Tellus (1994), 46B, 339–352
Printed in Belgium – all rights reserved

TELLUS
ISSN 0280–6509

Studies on the dry deposition of NO_2 to coniferous species at low NO_2 concentrations

By ALBERTO RONDÓN* and LENNART GRANAT, *Department of Meteorology, Stockholm University, S-106 91 Stockholm, Sweden*

(Manuscript received 26 February 1993; in final form 13 June 1994)

ABSTRACT

Measurements of the deposition of NO_2 to seedlings of Scots pine and Norway spruce at ppbv and sub ppbv levels were made in the laboratory using a flow through chamber technique. The results show that NO_2 deposition at air concentrations above 1 ppbv was governed by stomatal uptake. The possible influence of other factors controlling the NO_2 deposition was also explored. Mean NO_2 compensation points for both Scots pine and Norway spruce were lower than 0.2 ppbv, which can be considered negligible. Throughout the experiments, there was no evidence of internal resistance to NO_2 uptake by the seedlings. At low NO_2 concentrations (0.2–1 ppbv), the NO_2 flux was generally below the detection limit of the technique.

1. Introduction

The rôle of vegetation surfaces as a sink for atmospheric NO_2 has been extensively described in the literature (Hill, 1971; Hanson et al., 1989; Fowler, et al., 1989; Johansson, 1987; Granat and Hällgren, 1992; Rondón et al., 1993). In clean regions, far away from sources of NO and NO_2, the dry deposition of NO_2 to vegetation seems to play a minor role in the atmospheric balance of reactive nitrogen species (Johansson, 1987; Rondón et al., 1993). However, in more polluted areas, NO_2 deposition may account for a significant fraction of the total deposition of oxidized nitrogen compounds (Rondón et al., 1993; Hanson et al., 1989).

Measurements of the rates of exchange of NO_2 between the air and vegetation can be performed using micrometeorological and chamber methods (Fowler et al., 1989). The former method has the advantage over chamber techniques that it does not perturb the underlying surface conditions but it also has several theoretical and practical requirements that make it difficult to use above complex terrains such as forest canopies. With micrometeorological methods it is also difficult to distinguish between the flux to the canopy and to the forest floor. Chamber methods have been widely used both in laboratory and field experiments. They may perturb the plants if the experiments are run during long periods of time, but the possible bias can be minimized by controlling the environmental conditions in the chamber. Chamber methods are probably more appropriate when studying the processes and mechanisms controlling the deposition of gases to vegetation.

The deposition of atmospheric gases to plants can occur internally through stomatal uptake or externally on the cuticle. Highly reactive gases such as HNO_3 deposit readily to the external surfaces of leaves (Fowler et al., 1989; Hanson and Garten, 1992), whereas the plant stomata are generally the main deposition site for gases like SO_2, O_3 and NO_2. However, under certain environmental conditions of light and humidity, the cuticular deposition of O_3 may be a significant fraction of the total uptake (Rondón et al., 1993; Rondón, 1993). The results from NO_2 deposition experiments on alfalfa, soybean plants, and pine

* Corresponding author. Present affiliation: Atmospheric chemistry laboratory, IVIC, Apartado 21827, Caracas 1020-A, Venezuela.

and spruce trees at several ppbv NO_2 suggest that the deposition of NO_2 is mainly controlled by stomatal uptake (Hill, 1971; Wesely et al., 1982; Bengtson et al., 1982; Johansson, 1987; Hanson et al., 1989; Thoene et al., 1991; Rondón et al., 1993). With respect to NO_2 deposition to coniferous forests, very little has been done, especially at low concentrations representative for relatively clean areas, such as the boreal forests of the northern hemisphere (Skärby et al., 1981; Johansson, 1987; Hanson et al., 1989; Granat and Hällgren, 1992; Rondón et al., 1993). Most reports agree that the main deposition occurs through the stomata and not to the cuticle. However, Hanson et al. (1989) reported laboratory results conducted on red spruce, white pine and loblolly pine at mean NO_2 concentration of 33 ppbv, which showed that NO_2 needle conductance was 15 to 30% higher than stomatal conductance suggesting a possible deposition of NO_2 on the leaf and bark surfaces. At relatively high NO_2 concentrations the deposition is controlled by stomatal uptake, depending mainly on light intensity, relative humidity, temperature and water vapor deficit, and may be modelled in analogy to the exchange of water vapor. Johansson (1987) studied the deposition of NO_2 to Scots pine under field conditions of light and temperature. He found that the uptake was limited by both mesophyllic and stomatal resistances. At NO_2 concentrations between 1 and 3 ppbv, no uptake was detected. Bengtson et al. (1982) reported field and laboratory studies on the uptake of NO_x (NO and NO_2) to Scots pine needles. At concentrations ranging from 10 to 400 ppbv, they found that NO_2 uptake was determined by stomatal conductance. Thoene et al. (1991) measured the absorption of NO_2 to branches of spruce under laboratory conditions. At NO_2 concentration of 50 ppbv, the needle conductance and stomatal conductance for NO_2 were identical, which indicates a very small internal or mesophyllic resistance. However, in the range of NO_2 concentrations from 8 to 25 ppbv, they found that the uptake was limited by an internal resistance in accordance with the results reported by Johansson (1987). At 8 ppbv, the NO_2 needle conductance was only 18% of the stomatal conductance.

In a recent report, Rondón et al. (1993) present the results from field measurements on the exchange of NO and NO_2 between the air and shoots of Norway spruce and Scots pine. At a site in southern Sweden the NO_2 needle conductance and stomatal conductance were very similar in the whole range of NO_2 concentrations, from 0.4 to 12 ppbv. On the other hand, at a less polluted site in Central Sweden NO_2 needle conductance was lower than stomatal conductance. The compensation points reported for this site were in the range from 0.5–0.7 ppbv, somewhat lower than those reported previously at the same site by Johansson (1987).

The pathways for NO_2 assimilation by the vegetation are still not well understood. It has been suggested that NO_2 is taken up through the stomata and dissolved in the water around the mesophillic cells to produce NO_3^- and NO_2^- which are subsequently reduced and incorporated into amino acids. Reduction of NO_3^- and NO_2^- occur via enzymatic reactions involving nitrate reductase and nitrite reductase. The limiting step in this mechanism is the disproportionation of NO_2 in water, which is a second order reaction with respect to the NO_2 concentration. Field and laboratory experiments have clearly shown that the rate of uptake of NO_2 by plants is linearly correlated to the NO_2 concentration in the surrounding, which is contradictory to the idea mentioned above. The magnitude of measured NO_2 flux rate is also much higher than what would be expected by the slow process of NO_2 disproportionation in water. Ramge et al. (1992) have presented an alternative mechanism, based on the reaction of NO_2 with ascorbate present in apoplast, to explain the rate of uptake of NO_2 and its kinetic characteristics. Their model calculations reproduce the experimental data fairly well.

From the information on NO_2 deposition to coniferous species reviewed here, it is still not clear what the roles of the internal resistance and the internal NO_2 concentration are, in the control of NO_2 uptake. This question must be addressed before accurate modelling of NO_2 flux to the canopy can be done.

This paper presents results of the deposition of NO_2 to seedling of Scots pine and Norway spruce in the laboratory under controlled conditions of temperature, light intensity, relative humidity and concentrations of NO, NO_2 and O_3. Since most of the previous controversial results correspond to measurements made at low NO_2 concentrations which also are more relevant for most forest ecosystems, we have concentrated our effort to

evaluate the NO_2 exchange at concentrations varying from 0.2 to 30 ppbv.

