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Nitrogen oxides concentrations and soil emission fluxes in the Po Valley

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ABSTRACT

NO, NO_2 and O_3 measurements from the Ground-based Cloud Experiment (GCE) campaign 1989 in the Po Valley in fog and fog free situations are presented. Extremely high concentrations of NO up to 9700 nmole m^{-3} (217 ppbv) are shown. From the observations the fluxes are calculated using a flux-gradient-method. A detailed observation of the evolution of gas concentrations and fluxes during one observational day supports the significance of the oxidation of NO by O_3. The results strongly indicate that the soil is the main source of nitrogen oxides at this place.

1. Introduction

The nitrogen oxides NO and NO_2 play a key role in numerous important reactions in the atmosphere. Thus, not only the knowledge about the concentrations and their spatial and temporal distribution but also their sources and sinks are essential for our understanding of atmospheric chemistry.

The natural sources for the tropospheric nitrogen oxides are lightning, oxidation of ammonia and to a greater extent it is exhaled by soils. The largest anthropogenic processes are combustion of fossil fuels and biomass burning which make up more than half of the global NO_x-sources (Ehhalt and Drummond, 1982; Logan, 1983). Almost 100% of the NO_x emitted by natural as well as by antropogenic sources is emitted as NO.

The uncertainty in the amount of NO emission from soils is much larger than the uncertainty of other sources and sinks. In laboratory studies three mechanisms that may lead to the production of NO in soils have been identified: nitrification and denitrification by bacteria and chemical decomposition of nitrite, the so-called chemodenitrification (Firestone and Davidson, 1989; Galbally and Johansson, 1989). Numerous factors have been found to control the production and the emission of NO: soil temperature, soil pH, soil moisture and porosity, plant cover, soil organic carbon content, fertilization with organic or inorganic N-substances and the NO concentration in the air above the soil.

In most investigations, one of these factors dominated and masked the importance of the others. Williams and Fehsenfeld (1991) pointed out the importance of the soil temperature in various different ecosystems. They found an exponential increase in the NO-flux with increasing soil temperature in the range from 2–43°C. In an earlier study Williams et al. (1988) had found that fertilization is an important factor for the NO emission in agricultural areas. Similar results were obtained by Slemr and Seiler (1984) in their studies in Germany and Spain and by Johansson and Granat (1984) in Sweden. Equilibrium concentrations of NO (also called compensation points) have been reported by several authors (Johansson and Granat, 1984; Slemr and Seiler, 1991).

In this paper, we present measurements of very high NO concentrations obtained during the GCE campaign in the Po Valley in 1989. Furthermore fluxes of nitrogen oxides will be calculated from a

flux-gradient-method and the importance of the different factors controlling their magnitude will be discussed.

2. Experimental set-up

Measurements of the concentrations of the nitrogen oxides, ozone and of meteorological parameters have been performed during the Po Valley Fog Experiment in November 1989 at the measuring site at S. Pietro Capofiume as part of the EUROTRAC subproject GCE (Ground-based Cloud Experiment). The complete description of the observational site and the experimental set-up including details concerning the instrumentation is given elsewhere (Fuzzi et al., 1992). Here we concentrate on the measurements of NO, NO_2, O_3, windspeed, temperature and relative humidity, which are necessary to evaluate gas fluxes. The gas measurements were carried out at the tower in three levels (5, 25 and 50 m), the temperature and the relative humidity used were measured at 2 and 50 m, the windspeed due to problems with the instrumentation in 2 and 50 m were taken at 5 and 30 m.

3. Experimental results

Nitrogen oxides and ozone concentrations were measured from November 10 (16:00) to 17 November (12:00) with some shorter gaps, which are caused by either calibration interruptions or power failures. The period of November is characterized by a very high fog frequency (35% of the time). From 10 to 17 November we even observed 95 h of fog (see Fuzzi et al., 1992).

In the Fig. 1 (a–c), the time evolution of the $\frac{1}{2}$-h mean values of NO, NO_2 and O_3 for the entire period are reported for the three gas measuring heights of 5, 25 and 50 m. The figures are summarized in Table 1 with ranges, averages, and standard deviations of the $\frac{1}{2}$-h means together with the number of observations that were taken for the calculations.

The results show strong fluctuations of NO (Fig. 1a) with a long period of very low concentrations during fog event 2 and during noon hours, where high ozone values were reported (Fig. 1c). Maxima in NO concentrations can be observed in the hours after midnight with the highest value reaching up to 9684 nmol m^{-3} at the 5 m level on 17 November. The periods from 0:00 till 6:00 are characterized by the strongest vertical gradients in the concentrations with the highest values at the 5 m level and the lowest values at 50 m. This fact already indicates that the extraordinary high surface concentrations were caused by the soil. In contrast to this, ozone has its maxima around noontime. Prominent gradients were only formed on 15 November with an opposite direction as compared to NO. Ozone concentrations usually dropped below the detection limit around 18:00 when the sun had set. There are exceptions of this usual behaviour during the second half of event 2 with peak values around midnight or shortly later on 13 and 14 November. This finding is a strong indication for the mixing in or advection of aged air masses with higher ozone levels during these periods. Thus the locally generated NO is most likely oxidized by the ozone.

