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Field investigations of nitrogen dioxide (NO$_2$) exchange between plants and the atmosphere

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Abstract. The nitrogen dioxide (NO$_2$) exchange between the atmosphere and needles of *Picea abies* L. (Norway Spruce) was studied under uncontrolled field conditions using a dynamic chamber system. This system allows measurements of the flux density of the reactive NO-NO$_2$-O$_3$ triad and additionally of the non-reactive trace gases CO$_2$ and H$_2$O. For the NO$_2$ detection a highly NO$_2$ specific blue light converter was used, which was coupled to chemiluminescence detection of the photolysis product NO. This NO$_2$ converter excludes known interferences with other nitrogen compounds, which occur by using more unspecific NO$_2$ converters. Photo-chemical reactions of NO, NO$_2$, and O$_3$ inside the dynamic chamber were considered for the determination of NO$_2$ flux densities, NO$_2$ deposition velocities, as well as NO$_2$ compensation point concentrations. The calculations are based on a bi-variate weighted linear regression analysis (y- and x-errors considered). The NO$_2$ deposition velocities for spruce, based on projected needle area, ranged between 0.07 and 0.42 mm s^{-1}. The calculated NO$_2$ compensation point concentrations ranged from 2.4 ± 9.63 to 29.0 ± 16.30 nmol m^{-3} (0.05–0.65 ppb) but the compensation point concentrations were all not significant in terms of compensation point concentration is unequal to zero. These data challenge the existence of a NO$_2$ compensation point concentration for spruce. Our study resulted in lower values of NO$_2$ gas exchange flux densities, NO$_2$ deposition velocities and NO$_2$ compensation point concentrations in comparison to most previous studies. It is essential to use a more specific NO$_2$ analyzer than used in previous studies and to consider photo-chemical reactions between NO, NO$_2$, and O$_3$ inside the chamber.

1 Introduction

Nitrogen is an essential nutrient for all living organisms. Atmospheric N$_2$ is made available by biological fixation by procaryotic microorganisms delivering amino acids and ammonia, both of which can be taken up by higher plants. However, most of the nitrogen taken up by higher vegetation is introduced by nitrification performed by other groups of microorganisms which oxidize ammonia and deliver nitrate (NO$_3^-$) which is taken up by plant roots. Nitrate can also be reduced again to N$_2$ by microbial denitrification. In the course of both nitrification and denitrification, nitrogen monoxide (NO) can be released, oxidized to nitrogen dioxide (NO$_2$) and contribute to the atmospheric pool of these two nitrogen oxides, also termed NO$_x$ (Williams et al., 1992; Robertson and Groffman, 2007). NO and NO$_2$ are highly reactive trace gases in the atmosphere which influence its oxidation processes, the generation and destruction of ozone (O$_3$), and thus the atmospheric lifetime of various less reactive greenhouse gases. Both, NO and NO$_2$ are also produced by anthropogenic activities such as fossil fuel combustion, and they can be oxidized to nitrate and to nitric acid which is returned to the Earth's surface by dry and wet deposition. In the atmosphere, NO, NO$_2$, and O$_3$ are in a photostationary equilibrium, referred to as the NO-NO$_2$-O$_3$ triad (Seinfeld and Pandis, 2006).

In addition to the root uptake of NO$_3^-$, atmospheric NO$_2$ uptake may occur directly via plant stomata (Hanson et al., 1989; Hanson and Lindberg, 1991; Rondón et al., 1993; Neubert et al., 1993; Hereid and Monson, 2001; Sparks et al., 2001; Chaparro-Suarez et al., 2011). Plant metabolic consumption of NO$_2$ has been investigated by using the [15]N

isotope as a tracer (Nussbaum et al., 1993; Weber et al., 1995; Yoneyama et al., 2003). Dissolved in the apoplastic solution, NO_2 is disproportionated to nitrate and nitrite (NO_2^-), which are reduced to ammonium (NH_4^+) by the nitrate or nitrite reductase enzymes, respectively (Lea and Miflin, 1974; Thoene et al., 1991; Ammann et al., 1995; Maeck, 1995; Sakakibara et al., 1996; Tischner, 2000). Moreover, the reduction of NO_2 by apoplastic antioxidants, particularly ascorbate, has been proposed (Ramge et al., 1993). The theoretical calculations of Ramge et al. (1993) demonstrated sufficient rates to explain observed NO_2 leaf fluxes if the reactions between water and NO_2 and between NO_2 and ascorbate are taken into account. This direct role of ascorbate in the foliar uptake of NO_2 has been experimentally demonstrated by Teklemariam and Sparks (2006). They observed a significant correlation between leaf ascorbate concentrations and the NO_2 uptake by leaves. However, differences in apoplastic ascorbate concentrations between plant species and individuals as well environmental factors must be taken into account (Polle et al., 1995; Luwe, 1996). Another source for the apoplastic NO_2 is the uptake of NO and its oxidation to NO_2 (Ghaffari et al., 2005).

The NO_2 gas exchange between plants and the atmosphere is mainly controlled by concentration gradients inside/outside the leaves, the stomatal aperture and internal leaf resistances (the aerodynamic resistance is generally much smaller, Meixner, 1994). Plant stomatal regulation is affected by climatic factors like light, temperature, and water vapor pressure deficit. Several studies have demonstrated linear relationships between NO_2 uptake, stomatal conductance and increasing atmospheric NO_2 concentration (Johansson, 1987; Thoene at al., 1991, 1996; Chaparro-Suarez et al., 2011). Despite numerous investigations, NO_2 exchange between the atmosphere and plants is still a matter of debate. Emission of NO_2 is reported urging the discussion of bi-directional exchange and a corresponding so-called "compensation point". The NO_2 compensation point concentration defines that NO_2 concentration at which the NO_2 exchange is zero (as a net balance of NO_2 uptake and NO_2 emission). When ambient NO_2 concentrations are below the compensation point for NO_2, plants act as a source for NO_2. They turn out to be a NO_2 sink when ambient concentrations exceed the NO_2 compensation point. Previous studies reported NO_2 compensation point concentrations ranging from 0.3 to 3 ppb depending on tree species (Rondón et al., 1993; Thoene et al., 1996; Weber and Rennenberg, 1996; Sparks et al., 2001; Geßler et al., 2000, 2002; Hereid and Monson, 2001). But Lerdau et al. (2000) questioned the existence of such compensation points. For example, Jacob and Wofsy (1990) showed that even at ambient NO_2 concentrations of 0.2 to 0.4 ppb a strong uptake by plants is required to align measured NO_2 concentrations in the canopy with measured NO soil emission rates. Furthermore, a recent laboratory study on five European tree species, using a highly

specific NO_2 analyzer suggested at least considerable lower compensation point concentrations, and questioned the compensation point at all (Chaparro-Suarez et al., 2011).

The aim of this study was to investigate the stomatal NO_2 uptake of spruce (*Picea abies*) in order to identify NO_2 compensation point concentrations using a dynamic chamber system and a highly NO_2 specific measuring technique. In contrast to controlled laboratory measurements, typical field conditions do not exclude chemical reactions of NO and O_3 inside the plant chamber. Therefore, NO_2, NO, and O_3 concentrations were measured simultaneously at the inlet and the outlet of the dynamic chamber to determine the chemical source strength of NO_2 (reaction between NO and O_3) as well as the chemical sink of NO_2 (photolysis of NO_2 under daylight conditions). Furthermore, as NO_2 uptake is triggered by air chemistry, transport, and plant physiology also CO_2 and H_2O exchange rates were monitored. In this paper we present the field measurements only. The laboratory measurements have been presented in a recently published paper (Breuninger et al., 2012).

2 Material and methods

NO_2 uptake of *Picea abies* L. (Norway Spruce) was studied under field conditions during an intensive observation period of the EGER project (ExchanGE processes in mountainous Regions; see Foken et al., 2012) from 1 June to 15 July 2008 using dynamic plant chambers.

2.1 Plant material and site description

The EGER project took place at the field site "Weidenbrunnen" located in northeast Bavaria, Germany (Fichtelgebirge; $50°08'31''$ N, $11°52'01''$ E; 774 m a.s.l.). The area is best described as a mountainous area, mainly covered with forest and mixed with agricultural areas including meadows and lakes. It is located in the transition zone from maritime to continental climates with some maritime impact. Mean annual temperatures are 5 °C with extreme values of −20 °C during winter and +30 °C during summer time. Mean annual precipitation is 1162 mm (1971–2000; Foken, 2003). The spruce forest ecosystem resulted from intensive reforestation in the last century. The plant cover is dominated by *Picea abies* L. (Norway Spruce). The stand has a density of 1007 ha^{-1} (Alsheimer, 1997), a mean canopy height of 23 m (Serafimovich et al., 2008), an age of 56 yr, and a leaf area index (LAI) of 5.2 (Thomas and Foken, 2007).

For the gas exchange measurements the front part of an intact spruce branch was enclosed to around 40 cm length by the dynamic chamber. Branches of two different trees were monitored at the same time. For the determination of leaf area the enclosed branches were harvested at the end of the field experiment. The needles were scanned by a calibrated scanner system (DeskSCAN II, Hewlett-Packard,

USA) using an area determining software (SIZE, Müller, Germany). The total enclosed leaf areas were 0.99 m^2 (tree 1) and 1.02 m^2 (tree 2). As stomata are distributed over the whole needle surface in the case of spruce (amphistomatic leaves) the total leaf area to be taken into account was estimated by multiplication of the projected area with the factor 2.74 (Riederer et al., 1988). During the field measurements leaf area varied with leaf flushing and was interpolated retroactively for the individual measurement periods.

2.2 Set-up

2.2.1 Dynamic chamber system

For the gas exchange measurements a dynamic chamber system was used which consisted of thin transparent Teflon film (FEP) bags (Schäfer et al., 1992; Kesselmeier et al., 1996, 1997; Kuhn et al., 2000), which transmit 90 % of the photosynthetically active radiation and 70 % of the photolysis rate $j(NO_2)$ (Schäfer et al., 1992; Breuninger et al., 2012). In order to ensure a continuous turbulent mixing of the air inside the chambers and to minimize turbulent and boundary layer resistances, Teflon coated micro-fans mounted inside the chambers were installed (Meixner et al., 1997; Pape et al., 2009; Gut et al., 2002). Details are described in Breuninger et al. (2012).

