

Direct contribution of nitrogen deposition to nitrous oxide emissions in a temperate beech and spruce forest – a ^{15}N tracer study

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Abstract. The impact of atmospheric nitrogen (N) deposition on nitrous oxide (N_2O) emissions in forest ecosystems is still unclear. Our study assessed the direct contribution of N deposition to N_2O emissions in temperate forests exposed to chronic high N depositions using a ^{15}N labelling technique. In a Norway spruce stand (*Picea abies*) and in a beech stand (*Fagus sylvatica*) at the Solling, Germany, we used a low concentrated ^{15}N -labelled ammonium-nitrate solution to simulate N deposition. Nitrous oxide fluxes and ^{15}N isotope abundances in N_2O were measured using the closed chamber method combined with ^{15}N isotope analyses. Emissions of N_2O were higher in the beech stand ($2.6 \pm 0.6 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) than in the spruce stand ($0.3 \pm 0.1 \text{ kg N ha}^{-1} \text{ yr}^{-1}$). We observed a direct effect of N input on ^{15}N - N_2O emissions, which lasted for less than three weeks and was mainly caused by denitrification. No further increase in ^{15}N enrichment of N_2O occurred during a one-year experiment, which was probably due to immobilisation of deposited N. The annual emission factor for N_2O from deposited N was 0.1% for the spruce stand and 0.6% for the beech stand. Standard methods used in the literature applied to the same stands grossly overestimated emission factors with values of up to 25%. Only 6–13% of the total N_2O emissions were derived from direct N depositions. Whether the remaining emissions resulted from accumulated anthropogenic N depositions or native soil N, could not be distinguished with the applied methods. The ^{15}N tracer technique is a useful tool, which may improve estimates of the current contribution of N deposition to N_2O emissions.

1 Introduction

In Europe and in many other parts of the world, emissions of reactive nitrogen (N) have rapidly increased in the last decades mainly due to agricultural and industrial activities (e.g. Galloway et al., 2008; Vitousek et al., 1997). As a consequence, European forests have been exposed to high deposition rates of acidity and reactive N compounds (Berge et al., 1999). Pre-industrial European forests were supposed to be N-limited, however widespread N deposition has caused a shift in the forest's N status which under chronic N deposition may even lead to N-saturated conditions (Aber et al., 1998). Using N input-output balances, Brumme and Khanna (2008, 2009b) classified German forests into four groups with different N status that cover the complete N enrichment continuum. According to them “steady state type forests” with mull type humus (STFa: forests where deposited N is accumulating in trees only and not in the soil) were probably widespread in Europe in pre-industrial times. They assumed that soil acidification caused these forests to lose organic matter and mineral N from the soil changing them into “degradation type forests” (DTF: forests where the mineral soil has become a source of N and C). With further acid and N depositions, these forests would change into “accumulation type forests” (ATF: forests where deposited N and carbon is accumulating in the surface organic soil). At the end of the N enrichment continuum, forests could become another “steady state type forests” with moder type humus (STFb: forests where deposited N is accumulating in trees and not in soil). Fluxes of nitrous oxide (N_2O), which is an important greenhouse gas (IPCC, 2007) and contributes to the chemical destruction of the stratospheric ozone layer (Crutzen, 1979), may increase if the soil becomes a source of N (transition from STFa → DTF) and deposited N exceeds the storage capacity of the ecosystem (transition from



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ATF→STFb). Consequently, European forests with chronic acid and N deposition frequently act as considerable source for N₂O (e.g. Brumme and Beese, 1992; Butterbach-Bahl et al., 1998; Papen and Butterbach-Bahl, 1999; Skiba et al., 1999).

Temperate forest soils are estimated to add between 0.1 and 2.0 Tg N₂O-N yr⁻¹ to the atmosphere, which is between 0.6 and 11% of the total global N₂O emissions (Brumme et al., 2005; IPCC, 2001; Kroeze et al., 1999) indicating the high degree of uncertainty in the estimations. The role of atmospheric N depositions on N₂O emissions is highly unclear and is one of the reasons for this uncertainty (Pilegaard et al., 2006). The IPCC (2006) uses a default emission factor for N₂O of 0.01, which means that 1% of the N deposited in temperate forests contributes to N₂O emissions. The uncertainty of this emission factor is huge ranging from 0.002 to 0.05 where the higher fraction comes from deciduous forests and the lower fraction from coniferous forests (Brumme et al., 1999; Denier van der Gon and Bleeker, 2005). Tree species related differences in litter quality, litter structure, and soil moisture may play a role in the reported variation of emission factors, but still much uncertainty remains (Brumme et al., 1999; Pilegaard, 2006).

Three different approaches have been used to examine the impact of N depositions on N₂O fluxes: (1) regression analysis between N depositions and N₂O fluxes (e.g. Butterbach-Bahl et al., 1998), (2) comparison of similar forest ecosystems receiving different N loads (e.g. Skiba et al., 1999), and (3) N fertilisation experiments (e.g. Brumme and Beese, 1992). These approaches have the following limitations: (1) regression analysis between N depositions and N₂O fluxes requires a strong correlation, which can only occur if direct N₂O emission of deposited N is significant. Moreover, N deposition is usually correlated with similar factors (e.g. precipitation) that also control N₂O fluxes (Butterbach-Bahl et al., 1998; Kitzler et al., 2006a). (2) Comparing sites receiving different N loads has the limitation that sites are usually not completely comparable in climate and soil properties. Finally, (3) studies have shown that the application of mineral N to simulate N deposition does not commonly reflect the mode of chronic N depositions (Sitaula et al., 1995; Skiba and Smith, 2000).

The use of ¹⁵N isotopes as a tracer is potentially a useful technique to investigate the impact of N deposition on N₂O fluxes in forests. The ¹⁵N technique can be applied even if low direct N₂O emissions occur, it is independent of precipitation amount and does not cause artificially high mineral N concentrations in the soil. At present we are not aware of any study where the emission factor for N₂O from forest soils was estimated using ¹⁵N tracer techniques. In forest ecosystems the ¹⁵N tracing technique has only been used to distinguish between various sources of N₂O production (e.g. Ambus et al., 2006; Wolf and Brumme, 2002).

Our objectives were (i) to examine the direct contributions of ammonium (NH₄⁺) and nitrate (NO₃⁻) depositions to N₂O

emissions and (ii) to follow the effect for one year including the remineralisation of deposited and subsequently immobilised N. We hypothesise that (1) N depositions contribute considerably to direct N₂O emissions which is caused by the availability of mineral N independent of mineralisation and nitrification rates and (2) N depositions contribute to significant amounts of N₂O emissions over one-year because of remineralisation of deposited N. To test our hypotheses, we conducted (i) a short-term as well as (ii) a one-year long lasting in situ ¹⁵N tracer experiment in a coniferous and in a deciduous forest stand which both have been exposed to high atmospheric N depositions for decades.

2 Materials and methods

2.1 Study area

The study was carried out at the Solling plateau in Central Germany (51°46' N, 9°34' E; 500 m a.s.l.; mean annual temperature: 6.9 °C; annual precipitation: 1193 mm). The soil type is an acidic Dystric Cambisol (silt loam), which has developed in a loess solifluction layer overlying Triassic sandstone bedrock. The humus type is a typical moder. A detailed site description is given by Bredemeier et al. (1995, 1998) and by Brumme and Khanna (2009a). Experiments took place in a 74-yr-old Norway spruce stand (*Picea abies* (L.) Karst.) and in an adjacent 160-yr-old beech stand (*Fagus sylvatica*). Soil characteristics for both sites are presented in Table 1.

Both stands have been exposed to high N depositions for decades. In 2007 and 2008, stand deposition amounted to 33 kg N ha⁻¹ yr⁻¹ in the spruce stand with NH₄⁺-N:NO₃⁻-N:N_{org} in the ratios of 49:44:7 and to 20 kg N ha⁻¹ yr⁻¹ in the beech stand with a NH₄⁺-N:NO₃⁻-N:N_{org} ratio of 47:38:16. Stand N deposition was usually measured in monthly intervals in both stands and represents the sum of throughfall deposition and stemflow. Stemflow was negligible in the spruce stand. In the beech stand, data collection and chemical analyses were conducted by the Northwest German Forest Research Station (Meesenburg et al., 2009).

