**Biogeosciences**

# Controls over $N_2O$, $NO_x$ and $CO_2$ fluxes in a calcareous mountain forest soil

**B. Kitzler[1], S. Zechmeister-Boltenstern[1], C. Holtermann[2], U. Skiba[3], and K. Butterbach-Bahl[4]**

[1]Federal Research and Training Centre for Forests, Natural Hazards and Landscape (BFW), Seckendorff-Gudent-Weg 8, Vienna, Austria
[2]Sellenyg. 2–4/52, Vienna, Austria
[3]Institute of Terrestrial Ecology, Bush Estate, Penicuik, Midlothian EH26 OQB, Scotland
[4]Institute for Meteorology and Climate Research, Atmospheric Environmental Research, Forschungszentrum Karlsruhe, Kreuzeckbahnstraße 19, 82467, Garmisch-Partenkirchen, Germany

**Abstract.** We measured nitrogen oxides ($N_2O$ and $NO_x$), dinitrogen ($N_2$) and carbon dioxide ($CO_2$) emissions from a spruce-fir-beech forest soil in the North Tyrolean limestone Alps in Austria. The site received 10.6–11.9 kg N ha$^{-1}$ y$^{-1}$ nitrogen as bulk deposition. Fluxes of nitric oxide (NO) were measured by an automatic dynamic chamber system on an hourly basis over a two year period. Daily $N_2O$ emissions were obtained by a semi-automatic gas measuring system. In order to cover spatial variability biweekly manual measurements of $N_2O$ and $CO_2$ emissions were carried out in addition. For acquiring information on the effects of soil and meteorological conditions and of N-deposition on N-emissions we chose the auto-regression procedure (time-series analysis) as our means of investigation. Hence, we could exclude the data's autocorrelation in the course of the time. We found that soil temperature, soil moisture and bulk N-deposition followed by air temperature and precipitation were the most powerful influencing parameters effecting N-emissions. With these variables, up to 89% of observed temporal variations of N-emissions could be explained. During the two-year investigation period between 2.5 and 3.5% of deposited N was reemitted in form of $N_2O$ whereas only 0.2% were emitted as NO. At our mountain forest site the main end-product of microbial activity processes was $N_2$ and trace gases ($N_2O$ and NO) were only of minor importance.

## 1 Introduction

Nitrous oxide ($N_2O$) is a stable greenhouse gas in the troposphere and is involved directly in global warming. In the stratosphere it is responsible for the catalytic decomposition of ozone (Crutzen, 1979). The increase in the atmosphere is reported at present to be about 0.25% per year (IPCC, 2001). As the potential of global warming of $N_2O$ is 300 times higher than that of carbon dioxide ($CO_2$) a further increase of atmospheric $N_2O$ concentration might affect global climate even more in the future.

In contrast, nitric oxide (NO) is indirectly involved in global warming and contributes to the net production of radiative tropospheric ozone and photochemical air pollution (Crutzen, 1995; Firestone and Davidson, 1989; Williams et al., 1992).

The production of $N_2O$, NO, and $N_2$ in soils is mainly the result of nitrifying and denitrifying bacteria (e.g. Davidson et al., 2000; Conrad, 1996; Lovett et al., 2002). These microbial activity processes and thus the production rates of NO, $N_2O$ and $N_2$, are influenced by various factors. These drivers are temperature, precipitation, total N, availability of $O_2$, mineralization rate, respiration, texture and structure, available nitrogen, pH and tree species composition (Davidson et al., 2000; Ludwig et al., 2001; Simek and Cooper, 2002). As forest soils are generally not treated with N fertilizers, N deposition from the atmosphere which are mainly due to $NH_3$ release from agricultural practices and $NO_x$ release from combustion processes provides a considerable increase in mineral N input to forest soils. Atmospheric N-deposition is estimated to be at least 5 kg N ha$^{-1}$ y$^{-1}$ in most regions of Europe, but can reach up to 50 kg N ha$^{-1}$ y$^{-1}$ in Central and Northern Europe (NADP, 2002). Nitrogen surplus in forest

*Correspondence to:* B. Kitzler
(barbara.kitzler@bfw.gv.at)

**Table 1.** Site and soil characteristics of the investigation site Achenkirch.

| | |
|---|---|
| Location | 47°34′50″ N 11°38′21″ E |
| Vegetation | Aposerido-Fagetum caricetosum albae – Carici albae-Fagetum[a] |
| Stand age [yr] | 127 |
| Exposition, elevation [m] | N, 895 m a.s.l. |
| Tree height [m] | 19.1 |
| Basal area [m$^2$ ha$^{-1}$] | 40 |
| Soil type | Rendzic Leptosols/Chromic Cambisol |
| Soil texture | loam |
| Soil aciditiy 0–7 cm (pH CaCl$_2$) | 5.8–7.1 |
| C:N | 16–18 |
| Mean precipitation [mm] | 1733[b] |
| Mean air temp [°C] | 6.52[b] |
| Soil density [g cm$^{-3}$] | 0.6 |
| N$_{tot}$ [mg g$^{-1}$] 0–15 cm | 9[c] |
| C$_{org}$ [mg g$^{-1}$] 0–15 cm | 150[c] |

[a] Englisch and Starlinger 1995,
[b] Mean of years 1998–2003,
[c] Mutsch 2001.

soil can be stored as soil N, taken up by microbes and plants or leached into groundwater. It can alter the rates of microbial N- and C- turnover in soil or it can be nitrified and denitrified to gaseous products of NO, N$_2$O and N$_2$ (Skiba et al., 2004). Increased N-deposition can lead to changes in soil chemistry, forest composition and forest productivity.

A deposition of 12 kg ha$^{-1}$ y$^{-1}$ of nitrogen at the study site Achenkirch (AK) is moderate but exceeds Critical Loads according to the WHO-Guideline (WHO, 1995) for sensitive coniferous forest ecosystems (Smidt et al., 1996). In other alpine areas an input of up to 30 kg ha$^{-1}$ y$^{-1}$ was found (Herman et al., 2002) and increased flux rates of atmospheric greenhouse gas emissions (NO, N$_2$O, CO$_2$, CH$_4$) might be expected. However, only limited information is available about effects of atmospheric N deposition on the biosphere-atmosphere exchange of N trace gases in alpine forest ecosystems. For the estimation of global budgets such measurements are needed. During a two-year sampling period of CO$_2$, N$_2$O and NO$_x$ emissions, measurements were carried out in order to (1) investigate the trace gas exchange between a typical spruce-beech-fir forest soil in the limestone Alps and the atmosphere. Measurements were conducted in high temporal and spatial resolution to (2) get better estimates of annual emissions, (3) study the relationships between N-trace gas emissions and meteorological factors and soil parameters, (4) investigate if N-deposition affects N-emissions in these forest ecosystems and (5) find an appropriate statistical procedure to describe the relationships between N-emissions and their ecological drivers.

## 2 Material and methods

### 2.1 Investigation site and soil

The 127 year old forest is located in the Achental of the North Tyrolean limestone Alps, and was described by Englisch and Starlinger (1995) as a warm, central-montane spruce-fir-beech forest. The Mühleggerköpfl is a completely isolated hill, formed from dolomite, at a height of 895 m above sea level. The soils are mainly Rendzic Leptosols and Chromic Cambisol and are characterized by a high clay content and a low percentage of coarse material in the upper 10 cm. The soil properties are characterized by a high spatial heterogeneity. The depth of the A-horizon varies from 10–35 cm. For this horizon the organic matter content is very high (>10%). Mean pH is 6.42. (For site description see Table 1). A detailed description of the site is given in Herman et al. (2002).