The NO_2 data (Fig. 1b) show no such strong fluctuations and only minor gradients. The missing of a diurnal trend indicates that the nitrogen oxides at this measuring site are not caused by local automobile traffic.

Table 1. *Concentration ranges, mean values, standard deviations of the 1/2 h means of NO, NO_2 and O_3 for the three measuring heights, and the number of observations for 10 to 17 November*

	Range	Mean	Standard deviation	Number of $\frac{1}{2}$ h means
	(n mol m^{-3})			
NO				
5 m	61–9684	2190	2048	302
25 m	176–6999	1797	1554	302
50 m	20–5609	1276	1153	302
NO_2				
5 m	83–3705	1177	585	300
25 m	11–3944	1171	604	300
50 m	49–3193	1250	663	300
O_3				
5 m	0–2103	230	345	304
25 m	0–2273	275	406	304
50 m	0–2546	326	453	304

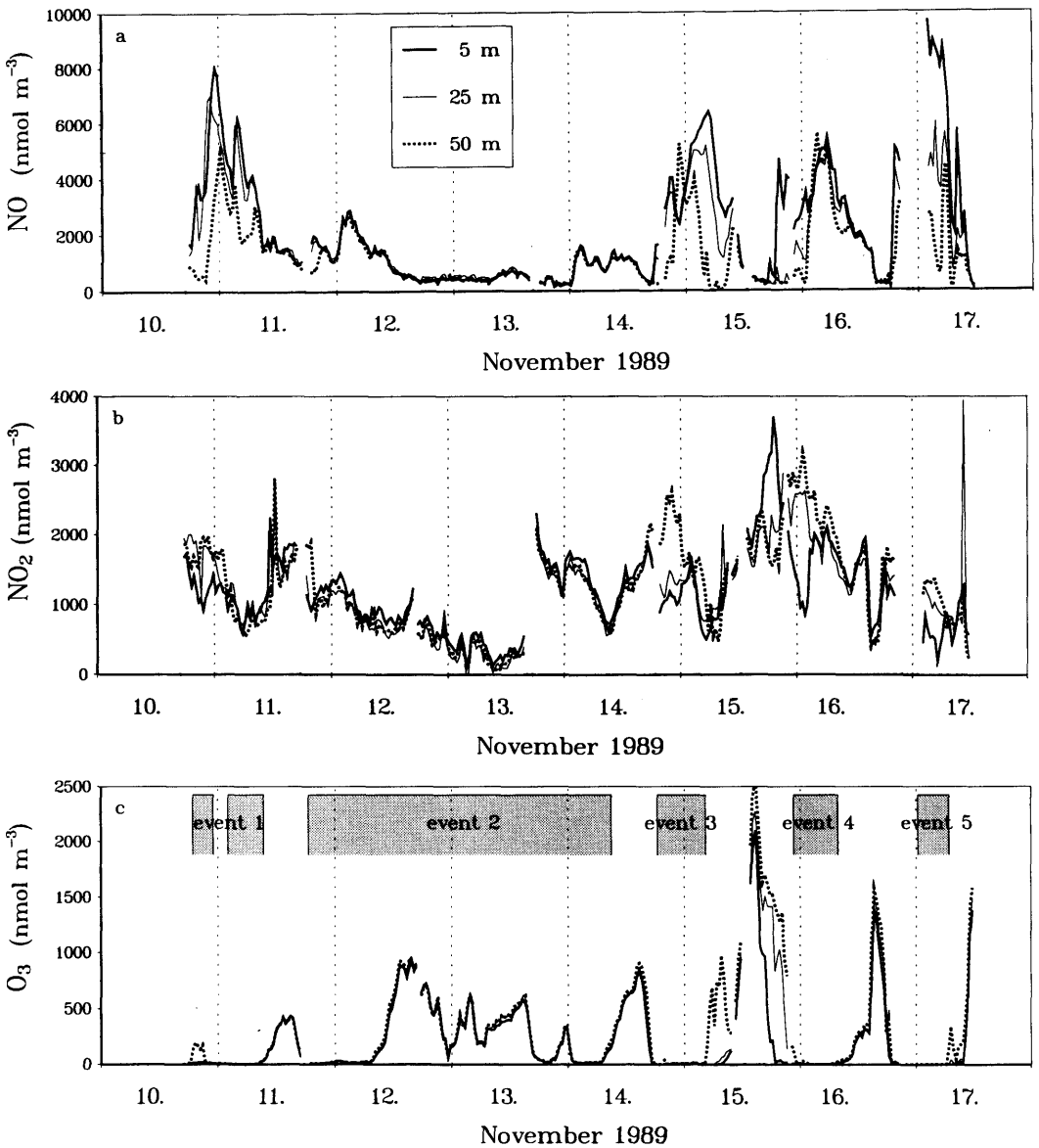

Fig. 1. Time evolution of NO, NO_2 and O_3. Data used are $\frac{1}{2}$-h mean values of concentrations at the three measuring heights. Verticals with dots illustrate 0:00.