2.2 Experimental design

We conducted the short-term experiment in August and September 2009 in order to examine the direct contribution of NH₄⁺ and NO₃⁻ depositions to N₂O emissions. Ten chamber bases were randomly installed in each stand, four of which were labelled once with ¹⁵NH₄NO₃ solution (named NH₄⁺-labelled) whereas the other four were labelled once with NH₄¹⁵NO₃ solution (named NO₃⁻-labelled; both contained 98 atom% ¹⁵N). Two chambers served as controls. We reduced the number of control chambers in favour of treated chambers because the temporal as well as spatial variability of emitted natural ¹⁵N in our previous studies in the beech

Table 1. Soil characteristics of the spruce and beech stands at the Solling site.

Soil depth and forest site	<i>n</i>	pH(H ₂ O)	<i>n</i>	Total organic carbon [mg C g ⁻¹]	Total nitrogen [mg N g ⁻¹]	C/N ratio	<i>n</i>	Bulk density [g cm ⁻³]	Humus mass [Mg ha ⁻¹]
Organic layer									
Spruce	3	3.6 (0.1) ^a	13	447 (13)	16.5 (0.4) ^a	27.2 (0.6) ^a	6		67.1 (4.4) ^a
Beech	3	4.0 (0.0) ^b	13	443 (12)	18.6 (0.7) ^b	24.1 (0.7) ^b	6		35.6 (1.9) ^b
0–5 cm									
Spruce	6	3.3 (0.0)	14	112 (7)	4.6 (0.3)	24.3 (0.8) ^a	4	0.76 (0.03)	
Beech	6	3.4 (0.0)	14	98 (11)	4.4 (0.3)	21.7 (1.4) ^b	6	0.89 (0.02)	
5–10 cm									
Spruce	5	3.5 (0.0)	13	39 (2) ^a	1.7 (0.1)	22.9 (0.8) ^a	5	1.00 (0.02)	
Beech	6	3.6 (0.0)	13	32 (2) ^b	1.7 (0.1)	19.8 (1.1) ^b	6	1.08 (0.04)	

At each layer, means (\pm SE) followed by different letters indicated differences among the spruce and beech stands (independent t-test or Mann-Whitney U-test at $P \leq 0.05$).

stand indicated low values (see Supplement). We added 0.7 L labelling solution per chamber base. The N concentration of the solution was 1.65 mg L⁻¹, which was within the range of the N concentrations measured in the throughfall. The labelled N was distributed down to 10 cm mineral soil depth within few hours after the application. In addition to the fluxes of N₂O and ¹⁵N-N₂O, we determined air and soil temperature, soil moisture, and extractable mineral N (N_{min} = NH₄⁺-N + NO₃⁻-N) content. Soil samples were taken at randomly chosen locations between the chamber bases. Measurements were conducted 3.5 h (spruce) and 5 h (beech), 24 h, 48 h, 7 days, and 21 days after the application of labelled N.

The one-year experiment was performed to examine the impact of NH₄⁺ and NO₃⁻ deposition on N₂O emissions including the remineralisation of the deposited N within one year. At both stands we randomly installed 17 chamber bases for gas flux measurements and soil sampling. Seven of the chamber bases received a ¹⁵NH₄NO₃ solution (named NH₄⁺-labelled; 98 atom % ¹⁵N) and another seven received a ¹⁵NH₄¹⁵NO₃ solution (named NH₄NO₃-labelled; 95 atom % ¹⁵N). Of the seven chamber bases, five were used for gas flux measurements whereas soil samples were taken in two chamber bases. Three chamber bases served as controls for N₂O and ¹⁵N-N₂O fluxes. All measurements as described above in the short-term experiment were also carried out in this experiment which was conducted from May 2007 to June 2008. Measurements were done every second week in the summer months and monthly in the winter months. Uncertainties that arise from the frequency of measurements are probably low. A published study done in our beech stand (Brumme and Beese, 1992) revealed that during the season with high emissions weekly measurements overestimated N₂O fluxes by 3% to 11% compared to measurements with an automatic chamber (five measurements per

day). Overestimation will presumably be lower when covering the whole year. The ¹⁵N solution was always applied one week before the gas flux measurements (18 applications over the year). For one N application in the one-year experiment, the amount of N and water added were equal to the amount added with one application in the short-term experiment. To each chamber receiving N we added the equivalent of 0.78 kg N ha⁻¹ yr⁻¹, which was 2.4% of the annual deposition in the spruce stand and 3.8% in the beech stand. The amount of water added was equivalent to 47 mm rain, which was approx. 4.8% of the annual precipitation.

2.3 N₂O and ¹⁵N-N₂O measurements

Fluxes of N₂O were measured using the closed chamber method (static, vented chambers made of PVC; area: 0.2665 m²; vol.: 18.9–29.3 L (beech), 27.5–34.7 L (spruce)). Gas samples of 100 mL were removed at three (May 2007 to January 2008) or four (February to June 2008 and 2009) regular time intervals following chamber closure (42 min at most) 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”. Analysis of N₂O was carried out with a gas chromatograph equipped with an EC detector (GC 14A, Shimadzu, Duisburg, Germany). Fluxes of N₂O were calculated from the linear change of N₂O concentrations in the chamber versus time, after fluxes were adjusted for air temperature and atmospheric pressure. We tested a quadratic model for some data, but no clear advantage of the non-linear model emerged from the statistical indicators for the goodness of fit. Additionally, N₂O fluxes calculated using the quadratic model were not significantly different from fluxes calculated using the linear model. We further think

that scattering of N_2O concentrations due to random errors during sampling and measurement were much larger than the effect of the chamber on the gas exchange and possible biases due to linear regression. The cumulative mean annual flux was calculated using the trapezoid rule. Samples for $^{15}\text{N}\text{-N}_2\text{O}$ analysis were collected in glass bottles (100 mL) closed with a butyl-hallow stopper at time point zero and after 24 to 28 min. Analysis of ^{15}N in N_2O was done using an isotope ratio mass spectrometer coupled with a pre-concentration unit (PreCon-GC-IRMS, Thermo Finnigan MAT, Bremen, Germany).

2.4 Chemical analyses

Mineral N was extracted after shaking 25 to 30 g fresh mineral soil with 100 mL 0.5 M K_2SO_4 solution or 15 g of the organic layer with 50 mL K_2SO_4 solution, using pre-washed filter papers. Extracts of K_2SO_4 were frozen until analysis. Mineral N analysis was carried out using continuous flow injection colorimetry (Cenco/Skalar Instruments, Breda, The Netherlands). The water content was determined gravimetrically. Soil bulk density was determined using undisturbed soil samples that were oven-dried at 105°C and sieved to 2 mm to remove stones and living roots. The mass of the organic layer was measured using a metal ring (594 cm^2). Organic layer samples were oven-dried at 60°C and living roots were removed. Total carbon and nitrogen measurements were done using a CNS Elemental Analyzer (Heraeus Elementar Vario EL, Hanau, Germany) and ^{15}N concentrations using a Delta C plus isotope ratio mass spectrometer (Finnigan MAT, Bremen, Germany). The pH was determined in distilled water (1:2.5 (v/v)) using 10 mL sieved soil or shredded organic material.

2.5 Calculation of ^{15}N abundance

Isotope abundances were expressed in absolute proportion [atom %]:

$$^{15}\text{N} \text{ [atom \%]} = \frac{^{15}\text{N}}{^{15}\text{N} + ^{14}\text{N}} \cdot 100 \quad (1)$$

The $^{15}\text{N}\text{-N}_2\text{O}$ abundance of N_2O emitted from the soil was calculated using the Keeling plot approach (Pataki et al., 2003; Tilsner et al., 2003):

$$^{15}\text{N}_{\text{emitted}} = \frac{^{15}\text{N}_{\text{chamber air}} \cdot c(\text{N}_2\text{O})_{\text{chamber air}} - ^{15}\text{N}_{\text{ambient air}} \cdot c(\text{N}_2\text{O})_{\text{ambient air}}}{c(\text{N}_2\text{O})_{\text{chamber air}} - c(\text{N}_2\text{O})_{\text{ambient air}}} \quad (2)$$

where $c(\text{N}_2\text{O})$ is the concentration of N_2O and ^{15}N is the abundance of ^{15}N in N_2O calculated as described in Eq. (1). The $^{15}\text{N}_{\text{emitted}}$ excess value was calculated by subtracting the $^{15}\text{N}_{\text{emitted}}$ value of the control chambers. The $^{15}\text{N}_{\text{emitted}}$ excess value was used to obtain the $^{15}\text{N}\text{-N}_2\text{O}$ excess flux. In case of negative N_2O fluxes the $^{15}\text{N}_{\text{emitted}}$ calculation was not applicable since $^{15}\text{N}\text{-N}_2\text{O}$ emissions occurred from labelled

soil but could not be quantified because we only measured net N_2O fluxes. Hence negative N_2O fluxes were omitted for $^{15}\text{N}\text{-N}_2\text{O}$ flux calculations, which included 35% of all flux values in the spruce stand and 17% of those in the beech stand.

