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# Field investigations of nitrogen dioxide (NO<sub>2</sub>) exchange between plants and the atmosphere

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## Abstract

The nitrogen dioxide (NO<sub>2</sub>) 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<sub>2</sub>-O<sub>3</sub> triad and additionally of the non-reactive trace gases CO<sub>2</sub> and H<sub>2</sub>O. For the NO<sub>2</sub> detection a highly NO<sub>2</sub> specific blue light converter was used, which was coupled to chemiluminescence detection of the photolysis product NO. This NO<sub>2</sub> converter excludes known interferences with other nitrogen compounds, which occur by using more unspecific NO<sub>2</sub> converters. Photo-chemical reactions of NO, NO<sub>2</sub>, and O<sub>3</sub> inside the dynamic chamber were considered for the determination of NO<sub>2</sub> flux densities, NO<sub>2</sub> deposition velocities, as well as NO<sub>2</sub> compensation point concentrations. The calculations based on a bi-variate weighted linear regression analysis ( $y$ - and  $x$ -errors considered). The NO<sub>2</sub> deposition velocities for spruce, based on projected needle area, ranged between 0.07 and 0.42 mm s<sup>-1</sup>. The calculated NO<sub>2</sub> compensation point concentrations ranged from 7.4 ± 6.40 to 29.0 ± 16.30 nmol m<sup>-3</sup> (0.17–0.65 ppb) but the compensation point concentrations were all not significant in terms of compensation point concentration is unequal zero. These data challenge the existence of a NO<sub>2</sub> compensation point concentration for spruce. Our study resulted in lower values of NO<sub>2</sub> gas exchange flux densities, NO<sub>2</sub> deposition velocities and NO<sub>2</sub> compensation point concentrations in comparison to most previous studies. It is essential to use a more specific NO<sub>2</sub> analyzer and to consider photo-chemical reactions between NO, NO<sub>2</sub>, and O<sub>3</sub> inside the chamber.

## 1 Introduction

Nitrogen is an essential nutrient for all living organisms. Atmospheric N<sub>2</sub> is made available by biological fixation through procaryotic microorganisms delivering amino acids and ammonia. Both compounds can be taken up by higher plants. However most of

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the nitrogen taken up by higher vegetation is introduced by nitrification performed by other groups of microorganisms oxidizing ammonia and delivering nitrate (NO<sub>3</sub><sup>-</sup>) which is taken up by plant roots. Nitrate can also be reduced again to N<sub>2</sub> by microbial denitrification. In course of both processes, nitrification and denitrification, nitrogen monoxide (NO) can be released, oxidized to nitrogen dioxide (NO<sub>2</sub>) and contribute to the atmospheric pool of these two nitrogen oxides, also termed NO<sub>x</sub> (Williams et al., 1992; Robertson and Groffman, 2007). NO and NO<sub>2</sub> are highly reactive trace gases in the atmosphere which influence its oxidation processes, the generation and destruction of ozone (O<sub>3</sub>), and thus the atmospheric lifetime of various less reactive greenhouse gases. Both, NO and NO<sub>2</sub> 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<sub>2</sub>, and O<sub>3</sub> are in a photostationary equilibrium, referred to as the NO-NO<sub>2</sub>-O<sub>3</sub> triad (Seinfeld and Pandis, 2006).

Additionally to the root uptake of NO<sub>3</sub><sup>-</sup> atmospheric NO<sub>2</sub> 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<sub>2</sub> has been investigated by using <sup>15</sup>N isotope as a tracer (Nussbaum et al., 1993; Weber et al., 1995; Yoneyama et al., 2003). Dissolved in the apoplastic solution, NO<sub>2</sub> is disproportionated to nitrate and nitrite (NO<sub>2</sub><sup>-</sup>), which are reduced to ammonium (NH<sub>4</sub><sup>+</sup>) by the enzymes nitrate or nitrite reductases, respectively (Lea and Mifflin, 1974; Thoene et al., 1991; Ammann et al., 1995; Maeck, 1995; Sakakibara et al., 1996; Tischner, 2000). Moreover, the reduction of NO<sub>2</sub> 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<sub>2</sub> leaf fluxes if the reactions between water and NO<sub>2</sub> and between NO<sub>2</sub> and ascorbate are taken into account. This direct role of ascorbate in the foliar uptake of NO<sub>2</sub> has been experimentally demonstrated by Teklemariam and Sparks (2006). They observed a significant correlation between

leaf ascorbate concentrations and the NO<sub>2</sub> uptake by leaves. However, differences of 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<sub>2</sub> is the uptake of NO and its oxidation to NO<sub>2</sub> (Ghaffari et al., 2005).

The NO<sub>2</sub> 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<sub>2</sub> uptake stomatal conductance and increasing atmospheric NO<sub>2</sub> concentration (Johansson, 1987; Thoene et al., 1991, 1996; Chaparro-Suarez et al., 2011). Despite numerous investigations, NO<sub>2</sub> exchange between atmosphere and plants is still a matter of debate. Emission of NO<sub>2</sub> is reported urging the discussion of bi-directional exchange and a corresponding so-called “compensation point”. The NO<sub>2</sub> compensation point concentration defines that NO<sub>2</sub> concentration at which the NO<sub>2</sub> exchange is zero (as a net balance of NO<sub>2</sub> uptake and NO<sub>2</sub> emission). When ambient NO<sub>2</sub> concentrations are below the compensation point for NO<sub>2</sub>, plants act as a source for NO<sub>2</sub>. Contrasting, they turn out to be a NO<sub>2</sub> sink when ambient concentrations are exceeding the NO<sub>2</sub> compensation point. Previous studies reported NO<sub>2</sub> 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<sub>2</sub> concentrations of 0.2 to 0.4 ppb a strong uptake by plants is required to align measured NO<sub>2</sub> concentrations in the canopy with measured NO soil emission rates. Furthermore, a recent laboratory study on five European tree species, applying a highly specific NO<sub>2</sub> analyzer suggested at

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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<sub>2</sub> uptake comparing field and laboratory measurements of spruce (*Picea abies*) in order to identify NO<sub>2</sub> compensation point concentrations using a dynamic chamber system and a highly NO<sub>2</sub> specific measuring technique. Contrasting controlled laboratory measurements typical field conditions do not exclude chemical reactions of NO and O<sub>3</sub> inside the plant chamber. Therefore, NO<sub>2</sub>, NO, and O<sub>3</sub> concentrations were measured simultaneously at the inlet and the outlet of the dynamic chamber to determine the chemical source strength of NO<sub>2</sub> (reaction between NO and O<sub>3</sub>) as well as the chemical sink of NO<sub>2</sub> (photolysis of NO<sub>2</sub> under daylight conditions). Furthermore, as NO<sub>2</sub> uptake is triggered by air chemistry, transport, and plant physiology also CO<sub>2</sub> and H<sub>2</sub>O exchange rates were monitored.