During the measurements two chambers acted as sample chambers and an identical but empty one as the reference chamber. The chambers were mounted at a height of 13 m (above ground). Additionally an inlet for sampling ambient air was installed at the same level. The chambers had an inner diameter of 40 cm, a height of 60 cm and a volume (V) of about 75 L. The air flow through the chambers (Q) was approximately 60 L min^{-1} which created a complete air exchange of the chamber within 75 s.

The reference chamber was used for the CO_2 and H_2O measurements which were made with a dual channel gas analyzer, enabling difference measurements between the sample chamber outlet and the reference. For the other trace gases we used single channel gas analyzers, so we had to measure the samples successively. The reference chamber was used to detect basic contamination in the system, adsorption/desorption, as well as to investigate gas-phase chemical reactions within the chamber volume and at the wall surface.

Photosynthetic active radiation (PAR) was measured outside the chambers with LiCor quantum sensors (model LI-190SA, LiCor, Lincoln, NE, USA). Temperature and relative humidity were monitored with combined temperature and relative humidity probes (Model MP100A, Rotronic, Switzerland). Air temperature and needle surface temperatures inside the chambers were recorded by Teflon covered thermocouples (0.005", Chromega™-Constantan, Omega, UK).

2.2.2 Trace gas analyzers

An infrared dual channel gas analyzer (LI-7000, LiCor, Lincoln, NE, USA) was used for the continuous determination of CO_2 and H_2O concentration differences between the reference and sample chambers. A second gas analyzer (LI-6262, LiCor, Lincoln, NE, USA) measured the absolute CO_2 and H_2O outside the chambers. O_3 was monitored with an UV-absorption analyzer (Model 49C, Thermo Fisher Scientific, Waltham, USA). For the detection of NO_2 we used a highly NO_2 specific blue light converter (photolytic converter, BLC) (manufactured by Droplet Measurement Technologies Inc., Colorado, USA) with subsequent chemiluminescence analysis of the generated NO (Model 42C, Thermo Fisher Scientific, Waltham, USA). The BLC converts NO_2 to NO at a wavelength of approximately 395 nm. For better accuracy and precision of the NO and NO_2 measurements the analyzer was operated with pure oxygen for the internal generation of ozone, necessary for the reaction with NO in the low pressure reaction chamber. The conversion efficiency of the BLC for NO_2 was 32–36.5 % under field conditions. The limit of detection (LOD) was defined as 3 times the standard deviation, which was obtained during zero-air measurements. Calibration was performed every seven days. The LOD for the NO concentration was 0.10 ppb and for NO_2 0.31 ppb. For more details of the analytical devices used and characterization of the dynamic plant chamber system see Breuninger et al. (2012).

As only one set of analyzers was used, their intakes were continuously switched to the corresponding inlet and outlet positions of the different dynamic chambers. The switching interval during field measurements was 4 min which resulted in four samples in a cycling time of 16 min.

2.3 Calculations

2.3.1 NO_2 exchange flux densities

The NO_2 exchange flux density F_{ex,NO_2} was calculated according to Eq. (1) based on the concentration differences between the outlet of the plant chamber (m_{s,NO_2} in nmol m^{-3}), which is equivalent to the concentration within the plant chamber provided the plant chamber's volume is well mixed by appropriate fans (Meixner et al., 1997; Pape et al., 2009), and the ingoing ambient air (m_{a,NO_2} in nmol m^{-3}), the chamber purging rate (Q in m^3 s^{-1}), and the enclosed leaf area (A_{leaf} in m^2). For the correct determination of NO_2 exchange flux densities F_{ex,NO_2}, NO_2 deposition velocities v_{dep,NO_2}, and NO_2 compensation point concentrations m_{comp,NO_2} under field conditions, photo-chemical reactions between NO, NO_2, and O_3 inside the chamber have to be considered. Relevant photo-chemical reactions are the oxidation of NO by O_3 to NO_2 and the regeneration of NO by the photolysis of NO_2 under daylight conditions. Consequently, the calculation of the photo-chemical reactions is based on the NO and

O_3 concentrations at the outlet of the plant chamber ($m_{s,NO}$ and m_{s,O_3} in nmol m^{-3}), the plant chamber's volume (V in m^3), the reaction coefficient of the NO + O_3 reaction (k in m^3 nmol^{-1} s^{-1}) (Atkinson et al., 2004), and the photolysis rate of NO_2 ($j(NO_2)$ in s^{-1}).

$$F_{ex,NO_2} = -\frac{Q}{A_{leaf}}\left(m_{a,NO_2} - m_{s,NO_2}\right.$$
$$\left. + \frac{V}{Q}k\,m_{s,NO}\,m_{s,O_3} - \frac{V}{Q}j\,(NO_2)\,m_{s,NO_2}\right) \qquad (1)$$

The dynamic chambers' mass balance equation for NO_2, which leads to the formulation of Eq. (1), is derived in Appendix A.

2.3.2 NO_2 deposition velocities and NO_2 compensation point concentrations

Deposition velocity (v_{dep,NO_2} in m s^{-1}) and compensation point concentration (m_{comp,NO_2} in nmol m^{-3}) are commonly determined from the linear relationship between F_{ex,NO_2} and m_{s,NO_2}, where v_{dep,NO_2} is the slope and m_{comp,NO_2} is the intersect of the corresponding regression line with the m_{s,NO_2}-axis. However, we decided to use the basically measured quantities, namely m_{a,NO_2} and m_{s,NO_2}, to avoid the calculation of the linear regression between F_{ex,NO_2} and m_{s,NO_2}. This is because the dependent variable F_{ex,NO_2} contains the independent variable m_{s,NO_2}. We used bi-variate weighted linear regression analysis to evaluate (graphically) the intercept (n_{NO_2}) and the slope (b_{NO_2}) of the regression line between measured m_{s,NO_2} and measured m_{a,NO_2}. However, the linear relationship between F_{ex,NO_2} and m_{s,NO_2} are still maintained:

$$F_{ex,NO_2} = \frac{\bar{Q}}{\bar{A}_{leaf}}\left(\frac{n_{NO_2}}{b_{NO_2}} - \frac{V}{\bar{Q}}\bar{k}\bar{m}_{s,NO}\bar{m}_{s,O_3}\right)$$
$$+ \frac{\bar{Q}}{\bar{A}_{leaf}}\left(1 - \frac{1}{b_{NO_2}} + \frac{V}{\bar{Q}}\bar{j}\,(NO_2)\right)\cdot m_{s,NO_2} \qquad (2)$$

The NO_2 deposition velocity (v_{dep,NO_2}) was determined by:

$$v_{dep,NO_2} = \frac{\bar{Q}}{\bar{A}_{leaf}}\left(\frac{1}{b_{NO_2}} - 1 - \frac{V}{\bar{Q}}\bar{j}\,(NO_2)\right) \qquad (3)$$

and the NO_2 compensation point concentration (m_{comp,NO_2}) by:

$$m_{comp,NO_2} = \frac{n_{NO_2} - b_{NO_2}\frac{V}{\bar{Q}}\bar{k}\bar{m}_{s,NO}\bar{m}_{s,O_3}}{1 - b_{NO_2} - b_{NO_2}\frac{V}{\bar{Q}}\bar{j}\,(NO_2)} \qquad (4)$$

where the quantities Q, A_{leaf}, $j(NO_2)$, k, m_{s,NO_2}, $m_{s,NO}$ and m_{s,O_3} with overbars represent mean values averaged over the same data set of the m_{a,NO_2} and m_{s,NO_2} measurements from which the quantities n_{NO_2} and b_{NO_2} have been derived. The derivation of Eqs. (2)–(4) are described in great detail in Breuninger et al. (2012). For the sake of completeness exchange

flux densities, deposition velocities, and compensation point concentrations of NO and O_3 are described there as well.

To decide whether or not a compensation point concentration was significant we tested the hypothesis whether or not the average of the compensation point concentration was different from zero. We applied the following limits: highly significantly ($\alpha = 0.999$), significantly ($\alpha = 0.99$), and likely ($\alpha = 0.95$). Therefore the limit for the statistical significance of $m_{comp,NO_2} \neq 0$ was greater than 95 %.

In Breuninger et al. (2012), we have simulated (random number application) the effect of different NO_2 detection limits (1.0, 0.1, and 0.01 ppb) on the minimum possible, but still highly significant NO_2 compensation point concentration considering several ambient and quality parameters (Fig. 2). For the given performance parameters of the NO/NO_2 analyzer used for this study, but otherwise optimal conditions, the minimum possible, but still highly significant NO_2 compensation point concentration would be < 0.1 ppb. Henceforth, when the term "negligible NO_2 compensation point concentration" is used, it should be understood as $m_{comp,NO_2} < 0.1$ ppb.

All trace gas concentrations were normalized for temperature and barometric pressure (0 °C, 1013.25 hPa).

2.3.3 Photosynthesis rates, transpiration rates, stomatal conductance

The CO_2 net exchange flux F_{ex,CO_2} (in µmol m^{-2} s^{-1}; photosynthetic uptake minus the simultaneously occurring respiration and photorespiration), and the transpiration rate F_{ex,H_2O} (in mmol m^{-2} s^{-1}) were calculated by use of the results of the infrared gas analyzer operated in differential mode. The calculation is based on the difference between the molar concentration at the outlets of the reference and plant chambers, the enclosed leaf area (A_{leaf}) and the chamber purging rate (Q) according to Eq. (1), but in this case without the chemical reaction terms.

The stomatal conductance for H_2O (g_{H_2O} in m s^{-1}) was calculated according to von Caemmerer and Farquhar (1981) from the transpiration rate and the humidity gradient, which is the difference between the absolute humidity inside the leaf and the absolute humidity of ambient air.

2.3.4 Standard errors of exchange flux densities, deposition velocities and compensation point concentrations

The standard errors of NO_2 exchange flux densities F_{ex,NO_2}, deposition velocities v_{dep,NO_2} and compensation point concentrations m_{comp,NO_2} were calculated by applying the generalized form of the Gaussian error propagation, which considers the dependence of all variables of the individual equation (Eqs. 1, 3 and 4) of each other (Taylor, 1982; Phillips et al., 2002). The general formulation of the standard error s_y

of a quantity $y = f(x_1, x_2, x_3, ..., x_n)$ reads as follows:

$$s_y^2 = \sum_{i=1}^{n} \left(\frac{\partial y}{\partial x_i} \cdot s_{x,i} \right)^2 + 2 \cdot \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \frac{\partial y}{\partial x_i} \cdot \frac{\partial y}{\partial x_j}$$
$$\cdot \, s_{x,i} \cdot s_{x,j} \cdot r \left(x_i ; x_j \right) \tag{5}$$

where $r(x_i; x_j)$ are the correlation coefficients between each pairs of all x_i and x_j. For a detailed listing of all error-prone variables and the derivatives of $\partial y / \partial x_i$ see Breuninger et al. (2012).