2.6 Recovery of ^{15}N in N_2O and N_t

The recovery of ^{15}N from the tracers in emitted N_2O (emission factor) and in soil N_t was calculated using atom % values for ^{15}N mass calculations:

$$^{15}\text{N} \text{ recovery [\%]} = \frac{m^{15}\text{N}_{\text{rec}}}{m^{15}\text{N}_{\text{Tracer}}} \cdot 100 \quad (3)$$

where $m^{15}\text{N}_{\text{rec}}$ could be $m^{15}\text{N}_{\text{N}_2\text{O}}$ or $m^{15}\text{N}_{\text{N}_t}$, respectively: $m^{15}\text{N}_{\text{N}_2\text{O}}$ is mass of emitted $^{15}\text{N}\text{-N}_2\text{O}$ excess in $\text{mg } ^{15}\text{N m}^{-2}$ per time interval considered; $m^{15}\text{N}_{\text{N}_t}$ is mass of $^{15}\text{N}\text{-N}_t$ excess in $\text{mg } ^{15}\text{N m}^{-2}$ after 19 tracer applications. Furthermore, $m^{15}\text{N}_{\text{Tracer}}$ is mass of ^{15}N excess in the tracer in $\text{mg } ^{15}\text{N m}^{-2}$ applied since the start of the corresponding experiment.

We used two approaches to estimate the mass of emitted $^{15}\text{N}\text{-N}_2\text{O}$ between two consecutive $^{15}\text{N}\text{-N}_2\text{O}$ flux measurements. In the first approach, we used the trapezoid rule. As indicated by the short-term experiment, this approach does not account for the peak emissions during the first week due to the fact that the emissions were measured one week after the application leading potentially to an underestimation of $^{15}\text{N}\text{-N}_2\text{O}$ fluxes whereas fluxes in the time interval between the measurement and the next tracer application were possibly overestimated. We therefore tested a second approach where we assumed that the $^{15}\text{N}\text{-N}_2\text{O}$ fluxes displayed the same temporal trend as observed in the short-term experiment. In this approach, the relative proportion of the tracer emission of one measuring day on the emissions of the time interval between consecutive tracer applications was estimated using the short-term experiment data (Eq. 4).

$$\text{relative proportion of Ms on Is [-]} = \frac{\text{mean}^{15}\text{N}\text{-N}_2\text{O}_{\text{Ms}}}{\text{mean}^{15}\text{N}\text{-N}_2\text{O}_{\text{Is}}} \quad (4)$$

where Ms is a measuring day of the short-term experiment (fluxes for days on which no measurement took place were interpolated from available measured data) and Is is the time interval between two consecutive tracer applications in which the measuring day lies. The mean $^{15}\text{N}\text{-N}_2\text{O}_{\text{Ms}}$ flux ($\text{ng } ^{15}\text{N m}^{-2} \text{ d}^{-1}$) represents the mean excess $^{15}\text{N}\text{-N}_2\text{O}$ flux of all replicates of one labelling treatment of the measuring day of the short-term experiment. The mean $^{15}\text{N}\text{-N}_2\text{O}_{\text{Is}}$ flux ($\text{ng } ^{15}\text{N m}^{-2} \text{ interval}^{-1}$) represents the cumulative mean excess $^{15}\text{N}\text{-N}_2\text{O}$ flux of all replicates of one labelling treatment of the time interval between two consecutive tracer applications of the short-term experiment. The tracer emission of a measuring day from the one-year experiment was then transformed into the tracer emission of the period between two

consecutive measurements by dividing it by its relative proportion (Eq. 5).

$$\text{cumulative } ^{15}\text{N-N}_2\text{O}_{\text{IL}} [\text{ng m}^{-2} \text{ interval}^{-1}] \quad (5)$$

$$= \frac{^{15}\text{N-N}_2\text{O}_{\text{ML}}}{\text{relative proportion of Ms on Is}}$$

where cumulative $^{15}\text{N-N}_2\text{O}_{\text{IL}}$ represents the cumulative excess $^{15}\text{N-N}_2\text{O}$ flux of a time interval between two consecutive tracer applications of the one-year experiment and $^{15}\text{N-N}_2\text{O}_{\text{ML}}$ ($\text{ng } ^{15}\text{N m}^{-2} \text{ d}^{-1}$) is the excess $^{15}\text{N-N}_2\text{O}$ flux of the measuring day in this interval. The relative proportion could only be estimated from the short-term experiment for the NH_4^+ -labelled and NO_3^- -labelled treatments. Thus, for the NH_4NO_3 -labelled treatment the mean of both proportions was used. Finally, the annual cumulative excess $^{15}\text{N-N}_2\text{O}$ flux was calculated by adding up the emissions of all measurement intervals.

Emission factors calculated by the two methods did not show any significant differences for a particular treatment and stand, indicating that the higher values of emissions during the first week of application were balanced by the lower emissions of the following week(s). Therefore, we only report results from the first approach.

Nitrous oxide derived from N deposition ($\text{N}_2\text{O-NDFD}$) was assessed by using the following equation:

$$\text{N}_2\text{O-NDFD} [\text{kg ha}^{-1} \text{ yr}^{-1}] = m\text{N}_{\text{dep}} \cdot \frac{\text{EF}}{100} \quad (6)$$

where $m\text{N}_{\text{dep}}$ is the mass of inorganic N of the stand deposition in $\text{kg ha}^{-1} \text{ yr}^{-1}$; EF is the emission factor (units in %).

2.7 Statistical analyses

Prior to analysis the assumptions of normality of residuals (Shapiro-Wilk or Cramer-von Mises test) and homogeneity of variances (Levene test) were tested. If necessary, we transformed (log and arcsine) data prior to analyses. Two independent sample means were tested for significant differences using the independent Student's t-test, the Welch-test, or the non parametric Mann-Whitney U-test. We used analysis of variance (ANOVA) for comparison of more than two sample means. The weighted harmonic mean was utilised for proportion data with different bases. These proportions were weighted prior to statistical analyses. Temporal pseudoreplication occurred with time series data (N_2O , $^{15}\text{N-N}_2\text{O}$) because measurements were repeatedly done using the same chamber bases. Therefore, we applied linear mixed effects models (Crawley, 2007; Gueorguieva and Krystal, 2004). We set up a basic model including the forest type (beech and spruce) or the different ^{15}N labelling (NH_4^+ -labelled, NO_3^- -labelled, NH_4NO_3 -labelled) as fixed effects and the spatial replication (individual chamber) nested in time as random effects. The model was extended by a variance function and by a first-order temporal autoregressive function if the extension increased the goodness of the fit of the model. The

Akaike Information Criterion was used to assess the relative goodness of the fit. Simple and multiple regressions were performed using ordinary linear regression models or, if residuals were autocorrelated, generalized least squares extended by an autoregressive moving average function. Autocorrelation was checked with the Durbin-Watson test and by plotting the autocorrelation function. A non-linear least-squares model was used to estimate parameters of the non-linear multiple regression. Effects were considered significant if $P \leq 0.05$. In the text results are reported as means ± 1 standard errors. Statistical analyses were carried out using R 2.10.1 (R Development Core Team, 2009).

3 Results

3.1 Annual N_2O fluxes

Fluxes of N_2O were significantly lower in the spruce stand than in the beech stand ($P < 0.0001$; Fig. 1a, b). Cumulative N_2O emissions were $0.3 \pm 0.1 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in the spruce stand and $2.6 \pm 0.6 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in the beech stand. The beech stand displayed a distinct seasonality of N_2O fluxes with high emissions during the summer months and low emissions during the winter months. Labelling did not increase N_2O fluxes since we observed no significant differences in N_2O fluxes between the NH_4^+ -labelled, NH_4NO_3 -labelled, and the control chambers (data not shown).

