AN EDDY-CORRELATION MEASUREMENT OF NO$_2$ FLUX TO VEGETATION AND COMPARISON TO O$_3$ FLUX*

M. L. WESELY and J. A. EASTVIES
Radiological and Environmental Research Division, Argonne National Laboratory, Argonne, IL 60439, U.S.A.

and

D. H. STEDMAN and E. D. YALVAC
Department of Atmospheric and Oceanic Science, University of Michigan, Ann Arbor, MI 48109, U.S.A.

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Abstract—Eddy-correlation measurements with a newly developed fast-response NO$_2$ sensor indicate that the deposition velocity at a height of about 6 m above a soybean field has a maximum value near 0.6 cm$^{-1}$ for NO$_2$ and is usually about 2/3 of that found for ozone. In these studies, over 90% of the NO$_2$ is NO, and the corresponding minimum surface resistance for NO$_2$ calculated as the quantity remaining after atmospheric resistances are subtracted is about 1.3 cm$^{-1}$, which is larger than expected on the basis of leaf stomatal resistance alone. Emission of NO from sites in the plant canopy and soil where NO$_2$ is deposited and reduced to NO or release of NO$_2$ as a result of biological activity may have lessened the downward fluxes of NO$_2$ as measured. During windy conditions at night, surface resistances are found to have values of about 1.8 s cm$^{-1}$ for NO$_2$ (again, greater than 90% NO) and 1.8 s cm$^{-1}$ for O$_3$, corresponding to deposition velocities of 0.05 cm s$^{-1}$ and 0.3 cm s$^{-1}$, respectively.

INTRODUCTION

Contaminants in the lower atmosphere are significantly affected by processes of removal and emission at the surface of the earth. Nitrogen oxides (NO$_x$ = NO + NO$_2$) are of interest because they can cause injurious biological effects and they strongly influence the photochemical production of other potentially-harmful substances, especially oxidants such as ozone. To estimate oxidant budgets for the lower atmosphere, the amount of nitrogen oxides present should be known (e.g. National Research Council, 1977). Also, knowledge of factors that control the amount of NO$_x$ in the atmosphere is important in studies of "acid rain", a subject receiving increasing attention at present.

Processes that control the exchange of trace gases between the atmosphere and the surface of the earth are highly varied, but a limiting factor can often be identified as the ability of the surface to "capture" the trace materials. This ability can thus determine the rate of cleansing of the lower atmosphere, and is highly dependent on the chemical and physical properties of the gases and surfaces considered. Important chemical properties of gases include solubility in water and the oxidizing or reducing potential, while the corresponding surface properties such as moisture content and the presence of easily reduced or oxidized compounds should be considered also.

Gases very soluble in water are usually taken up by vegetation at rates dependent on the sizes of leaf stomatal apertures on a plant canopy with a given number and distribution of stomata, while less-soluble gases are usually taken up more slowly (e.g. Hill, 1971). Highly-reactive gases, such as HF are usually removed quite efficiently by the outer leaf surfaces as well as through stomata (Benedict et al., 1965; Jacobson et al., 1966). However, there are many exceptions to such generalizations. The removal of ozone by vegetation, which is very weakly soluble in pure water and highly reactive with many surfaces, is rapid and controlled mainly by stomatal variations (Rich et al., 1970; Bennett et al., 1973; Wesely et al., 1978; Leuning et al., 1979). Apparently, ozone reacts strongly with compounds in the leaf (Thomson et al., 1966; Heath, 1975). For carbon dioxide, it is well known that removal by vegetation is somewhat controlled by the size of stomatal apertures, but is also lessened considerably by mesophyllic resistances dependent on processes of metabolism and photosynthesis.

The nature of NO and NO$_2$ deposition to vegetation in the field has not been determined yet. The major global source of NO$_2$ is natural biological action, but locally high levels are usually associated with man-made sources. Due to photochemistry, NO$_2$ usually predominates during the daytime. Both NO and NO$_2$ can affect plants, but NO$_2$ has more lasting, less reversible effects (Bennett and Hill, 1975). Chamber work by Bennett and Hill has shown that NO is taken up very slowly by alfalfa, while NO$_2$ is taken up rapidly. The uptake of NO$_2$ by wet surfaces should be

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approximately as large as that for highly-soluble gases such as SO₂, because NO₂ dissolves and reacts quickly in water to form nitrous and nitric acid. Another interesting feature found in the chamber work is that NO seems to be emitted from alfalfa exposed to NO₂, possibly because of conversion of NO₂ to NO in the chamber, perhaps by the vegetation (Hill, 1971).

