Biogeosciences

Laboratory measurements of nitric oxide release from forest soil with a thick organic layer under different understory types

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Abstract. Nitric oxide (NO) plays an important role in the photochemistry of the troposphere. NO from soil contributes up to 40% to the global budget of atmospheric NO. Soil NO emissions are primarily caused by biological activity (nitrification and denitrification), that occurs in the uppermost centimeter of the soil, a soil region often characterized by high contents of organic material. Most studies of NO emission potentials to date have investigated mineral soil layers. In our study we sampled soil organic matter under different understories (moss, grass, spruce and blueberries) in a humid mountainous Norway spruce forest plantation in the Fichtelgebirge (Germany). We performed laboratory incubation and flushing experiments using a customized chamber technique to determine the response of net potential NO flux to physical and chemical soil conditions (water content and temperature, bulk density, particle density, pH, C/N ratio, organic C, soil ammonium, soil nitrate). Net potential NO fluxes (in terms of mass of N) from soil samples taken under different understories ranged from 1.7–9.8 ng m^{-2} s^{-1} (soil sampled under grass and moss cover), 55.4–59.3 ng m^{-2} s^{-1} (soil sampled under spruce cover), and 43.7–114.6 ng m^{-2} s^{-1} (soil sampled under blueberry cover) at optimum water content and a soil temperature of 10 °C. The water content for optimum net potential NO flux ranged between 0.76 and 0.8 gravimetric soil moisture for moss covered soils, between 1.0 and 1.1 for grass covered soils, 1.1 and 1.2 for spruce covered soils, and 1.3 and 1.9 for blueberry covered soils. Effects of soil physical and chemical characteristics on net potential NO flux were statistically significant (0.01 probability level) only for NH$_4^+$. Therefore, as an alternative explanation for the differences in soil biogenic NO emission we consider more biological factors like understory vegetation type, amount of roots, and degree of mycorrhization; they have the potential to explain the observed differences of net potential NO fluxes.

1 Introduction

Nitric oxide (NO) is a reactive gas which plays a central role in the photochemistry of the troposphere (Crutzen, 1979). The photochemistry of NO and nitrogen dioxide (NO$_2$) is important for the generation/destruction of tropospheric ozone and, hence, regulates the oxidizing capacity of the troposphere. The oxidation products of NO (gaseous NO$_2$, nitrous and nitric acid, particulate nitrite and nitrate) also contribute to the generation of acid rain (Crutzen, 1979) affecting human health and plant productivity.

With respect to NO biosphere-atmosphere exchange, soils are of great interest due to the fact that NO biogenic emissions from soil contribute up to 40% to the global budget of atmospheric NO (Davidson and Kingerlee, 1997; Meixner, 1994; Denman et al., 2007; Rudolph and Conrad, 1996). Kesik et al. (2005) predicted that by 2039 soil NO emissions will increase by 9%. Soils have the potential for acting as a sink for atmospheric NO (Conrad, 1994). Only a few studies provide an indication of soils acting as a sink (Dunfield and Knowles, 1998; Skiba et al., 1994; Slemr and Seiler, 1991). The NO flux between soil and atmosphere is a result of microbial consumption and production of NO in the top

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soil layer. NO production and consumption occur simultaneously during nitrification and denitrification (Remde et al., 1989; Rudolph and Conrad, 1996; Skiba et al., 1997; Firestone and Davidson, 1989). In both soil microbial processes NO can be an intermediate, it can be released and also absorbed (Galbally, 1989).

In most cases the organic layer is the only soil layer in direct contact with the atmosphere. There are soils having an organic layer with a thickness of 10 cm or more; these thick organic layers are mostly a kind of moder or raw humus (Scheffer and Schachtschabel, 2002). Mineral soils under these organic layers are never in contact with the atmosphere. Hence, as shown by Gasche and Papen (1999), who examined soils under a spruce canopy, the most important layer for NO exchange is the uppermost organic layer. In their experiment with intact soil cores from a spruce forest site they found that the organic layer contributed over 86% to the NO emission from soil. It is also known that nitrification occurs predominantly in the first few centimeters of soils (Papke and Papen, 1998; Rudolph and Conrad, 1996; Laville et al., 2009; Venterea et al., 2005; Remde et al., 1993; Jambert et al., 1994). Venterea et al. (2005) found actually the highest NO production in the first centimeter. Organic soils support high nitrification and denitrification rates and may be important hot spots of NO emission (Guthrie and Duxbury, 1978). Denitrification, in contrast, normally occurs in deeper soil layers or in the water table. In this respect, the role of organic matter is potentially important (Jambert et al., 1994).

In forests the type of understory influences NO exchange between the soil and the trunk space (Jambert et al., 1994; Pilegaard et al., 1999). Most studies to date have focused on the influence of the overstory vegetation and/or soil nutrients (Fowler et al., 2009; Venterea et al., 2004; Pilegaard et al., 2006). As reported by Oberdorfer (1994), Norway spruce forests fall into a series of plant sociological associations, which are characterized by the main understory species present (e.g. *Calamagrostio villosae – Piceetum*). Within one individual forest stand the understory might be composed of patches characterized by different species (e.g. *Calamagrostis villosa*, *Vaccinium myrtillus*, *Deschampsia flexuosa*). There are only a few studies how plants influence the NO exchange between soil and atmosphere (Stöhr and Stremlau, 2006; Stöhr and Ullrich, 2002), and there is a considerable lack of knowledge in this area.

To investigate the effect of soil physical and chemical parameters and understory types on NO emission from thick organic layers of forest soils we carried out laboratory incubation and flushing experiments on soils sampled below various understory covers in a Norway spruce forest in south-eastern Germany.

2   Material and methods

2.1   Sample site

The field site is located at Weidenbrunnen (50°09′ N, 11°34′ E, 774 m above sea level) which is situated in the Fichtelgebirge Mountains, NE Bavaria, Germany. The site is mainly covered by 55-year-old Norway spruce (*Picea abies*) with significant variability in the understory. There are four different main understory types: moss, grass (*Deschampsia flexuosa* and *Calamagrostis villosa*), blueberries (*Vaccinium myrtillus*), and young spruce which cover 45, 19, 7 and 13%, respectively, of the total surface area of the Weidenbrunnen site (Behrendt, 2009). Mean annual air temperature of the Weidenbrunnen site is 5.3 °C, mean annual soil temperature is 6.3 °C, and mean annual precipitation is approximately 1160 mm (1971–2000; Foken, 2003; Falge et al., 2003). The soil type was classified as cambic podzol over granite (Subke et al., 2003), and the texture is sandy loam to loam, with relatively high clay content in the Bh horizon. The mineral soil is characterised by low pH values (<4). The soil litter and the organic horizon had a thickness between 5 and 9 cm (Behrendt, 2009). The organic layer is classified as a moder consisting of Oi, Oe, and Oa horizons. More details concerning the site can be found in Gerstberger et al. (2004).

2.2   Soil sampling and preparation

In September 2008, soil samples for the laboratory study on NO release were taken from the O horizon at patches below the main understory types: moss, grass, young spruce, and blueberries. An individual understory patch has been defined, such that one square meter of understory area has to be covered mainly (>50%) with the respective understory vegetation. Two samples were taken for each understory type, resulting in a total of eight soil samples (soil samples taken under moss: M1, M2, soil samples taken under grass: G1, G2, soil samples taken under spruce: S1, S2, soil samples taken under blueberries: B1, B2). The soil samples were air dried and then stored at 4 °C until analysis. All measurements were performed within 2 months after sampling.

For our laboratory studies of NO release rates, samples were sieved through a 16 mm mesh to homogenise the soil and, all green biomass was removed. This can be contrasted with previous studies of mineral soils and sands where samples were sieved through 2 mm mesh (van Dijk and Meixner, 2001; van Dijk et al., 2002; Feig et al., 2008; Yu et al., 2008; Gelfand et al., 2009). A 16 mm mesh was chosen, based on tests sieving Weidenbrunnen organic matter through 2, 4, 8, and 16 mm mesh sizes. These experiments showed, that sieving through a 2 mm mesh destroyed the structure of soil organic matter causing higher NO release rates than observed when sieving through 4, 8 and 16 mm meshes whose corresponding NO release rates were not significantly different from each other (see Fig. 1).
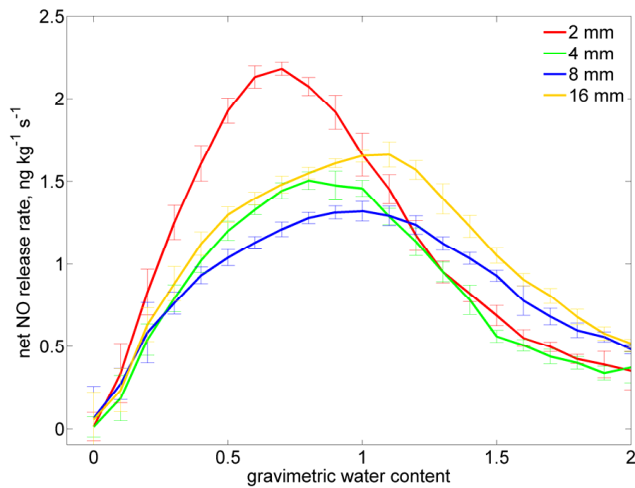
Fig. 1. The effect of sieving organic soil samples through sieves of different mesh sizes on the observed net NO release rates ($T_{soil} = 10\,°C$). Error bars show the standard deviation of the net NO release rate (expressed in terms of mass of nitrogen) averaged over bins of 0.1 gravimetric soil moisture.

