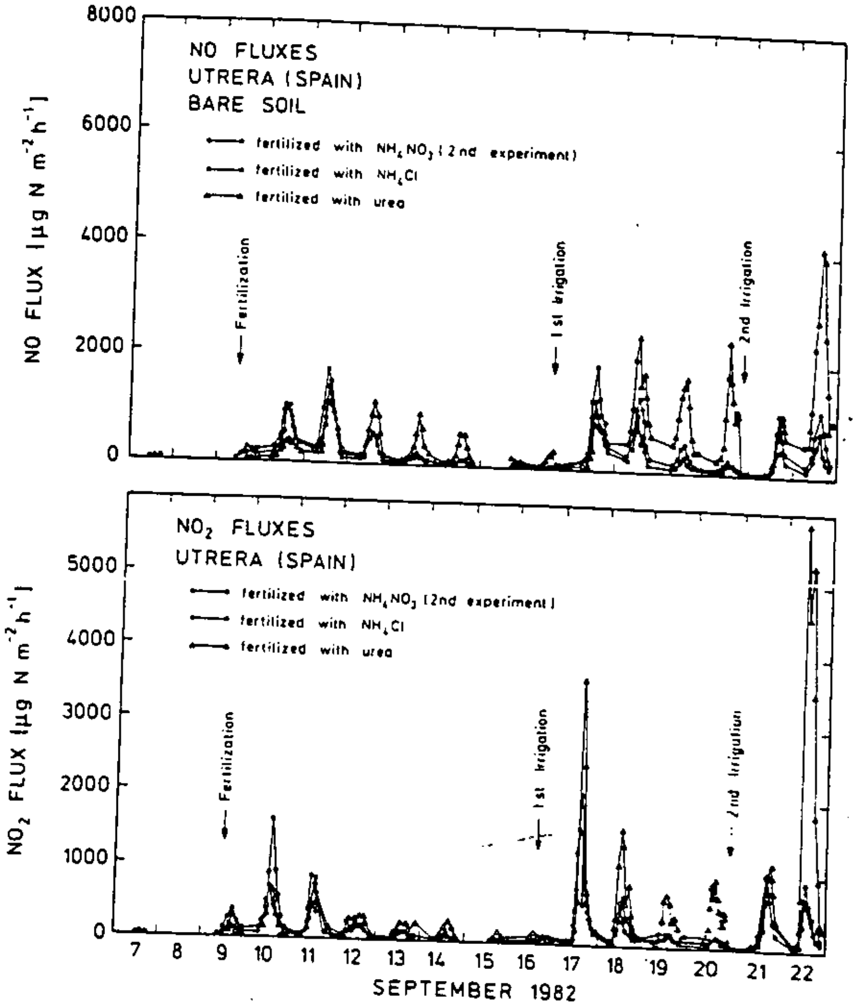

Fig. 7a. Influence of fertilization with NH_4NO_3, NH_4Cl and urea on the NO and NO_2 flux rates measured in Utrera on soils without vegetation.

the same dependence on type of mineral fertilizer observed for the NO and NO_2 emission (Conrad *et al.*, 1983), with considerably lower flux rates (see, e.g., Table IV). The higher NO and NO_2 emission from soils fertilized with ammonium fertilizer indicates that nitrification is much more efficient in producing nitrogen oxides than the denitrification. However, the possibility of additional NO_x production by denitrification of nitrite formed by nitrification (Schmidt, 1982) cannot be ruled out. The total NO flux was significantly reduced from the plant covered, NH_4Cl fertilized plot with a value of 55 mg NO–N m^{-2}

