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Pine forest: a negligible sink for atmospheric NO_x in rural Sweden

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ABSTRACT

A chamber technique was used to study the uptake of NO and NO_2 by branches of Scots Pine trees at concentrations ranging from about 1 ppbv (ambient levels) up to about 50 ppbv. The measurements were performed under field conditions of light intensity and temperature. Rates of photosynthesis and transpiration were determined from continuous measurements of CO_2 and water vapour.

The uptake of NO was small at all concentrations. The deposition rate per projected needle area was less than 0.1 mm s^{-1}. For NO_2, the uptake varied linearly with concentration. At high levels, the uptake was limited both by a stomatal and an internal resistance and a marked diurnal variation was observed. Typical deposition rates per projected needle area at concentrations larger than 10 ppbv were 1–2 mm s^{-1} during the day and 0.05–0.2 mm s^{-1} during the night. The internal resistance constituted between 3% and 60% of the total resistance to NO_2 uptake.

Contrary to observations made at high concentrations, no uptake of NO_2 could be detected when the concentration was decreased to 1 to 3 ppbv. Using a leaf area index of 3 m^2 m^{-2}, which is a typical value for a pine forest in Sweden, a deposition velocity per ground area of <1 mm s^{-1} is obtained. This is significantly lower than other values reported in the literature. Since the NO_2 concentration in the atmosphere of large rural areas covered with coniferous forest is of the same order of magnitude as that where no uptake of NO_2 was observed, this finding is of great importance for modelling of atmospheric chemistry and transport in the boundary layer. A comparison with the uptake of SO_2 and O_3 shows that daytime deposition velocities for these gases are a factor 10 larger than those for NO_2.

1. Introduction

Since the pioneering work by Hill (1971) concerning vegetation as a sink for pollutants, several investigators have repeatedly confirmed the absorption of NO_x by plants as well as non-vegetated surfaces (van Aalst, 1982; Voldner et al., 1986). Experiments using nitrogen-15 dioxide have demonstrated that gaseous NO_2 may serve as a source of nitrogen for plants (Rogers et al., 1979a). Rogers et al. (1979a) found that most of the $^{15}NO_2$ absorbed was incorporated into reduced nitrogen compounds. Their data suggest that the absorbed NO_2 formed nitrite, which is rapidly assimilated via nitrite reductase. Srivastava et al. (1975) demonstrated that the effect of NO_2 on the nitrate content and the nitrite reductase activity is strongly influenced by nutrient nitrogen level.

These and other results have led authors to suggest that incorporation of NO_x from the atmosphere may be either of benefit for the plants, when other forms of oxidized nitrogen are in short supply, or reduce growth of plants during conditions with high levels of NO_2 (Capron and Mansfield, 1977).

There are large gaps in our knowledge of the pathways for uptake of NO_2 as well as on the

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magnitude of the deposition velocity. Several studies have been using chamber techniques, where a part of a plant is placed in a ventilated chamber during controlled environmental conditions. Most of these studies have been performed at concentrations which are much higher than what has been found in the unpolluted atmosphere. Thus, Rogers et al. (1977) measured the uptake of NO_2 by Zea mays and soybean plants at concentrations ranging from 100 to 550 ppbv NO_2. The surface resistance for NO_2 was found to be strongly correlated with the stomatal resistance. A quantitative comparison using data reported by Rogers et al. (1979b) indicates that the stomatal resistance to diffusion of NO_2 is too large to explain the observed uptake (Farquhar et al., 1983). Similar results was obtained by Fuhrer and Erismann (1980). This indicates that in addition to the uptake of NO_2 through stomata, there is a flux to the surface of the leaves.

Bengtsson et al. (1982) studied the uptake of NO and NO_2 to pine needles in exposure systems where transpiration and photosynthesis were measured simultaneously. The uptake of NO_2 was studied at concentrations between 13 and 414 ppbv and was found to be determined by the stomatal conductance giving a deposition rate per total needle area of between 0.6 and 1.7 mm s^{-1} for the daytime and between 0.3 and 0.8 mm s^{-1} for nighttime. The uptake of NO was found to be about 10% of that for NO_2. No uptake of NO or NO_2 on the external surfaces of the needles could be observed and generally no internal resistance to NO_2 could be detected.

Another approach to study the exchange of gases is to use a micrometeorological technique. This has the advantage that the measurements are of minimal disturbance to the living plants. Wesley et al. (1982) studied the flux of NO_2 over a soybean-field using an eddy correlation technique. At the concentrations prevailing at the site of their measurements (between 8 and 50 ppbv) the deposition velocities (per ground area) varied from very small values during nighttime (0.5 mm s^{-1}) up to a maximum value of 5.6 mm s^{-1} during daytime. The deposition velocity for NO_2 was found to be smaller than what would be expected if the stomatal resistance was the only mechanism controlling the uptake at the surface. It was about 2/3 of that for O_3. The authors suggested that this was due to emission of NO from the soil and/or to an internal (mesophyllic) resistance to uptake of NO_2. The deposition velocity was probably even smaller than reported since the detection might have included some HNO_3, which is absorbed on vegetation much faster than NO_2 (Huebert, 1983).