For measurements of net NO release rates approx. 0.1 kg soil was placed into a Plexiglas cuvette, wetted with deionised water to a gravimetric water content >3 (using a spray can) and pre-incubated for 3 hours in a thermo-regulated cabinet to adapt to the soil temperature used during the corresponding NO release experiments. Former experiments showed that net NO release rates increase fairly proportionally with soil mass in the chambers up to 100 g, after which the slope declines. This indicates that from this soil mass onwards gas diffusion through the soil could be limiting. These results are similar to those of Remde et al. (1989) where the NO flux rate was shown to be proportional to the soil mass in the chamber up to 150 g. Above 150 g the relationship between NO flux and soil mass was no longer linear.

2.3 Soil physical and chemical characterization

In addition to samples for use in flux measurements, we took organic layer samples from each understory patch for the determination of soil pH, C/N ratio, organic C (C_{org}), soil nitrate (NO_3^-), soil ammonium (NH_4^+), bulk density (BD) and particle density (PD).

For the determination of soil pH the organic matter was homogenized and afterwards measured in a soil-to-water suspension (1:2.5) using a glass electrode (SenTix®, WTW, Germany). The C/N ratio was measured with an elementary analyzer (Flash EA 1112, Thermoquest, Germany). C_{org} was determined by the mean difference of 5 g (air dried) of the soil sample and 5 g dried at 430 °C in a muffle furnace (until constant weight was achieved). The ammonium and nitrate concentrations in extracts of the soil samples were measured by spectrometry (FIA-lab, MLE, Germany). For
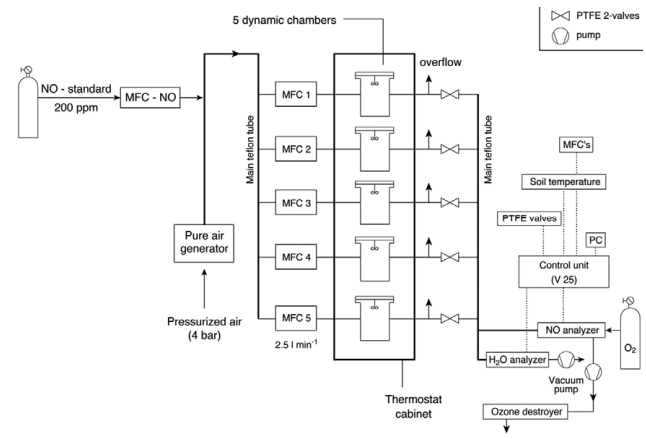

Fig. 2. Experimental setup for laboratory investigation of net NO release rates on soil samples (details, see Sect. 2.4).

determination of the soil bulk density, undisturbed soil samples were taken using a spade and afterwards dimensioned. Then the samples were dried at 60 °C for 24 h. From each patch we took three soil cores and individual quantities were averaged over these. Particle density of the soil sample was determined by a heliumpycnometer (AccuPyc II 1340, Micromeritics, USA) after sieving soil samples through a 2 mm mesh.

2.4 Laboratory setup

Net NO release rates from soil samples were determined using an automated laboratory system. A detailed description of our experimental setup is given in van Dijk and Meixner (2001); here we give only a short description of the most recent state of the setup (see Fig. 2).

Pressurized air is passed through a pure air generator (PAG 003, ECOPHYSICS, Switzerland) to provide dry and NO-free air. This NO-free air supplied five Plexiglas cuvettes (four incubation cuvettes and one empty reference cuvette). The volume of each cuvette was $9.7 \times 10^{-4}\,m^3$ (0.97 l)) and each was flushed with a continuous flow of $4.2 \times 10^{-5}\,m^3\,s^{-1}$ (2.5 l min^{-1}) of dry NO-free air, as controlled by five mass flow controllers (MFC, Mass-Flo, 5000 sccm range, MKS instruments, USA), one for each cuvette. The headspace volume of each cuvette is well mixed by a teflonized micro-fan (Micronel®, USA). The outlet of each cuvette was connected to a switching valve. Every two minutes one cuvette was switched to be the "active" cuvette (i.e., connected to the analyzers, while the remaining four cuvettes were still purged), so that all five cuvettes were measured within 10 min. The valves provided necessary sample air to a chemi-luminescence detector, NO-analyser (Model 42i Trace Level, Thermo Electron Corporation, USA; detection limit: 250 ppt (3σ)) and a CO$_2$-/H$_2$O-analyzer (Li-cor 840, Licor, USA). Instead of ambient air we operated the NO-analyser with pure oxygen (O$_2$) to obtain a better accuracy and precision of

the NO mixing ratio measurements, particularly at low mixing ratios.

The NO-analyser was calibrated using a gas phase titration unit (GPT, 146 C Dynamic Gas Calibrator, Thermo Electron Corporation, USA). For operating the GPT we used NO-free air from the PAG 003 and an NO gas standard (5.02 ppm NO, Air Liquide, Germany). The determination of the soil NO compensation mixing ratio (Conrad, 1994) requires the flushing of incubated soil samples with enhanced NO mixing ratios (resulting in reduced or even negative net NO release rates, i.e. NO uptake by the soil). Hence, NO standard gas (200 ppm NO, Air Liquide, Germany) was diluted into the air flow from the PAG 003 via a mass flow controller (Flow EL, Bronkhorst, Germany).

All connections and tubes consisted of polytetrafluorethylene (PTFE). A homebuilt control unit (V25) was controlling the entire laboratory system and, in combination with a computer, was also used for data acquisition (see Fig. 2).

To determine the temperature response of the net NO release we performed a total of four experiments, each on another sub-sample of the original understory soil sample. The sub-samples were identically pre-treated. Incubations were at 10 °C and 20 °C, corresponding flushing was either with dry, NO-free air, or with air containing 133 ppb of NO. Since every experiment begins with a wetted soil sample and the flushing air is completely dry, the gravimetric water content (θ) of the samples declines during each experiment as evaporating water leaves the cuvette with the flushing air flow. Gravimetric soil moisture content was measured by tracking the loss of water vapour throughout the measurement period and relating this temporal integral to the gravimetric soil moisture content observed at the start and end of the measurement period. Soil samples are completely dry within 4 to 7 days. This procedure provides us the response of the net NO release rates over the entire range of gravimetric soil moisture (>4 to 0). Gravimetric soil moisture ranging from 0 to 4 corresponds to a water filled pore space (WFPS) from 0 to 0.7.

The NO release rate is a product of NO consumption and NO production, because both processes occur simultaneously in the topsoil (Rudolph and Conrad, 1996; Conrad, 1994). Consequently, the observed NO release rate, J (see Eq. 1), is always a net release rate. If NO consumption overrides the NO production in the soil sample, then J becomes negative. However, this only occurs if the the NO mixing ratio in the reference cuvette, $m_{NO,ref}$, exceeds the NO mixing ratio in the headspace of a sample cuvette (which is equal to the corresponding outlet NO mixing ratio, $m_{NO,out}$, due to well-mixed conditions within each sample cuvette).

2.5 Calculation and fitting the net NO release rate

For a given constant incubation temperature (10 °C, 20 °C) we derived from our laboratory data the net NO release rate $J=J(\theta)$ (in ng NO (in terms of mass of nitrogen) per mass of (dry) soil (kg) and time (s)) as a function of the gravimetric soil moisture (θ) of the soil samples. $J(\theta)$ was calculated from the NO mixing ratio difference between the reference cuvette ($m_{NO,ref}$, in ppb) and the soil incubation cuvettes ($m_{NO,out}$, in ppb):

$$J(\theta) = \frac{Q}{M_{soil}}(m_{NO,out} - m_{NO,ref}) \cdot \frac{M_N}{V_m} \times 10^{-3} \qquad (1)$$

where Q is the flow through the cuvette (m^3 s^{-1}), M_{soil} is the dry mass of the soil sample (kg), $M_N/V_m \cdot 10^{-3}$ is the conversion factor (ppb to ng m^{-3}), where M_N is the molecular weight of nitrogen (14.0076 kg kmol^{-1}) and V_m is the molar volume (m^3 kmol^{-1}) at actual temperature and standard pressure (1013.25 hPa).

Individual data of measured net NO release rates were fitted with a 3 parameter function (Eq. 2) modified from that given by Meixner and Yang (2006) in order to yield two of the three parameters as measured quantities (θ_{opt}, J_{opt}):

$$J(\theta) = J_{opt} \cdot (\frac{\theta}{\theta_{opt}})^b \cdot \exp(b\left(1 - \frac{\theta}{\theta_{opt}}\right)) \qquad (2)$$

where θ_{opt} is the gravimetric water content where the optimum net NO release rate ($J_{opt}:=J(\theta_{opt})$) is observed, and b characterizes the width of the fitting curve. The gnuplot® software (www.gnuplot.info, see copyright information) was used for fitting.