3.2 Short-term ^{15}N tracer experiment

In the spruce stand, the application of the $\text{NH}_4^{15}\text{NO}_3$ tracer caused an immediate and significant increase in $^{15}\text{N-N}_2\text{O}$ fluxes (Fig. 2a). Subsequently, $^{15}\text{N-N}_2\text{O}$ emissions decreased again and no significant differences in $^{15}\text{N-N}_2\text{O}$ fluxes were found three weeks after the $\text{NH}_4^{15}\text{NO}_3$ tracer application compared to the reference value (pre-measurement at zero hours). Application of the $^{15}\text{NH}_4\text{NO}_3$ tracer also caused a significant increase in $^{15}\text{N-N}_2\text{O}$ fluxes 3.5 h after the addition, but the increase was smaller than in the NO_3^- -labelled plots (Fig. 2a). After one week no significant differences in $^{15}\text{N-N}_2\text{O}$ fluxes occurred in the NH_4^+ -labelled plots of the spruce stand compared to the reference.

In the beech stand, a similar temporal pattern as in the spruce stand was found after tracer application. In the NO_3^- -labelled plots, we observed an immediate strong and significant increase in $^{15}\text{N-N}_2\text{O}$ fluxes (Fig. 2b). After one week, $^{15}\text{N-N}_2\text{O}$ fluxes had decreased and no differences compared to the reference measurement were observed. The application of the $^{15}\text{NH}_4\text{NO}_3$ tracer only slightly but significantly increased $^{15}\text{N-N}_2\text{O}$ fluxes and again one week after the tracer addition no significant differences existed when compared to the reference value (Fig. 2b). In both spruce and beech stands, the NO_3^- -labelled plots displayed three times higher EFs during the first week compared to the NH_4^+ -labelled plots (Table 2). For the first three weeks, the EFs calculated

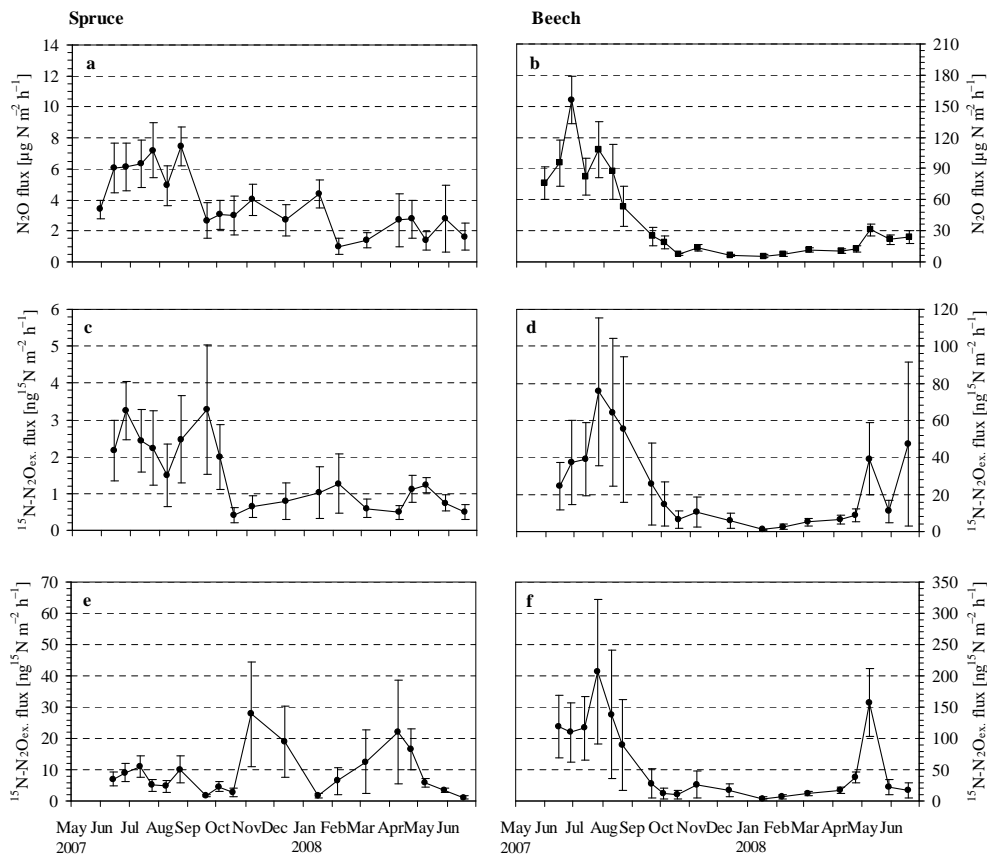


Fig. 1. Mean (\pm SE, $n = 13$) N_2O fluxes (**a, b**) and mean (\pm SE, $n = 5$) $^{15}\text{N-N}_2\text{O}$ excess fluxes of the NH_4^+ -labelled treatments (**c, d**) and NH_4NO_3 (double)-labelled treatments (**e, f**) of the spruce stand (**a, c, e**) and beech stand (**b, d, f**). Please note the different scales.

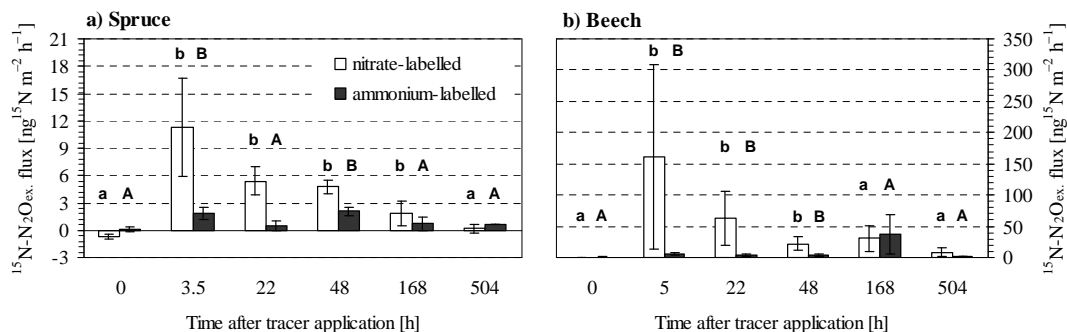


Fig. 2. Mean (\pm SE, $n = 4$) $^{15}\text{N-N}_2\text{O}$ excess fluxes in the spruce stand (**a**) and beech stand (**b**) during the short-term experiment. Fluxes are given for the NO_3^- -labelled and NH_4^+ -labelled treatments before (zero hours) and after the tracer application. Means followed by the same letter indicated no significant differences in $^{15}\text{N-N}_2\text{O}$ excess fluxes of one labelling treatment (NO_3^- - or NH_4^+ -labelled) between zero hours and the time points after the tracer application (mixed effects models with linear contrasts at $P \leq 0.05$). Please note the different scales.

for the NO_3^- -labelled plots were approx. three times higher than the EFs calculated for the NH_4^+ -labelled plots as well (Table 2). But in the beech stand, the difference between the EFs of the NO_3^- -labelled and NH_4^+ -labelled plots decreased and the EF values of the NH_4^+ -labelled plots were 70% of the EF values of the NO_3^- -labelled plots (Table 2).

However, for each stand differences in $^{15}\text{N-N}_2\text{O}$ emissions between NH_4^+ -labelled chambers and NO_3^- -labelled chambers were not significant. Moreover, differences in $^{15}\text{N-N}_2\text{O}$ emissions of the NO_3^- -labelled chambers between both stands were not significant, but $^{15}\text{N-N}_2\text{O}$ fluxes of the NH_4^+ -labelled chambers were significantly higher in the beech stand than in the spruce stand ($P = 0.029$).

Table 2. Emission factors (EFs) of N₂O during the first week and the first three weeks following tracer application in the spruce and beech stands. The emission factors were derived from the NH₄⁺-labelled and NO₃⁻-labelled treatments of the short-term experiment (*n* = 4).

Tracer	EF (1 week) [%]			EF (3 weeks) [%]		
	NH ₄ ⁺	NO ₃ ⁻	NH ₄ NO ₃ [*]	NH ₄ ⁺	NO ₃ ⁻	NH ₄ NO ₃ [*]
Spruce	0.01 (0.00)	0.03 (0.01)	0.02 (0.01)	0.02 (0.01)	0.05 (0.02)	0.04 (0.01)
Beech	0.12 (0.09)	0.31 (0.18)	0.22 (0.10)	0.43 (0.33)	0.62 (0.33)	0.54 (0.22)

Means (± SE); no significant differences were detected among stands, labellings, and EFs.

