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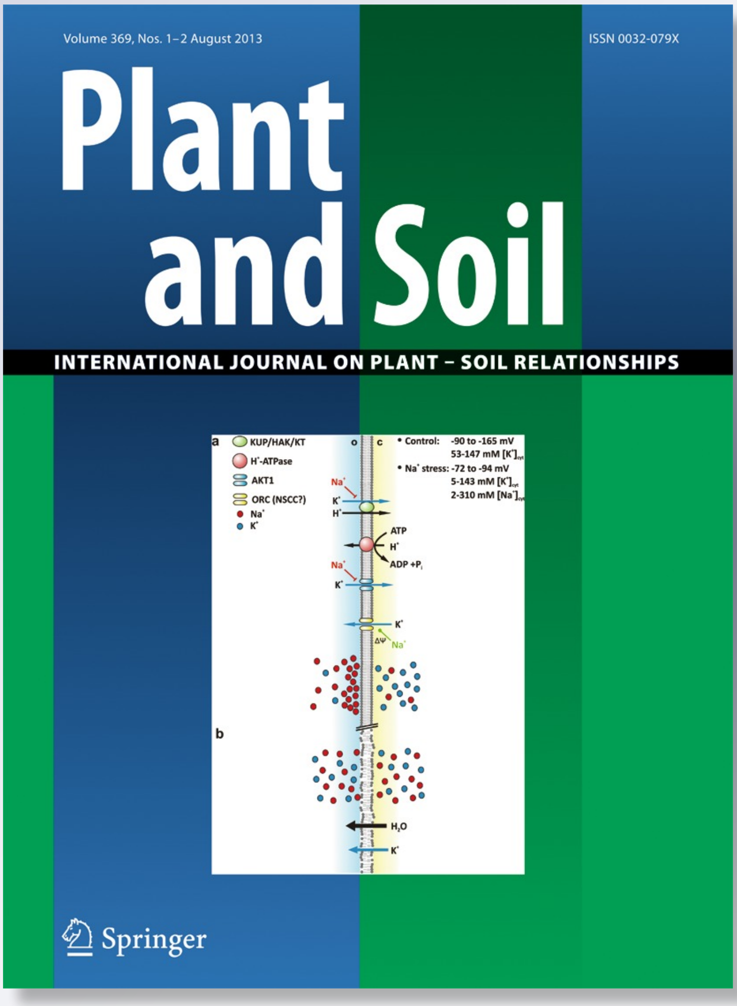

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REGULAR ARTICLE

Regulation of N_2O and NO_x emission patterns in six acid temperate beech forest soils by soil gas diffusivity, N turnover, and atmospheric NO_x concentrations

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Abstract

Aims Low gas diffusivity of the litter layer is held responsible for high seasonal nitrous oxide (N_2O) and low nitric oxide (NO) emissions from acid beech forest soils with moder type humus. The objectives were (i) to evaluate whether these beech forest soils generally exhibit high seasonal N_2O emissions and (ii) to assess the influence of gas diffusivity and nitrogen (N) mineralisation on N oxide fluxes.

Methods We measured N_2O and NO_x ($NO + NO_2$) fluxes in six German beech stands and determined net N turnover rates and gas diffusivity of soil samples taken at each chamber.

Results High N_2O emissions (up to 113 μgN $m^{-2}h^{-1}$) were only observed at one beech stand. Net nitrification of the organic layer and soil gas diffusivity explained 77 % of the variation in N_2O fluxes (P=0.001). Fluxes of NO_x were low (−6.3 to 12.3 μgN $m^{-2}h^{-1}$) and appeared to be controlled by NO_x concentrations in the forest air.

Conclusions Low soil gas diffusivity and high N turnover rates promoted high N_2O losses in times of high soil respiration but were not necessarily associated with moder type humus. High seasonal emissions are probably less common in German beech forests than previously assumed.

Keywords Soil gas diffusivity · Nitrous oxide · Nitric oxide · N mineralisation · Seasonal emission patterns · Penman-Millington-Quirk model

Introduction

Temperate forest soils have been identified as a considerable source for the trace gases nitrous oxide (N_2O) and nitric oxide (NO) in particular when forests are exposed to high nitrogen (N) depositions (e.g., Brumme and Beese 1992; Papen and Butterbach-Bahl 1999; Skiba et al. 1999; van Dijk and Duyzer 1999). Nitrous oxide is a potent greenhouse gas and contributes to the catalytic decomposition of stratospheric ozone (Crutzen 1979; IPCC 2007). Nitrogen dioxide (NO_2) and NO ($NO_2 + NO = NO_x$) are indirectly involved in global warming through the production of radiative tropospheric ozone and contribute to the formation of acid rain (Crutzen 1979; Logan 1983).

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N. Eickenscheidt · R. Brumme
Soil Science of Tropical and Subtropical Ecosystems,
Büsgen Institute, University of Göttingen,
Büsgenweg 2,
37077 Göttingen, Germany

Present Address:
N. Eickenscheidt (✉)
Thünen Institute for Forest Ecosystems, Federal Research
Institute for Rural Areas, Forestry and Fisheries,
Alfred-Möller-Strasse 1,
16225 Eberswalde, Germany
e-mail: nadine.eickenscheidt@ti.bund.de

Several studies have reported that in general N_2O emissions from deciduous forests were higher than those from coniferous forests (e.g., Brumme et al. 1999; Papen and Butterbach-Bahl 1999) whereas this seems to be reversed for NO emissions (e.g., Pilegaard et al. 2006; van Dijk and Duyzer 1999). Differences in litter quality and quantity are held responsible for these observations (e.g., Papen and Butterbach-Bahl 1999). Soil N turnover rates are typically higher in deciduous forests than in coniferous forests due to the higher degradability of the litter (e.g., Ambus et al. 2006). Furthermore, the horizontal laminar structure of the litter layer in beech forests on acid soils has been found to function as a gas diffusion barrier (Ball et al. 1997; Brumme and Borken 2009). Low gas diffusivity was responsible for high N_2O emissions during times of high soil respiration in a beech forest with moder type humus in contrast to a beech forest with mull type humus and a coniferous forest with moder type humus, which exhibited low emissions (Brumme et al. 1999). A literature review revealed that deciduous forests with mull type humus and acid coniferous forests with moder type humus, whose litter layer is thick but well-aerated, showed low non-seasonal emissions whereas deciduous forest with moder type humus showed a seasonal emission pattern with high summer emissions (Ball et al. 1997; Brumme and Borken 2009; Brumme et al. 1999). Brumme et al. (1999) defined three types of N_2O emission patterns in temperate forests: (i) the seasonal emission pattern (SEP) with high N_2O emissions in wet summer months, (ii) the background emission pattern (BEP) with low N_2O emissions during the whole year, and (iii) the event emission pattern (EEP) with N_2O emissions during freezing/thawing periods or after rewetting. The authors hypothesised that soil gas diffusivity of the organic layer was mainly responsible for these differences whereas N was not a limiting factor under the high N load in most of the temperate zone.

Firestone and Davidson (1989) proposed the conceptual ‘hole-in-the-pipe’ (HIP) model which postulates two levels of regulation of N oxide emissions from soils: (i) the sum of total N oxide production is a function of N availability, specifically of nitrification and denitrification rates (rate of N moving ‘through the pipe’) and (ii) the ratio of released gases (NO, N_2O, N_2) is a function of environmental factors such as O_2 availability and pH, which define the size of ‘holes in the pipe’ (Davidson et al. 2000). Whether aerobic nitrification or anaerobic denitrification prevails, depends on O_2 availability, which is controlled by gas diffusivity of the soil and O_2 consumption by microorganisms and roots (Bollmann and Conrad 1998; Brumme et al. 1999; Smith et al. 2003). In contrast to N_2O emissions, which are mainly derived from denitrification, NO emissions are probably the result of nitrification or chemodenitrification (Ambus et al. 2006; Wolf and Brumme 2002; van Cleemput and Samater 1996). The O_2 and N mineralisation dynamics might thus be the most important drivers for high N_2O emissions and have been assumed to be responsible for seasonal emission patterns in the rainy seasons of the tropics and moist summer periods in the temperate regions (Brumme et al. 2005). However, to date N oxide fluxes, mineralisation and nitrification rates, and soil gas diffusivity have not been measured simultaneously at forest sites.