It has been frequently shown, that there is a linear relationship between the net NO release rate (J) and the headspace NO mixing ratio ($m_{NO,out}$) (Remde et al., 1989; van Dijk and Meixner, 2001; van Dijk et al., 2002; Ludwig et al., 2001):

$$J = P - K = P - k \cdot m_{NO,out} \cdot \frac{M_N}{V_m} \times 10^{-3} \qquad (3)$$

Equation (3) implies that the NO production rate P (ng kg^{-1} s^{-1}) is independent of the cuvette's headspace NO mixing ratio ($m_{NO,out}$), whereas the first-order NO consumption rate, K (ng kg^{-1} s^{-1}), is dependent on it. The NO consumption coefficient k (m^3 kg^{-1} s^{-1}) is determined from the slope of Eq. (3). To obtain this slope, we used two incubation data sets: namely at $m_{NO,ref} = 0$ ppb and $m_{NO,ref} = 133$ ppb,

$$k(\theta) = \qquad (4)$$
$$\frac{\Delta J_{NO}}{\Delta [NO]} - \frac{J(m_{NO,out,high}) - J(m_{NO,out,low})}{m_{NO,out,high} - m_{NO,out,low}} \cdot \frac{V_m}{M_N} \times 10^{-3}$$

where $m_{NO,out,low}$ is the actual NO mixing ratio (ppb) in the headspace of the cuvette under flushing with NO free air and $m_{NO,out,high}$ is the actual NO mixing ratio in the cuvette under flushing with 133 ppb NO. Having determined k, the NO production rate P was calculated from Eq. (3) and corresponding NO net release rates J from Eq. (1).

Finally, Eq. (3) is extended to describe the net NO release rate, for each soil sample, as a function of the main influencing variables, headspace NO mixing ratio ($m_{NO,out}$), gravimetric water content (θ) and soil temperature (T_{soil}). For

the temperature dependence we used the Q_{10} values (see Sect. 2.8), as a "temperature amplification factor" (Feig et al., 2008):

$$J(m_{NO,out}, \theta, T_P \text{soil}) = \quad (5)$$

$$P(\theta, T_{soil}) - k(\theta, T_{soil}) \cdot m_{NO,out} \cdot \frac{M_N}{V_m} \times 10^{-3}$$

2.6 NO compensation point mixing ratio

The existence of a NO compensation point mixing ratio ($m_{NO,comp}$) has been clearly demonstrated (Remde et al., 1989; van Dijk and Meixner, 2001; Conrad, 1994; Gelfand et al., 2009; Feig et al., 2008; Otter et al., 1999; Johansson and Granat, 1984). Considering Eq. (5) $m_{NO,comp}$ is the mixing ratio ($m_{NO,out}$) at which the rate of NO production P equals the rate of NO consumption K, so that the net NO release rate between soil and the headspace is zero ($J = 0$). Hence, from Eq. (6) $m_{NO,comp}$ is calculated in terms of gravimetric soil water content and soil temperature.

$$m_{NO,comp}(\theta, T_{soil}) = \frac{P(\theta, T_{soil})}{k(\theta, T_{soil})} \cdot \frac{V_m}{M_N} \times 10^{-3} \quad (6)$$

2.7 Net potential NO flux

To relate the net NO release rate, which is expressed in ng NO per mass of soil and time, to the net potential NO flux, which is expressed in ng NO per soil area and time, we used the following equation, originally presented by Galbally and Johansson (1989), which has been used in modified forms already by Otter et al. (1999), van Dijk and Meixner (2001), Feig et al. (2008), Gelfand (2009), Yu et al. (2008).

$$F_{NO}(\theta, T_{soil}) = \sqrt{D_p(\theta) \cdot BD \cdot k(\theta, T_{soil})} \quad (7)$$

$$\cdot \left(\frac{P(\theta, T_{soil})}{k(\theta, T_{soil})} - m_{NO,out} \cdot \frac{M_N}{V_m} \times 10^{-3} \right)$$

F_{NO} is the desired net potential NO flux (ng m^{-2} s^{-1}), BD is the bulk density of soil (kg m^{-3}), D$_p$ is the effective diffusion coefficient of NO in soil (in m^2 s^{-1}) according to Millington and Quirk (1960) (see Sect. 2.9).

2.8 Calculation of the Q_{10} value

The temperature dependence of the net potential NO flux was determined by using net NO release rates obtained for two soil temperatures, namely those at 10 °C and 20 °C. The temperature dependence usually shows an exponential increase and can be expressed by the ratio of two net potential NO fluxes, at soil temperatures 10 °C apart. The Q_{10} values used for this study were calculated from the net potential NO fluxes at optimum gravimetric soil moisture (θ_{opt}):

$$Q_{10}(\theta_{opt}) = \frac{F_{NO}(\theta_{opt}, T_{soil} = 20 °C)}{F_{NO}(\theta_{opt}, T_{soil} = 10 °C)} \quad (8)$$

Table 1. Mathematical formulations for the calculation of the effective diffusion coefficient in soil. ϵ is the soil air-filled porosity in m^3 (soil air) m^{-3} (soil), Φ is the soil total porosity in m^3 (pores) m^{-3} (soil) and D_0 is the gas diffusion coefficient in free air (1.99×10^{-5} m^2 s^{-1}).

Moldrup (2000)	Millington (1959)	Millington & Quirk (1961)
$D_p = \frac{\epsilon^{2.5}}{\Phi}$	$D_p = \epsilon^{3/2} \cdot D_0$	$D_p = \frac{\epsilon^{10/3}}{\Phi^2} \cdot D_0$

2.9 Effective diffusion of NO in soil air

The effective gas diffusion coefficient of NO in soil air is an important parameter for deriving the net potential NO flux from NO production and NO consumption rates (Bollmann and Conrad, 1998). Since we do not have measurements of the effective soil diffusion coefficient (D_p) at the Weidenbrunnen site, we estimated the diffusion coefficient through available functional relationships. The choice of the proper diffusivity coefficient function is not trivial, particularly for organic soils (Kapiluto et al., 2007). Therefore, we tested different functions namely those of Moldrup et al. (2000), Millington (1959) and Millington and Quirk (1960) which are given in Table 1. In these functions the following measured variables were used:

– soil total porosity (Φ), calculated from the soil bulk density (BD) and the particle density (PD) of the soil sample; both parameters measured directly on the soil samples:

$$\Phi = 1 - \frac{BD}{PD} \quad (9)$$

– soil air filled porosity (ϵ) calculated from the soil bulk density, the density of water (WD), and the the soil total porosity (Φ):

$$\epsilon = 1 - \theta \frac{BD}{WD} \cdot \frac{1}{\Phi} \quad (10)$$

We calculated net potential NO fluxes (see Sect. 2.7) using the three different effective NO diffusion coefficients. One example for a soil sample from a grass covered patch is shown in Fig. 3. Net potential fluxes exhibit different maxima with a shifting value for the optimum water content for NO production due to the different exponents for ϵ. According to Moldrup (personal communication, 2009), the Millington and Quirk approach describes the effective gas diffusion coefficient best for soil organic matter; therefore the potential NO fluxes of this paper have been calculated using the formulation by Millington and Quirk (1960).
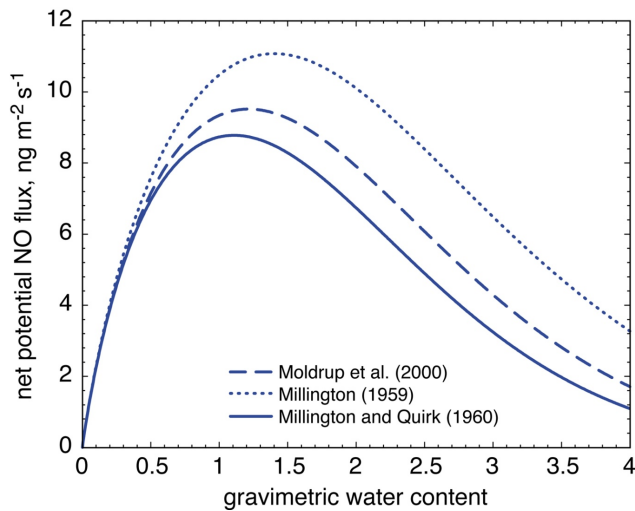
Fig. 3. Net potential NO flux at $10\,^{\circ}$C from a grass covered patch (all expressed in terms of mass of nitrogen). The net potential NO fluxes were calculated according to Eq. (8) applying effective soil diffusion coefficients by Moldrup et al. (2000), Millington (1959) and Millington and Quirk (1960) (see Table 1).

2.10 Error estimation of NO release measurements

The errors in the net NO release rate were determined using the individual errors of all quantities on the right hand site of Eq. (1). We specified these errors as followed:

– The error in the soil weight (M_{soil}) measurements was set to the accuracy of the balance (PG-S Delta Range®, Mettler-Toledo, Switzerland) provided by the manufacturer: $0.001\,\mathrm{kg}$ (for a mass $<1.0\,\mathrm{kg}$).

– The error of the mass flow rate through the cuvette (Q) was found as $1.68\times10^{-8}\,\mathrm{m^3\,s^{-1}}$ (i.e. the standard deviation of all individual mean flux rates of a corresponding experiment with n=798).

– The error of the mixing ratio in the headspace of a soil cuvette ($m_{\mathrm{NO,out}}$) was determined by using every NO mixing ratio measurement: for $m_{\mathrm{NO,ref}}$=0 ppb the error was <0.1 ppb, for $m_{\mathrm{NO,ref}}$=133 ppb the error was <0.6 ppb.

– The error of the reference cuvette ($m_{\mathrm{NO,ref}}$) was determined in the same way, resulting in an error of <0.1 ppb ($m_{\mathrm{NO,ref}}=0$ ppb), and <0.4 ppb ($m_{\mathrm{NO,ref}}$=133 ppb).