Delany and Davies (1983) measured the dry deposition of NO_x and O_3 over a cut grass field using a gradient method. The deposition velocities were similar to the values found by Wesley et al. (1982) and ranged between 1 and 6 mm s^{-1}. The NO_x concentrations were between 8 to 24 ppbv and their data confirm the finding by Wesley et al. (1982) that the deposition velocities for NO_x are lower than those for O_3 and that there is a significant internal resistance for NO_2.

From the results cited above it seems as if the pathway for the deposition of NO_2 changes as the concentration decrease. At high concentrations the deposition velocity exceeds the stomatal conductance and an uptake to the external surfaces of the leaves is observed. In the micrometeorological studies, which have been performed at ambient concentrations, the deposition seems to be limited both by a resistance to diffusion through stomata and an internal (mesophyllic) resistance. However, it is by no means clear how to interpret the results from the latter measurements. Firstly, since the eddy correlation and gradient technique only gives the net fluxes the magnitude of the contribution of a possible NO emission from the soil is unknown. Secondly, a complete analysis of the results obtained from micrometeorological measurements should include an analysis of the photochemistry of the NO_x-O_3 system, which occur on a time scale comparable to that of the deposition/emission processes at the surface (Duyzer et al., 1983). The results by Duyzer et al. (1983) suggest that, on some occasions, chemical reactions rather than deposition may be determining the gradients of the individual gases (NO, NO_2).

The present study was undertaken to investigate the uptake of NO_x by Scots pine trees at several different concentrations, including ambient levels. For these measurements a flow-through chamber system for branches *in vitro* was used. With this technique it is possible to study the uptake/emission at the surface independent of turbulent transport and chemical interactions of gases in the atmosphere.

2. Experimental

2.1. *Experimental design*

The basic experimental system has been described earlier (Johansson et al. 1983a). Part of a branch (1.5 10^{-2} to 2.5 10^{-2} m^2 projected needle area) was enclosed in a chamber which was ventilated with a continuous airflow of about 5 l min^{-1}. Branches at some different heights of pine trees were studied. The rates of photosynthesis, transpiration and NO_x (= NO + NO_2) exchange were determined from simultaneous measurements of CO_2, water vapour and NO_x. Ozone was removed from the air entering the system in order to avoid chemical reactions between NO_x and O_3 in the chamber. Much attention has been paid to keep the microclimate inside the chamber as close as possible to the conditions of the natural environment. Thus, both the temperature and the concentration of CO_2 inside the chamber could be actively controlled.

Different concentrations of NO and NO_2 in the chamber were achieved by addition from permeation tubes placed in a constant temperature water bath or gas mixtures in cylinders containing ppm levels of NO or NO_2 in N_2. The concentration was varied from about 1 ppbv up to 60 ppbv. Generally the gas exchange by each branch was studied for a one week period. Frequent measurements with an empty chamber showed no uptake of NO or NO_2 on the inside walls. Since O_3 was removed from the air entering the chamber there was no oxidation of NO to NO_2. Some NO_2 was photolysed to NO but since there was no uptake of NO by the shoots could the difference in the concentration of NO_x between inlet and outlet of the chamber be attributed solely to an exchange of NO_2.

2.2. *Site description*

The measurements were performed at two different sites. The site at Jädraås is situated 240 km N of Stockholm far from large sources of pollutants. It is a 20 to 25 year old stand of Scots pine (Pinus sylvestris L.) at the Swedish Coniferous Forest Project site, Ivantjärnsheden. The site has been extensively analysed from many aspects, biotic as well as abiotic. Detailed characteristics regarding vegetation cover, nutrient status of the soil and climatic data are given in Axelsson and Bråkenhielm (1980). Sörentorp, which is located only 10 km north of Stockholm may experience quite high levels of NO_x, especially during the morning and in the afternoon due to the proximity of the city of Stockholm. It is a rather open parklike forest dominated by Scots pine mixed with Norway spruce, silver birch and aspen. The stand is approximately 75 to 80 years old.

2.3. *Equipment*

The chambers were made from transparent 0.025 mm FEP-Teflon film, which transmits 95% of the visible and infrared light (E. I. Du Pont De Nemours and Co.). The volume was 5 to 10 litres and propellers were mounted inside to mix the air and keep the turbulent transfer of gases constant. The temperature in the ambient air and inside the chamber was continuously monitored using semiconductors (AD 590). To keep the air temperature inside the chamber as close as possible to that of the environment, peltier cooled aluminium bodies coated with a thin layer of Teflon were used as heat sinks and were mounted inside the chamber.

Photosynthetically active radiation (400 to 700 nm) was continuously registered with a quantum sensor (Li-190 SB, Li-Cor inc., USA). The projected area of the needles was determined using a Leaf area meter (Lambda Li 3000, Lambda Instrument Company, USA). This area is used in the calculations of the conductances and fluxes.