## 2 Material and methods

NO<sub>2</sub> 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

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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<sup>-1</sup> (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 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<sup>2</sup> (tree 1) and 1.02 m<sup>2</sup> (tree 2). As stomata are distributed over the whole needle surface in 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 flush and was interpolated retroactively for the individual measurement periods.

## 2.2 Set-up

### 2.2.1 Dynamic chamber system

For the measurements of gas exchange a dynamic chamber system was used based on bags consisting of a thin transparent Teflon film (FEP) (Schäfer et al., 1992; Kesselmeier et al., 1996, 1997; Kuhn et al., 2000), which transmits 90 % of the photosynthetically active radiation and 70 % of the photolysis rate  $j(\text{NO}_2)$  (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 (see Meixner et al., 1997; Pape et al., 2009; Gut et al., 2002). Details are described in Breuninger et al. (2012).

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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<sup>-1</sup> which achieved a complete air exchange of the chamber within 75 s.

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<sup>TM</sup>-Constantan, Omega, UK).

### 2.2.2 Trace gas analyzers

An infrared dual channel gas analyzer (LI-7000, LiCor, Lincoln, NE, USA) was used for continuous determination of CO<sub>2</sub> and H<sub>2</sub>O concentration differences between reference and sample chamber. A second gas analyzer (LI-6262, LiCor, Lincoln, NE, USA) measured the absolute CO<sub>2</sub> and H<sub>2</sub>O outside the chambers. O<sub>3</sub> was monitored with an UV-absorption analyzer (Model 49C, Thermo Fisher Scientific, Waltham, USA). For NO<sub>2</sub> detection we used a highly NO<sub>2</sub> 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<sub>2</sub> to NO at a wavelength of approximately 395 nm. In contrast to widely used molybdenum converters, which overestimate the true values of NO<sub>2</sub> 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), such interferences were found to be negligible with photolytic converters (Fehsenfeld et al., 1990; Ryerson et al., 2000). Thus, photolysis is





the calculation of the photo-chemical reactions based on the NO and O<sub>3</sub> concentrations at the outlet of the plant chamber ( $m_{s,NO}$  and  $m_{s,O_3}$  in nmol m<sup>-3</sup>), the plant chamber's volume ( $V$  in m<sup>3</sup>), the reaction coefficient of the NO + O<sub>3</sub> reaction ( $k$  in m<sup>3</sup> nmol<sup>-1</sup> s<sup>-1</sup>) (Atkinson et al., 2004), and the photolysis rate of NO<sub>2</sub> ( $j(NO_2)$  in s<sup>-1</sup>).

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

Dynamic chambers' mass balance equation for NO<sub>2</sub>, which leads to the formulation of Eq. (1), is derived in Appendix A.

### 2.3.2 NO<sub>2</sub> deposition velocities and NO<sub>2</sub> compensation point concentrations

Deposition velocity ( $v_{dep,NO_2}$  in ms<sup>-1</sup>) and compensation point concentration ( $m_{comp,NO_2}$  in nmol m<sup>-3</sup>) 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 intercept 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 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:

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

The NO<sub>2</sub> deposition velocity ( $v_{dep,NO_2}$ ) was determined by:

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

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and the NO<sub>2</sub> compensation point concentration ( $m_{\text{comp,NO}_2}$ ) by:

$$m_{\text{comp,NO}_2} = \frac{n_{\text{NO}_2} - b_{\text{NO}_2} \frac{V}{Q} \bar{k} \bar{m}_{\text{s,NO}} \bar{m}_{\text{s,O}_3}}{1 - b_{\text{NO}_2} - b_{\text{NO}_2} \frac{V}{Q} \bar{j}(\text{NO}_2)} \quad (4)$$

where the quantities  $Q$ ,  $A_{\text{leaf}}$ ,  $j(\text{NO}_2)$ ,  $k$ ,  $m_{\text{s,NO}_2}$ ,  $m_{\text{s,NO}}$  and  $m_{\text{s,O}_3}$  with overbars represent mean values averaged over the same data set of the  $m_{\text{a,NO}_2}$  and  $m_{\text{s,NO}_2}$  measurements from which the quantities  $n_{\text{NO}_2}$  and  $b_{\text{NO}_2}$  have been derived. 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<sub>3</sub> are described there as well.

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<sub>2</sub> net exchange flux  $F_{\text{ex,CO}_2}$  (in  $\mu\text{mol m}^{-2} \text{s}^{-1}$ ; photosynthetic uptake minus the simultaneously proceeding respiration and photorespiration), and the transpiration rate  $F_{\text{ex,H}_2\text{O}}$  (in  $\text{mmol m}^{-2} \text{s}^{-1}$ ) 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 reference and plant chamber, the enclosed leaf area ( $A_{\text{leaf}}$ ) and the chamber purging rate ( $Q$ ) according to Eq. (1), but in this case without the terms of chemical reactions.

The stomatal conductance for H<sub>2</sub>O ( $g_{\text{H}_2\text{O}}$  in  $\text{m s}^{-1}$ ) 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.

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

The standard errors of NO<sub>2</sub> exchange flux densities  $F_{\text{ex,NO}_2}$ , deposition velocities  $V_{\text{dep,NO}_2}$  and compensation point concentrations  $m_{\text{comp,NO}_2}$  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 and 3–4) of each other (Taylor, 1982; Phillips et al., 2002). The general formulation of the standard error  $s_y$  of a quantity  $y = f(x_1, x_2, x_3, \dots, x_n)$  reads as follows:

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

where  $r(x_i; x_j)$  are the correlation coefficients between each pairs of all  $x_i$  and  $x_j$ . For detail 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<sub>2</sub> and H<sub>2</sub>O needle gas exchange in response to temperature, radiation, CO<sub>2</sub> 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 control and enclosed spruce needles were measured according to validated analytical methods by the Bayreuth Center of Ecology and Environmental Research (BayCEER).

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## 2.5 Significance of NO<sub>2</sub> concentration differences

Before calculating the NO<sub>2</sub> exchange flux density ( $F_{\text{ex,NO}_2}$ ) the difference of the gas concentrations at the inlet and the outlet of the dynamic chamber  $\Delta m_{\text{NO}_2} = (m_{\text{a,NO}_2} - m_{\text{s,NO}_2})$ , i.e. the major component of this calculation, was checked for significance by application of a t-test taking into account the individual concentration measurements of  $m_{\text{s,NO}_2}$  and  $m_{\text{a,NO}_2}$  during one measurement cycle (4 min). Outliers in the data sets were identified by the Nalimov-test. Concentration differences  $\Delta m_{\text{NO}_2}$  with statistical significance below 99 % ( $\alpha < 0.99$ ) were not included in subsequent calculations.