The objective of this study was to determine the gas fluxes of N_2O and NO_x along a gradient from F-mull to moder/mor type humus with different soil texture under high N deposition loads. At two field campaigns in six beech forests, in-situ fluxes of N_2O and NO_x were measured and lab experiments were performed to determine N mineralisation, nitrification, and gas diffusivity. In this study the following questions were addressed: (i) Do acid temperate beech forest soils with organic layers consisting of moder type humus exhibit high seasonal N_2O emissions and low NO_x emissions? (ii) Is gas diffusivity the key driver that controls the release of N oxides?

Materials and methods

Study sites

The study was conducted at six beech stands (*Fagus sylvatica*), which were part of the German Level II monitoring programme (Forest Intensive Monitoring Programme of the UNECE; Table 1). The beech stands were > 100 years old and were characterised by acid soil conditions. The soil types were Dystric Cambisols, but sites differed in particle size distributions, humus type, and climatic conditions. The surface organic layer type ranged from F-mull to moder/mor type humus. The stands have been exposed to atmospheric N loads ranging from 15 to 24 kgN $ha^{-1}year^{-1}$. The site characteristics and soil properties are presented in Tables 1 and 2. The Hünfeld site had probably been limed in the past.

Table 1 Site characteristics of the six Level II monitoring beech stands in Germany

	Haard	Neuhäusel	Biebergemünd	Hünfeld	Lüss	Solling
Level II identifier	503	704	604	601	301	304
Elevation [m]	70	390	450	410	101–150	500
Precipitation [$mmyr^{-1}$]	880	956	1037	706	784	1193
Mean temperature [°C]	9.5	8.1	7.6	7.2	8.0	6.9
Soil parent material	Cover sand over Haltener Sand	Pumic or loess solifluction layer over quartzite	Loess solifluction layer over Triassic sandstone	Loess solifluction layer over Triassic sandstone	Pleistocenic sands	Loess solifluction layer over Triassic sandstone
Humus type	Moder/Mor	F-Mull	Moder	F-Mull	Moder	Moder
Height org. layer [cm]	9.6	4.2	4.3	3.8	6.0	5.2
NO_3 deposition [$kgNha^{-1}year^{-1}$]	8.3	9.9	11.5	11.4	6.4	9.5
NH_4 deposition [$kgNha^{-1}year^{-1}$]	15.3	8.8	8.3	7.4	8.7	12.1
Throughfall N_{min} deposition [$kgNha^{-1}year^{-1}$]	23.6	18.7	19.9	18.8	15.2	21.6
N leaching [$kgNha^{-1}year^{-1}$]	16	6	2	0	0	1
N uptake [$kgNha^{-1}year^{-1}$]	13	6	17	14	6	11

Data derived from Haussmann and Lux (1997), Brumme and Khanna (2008, 2009), Gehrmann (pers. communication, 2009), Meesenburg (pers. communication, 2009), and from 'www.wald-rlp.de' (accessed 2010)

Soil properties

At the Solling site, soil samples for soil characterisation were taken in December 2007. At the other five sites, soil samples were taken in October 2009. The mass of the organic layer was determined using a metal ring (594 cm^2). Organic layer samples were oven-dried at 60 °C, living roots were removed, and organic material was shredded and ground for further analyses. Soil bulk density of the mineral soil was determined on undisturbed soil samples (0–5 and 5–10 cm depths; 250 cm^3), which were oven-dried at 105 °C and corrected for the volume of roots and stones > 2 mm. Mineral soil samples were oven-dried at 60 °C, sieved, and ground for further analyses. Organic carbon and total nitrogen concentrations were determined using a CNS Elemental Analyzer (Heraeus Elementar Vario EL, Hanau, Germany). Sieved mineral soil or shredded organic material (10 mL) was used for pH measurements conducted in distilled water (1:2.5 (v/v)).

The effective cation exchange capacity (CEC) was determined according to König and Fortmann (1996). In short, soil samples were percolated with 100 mL 1 M NH_4Cl solution for 4 h and the cations were quantified using an ICP-AES (Spectro Analytical Instruments, Kleve, Germany). Exchangeable protons were calculated from the pH of the NH_4Cl solution before and after percolation. Cation exchange capacity was calculated as the sum of the exchangeable Na, K, Ca, Mg, Mn, Fe, Al, and H ions whereas the base saturation (BS) was calculated as the sum of base cations (Na, K, Ca, and Mg) as percent of CEC. The particle size distribution was determined using the sieving and pipette method described by Schlichting et al. (1995). Briefly, organic matter and Fe oxides were destroyed using 30 % H_2O_2 and 4 % Na-dithionite-citrate before wet sieving of the sand and coarse silt fraction (≥ 20 µm). Afterwards, sedimentary fractionation according to the Atterberg method (Schlichting et al. 1995) was conducted at 25 °C for 21 h (30 cm fall height).

N_2O and NO_x flux rates

Gas flux measurements were conducted during two field campaigns in May and July 2009. These months were chosen since high emissions were expected at sites with seasonal emission patterns. Five chamber

Table 2 Soil properties of the six German beech stands

	Haard	Neuhäusel	Biebergemünd	Hünfeld	Lüss	Solling
Sand [%]	63.4 (1.0)^{a}	23.6 (2.3)^{b}	57.7 (0.7)^{c}	54.4 (1.3)^{c}	78.8 (0.8)^{d}	22.2 (0.6)^{b}
Silt [%]	31.0 (0.9)^{a}	52.7 (2.0)^{b}	29.8 (0.6)^{a}	36.2 (1.5)^{c}	17.4 (0.7)^{d}	52.9 (0.5)^{b}
Clay [%]	5.6 (0.2)^{a}	23.7 (1.5)^{b}	12.5 (0.4)^{c}	9.4 (0.3)^{d}	3.8 (0.4)^{e}	24.8 (0.4)^{b}
Mass org. layer [Mgha^{-1}]	309 (38)^{a}	50 (10)^{bd}	56 (12)^{b}	40 (6)^{bd}	184 (7)^{c}	36 (7)^{d}
BD 0–5 cm [gcm^{-3}]	1.36 (0.13)^{a}	0.83 (0.08)^{c}	0.93 (0.09)^{bc}	1.18 (0.17)^{ab}	1.35 (0.28)^{a}	0.89 (0.06)^{c}
BD 5–10 cm [gcm^{-3}]	1.55 (0.07)^{a}	1.07 (0.11)^{b}	0.92 (0.09)^{b}	1.50 (0.04)^{a}	1.57 (0.11)^{a}	1.08 (0.13)^{b}
C content org. layer [%]	39.9 (0.9)^{a}	30.8 (2.9)^{b}	32.5 (1.0)^{b}	35.6 (2.4)^{ab}	33.5 (4.3)^{ab}	45.5 (0.4)^{c}
N content org. layer [%]	1.86 (0.06)^{ac}	1.36 (0.10)^{b}	1.54 (0.07)^{ab}	1.23 (0.05)^{b}	1.33 (0.16)^{b}	2.07 (0.07)^{c}
C/N ratio organic layer	21.5 (0.5)^{a}	22.6 (0.9)^{a}	21.2 (0.6)^{a}	28.9 (1.8)^{b}	25.1 (0.8)^{ab}	22.1 (0.7)^{a}
C content 0–5 cm [%]	14.17 (1.42)^{a}	6.92 (1.19)^{bc}	5.87 (0.62)^{c}	3.25 (0.59)^{d}	5.61 (0.91)^{cd}	9.70 (0.84)^{abc}
N content 0–5 cm [%]	0.57 (0.07)^{a}	0.38 (0.07)^{bc}	0.26 (0.03)^{cd}	0.15 (0.02)^{d}	0.23 (0.03)^{d}	0.47 (0.04)^{abc}
C/N ratio 0–5 cm	25.3 (1.0)^{a}	18.2 (0.5)^{c}	22.3 (0.5)^{ad}	21.7 (0.9)^{bde}	24.2 (0.3)^{ae}	20.7 (0.3)^{bcd}
pH (H_2O) 0–5 cm	3.6 (0.0)^{a}	4.1 (0.1)^{b}	3.7 (0.0)^{c}	4.3 (0.1)^{b}	3.7 (0.0)^{c}	3.5 (0.0)^{d}
CEC 0–5 cm [mmol$_c$ kg^{-1}]	108 (10)^{a}	101 (8)^{ac}	77 (3)^{bc}	56 (5)^{b}	49 (7)^{b}	139 (6)^{d}
BS 0–5 cm [%]	6.7 (0.6)^{a}	8.1 (1.2)^{a}	7.0 (0.8)^{a}	45.1 (8.5)^{b}	10.8 (0.9)^{a}	10.0 (1.4)^{a}