This work is a continuation of efforts to measure and parameterize the dry-deposition rates of various atmospheric contaminants in natural conditions. The nature of the vertical flux of NO₂, mostly NO₂ during this experiment, above a common agricultural field, soybeans (Glycine max. L. Merr.), is investigated. Comparisons with simultaneous measurements of ozone flux are made. The eddy-correlation techniques used and the theoretical approach applied are largely explained elsewhere (Wesely et al., 1977; Wesely et al., 1978), and are only briefly outlined here. The main limitation to the study of NO₂ flux by eddy correlation in the field is the lack of a suitably sensitive and fast-responding sensor for the gas. The sensor used in this study is the first designed specially for eddy correlation measurements.

EXPERIMENTAL PROCEDURES

Eddy-correlation measurements of the vertical fluxes of momentum, heat, water vapor, ozone, and NO₂ (NO + NO₂) were taken during August, 1979, near Manheim, in Lancaster County, Pennsylvania, U.S.A. Sampling points were about 5.1 m above the aerodynamic displacement height of a soybean canopy, which was about 0.9 m tall. The soybeans were near a maximum in vigor and amount of ground cover.

The site had been carefully chosen to provide a large uniform surface upwind of the sampling point, in order that measurements be taken in an atmospheric surface layer in “equilibrium” with the surface. Fetch-to-height ratios were greater than 100 during collection of the data reported here. Thus, the vertical fluxes at the sampling height of 5.1 m should have been practically the same as those that would have been found much closer to the surface in representative portions of the field.

Data were collected with a minicomputer and digital-tape system at a rate of 20 s⁻¹, and were analyzed in real time as well as later in a more thorough analysis of the tapes. Some of the sensors had notably large response and delay times, near 1 s, so that some corrections were applied to account for the poorly-detected high frequencies that are associated with the vertical fluxes. See Wesely et al. (1978) for a brief explanation of the corrections, along with descriptions of the wind, temperature, and ozone sensors. One of the two ozone sensors employed chemiluminescent reaction with NO (Eastman and Stedman, 1977) and one employed chemiluminescent reaction with C₂H₄ (Wesely et al., 1981). A commercially-available Lyman-alpha hygrometer was used to measure humidity fluctuations.

The instrument used to measure the concentration of NO₂ employed the chemiluminescent reaction of NO and O₂ (Stedman et al., 1972, and references therein). Upstream of the instrument and near the sampling point, a converter (containing molybdenum metal turnings at about 400°C and manufactured by Columbia Scientific*) was used to reduce NO₂ in the sampled air to NO. The NO detection system was specially designed to provide sensitivity and detection limits much lower than commercial NO detectors. The system delay time in the field was 0.6 s and the response time 0.15 s. Efficient mixing of sample air and ozone was accomplished in a reaction chamber designed by M. McFarland of the NOAA Aeronomy Laboratory, Boulder, CO (McFarland et al., 1979). The intensity of light from chemiluminescence was measured by a red-sensitive photomultiplier tube (EMI 9658A*) maintained at −50°C, and operated in the pulse counting mode. The detector background signal, or “zero” level, was obtained by altering the flow route so that the O₂ and sample air were mixed in a pre-reactor vessel, so that chemiluminescence was completed before the sample air entered the reaction chamber and thus was out of view of the photomultiplier tube.

The sample air flow was limited by a glass capillary intake. At the typical sample flow rate of 40 s⁻¹, the pressure in the inlet plumbing was close to that in the reaction chamber itself, less than 1333 Pa (1 atm). The low pressure in the inlet minimized losses of NO₂ to the tubing walls. The conversion efficiency was found to be stable and greater than 97%, at concentration of 1–30 ppb. This measurement of efficiency used a NO₂/O₂ titration technique which is independent of flow rates and of absolute concentrations of source gases (Stedman, 1976). Knowledge of the conversion efficiency allowed “absolute” standards of both NO and NO₂ to be used in calibration.

An important aspect of this detector is that, while the chemiluminescence intrinsically measures NO, use of the converter in the intake system causes the sum (NO₂) of NO and other materials which can be coverted to NO to be detected. If vegetation or other surface materials were oxidized by NO₂ and some of the NO₂ thus reduced to NO re-emitted, then a lessened net NO₂ flux would be measured. In fact, the re-emitted NO would react rapidly with normal ambient ozone to produce NO₂, the lifetime of NO emitted into air with 50 ppb of ozone is about 50 s. Thus, some of the conversion would take place below the eddy-correlation sampling point, causing the apparent ozone flux at that height to increase slightly and the NO₂ (as well as NO₃) flux to decrease. Of course, other sources of NO at the surface, such as bacterial production in the soil, would also lessen the measured downward flux of NO₂.