Application of Gaussian error propagation to Eq. (1) resulted in an error in the optimum net NO release rate (J_{opt}) of less than 8%.

The detection limit for the net NO release rate obtained by our laboratory system was determined by Feig et al. (2008) and Gelfand et al. (2009) using inert glass beads and autoclaved soils. The "blank" net NO release
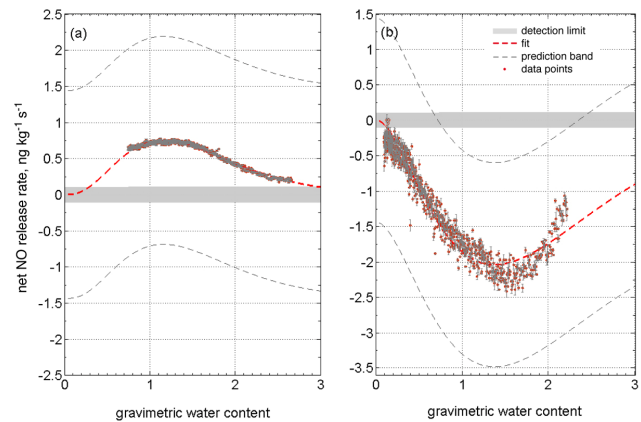

Fig. 4.   **(a)** measured net NO release rates (red dots) at $m_{\mathrm{NO,ref}}=0$ ppb and fitted net NO release rates (red dashed line), for a soil samples covered with moss. **(b)** measured net NO release rates (red dots) at $m_{\mathrm{NO,ref}}$=133 ppb and fitted net NO release rates (red dashed line), for a moss covered soil. The grey shaded band indicates the detection of the net NO release rate obtained through our laboratory system. Error bars (grey whiskers) on each individual data point have been calculated by the Gaussian error propagation (see Sect. 2.10). NO release rates in both panels have been obtained for $T_{\mathrm{soil}}=20\,^{\circ}$C.

rate from the inert glass beads was $0.02\,\mathrm{ng\,kg^{-1}\,s^{-1}}$ with a random deviation of $0.02\,\mathrm{ng\,kg^{-1}\,s^{-1}}$ and for autoclaved soils it was $0.05\,\mathrm{ng\,kg^{-1}\,s^{-1}}$ with a random deviation of $0.02\,\mathrm{ng\,kg^{-1}\,s^{-1}}$. Feig et al. (2008) defined the detection limit of the net NO release rate as $0.08\,\mathrm{ng\,kg^{-1}\,s^{-1}}$ (i.e. mean net NO release rate of glass beads plus three times its standard deviation). The detection limit of the autoclaved soils was calculated the same way and resulted in a detection limit of $0.11\,\mathrm{ng\,kg^{-1}\,s^{-1}}$. Therefore, the more conservative estimate from the autoclaved soils was used as the detection limit of net NO release rates determined by our laboratory system.

In Fig. 4a and b, we present the net NO release rate calculated from the difference in the data points of NO mixing ratio (see Eq. 1) and the corresponding fit (see Eq. 2) for a soil samples under moss. Fig. 4 also shows the individual errors of J (by Gaussian error propagation; grey whiskers) and the detection limit of J (grey shadow band).

For the fit of the data according to Eq. (2), prediction bands (PB) were calculated at a confidence level of 95% using the procedure given by Olive (2007) (Eq. 2.6 in the work by Olive). The prediction bands show for a prescribed probability, the values of one or more hypothetical observations that could be drawn from the same population from which the given data was sampled.
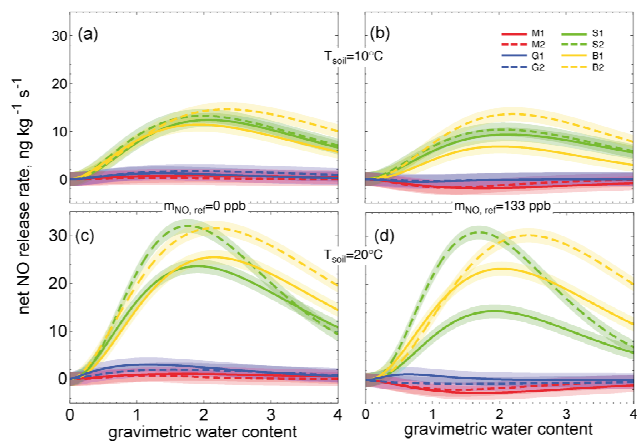
Fig. 5. Net NO release rates fitted through experimental results by Eq. (2) (see Sect. 2.4) at **(a)** $T_{soil}=10\,°C$ and $m_{NO,ref}=0\,ppb$, **(b)** $T_{soil}=10\,°C$ and $m_{NO,ref}=133\,ppb$, **(c)** $T_{soil}=20\,°C$ and $m_{NO,ref}=0\,ppb$ NO and **(d)** $T_{soil}=20\,°C$ and $m_{NO,ref}=133\,ppb$ (all expressed in terms of mass of nitrogen). The transparent bands are the prediction bands of each line (95% confidence level).

3 Results

3.1 Net NO release rates

Figures 5a–d present net NO release rates obtained from soil samples taken under moss, grass, spruce and blueberry cover at two temperatures (upper panels: 10 °C, and lower panels: 20 °C) and two NO mixing ratios (left panels: $m_{NO,ref}=0\,ppb$ and right panels: $m_{NO,ref}=133\,ppb$). The curves are the result of corresponding fitting (Eq. 2) to measured data as described in section 2.5. At incubation with NO free air higher net NO release rates occurred from soil samples taken under spruce (S1, S2) and blueberry (B1, B2) cover than under moss (M1, M2) and grass (G1, G2) cover. Maximum NO release rates at $T_{soil}=10\,°C$ and 20 °C were 12.4 and 23.6 ng kg^{-1} s^{-1} for S1, 13.2 and 32.0 ng kg^{-1} s^{-1} for S2, 11.4 and 25.5 ng kg^{-1} s^{-1} for B1, and 14.6 and 33.6 ng kg^{-1} s^{-1} for B2. Similarly, when incubated with 133 ppb NO, soil samples taken under spruce (S1: 9.3 and 14.4 ng kg^{-1} s^{-1}, S2: 10.4 and 30.8 ng kg^{-1} s^{-1}) and blueberry (B1: 6.8 and 23.6 ng kg^{-1} s^{-1}, B2: 13.6 and 30.2 ng kg^{-1} s^{-1}) cover showed the highest net NO release rates. In contrast, soil samples taken under moss and grass cover showed small net NO release rates when flushed with NO free air (Fig. 5a, c). When flushed with air containing 133 ppb NO, negative net NO release rates occurred for the soil samples S1, S2 and G2. In these cases the flushing NO mixing ratio of 133 ppb was obviously higher than the NO compensation mixing ratio ($m_{NO,comp}$) of the corresponding soil samples (see section 2.7), and the NO consumption rate (K) has exceeded the NO production rate (P) in these soil samples.
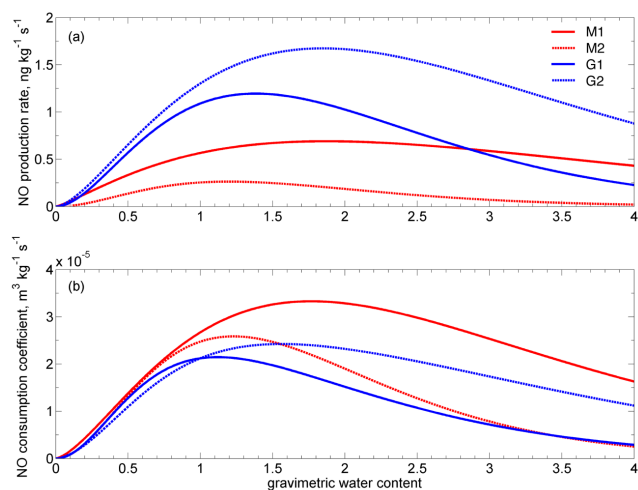

Fig. 6. **(a)** NO production at $T_{soil}=10\,°C$ and **(b)** NO consumption coefficient at $T_{soil}=10\,°C$ from soil samples taken under moss and grass cover (all expressed in terms of mass of nitrogen). The red lines show the production and consumption coefficient of soil samples taken under moss covered patches and the blue lines of soil samples taken under grass covered patches.

Net NO release rates reached their maxima between 0.64 (G1) and 2.41 (B2) gravimetric water content. The soil moisture, where the optimum net NO release rate is observed, is called the optimum soil moisture ($θ_{opt}$ in Eq. 3). Generally, highest values of $θ_{opt}$ were observed for S1, S2, B1 and B2.

At gravimetric soil moisture of 4 the net NO release rates do not become zero. That is due to the fact that the samples were not waterlogged at gravimetric soil moisture of 4. Therefore, nitrifiers and denitrifiers might be still supplied with oxygen.

However, the curves differ for optimum soil moistures and higher than these. The net NO release rates from S1 and S2 were not significantly different from each other using either flushing at $T_{soil}=10\,°C$, but significantly differ at $T_{soil}=20\,°C$. No significant differences could be observed between the two samples taken under moss cover, or the two samples taken under grass cover. Net NO release rate of soil samples taken under blueberry cover were similar only in a range between 0 and 1.4 gravimetric water content and only in the treatment with NO free air and at $T_{soil}=10\,°C$.