Among the stands, means (± SE, n=5) followed by the same letter were not significantly different (ANOVA, Tukey HSD-test at $P\leq 0.05$). For the Solling site, six replicates were taken for bulk density and organic layer mass and at the other stands four replicates were taken for the organic layer mass. Soil sampling at the Solling site was conducted in December 2007 and at the other stands in October 2009. BD stands for bulk density of the mineral soil; CEC for effective cation exchange capacity, and BS for base saturation

bases (PVC; area: 0.07 m^2) were randomly distributed at each site and inserted approx. 3 cm into the soil 0.5–1 h before measurements. The chambers that were used for both N_2O and NO_x measurements were vented and were made of PVC. The enclosed mean air volume was 17.6 L. During the gas flux measurements, air and soil temperature (in 5 cm soil depth) was determined. For N_2O flux measurements, the closed chamber method was used. Gas samples were taken in pre-evacuated glass flasks (100 mL) at 0, 15, 30, and 45 min after chamber closure, using a portable gas sampler equipped with a pressure sensor (Loftfield et al. 1997). The pressure sensor was used to check the leak tightness of the evacuated glass bottles prior to sampling and to ensure that bottles were completely filled with "chamber air". The samples were stored for 1 week at most and were analysed with a gas chromatograph equipped with an autosampler and an EC detector (GC 14A, Shimadzu, Duisburg, Germany). For NO_x flux measurements, an open dynamic chamber method combined with a portable battery operated NO_x analyser (Scintrex Unisearch, Ontario, Canada) was used. Calibration was conducted in the field before and after chamber measurements using a NO standard gas (3000 ppbv NO in N_2; Air Liquide GmbH, Germany). Nitric oxide was oxidised to NO_2 by a solid CrO_3 catalyst before NO_2 detection by luminol chemiluminescence (Scintrex LMA-3 chemiluminescence detector) whereas NO_2 produced in the soil or in the chamber was directly measured by the detector. Air humidity was measured and was kept below 50 % to ensure the conversion of NO by the CrO_3 catalyst. A Teflon tube connected the analyser to a chamber, which was placed on the chamber base for 5 min. The total mean air flow through the chamber was 0.9 Lmin^{-1}. Concentrations of NO_x were logged every 5 s using a CR510 data logger (Campbell Scientific, Utah, USA). This NO_x measurement was described by Köhler et al. (2009) and by Williams and Davidson (1993) who also compared the luminol chemiluminescence method with the NO/O_3 chemiluminescence method.

In July 2009, we additionally measured N_2O fluxes and heterotrophic CO_2 respiration rates in the laboratory on undisturbed soil sample (PVC columns, height: 0–9 cm and 0–19 cm, diameter: 15.1 cm). The aim was to obtain the N_2O fluxes of the columns since these columns were also used for the determination of the N_2 diffusion coefficients and additionally to assess the influence of increased soil temperature and CO_2 respiration (as indicator for O_2 consumption) on N_2O fluxes. The bottom of the PVC column, which contained the soil sample, was ait-tightly fixed on a PVC block and a chamber (PVC, area: 0.018 m^2;

enclosed air volume: 2.8 L) was air-tightly fixed to the top of the column. The first sample (time point zero) was taken above the soil surface immediately before chamber closure. Further samples were removed 5, 10, and 15 min after chamber closure. Samples were removed using a syringe and the sample (3 mL) was directly inserted into the gas chromatograph (GC 14A, Shimadzu, Duisburg, Germany) for simultaneous N_2O and CO_2 measurements.

All gas fluxes (N_2O, NO_x, and CO_2) were calculated from the linear increase or decrease of gas concentration in the chamber versus time and were adjusted for air temperature and atmospheric pressure (Eickenscheidt et al. 2011; Köhler et al. 2009).

Net N mineralisation rates

In May and July 2009, five PVC columns (height: approx. 0–19 cm, diameter: 15.1 cm) were inserted into the organic layer and upper mineral soil next to the chambers after gas flux measurements to determine net nitrification and mineralisation rates. The PVC columns were excavated and stored in PE bags. The soil samples were cooled during transport. In the laboratory, the organic layer and the upper 5 cm mineral soil of each column were separately mixed and a part of the soil (t0 samples) was removed for preparation of soil mineral N (N_{min}) extracts and for gravimetrical soil water determination. The remaining part (t1 sample) was incubated in PE bags in the laboratory at the soil temperatures (in 5 cm soil depth) during soil sampling, which were 9 °C in May and 13.5 °C in July (Table 3). After 14 days, the incubated, disturbed soil samples were extracted using the same procedure as for the t0 samples.

For soil extraction, 100 mL 0.5 M K_2SO_4 solution was added to 30 g fresh soil or 50 mL K_2SO_4 solution to 15 g of the organic layer. The excess was filtered after shaking the sample solution for 1 h. The extracts remained frozen until N_{min} analysis was done. The concentrations of extractable ammonium (NH_4^+) and nitrate (NO_3^-) were determined using a continuous flow injection colorimeter (Cenco/Skalar Instruments, Breda, The Netherlands). The NO_3^--N and NH_4^+-N contents at the beginning and at the end of the incubation were used to calculate the net nitrification and mineralisation rates.

Gas diffusion coefficients

Although the gas diffusion coefficient of O_2 was the target of this experiment, N_2 was chosen as experimental gas, since its molecular mass is similar to that of O_2 and its concentration in the air is comparatively constant. The production of N_2 was not measured during the experiment but we think that both consumption and production of N_2 during the experiment could be neglected. A laboratory study by Wolf and Brumme (2003) examined the formation of N_2 in soil columns of the mineral soil and humus layer of the Solling beech stand. This stand was also investigated in the present study and probably had the highest N_2 emissions regarding the six beech stands due to having the highest soil water contents. Dinitrogen was produced in the Solling soil but the N_2/N_2O-ratio was well below 1. Even when assuming N_2 emissions equal or two-fold than N_2O emissions during the laboratory experiment, produced N_2 in total pore air of the soil columns was negligible considering that 78 % of the atmospheric air that diffused into the soil

Table 3 Soil temperature in 5 cm soil depth during the field measurements in May and July 2009, mean (± SE, $n=5$) water content of 0–5 cm soil depth during the field measurements, and mean (± SE, $n=5$) water content of the 0–9 cm soil columns (lab$_9$) and 0–19 cm soil columns (lab$_{19}$) during the laboratory measurements