It is possible that the O₂ and NO₂ sensors could interfere with each other because the NO₂ sensor produces large excesses of O₂ and the O₂ sensor produces excess NO₂. However, the outlets for these unwanted gas products are easily placed downwind of the sampling points, thus avoiding the problem.

RESULTS AND DISCUSSION

Fluxes and concentrations

Figure 1 summarizes the measurements, which encompass nearly 24 h of data collection. A full diurnal cycle of measurements is desirable in order to study the entire range of resistances associated with soybean leaf stomata which, as is well known, close at night and open in the daytime. For the night considered, the winds were sufficiently strong to allow successful use of the eddy-correlation apparatus; very light winds at night often result in greatly damped turbulence confined to relatively high frequencies, which prevents effective use of the rather slow-response instruments for eddy-correlation. Also, with light winds and strong surface cooling at night, the formulations currently available to describe flux-gradient relationships in the

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* This does not connote approval or recommendation of the product by sponsors of this work, Argonne National Laboratory, or the University of Michigan, to the exclusion of other products which may be suitable.
An eddy-correlation measurement of \( \text{NO}_2 \) flux to vegetation and comparison to \( \text{O}_3 \) flux

The energy balance terms shown in the lower portion of Fig. 1 depict a rather common situation for well-watered soybeans under mostly cloudless skies. The large variations evident between 1200 and 1600 h Eastern Standard Time (EST) are due to scattered clouds. The latent heat flux \( L, E \) is large and the sensible heat flux seems suppressed during the daytime, which is suggestive of heat advection. In the authors' experience, such a case of mild heat advection is not unusual for soybeans with a good supply of soil moisture; it is not known whether this was large-scale advection or local advection from the nearby fields.

The two ozone sensors provide nearly identical values of the vertical flux, which quite closely parallel the trends in \( L, E \). The flux of \( \text{NO}_2 \) at times has similar trends, but is occasionally directed upward, a confusing factor. While the possibility that the surface was a source of \( \text{NO}_2 \) at times cannot be totally discarded, it is likely that the "noise" inherent in this preliminary version of the \( \text{NO}_2 \) sensor caused some spurious readings that were particularly strong at these times. Indeed, most of the variability in the \( \text{NO}_2 \) fluxes from 1/2 h to 1/2 h does not seem to be correlated with any of the other factors considered, and thus could be due to the noisiness of the sensor. For frequencies greater than 1 Hz, a large amount of noise was noted in the output signal of the \( \text{NO}_2 \) sensor. This noise was random in the sense that it was not correlated with vertical wind speed, and thus should not have systematically altered the \( \text{NO}_2 \) fluxes.

Surface resistances

To eliminate some of the seemingly random variations of \( \text{NO}_2 \) flux and thus obtain a clearer picture of the processes that control the flux, data are averaged over at least two 1/2 h intervals. Then a residual surface resistance \( r_c \) is calculated following the procedures of Wesely and Hicks (1977):

\[
r_c = c_0 - r_a - r_s.
\]

where the deposition velocity \( c_0 \) is the negative of the ratio of the measured flux (positive when directed upward) to the concentration at the height of measurement, the aerodynamic resistance \( r_a \) from the sample point to near the surface is estimated on the basis of some of the micrometeorological flux measurements and inferred surface physical
properties, and the boundary-layer resistance $r_c$ of the quasi-laminar air sublayer enveloping surface elements is calculated based on momentum flux and surface roughness. According to Equation (1), $r_c$ is the resistance that remains after all aerodynamic resistances above the surface elements are removed and thus represents the bulk resistance of the plant canopy and soil to uptake, as seen from above. Notably, $r_c$ results from a highly stylized formulation and is difficult to relate precisely to the properties of any one surface element such as leaf, stem, or particular area of soil surface. Similar resistances are calculated for water vapor and ozone, which should mainly represent the bulk canopy stomatal resistance, with perhaps some lessening due to evaporation from the soil or ozone destruction at the soil and outer plant surfaces.

For the night-time data between 1915 and 0315 h, the average surface resistances for $H_2O$, $O_3$, and $NO_2$ are $3.0 \pm 0.74 \text{scm}^{-1}$ for 13 1.2 h samples, $1.8 \pm 0.4 \text{scm}^{-1}$ for 13 samples, and $15 \pm 2 \text{scm}^{-1}$ for 11 samples, respectively. These are logarithmic averages, which are appropriate because of nearly log-normal distributions, as are typically found in resistance data. Also, the two cases of $NO_2$ flux being directed upward are not used; the value $15 \text{scm}^{-1}$ thus represents a lower limit. These averages indicate that, while evaporation from the soil was significant and ozone destruction at the soil and possibly the outer plant surfaces was rather large, the net flux of $NO_2$ was severely limited. Hence, it appears that penetration of well-mixed air into the plant canopy and down to the soil surface was substantial, and that ozone is much more easily removed than $NO_2$ from the air by soil and plants with stomata closed. Of course, there remains the possibility that $NO$ emitted from the soil as a result of microbial activity or of reduction of $NO_2$ to $NO$ at the surface could have substantially decreased the net flux of $NO_2$.