* The EF for the NH₄NO₃-labelled treatment was obtained by calculating the mean of the NH₄⁺-labelled and NO₃⁻-labelled treatments of the short-term experiment (*n* = 8).

Table 3. Cumulative N₂O and ¹⁵N-N₂O emissions, one-year emission factor (EF), N₂O derived from deposition (N₂O-NDFD), ratio of N₂O-NDFD to total N₂O emissions, and recovery of ¹⁵N tracer in N_t of the organic layer and the upper 10 cm of mineral soil. Results are derived from the NH₄⁺-labelled and NH₄NO₃-labelled treatments of the one-year experiment.

	Labelling	N ₂ O	¹⁵ N-N ₂ O	EF	N ₂ O-NDFD	N ₂ O-NDFD/ N ₂ O-N* [%]	Recovery in N _t
		[kg N ha ⁻¹ yr ⁻¹]	[g ¹⁵ N ha ⁻¹ yr ⁻¹]	[%]	[g N ha ⁻¹ yr ⁻¹]		[%]
Spruce	NH ₄ ⁺	0.26 (0.06) ^{aA}	0.12 (0.04) ^{aA}	0.03 (0.01) ^{aA}	9.4 (3.0) ^{aA}	3.6 (1.1) ^{aA}	59.2 (11.6) ^{aA}
	NH ₄ NO ₃	0.30 (0.13) ^{aA}	0.91 (0.47) ^{aB}	0.12 (0.06) ^{aA}	37.9 (19.3) ^{aA}	12.5 (6.4) ^{aA}	36.6 (6.6) ^{aA}
Beech	NH ₄ ⁺	3.15 (1.26) ^{bA}	1.79 (1.10) ^{bA}	0.46 (0.29) ^{aA}	79.6 (49.0) ^{aA}	2.5 (1.6) ^{aA}	41.7 (7.2) ^{aA}
	NH ₄ NO ₃	1.75 (1.90) ^{bA}	4.28 (2.18) ^{bA}	0.58 (0.29) ^{aA}	99.3 (50.5) ^{aA}	5.7 (2.9) ^{aA}	20.7 (3.1) ^{aB}

Means (± SE; *n* = 5 for N₂O, ¹⁵N-N₂O, EF, N₂O-NDFD, and N₂O-NDFD/N₂O-N and *n* = 4 for recovery in N_t) followed by the same lower-case letters indicated no significant differences among both stands and the same labelling treatments. Means followed by the same capital letters indicated no significant differences among different labelling treatments within one stand (independent t-test at *P* ≤ 0.05).

* The ratio N₂O-NDFD/N₂O-N represented the weighted harmonic mean with corresponding SE.

Within one stand, fluxes of total N₂O were not significantly different in time during the short-term experiment and were 10-times higher in the beech stand (22.8 ± 3.6 μg N m⁻² h⁻¹) than in the spruce stand (2.2 ± 0.5 μg N m⁻² h⁻¹; *P* = 0.009). Since no changes were observed in fluxes we assumed that total N₂O fluxes were not changed by the tracer application. The same was true for the contents of NH₄⁺, NO₃⁻ and soil moisture, which remained unchanged during the period of the short-term experiment.

3.3 One-year ¹⁵N tracer experiment

In the spruce stand, fluxes of ¹⁵N-N₂O were significantly higher in the NH₄NO₃-labelled treatment than in the NH₄⁺-labelled treatment (*P* = 0.0014), though N₂O fluxes were not significantly different between the two labelled treatments (Fig. 1a, c, e, Table 3). Fluxes of ¹⁵N-N₂O and N₂O were positively correlated for both labellings individually (*P* ≤ 0.05). Emissions of ¹⁵N-N₂O of the NH₄NO₃-labelled treatment displayed high variability especially during the winter months when nitrate availability was low and any addition of nitrate with the NH₄NO₃ treatment may have contributed significantly to the ¹⁵N-N₂O fluxes in the spruce stand (Fig. 1e). We did not observe continuous enrichment of ¹⁵N in N₂O during the one-year experiment. The mean annual fraction of ¹⁵N-N₂O on total N₂O-N was 0.04% (0.00–

0.22%) for the NH₄⁺-labelled treatment and 0.21% (0.01–0.71%) for the NH₄NO₃-labelled treatment. In the beech stand, we observed no significant differences in ¹⁵N-N₂O fluxes between both treatments and beginning in July (1.5 months after the first labelling event), they followed a similar seasonal trend as the total N₂O flux in both treatments (Fig. 1b, d, f, Table 3). Fluxes of ¹⁵N-N₂O and N₂O displayed strong correlations for both treatments (*P* ≤ 0.0001). The fraction of ¹⁵N-N₂O on N₂O-N averages 0.06% (0.00–0.22%) for the NH₄⁺-labelled treatment and 0.19% (0.04–0.49%) for the NH₄NO₃-labelled treatment. In both treatments ¹⁵N-N₂O emissions were significantly higher in the deciduous stand than in the coniferous stand (*P* ≤ 0.05; Table 3).

Using the EF values approx. 0.12% (spruce) to 0.58% (beech) of the inorganic throughfall N deposition was lost as N₂O within one year, which corresponded to 12.5% (spruce) and 5.7% (beech) of the total annual N₂O emissions (N₂O-NDFD/N₂O-N, Table 3). For the spruce stand, the EFs of the first week and first three weeks were significantly lower than the EF of one year (*P* = 0.03) but no significant differences among EFs were found for the beech stand (Tables 2, 3).

We recovered a large fraction of 59% (spruce) and 42% (beech) of the applied NH₄⁺ in N_t of the organic layer and the surface 10 cm of the mineral soil (Table 3). In contrast, the recovery of NO₃⁻ tracer in N_t of the NH₄NO₃-treatment

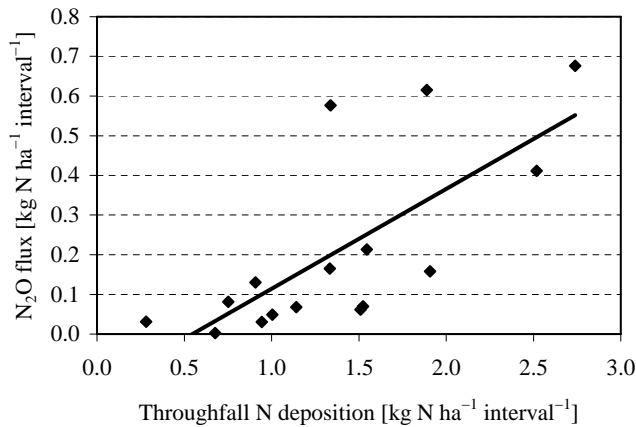


Fig. 3. Relationship between N_2O fluxes (y) and total throughfall N depositions (x) in the beech stand from May 2007 to June 2008 ($y = x \cdot 0.25 (\pm 0.06) - 0.14 (\pm 0.09)$; $r^2 = 0.53$, $P = 0.001$, $df = 14$).

(obtained by subtracting the recovery in the NH_4^+ treatment) was negligible in the beech stand and less than 10% in the spruce stand.

3.4 Relationship of N_2O flux rates to throughfall N depositions

In the beech stand, N_2O fluxes were positively correlated with total throughfall N depositions ($P = 0.001$; Fig. 3, Table 4) and with NH_4^+ -N depositions ($P = 0.001$; Table 4). The slope of the regression equation, which described the modelled relationship between measured N_2O fluxes and measured N depositions, indicated the fraction of throughfall N deposition emitted as N_2O . The fraction was 25%. However, both N_2O fluxes ($P < 0.0001$; Fig. 4) and throughfall N deposition were also positively related with soil temperature (N deposition = temperature $\cdot 0.09 (\pm 0.03) + 0.70 (\pm 0.27)$, $r^2 = 0.37$, $P = 0.01$, $df = 14$). When soil temperature was included in the regression equation the calculated EF was reduced from 25% to 8.6% (Fig. 4). Throughfall deposition was further positively correlated with precipitation ($P = 0.004$; not shown). For the spruce stand, we did not observe significant correlations between N_2O fluxes with N depositions. However N_2O fluxes were positively correlated with precipitation (Table 4).