	Soil temperature [°C]		Water content 0–5 cm [gg^{-1}]		Water content lab$_9$ [gg^{-1}]		Water content lab$_{19}$ [gg^{-1}]	
	May	July	May	July	May	July	May	July
Haard	9.6	13.1	0.72 (0.11)^{ab}	0.64 (0.09)^{ab}	1.51 (0.31)^{a}	0.80 (0.11)^{ab}	0.47 (0.06)^{a}	0.45 (0.02)^{a}
Neuhäusel	8.0	12.5	0.59 (0.05)^{abc}	0.50 (0.08)^{abc}	0.55 (0.03)^{b}	0.54 (0.02)^{ac}	0.43 (0.03)^{a}	0.39 (0.06)^{a}
Biebergemünd	8.1	13.3	0.41 (0.03)^{bc}	0.33 (0.03)^{bc}	0.46 (0.04)^{b}	0.38 (0.03)^{ac}	0.30 (0.01)^{b}	0.28 (0.01)^{b}
Hünfeld	8.2	14.3	0.34 (0.02)^{c}	0.24 (0.02)^{c}	0.43 (0.01)^{b}	0.26 (0.02)^{c}	0.26 (0.01)^{b}	0.21 (0.01)^{b}
Lüss	9.8	14.1	0.69 (0.10)^{ab}	0.36 (0.10)^{bc}	0.91 (0.18)^{ab}	0.69 (0.11)^{abc}	0.29 (0.02)^{b}	0.26 (0.02)^{b}
Solling	8.8	13.9	0.85 (0.08)^{a}	0.73 (0.10)^{a}	1.09 (0.17)^{ab}	1.09 (0.21)^{b}	0.46 (0.03)^{a}	0.46 (0.02)^{a}

For each site, means followed by the same letter were not significantly different (ANOVA, Tukey HSD-test at $P\leq0.05$)

column is N_2. To determine the apparent diffusion coefficient (*Ds*) of N_2 in the soil, we collected one undisturbed soil column (height: approx. 0–19 cm, diameter: 15.1 cm) per site from each of the five chambers per site in May and July 2009 after conducting the gas flux measurements. In July 2009, an additional column (height: approx. 0–9 cm, diameter: 15.1 cm) per chamber was taken next to each chamber for measurement of *Ds*. In May 2009, we determined the diffusion coefficient for the whole column and, then, after cutting off the lower part, also for the upper 0–9 cm of the column. The undisturbed soil samples were stored in PE bags at 9 °C in May and at 13.5 °C in July. The temperatures corresponded to the mean soil temperatures in 5 cm soil depth during the sampling. Before determination of the diffusion coefficient, soil columns were acclimatised to room temperature (25 °C in May and 27.5 °C in July) for one night. The 'one-chamber' method was used where soil columns were placed on a chamber (height: 15.6 cm; diameter: 15.1 cm) and the upper surface of the soil sample was exposed to the atmosphere (Flühler 1972; Teepe 1999). The gas leakage rate was examined for each chamber before soil samples were analysed. A mesh prevented soil loss into the chamber. A magnetic stirrer at the bottom of the chamber provided a homogenisation of the gas mixture. The chamber was equipped with two valves to flush the chamber and a septum to take gas samples with a syringe. The chamber was flushed with argon to decrease the N_2 concentration in the chamber to 2–6 %. Gas samples (2 mL) were removed at several time points, depending on the rate of N_2 increase in the chamber. Usually six gas samples were collected over a period up to 4 h (for the 0–19 cm soil samples) and up to 1.5 h (for the 0–9 cm soil samples). Analyses of N_2 were conducted with a gas chromatograph coupled to a thermal conductivity detector (80 °C) following separation of N_2 and O_2 by a molecular sieve (3 m column; 80 °C) (Delsi Instruments ENICA 21).

Fick's first law describes the rate of gas diffusion under stationary conditions (Flühler 1972). However, for the present experiment quasi steady state conditions were assumed, i.e., that the gradient of N_2 changed with time but was locally constant at a specific time, and the gas diffusion rate changed with time (Flühler 1972; Teepe 1999). Thus, Fick's first law was combined with these assumptions (Eq. 1):

$$\frac{\mathrm{d}(\mathrm{c_C(t)} - \mathrm{c_A})}{\mathrm{dt}} \cdot \frac{V_C}{A} = -Ds \cdot \frac{c_C(t) - c_A}{z} \tag{1}$$

where

dc	Local difference in the gas concentration [$\mathrm{cm^3\,cm^{-3}}$]
$c_C(t)$	Gas concentration in the chamber at time point t
c_A	Gas concentration in ambient air, constant
dc/dt	Temporal change in the gas concentration [$\mathrm{s^{-1}}$]
V_C	Chamber volume [$\mathrm{cm^3}$], constant
A	Cross section area of the soil sample and chamber [$\mathrm{cm^2}$], constant
Ds	Apparent diffusion coefficient of N_2 in the soil [$\mathrm{cm^2\,s^{-1}}$]
z	Length of the soil sample [cm], varied

Rearrangement of Eq. 1 to solve for *Ds* and integration in the limits of integration t=0,c_C(0) and t=t', c_C(t') gives (Eq. 2):

$$Ds = \frac{2.3 \cdot V_C \cdot z}{A} \cdot \frac{1}{t'} \cdot \log\left(\frac{c_C(0) - c_A}{c_C(t') - c_A}\right) \tag{2}$$

For comparison of samples, independent of the gases used, the apparent diffusion coefficient *Ds* was expressed relative to that in free air *Da* (*Ds*/*Da*; *Da*= 0.199 $\mathrm{cm^2\,s^{-1}}$; Teepe 1999). Since gas diffusion in soils is in particular dependent on air-filled porosity ε, *Ds*/*Da* was described as function of ε. For this, the total soil porosity (Φ) and ε of each soil sample was calculated. Particle density of minerals was assumed to be 2.65 $\mathrm{g\,cm^{-3}}$ and density of organic matter was assumed to be 1.5 $\mathrm{g\,cm^{-3}}$. A power function model (Table 4, Fig. 1) and the Penman-Millington-Quirk (PMQ) model (Eq. 3, Table 4; Moldrup et al. 1997) provided the best residual-based goodness of fit.

$$\frac{Ds}{Da} = 0.66 \cdot \Phi \cdot \left(\frac{\varepsilon}{\Phi}\right)^{\frac{(12-m)}{3}} \tag{3}$$

Moldrup et al. (1997) suggest a tortuosity parameter m=3 for undisturbed soils. This value also gave best model fits for the sandy Lüss site. However, for the fine-textured soils the models performed better with lower values for m indicating even higher tortuosity of soils (Table 4).

Table 4 Values of fitted parameters for the power function and PMQ_{mod} models, which predict the relative N_2 gas diffusivity *Ds*/*Da* of 0–9 cm soil columns and of 0–19 cm soil columns. Model fitting was conducted separately for the Lüss site due to the high sand content of approx. 80 %. Data from the Haard site was omitted due to the thick organic layer. For parameter fitting, sites were further separated according to soil texture for the 0–19 cm columns (see Table 2)

	$Ds/Da = B \cdot \varepsilon^k$		PMQ_{mod}
	B	*k*	*m*
0–9 cm column			
N,B,H,S-sites	1.22	3.9	−0.4
L-site	0.73	2.2	3.0
0–19 cm column			
N,S-sites	0.68	2.4	2.1
B,H-sites	0.39	1.8	0.2
L-site	0.22	0.9	3.3

N Neuhäusel, *B* Biebergemünd, *H* Hünfeld, *S* Solling, *L* Lüss

Statistical analyses

Analysis of variance (ANOVA) and the Tukey HSD-test were used for comparisons of sites. The assumptions of normality of residuals (KS test or Cramer-von Mises test) and homogeneity of variances (Levene test) were tested prior to analysis. Where necessary, data were log or box-cox transformed. We used the Kruskal-Wallis H-test in case normality of residual errors was not obtained. Simple and multiple regression analyses were carried out. The minimal adequate model was obtained using Akaike's Information Criterion (AIC). Due to non-normality of residual errors, regressions on field N_2O fluxes were performed using mean values of the replication chambers. Multiple regressions on NO_x fluxes were also performed using mean values since NO_x concentration measurements in forest air were not replicated. Effects were considered significant if $P \leq 0.05$. Results are reported as means±1 standard errors. Statistical analyses were carried out using R 2.12.0 (R Development Core Team 2010).