2.4 Control of plant-physiological conditions

As long-term field measurements may affect the enclosed plant parts we performed control experiments to check plant metabolic integrity. We determined the photosynthetic capacity of the enclosed spruce needles in comparison to a non-enclosed control. These measurements of in-situ CO_2 and H_2O needle gas exchange in response to temperature, radiation, CO_2 mixing ratio and relative humidity were performed with a portable gas exchange system (WALZ GFS3000, Walz, Effeltrich/Germany). Light-response curves allowed the determination of the light compensation point (I_c) and the light saturation point (I_s). Furthermore, inorganic nutrient content (calcium, potassium, magnesium, manganese, phosphorus, sulfur, carbon and nitrogen) of the control and enclosed spruce needles were measured according to validated analytical methods by the **Bay**reuth **C**enter of **E**cology and **E**nvironmental **R**esearch (BayCEER). Therefore at first all the samples were ground by a ball mill. Carbon and nitrogen were measured by a C/H/N elemental analyzer by combusting the sample in an oxygen stream at temperatures of 900 °C with subsequent measurement by a thermal conductivity detector. The other elements were measured by using inductively coupled plasma optical emission spectrometry (ICP-OES).

2.5 Significance of NO2 concentration differences

Before calculating the NO_2 exchange flux density (F_{ex,NO_2}) the difference of the gas concentrations at the inlet and the outlet of the dynamic chamber $\Delta m_{NO_2} = (m_{a,NO_2} - m_{s,NO_2})$, i.e. the major component of this calculation, was checked for significance by the application of a t-test taking into account the individual concentration measurements of m_{s,NO_2} and m_{a,NO_2} during one measurement cycle (4 min). Outliers in the data sets were identified by the Nalimov-test. Concentration differences Δm_{NO_2} with statistical significance below 99 % ($\alpha < 0.99$) were not included in subsequent calculations. During the field experiment nearly 3000 pairs of $m_{a,i}$ and $m_{s,i}$ were obtained. After applying the significance criterion and the LOD around 60 % of the NO_2 data pairs remained (see Breuninger et al., 2012).

Table 1. Overview of the ambient measurements. Parameters were measured near the dynamic plant chambers (16 m above ground within the canopy) except for global radiation, which was recorded above the canopy (31 m above ground).

|	average	range
NO, ppb	0.19 ± 0.17	0.07–2.89
NO$_2$, ppb	2.46 ± 1.42	0.42–21.49
O$_3$, ppb	47.12 ± 11.67	19.00–77.10
CO$_2$, ppm	380 ± 8	293–409
H$_2$O, ppth	13 ± 2.6	7–25
relative humidity, %	70.5 ± 17.4	31.2–99.9
temperature, °C	14.4 ± 4.5	3.8–27.7
PAR, μmol m^{-2} s^{-1}	$265 \pm 402^*$	0–1910*
global radiation, W m^{-2}	$232 \pm 276^*$	0–1005*

* Daytime only data.

3 Results

3.1 Microclimatic conditions

Ambient concentrations of NO, NO_2, O_3, CO_2, and H_2O, relative humidity and air temperature were recorded during the entire EGER experiment (Table 1). Global radiation was determined on the top of the tower (31 m above ground, 8 m above the canopy). NO concentrations were mostly near the detection limit with some sporadic peaks. The NO_2 concentration varied between 0.4 and 21.5 ppb. The diel course exhibited generally higher NO_2 concentrations at night. O_3 mixing ratios ranged between 3 and 78 ppb with a gradual decline in the morning hours. Air temperature ranged from 4 to 28 °C with a mean temperature of 14 °C.

3.2 Plant physiological conditions after long-term enclosure

Plant physiological processes such as photosynthesis and stomatal regulation can be affected by pollutants and the availability of mineral nutrition. CO_2 response and light response of CO_2 uptake are reported as quantitative measures (Selinger et al., 1986). With regard to that, an overview of the photosynthetic capacity of enclosed and control branches is given in Fig. 1. We distinguished between control (non-enclosed during the whole campaign) and enclosed branches as well as between young and older needles. The latter differentiation was made because CO_2 exchange rates may differ with needle age (Grennfelt et al., 1983; Wallin et al., 1992). The photosynthesis rates of our younger needles were around 50 % higher than the rate of the older needles. But enclosed and control needles were found to behave very similarly. The light compensation point (I_c) was in the range of 40 to 70 μmol photons m^{-2} s^{-1} and light saturation (I_s) was reached between 500 and 1100 μmol photons m^{-2} s^{-1}.
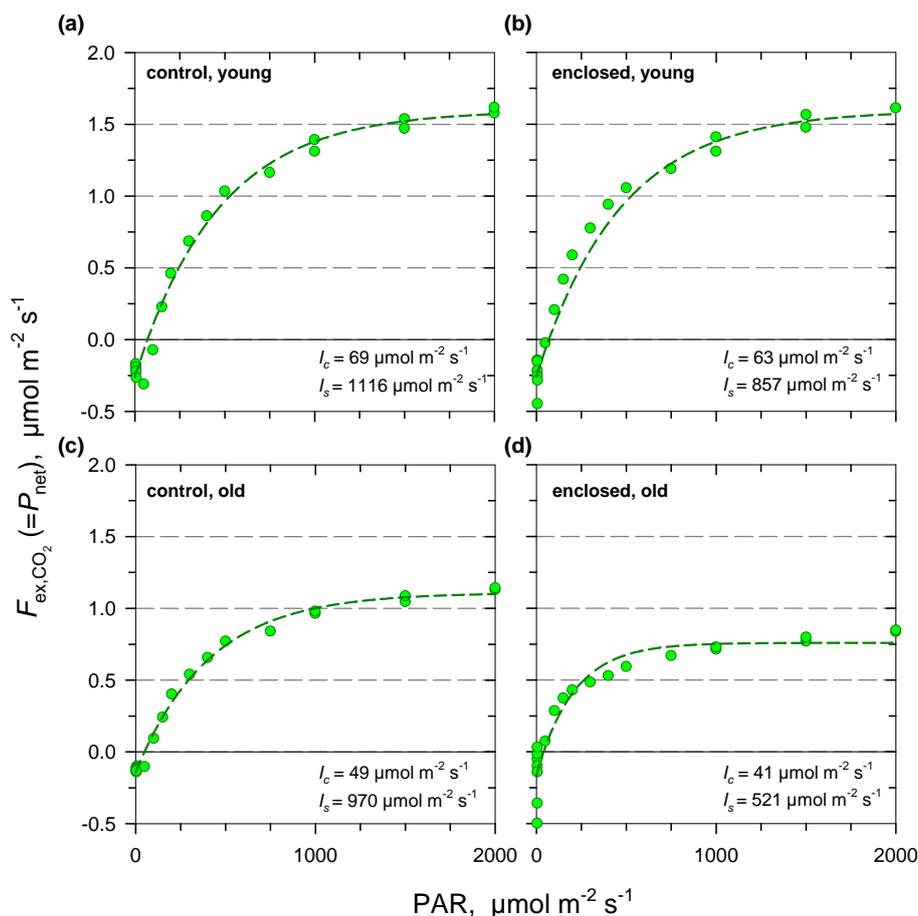
Fig. 1. Photosynthetic light response curves at ambient CO_2 concentration (370–390 ppm) of control and enclosed spruce needles. **(a)** Young control needles, **(b)** young enclosed needles, **(c)** older control needles, **(d)** older enclosed needles.

Additionally, we checked the changes of needles' nutrient content due to the enclosure. A nutrient composition analysis of our needles (total carbon and nitrate concentrations as well as calcium, magnesium, manganese, phosphate and sulfur) exhibited no substantial differences between the control and enclosed needles, except the potassium content which differed significantly between young control (6.9 mg g^{-1} dw) and enclosed needles (8.6 mg g^{-1} dw).

3.3 Overview of plant chamber measurements

An overview of the atmospheric concentrations of NO, NO_2, and O_3, as well as their exchange flux densities are reported in Table 2 together with the enclosure data of photosynthesis, transpiration, leaf conductance, light and temperature covering the entire period of the EGER field campaign. Corresponding diurnal variations of exchange flux densities of CO_2, H_2O, NO, NO_2 and O_3 for spruce (plant chamber 1) for the entire study are presented in Fig. 2. NO concentrations ($m_{s,NO}$) inside the two sample chambers were on average 0.16 ppb during the day and 0.1 ppb at night approaching the limit of detection of the analyzer

(LOD(m_{NO}) = 0.1 ppb = 4.46 nmol m^{-3}). NO_2 concentrations (m_{s,NO_2}) ranged always above the limit of detection (LOD(m_{NO_2}) = 0.31 ppb = 13.8 nmol m^{-3}) with means for day and night around 2 ppb. High concentrations were observed peaking at 17 ppb for NO_2 and at 1.8 ppb for NO caused by rush-hour traffic in the morning between 06:00 and 12:00 resulting from a public road near the site. O_3 concentrations (m_{s,O_3}) were 40 ppb on average. Both branches displayed similar photosynthesis (F_{ex,CO_2}), transpiration (F_{ex,H_2O}) as well as leaf conductances of H_2O (g_{H_2O}).