## 3 Results

### 3.1 Microclimatic conditions

Ambient concentrations of NO, NO<sub>2</sub>, O<sub>3</sub>, CO<sub>2</sub>, and H<sub>2</sub>O, 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 found around the detection limit with some sporadic peaks. The NO<sub>2</sub> concentration varied between 0.4 and 21.5 ppb. The diel course exhibited generally higher NO<sub>2</sub> concentrations at night. O<sub>3</sub> 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 availability of mineral nutrition. CO<sub>2</sub> response and light response of CO<sub>2</sub> 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

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the whole campaign) and enclosed branches as well as between young and older needles. The latter differentiation was made because CO<sub>2</sub> 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, respectively. The light compensation point ( $I_c$ ) was found in a range of 40 to 70  $\mu\text{mol photons m}^{-2} \text{s}^{-1}$  and light saturation ( $I_s$ ) was reached between 500 and 1100  $\mu\text{mol photons m}^{-2} \text{s}^{-1}$ .

Mineral nutrients 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). Therefore, we checked the nutrient content of the needles concentration changes 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 control and enclosed needles, except the potassium content which differed significantly comparing young control (6.9  $\text{mg g}^{-1} \text{dw}$ ) and enclosed needles (8.6  $\text{mg g}^{-1} \text{dw}$ ). However, as the low concentration of potassium in the young needles does 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.

### 3.3 Overview of plant chamber measurements

An overview of the atmospheric concentrations of NO, NO<sub>2</sub>, and O<sub>3</sub>, 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<sub>2</sub>, H<sub>2</sub>O, NO, NO<sub>2</sub>, and O<sub>3</sub> 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 at day and 0.1 ppb at night approaching the limit of detection of the analyzer ( $LOD(m_{NO}) = 0.1 \text{ ppb} = 4.46 \text{ nmol m}^{-3}$ ).  $NO_2$  concentrations ( $m_{s,NO_2}$ ) ranged always above the limit of detection ( $LOD(m_{NO_2}) = 0.31 \text{ ppb} = 13.8 \text{ nmol m}^{-3}$ ) with means at 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 to the site.  $O_3$  concentrations ( $m_{s,O_3}$ ) were on average 40 ppb. 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 $NO_2$ 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 guidance 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 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) day time 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 ( $\sim 1.1 \text{ km}$ ). A closer look by leaf conductance classification furthers the understanding of the exchange (Fig. 4, plant chamber 1; Fig. 5, plant chamber 2). Deposition

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velocity  $v_{\text{dep,NO}_2}$  and compensation point concentration  $m_{\text{comp,NO}_2}$  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 ( $m_{\text{a,NO}_2}$  and  $m_{\text{s,NO}_2}$ ) from spruce showed a strong correlation between  $m_{\text{a,NO}_2}$  and  $m_{\text{s,NO}_2}$ . The regression coefficient  $R^2(m_{\text{a,NO}_2}, m_{\text{s,NO}_2})$  reached values between 0.8709 and 0.9951. The deposition velocity  $v_{\text{dep,NO}_2}$  derived from this analysis ranged between 0.07 and 0.42  $\text{mms}^{-1}$ , and was found clearly increasing with leaf conductance. Both spruce branches showed a linearly correlated increase of  $\text{NO}_2$  uptake with increasing leaf conductance. This circumstance is presented in Fig. 6, where the calculated deposition velocities  $v_{\text{dep,NO}_2}$  were plotted against stomatal leaf conductance  $g_{\text{H}_2\text{O}}$ .

The  $\text{NO}_2$  compensation point concentrations  $m_{\text{comp,NO}_2}$  were found between  $2.4 \pm 9.63$  and  $29.0 \pm 16.30 \text{ nmol m}^{-3}$  (0.05–0.65 ppb), however, with significance probabilities for  $m_{\text{comp,NO}_2} \neq 0$  ranging from 19.98 % to 91.22 % (i.e. unlikely probabilities for  $m_{\text{comp,NO}_2} \neq 0$ ).

## 4 Discussion

### 4.1 Effects on enclosed plants

Application of a chamber system with enclosed 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 not 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

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5 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  $\text{CO}_2$  and optimal temperature ( $I_c = 30\text{--}40\ \mu\text{mol photons m}^{-2}\ \text{s}^{-1}$ ,  $I_s = 800\text{--}1000\ \mu\text{mol photons m}^{-2}\ \text{s}^{-1}$ ; Larcher, 2003).

10 The analysis of the nutrient composition of the needles also resulted in no obvious differences. Only for potassium differences were noticeable. The higher concentration of potassium was found for the young enclosed needles but the concentration was in a normal range, which is specified in literature to be between 5 and 70  $\text{mg g}^{-1}\ \text{dw}$  (Frey, 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.

15 In summary we like to state, that our data sets give good reasons to assume that the enclosed branches were not harmed by the chambers.

## 4.2 $\text{NO}_2$ exchange with leaves

20 Under field conditions an increase of  $\text{NO}_2$  uptake was found in relation to increasing  $\text{NO}_2$  concentrations. This agrees with previous studies (Rondón et al., 1993; Thoene et al., 1991; Weber and Rennenberg, 1996; Geßler et al., 2002; Chaparro-Suarez et al., 2011) and confirms the assumption that  $\text{NO}_2$  exchange is driven by the  $\text{NO}_2$  concentration difference between atmosphere and the gaseous phase of the leaf interior. Up to now,  $\text{NO}_2$  emission has been found only at (very) low  $\text{NO}_2$  concentrations.  $\text{NO}_2$  emissions have been measured within several studies. Teklemariam and Sparks (2006) reported emissions from four species (wheat, corn, sunflower, Madagascar periwinkle) to range between 36.8 and 101.0  $\text{pmol m}^{-2}\ \text{s}^{-1}$ . Sparks et al. (2001) observed  $\text{NO}_2$

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emissions up to  $50 \text{ pmol m}^{-2} \text{ s}^{-1}$  from several tropical trees and Hereid and Monson (2001) from field-grown corn.  $\text{NO}_2$  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  $\text{NO}_2$  from spruces varied between 0.07 and  $58 \text{ pmol m}^{-2} \text{ s}^{-1}$  measured at mean  $\text{NO}_2$  concentrations of  $67.3 \text{ nmol m}^{-3}$  (1.5 ppb).