We also calculated EFs according to the fraction method, where EFs are calculated by relating measured total N_2O emissions to measured N depositions (for the calculation see notes of Table 5). The EFs obtained from this approach were 0.9% for the spruce stand and 13% for the beech stand.

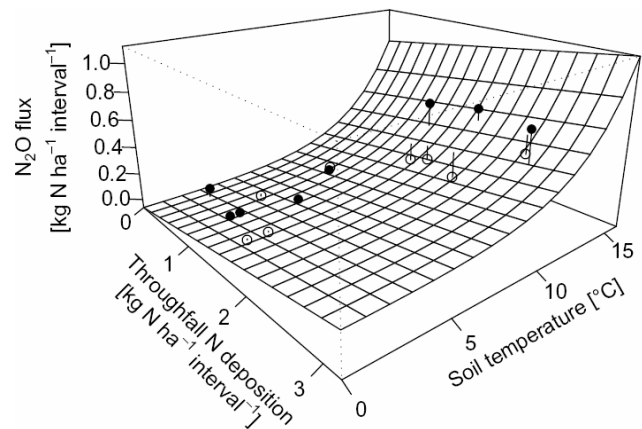


Fig. 4. Relationship of N_2O fluxes (y) to throughfall N depositions (x_1) and soil temperatures in 5 cm soil depth (x_2) ($y = 0.086 (\pm 0.063) \cdot x_1 + 0.001 (\pm 0.000) \cdot \exp(0.468 (\pm 0.242) \cdot x_2) - 0.042 (\pm 0.073)$; $r^2 = 0.78$, $P < 0.0001$, $df = 13$). The measured data are indicated as points, where black points are located above the surface area and white points are located below the surface area. The solid lines indicate the deviations of measured data from the model.

4 Discussion

4.1 Annual N_2O fluxes

The relatively low N_2O fluxes from the spruce stand and the higher N_2O fluxes from the beech stand were within the range of N_2O emissions reported for other temperate coniferous and deciduous forests (Butterbach-Bahl et al., 2001; Macdonald et al., 1997; Oura et al., 2001; Zechmeister-Boltenstern, 2002; see also Table 5). The compiled values from literature (Table 5) further support the observation that deciduous forests generally tend to be a higher source for N_2O ($> 20 \mu\text{g N}_2\text{O-N m}^{-2} \text{h}^{-1}$) than coniferous forests ($< 10 \mu\text{g N}_2\text{O-N m}^{-2} \text{h}^{-1}$). We attributed the differences in N_2O fluxes between the investigated forest types to the differences in the structure and quality of the litter (e.g. pH, C/N ratio; see Table 1). The laminar structure of the beech litter on the surface of the moder type humus may have reduced gas diffusivity, whereas the needle litter of spruce may have created a well-aerated organic layer as was reported by Ball et al. (1997) for the Solling sites. As a result, the high N_2O emissions during the summer months were possibly produced by denitrification in anaerobic micro-sites in the soil due to high oxygen consumption by microorganisms and plants during high summer temperatures (Brumme et al., 1999). Wolf and Brumme (2002) identified denitrification as main process for N_2O production in the same beech stand which was investigated in the present study.

Net uptake of N_2O , as we observed in single chambers, may be ascribed to consumption of N_2O during denitrification to N_2 (Kroeze et al., 2007). The review by Kroeze et al. (2007) revealed that uptake of N_2O may occur at low

Table 4. Results of the regression analyses of N₂O-N fluxes and throughfall N depositions (total N, NH₄⁺-N, NO₃⁻-N, and organic N depositions) and precipitation.

	N _{total}			NH ₄ ⁺ -N			NO ₃ ⁻ -N			N _{org}			Precipitation		
	r ²	P	df	r ²	P	df	r ²	P	df	r ²	P	df	r ²	P	df
Spruce	—	ns	—	—	ns	—	—	ns	—	—	ns	—	0.30	0.042	12
Beech	0.53	0.001	14	0.53	0.001	14	—	ns	—	—	ns	—	—	ns	—

ns is not significant.

oxygen and NO₃⁻ availability, even at fertilised sites, and that sites with small N₂O fluxes may change from sources to sinks depending on the soil conditions. At the beech stand, negative N₂O fluxes were almost exclusively measured during the winter months where soil moisture was high and soil NO₃⁻ concentrations were close to zero.

4.2 Temporal dynamics of N₂O emissions derived from N deposition

The immediate increase in ¹⁵N-N₂O fluxes that occurred within 3.5–5 h in the short-term experiment after NH₄¹⁵NO₃ and ¹⁵NH₄NO₃ tracer application indicates that deposited N contributed promptly to N₂O production. However, the contribution of N deposition to N₂O fluxes decreased within the following three weeks. In the spruce stand release of N₂O derived from the ¹⁵N label occurred over a longer period than in the beech stand, where loss of deposited N as N₂O occurred entirely during the first three weeks. This short-lived increase in ¹⁵N-N₂O emissions, which lasted approx. three weeks, was probably related to biotic and abiotic immobilisation of added N and to dilution processes. In contrast to our hypotheses, the repeated application of ¹⁵N labelled N did not lead to any further increase in ¹⁵N enrichment of N₂O emitted during the one-year experiment. This indicates that the main effect of N deposition on N₂O fluxes occurs when the mineral N enters the soil system (“short-lived effects”). The absence of “medium-term” effect (up to one year) may be explained by continual immobilisation of N during the related additions and by the lack of any remobilisation of the immobilised N. Our recovery of NH₄NO₃ tracer in soil N_t also showed that a great proportion of N deposition was retained in the soil. Our finding was supported by output analysis by Brumme and Khanna (2009b) and Feng et al. (2008), which indicated that in both systems (spruce and beech) the deposited N was predominantly retained despite the amount of N deposition was in excess of that required for plant increment.

4.3 Processes of N₂O emissions derived from N deposition

The greater increase in ¹⁵N-N₂O fluxes after NO₃⁻ tracer application than after NH₄⁺ tracer application suggests that den-

itrification was the dominant process for the input-derived emissions at both sites. Water addition probably created additional anaerobic micro-sites resulting in favourable conditions for denitrification, which mimics conditions when natural wet N deposition occurs. Denitrification was also found to be the dominant process at our beech stand at the Solling site by Wolf and Brumme (2002). The smaller ¹⁵N-N₂O flux increase after ¹⁵NH₄NO₃ tracer application was probably caused by low activity of nitrifiers in these acid soils and the weak competition of nitrifiers for available NH₄⁺ (Corre and Lamersdorf, 2004 (study conducted at Solling); Rennenberg et al., 1998). Fertilisation with (NH₄)₂SO₄ also delayed an increase in N₂O emissions by 14 days at our beech stand (Brumme and Beese, 1992), indicating low activity of nitrifiers and thus a delay of denitrification. In contrast, rapid increases in N₂O fluxes have been reported after fertilisation with NO₃⁻-containing fertilisers of coniferous forests (Klemetsson et al., 1997; Macdonald et al., 1997; Sitaula et al., 1995).

For both stands, the fraction of ¹⁵N-N₂O on N₂O-N of 0.05% for the NH₄⁺-labelled treatment and of 0.20% for the NH₄NO₃-labelled treatment of the one-year experiment suggests that the contribution of NH₄⁺ to N₂O emissions was 25% and of NO₃⁻ 75%. Similar results were presented by Ambus et al. (2006) who showed that 62% of N₂O emissions in 11 European forests were derived from NO₃⁻ and 34% were derived from NH₄⁺.

4.4 Contribution of N deposition to N₂O emissions

The compilation of published studies on this subject showed a huge range of results for the impact of N input on N₂O fluxes in temperate forests similar as we found in our study (Table 5). Our study indicated that the emission factor (EF) depended on the method used for its calculation. The EF_R value of 25% for our beech stand, which was calculated by using the regression method, was higher than the EF_F values, which were obtained by the fraction method and ranged from 0.9% (spruce) to 13% (beech). The EF_R and EF_F were again both higher than the EF_{15N} values derived from our ¹⁵N tracer study (0.1% for spruce and 0.6% for beech stands). Further, a EF_{FB} value (obtained from N fertilisation experiments; for calculations see notes of Table 5) of 1.6% was calculated for

Table 5. Compilation of published studies that investigated the impact of N input on N₂O fluxes from deciduous and coniferous temperate forest soils. Studies are divided into fertilisation, deposition, and ¹⁵N tracer experiments. The emission factor (EF) for N₂O is given for one year if not differently indicated.

