Direct Measurements of Nitrogen Oxides and Ozone Fluxes over Grassland

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Abstract. Using the eddy correlation method, fluxes of nitric oxide, nitrogen dioxide, ozone, water, and sensible heat were measured at a site 20 km north of Denver, Colorado over mature crested wheat grass, 0.75 m high in late June and early July. During this period the weather was fair with no synoptic disturbances. In the early morning a well-mixed diluted urban pollution plume traversed the site, by late morning aged pollution had mixed downward into the local boundary layer, and by afternoon the air came from a relatively unpolluted area of the high plains. The mean trace gas concentrations reflect this repeated pattern of local air flow. The fluxes of the trace gases were influenced both by the variation of the means and by other factors including temperature and biological activity. Ozone fluxes were found to be always negative and proportional to the mean, with an average deposition velocity for this case of about 0.006 m s^{-1}. For the oxides of nitrogen this simple treatment was not appropriate. Both deposition and emission were observed, generally deposition predominated in the morning and emission in the afternoon with observed variations in the fluxes of $NO_x = NO + NO_2$ from -0.3 to $+0.2$ ppbv m s^{-1}.

1. Introduction

The oxides of nitrogen ($NO_x = NO + NO_2$) are important constituents of the odd nitrogen complement of the atmosphere. They play a crucial role in atmospheric chemistry, being involved in the mechanism defining both atmospheric oxidant capacity and atmospheric acidity. Their atmospheric concentrations are quite variable due to their reactivity and their diverse source and removal terms.

Recent literature reviews of atmospheric measurements of nitrogen oxides (Hahn and Crutzen, 1982; Ehhalt and Drummond, 1982; Logan, 1983) have presented estimates of the strengths of the different sources and sinks. A major uncertainty is the contribution which the earth's surface flux makes to the atmospheric budget. Ehhalt and Drummond (1982), for example, estimate that between 5 and 17% of the overall NO_x atmospheric source could be due to soil emission. Hahn and Crutzen (1982) estimate between 0 and

50%, and Logan (1983) estimates that soil emission is of the order of 5–15%, while dry deposition to plants accounts for about 30% of the removal.

The biosphere interacts with the atmospheric nitrogen cycle in a complex fashion, and both emission and deposition of nitrogen oxides as well as other nitrogen species occur simultaneously. Nitrogen is a critical component of the biosphere and is intricately involved in all life forms. Nitrogen in living tissue is mainly in the amino (3–) form. Green plants are capable of expending photosynthetic energy to effect the reduction of oxidized nitrogen compounds to the amino form. In addition, many plants (such as the legumes) act as hosts by providing nutrients to microorganisms capable of fixing molecular nitrogen to be incorporated into the biosphere as amino nitrogen. Death and excretion make this reduced nitrogen available for nitrification.

Under anoxic conditions this nitrite and nitrate can be utilized by microorganisms as oxidants leading to denitrification; i.e., the reduction of nitrite and nitrate. During both nitrification and denitrification, loss of nitrogen from the system can occur. Molecular nitrogen (0), nitrous oxide (1+), nitric oxide (2+) and nitrogen dioxide (4+) production have all been reported (Wetselaar and Farquhar, 1980). Many different microorganisms are involved and the microbial metabolic processes differ in their reponse to different conditions. Therefore the emission of N_2, N_2O, NO, and NO_2 vary greatly. (For a review of nitrification and denitrification, see McElroy et al., 1977).

The mechanisms of nitrification and denitrification, and the involvement of N_2, N_2O, NO and NO_2 in these processes has been studied by, e.g., Myers et al. (1979). Soils have been studied in the laboratory to investigate the emissions of these gases under various conditions (e.g., Lipschultz et al., 1981, McKenney et al., 1982) but most field work has focused on the study of N_2O emission (e.g., Cicerone et al., 1978).

The surface depositional flux or dry deposition of nitrogen oxides has received considerable attention due to their role in acid deposition. In polluted areas the interaction of oxides of nitrogen with vegetation is potentially important in removing these species from the atmosphere. A survey of the literature by Voldner et al. (1985), which was carried out to provide better data for acid deposition models, concludes that little is known about the depositional flux of nitrogen oxides.

Most previous workers investigating the emission of oxides of nitrogen (Kim, 1973; Galbally and Roy, 1978, 1981; Johansson and Granat, 1984; Slemr and Seiler, 1984) have used enclosure techniques. Relatively small chambers (< 0.5 m^2, < 0.25 m^3) were placed on the surface and changes of concentration monitored. Both static and flow-through systems have been used and great care was taken to avoid unneccessary perturbation of the soil/microbe/plant/atmosphere system. The nitrogen balance of this system, however, is quite mutable and even a small disturbance such as restricting the water flux may have the effect of changing the emission flux. One indication of the ease with which the system is modified lies in the areal variability which has been reported in previous work. Johansson and Granat (1984) discuss this in their paper and quote factors of > 10 variation in emission from seemingly uniform surfaces. The other authors report similar results.

Under field conditions, the mineralization of soil organic nitrogen to yield available

ammonium and nitrate, the effect of precipitation and evaporation in changing soil moisture distribution, the wet and dry deposition of NO_x, HNO_3, NH_3 and of aerosol NH_4^+ and NO_3^- are all factors controlling nitrogen species emissions. Any interference with conditions can readily change the balance of the nitrogen reaction scheme and hence the production or uptake of nitrogen gases.

These considerations reinforce the desirability of employing direct flux measurement techniques, which allow the natural system to remain completely unperturbed and yield a measurement over a several hectare area.