NO was detected using a NO/O_3 chemiluminescence analyser (TECO 14D), modified to increase the sensitivity (Delany et al., 1982). NO_2 was first converted to NO by passing the air through a tube packed with ferrous sulphate. The conversion efficiency was measured by titration of NO with O_3 and was found to be larger than 95%. This technique has been used earlier in monitoring of the concentrations of NO_2 in air (e.g., Dickerson, 1984). Calibration was made by diluting gas mixtures with 1 ppm NO in N_2 (Alfax, Malmö, Sweden). The detection limit is about 0.2 ppbv. The only interference reported are from PAN, of which 10% is converted to NO and from HNO_2 which has been found to be converted to NO with a 100% efficiency (Dickerson, 1984). If at all present in the ambient air at the sites, HNO_2 is expected to be trapped in the inlet system before reaching the analyser.

Tests showed no significant interference effects on the NO_x-instrument from even drastic changes in the water vapour and CO_2 concentration. Some olefins are potentially interfering compounds due to their rapid reaction with ozone. However, tests have shown no significant interfering effects from propylene (Drummond et al., 1985), ethylene (McKenney et al., 1982) or acethylene (Johansson and Galbally, 1984). CO_2 was measured using an IR gas analyser (Unor 2, H. Maihak, Germany). Tubes packed with calcium chloride were used to dry the air before the CO_2 analyser. Dew point mirrors (EG&G, International Inc. USA) were used to measure the concentration of water vapour.

2.4. *Calculations*

The flux to the branch was obtained from:

$$J = Q(C_o - C_e)/A, \qquad (1)$$

where Q is the air flow rate through the chamber, $(C_o - C_e)$ is the difference in concentration between the inlet and outlet of the chamber and A is the *projected* needle area of the branch.

In analogy with the definition of the deposition velocity as the ratio of the measured flux to the concentration at some reference height a deposition rate per projected needle area was calculated as:

$$v_n = J/C_e \qquad (2)$$

(For a well-mixed chamber the concentration at the outlet of the chamber, C_e, is equal to that inside.) The transpiration rate was obtained as:

$$\mathrm{TR} = Q(x_o - x_e)/A, \qquad (3)$$

where $(x_o - x_e)$ is the difference in the concentration of water vapour between the inlet and outlet of the chamber. The stomatal conductance to transpiration, $k_{s,w}$, is defined in:

$$\mathrm{TR} = (x_s - x_e)/(1/k_{s,w} + r_a), \qquad (4)$$

where x_s is the concentration of water vapour inside the stomatal cavities (i.e., air saturated at needle temperature) and r_a is the aerodynamic resistance to transfer of water vapour (see below). The saturated concentration of water vapour was obtained by assuming that the needle temperature was equal to the temperature of the air in the chamber.

The actual uptake of NO_2 was compared with a potential uptake that would occur if the only limiting factor was the stomatal resistance, i.e., if the concentration of NO_2 inside the stomata was zero and the uptake on the external surfaces of the needles (cuticula) could be neglected. The potential uptake of NO_2 was calculated from the relation:

$$J_p = k_s(C_e - 0), \qquad (5)$$

where k_s is a stomatal conductance for NO_2, which was obtained from:

$$k_s = k_{s,w}(D/D_w), \qquad (6)$$

where D_w and D are the diffusivities of water vapour and NO_2 in air, respectively. The quotient between the diffusion coefficients was assumed to be equal to the square root of the ratio of the molecular weight of water to that of NO_2. This is in analogy to the relation commonly used to obtain the stomatal conductance for CO_2 (Jarvis, 1971).

As indicated earlier, two assumptions were made in order to determine the stomatal conductance; (i) the needle temperature is equal to that of the air inside the chamber, (ii) the water vapour concentration inside the stomatal cavities equals that of saturation at the needle temperature. During drought periods the vapour pressure inside the stomatal cavities may be reduced (Jarvis, 1971). In that case the value of the stomatal conductance, as calculated from eq. (4), would be too small and the internal resistance would be overestimated. On the other hand, if the needle temperature is actually larger than the chamber air temperature, then the stomatal resistance obtained is too large and the internal resistance would be underestimated. It seems to be an open question, whether or not the stomatal cavities are saturated (Jarvis, 1971). One way to investigate the water status of the needles is to measure their water potential. The measurements by Milthorpe (1961, as cited in Jarvis, 1971) indicate that for water potentials between 0 and −20 bar and relative humidities up to 80%, the error in the stomatal conductance by assuming saturation in the cavities is less than 10%. For the Scots pine trees at Jädraås the water potential has been found to range from 0 to −16 bar (Mattson-Djos and Hellkvist, 1977). The assumption that the needle temperature equals the air temperature is probably also fairly reasonable for conifer needles since they have a small boundary layer thickness, which increases the rate of sensible heat transfer (Jarvis, 1971). Only during periods with high incoming light intensity, deviation of needle temperature from chamber air temperature might be expected to occur.