Forest type	Type of N input	N ₂ O [μg N m ⁻² h ⁻¹]	Emission factor [%]	Method used	Treatment	Reference
Deciduous	Fertilisation	0.68	0.03 ^e	EF _{FB}	NH ₄ NO ₃ -fertilised (120 (1. yr) and 150 (2. yr) kg N ha ⁻¹ yr ⁻¹ ; chronic N addition exp.; measurement in the 2. yr; USA)	Bowden et al. (1991)
		0.57	0.06 ^e	EF _{FB}	NH ₄ NO ₃ -fertilised (37 (1. yr) and 50 (2. yr) kg N ha ⁻¹ yr ⁻¹ ; chronic N addition exp.; measurement in the 2. yr; USA)	
		0.23			Unfertilised (USA)	
		89	1.6	EF _{FB}	(NH ₄) ₂ SO ₄ -fertilised (140 kg N ha ⁻¹ yr ⁻¹ ; chronic N addition exp.; measurement in the 6. and 7. yr; Germany)	Brumme and Beese (1992)
		64	16 ^e	EF _F	Unfertilised (35 kg N ha ⁻¹ yr ⁻¹ deposition; Germany)	
		< 10	< 0.3	EF _F	NH ₄ NO ₃ -fertilised (150 kg N ha ⁻¹ yr ⁻¹ ; chronic N addition exp.; measurement in the 13. yr; USA)	Venterea et al. (2003)
		< 10	< 0.3	EF _F	NH ₄ NO ₃ -fertilised (50 kg N ha ⁻¹ yr ⁻¹ ; chronic N addition exp.; measurement in the 13. yr; USA)	
		< 10	< 0.3	EF _F	Unfertilised (8 kg N ha ⁻¹ yr ⁻¹ wet + dry deposition; USA)	
	Deposition	5.7	2 ^e	EF _F	25.6 kg N ha ⁻¹ yr ⁻¹ throughfall + stemflow dep. (Denmark)	Beier et al. (2001)
		83.3	22 ^e	EF _F	33 kg N ha ⁻¹ yr ⁻¹ wet deposition (Germany)	Brumme et al. (1999)
		9.1	2.4 ^e	EF _F	33 kg N ha ⁻¹ yr ⁻¹ wet deposition (Germany)	
		1.9	0.6 ^e	EF _F	28 kg N ha ⁻¹ yr ⁻¹ throughfall deposition (Germany)	
		7.2	2.4 ^e	EF _F	26 kg N ha ⁻¹ yr ⁻¹ throughfall deposition (Germany)	
		4.7	1.9 ^e	EF _F	21 kg N ha ⁻¹ yr ⁻¹ throughfall deposition (Germany)	
		7.3–9.0	~ 3.5 ^e	EF _F	20.2 kg N ha ⁻¹ yr ⁻¹ wet deposition (Austria)	Kitzler et al. (2006a) ³
		5.9–7.4	~ 4.6 ^e	EF _F	12.6 kg N ha ⁻¹ yr ⁻¹ wet deposition (Austria)	
		2.3	1.27	EF _F	15.7 kg N ha ⁻¹ yr ⁻¹ throughfall deposition (Japan)	Oura et al. (2001)
		58.4	10	EF _R	20 kg N ha ⁻¹ yr ⁻¹ wet deposition (Germany)	Papen and Butterbach-Bahl (1999)
		29.7	25; 13	EF _R , EF _F	20 kg N ha ⁻¹ yr ⁻¹ throughfall + stemflow dep. (Germany)	This study
¹⁵ N tracer	29.7	0.6	EF _{15N}	20 kg N ha ⁻¹ yr ⁻¹ throughfall + stemflow dep. (Germany)	This study	

a long-term fertilisation experiment at our beech stand where 140 kg N ha⁻¹ yr⁻¹ were applied over a 5–6 yr period (Table 5; Brumme and Beese, 1992).

In literature EF_R values were among the highest reported. For example, a study in southern Germany reported an EF_R of 10% for a beech stand (5.1 kg N₂O-N ha⁻¹ yr⁻¹) and 0.5% for a spruce stand (1.4 kg N₂O-N ha⁻¹ yr⁻¹) using the regression approach (Papen and Butterbach-Bahl, 1999; Table 5). Denier van der Gon and Bleeker (2005) combined results from several studies conducted in temperate forests and found an EF_R value of 6.3% for deciduous forests and of 1.4% for coniferous forests. A positive correlation of N₂O + NO fluxes with N deposition was also reported for 15 European forests exposed to different rates of N deposition where between 2% and 32% of total N deposition were emitted as N₂O + NO (Pilegaard et al., 2006). Emission factors EF_F

show a wide range from <0.1% to 22% for both forest types (Table 5). Using the fraction method, Denier van der Gon and Bleeker (2005) found an average EF_F of 2.4% for coniferous forests and of 6.5% for deciduous forests. The EF_{FB} based on fertilised plots ranged from 0.1% to 0.9% for the coniferous forests and from 0.03% to 1.6% for the deciduous forests (Table 5). The results of EF estimations can be summarised as follows:

$$EF_{15N} \approx EF_{FB} \ll EF_F \approx EF_R \quad (7)$$

What factors cause the large differences in EFs when calculated employing different methods? The fraction of N₂O derived from inorganic N deposition was relatively small (13% on spruce and 6% on beech stands) indicating that sources other than direct N deposition were involved in N₂O emissions. The EF_{FB} considers such background emissions

Table 5. Continued.

Forest type	Type of N input	N ₂ O [$\mu\text{g N m}^{-2} \text{h}^{-1}$]	Emission factor [%]	Method used	Treatment	Reference
Coniferous	Fertilisation	4.0	0.1 ^e	EF _{FB}	NH ₄ NO ₃ -fertilised (120 (1. yr) and 150 (2. yr) kg N ha ⁻¹ yr ⁻¹ ; chronic N addition exp.; measurement in the 2. yr; USA)	Bowden et al. (1991)
		3.0	0.5 ^e	EF _{FB}	NH ₄ NO ₃ -fertilised (37 (1. yr) and 50 (2. yr) kg N ha ⁻¹ yr ⁻¹ ; chronic N addition exp.; measurement in the 2. yr; USA)	
		0.8			Unfertilised (USA)	
		3.11	0.35	EF _F	NH ₄ Cl-fertilised (31.4 kg N ha ⁻¹ yr ⁻¹ ; chronic N addition exp.; measurement in the beginning of the 3. yr (only growing season), estimated annual N ₂ O flux of 0.11 kg N ha ⁻¹ yr ⁻¹); USA	Castro et al. (1993)
		-1.12			Unfertilised (10 kg N ha ⁻¹ yr ⁻¹ wet + dry deposition; measurement only in the growing season); USA	
		1.1 (drained); 2.9 (wet)	0.1 (drained) 0.6 (wet) ^e	EF _{FB}	NH ₄ NO ₃ -fertilised (35 kg N ha ⁻¹ yr ⁻¹ in small doses; chronic N addition exp.; measurement after 2 yr; Sweden)	Klemetsson et al. (1997)
		0.8 (drained); 1.3 (wet)			Unfertilised (12 kg N ha ⁻¹ yr ⁻¹ deposition; Sweden)	
		0.9	< 0.1 ^e	EF _F	(NH ₄) ₂ SO ₄ -fertilised (150 kg N ha ⁻¹ ; single dose; measurement in the first 3 yr; Germany)	Papen et al. (2001)
		-1.0			Unfertilised (Germany)	
		45.8	0.93 (1 month)	EF _{FB}	NH ₄ NO ₃ -fertilised (90 kg N ha ⁻¹ ; single dose; measurement over 1 month; Norway)	Sitaula et al. (1995) ^b
		21.7	0.94 (1 month)	EF _{FB}	NH ₄ NO ₃ -fertilised (30 kg N ha ⁻¹ ; single dose; measurement over 1 month; Norway)	
		8.3			Unfertilised (Norway)	
		5.7	0.6 ^e	EF _{FB}	Acid mist-fertilised (96 kg N ha ⁻¹ yr ⁻¹ ; chronic N addition exp.; measurement after 2 yr; UK)	Skiba et al. (1998, 1999)
		0.5	0.2 ^e	EF _{FB}	Acid mist-fertilised (48 kg N ha ⁻¹ yr ⁻¹ ; chronic N addition exp.; measurement in the 3. yr, UK)	
		-0.3			Unfertilised (6.7 kg N ha ⁻¹ yr ⁻¹ wet + dry deposition; UK)	
		< 10	< 0.3	EF _F	NH ₄ NO ₃ -fertilised (150 kg N ha ⁻¹ yr ⁻¹ ; chronic N addition exp.; measurement in the 13. yr; USA)	Venterea et al. (2003)
< 10	< 0.3	EF _F	NH ₄ NO ₃ -fertilised (50 kg N ha ⁻¹ yr ⁻¹ ; chronic N addition exp.; measurement in the 13. yr; USA)			
< 10	< 0.3	EF _F	Unfertilised (8 kg N ha ⁻¹ yr ⁻¹ wet + dry deposition; USA)			

e.g. from unfertilised plots in fertilisation experiments. In contrast to EF_{FB}, the EF_F does not distinguish between possible background emissions and emissions directly derived from N deposition. Consequently values of EF_F of the fraction method will overestimate direct N₂O emissions from deposition because it does not correct for such possible N₂O background emissions.