The concentrations observed during the Po Valley Fog Experiment were not unusual for the measuring site. Continuous observations of NO, NO_2 and O_3 during October and November 1989 at ground level (2 m) confirm the order of magnitude for the concentrations found during the GCE campaign.

4. Determination of NO fluxes

4.1. Model conception

To estimate reliable NO fluxes a so-called flux-gradient-method was used. It is based on the assumption that the flux of a constituent x is

proportional to the gradient of the temporal mean value of x (Stull, 1988):

$$F_x = -k_x \frac{\partial x}{\partial z}, \tag{1}$$

where F_x is the vertical flux, $\partial x/\partial z$ is the gradient and k_x is the eddy diffusivity for x. This method in addition makes use of the constant-flux-hypothesis, which means, that the flux is independent of the height z (Dyer and Hicks, 1970):

$$\frac{\partial F_x}{\partial z} = 0. \tag{2}$$

As a result of similarity theory it is possible to write F_x as the product of the friction velocity u_* and the constituent scale x_*:

$$F_x = -u_* \cdot x_*. \tag{3}$$

u_* and x_* can be derived from the following similarity relations (Stull, 1988):

$$\frac{\kappa z}{x_*}\frac{\partial x}{\partial z} = \Phi_x\left(\frac{z}{L}\right). \tag{4}$$

κ is the von Karman constant with a value of 0.4 and z is the altitude. $\Phi_x(z/L)$ is the dimensionless gradient for x. In neutral conditions this term is equal to 1. For non-neutral conditions Clarke (1970) and Delsol et al. (1971) have estimated the functional form for the dimensionless windshear $\Phi_u(z/L)$ based on field experiments:

$$\Phi_u\left(\frac{z}{L}\right) = \begin{cases} \left(1 - 15\frac{z}{L}\right)^{-11/40} & \text{for } L < 0 \\ 1 & \text{for } L = 0 \\ \dfrac{\left(1 + 5\frac{z}{L}\right)}{\left(1 + 0.0079\frac{z}{L} + 0.0395\left(\frac{z}{L}\right)^2\right)} & \text{for } L > z \\ 6\Big/\left(1 + 0.0474\frac{z}{L}\right) & \text{for } L < z \end{cases} \tag{5}$$

where L is the Monin-Obukhov-length given as:

$$L = \frac{u_*^2 \Theta^S}{\kappa g(\Theta_* + 0.608 q_* \Theta^S)}, \tag{6}$$

and Θ^S is the spatial mean potential temperature, g is the acceleration due to gravity, Θ_* and q_* are the scales of the potential temperature and the specific humidity, respectively. In stable conditions the dimensionless potential temperature gradient $\Phi_\Theta(z/L)$, the dimensionless moisture gradient $\Phi_q(z/L)$ and the dimensionless pollutant gradient $\Phi_c(z/L)$ were assumed to be equal to $\Phi_u(z/L)$, otherwise they are equal to $\Phi_u^2(z/L)$. Integrating equation (4) from 5 to 50 m and applying it to the observed mean horizontal windspeed, the mean potential temperature, and the mean specific humidity together with equation (6) a system of 4 equations for the 4 unknown variables L, u_*, Θ_*, q_* results. Integrating eq. (4) from 5 and 50 m with respect to the mean observed pollutant concentration c in these levels makes it possible to calculate c_*. Finally the vertical flux F_c between 5 and 50 m can be determined with eq. (3).

In order to consider sources or sinks due to chemistry the two following very fast reactions are important:

$$\begin{aligned} &NO + O_3 \rightarrow NO_2 + O_2 \\ &NO_2 + h\nu \rightarrow NO + O. \end{aligned} \tag{7}$$

Since the ozone concentrations during night time were in most cases very low, the influence of both reactions for the resulting deposition fluxes can be neglected. Models taking these chemical transformations into account (e.g., Parrish et al., 1987) are therefore impracticable for our situation. During the day a very complex chemistry including ozone, hydroxyl- and other radicals as well as radiation can lead to significant deviations from the simple descriptions of eq. (7). That is why we refrained from including eq. (7) in our model.