3.2 NO production rates, NO consumption coefficients, and NO compensation point mixing ratios

Exemplary results of NO production rate and NO consumption coefficient as a function of gravimetric soil water content for $T_{soil}=10\,°C$ are shown in Fig. 6a and 6b (for soil samples taken under moss and grass cover). The NO production rate P (also expressed in ng kg^{-1} s^{-1}) is nearly as high as the net NO release rate at $m_{NO,ref}=0\,ppb$. The NO production rate exponentially increased with soil moisture
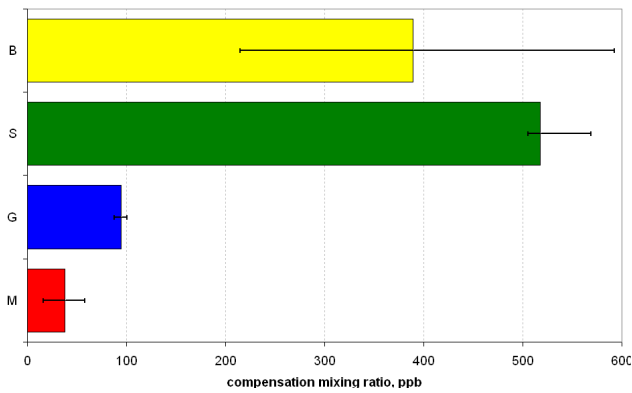
Fig. 7. Median NO compensation point mixing ratios, $m_{\mathrm{NO,comp}}$ (Eq. 7, Sect. 2.7), for all soil probes taken under the different understory types of the Weidenbrunnen site at 1 ± 0.1 gravimetric soil moisture and $T_{\mathrm{soil}} = 10\,^{\circ}\mathrm{C}$. The bars indicate the range between the 25% and 75% percentile of the data ($n = 10$, for each understory type data set).

to a maximum value followed by a moderate decrease at higher soil moistures. This optimum shape of the NO production rate has been explained by substrate limitation under very dry conditions, and O_2-diffusion limitation under very wet conditions (Davidson et al., 1993; Meixner, 1994; Rudolph and Conrad, 1996; Meixner and Yang, 2006; Skopp et al., 1990). The lowest optimum NO production rates were found at $T_{\mathrm{soil}}=10\,^{\circ}\mathrm{C}$ for M1 and M2 with 0.7 and 0.3 $\mathrm{ng\,kg^{-1}\,s^{-1}}$. G1 and G2 revealed optima of 1.2 and 1.7 $\mathrm{ng\,kg^{-1}\,s^{-1}}$. S1 and S2 yield optimum NO production rates of 12.0 and 12.8 $\mathrm{ng\,kg^{-1}\,s^{-1}}$, and B1 and B2 of 10.9 and 14.5 $\mathrm{ng\,kg^{-1}\,s^{-1}}$(see Table 2). The NO production rate at 20 °C showed generally higher values at optimum soil moisture. The optimum NO production rate for M1 and M2 at $T_{\mathrm{soil}}=20\,^{\circ}\mathrm{C}$ were 1.1 and 0.7 $\mathrm{ng\,kg^{-1}\,s^{-1}}$, for G1 and G2 3.0 and 2.0 $\mathrm{ng\,kg^{-1}\,s^{-1}}$, 21.4 and 31.6 $\mathrm{ng\,kg^{-1}\,s^{-1}}$ for S1 and S2, and for B1 and B2 24.8 and 31.2 $\mathrm{ng\,kg^{-1}\,s^{-1}}$ (see Table 2).

The NO consumption coefficient (k, see Eq. 4) is expressed in $\mathrm{m^3\,kg^{-1}\,s^{-1}}$. For our samples, we measured maximum NO consumption coefficients for M1 and M2 of $3\times10^{-5}\,\mathrm{m^3\,kg^{-1}\,s^{-1}}$, for G1 and G2 $2\times10^{-5}\,\mathrm{m^3\,kg^{-1}\,s^{-1}}$ for both, $4\times10^{-5}\,\mathrm{m^3\,kg^{-1}\,s^{-1}}$ for S1 and S2 and 6×10^{-5} and $3\times10^{-5}\,\mathrm{m^3\,kg^{-1}\,s^{-1}}$ for B1 and B2 (all values for $T_{\mathrm{soil}}=10\,^{\circ}\mathrm{C}$, see Table 3 for NO consumption at $T_{\mathrm{soil}}=20\,^{\circ}\mathrm{C}$).

Fig. 7 presents mean NO compensation point mixing ratios ($m_{\mathrm{NO,comp}}$) for all eight soil samples at gravimetric soil moisture of 1 ± 0.1 which is at the upper end of gravimetric soil moistures observed at the sample site (Behrendt, 2009). The $m_{\mathrm{NO,comp}}$ varies over a wide range. Soil samples taken under moss and grass cover showed small $m_{\mathrm{NO,comp}}$ (38 ppb and 94 ppb) compared to soil samples taken under spruce and blueberry cover which exhibited considerable higher $m_{\mathrm{NO,comp}}$ (518 ppb and 389 ppb).
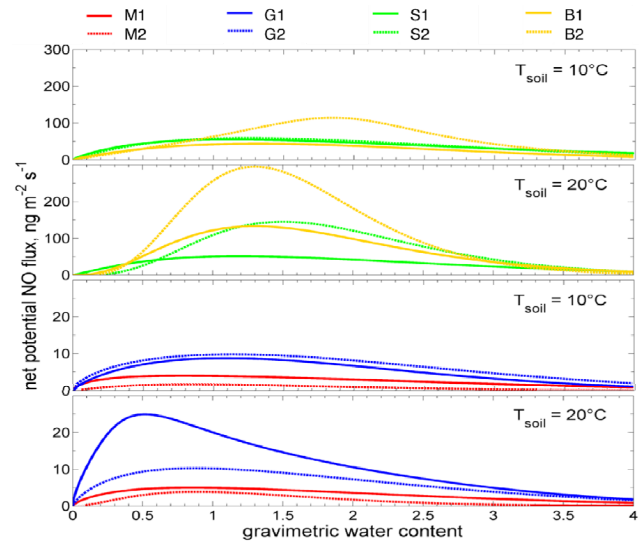

Fig. 8. Net potential NO flux (all expressed in terms of mass of nitrogen) at 10 °C and 20 °C from soil samples taken under moss, spruce and blueberry covered patches (note different scales of the y-axes).

3.3 Net potential NO fluxes

Net potential NO fluxes derived from measured net NO release rates from soil samples taken under different understory covers are given in Fig. 8. It is remarkable, that the net potential NO fluxes from soil samples taken under spruce and blueberry cover were approximately 10-fold higher than net potential NO fluxes from soil samples taken under moss and grass cover (note different scales of y-axes in Fig. 8). The optimum NO fluxes at $T_{\mathrm{soil}}=10\,^{\circ}\mathrm{C}$ ranged between 1.7 $\mathrm{ng\,m^{-2}\,s^{-1}}$ (M2) and 114.6 $\mathrm{ng\,m^{-2}\,s^{-1}}$ (B2). The position of the optimum gravimetric water content varied between the different curves. The optimum gravimetric water content for $T_{\mathrm{soil}}=10\,^{\circ}\mathrm{C}$ was 0.8 for M1 and M2, 1.1 for G1 and G2, 1.3 for S1 and S2 and 1.3 for B1 and 1.5 for B2 gravimetric soil moisture (also see Table 2). For flushing at $T_{\mathrm{soil}}=20\,^{\circ}\mathrm{C}$, optimum net potential NO fluxes were, except for S1, always higher at the higher incubation temperature. They ranged between 3.9 $\mathrm{ng\,m^{-2}\,s^{-1}}$(M2) and 295 $\mathrm{ng\,m^{-2}\,s^{-1}}$ (B2) (see Table 2). Optimum gravimetric water content for $T_{\mathrm{soil}}=20\,^{\circ}\mathrm{C}$ were 0.8 and 0.9 for M1 and M2, 0.5 and 0.8 for G1 and G2, 1.2 and 1.5 for S1 and S2, and 1.3 for B1 and B2.

3.4 Temperature dependence (Q_{10} values)

Optimum net potential NO fluxes measured at two different soil temperatures (10 °C and 20 °C) allowed us to estimate Q_{10} values for each soil sample of the Weidenbrunnen site and data are given in Table 2. For S1 we derived the lowest Q_{10} value (0.92). B1 showed the highest Q_{10} value of 3.04.