### 2.2 N$_2$O and CO$_2$ flux measurements

Gas measurements were carried out as described in Kitzler et al. (2006). Gas samples of four manually operated chambers (area: 1 m$^2$, volume: 80 l) were taken biweekly from May 2002 until July 2004. Duplicate air samples from the chambers were taken after 0, 1 and 2 h and injected into gas tight head-space vials (20 ml). Linearity of emission was always tested. We never observed a flattening of the N$_2$O increase in our chambers, which would indicate an approach of the compensation point for N$_2$O. Additional measurements every 15 minutes showed that the increase in N$_2$O concentrations remained linear for up to 4 hours (Zechmeister-Boltenstern et al., 2002).

Daily (1/day) samples were taken by the automatic gas sampling system (AGPS – patent DE 198 52 859) and vials were collected every two weeks. The system is described in detail by Kitzler et al. (2006). Gas samples were stored at 4°C until analysis.

Gas samples were automatically drawn at 6 a.m. The time was chosen based on observations that emission rates were higher in the morning. Seven diurnal measurements at different times of the year showed, that between 4 and 10 a.m. and again in the afternoon slightly higher emissions were measured, but no regular daily trend could be observed. Furthermore, a high variability was detected on successive days. At each manual sampling time we made a measurement with the AGPS to ensure, that with our timing of the AGPS system reliable estimates can be made. The N$_2$O concentrations of manually and automatically drawn samples were of similar magnitude and well within the range of spatial variability. In order to avoid freezing of the covering case on the sealing plate, the thermostat was set to 1°C and there were no measurements conducted below this temperature. During winter no automatic measurements were carried out, but manual measurements were carried out as long as the site was accessible. Emissions of N$_2$O ($\mu$g N m$^{-2}$ h$^{-1}$)

and $CO_2$ ($mg\,C\,m^{-2}\,h^{-1}$) were determined by the linear increase of the mixing ratio within the incubation period. Nitrous oxide and $CO_2$ fluxes were calculated as described in IAEA (1992). Annual rates were calculated by weighting hourly emission rates with the exact period between sampling times. Emissions from the manual system are presented for the first investigation year (May 2002–April 2003) and for the second investigation year (May 2003–April 2004). With the AGPS ($N_2O$-N AGPS) no measurements were made during winter, calculated emissions are presented for June–November 2002 and May–November 2003. A gas chromatograph (HP 5890 Series II) with a $^{63}$Ni-electron-capture detector (ECD), connected to an automatic sample-injection system (DANI HSS 86.50, HEADSPACE-SAMPLER) was used for $N_2O$ analysis. The oven, injector and detector temperatures were set at 120°C, 120°C and 330°C, respectively. A standard of $5\,\mu l\,l^{-1}\,N_2O$ (Linde Gas) was used and dilution series (5; 2.5; 1.25; 0.625; 0.25 vppm) were made regularly. Standards were placed after each batch of 12 samples. Dinitrogen in ECD-quality with a flow rate of $30\,ml\,min^{-1}$ served as carrier-gas. We quantified a minimum detectable $N_2O$ flux of $0.04\,\mu g\,N\,m^{-2}\,h^{-1}$ and the relative error falls below <17% with a median of 5%. Carbon dioxide was analysed by using a gas chromatograph (Hewlett-Packard 5890 II series) equipped with a thermal conductivity detector (TCD). Helium was used as carrier-gas (flow rate $10\,ml\,min^{-1}$); the $CO_2$ standard contained $10\,ml\,l^{-1}\,CO_2$ (Linde Gas) and dilution series (10 000; 5000; 2500; 1250; 500 vppm) were made regularly. Standards were placed after each batch of 12 samples. The detection limit for $CO_2$ flux was $0.001\,mg\,C\,m^{-2}\,h^{-1}$.

## 2.3 $NO_x$ flux measurements

Continuous measurements of $NO_x$ were completed by a fully automated system (Holtermann, 1996), at an hourly frequency. $NO_x$ was measured with a HORIBA APNA-360 chemoluminescence $NO_x$ analyzer (detection limit: 1 ppbv NO or $0.6\,\mu g\,NO$-$N\,m^{-2}\,h^{-1}$, 1 ppbv $NO_2$; flow rate: $1\,l\,min^{-1}$). The reading for $NO_x$ of the HORIBA analyzer refers to NO, $NO_2$ and other nitrogen compounds (PAN, $NH_3$, HONO, $HNO_3$, aerosol ammonium, nitrate and nitrite). We therefore use the terms NO and ($NO_x$-NO) further on. The median error was <15% and <35% for NO and $NO_x$-NO, respectively. Calibration was conducted monthly by using a HORIBA calibration unit (Transferstandard, ASGU-360, 0–600 ppb). The quality of calibration near the detection limit was <1%. To avoid reactions of NO and $O_3$ in the chambers, a filter cylinder, filled with Purafil and activated charcoal, was applied in front of the chambers in year 1 (May 2002–April 2003) as no ozone analyzer was available in this year. In the second year (May 2003–April 2004) we used an ozone analyzer (HORIBA APOA-360) for measuring $O_3$ concentrations within the chambers. Thus, the chemical reaction between NO and $O_3$ could be considered. No filter

was applied in this year.

Air samples were taken from 5 stainless steel chambers (ø=20 cm; Vol.=3.27 l), plus one reference chamber where the opening to the soil was sealed with a Plexiglas pane. Each chamber was closed (Plexiglas lid) for 5 min within which steady state was reached. For the calculation of the fluxes of the first year we followed the protocol of Schindlbacher et al. (2004), and for the second year the protocol of Butterbach-Bahl et al. (1997). For corrections in the tubings see also Beier and Schneewind (1991) and for corrections in the dynamic chambers Remde et al. (1993) and Ludwig (1994). For further details on analysis of gas samples and calculation of fluxes compare Kitzler et al. (2006). Ozone can strongly absorb to the chamber wall and to tubes and does effect the gas phase correction of NO and $NO_2$ fluxes. An error analysis indicated that $O_3$ absorption at the chamber walls was negligible and no correction of fluxes was deemed necessary. Even a 30% decrease of $O_3$ concentration would have changed the NO flux by less than $0.2\,\mu g\,N\,m^{-2}\,h^{-1}$ which is in our case smaller than the detection limit. The measured pressure deficit (Pressure sensor: PCLA 12X5D Sensor Technics) in our chambers is < than 0.6 Pa and irrelevant for N-fluxes. The residual aerodynamic resistance was determined as suggested by Ludwig (1994) and was $61\,s\,m^{-1}$. This value is in accordance to published values (55 and $60\,s\,m^{-1}$) by Meixner et al. (1997) and Gut et al. (2002).

## 2.4 Soil samples

Soil samples were taken approximately every two months. Extractable nitrogen was determined from litter layer (frame: $30\times30$ cm) and mineral soil (upper 7 cm), and analysed according to Kandeler (1995). Soil moisture was determined gravimetrically. The pH was measured in soil suspensions in $0.01\,M\,CaCl_2$ solution using a glass electrode. Additionally to these analysis, an acetylene ($C_2H_2$) inhibition experiment was carried out twice (May 2003 and August 2003). Acetylene inhibits the reduction of $N_2O$ to $N_2$ and is used to quantify the total N-emission ($N_2O$+$N_2$) that is produced via denitrification (Klemedtsson et al., 1990). Per sampling time 16 soil cores from the upper 5 cm mineral soil were incubated in airtight incubation cylinders (volume: 500 ml) and sealed with silicon grease. The headspace air of the cylinders was sampled (30 ml) at the beginning of the incubation period and after 4 h at a temperature of 25°C; thus allowing the determination of $N_2O$ production. Afterwards, acetylene was introduced into the head-space, exposing the soil core to 10 kPa acetylene. Gas sampling procedure and incubation of the acetylene treated samples was the same as for non treated samples. Gas samples were analyzed for $N_2O$ as described in Sect. 2.2. The difference between acetylene treated and untreated $N_2O$ production was calculated to be the $N_2$ production at the time of soil sampling (May 2003 and August 2003). Water filled pore space of soil samples was 43% and 46%.