3.4 NO₂ exchange flux density, deposition velocity and compensation point concentration

Consideration of potential compensation point concentration and determination of the deposition velocity require a certain amount of data obtained under comparable plant physiological adjustments. For that, a suitable guide is the stomatal conductance for H_2O (g_{H_2O}) because this parameter gives information about the condition of the plant affected by air temperature, radiation and water vapor deficit. Furthermore, NO_2 exchange is known to be strongly regulated by stomatal

Table 2. Overview of chamber measurements for spruce (*Picea abies*). Given are mean data from 4 min average values from day and night measurements. Values in brackets present the range of data.

	plant chamber 1		plant chamber 2	
	day[a]	night	day[a]	night
$m_{s,NO}$, ppb	0.16 ± 0.12	0.10 ± 0.04	0.16 ± 0.13	0.09 ± 0.04
	(0.10[b]–1.53)	(0.10[b]–0.35)	(0.10[b]–1.75)	(0.10[b]–0.35)
$F_{ex,NO}$, nmol m^{-2} s^{-1}	−0.006 ± 0.015	0.009 ± 0.005	−0.005 ± 0.007	0.010 ± 0.004
	(−0.110–0.044)	(0.002–0.019)	(−0.026–0.090)	(0.002–0.023)
m_{s,NO_2}, ppb	2.19 ± 1.35	2.28 ± 1.31	2.13 ± 1.27	2.30 ± 0.91
	(0.73–17.19)	(0.76–12.28)	(0.77–11.91)	(0.66–7.63)
F_{ex,NO_2}, nmol m^{-2} s^{-1}	−0.011 ± 0.015	−0.014 ± 0.025	−0.019 ± 0.020	−0.013 ± 0.022
	(−0.079–0.058)	(−0.414–0.085)	(−0.341–0.045)	(−0.205–0.155)
v_{dep,NO_2}, mm s^{-1}	0.19 ± 0.11		0.24 ± 0.11	
	(0.07–0.35)		(0.14–0.42)	
m_{s,O_3}, ppb	40.80 ± 11.88	37.41 ± 8.23	40.16 ± 11.88	40.42 ± 10.80
	(17.76–72.41)	(21.31–63.41)	(15.58–72.95)	(19.41–70.27)
F_{ex,O_3}, nmol m^{-2} s^{-1}	−0.367 ± 0.174	−0.019 ± 0.316	−0.386 ± 0.156	−0.180 ± 0.123
	(−1.153–0.086)	(−0.889–0.293)	(−1.167–0.152)	(−1.141–0.255)
v_{dep,O_3}, mm s^{-1}	0.22 ± 0.11		0.20 ± 0.09	
	(0.07–0.38)		(0.06–0.32)	
F_{ex,CO_2}, µmol m^{-2} s^{-1}	−0.57 ± 0.47	0.09 ± 0.07	−0.59 ± 0.45	0.13 ± 0.07
	(−2.66–0.20)	(−0.05–0.34)	(−2.01–0.24)	(−0.77–0.52)
F_{ex,H_2O}, mmol m^{-2} s^{-1}	0.07 ± 0.06	0.01 ± 0.01	0.09 ± 0.06	0.01 ± 0.01
	(0–0.39)	(0–0.03)	(0–0.28)	(0–0.03)
g_{H_2O}, cm s^{-1}	0.03 ± 0.04	0.01 ± 0.03	0.05 ± 0.06	0.01 ± 0.014
	(0–0.54)	(0–0.07)	(0–0.83)	(0–0.17)
T_{leaf}, °C	17.9 ± 4.7	11.3 ± 2.8	18.3 ± 4.9	13.3 ± 3.3
	(6.5–38.7)	(6.3–16.7)	(6.3–33.1)	(6.3–22.4)
RH$_{out}$, %	66.7 ± 17.5	85.4 ± 11.1	66.0 ± 17.8	79.0 ± 14.2
	(32.3–99.9)	(62.5–99.9)	(32.6–99.9)	(40.3–99.9)
PAR, µmol m^{-2} s^{-1}	231 ± 273	–	255 ± 280	–
	(0–1875)	–	(0–1848)	–

[a] Daytime values were used when global radiation $> 5\,\text{W}\,\text{m}^{-2}$, [b] Limit Of Detection (LOD).

conductance (Thoene et al., 1991; Geßler et al., 2000; Teklemariam and Sparks, 2006; Chaparro-Suarez et al., 2011). Hence, our data were classified into seven g_{H_2O} classes. Table 3 lists the ambient and plant conditions of the classes for each plant chamber.

Figure 3 shows the NO_2 exchange rates F_{ex,NO_2} in relation to NO_2 concentrations (at the outlet of plant chamber 1) without classification and only filtering for (a) daytime conditions, (b) significance of NO_2 concentration differences, and (c) for concentration peaks of NO, NO_2, and O_3 from the advection from the country road near to the site (~ 1.1 km). A closer look using leaf conductance classification furthers the understanding of the exchange (Fig. 4, plant chamber 1; Fig. 5, plant chamber 2). Deposition velocity v_{dep,NO_2} and compensation point concentration m_{comp,NO_2} was determined for each class. The details of statistical evaluation for all data are listed in Table 4. The behavior of both spruce branches was highly comparable to each other. The bi-variate regression analysis of the concentrations at the dynamic chambers' inlet and the outlet (m_{a,NO_2} and m_{s,NO_2}) for spruce showed a strong correlation between m_{a,NO_2} and m_{s,NO_2}. The regression coefficient $R^2(m_{a,NO_2}, m_{s,NO_2})$ reached values between 0.8709 and 0.9951. The deposition velocity v_{dep,NO_2} derived from this analysis ranged between 0.07 and 0.42 mm s^{-1}, and was found to clearly increase with leaf conductance. Both spruce branches showed a linearly correlated increase of NO_2 uptake with increasing leaf conductance. This circumstance is presented in Fig. 6, where the calculated deposition velocities v_{dep,NO_2} were plotted against stomatal leaf conductance g_{H_2O}.

The NO_2 compensation point concentrations m_{comp,NO_2} were between 2.4 ± 9.63 and 29.0 ± 16.30 nmol m^{-3} (0.05–0.65 ppb), however, with significance probabilities for $m_{comp,NO_2} \neq 0$ ranging from 19.98 to 91.22 %.
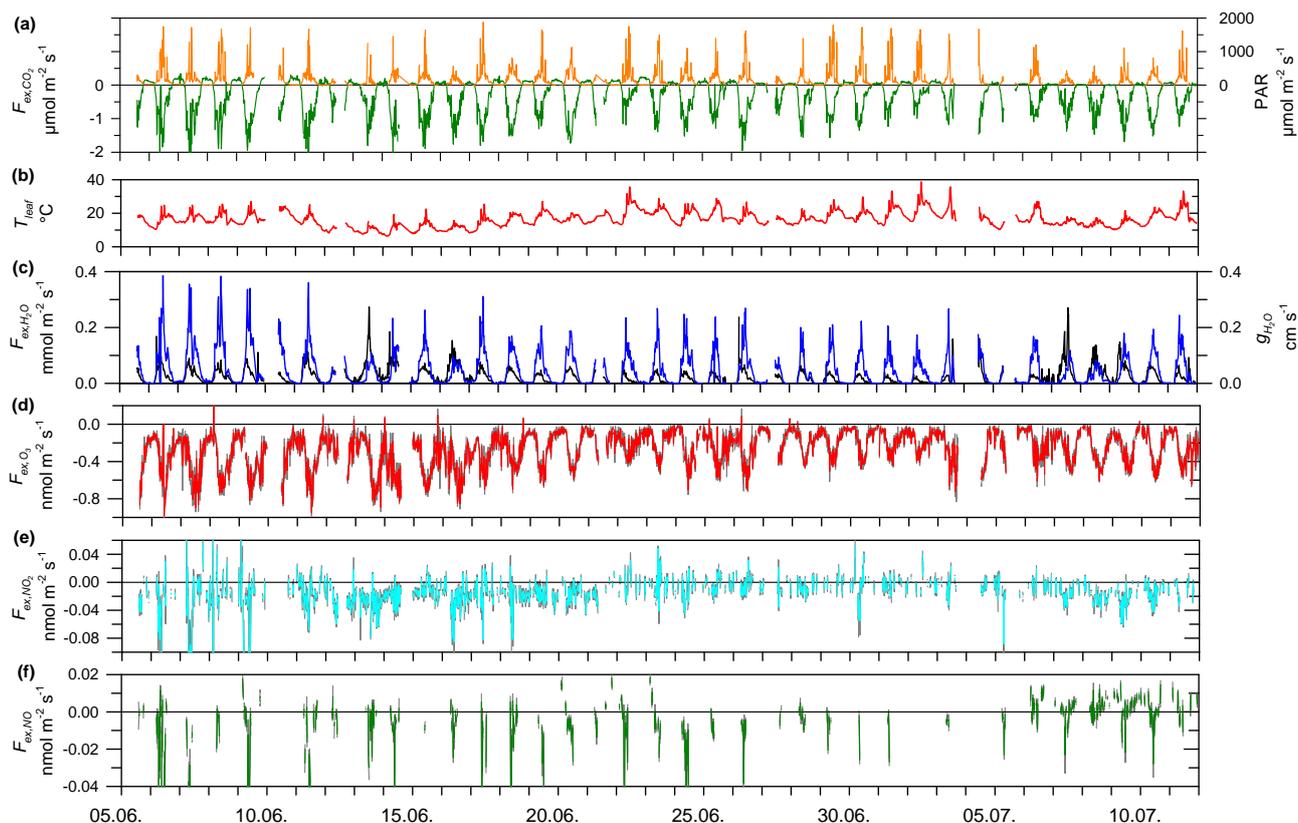
Fig. 2. Overview of exchange rates over the entire measurement period. **(a)** photosynthesis rate F_{ex,CO_2} (green line), PAR (orange line); **(b)** leaf temperature T_{leaf}; **(c)** transpiration rate F_{ex,H_2O} (blue line), leaf conductance (g_{H_2O}) (black line); **(d)** O_3 exchange flux F_{ex,O_3} (red line); **(e)** NO_2 exchange flux F_{ex,NO_2} (light blue line); **(f)** NO exchange flux $F_{ex,NO}$ (green line). F_{ex,O_3}, F_{ex,NO_2}, $F_{ex,NO}$ based on data pairs which were significant for $\Delta m_i = (m_{a,i} - m_{s,i})$ and their errors are shown as gray areas.

## 4   Discussion

4.1   Effects on enclosed plants

Application of a chamber system which encloses plants or parts of plants requires the control of plant conditions in order to be certain that observations and data are transferable and not created under unnatural conditions. It is important to make sure that the plant is not affected by the chamber, especially for long-term studies. Consequently, we controlled the status of the plants after field experiments. We could not identify visual differences between enclosed and non-enclosed plant material. Moreover, no variations in physiological performance were detectable. The photosynthetic capacities of enclosed and control needles were similar and in the same range as the results of independent measurements of photosynthetic light response curves of several spruce trees using the same gas exchange system during the same experiment period (data not shown). Also the differences of the light compensation points (I_c) and light saturation points (I_s) between enclosed and control needles were small. Our values correspond to literature values specified for sun shoots of coniferous trees under conditions of ambient CO_2

and optimal temperature ($I_c = 30$–40 µmol photons m^{-2} s^{-1}, $I_s = 800$–1000 µmol photons m^{-2} s^{-1}; Larcher, 2003).