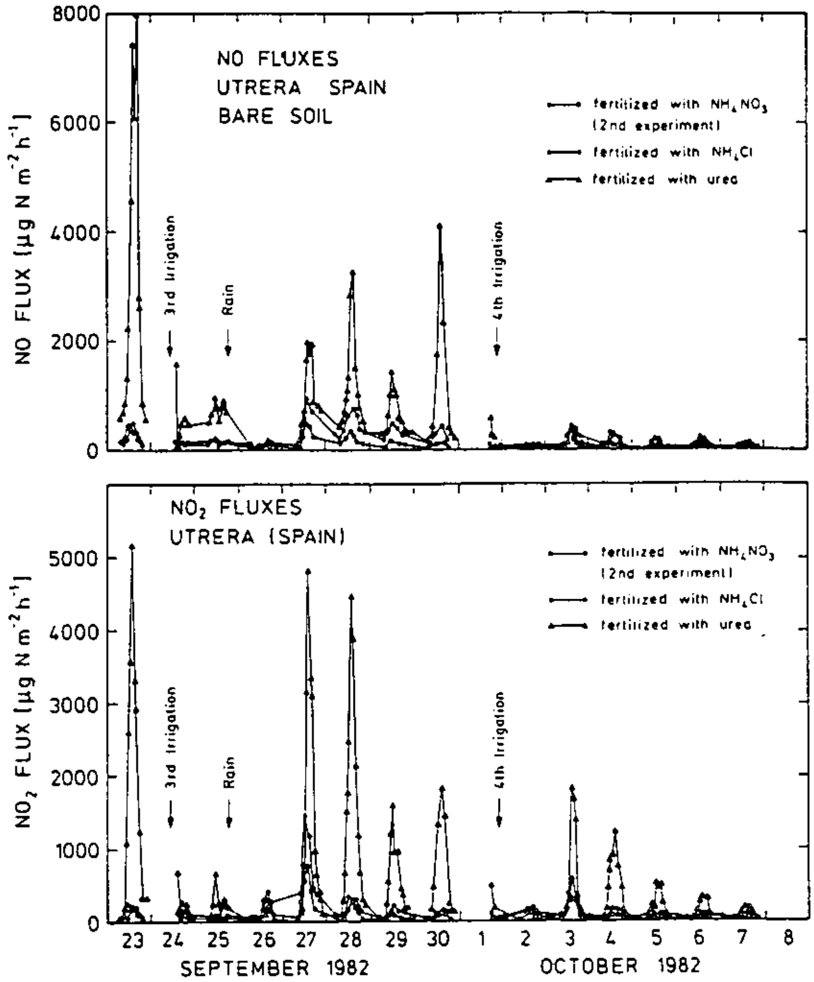

Fig. 7b. Continuation of Figure 7a.

compared to 155 mg m^{-2} from the bare soil plot (Table III). Even more pronounced is the difference between the total NO$_2$ fluxes of 6 and 119 mg NO$_2$–N m^{-2}, respectively.

The loss rates of mineral fertilizer N as NO$_x$ (NO + NO$_2$) expressed in percent of applied mineral fertilizer N vary between 0.11% for NaNO$_3$ and 5.4% for urea (see Tables III and IV). Despite the different climate and soil conditions, the loss rates obtained from measurements in Finthen and Utrera agree reasonably well and thus may be assumed to be representative of global conditions as a first approximation.

Table IV. Integrated NO, NO_2 and N_2O emission rates measured in Utrera, 9 September - 10 October, bare soil

Fertilizer	$\Sigma P(NO)$ (mg N m^{-2})	$\Sigma P(NO_2)$ (mg N m^{-2})	$\Sigma P(N_2O)$ (mg N m^{-2})	% applied fertilizer loss as			
				NO	NO_2	N_2O	Total
none	24.37	23.26	8.62	–	–	–	–
$NaNO_3$	38.45	37.12	–	0.14	0.14	–	0.28
NH_4NO_3	88.42	74.54	12.60	0.64	0.51	0.04	1.19
NH_4NO_3	101.81	79.43		0.77	0.56		1.37
NH_4Cl	147.66	83.40	–	1.23	0.60	–	1.83
urea	349.72	242.10	26.97	3.25	2.19	0.18	5.62