4.2. *Results*

Using the flux-gradient-method the Monin-Obukhov-length (MO-length) represents a useful tool to describe the stability of the atmospheric surface layer. Small positive MO-lengths up to about 30 m represent very stable situations, whereas MO-lengths > 100 m represent moderately stable situations. Negative MO-lengths characterize

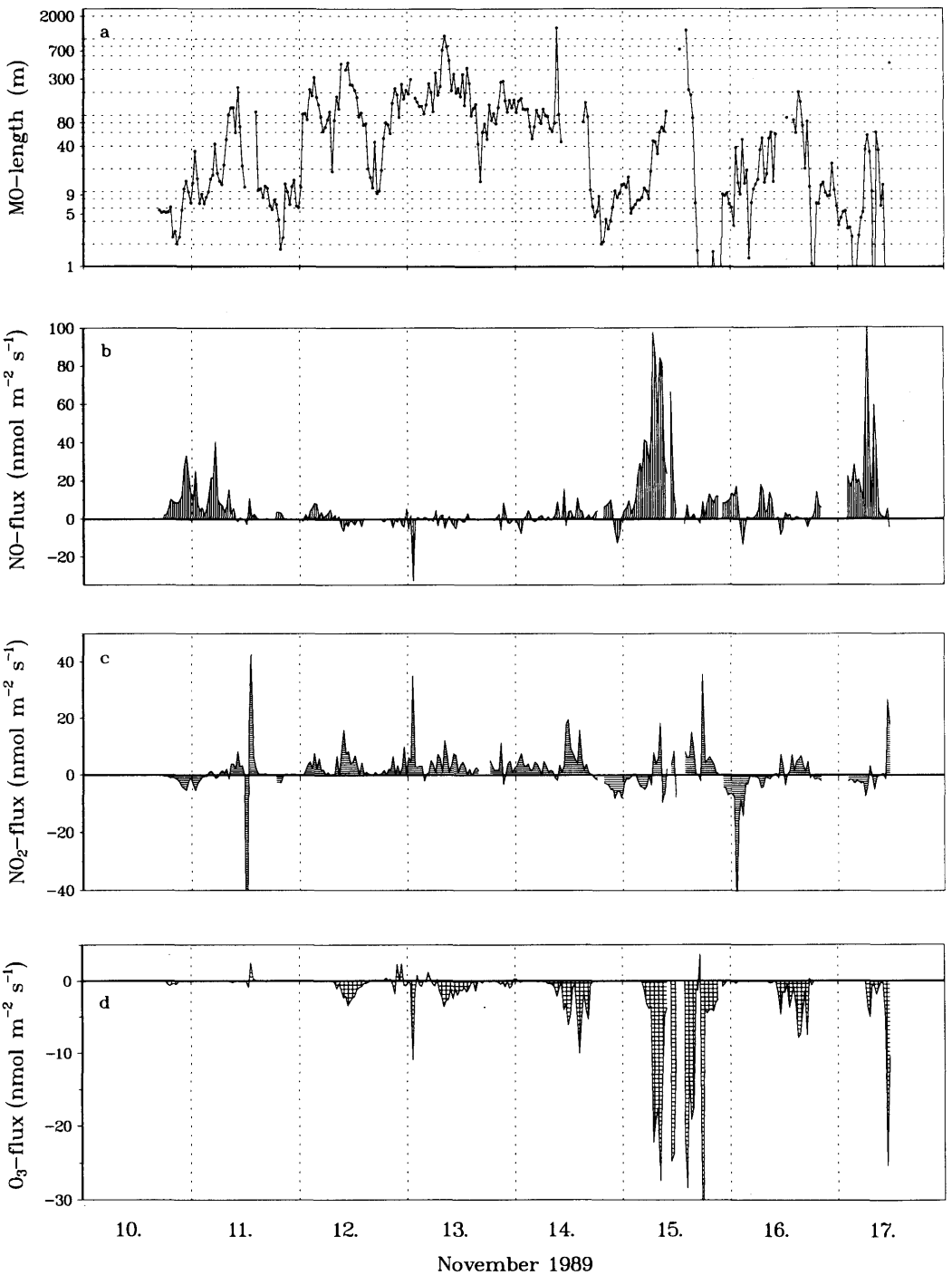

Fig. 2. Time evolution of the Monin-Obukhov-length together with the fluxes of NO, NO_2 and O_3 between 5 and 50 m.

unstable situations as they usually occur during sunshine periods. Thus, the MO-length gives an idea of the strength of the turbulent exchange. The time evolution of the MO-length is shown in Fig. 2a. (Negative values are removed but can be identified by the gaps in the graph during the daytime.) A diurnal trend can be seen for all fog free periods with very stable situations during the night-time hours and a change to more turbulent mixing during the daytime hours, as expected from theory (Stull, 1988). From the period of 12 to 14 November, however, almost no diurnal variations of the MO-length can be found. This was caused by the high reaching fog layer even persisting during daytime. The stratification in the 200 m high reaching fog layer was moderately stable and tented in some cases to near neutral conditions. The temporal evolution of the fluxes that were determined for NO, NO_2 and O_3 between 5 and 50 m are shown in Fig. 2 (b–d). Positive values indicate fluxes directed from the surface into the atmosphere, negative values indicate fluxes directed onto the surface.