Mineral nutrient concentrations may differ within species in relation to age and also between tissues (Bates, 1971; Foulds, 1993). Furthermore, it is known that the nutritional status influences the photochemical activity of plants (Pflüger and Mengel, 1972; Burns, 1992). For longer enclosure studies it is of interest that plant species efficiently withdraw nutrients from leaves prior to senescence (Langkamp and Dalling, 1982, 1983; Lohman et al., 1994; Buchanan-Wollaston, 1997). The analysis of the nutrient composition of the needles also showed no obvious differences, with the exception of potassium. The higher concentration of potassium was found for the young enclosed needles but the concentration was in a normal range, which is specified in the literature to be between 5 and 70 mg g^{-1} dw (Frey and Lösch, 2004). Potassium is needed during leaf development and it is responsible for the maintenance of the status of plasma swelling. A potassium deficit can be identified by tips of needles drying out and by premature shedding of needles (Larcher, 2003). Such symptoms were not observed. However, as the low concentration of potassium in the young

Table 3. Definition of the classes of leaf conductances, which were used for the classification of measured data. All displayed data are mean values. Leaf conductances (g_{H_2O}) are listed once calculated on basis of projected leaf area and once on total leaf surface area.

	class		1	2	3	4	5	6	7
	g_{H_2O} projected A_{leaf}	cm s^{-1}	0.01–0.025	0.025–0.06	0.06–0.08	0.08–0.1	0.1–0.13	0.13–0.16	0.16–1.0
	g_{H_2O} total A_{leaf}	cm s^{-1}	0.004–0.01	0.01–0.02	0.02–0.03	0.03–0.04	0.04–0.05	0.05–0.06	0.06–0.4
plant chamber 1	PAR	μmol m^{-2} s^{-1}	130 ± 261	200 ± 334	253 ± 311	279 ± 300	297 ± 312	355 ± 335	319 ± 365
	T_{air}	°C	18.8 ± 4.9	16.8 ± 4.9	16.5 ± 4.2	15.7 ± 3.7	14.3 ± 3.8	13.9 ± 3.6	12.0 ± 3.4
	RH	%	54 ± 17	64 ± 18	64 ± 16	67 ± 14	69 ± 14	70 ± 13	80 ± 14
	F_{ex,CO_2}	μmol m^{-2} s^{-1}	−0.15 ± 0.12	−0.37 ± 0.22	−0.62 ± 0.26	−0.74 ± 0.31	−0.86 ± 0.37	−1.02 ± 0.42	−1.05 ± 0.46
	F_{ex,H_2O}	mmol m^{-2} s^{-1}	0.03 ± 0.02	0.05 ± 0.04	0.08 ± 0.05	0.09 ± 0.05	0.10 ± 0.06	0.11 ± 0.07	0.09 ± 0.08
plant chamber 2	PAR	μmol m^{-2} s^{-1}	51 ± 158	157 ± 251	279 ± 353	336 ± 387	278 ± 290	320 ± 307	322 ± 329
	T_{air}	°C	16.9 ± 4.7	17.4 ± 5.1	17.4 ± 4.7	16.8 ± 4.2	15.8 ± 3.9	14.6 ± 3.7	12.6 ± 3.5
	RH	%	63 ± 19	61 ± 19	59 ± 17	61 ± 16	66 ± 14	69 ± 14	77 ± 16
	F_{ex,CO_2}	μmol m^{-2} s^{-1}	−0.03 ± 0.11	−0.25 ± 0.22	−0.53 ± 0.26	−0.67 ± 0.31	−0.77 ± 0.31	−0.88 ± 0.36	−0.98 ± 0.42
	F_{ex,H_2O}	mmol m^{-2} s^{-1}	0.02 ± 0.02	0.06 ± 0.05	0.10 ± 0.06	0.11 ± 0.07	0.11 ± 0.06	0.11 ± 0.06	0.09 ± 0.06
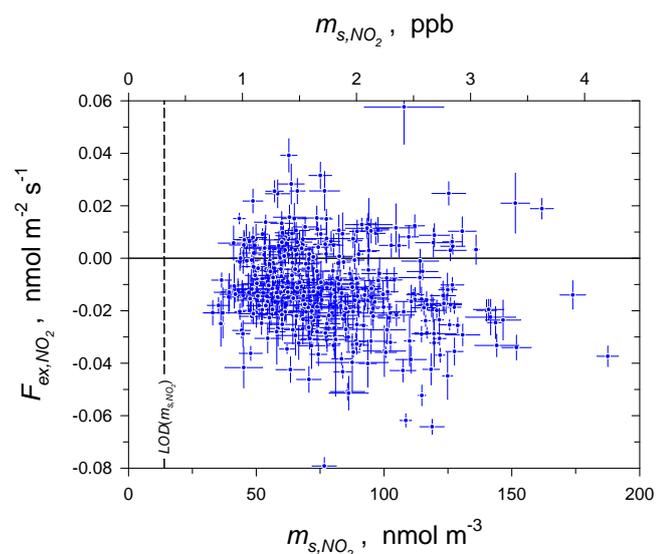
Fig. 3. NO$_2$ exchange flux density (F_{ex,NO_2}) vs. NO$_2$ concentration measured at the outlet of the dynamic plant chamber (m_{s,NO_2}) of *Picea abies* 1 over the entire measuring period. Data were filtered for daytime conditions, period of possible advection and significance of $\Delta m_{NO_2} = (m_{a,NO_2} - m_{s,NO_2})$. F_{ex,NO_2} were calculated according to Eq. (1), their standard errors according to Eq. (7).

needles did not reach potassium deficiency (Pflüger and Mengel, 1972; Sieghardt, 1988; Larcher, 2003), we do not consider these differences as a sign of a harmful effect of the chamber.

In summary our data sets give good reason to assume that the enclosed branches were not harmed by the chambers.

4.2 NO$_2$ exchange with leaves

Under field conditions an increase in NO$_2$ uptake was found in relation to increasing NO$_2$ concentrations. This agrees with previous studies (Rondón et al., 1993; Thoene et al., 1991; Weber and Rennenberg, 1996; Geßler et al., 2002; Chaparro-Suarez, 2011) and confirms the assumption that NO$_2$ exchange is driven by the NO$_2$ concentration difference between atmosphere and the gaseous phase of the leaf interior. Up to now, NO$_2$ emission has been found only at (very) low atmospheric NO$_2$ concentrations. NO$_2$ emissions have been measured in several studies. Teklemariam and Sparks (2006) reported emissions from four species (wheat, corn, sunflower, and Madagascar periwinkle) that ranged between 36.8 and 101.0 pmol m^{-2} s^{-1}. Sparks et al. (2001) observed NO$_2$ emissions up to 50 pmol m^{-2} s^{-1} from several tropical trees and Hereid and Monson (2001) from field-grown corn. NO$_2$ emissions from spruce needles were reported by Rondón et al. (1993) and Geßler et al. (2002). In the present study the significant leaf emission of NO$_2$ from spruces varied between 0.07 and 58 pmol m^{-2} s^{-1}. However, the emissions were very low compared to the NO$_2$ exchange flux densities. Furthermore, the released NO$_2$ may represent a release from the leaf surface instead of being an emission from inside the leaves. Evidence for this is given by the separation and classification of the NO$_2$ exchange flux densities for leaf conductance (see Figs. 4 and 5). It became apparent that at higher classes (i.e. higher leaf conductance) the NO$_2$ emission decreased and the compensation point concentration declined.