2. Experimental

2.1. Plant material and pre-treatment

The experiments were performed with 2 year old seedlings of Scots pine (*Pinus sylvestris L.*) and Norway spruce (*Picea abies L. Karst*). The plants were grown in 9 cm diameter pots in a nutrient rich commercial soil, and then divided into three groups which were then subjected to different pre-treatments. The first group was raised under ambient conditions on the roof of the laboratory at Stockholm University. The mean values of ambient NO_x and O_3 during the pre-treatment period, from May to August, were 8 ppbv and 31 ppbv, respectively.

Groups two and three were grown in plexiglas chambers under controlled conditions. A schematic diagram of the storage chamber and gas handling system is given in Fig. 1. The chambers were 85 cm long, 45 cm wide and 40 cm height and illuminated with metal halogen lamps (400 W) and ventilation fans to keep the chamber air well mixed. The light intensity at plant level was approximately 350 $\mu E\ m^{-2}\ s^{-1}$ during a light period of 14 h/day. The chambers were fed with ambient air, filtered with activated charcoal and subsequently humidified to control the relative humidity, at a flow rate of 70 l min^{-1}. After purification, the mean air concentrations of NO, NO_2 and O_3 were less than 0.2, 0.5 and 2 ppbv, respectively. One chamber was equipped with NO_2 and O_3 addition systems. NO_2 was added from pressurized gas bottles and O_3 generated using an UV light source and pure and dry oxygen.

2.2. Measuring chamber

The gas exchange between the shoots and the air was measured in a chamber made of 0.04 mm

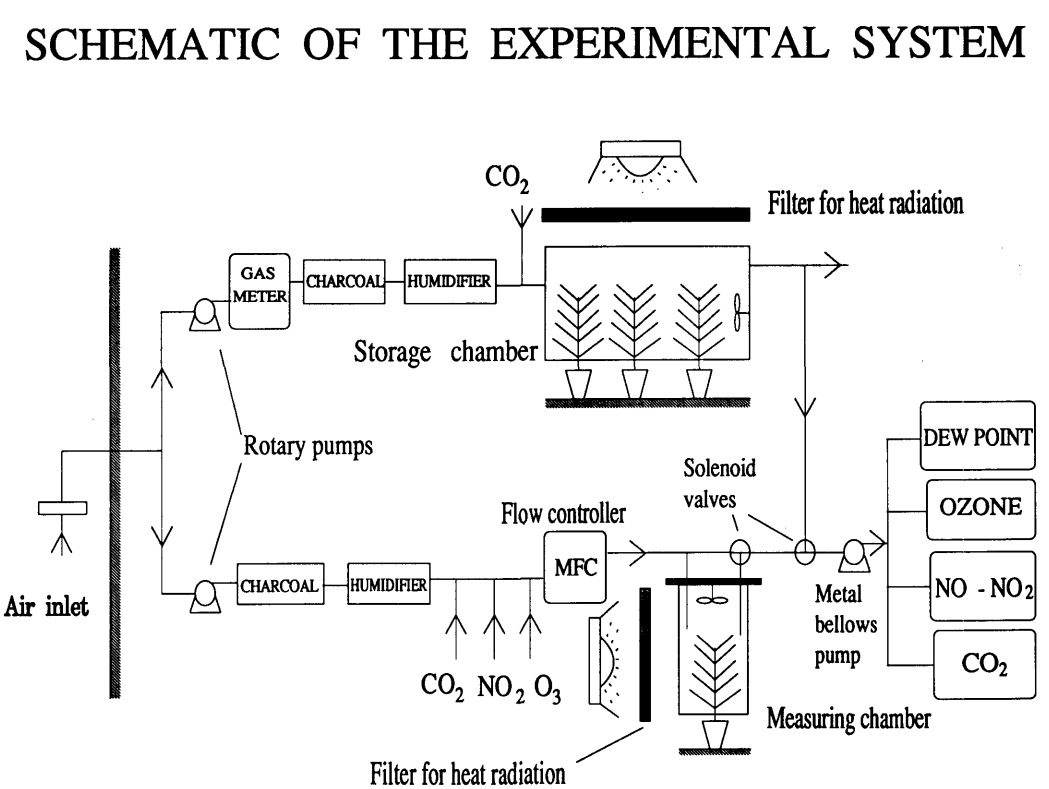

Fig. 1. Schematic of the experimental system.

teflon film. This type of chamber has been used previously in field experiments and was here slightly modified for the laboratory experiments. It has a cylindrical form with a base area of 315 cm^2 and 40 cm height. The chamber allows separation of the shoots from the soil to avoid gas exchange between the air and the soil. The air flow rate to the chamber was set to about 6 l min^{-1} and regulated by an electronic mass flow controller (i.e., the air was exchanged every 2 minutes). Ventilation fans were installed to mix the air and to minimize the aerodynamic and boundary layer resistances. The air temperature was measured using a shielded semiconductor (type AD 590). Photosynthetic active radiation (PAR) was measured with a LiCor 190 SB quantum sensor. A metal halogen lamp was used as light source. The UV light generated from the lamp was filtered through a plate filter while the heat radiation was dissipated by a water shield and external fans. A complete description of the operating modes in the system is given in Rondón et al., 1993.

2.3. *Analytical system*

NO was determined by a NO-O_3 chemiluminescence analyzer (TECAN CLD 770 Al ppt). NO_2 was measured by both photolytic and chemical ($FeSO_4$) conversion and subsequent detection of the NO produced (Fig. 2). The detection limit for NO and NO_2, defined as two times the standard deviation of the noise, was 0.05 and 0.2 ppbv, respectively. Calibration of the NO instrument was made by dilution of gas mixtures of NO in nitrogen. The photolytic converter was calibrated every 48 hours using an O_3-NO titration system. The conversion efficiency varied between 30 and 40%.

Parallel determinations of O_3, CO_2, and water vapor were also made. Description of the instruments and calibration procedures for these gases has been described by Rondón et al. (1993).

2.4. *Determination of nitrate reductase activity*

The analysis of the nitrate reductase activity in needles was made following the method in vivo reported by Wingsle et al. (1987). 200 mg fresh weight of one-year old needles were sampled in quadruplicate from each of the storage chambers, 3 hours after the light period started. The needles were cut into 2 mm segments and transferred to test tubes. The samples were incubated for 1 hour in the dark at 26°C, under continuous