The NO fluxes (Fig. 2b) showed most of the time emissions up to very high $\frac{1}{2}$-h mean values of more than 100 nmol $m^{-2} s^{-1}$. The NO_2 fluxes (Fig. 2c) showed both emissions with peak values of more than 40 nmol $m^{-2} s^{-1}$ and also in a few cases depositions of the same order of magnitude. As the O_3 concentrations increase in most cases with height the O_3 fluxes (Fig. 2d) are directed downward: In contrast to ozone the NO_2 concentrations are decreasing with height, resulting in upward fluxes. Surprisingly, this opposite behaviour occurred most of the time simultaneously. According to the high NO concentration near the surface we can assume that the oxidation of NO by O_3 causes the high NO_2 and low O_3 concentrations, that we found there.

5. Discussion of the fluxes of NO, NO_2 and O_3 on 15 November

Looking at Fig. 1 (a–c), we can see that on 15 November the concentrations of NO, NO_2 and O_3 had all high values and experienced strong changes. Furthermore this period was most of the time free of fog. This is why in the following section the evolution on this day will be studied in detail.

The concentrations of NO, NO_2 and O_3 at the three measuring heights with a time resolution of 6 min are shown in Fig. 3 (a–c). In order to interpret the fluxes resulting from the gas measurements one has also to study the evolution of the windspeed and temperature. The time history for the temperature (Fig. 4a) shows that except for daytime periods a strong inversion of up to 8°C in the first 50 m was observed. Between 10:00 and 15:00, however, the temperatures in 50 m were slightly below those in 5 m. The corresponding figure for the windspeed (Fig. 4b) shows that the windshear between 5 and 30 m dropped during the entire day except for the last two hours when a new fog field formed due to advection processes (see Wobrock et al., 1992). Between 0:00 and 10:00, the wind in the 2-m level was around 2 m s^{-1} while the wind aloft varied between 4 and 8 m s^{-1}. Around 10:00, the wind in the 5-m level increased to 3 m s^{-1} while the wind in 30 m dropped significantly. Around 15:00, the wind in both levels dropped to 1–2 m s^{-1} with almost no windshear.

Thus, we can identify 3 turbulent regimes illustrated by the Monin-Obukhov-length in Fig. 5a. The first period was characterized by very stable stratification with Monin-Obukhov-lengths below 30 m which increased to a moderately stable situation in the morning hours. After 10:00 the atmosphere became unstable which is displayed by the dots at the upper boundary of Fig. 5a. These represent negative Monin-Obukhov-lengths.

After 14:00 the Monin-Obukhov-length gradually dropped until 17:00 when an extremely stable condition was reached which was most likely caused by the lack of the vertical windshear.

Unfortunately in the periods from 10:00 to 10:30 as well as between 12:00 and 13:30 no gas measurements are available due to calibration breaks. However, the measurements at 11:00 and after 13:30 allow an interpolation for the missing values. The gradient of NO between 5 and 50 m is given in Fig. 3d and the resulting fluxes are shown in Fig. 5 (b–d). Starting from 14 November at sunset a constant increase in the NO concentrations (Fig. 1a) at all heights can be observed. At 2:00 on the 15th the NO concentration (Fig. 3a) at the 50 m level begins to decrease reaching values below the detection limit at about 5:00. At the 5 m level the concentrations constantly increased during this time resulting in a very steep gradient building up (Fig. 3d). During this situation with