2. Experimental

The method for measuring fluxes of NO, NO_2, O_3, H_2O and heat utilized in this study is the eddy correlation technique. A description of the theoretical and practical aspects of this technique is given elsewhere (for example, see Wesely and Hicks, 1977, and Wesely et al., 1978) and will only be briefly outlined here. Vertical air motion (w) and mixing ratio (s) are both measured with sufficient precision and time resolution to measure flux. The product of the departure of w and s from their mean values averaged over a time period long enough to give a statistically meaningful result defines the vertical flux $\overline{w's'}$. The measurement of w is obtained from a levelled sonic anemometer; the mean offset in the vertical velocity, presumably due to local flow distortion around the tower instruments and terrain variations, is removed before calculating the eddy flux. For measurement of surface fluxes, the required frequency response is several Hertz, and the required accuracy is a few percent of the range of variation measured within the time period used for the flux measurement which is typically about 20 min. The eddy correlation technique allowed the flux to be measured directly and with minimal perturbation of the study area.

The correlation technique defines the vertical flux through a horizontal plane at the location of the instruments. The flux originates over an area extending upwind of the instruments. With the instruments located several meters above the ground, as in this experiment, an area of several hectares contributed to the measured flux. With shifts of wind speed and direction, the particular area in this experiment changed but as the ground cover was quite uniform, these shifts did not affect the interpretation.

A considerable fetch upwind of the measurement location is required so that the surface layer is in equilibrium with the surface. The fetch must be sufficient to enable the turbulent structure of the surface layer to come into equilibrium with surface roughness elements and for the chemical source or sink characteristics of soil and vegetative cover to equilibrate with the surface layer air.

To avoid perturbation we restricted our measurements to periods when the wind did not pass through the tower and mast structures before it was sampled by the instruments. This unfortunately restricted our measurements to periods between 0700 and 1900 h.

The advection of an air mass with an enhanced concentration of a trace gas may cause an apparent transient flux. The air mass may cross the site first at a higher level and generates a down flux through the plane of the instruments at their height of several meters.

The effect, however, is essentially symmetrical with an up flux through the plane of the instruments following the passage of the air mass. This temporary phenomenon does not affect the definition of the absolute deposition or emission flux but merely contributes to the uncertainty. Other contributions to the uncertainty which do not change the absolute values include any instrumentation noise which is not correlated with vertical velocity. Thus, for example, although photomultiplier noise associated with the chemi-luminescence detectors limits the high frequency usefulness of the variance signals it does not affect the definition of fluxes although the coherence may be reduced and the measurement scatter increased. (For a discussion of this and related problems see Len-schow and Kristensen, 1985).

A research site was established at the Boulder Atmospheric Observatory, (BAO), 40 km north of Denver in the South Platte Basin and 25 km east of the foothills of the Front Range. The primary BAO facility is the 300 m tower instrumented for atmospheric research. The facility was utilized for both electric power and computer data management. (For a description of the facility, see Kaimal and Gaynor, 1983; maps and aerial views of the facility are given in Hooke, 1978). The BAO occupies approximately 45 ha. The site is on a slight rise and is well-drained. The soil, Weld loam, is a member of the Wiley-Colby-Weld complex and is an aeolian deposit of loam and silt loam (U.S.D.A., 1980). The reserve had been wheat land until the early 1970s, but since has been planted with crested wheat grass. The land surrounding the site is unirrigated and used mainly for the cultiva-tion of winter wheat with approximately equal areas in crop and fallow. A paved road runs along the south side of the reserve 800 m from the site and an unpaved, lightly travelled road is 500 m to the east. A major highway, I-25, is 2.5 km to the east. The area is rural but is within the influence of Denver pollution.

The diurnal surface wind pattern in the S. Platte River basin in the absence of strong synoptic effects (as was the case here) is quite repeatable (Johnson and Toth, 1985). At night, Denver pollution drains along the Platte Valley. Winds at the site, which is about 15 km west of the South Platte River are from the mountains to the west. During the morning, an upslope wind from the east typically develops because of solar heating of the sloping terrain. At ~0730 the upslope wind reaches the BAO and the Denver pollution, which had travelled down the Platte River Valley, is swept over the site. As the convective daytime boundary layer grows, overlying polluted air is mixed down the surface. Later in the day, however, this wind brings reasonably clean air from beyond the eastern edge of the valley. This upslope weakens in the late afternoon and is finally replaced by drainage flow. A radiation inversion caps the pollution near the surface in the stably stratified nocturnal boundary layer.

The field experiment extended from mid June 1983 to early July 1983. The first part of the period was used to establish the instrumentation and techniques. Although the spring of 1983 was wet, by the end of June the ground was dry and the last signifi-cant rainfall before the reported period (29 June to 7 July) occurred a week earlier. The crested wheat grass, which was approximately 0.75 m high, was green and just maturing at the time of the experiment.