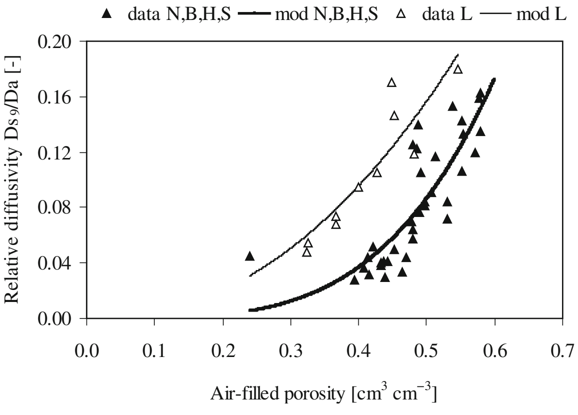

Fig. 1 Dependence of the relative diffusivity of N_2 (*Ds*/*Da*) of the 0–9 cm soil columns on air-filled porosity ε. Data of the Lüss site are very different, due to the high sand content of approx. 80 %, and therefore shown separately. A power function model was fitted to the data. The corresponding fitting parameters are presented in Table 4. Site abbreviations: N = Neuhäusel, B = Biebergemünd, H = Hünfeld, L = Lüss, and S = Solling

Results

Regulation of N_2O fluxes

Fluxes of N_2O were significantly different among the six stands in May 2009 ($P=0.001$; Fig.2a). The Solling site displayed the highest N_2O emissions of 36±11 $\mu gN\ m^{-2}h^{-1}$ followed by the sites Haard and Hünfeld with approx. 7 $\mu gN\ m^{-2}h^{-1}$ whereas net N_2O uptake was measured at the remaining sites. The second campaign in July displayed a similar pattern with high fluxes at the Solling site (113±68 $\mu gN\ m^{-2}h^{-1}$) but the fluxes among the sites were not significantly different because of high variability (Fig. 2a; Table 5).

The N_2O fluxes were positively and exponentially related to the water content of the organic layer, net nitrification rates of the organic layer, net N mineralisation rates of the organic layer, and negatively to the N_2 diffusion coefficient Ds_{19} (Table 6; Fig. 3). Using multiple regressions, N_2O fluxes (y) could be best explained by net nitrification of the organic layer ($x1$) and the diffusion coefficient Ds_{19} ($x2$; Eq. 4; Table 6).

$$\log(y + 3.5) = 0.5(\pm 0.2) \cdot x1 - 130.9(\pm 55.9) \cdot x2 + 2.7(\pm 1.0) \qquad (4)$$

The model fit was almost similarly good using net N mineralisation rates of the organic layer (instead of nitrification rates) and Ds_{19} as the predictors (Table 6). In addition, using the water content of the organic layer instead of the diffusion coefficient resulted in a similar goodness of model fits (Table 6). Simple as well as multiple regressions were not significant when omitting the data of the Solling site.

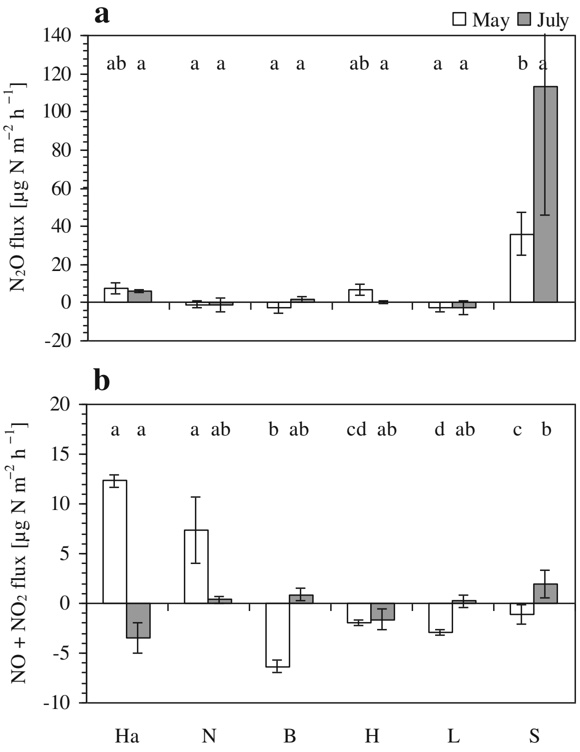

Fig. 2 Mean (± SE, n=5) N_2O fluxes (**a**) and NO + NO_2 fluxes (**b**) of the six beech stands in May and July 2009. Regarding 1 months, means followed by the same letter indicated no significant differences among stands (Kruskal-Wallis H-test or ANOVA, Tukey HSD-test at $P \leq 0.05$). Site abbreviations: Ha = Haard, N = Neuhäusel, B = Biebergemünd, H = Hünfeld, L = Lüss, and S = Solling

Higher N_2O fluxes were measured from the laboratory incubations at 27.5 °C compared to the field measurements at four out of six beech stands. However, significantly higher fluxes were only observed at the Solling site (P=0.001; Table 5). Fluxes of N_2O measured in the laboratory were best explained by net N mineralisation rates of the organic layer and *Ds* of the corresponding column (for 0–9 cm columns: P=0.0001, r^2=0.52, df=24 and for 0–19 cm columns: P=0.0002, r^2=0.49, df=26). There was no significant relationship between these N_2O fluxes and heterotrophic respiration rates measured in the laboratory, but both fluxes were highest at the Solling stand (Table 5).

Regulation of NO + NO_2 fluxes

Fluxes of NO_x were significantly different among the stands in May (P<0.0001) and July 2009 (P=0.017; Fig. 2b) and ranged from −6.3 to 12.3 µgN $m^{-2}h^{-1}$. In May, the Haard site displayed the highest fluxes followed by the Neuhäusel site and in July, the Solling site displayed the highest fluxes. All sites, except Neuhäusel site, showed negative fluxes at one of the two campaigns.

No significant simple and multiple regressions were observed among the NO_x fluxes and the control parameters. However, uptake of NO_x into the soil increased with increasing atmospheric NO_x concentrations (Fig. 4). In Fig. 4, two linear slopes could be distinguished, first a linear slope that contained the data of the Haard site at both measuring dates and of the Neuhäusel site in May and second, a linear slope that contained the remaining data. The significant influence of the NO_x concentration in the forest air on NO_x fluxes was indicated by multiple regression analysis but not by simple regression analysis. The minimal adequate regression model of all data (P= 0.11, r^2=0.52, df=8) contained the NO_x concentration in the forest air (P=0.04), the net nitrification rate of

Table 5 Mean (± SE, n=5) N_2O fluxes and heterotrophic CO_2 respiration rates measured in-situ at the six beech stands in July 2009 and in the laboratory at 0–9 cm soil columns (lab_9) and at 0–19 cm soil columns (lab_{19}), which both were taken at the six stands in July 2009

	N_2O flux, field [µgN$m^{-2}h^{-1}$]	N_2O flux, lab_9 [µgN$m^{-2}h^{-1}$]	N_2O flux, lab_{19} [µgN$m^{-2}h^{-1}$]	CO_2 flux, lab_9 [mg C $m^{-2}h^{-1}$]	CO_2 flux, lab_{19} [mg C $m^{-2}h^{-1}$]
Haard	6.2 (0.5) ^{a}	45.2 (38.8) ^{a}	2.1 (6.4) ^{a}	196 (55) ^{ab}	249 (42) ^{a}
Neuhäusel	−1.2 (3.3) ^{a}	122.5 (122.2) ^{a}	131.9 (99.7) ^{a}	420 (102) ^{bc}	286 (55) ^{a}
Biebergemünd	1.6 (1.6) ^{a}	−1.5 (3.5) ^{a}	18.9 (20.5) ^{a}	251 (18) ^{ac}	368 (94) ^{a}
Hünfeld	0.2 (0.5) ^{a}	56.4 (38.8) ^{a}	29.6 (30.2) ^{a}	139 (17) ^{a}	305 (83) ^{a}
Lüss	−2.4 (3.7) ^{a}	0.0 (2.9) ^{a}	4.1 (5.2) ^{a}	193 (72) ^{a}	193 (30) ^{a}
Solling	113.3 (67.4) ^{a}	2233.8 (447.7) ^{b}	943.0 (442.8) ^{b}	518 (74) ^{c}	428 (127) ^{a}