The deposition rate of NO_2 can be regarded as the inverse of a resistance, which may be divided into an aerodynamic resistance, a resistance to diffusion to the cuticula and a resistance to diffusion through stomata (Unsworth, 1982). The aerodynamic resistance in the chamber was measured by substituting thick moistened filter paper for the needles. The paper was cut to have the approximate dimensions of pine needles. The resistance for water vapour was determined from measurements of the water vapour difference between inlet and outlet of the chamber, the temperature of the wetted paper and the air temperature. It was converted to an aerodynamic resistance for NO_2 by correcting for the different diffusivities of water vapour and NO_2 in air according to Farquhar et al. (1983). This resistance was found to be 0.03 s mm^{-1} and can be neglected in our calculation since the minimum measured total resistance is of the order of 0.3 s mm^{-1}. Then, if the concentration inside the stomata is zero, the total resistance, R, may be written as

$$1/R = v_n = 1/r_c + 1/(r_s + r_i), \tag{7}$$

where r_s is the stomatal resistance, r_i is the internal resistance and r_c is the cuticula resistance. The measurements cannot distinguish between uptake on the cuticula and uptake through stomata. If the flux to the cuticula is assumed to be zero (i.e., $1/r_c = 0$), this becomes

$$v_n = k_s/(1 + k_s r_i), \tag{8}$$

where $k_s = 1/r_s$.

For the internal concentrations, which will be presented in the results, one needs to consider interactions between water vapour and NO_2 molecules during transport through the stomatal pore (see Jarman (1974) and von Caemmerer and Farquhar (1981) who discussed the diffusion of carbon dioxide through stomata). When there is no net uptake of NO_2 by the branch, there is still a small concentration difference between the surrounding air and the air inside the stomata due to the flow of water vapour molecules out of the stomata (diffusiophoresis). A consequence of this is that when there is no net uptake of NO_2 is the concentration in the chamber larger than the concentration inside the stomatal cavities (later refered to as internal concentration). However, with the equations derived in von Caemmerer and Farquhar (1981) the correction would be less than 4%, which is well within the uncertainty of the measurements.

3. Results

Measurements were taken on 9 shoots during June, July and August at Jädraås in 1985 and during June and August at Sörentorp in 1984. Both current year and 1-year old shoots were studied. At Jädraås the trees were about 20 years old and measurements were made on the third whorl from top of the trees. At Sörentorp the trees were about 70 to 80 years old and measurements were performed on one of the lower whorls.

Figs. 1a, c shows the diurnal variation of the deposition rate per projected needle area for NO_2 (v_n) together with the stomatal conductance (k_s) for a 4-day period in July and August. The incoming light intensity and the rate of photosynthesis for the same period are presented in Figs. 1b, d. The temperature inside the chamber varied from a maximum value of 25°C during daytime to 6°C during nighttime and the relative humidity ranged from 80% during the day to about 50% during the night. Generally the temperature inside the chamber stayed within 2°C of that of the ambient air. However, during periods of high light intensity (above about 1000 $\mu E\ m^{-2}\ s^{-1}$), a difference of up to 6°C was observed. As indicated in Figs. 1a, c, the shoot was exposed to four different concentrations. At high concentrations the uptake of NO_2 showed a marked diurnal variation which was related to the opening of the stomata. Daytime values being an order of magnitude larger than those at night. Below a concentration of a few ppbv the deposition rate was zero or even negative. This is clearly illustrated when the concentation was decreased to 2.3 ppbv right after the period with 29 ppbv in August. Besides the diurnal variation of the stomatal conductance, there was a seasonal variation of this quantity with maximum values of 2