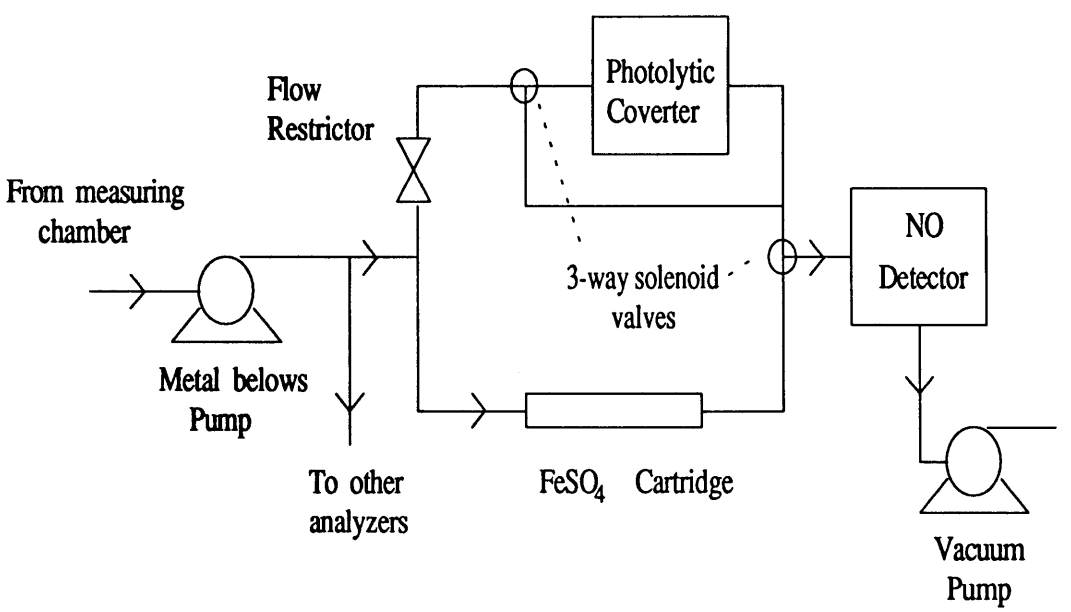

Fig. 2. Setup of the instruments for the comparison between the photolytic converter and the $FeSO_4$ reductor for the NO_2 analysis.

shaking. The incubation solution was 100 mM KH_2PO_4-KOH, 100 mM KNO_3 and 0.02% v/v Triton X-100 adjusted to pH 8 with a solution 1 M KOH. After incubation, 2×1 ml solution were transferred to test tubes for determination of nitrite and blank, respectively. Nitrite was determined by the diazotization reaction with a solution of sulfanilic acid and N-1-naphthylethylendiaminedihydrochloride. The results are expressed as nitrate reductase activity in nmol NO_2^- per g fresh weight per hour.

2.5. *Calculations*

A complete description of the relations employed to calculate the parameters used in this work is presented by Johansson (1987) and Rondón et al. (1993). Here we only include the definition of the most important quantities.

The needle conductance to NO_2 per projected needle area was calculated, in analogy to the definition of vertical deposition velocity, as the ratio of the flux to the concentration at a specific height:

$$g_{n,NO_2} = F_{NO_x}/C_{o,NO_2}, \quad (1)$$

where g_{n,NO_2} is the needle conductance per projected needle area, F_{NO_x} is the NO_x ($NO_x = NO + NO_2$) flux to or from the branch related to the projected needle area (considered positive when the flux is towards the branch), and C_{o,NO_2} is the NO_2 concentration at the chamber outlet. The NO_2 concentration at the chamber outlet, due to the well mixed conditions inside the chamber, is assumed identical to the NO_2 concentration in the chamber air. It have been previously shown that, due to the fact that NO is not exchanged between the branches and the air (Rondon et al., 1993; Johansson, 1987), one can assume that NO_2 flux is equal to the NO_x exchange rate. This approach avoid any limitations derived from the rapid exchange between NO and NO_2 that occurs in the chamber due to the reactions of NO with ozone and by the photolytical dissociation of NO_2.

The stomatal conductance for water vapor was calculated from measurements of the transpiration rate, assuming that the concentration of water vapor inside the stomata was equal to the saturation water vapor concentration at needle temperature, which in turn is assumed to be equal to the chamber air temperature (Johansson, 1987; Rondon et al. 1993). The stomatal conductance of NO_2 (K_{s,NO_2}) was calculated from the stomatal conductance of water vapor corrected for the difference in air diffusivities of NO_2 and water vapor (Johansson, 1987). The ratio between the diffusivity of NO_2 to the diffusivity of water vapor was assumed to be equal to the square root of the ratio of the molecular weight of water to that of NO_2.

The sum of the aerodynamic (r_a) and the boundary layer (r_b) resistances to the flux of NO_2 to pine branches in the chamber is about 0.03 s mm^{-1} (Johansson, 1987). This represents about 10% or less of the minimum total resistance. We have assumed that r_a and r_b can be neglected compared to the total surface resistance.

3. Results and discussion

3.1. *Chamber blank*

Chamber measurements of the rate of exchange of reactive trace gases between the air and vegetation at low concentrations involve serious difficulties due to the dynamic exchange of gases between the air and the chamber itself. In order to clarify these difficulties, we carried out a considerable number of experiments with an empty chamber.

In Table 1, we present the results from some NO_2 exchange measurements performed with empty chamber. The experimental system employed in this work uses only one chamber. Therefore, chamber blanks were made alternatively at the beginning and at the end of each experiment with the seedlings. Tests with empty chamber were carried out at different NO_2 concentration varying from 0.2 to 15 ppbv. It is evident from the data presented in Table 1 that there is a large variability in the behavior of the chamber, both in terms of the magnitude and sign of the exchange. At NO_2 concentrations below 2 ppbv, higher NO_2 concentrations were observed at the chamber outlet than at the inlet, which indicates a net emission of NO_2 from the chamber walls, possibly originated from NO_2 previously deposited on the chamber. The correction for chamber blank at NO_2 levels below 1 ppbv was 20 to 50%, which implies that results in that range of NO_2 concentrations are associated with a large uncertainty. At NO_2 concentrations

Table 1. *Chamber blank corrections at different NO_2 concentrations*

$[NO_2]$ (ppbv)	PAR ($\mu E\ m^{-2}\ s^{-1}$)	Temperature (°C)	Relative humidity (%)	$[NO_2]_i$-$[NO_2]_o$[a] (ppbv)	Blank[b] fraction (%)
0.2	290	25.8	38	−0.06	−23
0.2	0	22.4	47	−0.07	−35
0.7	450	25.1	49	−0.10	−20
0.8	0	22.3	53	−0.08	−10
1.3	450	25.5	42	−0.20	−21
1.3	0	22.1	46	−0.25	−26
3.7	360	25.7	42	0.3	+7
4.0	0	22.0	56	<0.05	<2
5.7	600	23.9	45	−0.2	−3
12.6	350	25.0	46	1.3	+10
13.7	0	21.7	56	0.35	+4

[a] Difference in NO_2 concentration between chamber inlet and outlet.
[b] Average fraction of the NO_2 lost or gain in the empty chamber related to the NO_2 concentration in the chamber air. (-) indicates a net gain of NO_2 in the chamber.

from 3 to 6 ppbv the exchange of NO_2 from or to the chamber was generally less than 10% of the actual NO_2 concentration. At higher NO_2 levels, from 10 to 15 ppbv, there was a net NO_2 deposition to the chamber components. These results suggest that there is a "compensation point" (NO_2 air concentration at which the net exchange between the air and the chamber is equal to zero) around 3 to 6 ppbv NO_2. The chamber blanks did not show any significant relationship with light intensity, temperature or relative humidity. These results illustrate some of the difficulties of working with teflon chambers at low NO_2 concentrations. A pre-exposure of teflon chambers to high levels of O_3 may help to reduce the reactivity of the teflon material with reactive gases. Another alternative to diminish blank problems could be to use a double-chamber system which could allow simultaneous correction during the experiments. However, we have not investigate if the presence of plants in the chamber changes the properties of the teflon surface, for example, due to deposition of organic substances emitted by the plants.