Table 2. Net potential NO flux (in terms of mass of nitrogen) calculated with the diffusion coefficient according to Millington and Quirk (1960); NO production rates (P_{opt}) and the NO consumption coefficients (k_{opt}) are calculated for $10\,°C$ and $20\,°C$ and the Q_{10} values. All values are at optimum gravimetric soil moisture (θ_{opt}).

soil samples	understory vegetation	optimum gravimetric water content (10 °C) [1]	optimum net potential NO flux (10 °C) (ng m^{-2} s^{-1})	optimum gravimetric water content (20 °C) [1]	optimun net potential NO flux (20 °C) (ng m^{-2} s^{-1})	P_{opt} (10 °C) (ng kg^{-1} s^{-1})	k_{opt} (10 °C) (m^3 kg^{-1} s^{-1})	P_{opt} (20 °C) (ng kg^{-1} s^{-1})	k_{opt} (20 °C) (m^3 kg^{-1} s^{-1})	Q_{10} [1]
M1	moss	0.8	4.0	0.8	5.0	0.7	3.3×10^{-5}	1.1	5.1×10^{-5}	1.25
M2	moss	0.8	1.7	0.9	3.9	0.3	2.6×10^{-5}	0.7	3.7×10^{-5}	2.29
G1	grass	1.1	8.8	0.5	24.9	1.2	2.1×10^{-5}	3.0	3.4×10^{-5}	2.83
G2	grass	1.1	9.8	0.9	10.3	1.7	2.4×10^{-5}	2.0	3.7×10^{-5}	1.05
S1	spruce	1.3	55.4	1.2	51.1	12.0	4×10^{-5}	21.4	1.4×10^{-5}	0.92
S2	spruce	1.3	59.3	1.5	145.0	12.8	3.7×10^{-5}	31.6	4.3×10^{-5}	2.45
B1	blueberry	1.3	43.7	1.3	133.0	10.9	6.1×10^{-5}	24.8	4.2×10^{-5}	3.04
B2	blueberry	1.5	114.6	1.3	295.0	14.5	2.8×10^{-5}	31.2	2.6×10^{-5}	2.6

3.5 Chemical and physical soil parameters

The results of analysis of different soil parameters including bulk density (BD), particle density (PD), soil pH, C/N ratio, organic carbon (c_{org}), soil ammonia (NH_4^+) and soil nitrate (NO_3^-) are summarized in Table 3. Soil bulk density ranged between 0.12 and $0.18\times10^3\,kg\,m^{-3}$, while PD ranged between 1.5 and $1.7\times10^3\,kg\,m^{-3}$. Soil pH was lowest (3.5) in soil samples taken under spruce cover (S1, S2) and highest (5.0) for soil samples taken under moss cover (M1, M2). C/N ratios for all soil samples taken from the organic layers are relatively low, but on average (16.2) close to the range reported in literature for other Norway spruce sites in the Fichtelgebirge (see Schmitt et al., 2008; Michel et al., 2006). C/N ratios varied only in a small range, namely between 14.7 and 18.4. For C_{org} the values ranged between 26.9% (M2) and 43.5% (S1). A higher variability has been found for soil NH_4^+. Lowest soil NH_4^+ values were found for S1 (56 mg kg^{-1}) and S2 (86 mg kg^{-1}) and the highest soil NH_4^+ values were found for G1 (207 mg kg^{-1}) and G2 (204 mg kg^{-1}) (expressed in mass of N). Soil NO_3^- ranged between 1 and 11 mg kg^{-1} (expressed in mass of N).

Pearson's product-moment-analyses were performed to test (a) net potential NO fluxes (at $T_{soil}=10\,°C$, $T_{soil}=20\,°C$), (b) NO production rates (at $T_{soil}=10\,°C$, $T_{soil}=20\,°C$) and (c) NO consumption coefficients (at $T_{soil}=10\,°C$, $T_{soil}=20\,°C$) for possible relationship with the physical and chemical soil parameters (soil pH, C_{org}, C/N ratio, soil NH_4^+, soil NO_3^- and PD).

The results obtained from Pearson's product-moment-analyses are presented in Table 4. Significant negative correlations (probability level of 0.1) were found only between soil NH_4^+ and NO production rate at $T_{soil}=10\,°C$, NO production rate at $T_{soil}=20\,°C$, and NO consumption coefficient at $T_{soil}=20\,°C$. The following correlations were not significant at a probability level of 0.1. Soil pH correlated negatively with all independent variables except for the consumption coefficient at $T_{soil}=10\,°C$. Positive correlations with the individual variables were found for soil C_{org} and also for C/N. Soil NO_3^- vs. independent variables showed positive correlations except for the NO consumption coefficient. Particle density correlated negatively with independent variables, except for the NO consumption coefficient.

4 Discussion

4.1 Comparison with other studies

During the last two decades, there has been a series of studies on biogenic NO emissions from soil in forest ecosystems (Papke and Papen, 1998; Pilegaard et al., 1999, 2006; Kesik et al., 2005; Johansson, 1984; Butterbach-Bahl et al., 2001, 2002; Lehmann, 2002). However, there are only a few studies examining spatial differences of NO fluxes within a forest (Gasche and Papen, 1999; Lehmann, 2002; Pilegaard et al., 1999; Nishina et al., 2009). Furthermore, the influence of soil organic matter on soil biogenic NO emissions has not been studied in detail and is consequently not well known. In most studies the effect of the dominant overstory or of the whole soil core (mineral and organic layer) was addressed by measurements using the dynamic chamber technique (Gasche and Papen, 1999; Butterbach-Bahl et al., 1997; Johansson, 1984).

During the last two decades, a series of field and laboratory studies clearly demonstrated, that NO fluxes, measured in the field by dynamic chamber techniques, were in good agreement with those NO fluxes, which have been derived from laboratory incubations on soils sampled from the top soil layer of dynamic chambers' enclosures (Meixner et al., 1997; van Dijk et al., 2002; Remde et al., 1993; Ludwig et al., 2001; Meixner and Yang, 2006; Otter et al., 1999). However, for more detailed investigations, laboratory studies are necessary, but only a few groups seem to have the facilities available to carry out laboratory measurements of

Table 3. Chemical and physical soil parameters from organic soil layers under different understories from Weidenbrunnen research site. NH_4^+ and NO_3^- are expressed in terms of mass of N.

soil samples	understory vegetation	bulk density $(10^3 \, kg \, m^{-3})$	particle density $(10^3 \, kg \, m^{-3})$	pH (measured in H_2O) [1]	C/N [1]	C_{org} [%]	NH_4^+ $mg \, kg^{-1}$ (dry soil)	NO_3^- $mg \, kg^{-1}$ (dry soil)
M1	moss	0.15	1.5	4.6	16.4	43.3	194	2
M2	moss	0.12	1.7	5	16.6	26.9	148	7
G1	grass	0.15	1.7	4.1	14.7	29.5	207	1
G2	grass	0.13	1.5	3.6	15.4	40.0	204	2
S1	spruce	0.14	1.6	3.5	16.9	43.5	56	2
S2	spruce	0.14	1.6	3.5	18.4	30.2	86	11
B1	blueberry	0.18	1.6	4.7	15.3	36.5	139	1
B2	blueberry	0.15	1.5	3.7	15.6	39.0	148	2

Table 4. Results of Pearson product moment correlation analysis of net NO release rates, net potential NO flux, NO production rate (P) and NO consumption coefficient (k) versus physical and chemical soil parameters.

	NO flux 10 °C	P 10 °C	k 10 °C	NO flux 20 °C	P 20 °C	k 20 °C
pH	−0.537	−0.523	0.206	−0.356	−0.468	−0.311
C_{org}	0.226	0.213	0.227	0.066	0.095	0.495
C/N	0.157	0.332	0.137	0.043	0.364	0.325
NH_4^+	−0.519	−0.739[a]	−0.467	−0.315	−0.698[a]	−0.662[a]
NO_3^-	0.061	0.172	−0.033	0.091	0.274	−0.083
PD	−0.367	−0.181	0.023	−0.387	−0.149	0.171

[a] Significant at the 0.10 probability level.

soil NO exchange (e.g. Bollmann et al., 1999; Ormeci et al., 1999; Schindlbacher et al., 2004; Feig et al., 2008; van Dijk and Meixner, 2001). Since laboratory studies are outnumbered, most of the following discussion is based on results from field measurements in spruce forests.

Pilegaard et al. (1999), applying a dynamic field chamber technique in a spruce forest site at Ulborg (Denmark), found low NO fluxes from moss covered soil. However, NO fluxes increased with closeness to standing tree trunks. For their forest soils which had a thick organic layer (4 cm), NO fluxes ranged between <0.3 and 66 ng m^{-2} s^{-1}. Similar results were presented by Gasche and Papen (2002) for the Höglwald forest (Germany). Their measurements, also employing a dynamic chamber technique, addressed the spatial distribution of NO fluxes along a tree-to-tree gradient. For 1997, annual mean NO fluxes of 29.2±0.9 ng m^{-2} s^{-1} were found for those chambers which were located closest to the stems, 18.4±0.5 ng m^{-2} s^{-1} for chambers approx. 4 m, and 12.3±0.4 ng m^{-2} s^{-1} for the chamber approx. 6 m apart from the stems. With closeness to trunks (living trees) the NO emissions increased significantly (between 1.6- and 2.6-fold). While for the Höglwald beech for-

est site, Gasche and Papen (2002) could explain an identical spatial effect with marked differences in soil physical and chemical soil parameters, there was no detailed explanation for the Höglwald spruce forest site. One reason could be that the nutrient supply from stem flow is negligible at this spruce forest site (Gasche and Papen, 2002). Butterbach-Bahl et al. (1997) reported mean monthly NO fluxes between 5.6 and 36.1 ng m^{-2} s^{-1} for the same Höglwald spruce forest site (July 1994 to June 1995). The site exhibits acidic soil pH values (2.7 to 3.6) in the organic layer. Again for the Höglwald spruce site, Gasche and Papen (1999) showed, that most of the NO emissions came from the organic layer and only a small contribution from the mineral soil. For the entire Höglwald site, they reported annual NO emission rates of 25.5±0.5 ng m^{-2} s^{-1} during 1994-1996. Very low NO fluxes (0.3±0.1 ng m^{-2} s^{-1}) were reported by Horváth et al. (2006) for a spruce forest site in NE Hungary (October 2002 to September 2003). Similar low NO fluxes were reported by Kitzler et al. (2006) for the spruce-fir-beech forest site of Achental (Austria) during the period of May 2002 to July 2004. Using a dynamic chamber technique, they found mean NO fluxes of only 0.2±0.02 ng m^{-2} s^{-1} for the

first year and mean NO fluxes of 0.14 ± 0.01 ng m^{-2} s^{-1} for the second year. However, the pH values at this site are very high (6.42).