Deposition fluxes of  $\text{NO}_2$  observed in our field study for spruce varied between  $-0.078$  and  $-0.018 \text{ nmol m}^{-2} \text{ s}^{-1}$ . These fluxes are much lower than  $\text{NO}_2$  deposition fluxes reported by Thoene et al. (1996), 1.88 to  $0.03 \text{ nmol m}^{-2} \text{ s}^{-1}$  for spruce, or Sparks et al. (2001), 1.55 to  $0.15 \text{ nmol m}^{-2} \text{ s}^{-1}$  for several tropical trees. These discrepancies to our values might be related to different detection techniques for  $\text{NO}_2$ . Thoene et al. (1996) used a non-specific molybdenum converter for  $\text{NO}_2$ , while Sparks et al. (2001) applied a liquid phase chemiluminescence detector (luminol reaction). Both techniques are interfering with other oxidized nitrogen compounds. Our data are based on the use of a blue light converter, which is highly specific for  $\text{NO}_2$  measurements. Very similar deposition fluxes up to  $0.3 \text{ nmol m}^{-2} \text{ s}^{-1}$  (at 5 ppb) were reported by Chaparro-Suarez et al. (2011) using a different photolytic converter (PLC 762, Ecophysics, Switzerland). Furthermore, our data are in close accordance with  $\text{NO}_2$  deposition fluxes reported by Geßler et al. (2002), ranging between 0.12 and  $0.02 \text{ nmol m}^{-2} \text{ s}^{-1}$ , also using an Ecophysics photolytic converter. Thus, discrepancies reported in the literature may be understood to be caused by the use of insufficiently specific  $\text{NO}_2$ -detection techniques.

### 4.3 Deposition velocities of $\text{NO}_2$

$\text{NO}_2$  deposition velocities exhibited values between 0.07 and  $0.42 \text{ mm s}^{-1}$  for spruce. These values were in accordance with the lowest up to now reported values of  $0.09 \text{ mm s}^{-1}$  for spruces under controlled field conditions (Geßler et al., 2002). In contrast, Thoene et al. (1991, 1996) described values ranging from 0.4 to  $0.9 \text{ mm s}^{-1}$  for laboratory measurements. Rondón et al. (1993) reported even much higher values from 1.8 to  $2.1 \text{ mm s}^{-1}$ .

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As indicated in the previous chapter, differences between data of our study and those of previous studies are most likely due to non-specific NO<sub>2</sub> analyzers applied in the previous studies. Furthermore, discrepancies may be also due to the fact, that some authors have neglected gas-phase reactions in the dynamic chambers at all, some excluded them by using corresponding set-ups, and some tried to consider them by application of an empty chamber (“reference chamber”) (Rondón et al., 1993; Geßler et al., 2000, 2001; Hereid and Monson, 2001; Sparks et al., 2001; Raivonen et al., 2009). Furthermore, different deposition velocities on 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 different performance of gas exchange depending on the needle ages are very rare.

Many of the reported NO<sub>2</sub> deposition velocities have been obtained by micrometeorological measurements (aerodynamic gradient or eddy covariance; corresponding data of NO<sub>2</sub> 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<sub>2</sub> deposition velocities (projected soil area) of 0.35 mm s<sup>-1</sup> are reported by Pilegaard et al. (1998) for wheat fields, and 2 to 6 mm s<sup>-1</sup> 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<sup>-1</sup> (Puxbaum and Gregori, 1998),  $v_{\text{dep, NO}_2} = 2 \text{ mm s}^{-1}$  for a deciduous forest were reported by Horii et al. (2004).

To compare deposition velocities measured over the canopy with those measured on 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  $v_{\text{dep NO}_2}^{\text{LAI, corrected}} = v_{\text{dep NO}_2}^{\text{LAI}} \cdot (1 - m_{\text{comp, NO}_2} / m_{\text{s, NO}_2})$ , where  $v_{\text{dep NO}_2}^{\text{LAI}}$  is the LAI converted deposition velocity,  $m_{\text{comp, NO}_2}$

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the NO<sub>2</sub> compensation point concentration (see Sect. 4.4) and  $m_{s,NO_2}$  is the mean NO<sub>2</sub> concentration during the period. Table 5 presents the corrected NO<sub>2</sub> deposition velocities determined for each class of leaf conductance. The application of this correction for the NO<sub>2</sub> compensation point concentration according to Rondón et al. (1993) effects 11–37 % lower deposition velocities. The average value of  $v_{dep,NO_2}^{LAI,corrected}$  was 0.98 mm s<sup>-1</sup>, which is one order of magnitude lower than the reported averaged and corrected NO<sub>2</sub> 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 probably differs upwards to the top of canopy and downwards to the ground of forest.

The demonstrated stomatal regulation of the NO<sub>2</sub> uptake fit in 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<sub>2</sub> deposition velocities of all investigated plants are well correlated with stomatal conductance. Obviously, the plant specific characteristics or the habitat conditions have only low effects on the uptake rate of NO<sub>2</sub>. This more comprehensive view intensified the impression that the NO<sub>2</sub> uptake rate of plants can be roughly estimated just by known stomatal conductance.

#### 4.4 Compensation point concentrations of NO<sub>2</sub>

In literature a wide range of NO<sub>2</sub> 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  $m_{\text{comp,NO}_2}$  between 0.1 and 0.7 ppb. These values are comparable to the values determined in this study, where the range of  $m_{\text{comp,NO}_2}$  determined for spruce needles under field conditions was estimated between  $7.4 \pm 6.40$  and  $29.0 \pm 16.30 \text{ nmol m}^{-3}$  (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 “unlikely”. Therefore, the existence of a NO<sub>2</sub> compensation point concentration for spruce is generally challenged. However, if a compensation point for NO<sub>2</sub> uptake would exist, the concentration will 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 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<sub>2</sub> emission from the forest at regions with small ambient NO<sub>2</sub> concentrations, which is not reported so far. These differences in the estimation of a compensation point concentration had 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 using different measurement techniques to detect the NO<sub>2</sub> concentrations. As mentioned above (see Sect. 2.2.2), most of the commonly used converters for the conversion of NO<sub>2</sub> to NO are not highly specific for NO<sub>2</sub>, therefore NO<sub>2</sub> concentrations will be overestimated. Previous studies demonstrated that molybdenum converters, for example, may oxidize 92 % of peroxyacetyl nitrate (PAN) and 98 % of nitric acid (HNO<sub>3</sub>) into NO (Winer et al., 1974; Grosjean and Harrison, 1985). The luminol technique is known for significant interferences with O<sub>3</sub> and PAN (25 %) especially at low NO<sub>2</sub> concentrations (Drummond et al., 1989; Kelly et al., 1990). 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 case of many reports it is not clear whether photo-chemical reactions of the NO-

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NO<sub>2</sub>-O<sub>3</sub> triad within the plant chambers were taken into account or an experimental setup was used which excluded reactions of NO<sub>2</sub> photochemistry (Geßler et al., 2000, 2001; Hereid and Monson, 2001; Sparks et al., 2001; Raivonen et al., 2009). During field measurements chemical reactions of the NO-NO<sub>2</sub>-O<sub>3</sub> triad must be regarded 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 (see Breuninger et al., 2012). However, this would not suffice to explain formerly reported high values of NO<sub>2</sub> compensation point concentration. 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 regression between exchange flux density  $F_{ex,NO_2}$  and the trace gas concentration at the outlet of the sample chamber  $m_{s,NO_2}$  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.