Figure 2 shows that values of surface resistances during the daytime of 16 August. There was an inadvertent release of nitrogen oxides in the vicinity of the $NO_2$ sensor at about 0845 h, possibly causing the appearance of an upward-directed flux of $NO_2$ near 0900 h (see Fig. 1). These cases of upward fluxes are not used in the analysis producing Fig. 2. Further, the raw $NO_2$ data are averaged over more than 1 1/2 h in order to smooth the variations of values of $r_c$ calculated. The overall trends of the three resistances plotted in Fig. 2 are similar and conform to the type of variation expected for bulk canopy stomatal resistance. That is, leaf stomata open fairly quickly in the morning and gradually close during late afternoon. Because of the rather strong winds and probably continued evaporation throughout the previous night, dewfall was probably not substantial on the leaves in the morning. Thus, the resistance for $H_2O$ during the morning and the other times shown in Fig. 2 should be representative of bulk canopy stomatal resistance, but probably lessened a little due to the effects of evaporation from the rather-wet soil surface. During late afternoon, the resistance to ozone removal seems to increase too rapidly, as the average value of $r_c = 1.8 \text{scm}^{-1}$ found for the previous night is exceeded.

An adequate explanation has not been found. Similar trends are seen on other days during transition to the very stable conditions that are rather common at night. During such stable conditions, aerodynamic resistances are very large, so that deposition velocities are extremely small regardless of the value of $r_c$. Thus, it is of little consequence that $r_c$ during night-time strongly-stable conditions is somewhat larger than suggested during night-time well-mixed conditions.

If the only mechanism controlling the surface resistance to $H_2O$ and $O_3$ flux were stomatal resistance, the differences in the rates of molecular diffusion in air through leaf stomatal openings should account for the differences in $H_2O$ and $O_3$ resistances. That is, the ratio of diffusivities (1.64) multiplied by $r_c$ for $H_2O$ should equal $r_c$ for $O_3$. However, $r_c$ for $O_3$ is substantially greater, which indicates that evaporation from the soil might be quite large, removal of $O_3$ at the soil surface might be weak, or that $O_3$ might be destroyed with considerably less than 100% efficiency at surfaces exposed in substomatal cavities. This situation is in contrast to that found recently for maize in drier soil, where ozone removal was considerably greater than expected on the basis of $H_2O$ resistance (Wesely et al., 1978).

Surface resistance to $NO_2$ removal is clearly much larger than would be expected if uptake through leaf stomata were limited only by molecular diffusion ($NO_2$ has about the same diffusivity in air as $O_3$). This could imply that mesophyllic resistance to $NO_2$ uptake is substantial, at least $0.5 \text{scm}^{-1}$, if the difference in Fig. 2 between the $r_c$'s for $O_3$ and $NO_2$ is taken as a guide.

Chamber work by Hill (1971), however, suggests that $NO_2$ uptake by vegetation is rapid, is limited mainly by stomatal resistance rather than mesophyllic resistance, and might be accompanied by substantial NO emission. It is possible that the situation in the
present study is similar. Research on different types of surfaces suggest that re-emission of a large portion of deposited NO₂ as NO might be fairly common (Judeikis and Wren, 1978). Also, soil bacteria release NO, perhaps at a greater rate during the daytime than at night because of warmer temperatures more favorable to microbial activity during the daytime. Let us assume, for example, that NO is released in substantial quantities from the vegetation and soil and is all rapidly converted to NO₂ in the atmosphere very close to the surface. Further, let us assume that the actual value of \( r_c \) for NO₂ is 0.7 cm⁻¹ near noon rather than the value of about 1.3 cm⁻¹ measured. This lower value should be a typical minimum value of bulk canopy stomatal resistance for gases with a diffusivity equal to that of NO₂ (Wesely and Hicks, 1977). It can then be calculated that roughly 50% of the NO₂ initially removed from the surface would seem to reappear in the atmosphere due to surface emissions. Even if very little of the NO emitted were converted to NO₂ by the time a height of several meters is reached, this mechanism of emission is still quite feasible since the sensor measured total NOₓ accomplished by conversion of any NO₂ to NO within the system. Conversion of NO to NO₂ at greater heights would still keep the concentration of NO as small as was observed.