3.2. *Photolytic and chemical reduction of NO_2*

One of the possible causes for the differences in the measurements of the NO_2 needle conductance to Scots pine performed by our group in central (Johansson, 1987; Rondón et al., 1993) and southern Sweden (Rondón et al., 1993) was initially attributed to differences in the instrumentation. A ferrous sulphate reductor was used in Jädraås (central Sweden) to convert NO_2 to NO while in Simlångsdalen (southern Sweden) a photolytic converter was employed. The hypothesis was that some N compounds may be emitted from the pine branches to produce interferences in the determination of NO_2 using the $FeSO_4$ converter. This would explain the lower deposition

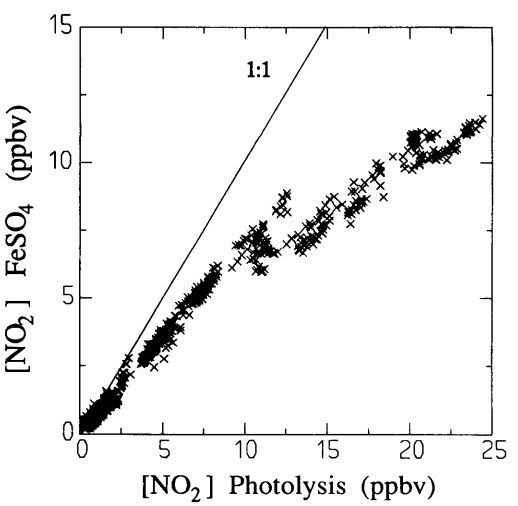

Fig. 3. Scatter plot of the NO_2 concentration measured using the $FeSO_4$ device versus the values obtained from the photolytic converter.

velocities measured in Jädraås compared to Simlångsdalen. There is experimental evidence that some N compounds like nitrous acid and peroxyacetylnitrate (PAN) produce significant positive interferences in the determination of airborne NO_2 using a $FeSO_4$ reductor (Gregory et al., 1990; Dickerson, 1984). To test this hypothesis we measured the deposition of NO_2 using both photolytic and $FeSO_4$ converters coupled to a NO analyzer. The setup of the system is shown in Fig. 2. To equalize the flow rate and pressure in the two lines a flow restrictor was placed in the photolytic converter line to compensate for the higher drop pressure in the $FeSO_4$ cartridge compared to the photolytic converter. The NO analyzer was calibrated through both lines every 6 h. The difference in the calibration factors for the two lines was always less than 10%, which is within the precision of the technique.

The results from the instrumental intercomparison are presented in Fig. 3. They show significant differences in the NO_2 concentrations measured by the two devices. NO_2 measured through the $FeSO_4$ line was systematically lower than the values from the photolytic converter. This could be due to an error in the calibration of the

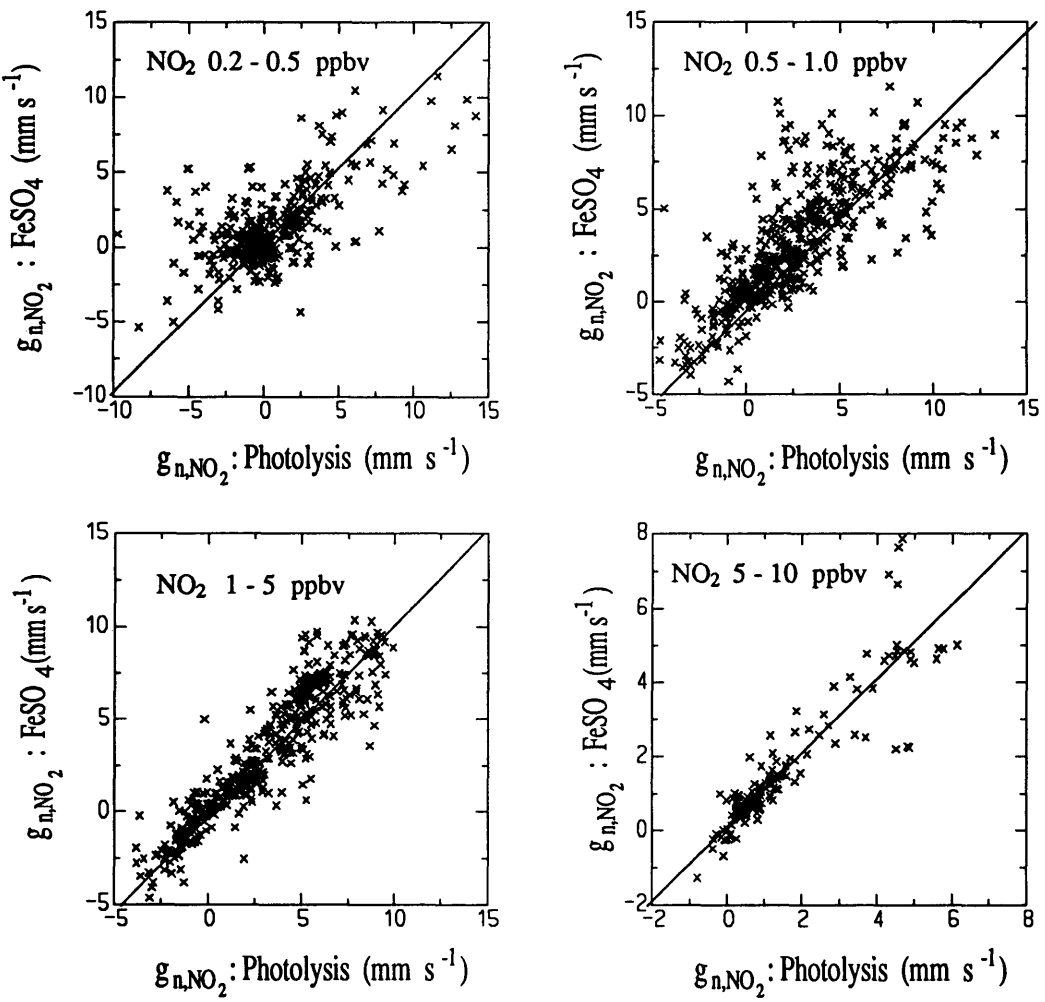

Fig. 4. Comparison between the values of NO_2 needle conductance measured with the $FeSO_4$ and photolytic converter devices at different NO_2 concentration ranges. (a) 0.2–0.5 ppbv, (b) 0.5–1 ppbv, (c) 1–5 ppbv, (d) 5–10 ppbv.

photolytic converter or to a low efficiency of the $FeSO_4$ cartridge. The photolytic converter was calibrated every 48 h and its efficiency was not recorded in the memory of the instrument until the precision of the calibrations was within $\pm 10\%$. For this reason, we are confident about the efficiency of the photolytic converter. An error of 10% in the measurements of NO_2-photolytic is not enough to explain the differences observed between the two devices. Despite the differences observed in the absolute NO_2 concentrations measured with the $FeSO_4$ and photolytic converters, there is a constant ratio (given by the slope of the curve in Fig. 3 between these variables in the range of NO_2 concentrations from 0.2 to 10 ppbv. This relationship between NO_2-$FeSO_4$ and NO_2-photolytic enables us to make an intercomparison of the NO_2 needle conductance measured by the two techniques in that range of NO_2 concentrations. The intercomparison is presented in Fig. 4 for several NO_2 concentration ranges. At NO_2 concentrations between 1 and 10 ppbv (Figs. 4c, d) there is a good relationship between the values with most of the measurements very close to the 1:1 line. At concentrations below 1 ppbv (Figs. 4a, b) there is a larger scatter in the data but the values are not systematically different. Based on these experiments, it seems unlikely that the observed difference in NO_2 deposition velocities at the two field sites in Sweden could be explained by chemical interferences in the analytical determination of NO_2.