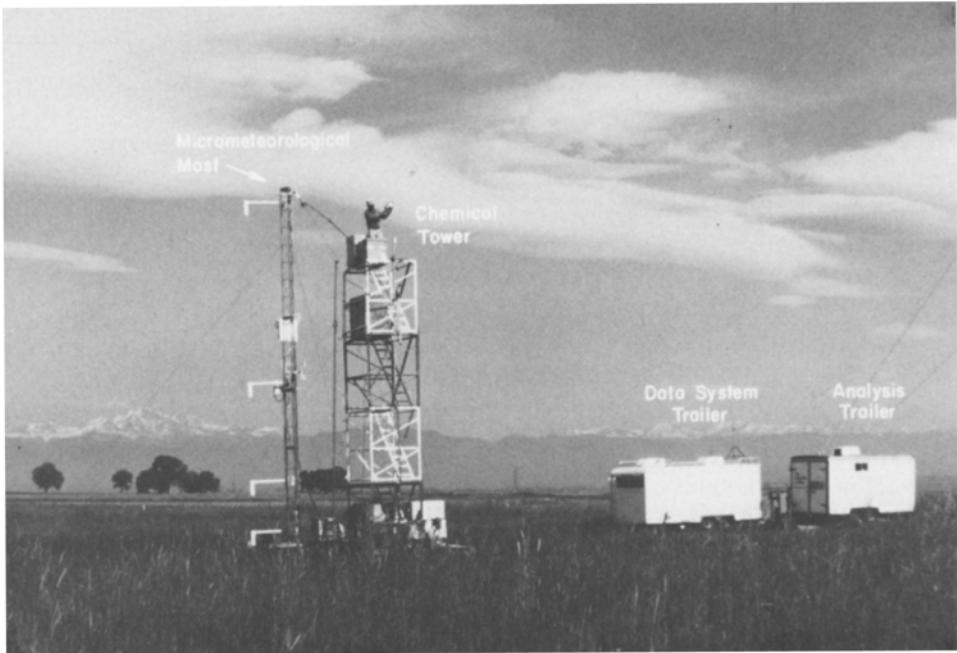The research towers and masts were erected in a north-south line to the east of the

Fig. 1. The research site viewed from the east indicating the configuration of the micrometeorological instruments and chemical sensors.

access track. The instruments were set out to function with wind directions between 45° to 180°. This orientation was chosen in order to investigate the daytime deposition/emission fluxes. Figure 1 shows the research installation viewed from the east indicating the configuration of the micrometeorological instruments and fast chemical sensors. Table I gives the characteristics of the instrumentation used.

A problem with the correlation technique for the determination of NO, NO_2, and O_3 fluxes is that the instrumentation is quite bulky and heavy. To prevent the instrument shelters and their support tower from perturbing the turbulence structure, the sonic anemometers, fast temperature sensors, and Lyman-α sensor head were mounted on a mast 3 m cross-wind from the tower. Teflon tubing (4 mm ID) was strung across the gap and the intakes positioned within 20 cm of the sonic anemometer sensor head. The flow control/pressure reducing elements of the O_3 and NO detectors were mounted at the outboard end of the intakes. This reduced the flow transit time delay to 0.3 s and 0.65 s for the O_3 and the NO detectors, respectively. The NO_2 detector operated at ambient pressure so that this procedure could not be used and a 2.5 s delay occurred. The time delays for the instruments were initially measured by bursting balloons filled with cigarette smoke in front of the sonic anemometer/chemical sensor intakes. These delay periods compared favourably with values calculated from the measured phase angles between the sensors (Lenschow *et al.*, 1982).

Two sets of sonic anemometers and fast temperature sensors were deployed on the

Table I.   Characteristics of the instrumentation used

Sonic Anemometer, EG & G Model 198-2 single axis modified by Applied Technologies 20 cm,
  sonic path pulsed at 200 Hz, resolution ± 0.007 m s^{-1} sampled at 10 Hz. (E.G. and G.,
  1973, Applied Technologies, 1983).
Platinum Thermometer, Air Model FT-1A, platinum resistance wire helical bobbin, resolution
  ± 1%, sampled at 10 Hz (AIR, 1982).
Lyman-α Hygrometer, NCAR/NSF Lyman-α hygrometer model LA-3, 2 cm absorption path,
  resolution ± 5%, sampled at 10 Hz (Buck and Post, 1976).
Nitrogen Dioxide Detector, chemiluminescence detector based upon the reaction of ambient
  NO_2 with luminol in liquid solution, with ozone removal prefilter, flow rate = 500 cm^3
  min^{-1}, delay time = 2.5 sec, response time (1/e) = 0.8 sec, resolution = detection limit
  (2σ at S/N = 1 for 1 sec) = 30 ppt, sampled at 10 Hz (Wendel *et al.*, 1983).
Nitric Oxide Detector, chemiluminescence detector based upon the reaction of ambient NO
  with O_3 in the gas phase, flowrate 2 l(STP) min^{-1}, delay time 0.6 sec, response time (1/e) =
  0.3 sec, resolution = detection limit (2σ at S/N = 1 for 1 sec) = 20 ppt, similar instrument
  to that described in Dickerson *et al.*, 1984.
Ozone Detector, chemiluminescence detector based upon the reaction of ambient O_3 with
  NO in the gas phase, flowrate delay time = 0.3 sec, response time (1/e) = 0.04 sec resolu-
  tion = detection limit (2σ at S/N = 1 for 1 sec) = 10 ppt, sampled at 10 Hz (Pearson and
  Stedman, 1980).
Computer Data System, BAO operating system (Kaimal and Gaynor, 1983).

mast; at 8 m and at 4 m height. The Lyman-α sensor was at 8 m and the results reported
here we obtained at this level.

The minimum height at which the sonic anemometer can resolve the bandwidth of
vertical velocity fluctuations that contributes to the vertical flux due to the path length
over which the vertical velocity is measured was estimated by Kristensen and Fitzjarrald
(1984) partly on the basis of the results of this study. They found that the 4 m minimum
height used here was overly conservative for a sonic anemometer averaging length of 20
cm, and that the height could be reduced to as low as 2 m and still resolve the high-
frequency contributions to the flux.

Data from the fast instruments were recorded at 10 s^{-1} on the BAO computer data
system and were later corrected for time delays and calibrated. Twenty minute spectra
and cospectra were calculated for w and NO, w and NO_2, w and O_3, w and H_2O and w
and T. Mean temperature, and wind speed and direction were also recorded.