Laboratory studies on undisturbed soil samples from the Weidenbrunnen site (approx. 300 m west of our site) resulted in NO fluxes between 2.6 and 12.9 ng m^{-2} s^{-1} (Muhr et al., 2008). This site is also a spruce site mainly covered with grass. Another laboratory study on mineral soil samples (taken just from the A horizon) were carried out at the Nagoya University Forest (Japan) site covered with Japanese cedar. The NO emissions ranged from 0.3 ng m^{-2} s^{-1} at high soil water contents (<92% WFPS) to 72.2 ng m^{-2} s^{-1} at low soil water contents (>29% WFPS)()(Nishina et al., 2009).

Our optimum net potential NO fluxes for soil samples taken under grass cover (8.8-9.8 ng m^{-2} s^{-1}, T_{soil}=10 °C, see Table 2) agree well with the (laboratory) results of Muhr et al. (2008). Also the results of Nishina et al. ()(2009) are in the range of our optimum net potential NO fluxes. However, their soil samples were taken from the mineral soil. Our results for soil samples taken under grass cover also overlap with the data given by Butterbach-Bahl et al. (1997) and Gasche and Papen (2002). Annual NO emission rates measured by Gasche and Papen (1999) range between our optimum net potential NO fluxes for soil samples taken under grass and spruce cover (and also for the B1 sample). Contrastingly, the NO fluxes found by Kitzler et al. (2006) and Horváth et al. (2006) are much lower than any of our optimum net potential NO fluxes. However, the Achental site is a mixed forest, and the soil exhibits a relatively high pH value (6.42). Relatively high values of the soil water content (average: 53% WFPS) characterized the soils of the Hungarian site (see Horváth et al., 2006). In contrast, the optimum soil water contents found in our study ranged between 18 and 27% WFPS (see equivalent gravimetric water contents in Table 2). Optimum net potential NO fluxes of our moss covered soils (if watered to 53% WFPS) would fall in the range of field fluxes observed by Horváth et al. (2006). In any case, our optimum net potential NO fluxes from soils under spruce and blueberries show higher values than any fluxes of the other studies mentioned above.

Net potential NO fluxes derived from laboratory experiments using the algorithm of Galbally and Johansson (1989) are particularly sensitive to changes in NO production rates and NO consumption coefficients and less sensitive to changes in diffusivity and soil bulk density (Rudolph and Conrad, 1996). In this respect, when comparing NO soil flux estimates (derived from laboratory incubation measurements), with data from literature, one should keep in mind, that the most up-to-date diffusion coefficient equations are basically applicable only to mineral soils. As gas diffusion in the organic layer can be substantially different, and uncertainties in determining diffusion coefficients in organic layers are still a matter of discussion (Moldrup, personal communication), we employed different mathematical formulations (see Table 1), and found that the choice of the diffusion coef-

ficient equation had an effect on the calculated NO flux (see Fig. 3). Depending on the diffusion coefficient, the NO fluxes had different magnitudes (factor of maximum 1.26 over the entire soil moisture range) and exhibited a shift in the position of the optimum flux (see Fig. 3). However, even using the correct effective diffusion coefficient, attention should be paid to its determination as the equation includes both the bulk and particle density. Both densities vary significantly between organic and mineral soil layers (e.g. Weidenbrunnen site: organic soil layers: BD: 0.14 ± 0.02, PD: 1.6 ± 0.07, n =8, mineral soil layers: BD: 0.88 ± 0.18, PD: 2.47 ± 0.06, n =8). If the effective diffusion coefficient has to be calculated, it is necessary to measure these quantities directly. Nevertheless, to reveal the uncertainties in diffusion through organic soil layers, further research, especially through field measurements of the diffusion coefficient, are most desirable.

Comparisons of NO production rates are not affected by the choice of diffusion coefficients. Therefore, only a few NO production rates are reported in the literature. Venterea and Rolston (2000) found mean NO production rates in a range of 9.4 to 18.7 ng kg^{-1} s^{-1} for agricultural soils from the Sacramento Valley of California. These values are comparable with our results of NO production rates (0.3-14.5 ng kg^{-1} s^{-1}). Remde et al. (1989) reported NO production rates twice as high as ours for a sandy clay loam under aerobic conditions (27.4 ± 1.8 ng kg^{-1} s^{-1}), yet much higher under anaerobic conditions (738 ± 21.6 ng kg^{-1} s^{-1}).

NO production rates reported in the literature are as rare as NO consumption coefficients. Values of the NO consumption coefficient (k) found in this study were in the range of 2×10^{-5} to 6×10^{-5} m^3 s^{-1} kg^{-1}. Soils from the Bolivian Amazon region showed k values under oxic conditions of 8×10^{-5} m^3 s^{-1} kg^{-1} (Koschorreck and Conrad, 1997). Feig et al. (2008) reported NO consumption coefficients between 5×10^{-5} and 26×10^{-5} m^3 s^{-1} kg^{-1}. However, these values were determined for desert soil with nearly no organic material inside at 25 °C in the laboratory, 15 °C more than for our studies. As biological processes usually increase by a factor of two with an increase in temperature of 10 °C (Kirschbaum, 1995; Davidson et al., 2006; Zheng et al., 2003), the higher values reported by Feig et al. (2008) are to be expected.

Only a few studies reported compensation point mixing ratios. Slemr and Seiler (1991) determined NO compensation point mixing ratio for agricultural soils between 0.3 and 5.5 ppb. Gasche and Papen (1999) found NO compensation point mixing ratios of 69.9 ± 9.6 ppb for a spruce forest soil in the Höglwald, Germany. Only for G1 and G2 we found NO compensation points in the low range of these studies. Soil samples taken under spruce and blueberry cover showed a much higher $m_{NO,comp}$. However, there are also studies which found higher NO compensation mixing ratios, e.g. ranging between 9 and 875 ppb for agriculture, meadow and forest soils (Gödde and Conrad, 2000). In view of the ambient NO mixing ratios observed at the Weidenbrunnen site, NO compensation point mixing ratios found in our study

demonstrate, that the soils there mainly act as a biogenic source for NO. Only when the ambient NO mixing ratio matches or falls below the NO compensation point mixing ratio will the soils become a sink for biogenic NO. Moravek (2008) observed ambient NO mixing ratios between 1 and 2 ppb at 5 cm above the forest floor (moss covered) and Plake (2009) found NO mixing ratios up to 4.2 ppb at 0.5 cm above the forest floor (moss covered), both at the Weidenbrunnen site. These mixing ratios are too low to change the NO flux from upward to downward directions.

Many studies have presented an exponential increase of soil NO emissions with increasing temperature. Generally, Q_{10} values are in the range of 2-3, a range valid for most biochemical processes (Koponen et al., 2006; Kirkman et al., 2002; van Dijk et al., 2002; Feig et al., 2008; Meixner and Yang, 2006; Smith et al., 2003). We obtained Q_{10} values for net potential NO fluxes between 0.92 and 3.04 (see Table 3). However, a Q_{10} value less than 1 (e.g. S1: 0.92) indicates a decrease of soil NO emission with increasing temperature.

4.2　Influence of soil chemical parameters on net potential NO flux

The processes which result in NO exchange are mainly influenced by soil temperature and soil moisture (Davidson and Kingerlee, 1997; Johansson and Granat, 1984; Skiba et al., 1997; Ludwig et al., 2001; Feig et al., 2008; Meixner, 1994; Meixner and Yang, 2006). Nevertheless, soil chemical and physical parameters may also affect the NO exchange (Nägele and Conrad, 1990a; Smith et al., 2003; Ludwig et al., 2001; Pilegaard et al., 2006; Kitzler et al., 2006; Laville et al., 2009; Gödde and Conrad, 2000).

For our soil samples from the Weidenbrunnen site we found no significant (probability level of 0.05) relationships between optimum net potential NO fluxes, NO production rates, or NO consumption coefficients with any physical or chemical soil parameters. However, on the 0.1 significance level we found negative correlations between soil NH_4^+ and (a) NO production rate (at $T_{soil}=10\,°C$), (b) NO production rate (at $T_{soil}=20\,°C$), and (c) NO consumption coefficient (at $T_{soil}=20\,°C$) (see Table 4). Also the NO consumption coefficient at $T_{soil}=10\,°C$ and the net potential NO fluxes showed a negative, but not significant correlation with soil NH_4^+. These negative correlations with soil NH_4^+ point to nitrification as the main converting process, because soil NH_4^+ must be available before nitrification may start. Denitrification is the conversion of NO_3^- to N_2O or N_2, and NO_3^- is necessary for the activation of denitrification. However, denitrification seems to play a smaller role for soils from the Weidenbrunnen site because we found no significant correlation between soil NO_3^- and other variables (see Table 4). Furthermore, nitrification may be lower from soil samples taken under moss and grass than from soil samples taken under spruce and blueberry cover. Therefore, the amount of soil NH_4^+ is higher at soil samples taken under moss and grass

than at soil samples taken under spruce and blueberry cover. Gödde and Conrad (2000) also found, that nitrification is the dominant process of NO production in the soil. In contrast to our study, Baumgärtner and Conrad (1992) found no significant correlation between the NO production rate and soil NH_4^+, but did find a significant correlation between the NO consumption coefficient and soil NH_4^+. However, they investigated mineral soil only. NO production and NO consumption processes are differently regulated (Dunfield and Knowles, 1998), so that both processes can respond independantly to changes in external factors. Gasche and Papen (1999) found a correlation between NO fluxes and soil NH_4^+ for the Höglwald spruce forest site as well as a correlation between NO fluxes and soil NO_3^-. Typically, 1-4% (sometimes more) of soil NH_4^+ is released from soil as NO (Dunfield and Knowles, 1998).