**Table 2.** Mean soil nitrogen [$\mu$g N g$^{-1}$ dw] and pH (CaCl$_2$) in the litter layer and in the upper 7 cm mineral soil in year 1 (May 2002–April 2003) and year 2 (May 2003–April 2004) at Achenkirch.

|  | year 1 | | year 2 | |
| --- | --- | --- | --- | --- |
| Litter layer | | | | |
| NH$_4^+$-N | 65.8 | (8.5) | 43.1 | (4.0) |
| NO$_3^-$-N | 31.4 | (4.4) | 18.3 | (2.2) |
| pH (CaCl$_2$) | 6.1 | (0.1) | 5.8 | (0.1) |
| Mineral soil | | | | |
| NH$_4^+$-N | 21.0 | (3.0) | 8.8 | (1.2) |
| NO$_3^-$-N | 1.5 | (0.3) | 2.1 | (0.3) |
| pH (CaCl$_2$) | 6.5 | (0.1) | 6.3 | (0.1) |

Note: Soil data are means with standard error in parenthesis.

**Table 3.** Sum of bulk and sum of NH$_3$ deposition [kg N ha$^{-1}$ y$^{-1}$] and precipitation via throughfall in year 1 (May 2002–April 2003) and year 2 (May 2003–April 2004) at the study site Achenkirch.

|  | year 1 | year 2 |
| --- | --- | --- |
| Precipitation [mm] | 1416 | 1067 |
| N-input by bulk deposition/throughfall [kg N ha$^{-1}$ y$^{-1}$] | | |
| NH$_4^+$-N | 3.5 | 4.6 |
| NO$_3^-$-N | 7.1 | 7.3 |
| **Sum of bulk deposition** | **10.6** | **11.9** |
| N-input by dry deposition [kg N ha$^{-1}$ y$^{-1}$] | | |
| NH$_3$-N | 0.56 | n.d. |

n.d. = not determined.

## 2.5 Meteorological data

Soil temperature (in °C, Vitel-thermisters) and soil moisture data (in %, Vitel – Theta probes) were quantified at a soil depth of 5, 15, 25 and 50 cm and stored in a data logger. Air temperature (°C) was measured with a LTK-592 C sensor (Inc. Sommer) at 2 m above ground in a standard weather station. Measuring interval was 4 h. As far as the manual gas sampling time was concerned, soil temperatures at a soil depth of 3 and 10 cm were additionally measured around the chambers. Daily precipitation was recorded by an ombrometer at the nearby meteorological station – Pumpwerk Achenkirch. The biweekly input below the crown was calculated from the crown throughfall collectors.

## 2.6 Deposition measurements

Dry N-deposition comprises NH$_3$ and NO$_2$, NO (if soil compensation mixing ratio is exceeded), HONO, HNO$_3$, PAN, aerosol ammonium, nitrate and nitrite. In this study, concentrations of NH$_3$ were captured by three passive diffusion tubes (Tang et al., 2001) and were analysed at CEH Edinburgh.

In this study the samplers were placed in the canopy at the investigation site at a height of 1.5 m and were changed monthly. Dry deposition velocities were assumed to be 3 mm s$^{-1}$ for NH$_3$ (Duyzer, personal communication). Bulk deposition was collected biweekly using 15 crown throughfall collectors. Bulk deposition was analysed for NH$_4^+$-N and NO$_3^-$-N (Dionex DX100 and Dionex 120). Concentration of NH$_3$ was measured in the first investigation year (May 2002–April 2003), whereas bulk deposition was measured in the first and the second investigation year (May 2003-April 2004).

## 2.7 Statistical analysis

Data were checked for normal distribution. The t-test or the nonparametric Wilcoxon-test was used for determining differences in soil emissions, soil chemical and N-deposition data between the investigation years. Pearson or Spearman rank correlation was used for determining relations between daily or biweekly emission data and soil, meteorological or deposition data. A moving average of 2 was applied for deposition data.

As variables are autocorrelated in the course of time (Durbin-Watson statistic), the autoregression procedure – GARCH ($p$, $q$) model (generalized autoregressive conditional heteroscedasticity model) – was used to detect influences of soil data, meteorological- or deposition data on N-emissions. Specifications of the GARCH model are described in detail in Kitzler et al. (2006). Variables that emerged to correlate best with N$_2$O and NO emissions and variables, whose effects on emissions were lagged, were incorporated in the models. Statistical analysis was either completed using SAS Enterpriseguide Version 2 or SAS Version 8. All differences reported were significant at $p < 0.05$ unless otherwise stated.

# 3 Results

## 3.1 Soil nitrogen and pH

Concentrations of extractable N in the litter layer were at their highest after litterfall in autumn and reached a maximum of 138 $\mu$g NH$_4^+$-N g$^{-1}$ dw (dry weight) and 80 $\mu$g NO$_3^-$-N g$^{-1}$ dw in September 2002 (Fig. 1). Mean NH$_4^+$-N and NO$_3^-$-N concentrations of the first year were considerably higher than the concentrations measured in the second year (Table 2). A similar seasonality was also observed with regard to N concentrations in the mineral soil. Here, up to 7.9 $\mu$g NO$_3^-$-N g$^{-1}$ dw (year 1) and up to 50 $\mu$g NH$_4^+$-N g$^{-1}$ dw (year 2) were reached in autumn. In the second
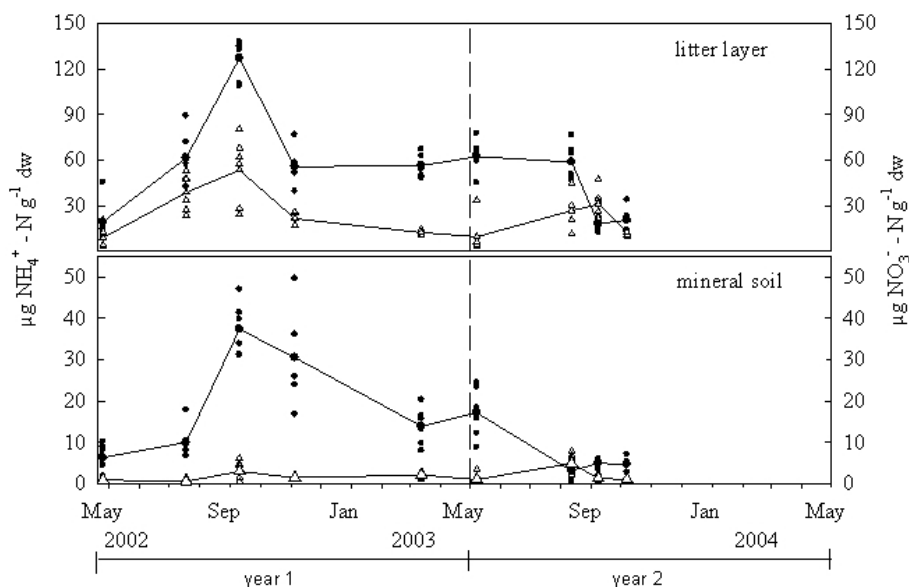
**Fig. 1.** Extractable NH$_4^+$-N (circles) and NO$_3^-$-N (triangles) in the litter layer and in the mineral soil at Achenkirch in the first investigation year (May 2002–April 2003) and the second investigation year (May 2003–April 2004). The straight line indicates the mean. Pooled samples (n=4) were taken from around the individual chambers.

year considerably lower NH$_4^+$-N concentrations were detected, particularly in autumn. Mean soil pH was 6.4 with a maximum of 7.0 and a minimum of 5.4. PH of the litter layer was generally lower (mean=5.9) and ranged from 5.1–7.1.