The fast NO and NO_2 sensors were calibrated at least once daily with dynamic dilution
of standard gases and the fast O_3 sensor was cross checked with a Dasibi ultraviolet ab-
sorption device.

The pressure-reducing process in the O_3 and NO sensors leads to an approximately
constant density in the reaction chamber, which means that the variable being measured
is mixing ratio with respect to moist air. The NO_2 sensor, on the other hand, measures
at atmospheric pressure, but its calibration depends upon the mass diffusivity of the NO_2
to the luminol solution. The mass flux to the luminol solution is approximately equal to
the kinematic diffusivity times the mixture density, which is a slowly varying function of
temperature, times the mixing ratio gradient. Laboratory tests have confirmed that the
NO_2 flux measurement is almost independent of pressure at the ambient atmospheric

pressure. Thus, all three sensors measure very nearly the mixing ratio with respect to moist air. Using the formulation of Webb *et al.* (1980), the fluxes need to be corrected for the density effects due to water vapor transport, but not heat transport. This correction amounts to less than about 10^{-4} m s^{-1} in terms of an emission velocity [i.e., (concentration flux)/(concentration gradient)] and thus is neglected.

3. Results

Figures 2a, b, c, d, and e are examples of the cospectra of w with NO_2, O_3, NO, H_2O, and T. The integrals of the plots are the net fluxes for the 20 minute period.

The cospectra for w and NO, and w and NO_2 have considerably more scatter than those for w and O_3, q and T, which is reflected in their smaller coherence. Part but not all of this reduced coherence is due to instrument noise. Instrument noise would predominantly affect the higher frequency part of the cospectra. We consider that surface flux is not the sole source of variance for NO and NO_2. Chemical reactions and horizontal variation in mean concentration may generate variance which could contribute to reducing the coherence of w and NO, and w and NO_2.
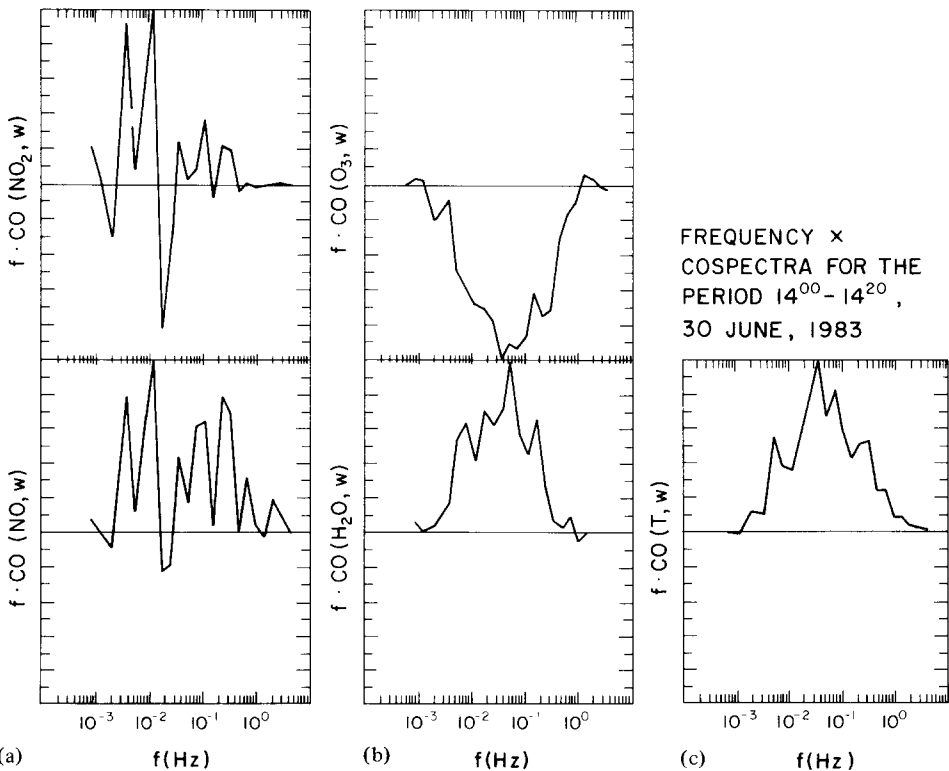