3.3. *Deposition of NO_2 to Scots pine and Norway spruce*

Measurements of NO_2 exchange on seedlings of Scots pine and Norway spruce were made for periods of 24 to 120 h. A typical result from the exposure of one of the plants to varying NO_2 concentration is presented in Fig. 5. At NO_2 concentrations higher than 10 ppbv NO_2, the needle conductance and the stomatal conductance, expressed per projected needle area, were practically identical. At relatively low NO_2 concentrations, below 2 ppbv, NO_2 needle conductance and stomatal conductance varied in the same way, but the precision of the measurements of needle conductance is somewhat lower. In general, the results from plants of the same species, but subjected to different pretreatments, were comparable in terms of the magnitude of NO_2 needle conductance, NO_2 stomatal conductance, and with respect to the relation between these two variables. Based on this fact, we treated the results in two main groups, one for the Scots pine and another for Norway spruce.

Results from the above experiments were evaluated to investigate the main controlling factors to the deposition process. Firstly, the measured NO_2 needle conductance was compared to the stomatal conductance. This comparison is presented in Figs. 6, 7 as scatter plots of needle conductance versus stomatal conductance, for pine and spruce, respectively. At NO_2 concentrations above 1–2 ppbv there is a good linear relationship between the two variables for both species. At NO_2 concentrations below 1–2 ppbv, the results show a large variability, most of the data points are within the detection limit of the technique (this detection limit for g_{n,NO_2} was calculated as a function of the minimum detectable NO_2 flux from or to the branch). The results from Figs. 6a, 7a indicate that at NO_2 concentrations higher than 1–2 ppbv, the NO_2 deposition rate is essentially controlled by the stomata openings. Similar results have been reported by Rondón et al. (1993) from measurements of the dry deposition to Scots pine and Norway spruce performed in southern Sweden. The curve derived from the linear regression analysis of the experimental data shows a slope slightly higher than 1. For Norway Spruce the slope was not statistically different than 1 at 99% confidence intervals but for Scots pine the slope was different than 1 at 96% confidence intervals. This may be an indication that a minor fraction of NO_2, of the order of 5 to 20%, is deposited on the external surfaces of the pine branches and the bark. For Scots pine, Hanson et al. (1989) have also reported some data that might be interpreted as a minor uptake of NO_2 on the bark and cuticle of different broadleaved and coniferous species.

The relation between NO_2 flux and NO_2 air concentration, in a narrow range of stomatal conductance ($k_{s,NO_2} \pm 0.5$ mm s^{-1}), are shown for Scots pine and Norway spruce in Figs. 8, 9, respectively. They show that the NO_2 flux to the branch is directly proportional to the NO_2 concentration, in agreement with results already reported by many authors (Hill, 1971; Skärby et al., 1981; Johansson, 1987; Hanson et al., 1989; Rondón et al., 1993). NO_2 compensation points were

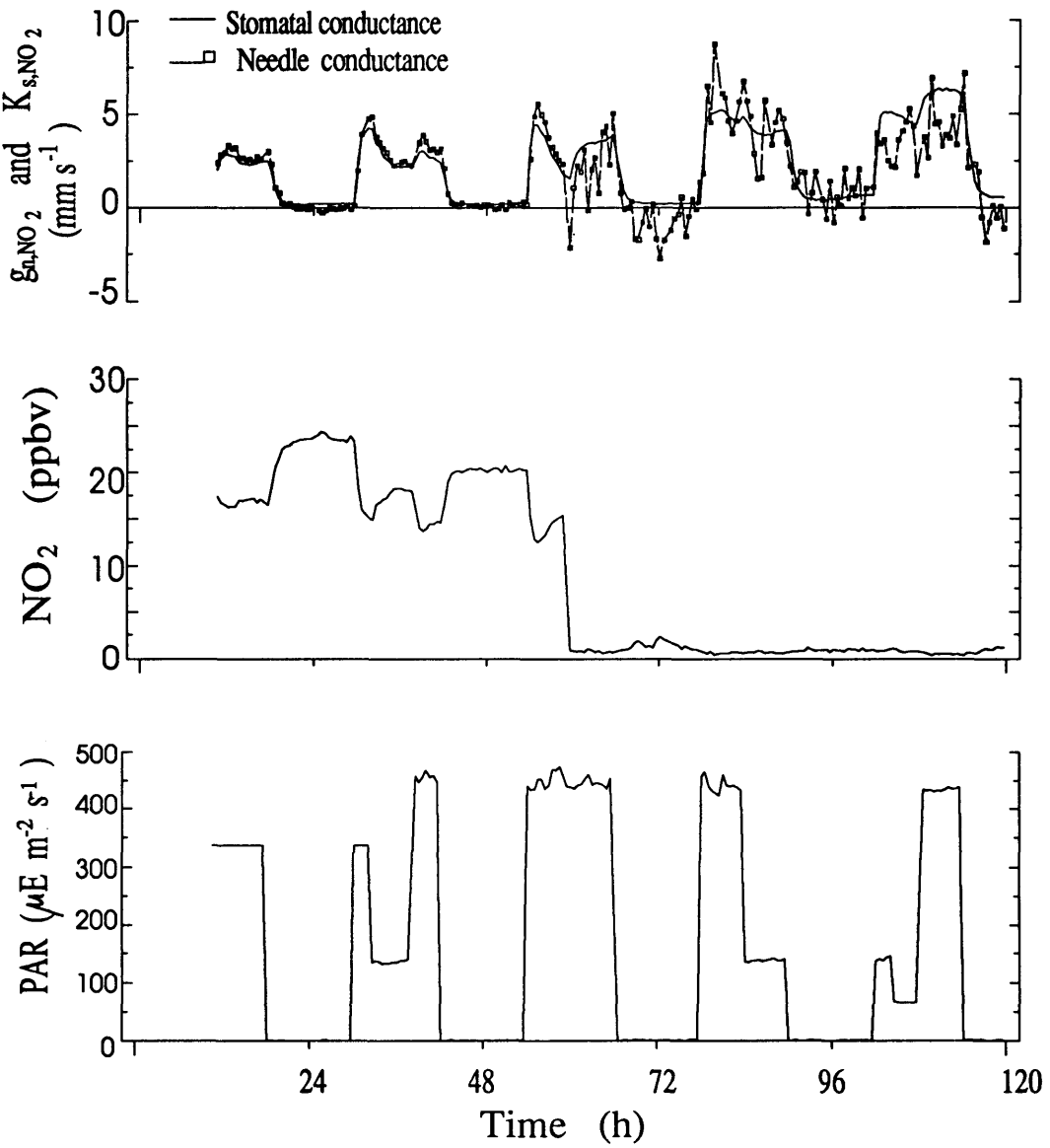

Fig. 5. Variation of NO_2 needle conductance and stomatal conductance referred to projected needle area for one Scots pine seedling exposed to several NO_2 concentrations at different PAR intensities.

derived for the studied species from the linear regression analysis of NO_2 flux versus NO_2 concentration, and correspond to the x-intercept at NO_2 flux equal to zero. The values are summarized in Table 2. They vary from <0.1 to 0.3 ppbv for pine and from <0.1 to 0.6 ppbv for spruce, which are comparable with the values derived in southern Sweden for Scots pine and Norway spruce (Rondón et al., 1993) but lower than the ones measured for Scots pine in central Sweden (Johansson, 1987; Rondón et al., 1993).