Deposition fluxes of NO$_2$ observed in our field study for spruce varied between −0.078 and −0.018 nmol m^{-2} s^{-1}. These fluxes are much lower than NO$_2$ deposition fluxes reported by Thoene et al. (1996) of 1.88 to 0.03 nmol m^{-2} s^{-1}
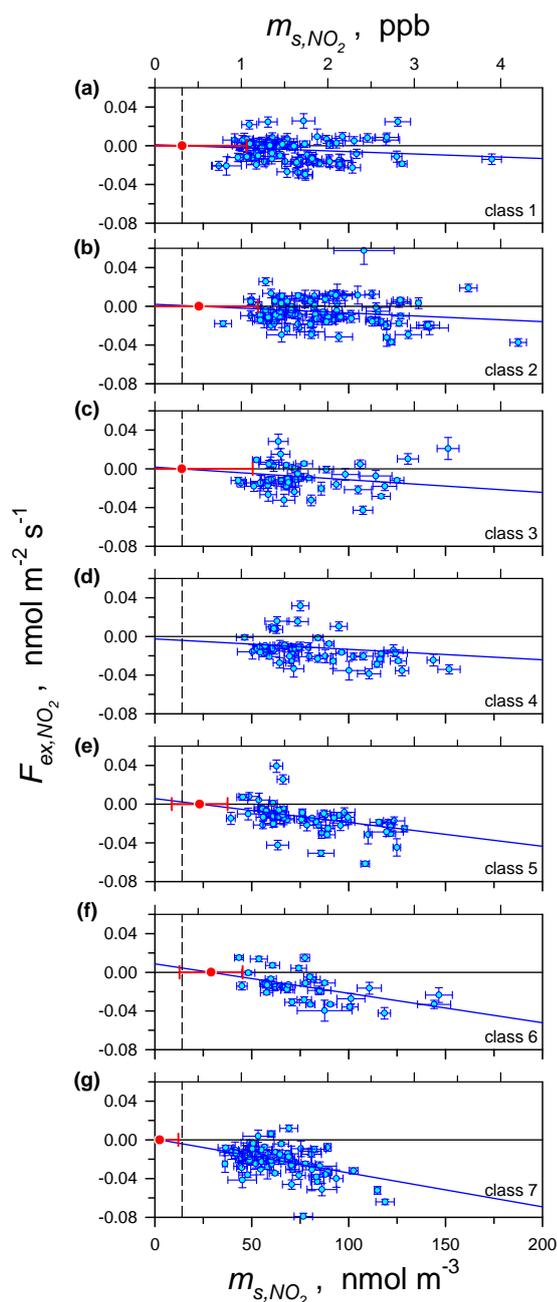
Fig. 4. NO$_2$ exchange flux densities ($F_{\mathrm{ex,NO_2}}$) of *Picea abies* 1 at various NO$_2$ concentrations measured at the outlet of the dynamic plant chamber ($m_{\mathrm{s,NO_2}}$). Data were filtered for daytime conditions and periods of possible advection. Only data pairs whose difference of NO$_2$ concentrations at the inlet and outlet of the dynamic plant chamber was statistically significant $\Delta m_{\mathrm{NO_2}} = (m_{\mathrm{a,NO_2}} - m_{\mathrm{s,NO_2}})$ were applied. Data were separated and classified for leaf conductance (class 1–7, **a–g**). NO$_2$ compensation point concentration ($m_{\mathrm{comp,NO_2}}$) is represented by red filled circle. Blue line is calculated according to Eq. (2) and represents $v_{\mathrm{dep,NO_2}}$. Dashed line indicates the limit of detection (3σ-definition) for NO$_2$ concentration measurements.
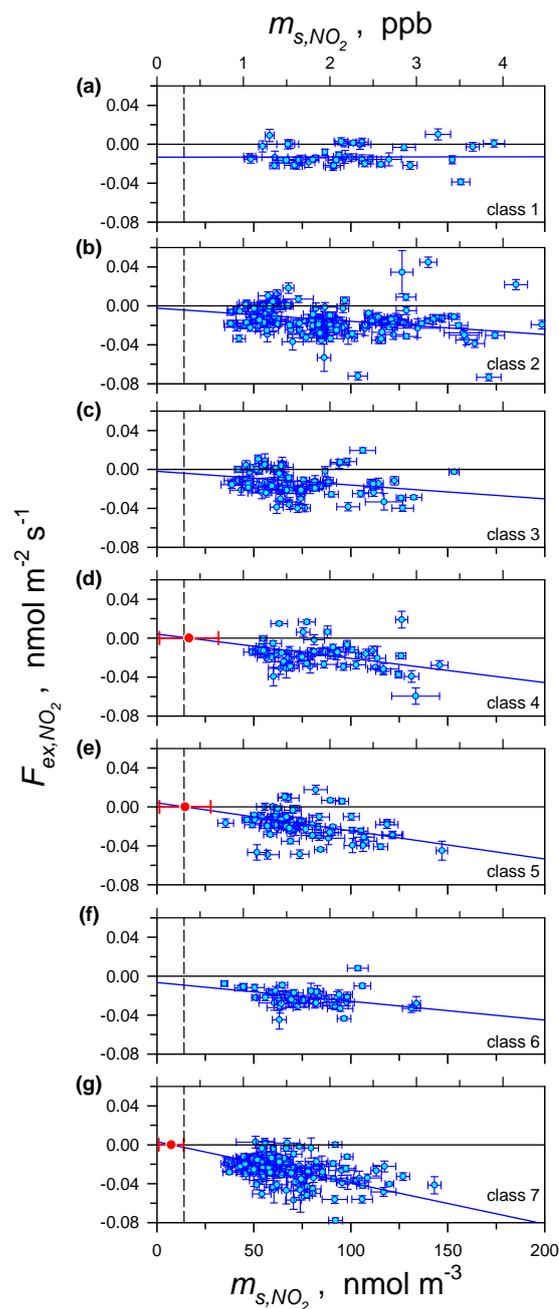
Fig. 5. NO$_2$ exchange flux densities ($F_{\mathrm{ex,NO_2}}$) of *Picea abies* 2 at various NO$_2$ concentrations measured at the outlet of the dynamic plant chamber ($m_{\mathrm{s,NO_2}}$). Data were filtered for day time conditions and period of possible advection. Only data pairs whose difference of NO$_2$ concentrations at the inlet and outlet of the dynamic plant chamber was statistical significant $\Delta m_{\mathrm{NO_2}} = (m_{\mathrm{a,NO_2}} - m_{\mathrm{s,NO_2}})$ were applied. Data were separated and classified for leaf conductance (class 1–7, **a–g**). NO$_2$ compensation point concentration ($m_{\mathrm{comp,NO_2}}$) is represented by red filled circle. Blue line is calculated according to Eq. (2) and represents $v_{\mathrm{dep,NO_2}}$. Dashed line indicates the limit of detection (3σ-definition) for NO$_2$ concentration measurements.
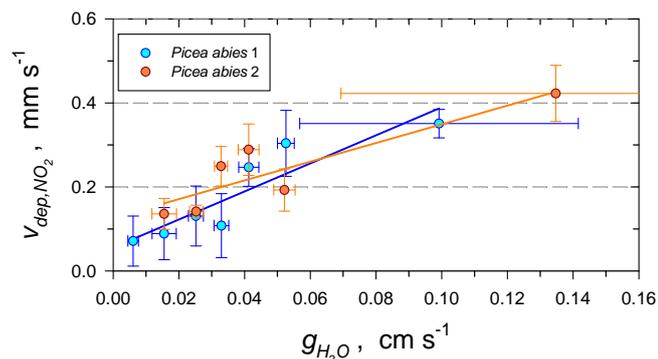
Fig. 6. NO_2 deposition velocities (v_{dep,NO_2}) in relationship to the stomatal leaf conductance (g_{H_2O}). Deposition velocities were determined for each class of leaf conductance (see Sect. 3.4) therefore v_{dep,NO_2} represents averages for these data sets.

for spruce, or by Sparks et al. (2001) of 1.55 to 0.15 nmol m^{-2} s^{-1} for several tropical trees. These discrepancies to our values might be related to different detection techniques for NO_2. Thoene et al. (1996) used a non-specific molybdenum converter for NO_2, while Sparks et al. (2001) used a liquid phase chemiluminescence detector (luminol reaction). Both techniques interfere with other oxidized nitrogen compounds. Our data are based on the use of a blue light converter, which is highly specific for NO_2 measurements. Very similar deposition fluxes of up to 0.3 nmol m^{-2} s^{-1} (at 5 ppb) were reported for five European tree species (*Betula pendula*, *Fagus sylvatica*, *Quercus robur*, *Quercus ilex*, *Pinus sylvestris)* by Chaparro-Suarez et al. (2011) using a different photolytic converter (PLC 762, Ecophysics, Switzerland). Furthermore, our data are in close accordance with NO_2 deposition fluxes reported by Geßler et al. (2002), ranging between 0.12 and 0.02 nmol m^{-2} s^{-1}, also using an Ecophysics photolytic converter. Thus, discrepancies reported in the literature may be understood to be caused by the use of insufficiently specific NO_2-detection techniques. However, it might be discussed, whether or not those measurements which have used either non-photolytic converters (molybdenum or ferrous sulphate) or the luminol technique are just measurement artefacts or reflect additional (extra?) fluxes of PAN, HONO, HNO$_3$, ethyl nitrite, and ethyl-, methyl-, n-propyl-, and n-butyl nitrate. All of these compounds generate positive interferences to the detection of NO_2, partly up to 100 % (see Table 2 in Breuninger et al, 2012). Therefore, if those compounds may be actually emitted from vegetation elements, either biologically or by surface (catalytic) reactions, then those measurements would be (a) an indication of additional N-fluxes (hard to quantify), but (b) would fake enhanced NO_2 compensation point concentrations.

4.3 Deposition velocities of NO_2

NO_2 deposition velocities exhibited values between 0.07 and 0.42 mm s^{-1} for spruce. These values were in accordance with the lowest values reported up to now of 0.09 mm s^{-1} for spruce under controlled field conditions (Geßler et al., 2002). In contrast, Thoene et al. (1991, 1996) described values ranging from 0.4 to 0.9 mm s^{-1} for laboratory measurements. Rondón et al. (1993) reported even much higher values from 1.8 to 2.1 mm s^{-1}.

As indicated in the previous section, differences between the data of our study and those of previous studies are most likely due to non-specific NO_2 analyzers applied in the previous studies. Furthermore, discrepancies may also be due to the fact that some authors have neglected gas-phase reactions in the dynamic chambers all together, some excluded them by using corresponding set-ups, and some tried to compensate them by application of an empty chamber ("reference chamber") (Rondón et al., 1993; Geßler et al., 2000, 2002; Hereid and Monson, 2001; Sparks et al., 2001; Raivonen et al., 2009). Furthermore, different deposition velocities at leaf level may be related to different ages of the enclosed plant material. Grennfelt et al. (1983) reported higher deposition velocities for 1-yr-old needles compared to current year needles. Unfortunately, studies about gas exchange differences depending on needle age are very rare.

Many of the reported NO_2 deposition velocities have been obtained by micrometeorological measurements (aerodynamic gradient or eddy covariance; corresponding data for NO_2 deposition velocity, for both foliar and non-foliar sites, refer usually to the projected (soil) area. However, those measurements generally do not consider gas exchange with the soil, surface reactions on soil and vegetation elements, and reactions with radicals. For example reactions with VOCs (emitted from plants) are involved, though not taken into account. NO_2 deposition velocities (projected soil area) of 0.35 mm s^{-1} are reported by Pilegaard et al. (1998) for wheat fields, and 2 to 6 mm s^{-1} for a fruit orchard by Walton et al. (1997). Monthly mean values (January to October) for an oak forest ranged between 0.2 and 6.4 mm s^{-1} (Puxbaum and Gregori, 1998), $v_{dep,NO_2} = 2$ mm s^{-1} for a deciduous forest were reported by Horii et al. (2004).