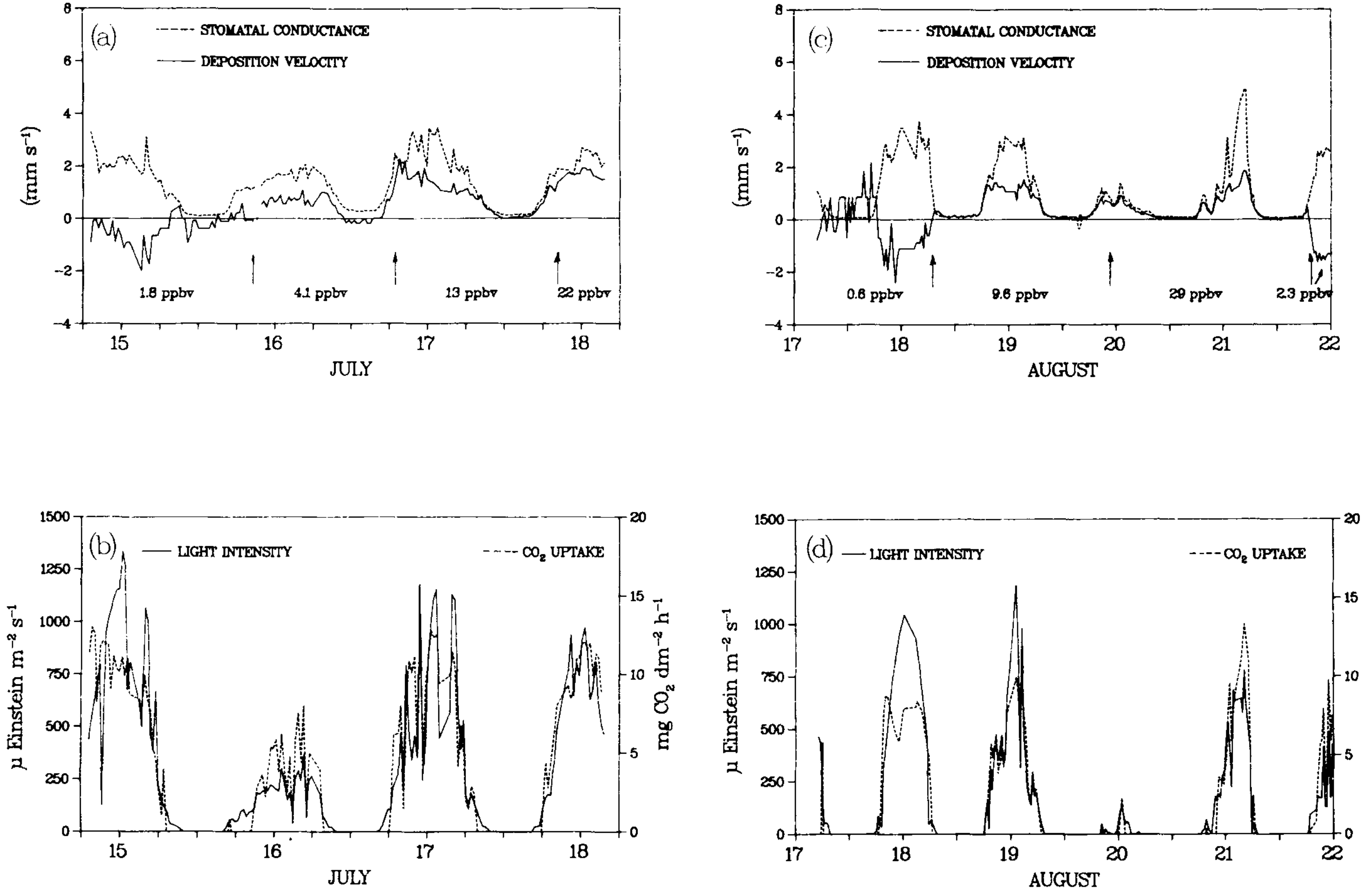

Fig. 1. (a) and (c) show the diurnal variation of stomatal conductance and deposition rate of NO_2 per projected needle area during a 4-day period in July and August, respectively. The arrows indicate a change in the NO_2 concentration. (b) and (d) show the diurnal variation of the incoming photosynthetical light (per ground area) and rate of uptake of CO_2 (per projected needle area) for the same period.

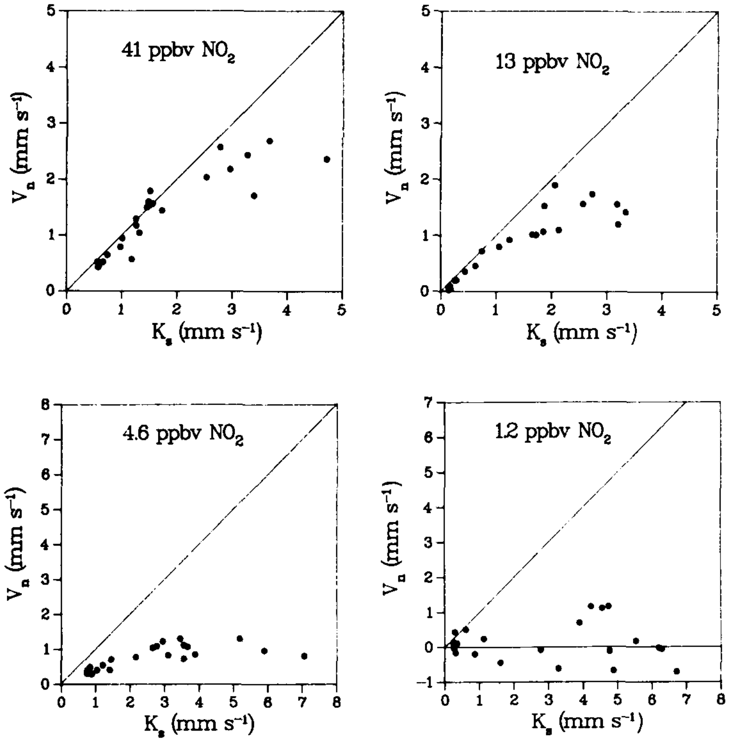

Fig. 2. Dry deposition rate (v_n) versus stomatal conductance (k_s) for NO_2 during four different concentrations. The values were calculated per projected needle area.

to 5 mm s^{-1} during daytime in July and August and about 1 to 2 mm s^{-1} in October (not shown).

The results shown in Figs. 1a, c demonstrates that the stomatal conductance is not the only factor controlling the uptake of NO_2. In Fig. 2 the stomatal conductance is plotted versus the deposition rate during periods with some different concentrations of NO_2. Each data point is an average over one hour during one to two days. At high concentrations of NO_2 the deposition rate was equal to or slightly less than the stomatal conductance. The effect of decreasing the concentration of NO_2 was to reduce the deposition velocity. The reduction relative to the stomatal conductance was more pronounced as the stomatal conductance increase. At a concentration of about 1 ppbv the deposition rate was essentially zero even at high values of the stomatal conductance.