In terms of the rôle of vegetation as sink for atmospheric NO_2, one can say from the results presented here and those reported for southern

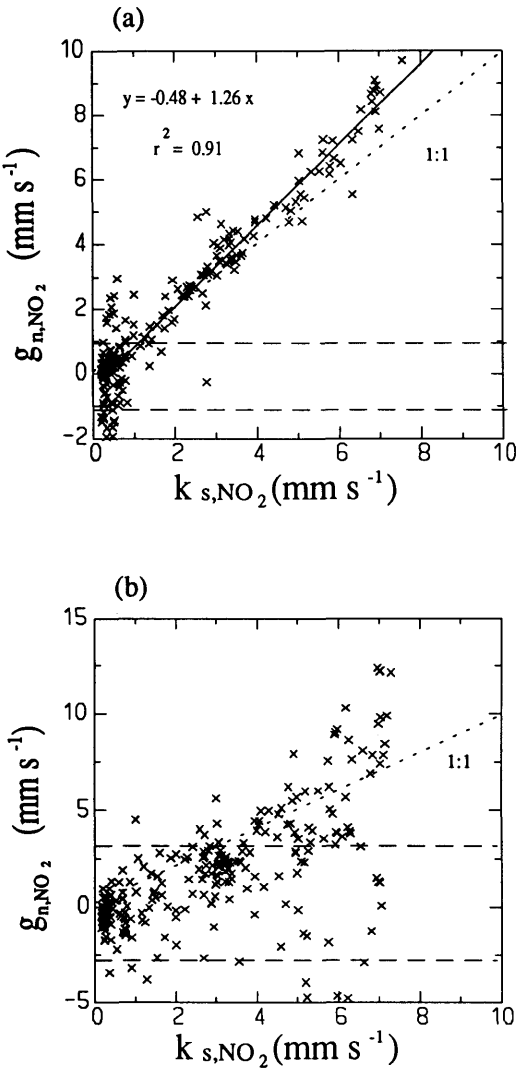

Fig. 6. Relation between NO_2 needle conductance and stomatal conductance per projected needle area for Scots pine at different range of NO_2 concentrations. (a) 1 to 30 ppbv, (b) 0.2 to 1 ppbv. The horizontal dashed lines indicate the detection limit of the g_{n,NO_2} measurements.

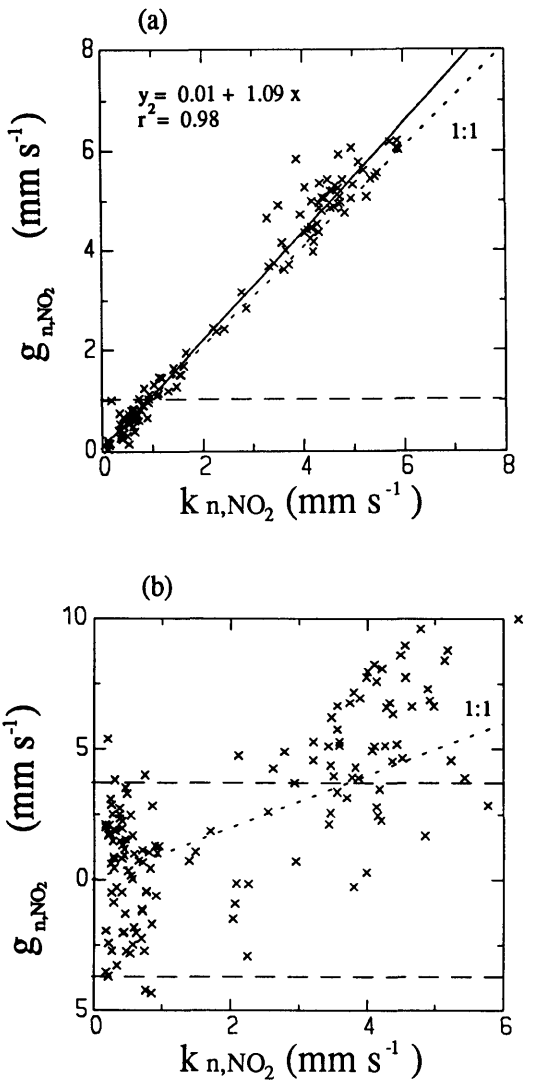

Fig. 7. Relation between NO_2 needle conductance and stomatal conductance per projected needle area for Norway spruce at different range of NO_2 concentrations. (a) 2 to 30 ppbv, (b) 0.2 to 2 ppbv. The horizontal dashed lines indicate the detection limit of the g_{n,NO_2} measurements.

Sweden by Rondon et al., 1993, that NO_2 uptake by coniferous species occurs even at sub-ppbv levels of NO_2, and that the rate of absorption can be predicted from measured or calculated values of stomatal conductance. Somewhat different results have been reported for Jädraås, central Sweden, by Johansson (1987) and Rondón et al. (1993), and laboratory experiments carried out by Thoene et al. (1991). In general, they reported that NO_2 uptake rate by coniferous species is smaller than the flux expected from calculated values of stomatal conductance. At air concentrations below 1–5 ppbv no uptake of NO_2 was measured. It is not clear what are the reason for the differences