### 3.2 Nitrogen input

In the two years of investigation, the N-input via throughfall amounted to 10.6 kg and 11.9 kg N ha$^{-1}$ y$^{-1}$ (Table 3). Ratio of deposited NO$_3^-$-N:NH$_4^+$-N is 1.7:1. In general, N from throughfall had its maximum in spring/early summer. In the second year, however, the highest bulk N-deposition was detected in autumn (Fig. 2). No relationship was found between precipitation rates and N-input. Concentrations of NH$_3$ were as high as 7.7 $\mu$g NH$_3$ m$^{-3}$ in the first year (May 2002–April 2003), respectively. The forest floor received 21.6 kg N ha$^{-1}$ y$^{-1}$ (1999) through litterfall (Herman et al., 2002).

### 3.3 Gas fluxes

### 3.3.1 CO$_2$ fluxes

Maximum CO$_2$ emissions were recorded in summer, following a seasonal course of air and soil temperature (Fig. 3a). In the first investigation year the summer peak was not as pronounced and summer emissions were significantly (p<0.01) smaller than in the following year. In late autumn emissions decreased steadily and reached a minimum in winter (0.0–0.2 mg CO$_2$-C m$^{-2}$ h$^{-1}$).

**Table 4.** Mean CO$_2$-C ( mg C m$^{-2}$ h$^{-1}$), N$_2$O-N and NO-N emissions ($\mu$g N m$^{-2}$ h$^{-1}$), minimum and maximum values and number of observations at Achenkirch. (year 1: May 2002–April 2003 and year 2: May 2003–April 2004). Mean NO-N emissions are calculated for a) June–November 2002 and b) May–November 2003.

|  |  | CO$_2$-C | N$_2$O-N | NO-N |
|---|---|---|---|---|
|  |  | [mg C m$^{-2}$ h$^{-1}$] | [$\mu$g N m$^{-2}$ h$^{-1}$] | |
| year 1 | mean | 11.6 | 4.5 | 0.7[a] |
|  | min-max | (0–56.4) | (−3.5–34.0) | (0.4–2.5) |
|  | N | 95 | 242 | 105 |
| year 2 | mean | 19.7 | 4.4 | 0.5[b] |
|  | min-max | (0.4–83.0) | (−2.9–40.6) | (−0.1–7.6) |
|  | N | 96 | 288 | 145 |

NO-N emissions are calculated for a) July–October 2002 and b) May–November 2003.

Mean CO$_2$ emission were 11.6±1.1 mg CO$_2$-C m$^{-2}$ h$^{-1}$ (year 1) and 19.7±2.0 mg CO$_2$-C m$^{-2}$ h$^{-1}$ (year 2) showing a significant difference between the two years (Table 4). At our site the cumulative soil respiration rate was 1.3±0.3 t C ha$^{-1}$ y$^{-1}$ (Table 5) with a 60% higher annual CO$_2$ production rate in year 2.

The most influencing parameters controlling CO$_2$ emissions were soil temperature at a soil depth of 3–25 cm (r$^2$=0.86) and air temperature (r$^2$=0.70).

**Table 5.** Measured and predicted CO$_2$-C ($\pm$ S.E) [kg C ha$^{-1}$ y$^{-1}$], N$_2$O-N emissions ($\pm$ S.E) [kg N ha$^{-1}$ y$^{-1}$] from the manual chambers for the two investigation years at the site Achenkirch (year 1: May 2002–April 2003 and year 2: May 2003–April 2004); N$_2$O-N (AGPS) and NO-N emissions [kg N ha$^{-1}$ y$^{-1}$] are calculated for a) June–November 2002 and b) May–November 2003.

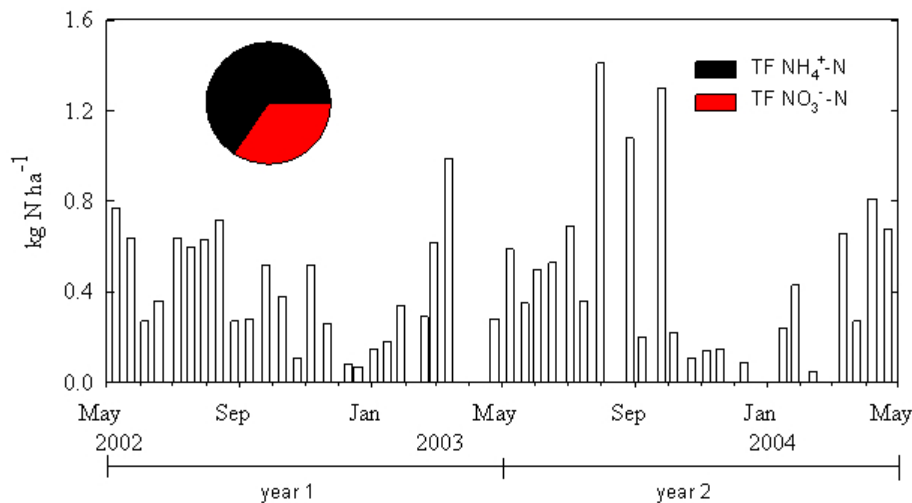| | CO$_2$-C | N$_2$O-N (manual) | | N$_2$O-N (AGPS) | | NO-N | |
|---|---|---|---|---|---|---|---|
| | kg C ha$^{-1}$ y$^{-1}$ | kg N ha$^{-1}$ y$^{-1}$ | | | | | |
| | measured | measured | predicted[1,2] | measured | predicted[3] | measured | predicted[4] |
| year 1 | 1020$\pm$241 | 0.30$\pm$0.11 | 0.36$\pm$0.04 0.33$\pm$0.03 | 0.22$\pm$0.02[a] | 0.28$\pm$0.01 | 0.03$\pm$0.002[a)] | 0.03$\pm$0.001 |
| year 2 | 1636$\pm$283 | 0.41$\pm$0.09 | 0.26$\pm$0.04 0.38$\pm$0.04 | 0.19$\pm$0.02[b] | 0.23$\pm$0.01 | 0.03$\pm$0.004[b] | 0.03$\pm$0.004 |

[1-4] Model 1–Model 4.



**Fig. 2.** Bar chart: Biweekly N-input (kg N ha$^{-1}$) at Achenkirch measured in the two investigation years. Pie chart: Portion of throughfall (TF NH$_4^+$-N, TF NO$_3^-$-N) on annual N-input (kg N ha$^{-1}$) in the first investigation year (May 2002–April 2003).

### 3.3.2 N$_2$O fluxes

Nitrous oxide emissions were mostly dependent on air and soil temperature, as well as on soil moisture. Figure 3b shows spatial and temporal variability during the investigation years. Spatial variation between the chambers was high (mean CV: 50%) and reached a maximum in winter (CV: 350%).