FREQUENCY ×
COSPECTRA FOR THE
PERIOD 14^{00}– 14^{20} ,
30 JUNE, 1983

Fig. 2. Cospectra of w and (a) NO_2, (b) O_3, (c) NO, (d) H_2O and (e) heat for the period 1983 June 30, 1400–1420, normalized for the maxima.
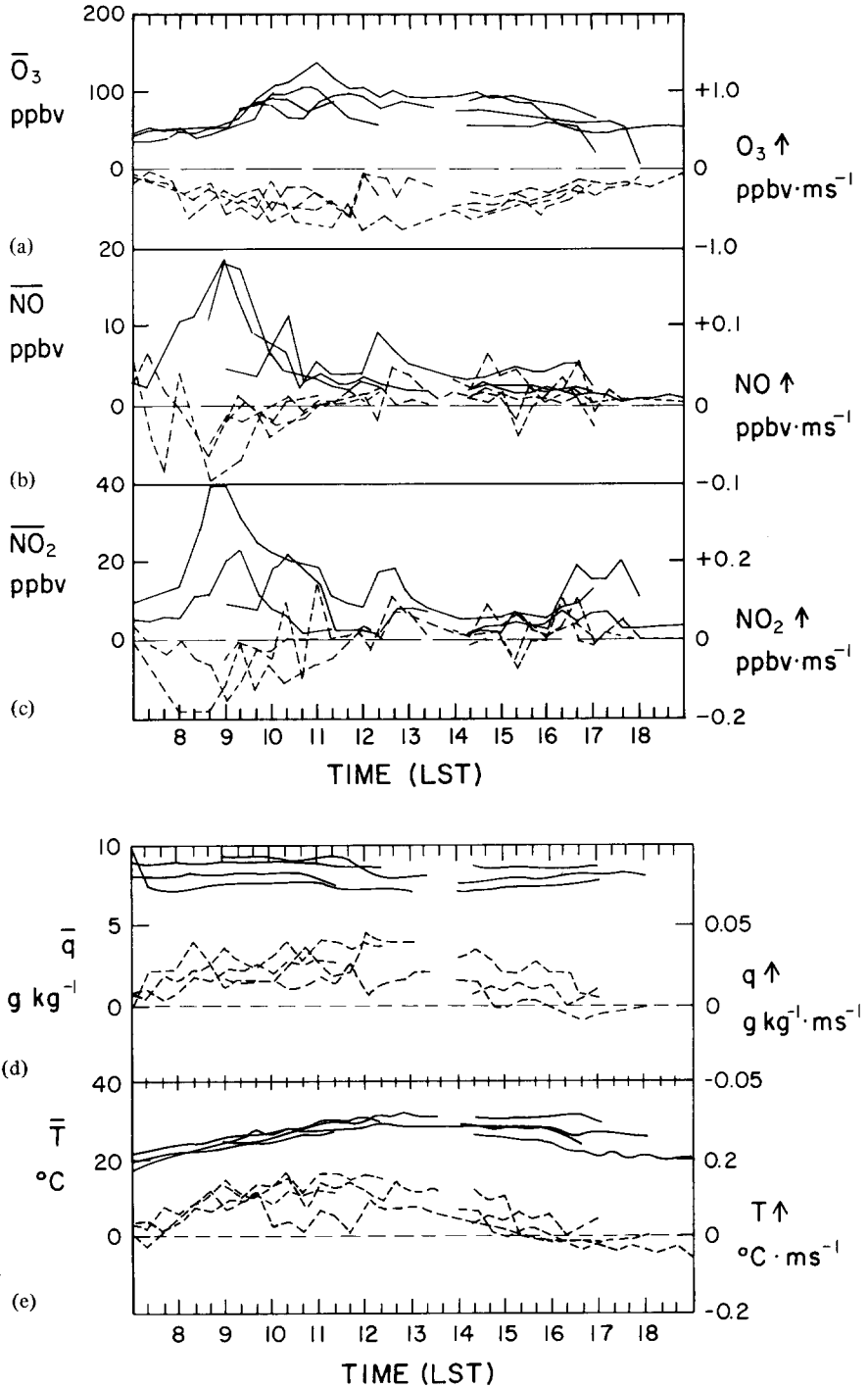
Fig. 3. Plots of 20 minute means (solid lines) and turbulent fluxes (broken lines) of (a) O_3, (b) NO, (c) NO_2, (d) H_2O and (e) heat for the daytime periods of 1983, June 29 and 30; July 1, 6 and 7.

Figures 3a, b, c, d, and e show plots of 20 minute means and fluxes for O_3, NO, NO_2, H_2O and heat at the 8 m level for the five daytime periods 29 and 30 June, 1, 6, and 7 July 1983. During these periods, all instruments were operating and wind direction was within the acceptable arc.

4. Discussion

The variations of the means reflect the manner in which the diurnal surface wind pattern in the South Platte Basin, coupled with the daily growth of the boundary layer, transports pollution from the Denver area to the research site. Ozone increases in the morning as photochemical production commences and as the deepening boundary layer taps the previous day's pollution. It decreases in the evening as the ozone is removed by dry deposition and chemical reaction. The nitrogen oxides show a major peak in the morning as the Denver pollution, which had drained northward along the South Platte Valley, is swept across the site by the daytime upslope wind. Lesser peaks occur at the noon and evening traffic peaks.

The O_3 flux variation represents a fairly simple response to the variation of the atmospheric mixing ratio. Figure 4 is a plot of flux divided by mean mixing ratio for 30 June 83. During the day, when turbulent mixing is well established, the deposition flux is proportional to the mean mixing ratio with a proportionality constant for this particular case of approximately -0.6 cm s^{-1}. This example indicates the usefulness of the deposition velocity concept when only a deposition flux is involved. Figure 5a is a different presentation of the same data where the time locus of the mean and flux is plotted. The locus moves down and to the right through the morning, remains there until afternoon and then returns.
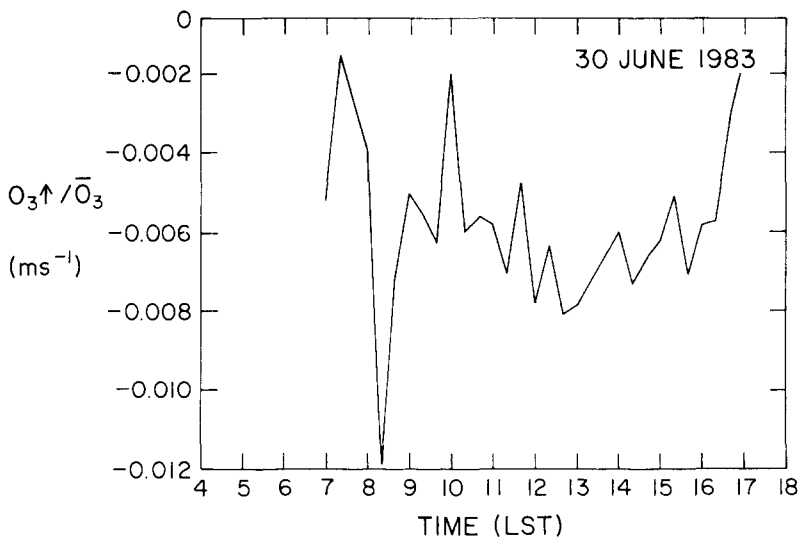