For each site, means followed by the same letter were not significantly different (ANOVA, Tukey HSD-test at $P \leq 0.05$). Gas flux measurements in the laboratory were conducted at 27.5 °C at field moisture

Table 6 *P*-values and coefficients of determination (r^2) for simple and multiple regression analyses between N_2O fluxes and control parameters

Control factor	N_2O flux [$\mu g N m^{-2} h^{-1}$] *P*-value	r^2
Simple regression		
Grav. water content O [$g g^{-1}$]	0.0154	0.46
Grav. water content M [$g g^{-1}$]	ns	
Temperature 5 cm depth [°C]	ns	
Net nitrification O [$mg N kg^{-1} d^{-1}$]	0.0020	0.63
Net mineralisation O [$mg N kg^{-1} d^{-1}$]	0.0016	0.65
Net nitrification M [$mg N kg^{-1} d^{-1}$]	ns	
Net mineralisation M [$mg N kg^{-1} d^{-1}$]	ns	
Ds_9 [$cm^2 s^{-1}$]	ns	
Ds_{19} [$cm^2 s^{-1}$]	0.0042	0.58
Air-filled porosity 0–9 cm [$cm^3 cm^{-3}$]	ns	
Air-filled porosity 0–19 cm [$cm^3 cm^{-3}$]	ns	
Multiple regression		
Water content O × nitrification O	0.0026	0.73
Water content O × mineralisation O	0.0016	0.76
Ds_{19} × nitrification O	0.0013	0.77
Ds_{19} × mineralisation O	0.0015	0.76

ns is not significant; O is organic layer; M is 0–5 cm mineral soil. Fluxes of N_2O were log-transformed for the analysis and $df=10$ for simple regressions and $df=9$ for multiple regressions

the organic layer ($P=0.09$), and Ds_9 ($P=0.14$), of which the atmospheric concentration of NO_x in the air was the only significant control parameter.

Regulation of the $N_2O + NO_x$ fluxes and the N_2O/NO_x ratio

The emission of the sum of N_2O and NO_x significantly and exponentially increased with increasing net nitrification rates ($P=0.002$, $r^2=0.64$, $df=10$) and net N mineralisation rates ($P=0.004$, $r^2=0.58$, $df=10$) of the organic layer. Results were similar to results from N_2O fluxes because of the strong impact of N_2O emissions from the Solling site. Due to occurrences of negative fluxes, calculation of the N_2O/NO_x ratio was not applicable for most sites.

Control parameters

Net rates of N mineralisation and nitrification of the organic layer ($P<0.0001$, Fig. 5) and surface 0–5 cm mineral soil ($P<0.001$, data not shown) significantly differed among the six stands in May and in July 2009. Highest rates were observed at the Solling site followed by the Neuhäusel site. Net nitrification could not be detected at the Lüss site and a negligible rate was detected at the Biebergemünd site.

Soil gas diffusivity was significantly different among the stands in May (0–19 cm: $P<0.0001$; 0–9 cm: $P=0.001$) and July (0–19 cm: $P=0.022$, Fig. 6a; 0–9 cm: $P<0.0001$, Fig. 6b). The lowest diffusivity was observed at the Solling site at both measuring dates followed by the Hünfeld site in July.

The water contents of the organic layer (Fig. 3d) and mineral soil (Table 3) were significantly different among the stands at both measuring dates ($P<0.0001$). The water content was highest at the Solling site at both dates followed by the sites Haard and Lüss (Fig. 3d). The annual precipitation sum was also highest at the Solling site. The water contents of the 0–9 cm columns and 0–19 cm columns (laboratory measurements) of the Solling and Haard sites were similar due to the high organic layer amount in columns of the Haard site (Table 3).

A linear positive relationship was observed between Ds_{19} and the sand content ($P=0.03$, $r^2=0.73$) and a linear negative relationship between Ds_{19} and the silt content ($P=0.03$, $r^2=0.72$), the clay content ($P=0.04$, $r^2=0.69$), and the water content of the organic layer ($P<0.001$, $r^2=0.73$).

Discussion

Regulation of N_2O fluxes by N turnover and soil anaerobicity

The present study demonstrated that N mineralisation and nitrification rates combined with an indicator for soil anaerobicity (gas diffusivity or water content) explained 73–77 % of the variation in N_2O fluxes. Similar relationships between N_2O fluxes and N turnover rates (e.g., Ambus et al. 2006; Gasche et al. 2002; Papen and Butterbach-Bahl 1999; Rosenkranz et al. 2006) and soil moisture (e.g., Rosenkranz et al. 2006; Schindlbacher et al. 2004) have previously been reported.

The present study indicated that gas diffusivity is only a slightly better predictor for N_2O fluxes when compared to the water content. This result was not expected since gas diffusivity provides information about the pore structure. Total pore volume of fine-textured soils is higher but most pores are smaller than those in coarse-textured soils

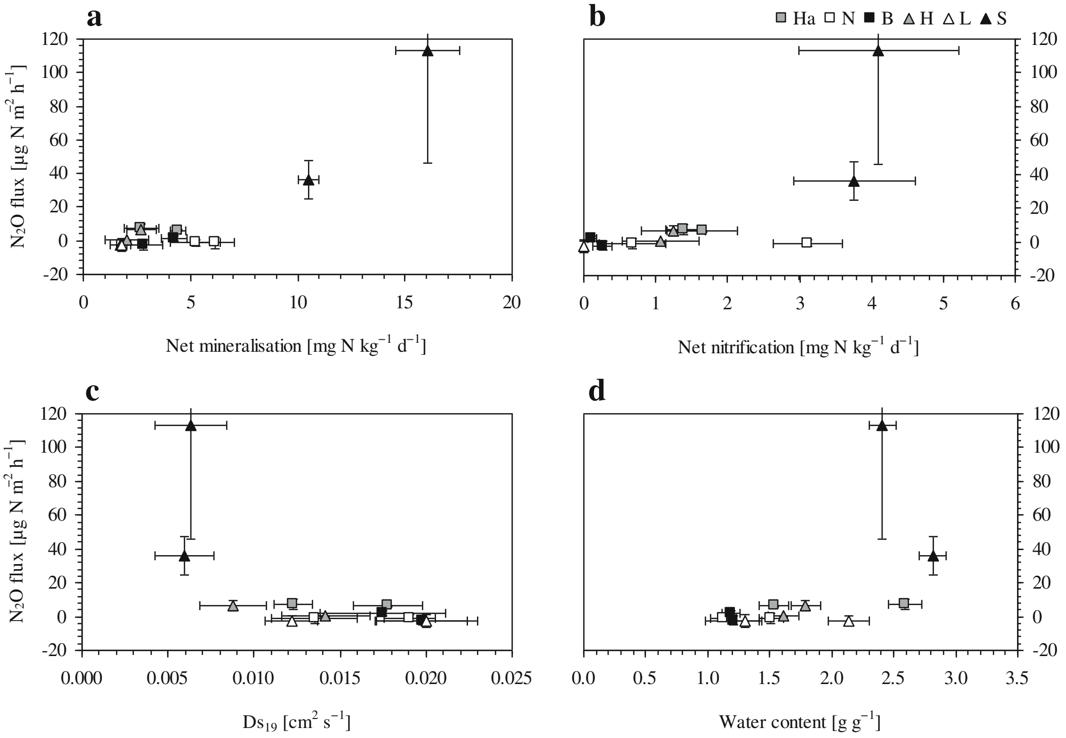

Fig. 3 Fluxes of N_2O of the six beech stands plotted against **a** net N mineralisation rates of the organic layer, **b** net nitrification rates of the organic layer, **c** apparent diffusion coefficients of N_2 of the 0–19 cm soil samples (Ds_{19}), and **d** gravimetric water contents of the organic layer. The mean values (n=5) from May and July 2009 are shown. Site abbreviations: Ha = Haard, N = Neuhäusel, B = Biebergemünd, H = Hünfeld, L = Lüss, and S = Solling

and molecular diffusion is slower through smaller pores (Currie 1961). This phenomenon is shown in Fig. 1 where the sandy soil of the Lüss site exhibits higher relative diffusivity compared to the more fine-textured soils at the same air-filled porosity. The observation that gas diffusivity predicted N_2O fluxes only slightly better than the water content may be ascribed to low diffusivity in water-filled anoxic micro-sites which is not sufficiently accounted for by diffusivity and water content of the whole soil column. In fine-textured soils anoxic micro-sites are created at lower soil water contents than in coarse-textured soils and thus, N_2O emissions are generally higher from fine-textured soils (Bollmann and Conrad 1998; Skiba and Smith 2000). In forests, soil moisture is as suitable as an indicator for soil anaerobicity as diffusivity, however, neither of them is sufficient to describe soil anaerobicity. The investigated beech stands in general had high air-filled porosities and high relative diffusivities, which may be due to continuous macropores possibly resulting from roots.