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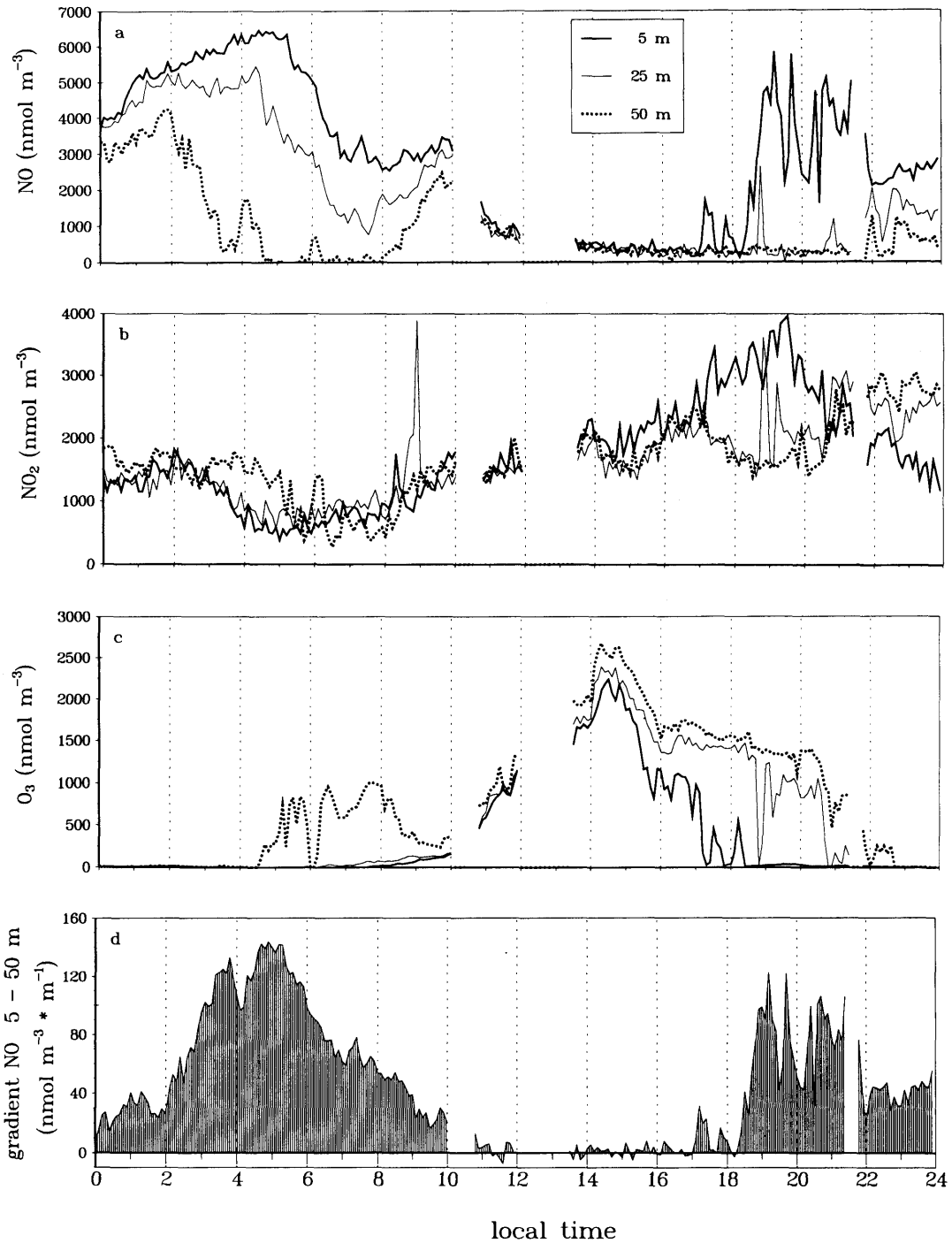

Fig. 3. 6-min mean values of the concentrations of NO, NO_2 and O_3 at the three measuring heights together with the gradient of NO between 5 and 50 m on 15 November.

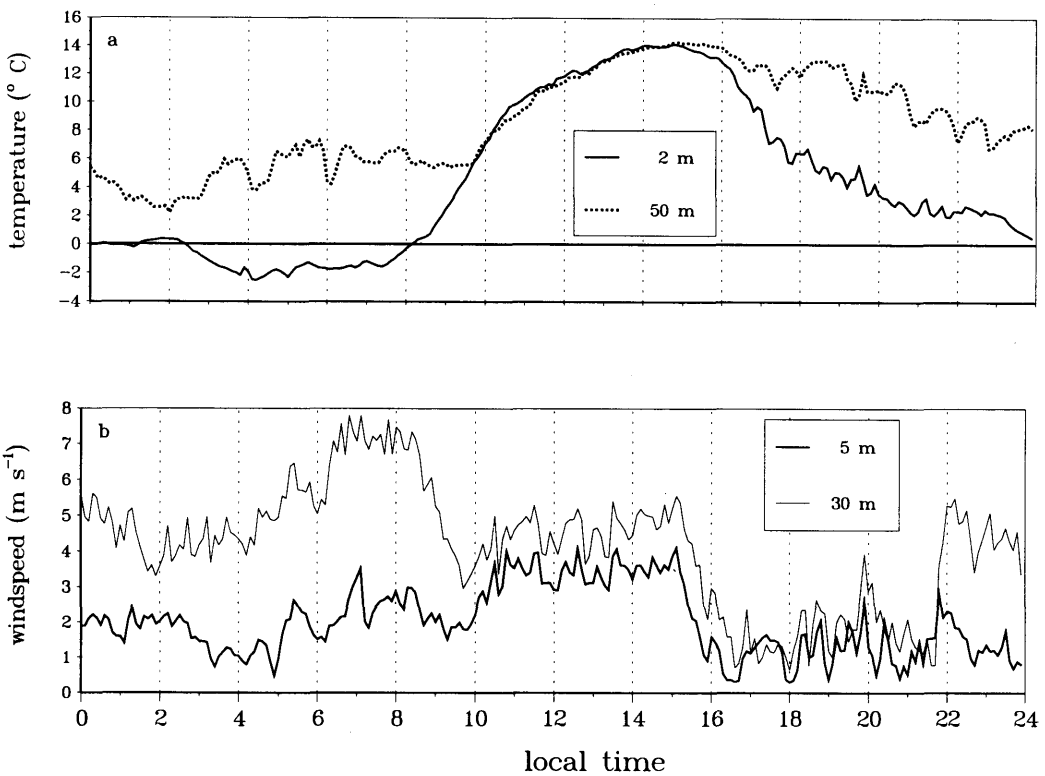

Fig. 4. Time evolution of the temperature and the windspeed for 15 November in two heights. Data used are 6-min mean values.

very low horizontal windspeeds around 1 m s^{-1} there was no significant change in wind direction. As the observation site was surrounded in the next 20–30 km only by grassland and harvested fields, effects due to horizontal advection from industrial plants or car traffic can be ruled out. During the stable stratification in the surface layer only extremely weak exchanges between the air at 5 and 50 m occurred. Consequently the increase in the NO concentration at the 5 m level strongly indicates the ground to be the dominant source.