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<sub>2</sub> 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 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 living even inside the apoplast of spruce needles. These organisms are able to metabolize  $\text{NH}_4^+$  and  $\text{NO}_2^-$  which is formed when  $\text{NO}_2$  dissolved in water. It must be assumed that  $\text{NO}_2$  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  $\text{NH}_3$  deposition fluxes significantly increased as consequence of metabolic activity of nitrifying bacteria. Possibly, this observation is also valid for  $\text{NO}_2$ .

## 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 behaved normally still after six weeks of enclosure.
2.  $\text{NO}_2$  deposition velocities ( $v_{\text{dep},\text{NO}_2}$ ) are positively correlated to leaf conductance. For spruce  $v_{\text{dep},\text{NO}_2}$  ranged between 0.07 and 0.42  $\text{mm s}^{-1}$ .
3. Estimates of  $\text{NO}_2$  deposition velocity per ground area (on a LAI basis) amounted to 0.98  $\text{mm s}^{-1}$  for the spruce stand.
4.  $\text{NO}_2$  compensation point concentrations ( $m_{\text{comp},\text{NO}_2}$ ) determined for spruce needles under uncontrolled field conditions ranged from  $7.4 \pm 6.40$  to  $29.0 \pm 16.30 \text{ nmol m}^{-3}$  (0.17–0.65 ppb) but are all “unlikely” in terms of  $m_{\text{comp},\text{NO}_2} \neq 0$ . This results challenge the existence of a  $\text{NO}_2$  compensation point concentration for spruce.
5. The constantly lower values of  $\text{NO}_2$  gas exchange flux densities,  $\text{NO}_2$  deposition velocities and  $\text{NO}_2$  compensation point concentrations in comparison to most

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previous studies are most likely due to using a more specific NO<sub>2</sub> analyzer with a blue light converter.

## Appendix A

### Mass balance equation of the trace gas NO<sub>2</sub> inside a dynamic plant chamber

5 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<sub>2</sub> may be written as:

$$10 \quad +F_{\text{in,NO}_2} - F_{\text{out,NO}_2} + F_{\text{wall}} + F_{\text{em,NO}_2} - F_{\text{dep,NO}_2} + F_{\text{prod,NO}_2} - F_{\text{dest,NO}_2} = 0 \quad (\text{A1})$$

where  $F_{\text{in,NO}_2}$  is the flux of trace gas NO<sub>2</sub> entering the plant chamber,  $F_{\text{out,NO}_2}$  the flux of NO<sub>2</sub> leaving the plant chamber,  $F_{\text{wall}}$  the flux to the inner chamber walls,  $F_{\text{em,NO}_2}$  the flux caused by emission from the leaves,  $F_{\text{dep,NO}_2}$  the flux caused by uptake to the leaves,  $F_{\text{prod,NO}_2}$  the flux into the plant chamber volumes caused by gas-phase production, and  $F_{\text{dest,NO}_2}$  is the flux out of the plant chamber's volume caused by gas-phase destruction.

15 The ingoing ( $F_{\text{in,NO}_2}$ ) and the outgoing ( $F_{\text{out,NO}_2}$ ) fluxes may be known by measurements. Considering the purging rate  $Q$  (m<sup>3</sup> s<sup>-1</sup>) and the molar concentration  $m_{\text{a,NO}_2}$  (nmol m<sup>-3</sup>) of trace gas NO<sub>2</sub> in ambient air (alternative the outlet of the reference chamber), the ingoing flux is defined by

$$20 \quad F_{\text{in,NO}_2} = Q \cdot m_{\text{a,NO}_2} \quad (\text{A2})$$

The outgoing flux leaving the chamber, considering the molar concentration at the outlet of the plant chamber ( $m_{\text{s,NO}_2}$  in nmol m<sup>-3</sup>), is defined by

$$25 \quad F_{\text{out,NO}_2} = Q \cdot m_{\text{s,NO}_2} \quad (\text{A3})$$

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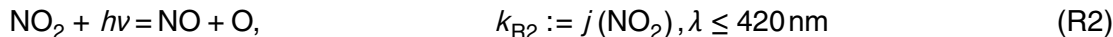
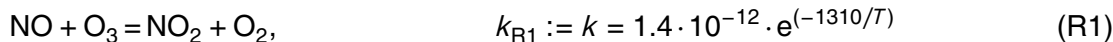
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The flux to the inner chamber wall  $F_{\text{wall}}$  must be quantified by corresponding laboratory experiments (e.g. Ludwig, 1994; Meixner et al., 1997; Breuninger et al., 2012). Using chemically inert material for the chamber walls  $F_{\text{wall}}$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

The gas-phase production and destruction of the trace gas  $\text{NO}_2$  are controlled by the photo-chemical reactions of the  $\text{NO-NO}_2\text{-O}_3$  triad:



The corresponding fluxes  $F_{\text{prod,NO}_2}$  and  $F_{\text{dest,NO}_2}$  can be formulated as:

$$F_{\text{prod,NO}_2} = \frac{V}{A_{\text{leaf}}} \cdot k \cdot m_{\text{s,NO}} \cdot m_{\text{s,O}_3} \quad (\text{A4})$$

and

$$F_{\text{dest,NO}_2} = \frac{V}{A_{\text{leaf}}} \cdot j(\text{NO}_2) \cdot m_{\text{s,NO}_2} \quad (\text{A5})$$

where  $V$  is the plant chamber's volume ( $\text{m}^3$ ),  $k$  the (temperature-dependent) reaction coefficient of the  $\text{NO} + \text{O}_3$  reaction ( $\text{m}^3 \text{nmol}^{-1} \text{s}^{-1}$ ) (Atkinson et al., 2004) and  $j(\text{NO}_2)$  ( $\text{s}^{-1}$ ) is the photolysis rate of Reaction (R2).

The unknown fluxes  $F_{\text{em,NO}_2}$  and  $F_{\text{dep,NO}_2}$  can be combined to the bi-directional "exchange flux"  $F_{\text{ex,NO}_2}$ :

$$F_{\text{ex,NO}_2} = +F_{\text{em,NO}_2} - F_{\text{dep,NO}_2} \quad (\text{A6})$$

Considering Eqs. (A1)–(A6) the balance equations of the exchange flux density  $F_{\text{ex,NO}_2}$  will read as follows:

$$F_{\text{ex,NO}_2} = -\frac{Q}{A_{\text{leaf}}} \left( m_{\text{a,NO}_2} - m_{\text{s,NO}_2} + \frac{V}{Q} k m_{\text{s,NO}} m_{\text{s,O}_3} - \frac{V}{Q} j(\text{NO}_2) m_{\text{s,NO}_2} \right) \quad (\text{A7})$$

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

	average	range
NO, ppb	0.19 ± 0.17	0.07–2.89
NO <sub>2</sub> , ppb	2.46 ± 1.42	0.42–21.49
O <sub>3</sub> , ppb	47.12 ± 11.67	19.00–77.10
CO <sub>2</sub> , ppm	380 ± 8	293–409
H <sub>2</sub> O, ppt	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 <sup>-2</sup> s <sup>-1</sup>	265 ± 402*	0–1910*
global radiation, W m <sup>-2</sup>	232 ± 276*	0–1005*

\* Daytime only data.