5. Discussion

The measurements carried out in Finthen and Utrera clearly demonstrate that soil, both fertilized and unfertilized, acts as a source for NO which confirms earlier results published by Galbally and Roy (1978). In addition, the measurements indicate that other nitrogeneous species, most likely NO_2, must be produced in the soil which are emitted into the atmosphere. The flux rates of both nitrogeneous species are quite comparable and are strongly dependent on the soil moisture as well as on the vegetation cover. Whereas the NO flux rates are positively correlated with soil temperature measured at a depth of 10 mm, the NO_2 flux rates correlate with the irradiation intensity.

The similar behaviour of the NO and N_2O flux rates strongly suggests that NO is produced by biological processes, most likely during denitrification and nitrification. This assumption is supported by laboratory measurements carried out by Nelson and Bremner (1970), John and Hollocher (1977), Smith and Chalk (1979, 1980a, 1980b), Lipschultz *et al.* (1981) and McKenney *et al.* (1982) who found NO to be one of the general products of nitrification and denitrification. Because of the positive correlation of the NO flux rate and soil temperature at a depth of 10 mm, the production of NO may occur predominantly in the upper soil layer.

NO_2 fluxes presented in this work were calculated as the difference between the NO_x and NO fluxes. The ambiguity of this ascription caused by the nonselective conversion of nitrogen species on molybdenum converter has already been mentioned. However, there are several reasons to believe that NO_2 is the major compound. First of all, high NO_2 flux rates were also measured by Makarov *et al.* (1963; 1969) and Kim (1973) using chemical techniques which were NO_2 specific (Cheng and Bremner, 1965). Furthermore, the NO_2 fluxes measured in this work, were found to be dependent on the difference of NO_x and NO mixing ratios in ambient air which generally is predominantly due to NO_2 (Kelly *et al.*, 1979); Shetter *et al.*, 1983). Finally, the differences between the NO and NO_2 flux patterns discussed later are compatible with the physicochemical properties of NO_2. However, although all this evidence suggests that NO_2 is the predominant species responsible for the difference between NO_x and NO fluxes, the existence

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of minor fluxes of other nitrogeneous species such as, e.g., methyl nitrite cannot be definitely eliminated.

The pattern of NO_2 flux rates indicates that the processes responsible for NO_2 emission are located in the uppermost soil layer or at the soil surface. Although NO_2 may also be produced in deeper soil layers, its solubility in water with subsequent conversion to NO_2^- and NO_3^- (Lee and Schwartz, 1981), its reactivity towards organic soil matter such as humic acids (Lee and Schartz, 1981) and its efficient absorption by the soil (Prather *et al.*, 1973) would effectively preclude its transport to the soil surface. NO, on the contrary, is much less soluble in water (Stephen and Stephen, 1963) and is not absorbed by the soil as effectively as NO_2 (Wesely *et al.*, 1982; Hill, 1971; Judeikis and Wren, 1980; Böttger *et al.*, 1980; Sehmel, 1980).

The process responsible for the emission of NO_2 from the soil is not known. The current biochemical models of nitrification and denitrification do not show NO_2 as a gaseous intermediate (Focht and Verstraete, 1977; Knowles, 1981; Firesteon, 1982; Garber and Hollocher, 1982; Schmidt, 1982) so that NO_2 might be produced by an abiological process. One possibility is the chemical decomposition of nitrite (Nelson and Bremner, 1970; Smith and Chalk, 1979, 1980a, 1980b), by

$$2\,HNO_2 \rightarrow NO + NO_2 + H_2O$$

Since nitrite is an obligate intermediate in the nitrification and denitrification, the chemical formation of NO_2 may be a common source of NO_2 in soils. Another possibility for NO_2 formation is the catalytic oxidation of NO to NO_2 proposed by Nelson and Bremner, (1970) and Prather and Miyamoto (1974). The existence of these two NO_2 production processes would suggest a strong link between the NO and NO_2 emissions which, however, was not observed. This indicates that other NO_2 sources in soil, e.g., by microbial activities, may exist. It is possible that NO_2 production in microbial studies has not been observed because NO_2 is effectively absorbed in the water media and therefore has not been detected in the gaseous phase.