Emission factors based on fertilised plots (EF_{FB}) were in the same order of magnitude in our study as our EF_{15N} values obtained by the ¹⁵N tracer method. However, strong increases in N₂O fluxes from the fertilised plots compared to the unfertilised control plots have been reported (Table 5),

which may result from the high mineral N concentrations following fertiliser application, which does not reflect conditions during atmospheric N deposition (Sitaula et al., 1995; Skiba and Smith, 2000) and may cause a positive priming effect (e.g. Fenn et al., 1998). Also the implicit assumption of the regression approach is that the N₂O emissions from N cycling are not affected by N depositions. However, this assumption may not be valid and may lead to artificially high estimates since both N deposition and N₂O fluxes are frequently positively related to a number of factors. Some of those factors also affect N₂O fluxes in a positive way causing systematic error of overestimating the EF_R values. For

Table 5. Continued.

Forest type	Type of N input	N ₂ O [μg N m ⁻² h ⁻¹]	Emission factor [%]	Method used	Treatment	Reference
Coniferous	Deposition	2.9	0.6 ^e	EF _F	41 kg N ha ⁻¹ yr ⁻¹ throughfall deposition (Germany)	Brumme et al. (1999)
		2.4	0.7 ^e	EF _F	31 kg N ha ⁻¹ yr ⁻¹ throughfall deposition (Germany)	
		14.8	6.5 ^e	EF _F	20 kg N ha ⁻¹ yr ⁻¹ throughfall deposition without N _{org} (Germany)	
		4–15	1.2–4.4 ^e	EF _F	30 kg N ha ⁻¹ yr ⁻¹ wet deposition (Germany)	Butterbach-Bahl et al. (1998) ^a
		–0.5–2.1	~1.3 ^e	EF _F	5–6 kg N ha ⁻¹ yr ⁻¹ wet deposition (Ireland)	
		16–32	~7–13 ^e	EF _F	20–22 kg N ha ⁻¹ yr ⁻¹ wet deposition (Germany)	Butterbach-Bahl et al. (2002) ^a
		5–10	~4.4 ^e	EF _F	~15 kg N ha ⁻¹ yr ⁻¹ wet deposition (Germany)	
		3.4–4.7	2.5–3.5	EF _F	10.6–11.9 kg N ha ⁻¹ yr ⁻¹ bulk deposition (Austria)	Kitzler et al. (2006b) ^c
		3.8	~1	EF _{FB}	~46.2 kg N ha ⁻¹ yr ⁻¹ total deposition (UK)	Macdonald et al. (1997)
		1.3		EF _{FB}	6.4 kg N ha ⁻¹ yr ⁻¹ total deposition (UK)	
		4.3	1.23	EF _F	30.6 kg N ha ⁻¹ yr ⁻¹ throughfall deposition (Japan)	Oura et al. (2001)
		16.4	0.5	EF _R	30 kg N ha ⁻¹ yr ⁻¹ wet deposition (Germany)	Papen and Butterbach-Bahl (1999)
		56	6	EF _{FB}	80.1 kg N ha ⁻¹ yr ⁻¹ NH ₃ dep from poultry farm; 30 m down-wind from farm (UK)	Skiba et al. (1998, 1999) ^d
		13		EF _{FB}	17.4 kg N ha ⁻¹ yr ⁻¹ NH ₃ dep from poultry farm; 250 m down-wind from farm (UK)	
		3.4	0.9	EF _F	33 kg N ha ⁻¹ yr ⁻¹ throughfall deposition (Germany)	This study
	¹⁵ N tracer	3.4	0.1	EF _{15N}	33 kg N ha ⁻¹ yr ⁻¹ throughfall deposition (Germany)	This study

EF_F: emission factor represented the fraction of N input that is re-emitted: $EF_F = \text{flux}/\text{N input} \cdot 100$. EF_{FB}: emission factor calculated for N fertilisation experiments or N deposition gradients, where N₂O background emissions are considered. Calculated for N fertilisation experiments: $EF_{FB} = (\text{flux from fertilised plot} - \text{flux from control plot})/\text{N amount in fertiliser} \cdot 100$. Calculated for N deposition gradients: $EF_{FB} = ((\text{flux at high N input} - \text{flux at background N input})/(\text{high N input} - \text{background N input})) \cdot 100$. EF_R: emission factors were derived from regression analyses between N₂O fluxes and N deposition rates. EF_{15N}: emission factors were derived from ¹⁵N tracer experiments; for calculations see this study.

^a The compared sites were similar in climatic and edaphic conditions.

^b Lysimeter study with re-established soil profiles from Scots pine forest.

^c Spruce-fir-beech forest.

^d Mixed woodland of pine, birch, oak, rowan, and elder.

^e Emission factor was calculated by the authors of this study.

an example, at times of high rainfall (and thus, high N deposition), high soil water content will stimulate denitrification and therefore N₂O fluxes, which originate mainly from N cycling in the soil and not from direct N deposition. The problem of complex relationships was further highlighted by the reduction of the calculated EF_R from 25% to 8.6% in our beech stand when soil temperature was included in the regression equation. Our study demonstrated that EF_{15N} values represent reliable and direct values of emissions by inorganic N depositions.

The low values of direct contribution of atmospheric depositions to N₂O emissions raise the question whether the background emissions are affected by decade long atmospheric N depositions, most of which may have been accumulated in the ecosystems. N cycling rates may have considerably changed due to long-term N depositions (Corre et al., 2007).

With the methods employed here it was not possible to assess the effect of accumulated anthropogenic N on the background N₂O emissions. However, the literature compilation indicates that, in general, soils with a similar forest type but with higher N depositions had higher N₂O emissions than soils exposed to lower N depositions (Table 5). Assuming that N₂O emissions were negligible before the onset of anthropogenic activity, the total contribution of N deposition to N₂O emission (direct and background emissions) is probably best described by the fraction of N₂O to current N deposition (EF_F). To obtain a representative EF_F value, mean values covering several years are necessary. This is illustrated by the mean EF_F value calculated for the beech stand from 1990 to 1998 (8.2% ± 0.7%) compared to the higher EF_F calculated for 2007 to 2008 when N depositions were comparably low and N₂O emissions were comparably high.

5 Conclusions

The ^{15}N tracer method proved to be a precise approach for quantifying the direct contribution of atmospheric N deposition to the emission of N_2O . The technique allows the simulation of atmospheric throughfall N deposition without artificial fertilisation. The method provides the possibility to investigate the impact of N deposition on N_2O emissions in forests also when direct emissions are low. In contrast to the regression approach, this method does not include artefacts which may result from controlling rainfall or temperature conditions, as both would influence N_2O fluxes and N depositions. There are no uncertainties resulting from the comparison of different sites (as when regarding deposition gradients), which are usually not completely comparable in climate and soil conditions. Furthermore, EFs when calculated from fertilised plots may result in artificially high N_2O emissions because the pulse in mineral N concentrations does not reflect the true atmospheric N depositions and may also cause positive priming effects on the N cycling in soils. Whereas most of the other methods overestimate the direct emissions, the ^{15}N tracer method is a useful tool to measure direct emissions or background emissions.

Supplementary material related to this article is available online at:
<http://www.biogeosciences.net/8/621/2011/bg-8-621-2011-supplement.pdf>.

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