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

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

<sup>a</sup> Daytime values were used when global radiation >5 W m<sup>-2</sup>.

\* Limit of detection (LOD).

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**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 conductance ( $g_{\text{H}_2\text{O}}$ ) 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	
$g_{\text{H}_2\text{O}}$ projected	$\text{cm s}^{-1}$	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	
	$A_{\text{leaf}}$								
$g_{\text{H}_2\text{O}}$ total	$\text{cm s}^{-1}$	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	
	$A_{\text{leaf}}$								
Plant chamber 1	PAR	$\mu\text{mol m}^{-2} \text{s}^{-1}$	130 ± 261	200 ± 334	253 ± 311	279 ± 300	297 ± 312	355 ± 335	319 ± 365
	$T_{\text{air}}$	$^{\circ}\text{C}$	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
	r.H.	%	54 ± 17	64 ± 18	64 ± 16	67 ± 14	69 ± 14	70 ± 13	80 ± 14
	$F_{\text{ex,CO}_2}$	$\mu\text{mol m}^{-2} \text{s}^{-1}$	-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
	$F_{\text{ex,H}_2\text{O}}$	$\text{mmol m}^{-2} \text{s}^{-1}$	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	$\mu\text{mol m}^{-2} \text{s}^{-1}$	51 ± 158	157 ± 251	279 ± 353	336 ± 387	278 ± 290	320 ± 307	322 ± 329
	$T_{\text{air}}$	$^{\circ}\text{C}$	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
	r.H.	%	63 ± 19	61 ± 19	59 ± 17	61 ± 16	66 ± 14	69 ± 14	77 ± 16
	$F_{\text{ex,CO}_2}$	$\mu\text{mol m}^{-2} \text{s}^{-1}$	-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
	$F_{\text{ex,H}_2\text{O}}$	$\text{mmol m}^{-2} \text{s}^{-1}$	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

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**Table 4.** Parameters of NO<sub>2</sub> field measurements of bi-variate weighted linear least-squares fitted 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 (classes 1–7). Only significant data of  $\Delta m_{NO_2} = (m_{a,NO_2} - m_{s,NO_2})$  were applied.

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

UL = “unlikely” probabilities for  $m_{comp,NO_2} \neq 0$  (see Sect. 3.4).

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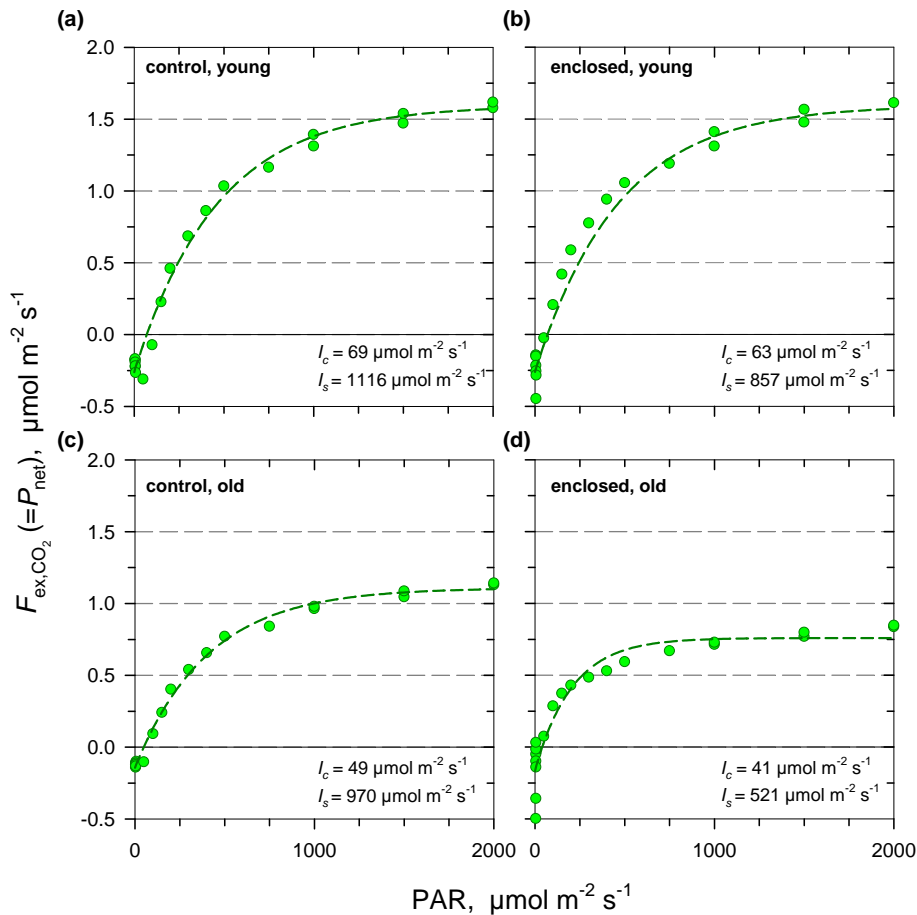

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**Table 5.** Averages of NO<sub>2</sub> deposition velocities ( $v_{\text{dep,NO}_2}$  in mm s<sup>-1</sup>) per ground area (LAI) and  $v_{\text{dep,NO}_2}^{\text{LAI}}$  corrected ( $v_{\text{dep,NO}_2}^{\text{LAI,corrected}}$  in mm s<sup>-1</sup>) for NO<sub>2</sub> compensation point concentration when compensation point was definable. LAI of Spruce forest (EGER) = 5.2.

class	<i>Picea abies 1</i>		<i>Picea abies 2</i>	
	$v_{\text{dep,NO}_2}^{\text{LAI}}$	$v_{\text{dep,NO}_2}^{\text{LAI,corrected}}$	$v_{\text{dep,NO}_2}^{\text{LAI}}$	$v_{\text{dep,NO}_2}^{\text{LAI,corrected}}$
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