For a constant stomatal conductance, the uptake of NO_2 increased linearly with the concentration (Fig. 3). Only the data corresponding to a narrow range of stomatal conductances have been chosen. The line corresponding to the measured uptake represents a linear regression. The square of the regression coefficient for the data shown in Fig. 3 averaged 0.95. Similar results were obtained when the uptake of NO_2 was measured at a range of NO_2 concentrations in short term (1 hour) experiments, during which the stomatal conductance did not change. The potential uptake shown in Fig. 3 corresponds to the maximum allowed flux based on the conductance to diffusion of NO_2 through stomata (eq. 5). The slope of the measured uptake versus concentration may be regarded as a *modified* deposition rate per projected needle area, according to:

$$v_{n,\mathrm{mod}} = J/C_e - C_i), \tag{9}$$

where C_i is the concentration at zero flux (hereafter termed "internal concentration"). The difference in the slopes between the potential and measured flux in Fig. 3, may be interpreted as

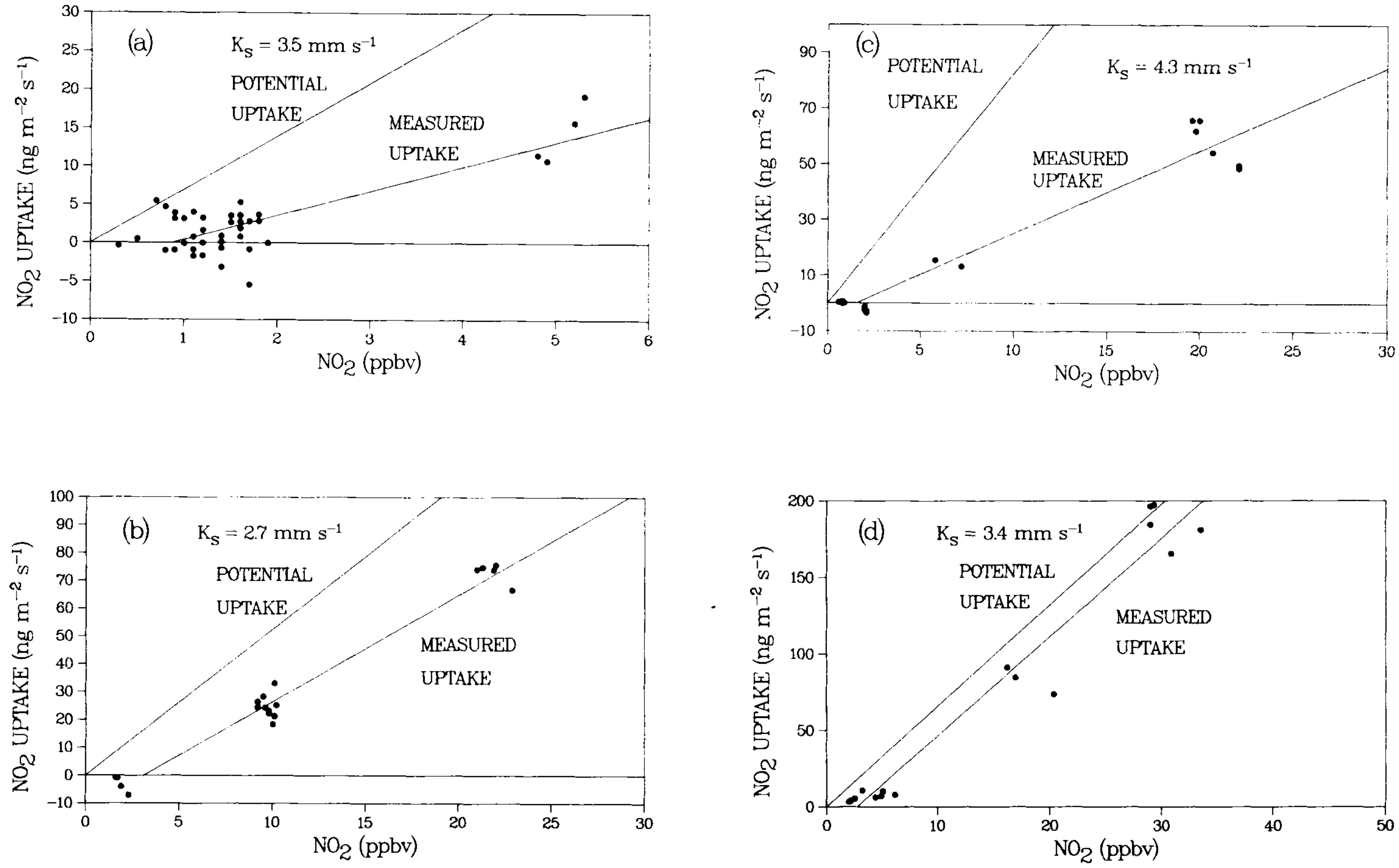

Fig. 3. The potential stomatal and measured uptake of NO_2 versus concentration for a constant stomatal conductance (k_s). The potential uptake is indicated by the line ($k_s C_e$) and the measured uptake by the points and the linear regression line. (a) = June, (b) = July and (c) = August at Jädraås and (d) = June at Sörentorp.