**Deposition velocities**

Deposition velocity, found as the ratio of the downward component of flux to the concentration at a specified height, incorporates the effects of both aerodynamic and surface properties, and thus is often more difficult to describe in general terms than a variable such as \( r_c \) that is meant to reflect only surface properties. Nevertheless, numerical models often use estimates of deposition velocity was an expedient to determine total removal at the surface from the atmosphere. For this reason, a brief summary of deposition velocities found in this experiment is appropriate. The nighttime average values found at a height of 5.2 m above the soybean field during 15 and 16 August are 0.29 cm s⁻¹ for ozone and 0.05 cm s⁻¹ for NO₂ (which again neglects the two cases of NO₃ flux directed upward). During the daytime, the deposition velocity has a maximum value of about 0.56 cm s⁻¹ for NO₂ and about 0.84 cm s⁻¹ for O₃. These and other estimates for the deposition velocity during daytime are easily calculated from the values of \( r_c \) shown in Fig. 2, with the additional information that the bulk gas-phase aerodynamic resistance above the leaves totals about 0.5 s cm⁻¹ between 0800 and 1600 h on 16 August. That is, deposition velocity is given approximately as \( \frac{1}{(r_c + 0.5)^{-1}} \).

A crude means of parameterizing deposition over large areas by use of \( r_c \) has been suggested recently by Sheih et al. (1979), for application in numerical models. It is assumed that aerodynamic resistances will be calculated independently in order to derive deposition velocities. Table 1 summarizes the present results in a form similar to that suggested by Sheih et al. Since these results are from only one day of measurements, further confirmation of the values in Table 1 is highly desirable. Of course, many types of surfaces need to be considered in order to consider large areas.

**Conclusions**

The removal of NO₂ from the atmosphere by a full-canopied soybean field is limited by a bulk surface resistance that is quite large at night, near 15 s cm⁻¹, and during daytime is 1.5-2.0 times as large as that for ozone. Ozone destruction at the field surface is rather large, corresponding to a calculated residual resistance of about 1.8 cm⁻¹ at night, which probably indicates a substantial uptake by the soil surface, and during daytime is near that expected if ozone were nearly perfectly removed at inner leaf surfaces. The corresponding deposition velocities are about 0.05 cm s⁻¹ for NO₂ and 0.3 cm s⁻¹ for O₃ at a height of 5-6 m during windy conditions at night, and vary to maximum values of slightly less than 0.6 cm s⁻¹ for NO₂ and slightly more than 0.8 cm s⁻¹ for O₃ during daytime. Actually, NO₂ was measured rather than NOₓ, but the NO portion was small enough, less than 10%, to be ignored in the present experiment.

The rather small deposition velocity for NO₂ during the daytime suggests that there might be a substantial mesophyllic resistance to NO₂ uptake amounting to at least 0.5 s cm⁻¹. This is somewhat unexpected since NO₂ dissociates rapidly in water and presumably also in the watery solution surrounding leaf cells. Apparently, the ability to be taken up by water can be secondary in importance to reactivity with inner leaf surfaces. Chamber work by Hill (1971) suggests that NO₂ is taken up quite effectively by alfalfa and is

<table>
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<th>Measurement period (h)</th>
<th>Stability category</th>
<th>Stability</th>
<th>( L ) (m)</th>
<th>( \bar{u} ) (m s⁻¹)</th>
<th>( r_c ) for O₃ (s cm⁻¹)</th>
<th>( r_c ) for NO₂ (s cm⁻¹)</th>
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<tr>
<td>0730-1600</td>
<td>A, B, C</td>
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<td>61 ± 9</td>
<td>3.7 ± 0.1</td>
<td>0.84 ± 0.04</td>
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<td>2.2 ± 0.1</td>
<td>2.4 ± 0.5</td>
<td>2.8 ± 1.6</td>
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<tr>
<td>1900-0330</td>
<td>E</td>
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<td>15 ± 5</td>
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<td>1.8 ± 0.4</td>
<td>15 ± 2</td>
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largely controlled by stomatal resistance, but that the uptake of NO₃ seems to be accompanied by a release of NO. It is possible that this mechanism lowered the apparent net uptake of NO₃ (measured as NO₂ in the present experiment). If so, then as much as 50% of the NO₂ initially removed from the atmosphere during the daytime could have been released as NO by the soybeans. More generally, any source of NO₂, whether from biological activity or from reduction of NOₓ to NO and subsequent entry into the atmosphere, could have caused the rather low values measured.

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