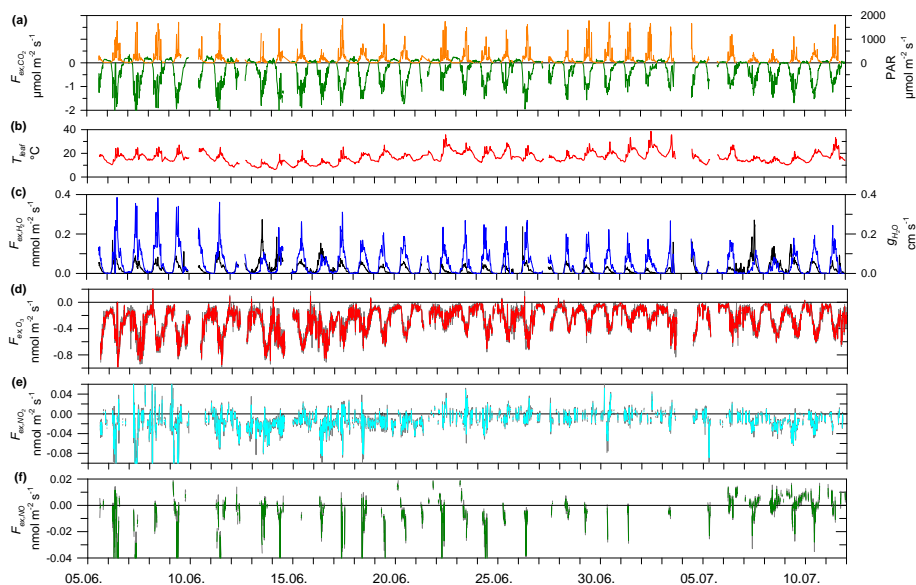
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**Fig. 1.** Photosynthetic light response curves at ambient  $\text{CO}_2$  concentration (370–390 ppm) of control and enclosed spruce needles. **(a)** Young control needles, **(b)** young enclosed needles, **(c)** older control needles, **(d)** older enclosed needles.

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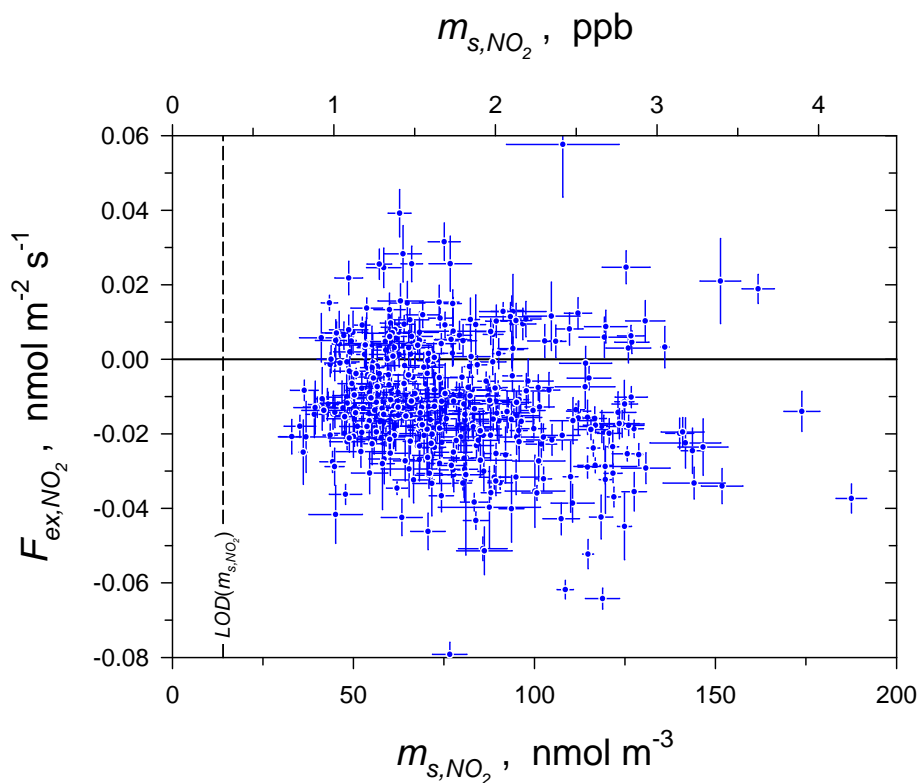


**Fig. 2.** Overview of exchange rates over the entire measuring period. **(a)** Photosynthesis rate  $F_{\text{ex},\text{CO}_2}$  (green line), PAR (orange line); **(b)** leaf temperature  $T_{\text{leaf}}$ ; **(c)** transpiration rate  $F_{\text{ex},\text{H}_2\text{O}}$  (blue line), leaf conductance ( $g_{\text{H}_2\text{O}}$ ) (black line); **(d)**  $\text{O}_3$  exchange flux  $F_{\text{ex},\text{O}_3}$  (red line); **(e)**  $\text{NO}_2$  exchange flux  $F_{\text{ex},\text{NO}_2}$  (light blue line); **(f)**  $\text{NO}$  exchange flux  $F_{\text{ex},\text{NO}}$  (green line).  $F_{\text{ex},\text{O}_3}$ ,  $F_{\text{ex},\text{NO}_2}$ ,  $F_{\text{ex},\text{NO}}$  based on data pairs which were significant for  $\Delta m_i = (m_{\text{a},i} - m_{\text{s},i})$  and their errors are shown as gray areas.

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**Fig. 3.** NO<sub>2</sub> exchange flux density ( $F_{\text{ex},\text{NO}_2}$ ) vs. NO<sub>2</sub> concentration measured at the outlet of the dynamic plant chamber ( $m_{\text{s},\text{NO}_2}$ ) of *Picea abies* 1 over the entire measuring period. Data were filtered for day time conditions, period of possible advection and significance of  $\Delta m_{\text{NO}_2} = (m_{\text{a},\text{NO}_2} - m_{\text{s},\text{NO}_2})$ .  $F_{\text{ex},\text{NO}_2}$  were calculated according to Eq. (1), their standard errors according to Eq. (7).

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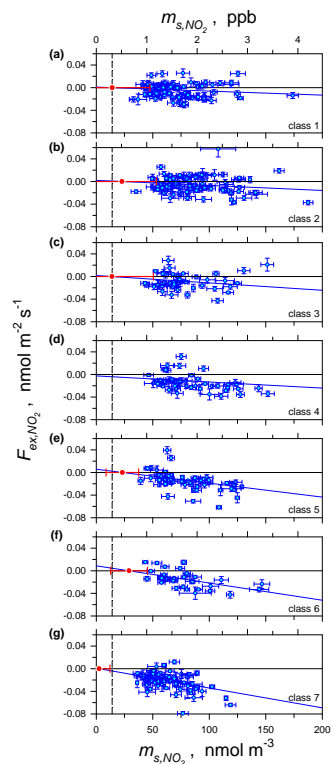
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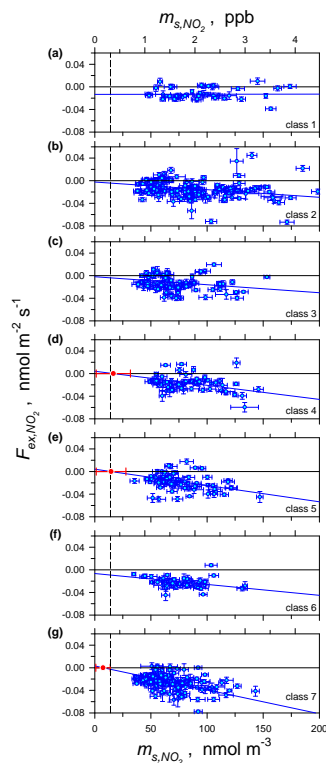
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**Fig. 4.** NO<sub>2</sub> exchange flux densities ( $F_{\text{ex,NO}_2}$ ) of *Picea abies* 1 at various NO<sub>2</sub> concentrations measured at the outlet of the dynamic plant chamber ( $m_{\text{s,NO}_2}$ ). Data were filtered for day time conditions and period of possible advection. Only data pairs whose difference of NO<sub>2</sub> concentrations at the inlet and outlet of the dynamic plant chamber was statistical significant  $\Delta m_{\text{NO}_2} = (m_{\text{a,NO}_2} - m_{\text{s,NO}_2})$  were applied. Data were separated and classified for leaf conductance (class 1–7, **a–g**). NO<sub>2</sub> compensation point concentration ( $m_{\text{comp,NO}_2}$ ) is represented by red filled circle. Blue line is calculated according to Eq. (2) and represents  $v_{\text{dep,NO}_2}$ . Dashed line indicates the limit of detection ( $3\sigma$ -definition) for NO<sub>2</sub> concentration measurements.