To compare deposition velocities measured over the canopy with those measured at leaf-level (dynamic chambers), deposition velocity data per projected needle area must be converted by multiplying the measured deposition velocity with the leaf area index (LAI). According to Rondón et al. (1993) the existence of a compensation point concentration can be also be considered by $v_{dep,NO_2}^{LAI,corrected} = v_{dep,NO_2}^{LAI} \cdot (1-m_{comp,NO_2}/m_{s,NO_2})$, where v_{dep,NO_2}^{LAI} is the LAI converted deposition velocity, m_{comp,NO_2} the NO_2 compensation point concentration (see Sect. 4.4) and m_{s,NO_2} is the mean NO_2 concentration during the period. Table 5 presents the corrected NO_2 deposition velocities determined for each class

Table 4. Parameters of NO_2 field measurements of bi-variate weighted linear least-squares fitting regression analysis (standard error of m_{s,NO_2} and m_{a,NO_2} considered). Data were separated for leaf conductance g_{H_2O} and classified into classes 1–7. Only significant data of $\Delta m_{NO_2} = (m_{a,NO_2} - m_{s,NO_2})$ were applied.

class	N [1]	$R^2(m_{a,NO_2}, m_{s,NO_2})$ [1]	m_{comp,NO_2} nmol m^{-3}	P($m_{comp,NO_2} \neq 0$?) %	v_{dep,NO_2} mm s^{-1}
Picea abies 1					
1	91	0.8939	14.0 ± 33.4	32.50 (ns)	0.07 ± 0.06
2	102	0.8886	22.7 ± 30.5	54.16 (ns)	0.09 ± 0.06
3	47	0.8709	13.9 ± 36.7	29.30 (ns)	0.13 ± 0.07
4	52	0.9401	-24.3 ± 35.6	50.11 (ns)	0.11 ± 0.08
5	55	0.9248	23.1 ± 14.4	88.43 (ns)	0.25 ± 0.05
6	35	0.9263	29.0 ± 16.3	91.22 (ns)	0.30 ± 0.08
7	75	0.8861	2.4 ± 9.6	19.98 (ns)	0.35 ± 0.03
Picea abies 2					
1	43	0.9702	6860 ± 12428	4.37 (ns)	-0.002 ± 0.04
2	165	0.9075	-16.7 ± 13.9	76.78 (ns)	0.14 ± 0.04
3	87	0.8783	-13.6 ± 19.5	51.48 (ns)	0.14 ± 0.02
4	59	0.8545	16.5 ± 15.3	71.75 (ns)	0.25 ± 0.05
5	74	0.9876	14.5 ± 13.2	72.44 (ns)	0.29 ± 0.06
6	43	0.8912	-34.0 ± 22.6	86.02 (ns)	0.19 ± 0.05
7	140	0.8106	7.4 ± 6.4	74.92 (ns)	0.42 ± 0.07

ns = not significantly different from zero for $m_{comp,NO_2} \neq 0$ (see Sect. 3.4).

of leaf conductance. The application of this correction for the NO_2 compensation point concentration according to Rondón et al. (1993) results in 11–37 % lower deposition velocities. The average value of $v_{dep,NO_2}^{LAI,corrected}$ was 0.98 mm s^{-1}, which is one order of magnitude lower than the reported averaged and corrected NO_2 deposition velocity per ground area for a spruce stand by Rondón et al. (1993). These large differences may be partly explained by fluctuations over the whole tree stand as argued by Rondón et al. (1993) who considered their converted deposition velocities to be upper limits measured at the tree top. We determined our values at branches in the middle of the canopy. The radiation intensity and thus the stomatal conductance in the forest probably differs upwards to the top of canopy and downwards to the ground.

The demonstrated stomatal regulation of the NO_2 uptake fits with the results of previous experiments with five European tree species (Chaparro-Suarez et al., 2011) and with laboratory studies of young spruce trees under controlled conditions (Breuninger et al., 2012). Figure 7 presents the deposition velocities in relationship to the stomatal conductance determined by this study in combination with the results of the studies mentioned before. Regardless of plant species or cultivation the NO_2 deposition velocities of all investigated plants are well correlated with stomatal conductance. Obviously, the plant specific characteristics or the habitat conditions have only small effects on the uptake rate of NO_2. This more comprehensive view intensified the impression that the NO_2 uptake rate of plants can be roughly

Table 5. Averages of NO_2 deposition velocities ($v_{dep,i}^{LAI}$ in mm s^{-1}) per ground area (LAI) and v_{dep,NO_2}^{LAI} corrected ($v_{dep,NO_2}^{LAI,corrected}$ in mm s^{-1}) for NO_2 compensation point concentration when compensation point was definable. LAI of Spruce forest (EGER) = 5.2.

| class | *Picea abies* 1 | | *Picea abies* 2 | |
	v_{dep,NO_2}^{LAI}	$v_{dep,NO_2}^{LAI,corrected}$	v_{dep,NO_2}^{LAI}	$v_{dep,NO_2}^{LAI,corrected}$
1	0.37	0.30	n.a.	n.a.
2	0.46	0.34	0.71	n.a.
3	0.68	0.56	0.74	n.a.
4	0.56	0.73	1.30	1.04
5	1.28	0.91	1.50	1.21
6	1.58	0.99	1.00	n.a.
7	1.82	1.75	2.20	1.96

n.a. = not available.

estimated just by knowing the stomatal conductance. Rondón and Granat (1994) also conclude that the relationship between NO_2 needle conductance and stomatal conductance was close to 1 : 1.

4.4 Compensation point concentrations of NO_2

In the literature a wide range of NO_2 compensation point concentrations (m_{comp,NO_2}) for spruce were reported, ranging from 0.1 to 1.7 ppb. Rondón et al. (1993) and Rondón and Granat (1994) described m_{comp,NO_2} between 0.1 and 0.7 ppb.
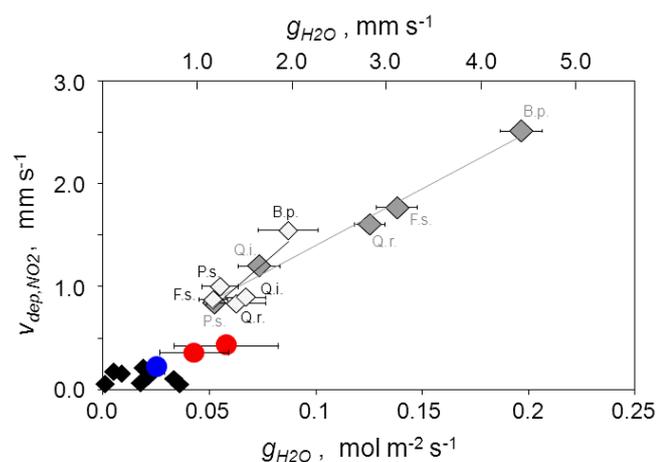
Fig. 7. Maximum NO_2 deposition velocities (v_{dep,NO_2}) in relation to their corresponding stomatal leaf conductance (g_{H_2O}) for five tree species (*Betula pendula*, *Fagus sylvatica*, *Quercus robur*, *Quercus ilex*, *Pinus sylvestris*) at two light intensities (light grey diamonds: PAR = 900 μmol m^{-2} s^{-1}; grey diamonds: PAR = 450 μmol m^{-2} s^{-1}; black diamonds: night time conditions) measured by Chaparro-Suarez et al. (2011), for *Picea abies* measured in the present study (red filled circle), and for *Picea abies* measured under laboratory conditions (blue filled circle; data see Breuninger et al., 2012).

These values are comparable to the values determined in this study, where the range of m_{comp,NO_2} determined for spruce needles under field conditions was estimated to be between 7.4 ± 6.40 and 29.0 ± 16.30 nmol m^{-3} (0.17–0.65 ppb). But attention should be paid to the large errors of the compensation point concentrations, which can be 100 % or even more. Moreover, the significance probability of the compensation point concentrations in our study was always negligible. Therefore, the existence of a NO_2 compensation point concentration for spruce is generally challenged. However, if a compensation point for NO_2 uptake would exist, the concentration would be much less than 1 ppb. These considerations are in close accordance with laboratory experiments performed by Chaparro-Suarez et al. (2011) who also question the existence of a compensation point.

However, Thoene et al. (1996) determined a compensation point concentration of 1.64 ppb for spruce, and Geßler et al. (2002) values of 1.7 ppb. Such large values (above 1 ppb) would imply an almost constant NO_2 emission from the forest at regions with small ambient NO_2 concentrations, which have not been reported so far. These differences in the estimation of a compensation point concentration have led to some discussion (Lerdau et al., 2000). The discrepancy between the values determined in this study and those reported high values may be explained by the fact of using different measurement techniques to detect the NO_2 concentrations. As mentioned above (see Sect. 2.2.2), most of the commonly used converters for the conversion of NO_2 to NO are not

highly specific for NO_2, therefore NO_2 concentrations will be overestimated. Previous studies demonstrated that widely used molybdenum converters overestimate the true values of NO_2 because of substantial NO production from oxidized nitrogen compounds like peroxyacetyl nitrate (PAN) and nitric acid (Winer et al., 1974; Matthews et al., 1977; Grosjean and Harrison, 1985; Gehrig and Baumann, 1993; Steinbacher et al., 2007). For example, the processes may convert up to 92 % of peroxyacetyl nitrate (PAN) and 98 % of nitric acid (HNO_3) into NO (Winer et al., 1974; Grosjean and Harrison, 1985). The luminol technique is known for significant interferences with O_3 and PAN (25 %) especially at low NO_2 concentrations (Drummond et al., 1989; Kelly et al., 1990). Such interferences were found to be negligible with photolytic converters (Fehsenfeld et al., 1990; Ryerson et al., 2000). The highly specific blue light converter used in this study should minimize this source of error.

Another reason for different estimations of compensation point concentrations can be the application of different measurement setups and data analysis. In many reports it is not clear whether photochemical reactions of the NO-NO_2-O_3 triad within the plant chambers were taken into account or an experimental setup was used which excluded reactions of NO_2 photochemistry (Geßler et al., 2000, 2002; Hereid and Monson, 2001; Sparks et al., 2001; Raivonen et al., 2009). During field measurements chemical reactions of the NO-NO_2-O_3 triad must be regarded as being part of the natural conditions; therefore the measured values must be corrected. The impact of gas-phase reactions on compensation point concentrations is less than on deposition velocities. In Breuninger et al. (2012) we have differentiated our calculated NO_2 exchange flux densities into the (chamber) flux densities and the gas-phase flux densities (gas-phase production and destruction of NO-NO_2-O_3), so we could identify the fraction of the gas-phase reactions. For example for a selected leaf conductance category (high PAR radiation) the fraction of the gas-phase flux densities at the exchange flux density of NO_2 was just +8 %, but in particular cases it could be +22 % or −12 %, respectively. However, this would not suffice to explain formerly reported high values of NO_2 compensation point concentrations. Furthermore, another source for the discrepancy could be whether deposition velocities and compensation point concentrations were determined by applying simple linear regression (no errors considered at all) or bi-variate weighted linear regression (y- and x-errors considered). The bi-variate regression is preferred to any standard forms of linear regression analysis, since (a) both concentrations, m_{a,NO_2} and m_{s,NO_2}, are measured with identical analyzers, (b) corresponding standard errors are of the same order of magnitude, and (c) errors are usually large (for m_{s,NO_2} and m_{a,NO_2}, as well as for F_{ex,NO_2}) due to the fact that NO analyzers have in most cases measured at the lower end of their capabilities. In most of the previous studies simple linear regressions between exchange flux density $F_{ex,i}$ and the trace gas concentration at the outlet of the sample

chamber $m_{s,i}$ were applied (Rondón et al., 1993; Rondón and Granat, 1994; Thoene et al., 1996; Sparks et al., 2001; Hereid and Monson, 2001), only Geßler et al. (2000, 2002) applied a bi-variate algorithm.