Interesting is the observation of NO/NO_2 equilibrium values which indicate the existence of production and destruction processes occurring simultaneously in the soil or at the soil surface. The absolute value of equilibrium mixing ratios is dependent on several parameters, such as soil moisture, soil temperature, type of soil, fertilizer, etc. and varies between less than 1 ppbv and a few ppbv. In some cases, particularly in Finthen in the vicinity of large cities, the ambient NO and NO_2 mixing ratios exceeded the equilibrium values so that during these time periods the soil acted as a net sink of atmospheric NO and NO_2. Such situations may only occur in polluted areas so that uptake of atmospheric NO and NO_2 on the soil surface may be restricted to heavily populated and industrialized areas. NO and NO_2 uptake by soils has also been reported by Judeikis and Wren (1978), Hill (1971), Prather *et al.* (1973) and Prather and Miyamoto (1974).

Neglecting the results obtained during periods with highly polluted air, the average flux rates of NO and NO_2 measured on bare unfertilized soils in Finthen were approximately 10 μg N m^{-2} h^{-1} for NO_2 and 8 μg N m^{-2} h^{-1} for NO. In contrast, the results obtained on dry hot soils in Utrera show extremely high NO and NO_2 fluxes after the first irrigation which subsequently decreased with further irrigation, finally reaching mean values of 10 μg N m^{-2} h^{-1} for NO and for NO_2 comparable to those found in Finthen. This pattern agrees with the observations made by Dommergues (1977) on Moroccan soils showing that rain rapidly revived the nitrification activities after a long period of dryness. Furthermore, Patten *et al.* (1980) reported that drying of soil increased markedly the capacity of denitrification of nitrate. Therefore, it appears that because of the dry soil conditions and consequently low microbial activity, nitrients may have accumulated which then initiates very effective microbial processes shortly after the soil moisture exceeds a critical value.

The NO flux rates agree reasonably well with 2.2–26 μg N m^{-2} h^{-1} found by Galbally and Roy (1978) on grassland in Australia. In contrast, the NO_2 flux rates observed in our experiments are much lower than the figures of 26–105 μg N m^{-2} h^{-1} as reported by Makarov (1969) and 66–150 μg N m^{-2} h^{-1} as reported by Kim (1979). The different values may reflect the natural variability of the NO_2 emission from different ecosystems. Possibly, the higher NO_2 emissions found by those authors are due to artifacts caused by the applied sampling technique or oxidation of NO to NO_2 in the closed chamber.

The strong impact of plant cover on the NO and NO_2 flux rates may partially be due to the reduced soil temperature and higher soil moisture content causing lower production rates and favouring a higher uptake of NO_2 on the moist soil surfaces. In addition, NO and NO_2 might be metabolized by the plants (Rogers and Campbell, 1979) so that part of the NO and NO_2 emitted at the soil surface does not pass the plant canopy reducing the flux of these gases into the atmosphere. Furthermore, the root system providing easily available organic carbon to the soil may influence the microbial activity and thus the production and destruction rate of NO and NO_2 in the soil.

All experiments clearly demonstrate that the application of mineral fertilizer enhances the flux rates of NO and NO_2 from the soil into the atmosphere. The NO_x flux rates strongly depend on the oxidation state of the mineral fertilizer added. Highest flux rates were observed from soils fertilized with ammonium fertilizer suggesting that an oxidation process, e.g., nitrification, is the likely source of NO_x while denitrification seems to be less important. The fertilizer derived NO and NO_2 flux rates correspond to loss rates of 0.04 and 0.07% for $NaNO_3$ and 3.3 and 2.2% for urea, respectively, and thus exceed those found for N_2O (see, e.g., Conrad *et al.*, 1983). From production data of individual types of fertilizer (FAO, 1982) and assuming the figures observed to be representative for global conditions, the average fertilizer loss rates as NO and NO_2 are on the order of 1.6% for NO and 1.1% for NO_2.