After 10:00, the atmosphere became unstable with strong mixing of air close to the ground. Any NO produced by the soil was instantaneously oxidized within the first few meters above the ground by O_3 leading to increasing NO_2 concentrations (Fig. 3b) and strong fluxes of NO_2 and O_3 (Fig. 5c and 5d). Due to the reduced solar radiation also the O_3 concentrations decrease strongly in the afternoon.

The very stable period with very low windspeeds at all levels and a decoupling of the airmass at 5 m from that at 25 and 50 m began at 16:00. The NO produced by the soil was oxidized by the O_3 present. The concentration of O_3 at 5 m decreased, that of NO_2 increased (Fig. 3b and 3c). Only after the O_3 dropped below the detection limit the NO concentrations increased at 18:15 (Fig. 3a). Very high NO concentrations of about 6000 nmol m^{-3} were reached within one hour. The very stable turbulent regime led to only minor fluxes though strong gradients were built up. The fluxes of O_3 and NO_2 (Fig. 5d and 5c) were directed into opposite directions, as already described in Section 4.

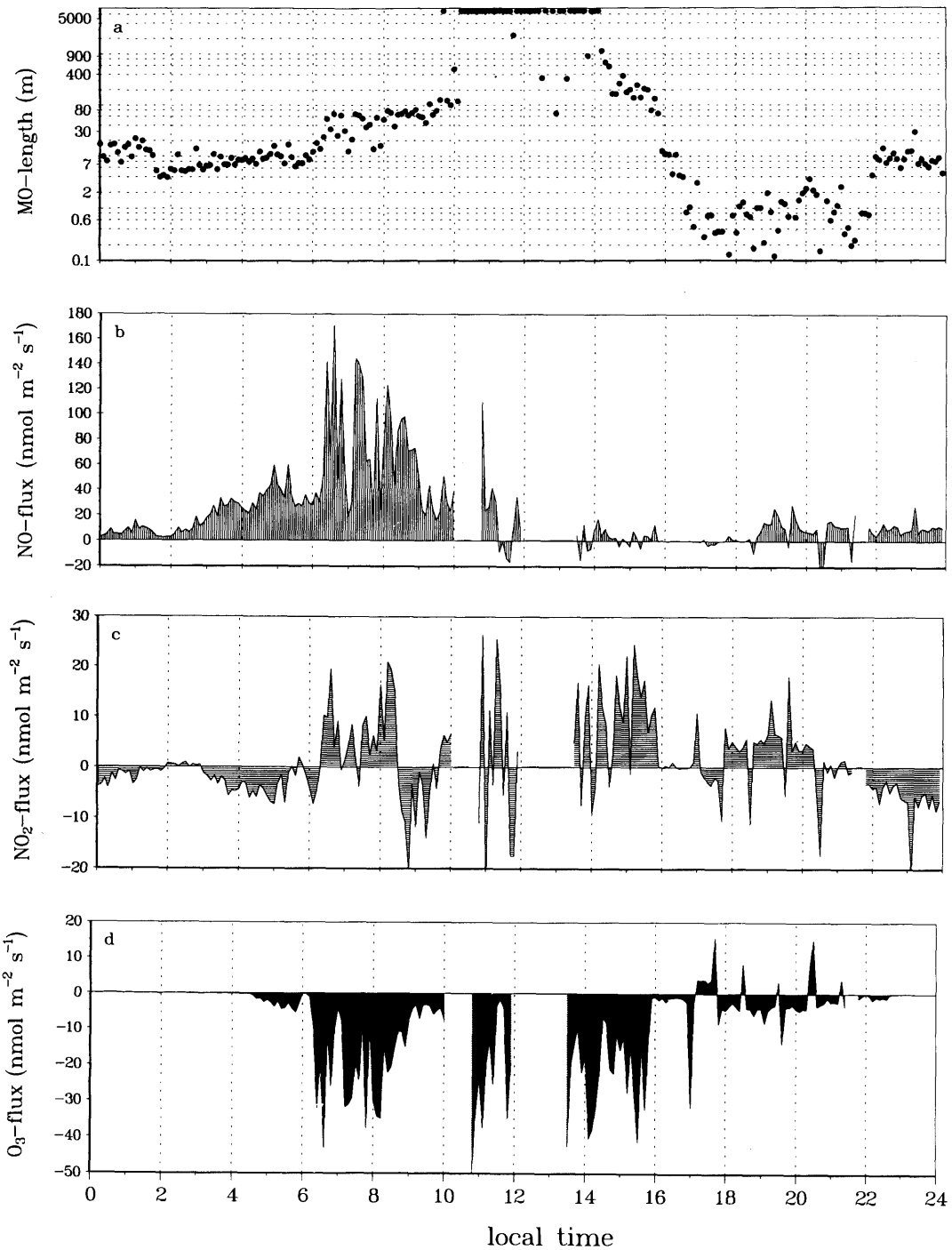

Fig. 5. Time evolution of the Monin-Obukhov-length for 15 November together with the fluxes of NO, NO_2 and O_3 between 5 and 50 m.

6. Parameters controlling the NO emissions

As was pointed out in the introduction, soil temperature, fertilization and the concentration of NO above ground have been identified as the most dominant factors controlling NO emissions. To show which of these possible factors plays the dominant part at our measuring site the dependence of the NO fluxes on soil temperatures was investigated and no trend to higher NO fluxes at higher temperatures was found.

In Fig. 6 the dependence of the NO fluxes on the NO concentrations in 5 m is shown. In contrast to the expectation of smaller positive fluxes with increasing concentrations there can not be seen a clear trend in the data. Some data even seem to point to an increase in fluxes with increasing concentrations whereas the highest fluxes of >50 nmol $m^{-2} s^{-1}$ were observed at relatively moderate concentrations of about 3500 nmol m^{-3}. This finding stands in clear contrast to the observations of compensation points by other authors (Johansson and Granat, 1984; Slemr and Seiler, 1991).