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**Fig. 5.**  $\text{NO}_2$  exchange flux densities ( $F_{\text{ex},\text{NO}_2}$ ) of *Picea abies* 2 at various  $\text{NO}_2$  concentrations measured at the outlet of the dynamic plant chamber ( $m_{\text{s},\text{NO}_2}$ ). Data were filtered for day time conditions and period of possible advection. Only data pairs whose difference of  $\text{NO}_2$  concentrations at the inlet and outlet of the dynamic plant chamber was statistical significant  $\Delta m_{\text{NO}_2} = (m_{\text{a},\text{NO}_2} - m_{\text{s}})$  were applied. Data were separated and classified for leaf conductance (class 1–7, **a–g**).  $\text{NO}_2$  compensation point concentration ( $m_{\text{comp},\text{NO}_2}$ ) is represented by red filled circle. Blue line is calculated according to Eq. (2) and represents  $v_{\text{dep},\text{NO}_2}$ . Dashed line indicates the limit of detection ( $3\sigma$ -definition) for  $\text{NO}_2$  concentration measurements.

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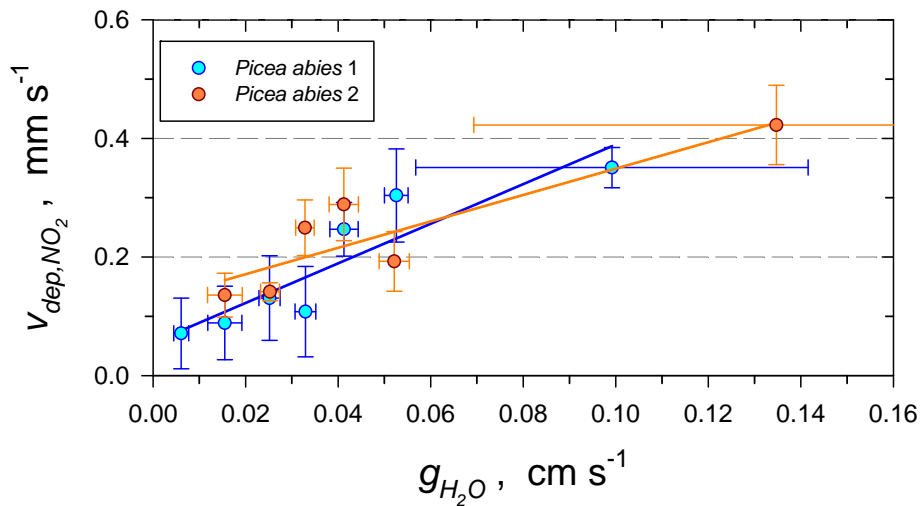
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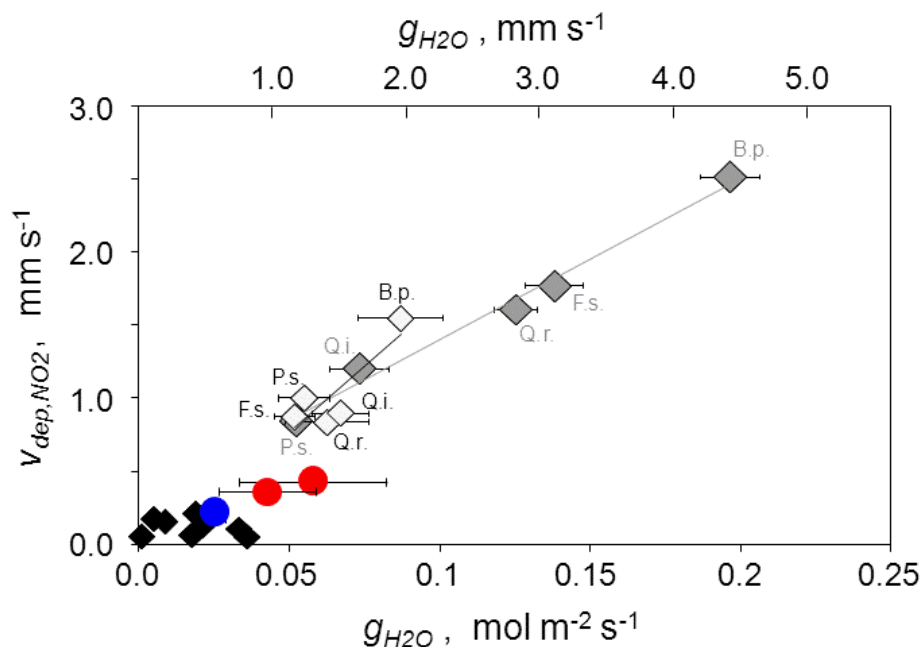
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**Fig. 6.** NO<sub>2</sub> deposition velocities ( $V_{dep,NO_2}$ ) in relationship to the stomatal leaf conductance ( $g_{H_2O}$ ). Deposition velocities were determined for each class of leaf conductance (see Sect. 3.4) therefore  $V_{dep,NO_2}$  represent averages for these data sets.

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**Fig. 7.** Maximally reached NO<sub>2</sub> deposition velocities ( $v_{\text{dep,NO}_2}$ ) in relation to their corresponding stomatal leaf conductance ( $g_{\text{H}_2\text{O}}$ ) for five tree species (*Betula pendula*, *Fagus sylvatica*, *Quercus robur*, *Quercus ilex*, *Pinus sylvestris*) at two light intensities (light grey diamonds: PAR = 900  $\mu\text{mol m}^{-2} \text{s}^{-1}$ ; grey diamonds: PAR = 450  $\mu\text{mol m}^{-2} \text{s}^{-1}$ ; 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).

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