Mean N$_2$O emissions averaged 4.4$\pm$0.3 $\mu$g N m$^{-2}$ h$^{-1}$ (Table 4). In the course of the year largest N$_2$O emissions were observed in summer 2003 (40.6 $\mu$g N m$^{-2}$ h$^{-1}$). Although we missed the summer peak with the manual chamber system in the first year, we were able to observe large N$_2$O emissions by the AGPS (Fig. 3b). During winter, when the site was covered with snow, a significant uptake of atmospheric N$_2$O (range: $-0.3$ to $-3.5$ $\mu$g N m$^{-2}$ h$^{-1}$) could be observed. Significant correlations could be found between C- and N-emissions, and soil, meteorological and N-input data (Table 6). Log-transformed N$_2$O fluxes measured by the manual system were positively correlated ($p<0.001$) to soil respiration rates ($r^2=0.58$), soil temperature in a depth of 3 and 10 cm ($r^2=0.64$) and air temperature ($r^2=0.58$). Correlation analysis between daily N$_2$O fluxes from the AGPS system and soil temperature revealed weaker but significant relationships ($r^2=0.27$, $p<0.001$).

Nitrate and NH$_4^+$ deposition via throughfall and NO$_3^-$ concentration in the mineral soil showed significant positive effects on N$_2$O fluxes ($r^2=0.26$, $r^2=0.25$, $p<0.001$ and $r^2=0.41$, $p<0.05$), even higher correlation was found with NO$_3^-$ concentration in the litter layer ($r^2=0.44$, $p<0.01$).

Simple regression models were insufficient for revealing dependencies of emission data, as residuals were correlated over time. Two GARCH models could be developed to predict N$_2$O emissions as measured with the manually operated system. Independent variables in model 1 were ($x_{1t}$) soil moisture at a soil depth of 5 cm and ($x_{2t}$) soil temperature at
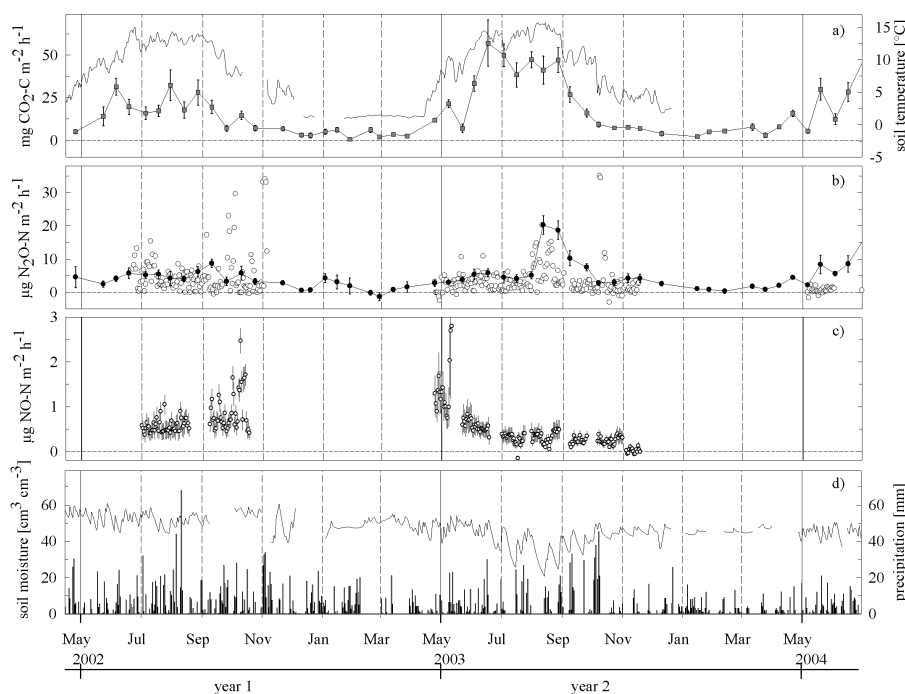
**Fig. 3. (a)** Mean CO$_2$ emissions (squares±S.E) measured with the manual chambers and soil temperature [5 cm] (line), **(b)** mean N$_2$O emissions from manual (dots±S.E) and automatic (circles) chambers, **(c)** mean NO emissions (±S.E) and, **(d)** daily precipitation (bars) and soil moisture [5 cm] (line) at the study site Achenkirch in the two investigation years.

**Table 6.** Matrix of Pearson correlation coefficients for significant relationships of mean N-emissions from manual chambers, AGPS system and dynamic chambers and soil-, meteorological- and N-input data at the site Achenkirch.

|  | lnN$_2$O-manual | | lnN$_2$O-AGPS | | lnNO | |
|---|---|---|---|---|---|---|
| CO$_2$ | 0.58 | *** | | | | |
| Air temperature | 0.58 | *** | 0.16 | * | | |
| Soil temperature | 0.64 | *** [a] | 0.27 | *** [b] | 0.19 | ** [b] |
| NO$_3^-$-N litter layer | 0.44 | ** | | | | |
| NO$_3^-$-N mineral soil | 0.41 | * | | | | |
| TF NO$_3^-$-N | 0.26 | *** | | | | |
| TF NH$_4^+$-N | 0.25 | *** | | | | |
| **TF sumN** | **0.31** | *** | | | | |
| DRY_NH$_3$-N | 0.37 | ** | | | | |

TF = throughfall, DRY = dry deposition. A moving average of 2 was applied to throughfall data. Soil temperature in [a] 3 and 10 cm and [b] in 5 cm. Asterisk indicates the statistic significance (* $p<0.05$, ** $p<0.01$, *** $p<0.001$).

a soil depth of 3 cm. As an effect of N-deposition on N$_2$O emission was discovered while carrying out the correlation analysis (Table 6), we included the monthly sum of nitrogen input (NO$_3^-$ and NH$_4^+$) via throughfall within model 2 and achieved an improvement of modelled N$_2$O emissions in comparison to simple regression analysis. Both models follow the GARCH (2, 1) process and revealed a $r^2$ of 0.89 (model 1) and $r^2$ of 0.83 (model 2) (Fig. 4). Daily N$_2$O emissions from the AGPS showed a high temporal variabil-

ity. Moreover, correlations with soil parameters were lower compared to the N$_2$O emissions measured by the spatially extended manual system. The GARCH model (Fig. 4, model 3 and Table 7) revealed that precipitation and air temperature on daily N$_2$O emissions are delayed by 8 days ($p<0.001$, $r^2=0.43$).

**Table 7.** Parameter estimation for the autoregression models 1 to 4 to predict $N_2O$ and NO emissions from the study site, Achenkirch. Parameters are based on data from the two investigation years. Intercept, regression coefficients of the independent variables ($x_1$) and ($x_2$) and significance level are shown for the individual models. a) in 5 cm, b) in 3 cm.

| Model | | | 1 | | 2 | | 3 | | 4 | |
|---|---|---|---|---|---|---|---|---|---|---|
| independent variable ($y_t$): | | | $N_2O$-manual | | $N_2O$-manual | | $N_2O$-AGPS | | NO | |
| Intercept: | $\beta_0$ | | −12.9481 | ** | 1.9971 | *** | 7.0895 | *** | 1.0429 | *** |
| regression coefficients of the independent variables ($x_1$) and ($x_2$) with significance level: | | | | | | | | | | |
| $\beta_1$ | ($x_1$) | soil moisture | 0.2885 | *** a) | | | | | −0.0034 | *a) |
| $\beta_1$ | ($x_1$) | bulk N deposition | | | −0.4061 | * | | | | |
| $\beta_1$ | ($x_1$) | precipitation | | | | | 0.0851 | *** | | |
| $\beta_2$ | ($x_2$) | soil temperature | 0.4753 | **b) | | | | | −0.0308 | *a) |
| $\beta_2$ | ($x_2$) | air temperature | | | | | −0.1992 | * | | |
| **total $R^2$**: | | | **0.89** | | **0.83** | | **0.43** | | **0.77** | |
| $n$ | | | 147 | | 213 | | 260 | | 217 | |

Regression coefficients and model parameters are statistically significant at the * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$ level. Bulk N deposition = $NO_3^-$-N and $NH_4^+$-N in the throughfall.