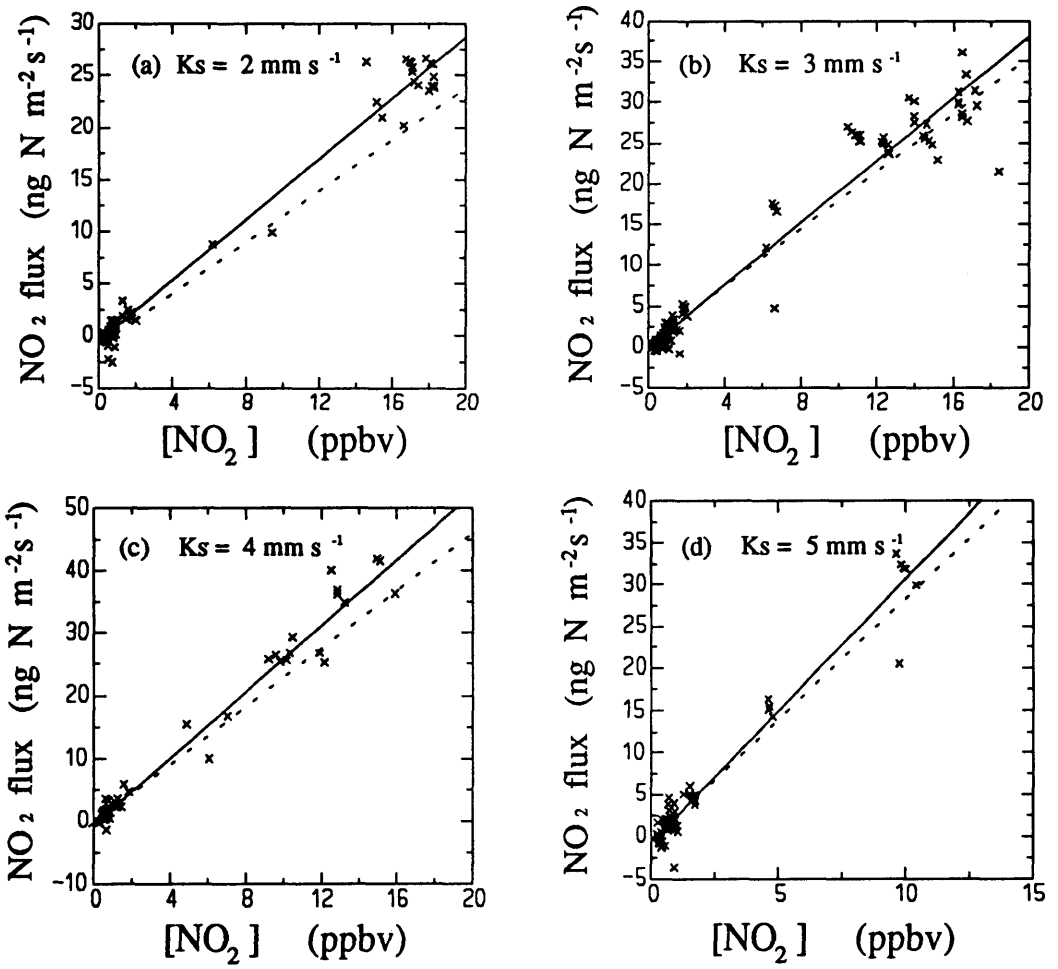

Fig. 8. The potential stomatal and measured fluxes of NO_2 for Scots pine as function of concentration for narrow ranges of stomatal conductance (value ± 0.5 mm s^{-1}). The potential flux is indicated by the dashed line and the measured flux by the data points and the linear regression line.

Table 2. *NO_2 compensation points (ppbv) as obtained from a regression analysis of the NO_2 uptake rate versus concentration for narrow ranges of stomatal conductances (see Figs. 8, 9)*

k_{s,NO_2} range (mm s^{-1})	Norway spruce	Scots pine
2 ± 0.5	0.6[a)]	0.3
3 ± 0.5	<0.1	<0.1
4 ± 0.5	<0.1	0.2
5 ± 0.5	<0.1	0.2

[a)] Different than zero at 98% confidence intervals. The rest of values are equal to zero at 99% confidence interval.

between those studies. Unidentified physiological factors might determine the capacity of plants to assimilate NO_2. These factors might in their turn be influenced by environmental conditions like for example soil nutrient levels, soil water stress and other climatic factors. Possible analytical differences may still be considered. In this work we have discarded the possibility that differences in the performance of various NO_2 converters as responsible for the observed discrepancies. Johansson (1987) has considered the possible effects of light hydrocarbons like propylene, ethylene and acetylene in the determination of NO. He concluded that these compounds do not show significant interfering

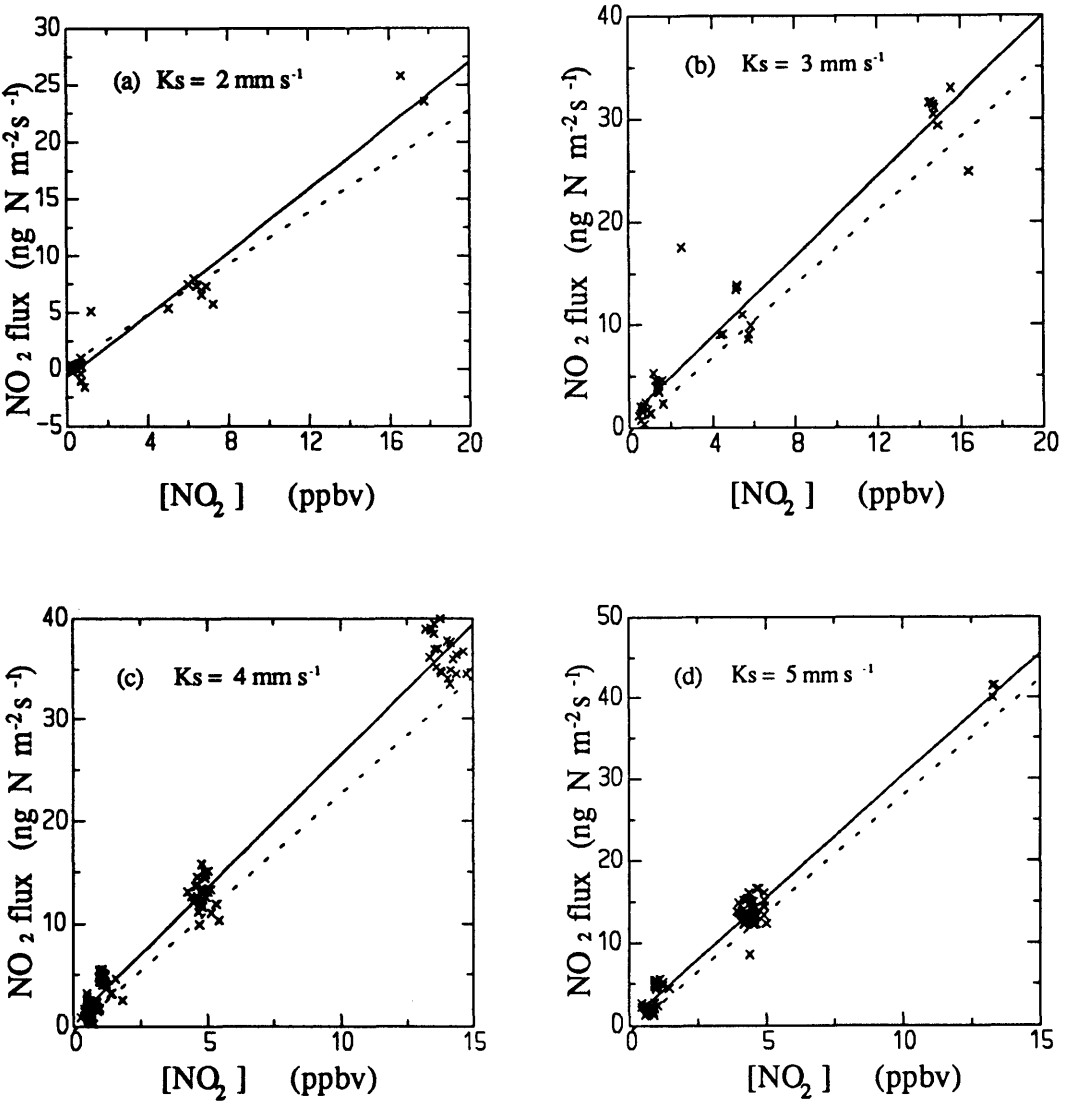

Fig. 9. The potential stomatal and measured fluxes of NO_2 for Norway spruce as function of concentration for narrow ranges of stomatal conductance (value ± 0.5 mm s^{-1}). The potential flux is indicated by the dashed line and the measured flux by the data points and the linear regression line.

effects. However, as far as we know, possible interferences from heavier unsaturated hydrocarbons (i.e., monoterpenes), due to reaction with ozone in the chamber of the NO analyzer, have not been evaluated. Further research is needed to explain the reason for the discrepancies observed between the different studies of NO_2 deposition at low concentrations.