Table 1. *The deposition velocity (modified), internal resistance and internal concentration as obtained from a regression analysis of the uptake of NO_2 versus concentration for five different branches and with constant stomatal conductance*

Site	Month	No. of values	Light intensity (μEinst m^{-2} s^{-1})		Net rate of photosynthesis (mg CO$_2$ dm^{-2} h^{-1})		Stomatal conductance (mm s^{-1})		Deposition velocity* (mm s^{-1})		Internal res. (s mm^{-1})	conc. (ppbv)
			mean	SD	mean	SD	mean	SD	mean	SD		
Sörentorp 59°26N 17°57E	June	17	100	65	nm†		3.4	0.2	3.3	0.2	0.01	2.7
		26	6	17	nm		1.2	0.1	1.2	0.2	0.05	1.2
	August	37	38	59	nm		2.4	0.2	1.6	0.1	0.20	1.0
		22	3	7	nm		1.2	0.1	0.60	0.1	0.80	1.0
Jädraås 60°48N 16°30E	June	43	640	429	14	5	3.6	0.5	1.7	0.2	0.31	0.9
		22	103	86	4	2	0.90	0.3	0.88	0.05	0.03	0.7
	July	20	764	294	16	2	2.7	0.5	2.0	0.1	0.13	3.1
		74	317	279	8	1	1.6	0.2	1.5	0.1	0.09	2.3
	August	20	633	239	12	2	4.3	0.5	1.5	0.1	0.43	1.5
		21	253	268	5	4	1.3	0.1	0.80	0.04	0.48	0.3

*This is a modified deposition velocity, $= J/(C_e - C_i)$, see text.
†nm = not measured.

being due to an internal (or mesophyllic) resistance.

The deposition rate for NO_2 (v_n, as defined in eq. 2), may then be formulated in terms of not only a stomatal conductance and an internal resistance but also an internal concentration:

$$v_n = k_s(1 - C_i/C_e)/(1 + k_s r_i). \qquad (10)$$

Such a dependence of the deposition rate on the concentration and an internal resistance is reflected in the data shown in Fig. 2. Both the internal concentration and the internal resistance tends to decrease v_n. The influence depends on the magnitude of the concentration and the stomatal conductance.

Five branches have been subjected to a range of different concentrations. Values of the (modified) deposition rate and the corresponding internal resistance and internal concentration were computed from the slopes and intercepts of the regression of the uptake versus concentration at two different stomatal conductances. These data together with the corresponding light intensity and rate of photosynthesis are presented in Table 1 and will be discussed below.

4. Discussion

4.1. Deposition velocities

No uptake of NO could be detected over the whole concentration range surveyed. Hence, the deposition velocity was found to be less than 0.1 mm s^{-1}. Similar results were presented for Scots pine by Bengtsson et al. (1982). The surface resistance to uptake of NO by alfalfa has been observed to be about 20 times larger than the uptake of NO_2 (Hill, 1971).

The deposition velocity for NO_2 obtained at high concentrations (> 10 ppbv) are very close to that reported by Bengtsson et al. (1982) who made similar measurements at the same site. As in the present study they found that the rate of uptake was closely related to the stomatal conductance with no residual uptake of NO_2 on surfaces outside stomata.

The uptake of SO_2 and O_3 by shoots of Scots pine trees has been studied in earlier measurements using the same system (Johansson et al., 1983b). There is a profound difference in the behaviour of these gases compared to that of NO_2 with respect to the pattern of deposition as well as the magnitude. For both SO_2 and O_3 a significant deposition on the surface of the needles was observed in addition to the uptake via stomata. Other measurements have, however, observed the presence of an internal resistance also for SO_2 (Hällgren et al., 1982; Fowler and Cape, 1983). A comparison of the magnitude of the deposition velocities at a concentration of a few ppbv, indicates that the daytime deposition rate for SO_2 and O_3 may be up to a factor of 10 larger than that for NO_2.

4.2. *Internal resistance*

In order to examine the internal resistance to diffusion of NO_2 through the stomata a few different values of the stomatal conductance were used as illustrated in Fig. 3 and Table 1. (It was assumed that the uptake on the surface outside the stomata of the needles was negligible.) The range of stomatal conductances chosen was somewhat different for different shoots depending on natural variations in the stomatal conductance during the measurements of NO_2 uptake at different concentrations. The internal resistance was found to vary from 0.01 to 0.8 s mm^{-1} constituting up to 62% of the total resistance (Table 1). On the average it does not seem to be related to the stomatal conductance; the mean value for the higher and lower stomatal conductance in Table 1 is 0.22 and 0.29 s mm^{-1}, respectively. Since the measured uptake of NO_2 seems to vary linearly with concentration (Fig. 3), the internal resistance is independent of the concentration at these levels.

In contrast to the present study, Bengtsson et al. (1982) did not find any significant internal resistance for NO_2. The uptake was limited by an internal resistance only when the shoot had been exposed to high concentrations (110 ppbv) for a long period of time or when the plants were under water stress conditions. An adequate explanation for this discrepancy in the results has not been found.

4.3. *The uptake of NO_2 at low concentrations*

At concentrations of a few ppbv and below a spurious production of NO_2 in the empty chamber was detected. Although a correction was made, this contributes to the uncertainty in the determination of the concentration with zero uptake. In order to minimize the influence of this artificial production, the data obtained at higher concentrations was also included in the regression analysis of the uptake of NO_2 versus concentration (Fig. 3). The internal concentrations obtained from the regression ranged from 0.3 to about 3 ppbv (Table 1). The lower values for each branch are associated with the lower stomatal conductance, light intensity and rate of photosynthesis.