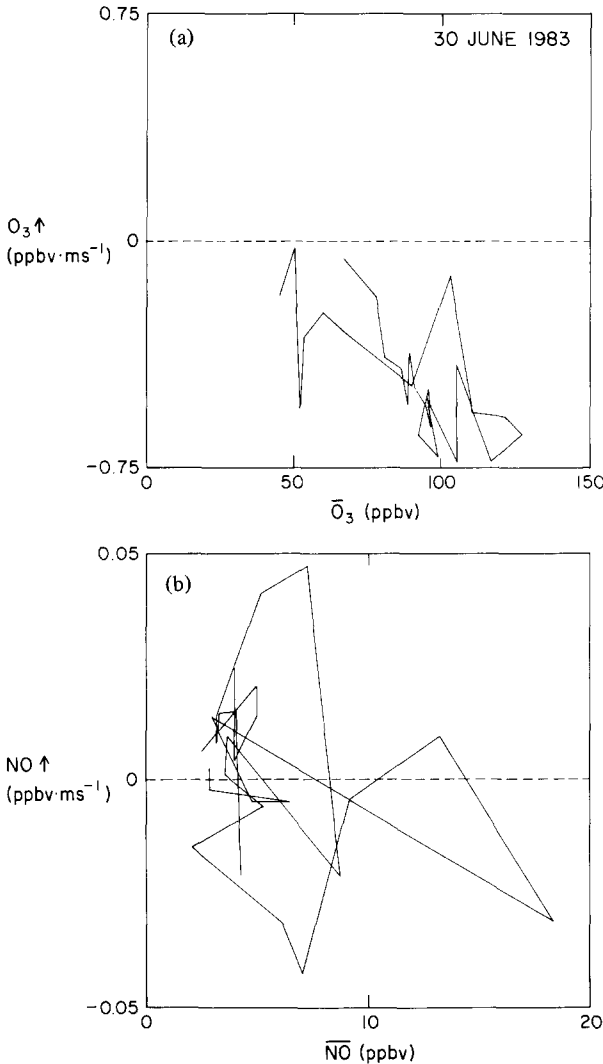Fig. 4. The ozone flux/ozone mean ratio plot for 1985, June 30.

Fig. 5. The time locus of the flux versus the mean for 1985, June 30 of (a) O_3 and (b) NO.

Figure 5b is the time locus of the NO mean and flux for the same day. In contrast to O_3 the situation for NO is more complex. — First, because of chemical reactivity, the measured NO flux at 8 m is actually proportional to the NO_x flux which is conserved (Lenschow and Delany, 1986). We assume here, however, that the measured NO flux at 8 m is proportional to the surface NO flux. Second, simple relationship between means and fluxes does not apply. The flux of NO is bidirectional; an emission flux competes with a deposition flux. Thus, a turbulent deposition flux of NO like that of O_3 is proportional to the atmospheric concentration whilst the emission flux is dependent upon the production of NO within the soil and its transport to the atmosphere.

The bidirectionality of NO flux has been described previously when chamber or enclosure techniques were used (Galbally and Roy, 1978, 1981; Johansson and Granat,

1984). These investigators found that the NO concentration in their enclosures approached a constant value which Galbally termed a compensation level. Lower initial concentrations increased to this value and, if the initial concentration were enhanced, it decreased to the same value. The adjustment in enclosure concentration was quite rapid with an exponential form

$$\frac{c}{c_0} = 1 - e^{-kt}$$

where k lay between 0.3×10^{-3} and 1.5×10^{-3} s^{-1} (an exponential response of between 11 and 50 min). These compensation levels were not uniform but varied for different soil/plant systems from 3 to 150 ppbv (Galbally, personal communication in Johansson and Granat, 1984). Johansson and Granat (1984) observed that such a situation could result from either of two mechanisms. If source and sink corresponded to identical regions in the soil as in a classic sorption system, then the increase of atmospheric [NO] would lead to an increase in the soil gas [NO] until the free energy of the soil gas was equal to that of the source. The flux would then tend to zero as the free energy difference disappeared. A second explanation is that emission and deposition occur independently, with distinct source and sink regions. Increased atmospheric NO would increase the deposition until it equalled the emission. The net flux would then be zero. The enclosure technique for defining flux cannot distinguish between the two possibilities as flux is inferred from the change of the mean. The correlation technique allows one to assess the relevance of the concepts of deposition velocity and compensation level since fluxes and concentrations are determined separately. Examination of Figure 5b, which is the locus of the NO mean mixing ratio versus NO flux, indicates the difference in the two interpretations. If a compensation level mechanism controlled the balance of deposition and emission, the locus would take on the appearance of a slanted line cutting the mixing ratio mean axis at the compensation level. The locus does not behave in this fashion.

A comparison of the NO mean mixing ratio (Figure 6a) and the NO flux (Figure 6c) is also instructive. Figure 6b indicates the form which the flux trace could be expected to exhibit if a simple compensation level and deposition velocity were applied to the mean trace shown in Figure 6a. A best fit for the expression

$$(\overline{NO} - CL)V_d = NO\uparrow$$

was obtained with the compensation level $CL = 10.8$ ppb and the deposition velocity $V_d = -0.0035$ $m\ s^{-1}$. There is some similarity between the derived flux and the directly measured flux shown in Figure 6c, but significant differences are also apparent.