Our measuring site is situated in an agricultural area that is heavily fertilized with urea and other N-substances as described by Fuzzi et al. (1992). In this situation the soil's N-content seems to be so high and the reservoir for NO emissions seems to be so strong that the factors soil temperature and NO concentration in the air above ground are probably totally masked.

7. Conclusion

The gas measurements at a rural site showed very high NO concentrations near the ground of up to 9700 nmol m^{-3}. Such high values are usually only reached in urban regions where they are caused by automobile exhausts. At our measuring site they are caused most likely by soil emissions, as was shown by the estimation of fluxes for the nitrogen oxides as well as for ozone. As our observation site was surrounded in the adjacent 35 km only by villages without industry and the next busy trafficroads were more than 20 km away, we can rule out the advection of NO from anthropogenic sources. Furthermore no dependence of the magnitude of the NO concentration or gradient from the winddirection was observed. The mean NO flux of 6.5 nmol $m^{-2} s^{-1}$ for the entire period as it was estimated is in good agreement with results of comparable measuring sites. Williams et al. (1988) determined a mean of 5.9 nmol $m^{-2} s^{-1}$ for a fertilized cropland under temperate conditions. Slemr and Seiler (1991) in their investigation

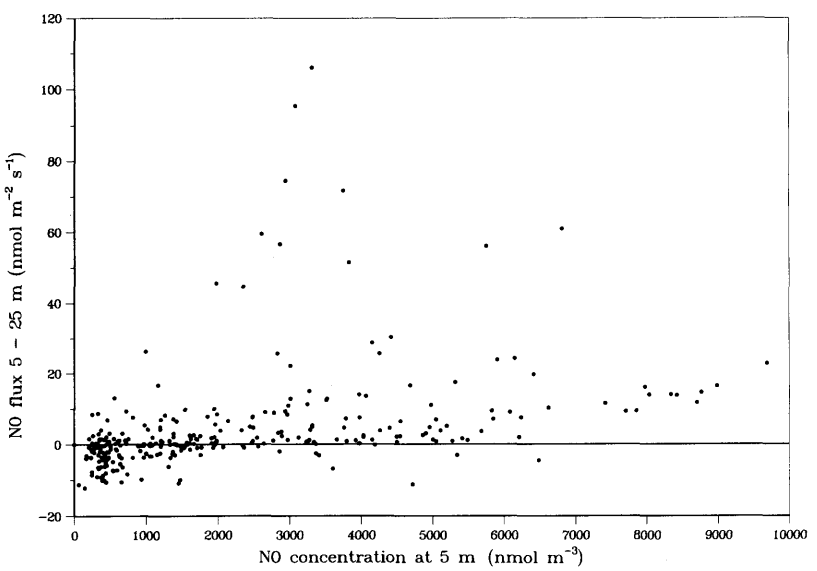

Fig. 6. Dependence of the NO flux on the NO concentration.

of soils fertilized with urea in Spain found fluxes of up to 130 nmol $m^{-2} s^{-1}$ and more, which compare well with the maxima of more than 100 nmol $m^{-2} s^{-1}$ at our site. Thus, heavily fertilized agricultural areas as the Po Valley seem to represent a source of nitrogen oxides that cannot be neglected in calculations of global N-cycles.

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