As the concentration in the chamber is decreased below the internal concentration indications of an emission of NO_2 can be seen. The possibility that this could be explained in terms of some interfering compound on the NO_x analyser has been examined by passing the air through a tube with ferrous sulphate, which converts all NO_2 to NO and subsequently adding excess O_3 in a reactor volume, where NO is converted to NO_2. Since the NO signal was lost after the addition of O_3 and almost totally recovered after a second tube with ferrous sulphate it seems improbable that the emission emanates from another compound than NO_2 (e.g., organic nitrates, see also under Subsection 2.3).

Although, the possibility of an emission of NO_2 during periods with very low concentrations is interesting from a plant physiologists point of view, it appears to be of little quantitative importance as a source of NO_x for the atmosphere. The reason is that the concentrations found in rural air in Sweden (Sjödin and Grennfelt, 1984) are similar to the internal concentration.

There seems to be no measurements of the uptake of NO_x to plants at concentrations as low as a few ppbv. Results recently reviewed by Galbally (1985), show that for the plant-soil system, an NO emission from the soil is counterbalanced by an uptake of NO_2. Thus, depending on the atmospheric concentrations of NO and NO_2, the exchange may vary from net emission to net uptake (Galbally et al., 1985). Farquhar et al. (1980) measured the uptake of NH_3 by *Phaseolus vulgaris L.* and the qualitative results were similar to those presented here for NO_2. The uptake was found to be linearly related to the concentration and was zero at a finite concentration of a few ppb's. Below this concentration, they observed an emission of NH_3 or some volatile amine.

As NO_x, O_3 and SO_2 usually occur together in the atmosphere, there is a danger in studying the exchange of these gases separately. For example, it has been shown that SO_2 combined with NO_2 (both at high concentrations) have a synergistic effect on the inhibition of photosynthesis in alfalfa (see review by Wellburn, 1982). However, an examination of earlier measurements (Johansson et al., 1983b), where the uptake of NO_x, O_3 and SO_2 were studied simultaneously does not seem to show any increased uptake of NO_2 due to the presence of SO_2 and O_3.

4.4. *Deposition to the canopy*

Proceeding from a deposition rate per projected needle area to a deposition velocity per ground area (v_g), it is necessary to consider the spatial distribution of needle area together with the variation of the mass transfer resistances and possibly also the variation of the internal concentration within the canopy. Rather extensive measurements of the variation of leaf area index (LAI = projected needle area per ground area) and stomatal resistance within the forest at Jädraås have been performed by Halldin, 1985) and Linder and Troeng, (1980), respectively. However, at this stage only an approximate estimate of the deposition velocity for NO_2 to the forest seems justified since there is no information on the spatial variation of the internal resistance and internal concentration.

To illustrate the influence of the concentration of NO_2 on the deposition to the forest, two cases may be considered. In the case when the concentration is larger than 10 ppbv, which corresponds to the levels during the measurements by Delany and Davies (1983) and Wesley et al. (1982), the influence of C_i on the deposition velocity may be neglected. For an internal resistance of between 0.1 and 0.4 s mm^{-1} and a typical day-time stomatal conductance of 3 mm s^{-1}, the deposition rate per projected needle area will be between 2.3 and 1.4 mm s^{-1} (cf. eq. 8). As the atmospheric resistance for NO_2 over and within a forest constitutes only about 10% of the total resistance to uptake, even at modest wind speeds (Fowler, 1984), this deposition rate may be multiplied by the average LAI to obtain a deposition velocity per ground area. Thus, using a LAI of 3, which is representative for the Scots pine forest at Jädraås, a depsotion velocity per ground area of between 7 and 4 mm s^{-1} is obtained. This is similar to the estimates of the deposition velocity to a forest given by Fowler (1984) and to the results obtained for short field crops (Delany and Davies, 1983; Wesley et al., 1982).

In the case when the concentration is equal to C_i, the deposition rate per projected needle area is estimated to be less than 0.4 mm s^{-1}. With a LAI of 3, this corresponds to a deposition velocity to the forest of less than 1 mm s^{-1}. This is at least a factor 4 lower than the values obtained at high concentrations.

5. Conclusions

This study support the results already obtained by others that:

- at NO_2 concentrations of several tens of ppbv, the removal from the atmosphere is under biological control. The removal rate is governed by the stomatal conductance, with a negligible deposition to the external surfaces of the needles. In addition to the stomatal resistance an internal resistance to uptake of NO_2 was observed.
- the uptake of NO is much smaller than that of NO_2.

An important novel finding is that the uptake of NO_2 becomes essentially zero at a concentration, which corresponds approximately to the levels found in rural air in Sweden. This result is of great importance for budget calculations and long range transport modelling since NO and NO_2 are key species in determining the concentration of the highly reactive OH radical, which in turn have a large influence on the rate of removal of several other species in the atmosphere. If dry deposition of NO_2 is negligible, relatively more NO_x than previously thought may remain in the atmosphere and subsequently be converted to HNO_3, which is ultimately removed by rainout and dry deposition.

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