### 3.3.3   $NO_x$ fluxes

Mean NO emissions were $0.7 \pm 0.04\,\mu g\,N\,m^{-2}\,h^{-1}$ and hence significantly larger in the first year ($p < 0.001$) compared to the second year ($0.5 \pm 0.07\,\mu g\,N\,m^{-2}\,h^{-1}$) when low soil N concentrations were measured. Mean NO emissions were generally smaller than $N_2O$ emission rates. A consistent seasonal trend could not be observed: In the first year largest emissions occurred in autumn, whereas in the second year maximum emissions were measured in spring (Fig. 3c). ($NO_x$-NO) was deposited with a mean of $-0.3 \pm 0.1\,\mu g\,N\,m^{-2}\,h^{-1}$ (year 2).

Correlation analysis (Table 6) revealed a weak positive relationship between mean daily NO fluxes and soil temperature at the soil depth of 5 cm ($r^2 = 0.19$, $p < 0.5$). No valid statistical explanation could be given to characterize NO emissions by a simple regression model. By using the autoregression procedure, however, a GARCH (1,1) model could be developed to predict daily NO emissions of our site (Fig. 4, model 4). Through a mean of daily soil moisture content ($x_{1t}$) and soil temperature ($x_{2t}$) at a soil depth of 5 cm, predictions of mean daily NO emissions could be carried out with an $r^2$ of 0.77 (Table 7). This model revealed a time lag of 2, signifying that the independent variables have an influence on NO emissions over two days.

### 3.3.4   Acetylene inhibition

Acetylene inhibits the reduction of $N_2O$ to $N_2$. The total N-emission due to denitrification can be measured. The production of $N_2O$ in $C_2H_2$-treated samples was between 101 and 4200% (median: 266%) of the samples without inhibition. The ratio of $N_2O$-N:$N_2$-N was 1:6. Mean $N_2$ production ($\pm$ S.E) at a WFPS of 43% and 46% was $11.6 \pm 1.4\,\mu g\,N\,m^{-2}\,h^{-1}$ and $19.1 \pm 3.9\,\mu g\,N\,m^{-2}\,h^{-1}$.

## 4   Discussion

### 4.1   $CO_2$ fluxes

Carbon dioxide emissions, a measure for general microbial activity, followed a typical seasonal trend, with highest rates in summer, when mineralization of organic matter occurs. Lowest rates were measured in winter. Organic carbon is converted to $CO_2$ during mineralization. This process is strongly dependent on soil temperature and soil moisture. At our site, soil temperature at a soil depth of 3 and 10 cm was mostly responsible for temporal variation in soil respiration. This finding is in good agreement with results from other studies (Epron et al., 1999; Merino et al., 2004). Soil moisture also showed a significant effect on soil respiration rates. Carbon dioxide release was reduced during periods of heavy rain (summer 2002), when the water content was between 50–65%, probably as a consequence of $O_2$ deficiency in soil due to diffusion restrictions (Howard and Howard, 1993). The cumulative soil respiration rates at our site (1–1.6 t $CO_2$-C ha$^{-1}$ y$^{-1}$) are lower than values for temperate coniferous forests reported by Raich and Schlesinger (1992).

### 4.2   $N_2O$ fluxes

At our site, seasonal variations in $N_2O$ emissions followed mainly the annual changes in soil temperature, soil moisture and the availability of N in the soil. Largest emissions were thus observed during summer/autumn. Although, we missed out on the summer peak in year 2002 through the manual

chamber system (biweekly sampling), we were able to observe large emissions by the AGPS.

Soil temperature and soil moisture were the most important factors controlling $N_2O$ emissions. Those parameters affect microorganisms and their metabolism and, hence, the production and consumption of N trace gases in soils (Conrad, 1996). The air-filled porosity controls the movement of the gases towards and away from the atmosphere; it also affects soil aeration, and, thus, indirectly controls the capacity of the soil for producing or consuming soil-produced trace-gases (Smith et al., 2003; Davidson et al., 2000). In a laboratory parameterisation study, Schindlbacher et al. (2004) found for the AK site a $N_2O$ emission maximum at a soil moisture range of 60%–90% water filled pore space (WFPS) which corresponds to a water content of 53–80%. In the field we found, beside the peak in August 2003, that maximum $N_2O$ emissions occurred at soil moisture values in the range of 50%–65%, i.e. in accordance to the laboratory results of Schindlbacher et al. (2004). With the GARCH model 1 $N_2O$ emissions could be predicted best using soil moisture and soil temperature as predictors ($r^2=0.89$). Within the model, soil moisture showed a highly significant effect ($p<0.001$); an effect of soil temperature was also visible ($p<0.01$). Furthermore, high precipitation and low air temperature showed a significant effect on $N_2O$ emissions with a lag of $\sim$8 days (model 3). We hypothesize that these adverse conditions for microbes may be comparable to the effects observed after freeze-thaw events. In a microcosm experiment Sharma et al. (2006) found that maximum $N_2O$ emissions occurred $\sim$8 days after thawing.

Largest emissions were observed in the second year in August. There are various parameters that might have contributed to the $N_2O$ peak. Even at this site, where soil moisture is generally high, the water content during the European drought period of summer 2003 decreased to 30%. After a rainfall event soil moisture increased again and may have caused an increase in microbial activity. On the other hand, the actual level of N-deposition and the $NO_3^-$ pool in the soil might have played an important role in the sudden release of $N_2O$ (Davidson et al., 2000). Highest amounts in $NO_3^-$ and $NH_4^+$ via throughfall reached the forest floor in August. Although, throughout the study bulk N-deposition accounted for up to only 31% of the variation in $N_2O$ emission (correlation analysis), a strong relationship was apparent between the two factors. This high $N_2O$ peak coincided with significant larger available soil N concentrations, in particular soil $NO_3^-$. Using model 2 the relationship between biweekly measured $N_2O$ emissions and biweekly sum of nitrogen input ($NO_3^-$ and $NH_4^+$) via throughfall was found by a high $r^2$ (0.83). The time series analysis revealed a highly significant ($p<0.001$) lagged effect of reduced bulk N-deposition on $N_2O$ emission for a 3-month period. Model 1 also revealed that past environmental conditions (3 months) of high soil moisture and temperature can significantly affect actual
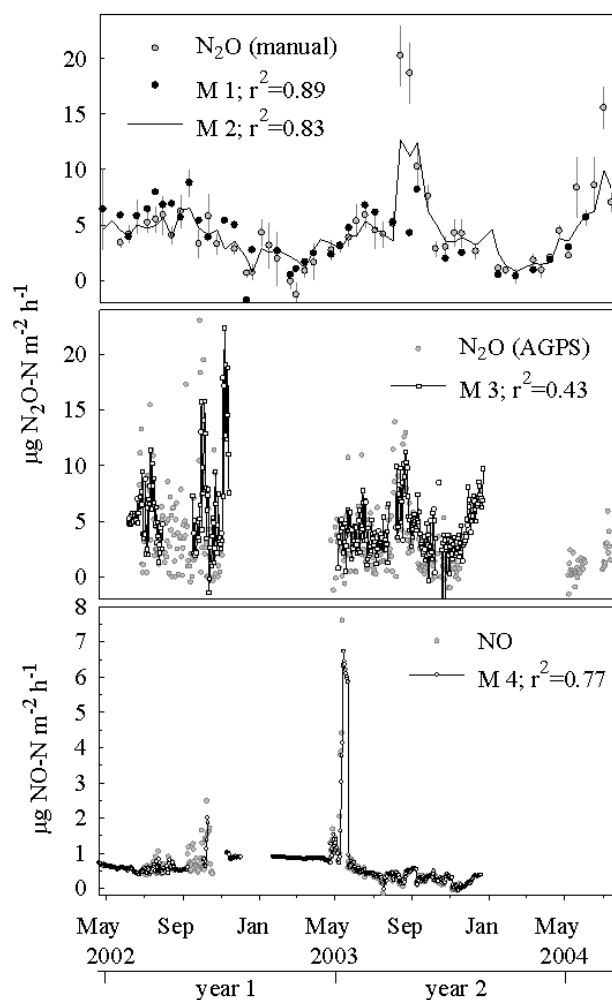