The other parameters showed no significant correlations (<0.1). As the research site, a typical even-aged monoculture, is relatively small (1.4 ha), soil parameters vary only over a small range (see also Behrendt, 2009). This makes it difficult or impossible to establish significant correlations between the other soil chemical or physical parameters and net potential NO fluxes.

Nevertheless, net potential NO fluxes showed a weak relationship with soil pH values. During laboratory incubation measurements, there might have been microsites in the soil samples with a soil pH different from the measured mean pH, indicating that nitrification occurred in microsites having pH higher than the surrounding soil ()(Paavolainen and Smolander, 1998). That could also be a reason for the relatively high NO emission despite of the low pH values. A pH value between 7 and 8 is ideal for nitrification. However, Paavolainen and Smolander ()(1998) reported coniferous soils that exhibited acid-tolerant nitrification. In this respect, a series of studies reported relationships between NO exchange processes and soil pH (Gödde and Conrad, 2000; Venterea et al., 2004; Nägele and Conrad, 1990b). There is also an enhanced chemical NO production from nitrite at low soil pH (Cleemput and Baert, 1984), which can happen even if nitrite does not accumulate to detectable amounts. In contrast, other studies found no strong relationships between NO exchange and soil pH (Dunfield and Knowles, 1998).

4.3　Influence of the understory type on net potential NO flux

A number of studies have detected effects of vegetation on NO emissions (Meixner et al., 1997; Feig et al., 2008; Davidson, 1991; Martin and Asner, 2005; Pilegaard et al., 1999). Our study suggests a strong relationship between understory type and the amount of net potential NO flux. As this relationship can hardly be explained by the measured physical and chemical soil parameters alone, it may originate from the complex biological interactions between plants and their soil environment. Because plant species differ in quantity

and quality of resources that they return to soil,individual plant species may have important effects on componentsof the soil biota and the processes that they regulate (Wardle et al., 2004). Carbon derived from plant litter mainly influences the decomposer communities. In addition, providing carbon to the rhizosphere creates a hot spot for microbial activity in the soil. For example the size and the density of the nitrifier and denitrifier communities are strongly influenced by plant roots (Philippot et al., 2009).

In our experiments, soils were sieved through a 16 mm sieve and kept at 4 °C for up to 2 months. Sieving may have removed the majority of roots but it cannot be excluded that fine roots passed the meshes resulting in a soil sample containing litter, roots, rhizosphere and root free soil. Stöhr and Ullrich (2002), and Stöhr and Stremlau (2006) demonstrated that roots can generate NO. The contribution of living roots to the observed net potential NO fluxes in our experiments should be rather low because most fine roots were removed by sieving. However, biochemical reactions of intact fine roots of spruce when stored in soil at 4 °C are unchanged for up to 4 weeks and then slowly decline (Pritsch, unpublished results). Thus it cannot be excluded that a minor part of the observed NO emissions came directly from those fine roots that were not removed by sieving.

A more likely explanation for the different net potential NO fluxes is that litter type and the influence of root exudates influenced functions of the soil microbial communities under the respective understory plants. Rhizosphere effects i.e. the influence of roots on NO emission rates was found by Slemr and Seiler (1991). Vos et al. (1994) measured 2 to 12-fold higher NO emissions from plots covered with green manure than from fallow plots, probably caused by increased microbial activity in the rhizosphere of the green manure plots compared to the bare soil. Unfortunately, no field studies exist examining the influence of plant roots on NO emissions. A few studies have shown a strong influence of roots on nitrous oxide emissions (Mosier et al., 1990) and it is generally accepted that denitrification is highest in the rhizosphere and decreases with distance from plant roots (Smith and Tiedje, 1979).

According to our study, net potential NO fluxes as well as NO production rates, NO consumption coefficients, and net NO release rates displayed the highest values for soil samples taken under spruce and blueberry covered soils and the lowest values for soil samples taken under moss and grass covered soils. Our results on small net potential NO fluxes from soils taken under moss cover are in accordance with findings of Pilegaard et al. (1999). They suspected that mosses retain nutrients from throughfall but also hypothesized that moss cover simply reflects other factors such as canopy density and water availability. Similarly small net potential NO fluxes were found for soil samples collected under grass cover in our study. *Deschampsia flexuosa* has a high potential to take up nitrogen in various forms and in competition to microbes (Harrison et al., 2008). This may explain a possibly reduced

potential of its microbial communities in nitrogen cycling. The role of its arbuscular mycorrhizal (AM) associates has not been studied at the field site but colonisation by AM seems to be low on acidic soils (Göransson et al., 2008). Inferior competition of microbial communities under moss and grass cover therefore could explain low NO emissions.

Soils taken under blueberry and spruce cover, in contrast, produced high net potential NO fluxes. Both plant species are associated with asco- and basidiomycetes forming ericoid mycorrhizae (blueberry), respectively ectomycorrhizae (spruce). NO accumulation can occur in mycorrhizal symbioses (Stöhr and Stremlau, 2006). Wallenda et al. (2000) also demonstrated that intact mycorrhizal roots of Norway spruce took up substantial amounts of NH_4^+. This NH_4^+ may act as precursor of nitrification. During nitrification NO can be released as an intermediate. However, due to the fact that only very few roots may have been present and in an active state NO released from mycorrhizae may be of minor relevance. The 10 fold higher NO fluxes from the soils beneath spruce and blueberry are difficult to explain from our data. One factor may be that both plants produce litter types rich in lignin and phenolics (Adamczyk et al., 2008). Tannins formed in degradation of these litter types can form complexes with proteins. Protein phenol complexes can be degraded by ericoid mycorrhizal fungi and saprotrophic fungi but not by ectomycorrhizal fungi (Wu et al., 2003). It has been suggested that relatively more dissolved organic nitrogen (DON) compared to inorganic nitrogen is released upon degradation of these phenol rich litters (cf. from (Hofland-Zijlstra and Berendse, 2010). Since DON as a possible substrate for nitrification and N-mineralisation has not been measured in our study it can only be speculated if nitrogen sources other than NH_4^+ could explain the high NO net release or which part of the soil microflora may have contributed to the results. It could be speculated that fungi as decomposers may have played a role in this process. In a beech forest, measurements of nitrous oxide (N_2O) emission from forest floor samples indicated that net N_2O production was the result of predominantly fungal N_2O production and predominantly bacterial N_2O consumption (Blagodatskaya et al., 2010).

Altogether our results indicate a challenging field for unravelling the underlying processes of different understory plants on NO net release from forest soils.

5 Conclusion

In this study, we investigated the net potential NO fluxes from soil samples of the organic layers of a spruce forest soil covered with four different understory types (moss, grass, spruce and blueberry).

Observed net NO release rates of soil samples taken under moss and grass cover indicated a high potential for NO consumption, resulting in very low net potential NO fluxes

from soil samples taken under these understory types. In strong contrast, soil samples taken under spruce and blueberry cover showed 10 fold higher net potential NO fluxes, than those taken under moss and grass cover.

Therefore, it is an important lesson of this study, that more attention must be paid to small scale heterogeneity of understory vegetation, when quantification of the biogenic NO emission from a (spruce) forest floor is attempted.

Analysis of the compensation point mixing ratios indicated that measured ambient mixing ratios of NO at 0.5 cm above the forest floor of the field site were – even for the soil samples taken under moss and grass cover – too low to change the soil NO flux from upward to downward directions.

Further research investigating effective soil diffusion coefficients is very desirable. The net potential NO flux calculated with the diffusion coefficient according to Millington (1959) is 1.26 fold higher than the net potential NO flux calculated with diffusion coefficients according to Millington and Quirk (1960). Also the position of the optimum NO flux shifts depending on the choice of the diffusion coefficient.

While the understory type seems to be an important variable controlling NO exchange processes, corresponding soil nutrients played generally a less important role. The only exception was for NH_4^+, the precursor of NO_3^- in the nitrification process. This implies that nitrification was the limiting factor of NO production for the investigated soils, whereas denitrification played an obviously smaller role. It is remarkable that high NO emissions were observed for soils under woody understory types; this may be related to soil chemical processes in the vicinity of mycorrhized roots, but further studies are certainly necessary for confirmation. As the establishment of different understory types is related to the availability of light at the forest floor as a result of forest thinning, management practises are likely to have important consequences on the net soil NO emission from a forested site.

Coniferous forest soils in temperate humid climates are characterized by thick organic layers of moder or raw humus forms. Organic layers of our soils had a much higher potential (over 2.5 fold) for NO emission than the corresponding mineral soil layers. Hence quantification of net potential NO fluxes of the O horizons of temperate forest soils is an important step for (a) comparison of laboratory and field measurements, (b) up-scaling from laboratory to field scale fluxes (by areal information on understory distribution), and (c) extrapolation from field site results to larger scales (e.g. regional).

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