The rapid adsorption/desorption response to changing NO concentration is probably a function of NO uptake and release on leaf surfaces or in leaf tissue fluids. The more important overall control of emission, however, is not by the plant tissue but is by microbial activity in the soil. Microbes metabolize nitrogen compounds and generate nitric oxide. Subsequent transport delivers the NO to the atmosphere.

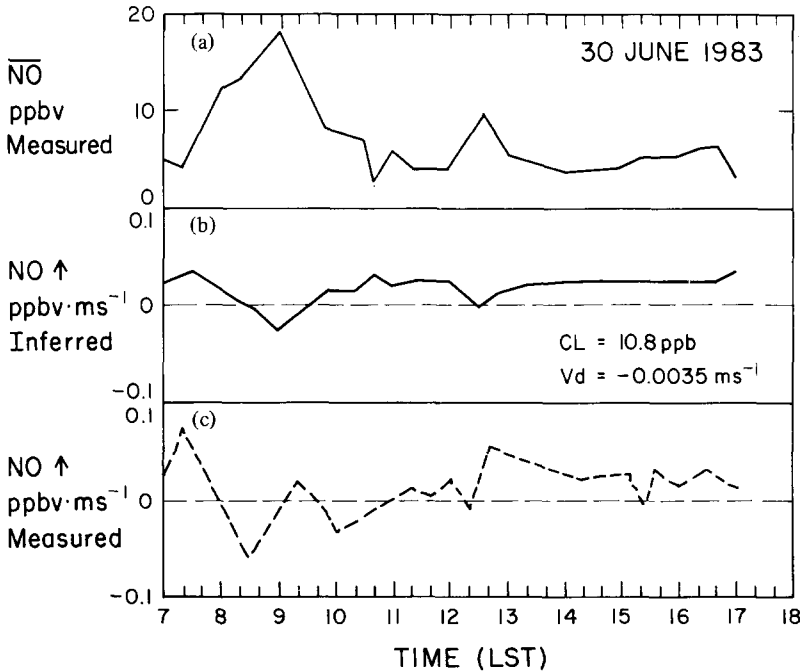Figure 7 illustrates values of NO fluxes reported in the literature and compares them with the results of this work.

Fig. 6. (a) The NO mean for 1983, June 30, (b) the calculated NO flux using a compensation level of 10.8 ppb and a deposition velocity of −0.0035 m s⁻¹ and (c) the measured NO flux.

The mechanism controlling the net flux of oxides of nitrogen at the site can be postulated as follows: Oxides of nitrogen in the atmosphere are deposited on the wheat grass and are taken into the leaves via the stomata. They dissolve in the plant fluids and are in short-term equilibrium with the atmosphere, capable of desorption. On a longer time scale, the excess is hydrolyzed and incorporated as nitrate in the plant system which can be transported throughout the plant. In the soil, microbial activity generates NO together with N_2 and N_2O as byproducts of nitrification and/or denitrification utilizing local excesses of nitrogen compounds. The production rate is dependent upon soil temperature, the supply of fixed nitrogen, the redox potential, soil moisture and other conditions. Transport from the generation zone to the atmosphere is either via diffusion through the soil or via the plant roots and vascular system in association with the transpiration of water. For the case reported here, the atmospheric release of oxides of nitrogen seems to commence about noon and decrease later in the afternoon. The evidence presented here indicates that the soil production of NO is temperature dependent, and starts only when the diurnal temperature wave has reached the appropriate depth. Transport to the atmosphere is associated with transpiration, as it ceased in the evening as the water vapor flux vanished.

Figure 8 illustrates this proposed hypothesis. The mean for the oxides of nitrogen varies throughout the day and generates via turbulent transport a deposition flux. The sum of this deposition flux and the emission flux yields the observed net flux.