3.4. Nitrate reductase activity and NO_2 uptake

Nitrate reductase activity (NRA) was determined in samples of one year old needles during a period of 12 days. In total, five determinations of quadruplicate samples from each species and group were made during this experiment. The idea was see if changes in the range of NO_2 concentra-

Table 3. *Nitrate reductase activity [nmol NO_2^- (g fresh weight)$^{-1}$ h^{-1} ± standard deviation] in one-year old needles of Norway spruce and Scots pine*

Date	Norway spruce		Scots pine	
	clean chamber	NO_2 chamber	clean chamber	NO_2 chamber
27 June	64 ± 56	155 ± 73	503 ± 208	436 ± 188
1 July	83 ± 75	5 ± 3	228 ± 98	454 ± 175
3 July	29 ± 18	9 ± 13	243 ± 126	281 ± 115
5 July	78 ± 86	16 ± 17	135 ± 72	391 ± 87
8 July	29 ± 26	33 ± 43	318 ± 80	299 ± 80

Plants in the clean chamber (chamber 1) were exposed to NO_2 air concentrations lower than 0.2 ppbv and plants in the NO_2 chamber (chamber 2) were subjected to an increasing NO_2 concentrations in the range from 0.2 to 1 ppbv. Each value is the average from 4 different plants.

tions typically found in Scandinavian forests would produce variations in NRA. The results are shown in Table 3. Air concentrations of NO_2 in chamber 1 were always lower than 0.2 ppbv. Mean NO_2 concentrations in chamber 2 (varying NO_2 concentrations) varied from 0.2 to 0.4 ppbv between 27 June and 1 July and from 0.4 to 1 ppbv between 1 and 8 July. There was a large variability in NRA between plants of the same species and subjected to the same treatment, which is illustrated by the high values of the standard deviations. NRA for Scots pine was always much higher than for Norway spruce. However, we did not find differences between the two species in the relation between NO_2 needle conductance and stomatal conductance nor in the magnitude of these variables. This may indicate that NRA is not a determinant factor in controlling NO_2 uptake, and thus, NO_2 assimilation by plants should involve other important biochemical reactions. No systematic variation in the NRA levels was observed over the time period of the experiments for the two species. They varied randomly with a minor tendency to decrease with time. These preliminary results suggest that, contrary to observations of induced NRA by fumigation at relatively high NO_2 concentrations (Wingsle et al., 1987; Thoene et al., 1991), it is difficult to induce NRA by varying NO_2 in the range of concentrations relevant for most rural ecosystems in Scandinavia.

4. Conclusions

The results found in this work during measurements of the exchange of NO_2 between the air and seedlings of Scots pine and Norway spruce have shown that:

(i) the relationship between NO_2 needle conductance and stomatal conductance was found to be close to 1:1 at NO_2 concentrations above 1 ppbv, and show a variability of the same order as the analytical precision between 0.2 and 1 ppbv;

(ii) internal resistance to NO_2 uptake was not observed;

(iii) the compensation points were very low, generally less than 0.2 ppbv;

(iv) the NO_2 deposition to the external surfaces of the needles and to the bark was a minor fraction of the total deposition.

It can be concluded from the above that dry deposition of NO_2 to seedlings of Scots pine and Norway spruce, at NO_2 concentrations above 1 ppbv, is controlled by the stomatal conductance. If these results are representative for field conditions of large forested areas, it may be possible to make an acceptable estimate of the surface resistance to NO_2 uptake by calculations based on canopy stomatal conductance.

5. Acknowledgements

We are grateful to Leif Bäcklin for his valuable assistance during the measurements. Thanks are due to Dr. Christer Johansson and Professor Henning Rodhe for their suggestions and constructive criticism during the experiments and preparation of this paper. Special thanks to Dr. Robert Janson for many helpful discussions.

Thanks are also due to Dr. Jan-Erik Hällgren for helping us during the planning stage of the experiments and for his support with some important instrumentation. We also want to thank Berit Bergström for her help with the analysis of NRA. This work was supported by the National Swedish Environmental Protection Board, under contract 5620301-1.

REFERENCES

Bengtson, C., Grennfelt, P., Boström, C.-Å., Troeng, E., Skärby, L., Sjödin, Å. and Petersson, K. 1982. Deposition and uptake of nitrogen oxides in Scots pine needles (*Pinus sylvestris L.*). *Report IVL-B 647.* Institute for Water and Air Pollution Research, Gothenburg, Sweden.

Dickerson, R. R. 1984. Measurements of reactive nitrogen compounds in the free troposphere. *Atmos. Environ.* **18**, 2585–2594.

Fowler, D., Cape, J. N. and Unsworth, M. H. 1989. Deposition of atmospheric pollutants on forests. *Phil. Trans. R. Soc. Lond.* **B324**, 247–265.

Granat, L. and Hällgren, J.-E. 1992. Relation between estimated dry deposition and throughfall in a coniferous forest exposed to controlled levels of SO_2 and NO_2. *Environ. Pollut.* **75**, 237–242.

Gregory, G. L. et al. 1990. An intercomparison of airborne nitrogen dioxide instruments. *J. Geophys. Res.* **95D**, 10103–10127.

Hanson, P. J. and Garten, C. T. 1992. Deposition of $H^{15}NO_3$ vapour to white oak, rep maple and loblolly pine foliage: experimental observations and a generalized model. *The New Phytologist* **122**, 329–337.

Hanson, P. J., Rott, K., Taylor, G. E., Jr., Gunderson, C. A., Lindberg, S. E. and Ross-Todd, B. M. 1989. NO_2 deposition to elements representative of a forest landscape. *Atmos. Environ.* **23**, 1783–1794.

Hill, C. 1971. Vegetation: a sink for atmospheric pollutants. *J. of the Air Pollut. Control Ass.* **21**, 341–346.

Johansson, C. 1987. Pine Forest: a negligible sink for atmospheric NO_x in rural Sweden. *Tellus* **39B**, 426–438.

Ramge, P., Badeck, F.-W., Plöchl, M. and Kohlmaier, G. H. 1992. Elimination reactions of nitrogen dioxide in leaf tissues. In: *Field measurements and interpretation of species related to photo-oxidants and acid deposition* (eds. G. Angeletti et al.). Air Pollution Research Report 39. Commission of the European communities, Brussels, 311–318.

Rondón, A., Johansson, C. and Granat, L. 1993. Dry deposition of nitrogen dioxide and ozone to coniferous forests. *J. Geophys. Res.* **98D**, 5159–5172.

Rondón, A. 1993. *Atmosphere-surface exchange of nitrogen oxides and ozone.* Ph.D. Thesis, Department of Meteorology, Stockholm University, Sweden.

Skärby, L., Bengtson, C., Boström, C.-Å., Grennfelt, P. and Troeng, E. 1981. Uptake of NO_x in Scots pine. *Silva Fennica* **15**, 396–398.

Thoene, B., Schröder, P., Papen, H., Egger, A. and Rennenberg, H. 1991. Absorption of atmospheric NO_2 by spruce (*Picea abies* L. Karst.) trees. I. NO_2 influx and its correlation with nitrate reduction. *New Phytol.* **117**, 575–585.

Wesely, M., Eastman, J., Stedman, D. and Yalvac, E. 1982. An eddy correlation measurement of NO_2 flux to vegetation and comparison with O_3 flux. *Atmos. Environ.* **16**, 815–820.

Wingsle, G., Näsholm, T., Lundmark, T. and Ericsson, A. 1987. Induction of nitrate reductase in needles of Scots pine seedlings by NO_x and NO_3^-. *Physiol. Plantarum* **70**, 399–403.