In view of the large demand for a rough estimate of global NO/NO_2, the flux rates from these admittedly very limited *in-situ* measurements may be extrapolated to the global NO_x cycle. The figures calculated for the NO and NO_2 fluxes from natural and fertilized soils are summarized in Table V together with information on NO_x production by other processes reported by Crutzen (1983) and Ehhalt and Drummond (1982). The estimate of 1.7 Tg NO_x–N yr^{-1} derived from the application of mineral fertilizer is based on an average loss rate of 1.6% for NO and 1.1% for NO_2 as well as a global nitrogen fertilizer production of 60 Tg N yr^{-1} for 1980. This estimate might be an upper

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Table V. Estimates of NO_x soil source strength and total emission (in Tg N yr^{-1})

	This work	Crutzen (1983)	Ehhalt and Drummond (1982)
(A) from mineral fertilizers	<1.7		
(B) from unfertilized soils	7		
(C) from animal excreta	<2		
Total soil source strength	<11	1–15	1–10
Fossil fuel burning		12–20	8–19
Biomass burning		10–40	6–16
Lightning		1–10	2–8
Total NO_x		24–85	17–53

limit for fertilizer derived NO_x flux since part of the mineral fertilizer is applied to plant covered fields so that part of the NO_x emitted from the soils may be taken up by plants.

The figure of 7 Tg NO_x–N yr^{-1} estimated for the flux of NO_x from natural unfertilized soils is based on the assumption that the NO_x flux rates measured on unfertilized bare soils in Finthen and Utrera are representative only for approximately half of the total land surface and that the other half does not act as a source of NO_x because of vegetation cover. The given estimate takes also into account that due to the strong temperature dependence, the NO_x flux should show significant seasonal variations. As a first approximation, it is assumed that the NO_x flux from land areas north and south of 30° latitude does not contribute to the atmospheric NO_x cycle for a period of 6 months per year. Polar regions are not considered to be active with respect to the NO and NO_2 production.

Additional NO_x may be emitted from the soil by the production of animal excreta – mainly urea – whose degradation causes an enhanced NO_x production as shown by the experiment in Utrera using urea fertilizer. The total production of urea by animals is estimated by Böttger *et al.* (1980) to be approximately 40 Tg urea N yr^{-1} which may result in an NO_x flux of about 2 TG NO_x–N yr^{-1}. This figure might be overestimated since part of the urea is emitted in vegetated areas which may reduce the NO_x emission from the soil into the atmosphere.

Summarizing the individual NO_x sources, we obtain an upper limit of the total NO_x emission from soils into the atmosphere of about 11 Tg NO_x–N yr^{-1}. This figure is certainly far from definite. Additional measurements over extended periods of time and in other climatic regions are urgently needed to verify the figure given above. It is noteworthy, however, that the flux of 11 Tg NO_x–N yr^{-1} as estimated in this paper agrees reasonably well with theoretical estimates (5.5 Tg N yr^{-1} given by Ehhalt and Drummond, 1982) and is also within the range of 1–15 Tg N yr^{-1} as reported by Crutzen (1983).

Compared to the other major sources of NO_x compiled in Table V, the flux of NO_x into the atmosphere contributes substantially to the global NO_x cycle. The influence of NO_x flux from the soil becomes even more important if one takes into account that the NO_x production by combustion of fossil fuel representing predominant sources of atmospheric NO_x is restricted to relatively small areas and because of its short residence time, NO_x will not be transported over long distances. Thus, in remote continental areas, the NO_x flux from the soil may be the dominant NO_x source and therefore will significantly influence the atmospheric chemistry.

Acknowledgements

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