**Fig. 4.** Predicted versus measured $N_2O$ and NO emissions at Achenkirch in the two investigation years. Independent variables are soil moisture and soil temperature for model 1 (M 1) and model 4 (M 4); N-deposition ($NH_4^+$-N and $NO_3^-$-N) for model 2 (M 2) and, precipitation and air temperature for model 3 (M 3).

$N_2O$ emissions. Explanations for this phenomenon can only be hypothetical. It has been observed that nitrogen in microbes may have a turnover rate of $\sim$3 months (Tietema and van Dam, 1996). According to the theories of microbial stochiometry (Schimel and Weintraub, 2003) microbes tend to immobilize nitrogen from the soil solution and use it for cell growth at times when it is the limiting nutrient. This could be the case during favourable growth conditions of soil moisture and high temperatures but little N-input. After $\sim$3 months microbial death may occur, which may lead to enhanced N-release and $N_2O$ emissions as observed in beech forests (Zechmeister-Boltenstern et al., 2002).

The soil at the Mühleggerköpfl is typically moist (mean 55%) and denitrification may have been the main source of $N_2O$ emissions throughout the year. A high pH value is also one of the factors that provide favourable conditions

for denitrification at the site. Previous studies (Härtel et al., 2002) have indicated that complete nitrification takes place at our site and that it is of major importance for N$_2$O emission. $^{15}$NO$_3^-$ was strongly immobilized. Furthermore, close C/N-ratios (16–18) suggest favourable conditions for N-mineralization and nitrification (Herman et al., 2002). It was in August/September that nitrate concentration increased and we suppose that the high N$_2$O peak in the second year is the product of nitrification.

At our site winter emissions were generally small and the site even functioned as a sink for N$_2$O. Butterbach-Bahl et al. (2002) detected negative N$_2$O fluxes in pine forests with moderate N-deposition whereas a pine forest with high N-loads exclusively functioned as a source of N$_2$O during winter. On the other hand winter emissions, comparable to the ones during the year (January 2003; $4.3 \pm 1.3 \, \mu$g N$_2$O-N m$^{-2}$ h$^{-1}$), could be observed after freeze-thaw events. These large emissions were either a result of enhanced denitrification activity or could be due to the physical release of accumulated N$_2$O in the snow or in the soil (Teepe et al., 2001).

## 4.3 NO$_x$ fluxes

The production of NO is strongly dependent on climate and varies considerable with soil temperature and soil moisture (Davidson et al., 2000; Ludwig et al., 2001; Van Dijk et al., 2002). The optimum soil temperature (20°C), as detected in laboratory studies by Schindlbacher et al. (2004), could not be confirmed in the field experiment, where largest NO emissions were measured at 8–10°C soil temperature; maximum soil temperature in the field was 16°C. Optimum WFPS in the field for NO emission was found to be at 30–45% WFPS (water content 27–40%) and was, thus, higher than in laboratory studies (Schindlbacher et al., 2004). In the field largest NO emissions were found in autumn and in spring, when soil water content was between 45–50%. Large spring emissions were detected in May, when soil was moistened and soil temperature increased. With the GARCH procedure a relationship between NO emissions and soil moisture and soil temperature could be found with an $r^2$=0.77 (model 4). Autoregressive parameters were estimated for a time-lag of 2 days; i.e. NO emissions were especially promoted when soils had been colder and drier ∼2 days before.

Soil nitrogen content contributed to large NO emission in autumn, where highest NO$_3^-$ and NH$_4^+$ concentrations were measured. As in autumn 2003 the N-pool (especially extractable NH$_4^+$) in the soil and the litter layer was low compared to concentrations measured in autumn 2002 no increase in NO emissions could be detected. The effect of rewetting the soil as it was found for N$_2$O emissions could not be seen for NO emissions.

Soil acidity is supposed to be an important factor promoting N-emissions from forest soils influenced by atmospheric nitrogen deposition (Li et al., 2000 and Venterea et al., 2003). Soils with a pH of 7–8 are supposed to produce higher amounts of N$_2$ (Simek and Cooper, 2002) but revealed an order of magnitude larger N$_2$O emissions than soils with a pH between 4 and 6 (Vermoesen et al., 1996). A soil pH of 6.7–7.1 measured at our limestone site restricts self-decomposition of HNO$_2$ and might, therefore, be responsible for small NO fluxes (Van Cleemput and Samater, 1996). Beside the high pH and the high microbial biomass (Härtel et al., 2002), the well-balanced community composition of the microflora could be a reason for small NO-fluxes. Results of PLFA (Phospholipid fatty-acid analysis) studies of European soils by (Zechmeister-Boltenstern, unpublished) showed that at acidic high N-input sites the microbes are under stress which leads to structural changes of their cell membranes. This could cause losses of intermediate products in the nitrification or denitrification pathway and could, thereby, lead to larger NO and N$_2$O emissions. The assumption of a well-balanced microflora was supported by the acetylene inhibition experiment.

## 4.4 Annual N-emissions

At our site the N release was between 0.3 and 0.4 kg N$_2$O-N ha$^{-1}$ y$^{-1}$, and 0.03 kg NO-N ha$^{-1}$ y$^{-1}$ (Table 5). These values correspond to a yearly release of actual N input of 2.5–3.5% in form of N$_2$O-N and 0.2% in form of NO-N and are located in the lower reported percentage of deposited N which is 0–16% (N$_2$O-N) and 0–10% (NO-N) (Skiba et al., 2004). According to the acetylene inhibition method the ratio of N$_2$:N$_2$O was 6.0. The estimated annual N$_2$ emission is therefore 2.2 kg N ha$^{-1}$. The ratio of N$_2$:N$_2$O is considerably higher than in previous investigations of forests (0–0.4; Wolf and Brumme, 2003; Brumme et al., 1999; Mogge et al., 1998). Our estimation is based on only two measurements. Conclusions need to drawn cautiously because the N$_2$ production changes with changing WFPS% (Davidson et al., 2000). However, it can be hypothesized that the deposited N from the atmosphere is mainly emitted as N$_2$ at this limestone site.

The magnitude of N$_2$O-N emissions from our site is consistent with values reported of other coniferous forests (MacDonald et al., 1997; Papen and Butterbach-Bahl, 1999; Butterbach-Bahl et al., 2002) and limed beech forests (Borken and Brumme, 1997). Higher emissions (16–35 N$_2$O-N m$^{-2}$ h$^{-1}$) have been measured from acidic soils of N-enriched coniferous forests (Papen and Butterbach-Bahl, 1999; Butterbach-Bahl et al., 2002) and from deciduous forests (1.5–5.6 kg N$_2$O-N ha$^{-1}$ y$^{-1}$) with low pH (Brumme and Beese, 1992; Borken and Brumme, 1997).