Nitric oxide transport via the plant vascular system suggests a transport mechanism
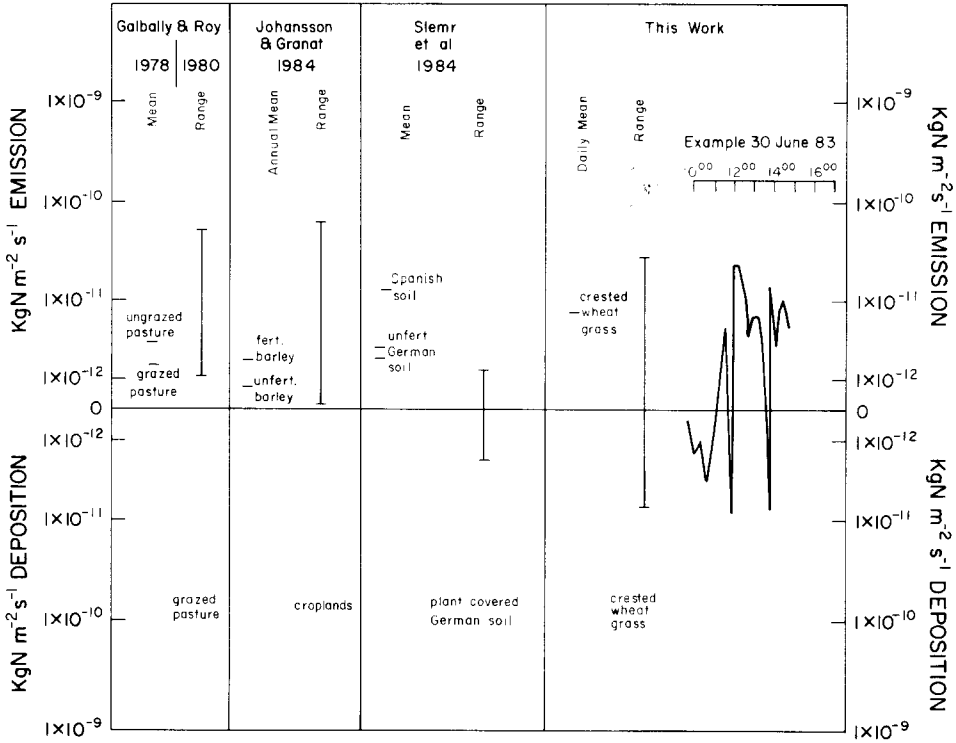
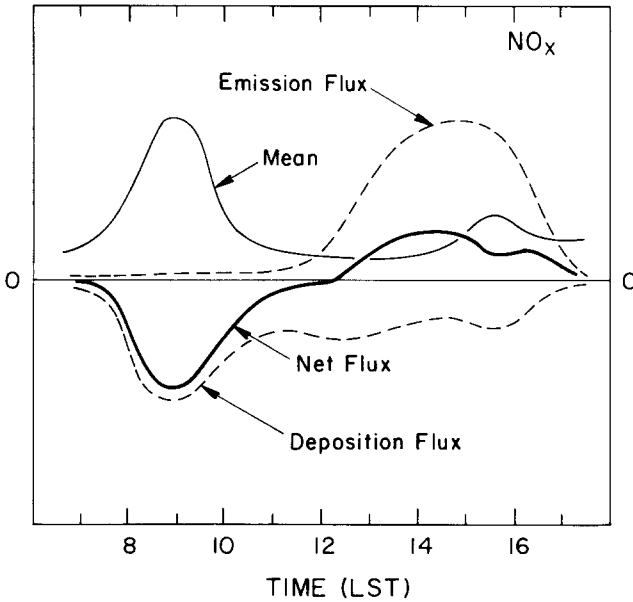Fig. 7. Ranges and mean values of NO flux reported in the literature.

Fig. 8. A postulated relationship between deposition, emission and resultant flux of oxides of nitrogen throughout the daytime period.

complementary to the one presented by Johansson and Granat (1984) and by Slemr and Seiler (1984). They found that the emission flux was greater from bare soil than from vegetation covered soil and that the nitric oxide was produced in the top few centimeters of the soil and diffused out into the atmosphere.

The chamber method may inhibit the transpiration water flux and consequently, transport via the vascular system. On the other hand, given the difference in the experimental sites and the variability of nitrogen emissions, even from apparently homogeneous areas, it is possible that both mechanisms may be important under different conditions. Clearly, more areas must be studied.

The specific question of the emission of nitrogen dioxide has not been very well defined in the literature. Makarov (1969) reported emission of nitrogen dioxide but did not report measurements of nitric oxide. This could have been due to the analytical scheme used. Kim (1973) likewise reported emission of NO_2 but again the analysis method used was not efficient for NO. Another issue that needs further study is the relative contribution of NO and NO_2 emission to the total NO_x flux. The chemical reaction time for the $NO-NO_2-O_3$ triad is shorter than the time required for the species to diffuse from the surface to the observation height. As a result, neglecting other chemical reactions, the ratio of the NO flux to the NO_2 flux at observation height should be approximately equal to the ratio of their concentrations at that height. Only the total NO_x flux is conserved and we cannot distinguish between the relative contributions of NO and NO_2 fluxes at the surface. (This aspect of the measurement of the surface fluxes of the oxides of nitrogen will be discussed further and more rigorously in Lenschow and Delany, 1986).

Galbally and Roy (1978) indicate that NO_2 emission is $< 3\%$ that of NO whereas Rosswall (1982) put the value as high as 50%. Johansson and Granat (1984), using a flow chamber and specifically removing atmospheric ozone which can generate an apparent flux of NO_2, found that the flux of NO_2 $(= NO_x - NO)$ was less than 10% of the NO flux.

In a study of the surface flux of nitrogen oxides (NO_x) Wesely et al. (1982) found the net flux over soybeans to be depositional. The concentration ratio, $[NO]/[NO_2]$ was ~ 0.1 and the authors conjectured that the flux of oxides of nitrogen $(NO_2 + NO = NO_x)$ under these conditions was dominated by the rapid uptake of NO_2 by vegetation.

Emission of nitrogen dioxide from the soil/microbe/plant systems can result either from biological activity or from chemodenitrification as a result of acidification of nitrites (Smith and Chalk, 1980). Slemr and Seiler (1984) in their enclosure experiments found that whereas the NO emission was correlated with soil temperature, the NO_2 flux was correlated with radiation intensity. This they interpret to indicate that whilst NO was produced by biological functions the NO_2 could result from abiological processes.

There is also the possibility that ozone deposited on vegetation surfaces either acts directly or via ozonolysis products to oxidize nitric oxide before it is emitted. Approximately ten times as much ozone is deposited as nitric oxide is emitted and so the process need not be very efficient to influence the nitrogen dioxide and nitric oxide emission fluxes.

5. Conclusions

The flux of ozone to the vegetation surface is determined by the atmospheric concentration and for a particular case it is possible to utilize the deposition velocity to relate the atmospheric mean to the deposition flux. This velocity is, of course, different for different vegetation and surface conditions; for the case discussed here, we found it to be 0.006 m s^{-1}.

For the oxides of nitrogen (NO and NO$_2$) such a simple relationship does not apply. Emission as well as deposition occurs and the net flux is the sum of the two components. The deposition flux is determined by the atmospheric concentration and thus is analogous to ozone deposition. However, the emission flux is driven by an entire complex of physical, chemical, and biological factors.

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