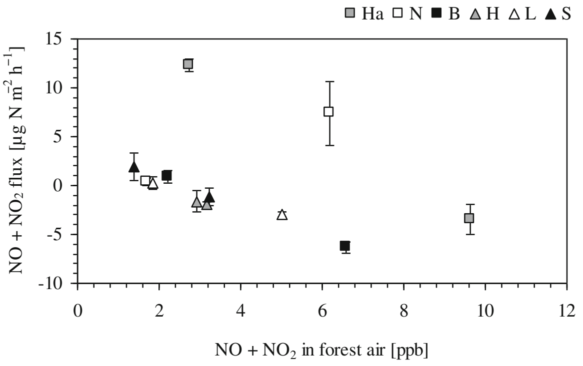

Fig. 4 Mean (± SE, n=5) NO + NO_2 fluxes plotted against NO + NO_2 concentrations in the forest air of the six beech stands. Mean fluxes were derived from measurements in May and July 2009. Site abbreviations: Ha = Haard, N = Neuhäusel, B = Biebergemünd, H = Hünfeld, L = Lüss, and S = Solling

Explanation for seasonal N_2O emission patterns

Nitrous oxide fluxes did not follow a gradual change with any of the measured regulators. Instead, N_2O emissions abruptly increased and suggested that more

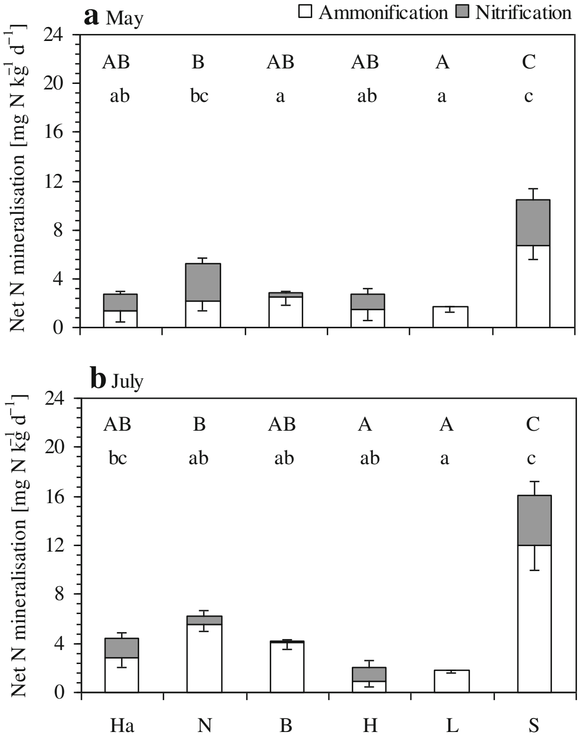

Fig. 5 Mean (± SE, n=5) net N mineralisation rates of the organic layer of the six beech stands measured on disturbed soil samples taken in **a** May and **b** July 2009. Upward error bars belong to net nitrification rates and downward error bars to net ammonification rates. Among stands, means followed by the same letter indicated no significant differences (ANOVA, Tukey HSD-test at $P\leq0.05$). Lower case letters belong to net nitrification rates and upper case letter to total net N mineralisation rates. Site abbreviations: Ha = Haard, N = Neuhäusel, B = Biebergemünd, H = Hünfeld, L = Lüss, and S = Solling

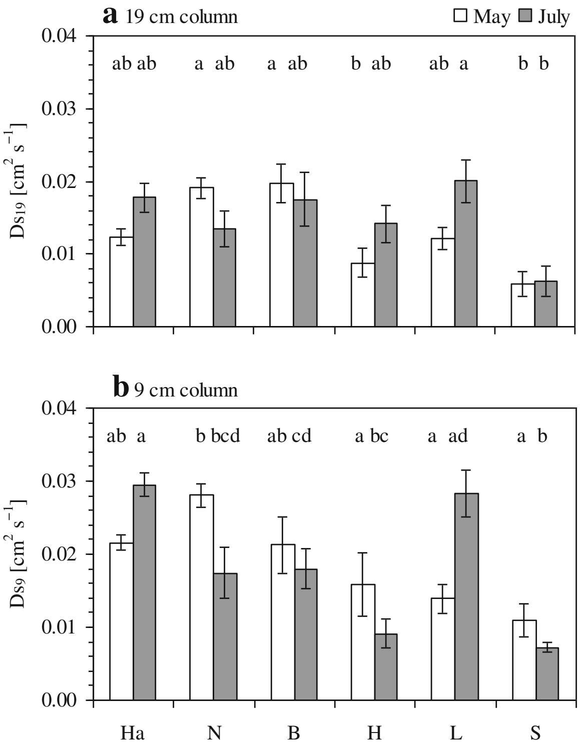

Fig. 6 Mean (± SE, n=5) apparent diffusion coefficients of N_2 given for the six beech stands, which were measured **a** on 0–19 cm soil samples (Ds_{19}) and **b** on 0–9 cm soil samples (Ds_9) taken in May and July 2009. Regarding 1 months, stand means followed by the same letter indicated no significant differences (ANOVA, Tukey HSD-test at $P\leq0.05$). Site abbreviations: Ha = Haard, N = Neuhäusel, B = Biebergemünd, H = Hünfeld, L = Lüss, and S = Solling

than one parameter has to be in a critical range for high emissions of N_2O in forest stands. Not even significant relationships between N_2O fluxes and N turnover and anaerobicity were observed when omitting the Solling site, which displayed exceptionally high N_2O emissions compared to the other five beech stands. The Solling site has previously been described as seasonal N_2O emission type (SEP) with high N_2O losses from denitrification during summer months and low emissions during winter months (Brumme et al. 1999; Eickenscheidt et al. 2011; Wolf and Brumme 2002). For a 10-year measuring period the N_2O emissions ranged annually from 1.1 to 3.0 kgN ha^{-1}year^{-1} (mean of 1.9 kgN ha^{-1}year^{-1}; Brumme and Borken 2009). One reason for the abrupt change in N_2O emissions is low gas diffusivity in combination with high N turnover (Ball et al. 1997; Brumme 1995). In times of high soil moisture and high soil respiration in summer months, when high N turnover provides the necessary nitrate for denitrification, it is the low gas diffusivity which restricts the O_2 supply for microorganisms and causes a change from aerobic to nitrate respiration.

The observed significant increase in N_2O emissions in the laboratory compared to the field by up to a factor of twenty (Table 5) supports the hypothesis of a temperature driven effect on O_2 reduction by microbial respiration. Since temperature increased processes like mineralisation, nitrification, and respiration two to three times per 10 °C (Brumme et al. 2009), according to the rule of van't Hoff, the observed 20-fold increase in N_2O emissions may only be explained by the theory of the development of anaerobic volumetric zones. Smith et al. (2003) revealed that a linear increase in temperature creates an exponential increase in anaerobic soil volume fraction due to respiratory O_2 consumption.