In Breuninger et al. (2012), we have analyzed the effect of applying simple linear regression or bi-variate weighted linear regression (see Table 7 there). Applying simple linear regression instead of bi-variate weighted linear regression analysis does not lead to considerably different values, neither of NO_2 compensation point concentrations nor NO_2 deposition velocities. However, the statistical significance of $m_{comp,NO_2} \neq 0$ changes from "highly significant ($P = 0.999$)", if simple linear regression is applied, to "unlikely ($P < 0.95$)", if we used bi-variate weighted linear regression analysis.

Other issues potentially contributing to the observed differences, could be different plant materials used or different habitat conditions. Previous studies suggest that mesophyllic characteristics like leaf ascorbate concentration may influence NO_2 exchange rates (Ramge et al., 1993; Teklemariam and Sparks, 2006). The apoplastic ascorbate concentration varies with species, environmental conditions (Polle et al., 1995; Schwanz et al., 1996) and stage of development (Luwe, 1996). Another reason could be a different colonization of the trees by chemolithoautotrophic nitrifying bacteria. It is known that these bacteria colonize the phyllosphere of trees. Heuser and Zimmer (2003) demonstrated autotrophic nitrite oxidizers on the leaf surface of English oak (*Quercus robur* L.) and Papen et al. (2002) detected them on spruce needles. Teuber (2003) was able to verify nitrifying bacteria even living inside the apoplast of spruce needles. These organisms are able to metabolize NH_4^+ and NO_2^- which is formed when NO_2 is dissolved in water. It must be assumed that NO_2 uptake and compensation point concentration will differ if plants are colonized by nitrifiers or not. From previous studies (Papen et al., 2002) it is known that NH_3 deposition fluxes significantly increased as a consequence of metabolic activity of nitrifying bacteria. Possibly, this observation is also valid for NO_2.

5   Conclusions

1. The control of plant conditions and the plant nutrient composition after field measurements indicated that the enclosed branches were not harmed by the dynamic plant chambers and still behaved normally after six weeks of enclosure.

2. NO_2 deposition velocities (v_{dep,NO_2}) are positively correlated to leaf conductance. For spruce v_{dep,NO_2} ranged between 0.07 and 0.42 mm s^{-1}.

3. Estimates of NO_2 deposition velocity per ground area (on a LAI basis) amounted to 0.98 mm s^{-1} for the spruce stand.

4. NO_2 compensation point concentrations (m_{comp,NO_2}) determined for spruce needles under uncontrolled field conditions ranged from 2.4 ± 9.63 to 29.0 ± 16.30 nmol m^{-3} (0.05–0.65 ppb) but are all negligible in terms of $m_{comp,NO_2} \neq 0$. These results challenge the existence of a NO_2 compensation point concentration for spruce.

5. The constantly lower values of NO_2 gas exchange flux densities, NO_2 deposition velocities and NO_2 compensation point concentrations in comparison to most previous studies are most likely due to using a more specific NO_2 analyzer with a blue light converter.

Appendix A

Mass balance equation of the trace gas NO_2 inside a dynamic plant chamber

Assuming steady-state conditions within the dynamic chamber and considering the convention fluxes into (out of) the plant chamber's volume are counted positive (negative), the dynamic chamber's mass balance equation of the trace gas NO_2 may be written as:

$$+ F_{in,NO_2} - F_{out,NO_2} + F_{wall} + F_{em,NO_2} - F_{dep,NO_2}$$
$$+ F_{prod,NO_2} - F_{dest,NO_2} = 0 \quad\quad (A1)$$

where F_{in,NO_2} is the flux of trace gas NO_2 entering the plant chamber, F_{out,NO_2} the flux of NO_2 leaving the plant chamber, F_{wall} the flux to the inner chamber walls, F_{em,NO_2} the flux caused by emission from the leaves, F_{dep,NO_2} the flux caused by uptake to the leaves, F_{prod,NO_2} the flux into the plant chamber volumes caused by gas-phase production, and F_{dest,NO_2} is the flux out of the plant chamber's volume caused by gas-phase destruction.

The ingoing (F_{in,NO_2}) and the outgoing (F_{out,NO_2}) fluxes may be known by measurements. Considering the purging rate Q (m^3 s^{-1}) and the molar concentration m_{a,NO_2} (nmol m^{-3}) of trace gas NO_2 in ambient air (alternative the

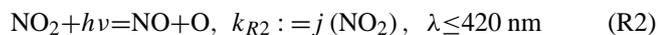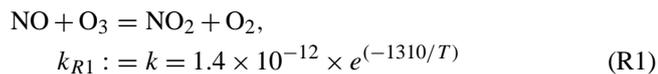outlet of the reference chamber), the ingoing flux is defined by

$$F_{in,NO_2} = Q \cdot m_{a,NO_2} \tag{A2}$$

The outgoing flux leaving the chamber, considering the molar concentration at the outlet of the plant chamber (m_{s,NO_2} in $nmol\,m^{-3}$), is defined by

$$F_{out,NO_2} = Q \cdot m_{s,NO_2} \tag{A3}$$

The flux to the inner chamber wall F_{wall} must be quantified by corresponding laboratory experiments (e.g. Ludwig, 1994; Meixner et al., 1997; Chaparro-Suarez et al., 2011; Breuninger et al., 2012). Using chemically inert material for the chamber walls F_{wall} can be neglected.

The gas-phase production and destruction of the trace gas NO_2 are controlled by the photo-chemical reactions of the NO-NO_2-O_3 triad:

$$NO + O_3 = NO_2 + O_2,$$
$$k_{R1} := k = 1.4 \times 10^{-12} \times e^{(-1310/T)} \tag{R1}$$

$$NO_2 + h\nu = NO + O, \quad k_{R2} := j\,(NO_2), \quad \lambda \le 420 \text{ nm} \tag{R2}$$

The corresponding fluxes F_{prod,NO_2} and F_{dest,NO_2} can be formulated as:

$$F_{prod,NO_2} = \frac{V}{A_{leaf}} \cdot k \cdot m_{s,NO} \cdot m_{s,O_3} \tag{A4}$$

and

$$F_{dest,NO_2} = \frac{V}{A_{leaf}} \cdot j\,(NO_2) \cdot m_{s,NO_2} \tag{A5}$$

where V is the plant chamber's volume (m^3), k the (temperature-dependent) reaction coefficient of the $NO + O_3$ reaction ($m^3\,nmol^{-1}\,s^{-1}$) (Atkinson et al., 2004) and $j(NO_2)$ (s^{-1}) is the photolysis rate of Reaction (R2).

The unknown fluxes F_{em,NO_2} and F_{dep,NO_2} can be combined to the bi-directional "exchange flux" F_{ex,NO_2}:

$$F_{ex,NO_2} = +F_{em,NO_2} - F_{dep,NO_2} \tag{A6}$$

Considering Eqs. (A1)–(A6) the balance equations of the exchange flux density F_{ex,NO_2} will read as follows:

$$F_{ex,NO_2} = -\frac{Q}{A_{leaf}} \left(m_{a,NO_2} - m_{s,NO_2} \right.$$
$$\left. + \frac{V}{Q} k\, m_{s,NO} m_{s,O_3} - \frac{V}{Q} j\,(NO_2)\, m_{s,NO_2} \right) \tag{A7}$$

Appendix B

List of symbols and abbreviations

A_{leaf}	leaf area	m^2
BLC	Blue Light Converter	
b_{NO_2}	slope of regression analysis of trace gas NO_2	$nmol\,m^{-3}$
F_{ex,CO_2}	CO_2 net exchange flux density	$\mu mol\,m^{-2}\,s^{-1}$
F_{ex,H_2O}	transpiration rate	$mmol\,m^{-2}\,s^{-1}$
F_{ex,NO_2}	exchange flux density of trace gas NO_2	$nmol\,m^{-2}\,s^{-1}$
g_{H_2O}	stomatal conductance for H_2O	$m\,s^{-1}$
I_c	light compensation point	$\mu mol\,photons\,m^{-2}\,s^{-1}$
I_s	light saturation point	$\mu mol\,photons\,m^{-2}\,s^{-1}$
$j(NO_2)$	photolysis rate of NO_2 ($\lambda \le 420$ nm)	s^{-1}
k	rate constant for chemical reactions	$cm^3\,molecule^{-1}\,s^{-1}$
LAI	leaf area index	–
LOD	limit of detection	$nmol\,m^{-3}$, ppb
$m_{a,i}$	molar concentration in ambient air of gas i	$nmol\,m^{-3}$, ppb
$m_{s,i}$	molar concentration within plant chamber of gas i	$nmol\,m^{-3}$, ppb
m_{comp,NO_2}	compensation point concentration of trace gas NO_2	$nmol\,m^{-3}$ or ppb
n_{NO_2}	intercept of regression analysis of trace gas NO_2	$nmol\,m^{-3}$
N	number of samples	–
PAR	photosynthetically active radiation	$\mu mol\,m^{-2}\,s^{-1}$
Q	purging rate	$m^3\,s^{-1}$
R^2	regression coefficient	–
s	standard error	
T	temperature	°C or K
V	chamber volume	m^3
v_{dep,NO_2}	deposition velocity of trace gas NO_2 (quantity is chamber-specific, see Breuninger et al., 2012)	$m\,s^{-1}$
v_{dep,NO_2}^{LAI}	LAI converted deposition velocity	$m\,s^{-1}$
$v_{dep,NO_2}^{LAI,corrected}$	LAI converted deposition velocity considered m_{comp,NO_2}	$m\,s^{-1}$

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