Low gas diffusivity at the Solling site can be attributed to the fine-textured soil, a moder type humus of tightly-packed laminar beech leaves, and high annual precipitation causing high soil water contents. The determined relative diffusion coefficients of the beech stand at the Solling site were in good accordance with the results of Ball et al. (1997). They showed that the diffusivity of the organic layer was similarly low than from the upper mineral soil at the Solling site whereas higher values were measured at an adjacent limed plot. Liming reduced N_2O emissions by 73 % at the Solling site (Ball et al. 1997; Brumme and Beese 1992). The observation was attributed to an alteration of the structure of the organic layer by earthworms (Borken and Brumme 1997). High N mineralisation and nitrification rates at the Solling site despite low soil pH may be attributed to a better nutrient status and high N depositions compared to the other sites. High nitrification rates have previously been reported for this stand by Eickenscheidt and Brumme (2013) and by Meiwes et al. (1998).

Potential for high N_2O emissions at forests with low background emissions under changing environmental conditions

Five out of the six beech stands studied displayed low N_2O emissions and probably belonged to the background emission type (BEP). Likewise our observations, Brumme et al. (1999) found no correlations of N_2O fluxes with control parameters in forests with BEP. Low background fluxes of N_2O were reported in most studies (e.g., Brumme and Borken (2009) for beech forests with mull type humus; Butterbach-Bahl et al. (2002) for German Scots pine forests; Papen and Butterbach-Bahl et al. (1999) for a spruce forest).

The question arises whether changing climate conditions or management practise will move these forests from low to high seasonal N_2O emissions? It has been shown that soil compaction during harvesting increased the annual emissions of N_2O by up to 30-times (Teepe et al. 2004). Soil compaction reduced the macro pores and shifted all three beech forest from low background to high seasonal emissions. Brumme (1995) observed an increase in N_2O emission as a result of missing plant uptake after the establishment of a forest gap. Missing plant uptake increased the water and nitrate contents in the soil and increased the fluxes and the duration of emissions.

The flux measurements conducted in this study on undisturbed soil columns in the laboratory are not assignable to field conditions, but they indicate the potential of a stand for higher emissions of N_2O under changing environmental conditions. Since plant uptake was interrupted in the laboratory study, nitrate is not limiting denitrification processes as long as nitrification proceeds. Moreover, the higher temperature increased the microbial activity, N turnover and O_2 consumption and lead to optimal conditions for denitrification processes. Under these laboratory conditions, a significant increase in N_2O emissions up to a factor of 20 was observed at the Solling site, indicating that forests of the seasonal emission type had a very high potential for increasing emissions. Forest with background emissions react differently. The sandy texture and the missing nitrification at the Lüss site prevented any increase in N_2O emissions in contrast to the four other beech stands with BEP. Out of these sites, the Neuhäusel site showed the highest increase in N_2O emissions. The Neuhäusel site was similar to the Solling site in soil texture and net nitrification rates of the organic layer but showed higher gas diffusivity probably due to lower precipitation rates and differences in humus type (F-mull). Higher O_2 consumption probably created anaerobic zones at higher temperatures at the Neuhäusel site during the laboratory measurement.

In addition, the results from the Neuhäusel site indicated that texture is possibly more important for N_2O release from beech stands with mull type humus than humus type. High N_2O emissions of approx. 4 kgN ha^{-1} year^{-1} have also been reported from an acid beech forest soil in Austria, which had a high nitrification activity, high precipitation, and a loamy silt texture but a mull type humus (Zechmeister-Boltenstern et al. 2002). Hence, soil conditions at the depth of N_2O production are most important and Brumme et al. (1999) reported that the contribution of the organic layer to N_2O emissions in deciduous forests was low at mull type humus sites (2.2–7.4 %) compared to 53 % at the Solling site with moder type humus.

Atmospheric NO_x concentrations as key driver for NO_x fluxes

Fluxes of NO_x were low at all six sites and comparable to fluxes measured in beech stands by Beier et al.

(2001) and by Gasche and Papen (1999). The annual NO_x emissions amounted to 0.11±0.05 kgN ha^{-1} $year^{-1}$ at the Solling site in 2007–2008 (Eickenscheidt, unpublished data). However, most studies reported NO fluxes. When regarding net NO_x fluxes, high NO production rates may be balanced by NO_2 and NO uptake rates (Gasche and Papen 1999; Rosenkranz et al. 2006). Gasche and Papen (1999) reported net NO emission rates between 7.5 and 38.2 μgN $m^{-2}h^{-1}$ and simultaneous net NO_2 uptake rates between −25.9 and −6.8 μg N $m^{-2}h^{-1}$ from a German beech forest soil. Release of NO_x from soils may be the result of NO production via nitrification and denitrification (Davidson et al. 2000; Conrad 1996) or of NO_2 production via chemodenitrification in acid soils (van Cleemput and Samater 1996). Uptake of NO_x could be ascribed to abiotic NO_2 uptake, oxidative consumption of NO via nitrification, reductive consumption via denitrification, or consumption of NO by aerobic heterotrophic bacteria, respectively (Gasche and Papen 1999; Gödde and Conrad 2000; Pilegaard et al. 2006). The uptake of NO_x at the Haard site in July despite high gas diffusivity could possibly be attributed to a heavy rainfall event during the measurement.

Determination of net NO_x fluxes and thus presence of several different processes may be the reason for non-significant relationships with regulating factors as was the case in the present study. Fluxes of NO_x tended to increase with increasing diffusion coefficients (Ds_9) and net nitrification rates of the organic layer, which suggested that NO might be derived from nitrification. A positive correlation between NO emissions and nitrification rates was reported by e.g., Gasche and Papen (1999) and Gasche et al. (2002). Nitrification rates were similar for the sites Neuhäusel and Solling in May but the Neuhäusel site showed higher NO_x emissions most likely due to higher gas diffusivity compared to the Solling site where N_2O dominated. Fluxes of NO_x significantly depended on NO_x concentrations in the ambient air when also considering net nitrification and soil diffusivity in the regression analysis. Concentrations of NO (NO_x) in the ambient air have also been described as one of the main drivers for NO (NO_x) exchange between the atmosphere and soil by Eickenscheidt and Brumme (2012), Gasche and Papen (1999) and Ludwig et al. (2001). The higher compensation concentration of NO_x at the sites Haard and Neuhäusel (May) might be explained by comparable high nitrification rates and aerobic soil conditions. Anaerobic soil conditions probably resulted in NO consumption. Ludwig et al. (2001) proposed that higher compensation concentrations are typically associated with higher net nitrification rates. Gasche and Papen (1999) observed a high NO compensation concentration of > 75 ppbv from a southern German spruce forest, which had been exposed to chronic high N depositions and exhibited high nitrification rates. This spruce forest showed very high NO_2 uptake rates and a relationship between NO_2 uptake and inorganic N depositions. The authors concluded that N depositions increased NO emissions, which reacted with ozone to NO_2. The increase in NO_2 concentrations in ambient air in turn enhanced NO_2 uptake into the soil. This observation is in line with that of Beier et al. (2001), who observed NO_2 uptake at low NO emission rates in a beech stand and NO_2 upward fluxes at high NO emission rates as a result of the reaction of NO with ozone.

Conclusions

We demonstrated that the amount of N_2O emissions in German beech forest soils not only depends on net N mineralisation and nitrification rates but also on a temperature driven effect on O_2 consumption by microbial respiration. Consequently, anaerobic volumetric zones are developed in soils with low gas diffusivity, which in turn is the result of a combination of moder type humus on loamy soil under high annual precipitation. Hence, soil anaerobicity and high N turnover rates in wet summer result in high seasonal N_2O emissions from acid beech forest soils. However, moder type humus of acid beech soils is not necessarily associated with seasonal emission patterns. The results suggest that seasonal emission patterns are less common in German beech forests than previously assumed but they may increase under changing management or as a consequence of climate change. However, to confirm the stated conclusion, investigations from forests exhibiting seasonal pattern are necessary and more information about anaerobic micro-sites and their temporal and spatial dynamics are needed.

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