Nitric oxide emission measured in our study are small in comparison to other published NO fluxes from temperate coniferous forests. Our rates are in accordance with studies by Johansson, (1984) who reported annual NO emissions of 0.04 kg NO-N ha$^{-1}$ y$^{-1}$ from an unfertilized coniferous forest soil in Sweden. The majority of studies, however,

revealed significantly larger values. Pilegaard et al. (1999) and Butterbach-Bahl et al. (2002) found in moderately N-effected spruce forests annual NO emissions of 3.15 kg NO-N ha$^{-1}$ y$^{-1}$ and 3.1 $\mu$g NO-N m$^{-2}$ h$^{-1}$, respectively. It has to be taken into account that most of the reported data were measured at forest soils with low pH values; however, NO fluxes are reported to be significantly larger in more acidic soils compared to N$_2$O fluxes (Yamulki et al., 1997).

The employed GARCH model predicts NO fluxes with a higher $r^2$ than a regression model. Nitrous oxide emissions measured by manual chambers yielded an $r^2$ of 0.89 (model 1) and an $r^2$ of 0.83 (model 2). Through model 2, whith N-deposition as the only independent variable, annual emission rates were better than with model 1, where soil moisture and soil temperature were the independent variables. Especially in the second year, where large emissions (singular event) were detected in August, the predicted emissions with model 2 had a higher R-squared as with model 1. High variations in N$_2$O emissions measured by the AGPS led to an overestimation of N$_2$O emissions through model 3 (21–27%). Daily measured NO emissions were predicted with an $r^2$ of 0.77 (model 4) and also the high peak in May was captured. Annual simulated fluxes were in accordance with measured annual NO emissions.

We conclude that the GARCH model is better than a conventional regression analysis, because soil N-emissions can be modelled with a higher $r^2$. It reflects lagged effects of soil moisture, soil temperature, precipitation, air temperature and N-deposition on N-oxide emissions. The use of time-series models in GHG-flux investigations is a novel approach in soil science. So is the search for time-lagged responses of gas fluxes to environmental factors. At our site, NO emissions were three times smaller compared to N$_2$O emissions and total emissions of N were small compared to N-inputs. This may be attributed to the fact that in the limestone Alps soil pH is high, a large microbial biomass can be found and nitrogen is mainly emitted in the form of N$_2$. Alone in Austria, about a third of forests are on calcareous bedrock and this is the first report on processes determining N-oxides fluxes in these ecosystems.

## References

Beier, N. and Schneewind, R.: Chemical reactions of gases in tubes of probing systems and their influence on measured concentrations., Ann. Geophys., 9, 703—707, 1991, http://www.ann-geophys.net/9/703/1991/.

Borken, W. and Brumme, R.: Liming practice in temperate forest ecosystems and the effects on CO$_2$, N$_2$O and CH$_4$ fluxes, Soil Use and Management, 13, 251–257, 1997.

Brumme, R. and Beese, F.: Effects of liming and nitrogen fertilization on emissions of CO$_2$ and N$_2$O from temperate forest, J. Geophys. Res., 97, 12, 851–858, 1992.

Brumme, R., Borken, W., and Finke, S.: Hierachical control on nitrous oxide emission in forest ecosystems, Global Biogeochem. Cycl., 13, 1137–1148, 1999.

Butterbach-Bahl, K., Gasche, R., Breuer, L., and Papen, H.: Fluxes of NO and N$_2$O from temperate forest soils: impact of forest type, N deposition and of liming on NO and N$_2$O emissions, Nutr. Cycl. Agroecosys., 48, 79–90, 1997.

Butterbach-Bahl, K., Breuer, L., Gasche, R., Willibald, G., and Papen, H.: Exchange of trace gases between soils and the atmosphere in Scots pine forest ecosystems of the northeastern German lowlands: 1. Fluxes of N$_2$O, NO/NO$_2$ and CH$_4$ at forest sites with different N-deposition, For. Ecol. Manag., 167, 1–3, 123–134, 2002.

Conrad, R.: Soil microorganisms as controllers of atmospheric trace tases (H$_2$, CO, CH$_4$, OCS, N$_2$O, NO), Microbiol. Rev., 60, 609–640, 1996.

Crutzen, P. J.: The role of NO and NO$_2$ in the chemistry of the troposphere and stratosphere, Annu. Rev. Earth Planet. Sci., 7, 443–472, 1979.

Crutzen, P. J.: Ozone in the troposphere, in: Composition, Chemistry, and Climate of the Atmosphere, edited by: Signh, H. P., Van Nostrand Reinhold, New York, 349–393, 1995.

Davidson, E. A., Keller, M., Erickson, H. E., Verchot, L. V., and Veldkamp, E.: Testing a conceptual model of soil emissions of nitrous and nitric oxides, BioScience, 50, 667–680, 2000.

Englisch, M. and Starlinger, F.: Waldgesellschaften und Standorte im Bereich der Höhenprofile Achenkirch, FBVA-Bericht, 87, 25–54, 1995.

Epron, D., Farque, L., Lucot, E., and Badot, P. M.: Soil CO$_2$ efflux in a beech forest: the contribution of root respiration, Ann. For. Sci., 56, 4, 289–295, 1999.

Firestone, M. K. and Davidson, E. A.: Microbial Basis of NO and N$_2$O Production and Consumption in Soil, in: Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere, edited by: Andreae, M. O. and Schimel, D. S., John Wiley, New York, 7–21, 1989.

Gut, A., Scheibe, M., Rottenberger, S., Rummel, U., Welling, M., Ammann, C., Kirkham, G. A., Kuhn, U., Meixner, F. X., Kesselmeier, J., Lehmann, B. E., Schmidt, W., Müller, E., and Piedade, M. T. F.: Exchange fluxes of NO$_2$ and O$_3$ at soil leaf surfaces in an Amazonian rain forest, J. Geophys. Res., 107, 8060, doi:10.1029/2001JD000654, 2002.

Härtel, E., Zechmeister-Boltenstern, S., and Gerzabek, M.: Gaseous nitrogen losses from a forest site in the north Tyrolean limestone alps, Environm. Sci. Poll. Res., Special Issue 2, 23–30, 2002.

Herman, F., Smidt, S., Englisch, M., Feichtinger, F., Gerzabek, M., Haberhauer, G., Jandl, R., Kalina, M., and Zechmeister-Boltenstern, S.: Investitions of nitrogen fluxes and pools on

a limestone site in the Alps, ESPR – Environm. Sci. Poll. Res., 46–52, 2002.

Holtermann, C.: A transportable system for the on-line-measurement of NO$_x$ (NO, NO$_2$)-emission from soils, Die Bodenkultur, 47, 235–244, 1996.

Howard, D. M. and Howard, P. J.: Relationships between CO$_2$ evolution, moisture content and temperature for a range of soil types, Soil Biol. Biochem., 25, 1537–1546, 1993.

IAEA: Manual on measurements of methane and nitrous oxide emissions from agriculture, International Atomic Energy Agency, Vienna, 90, 1992.

IPCC: Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel of Climate Change, in: Cambridge University Press, edited by: Houghton, J. T., Ding, Y., Griggs, D. J., Noguer, M., Van der Linden, P. J., and Xiaosu, D., Cambridge, UK and New York, NY, USA, 881p., 2001.

Johansson, C.: Field measurements of emission of nitric oxide from fertilized and unfertilized forest soils in Sweden, J. Atmos. Chem., 1, 429–442, 1984.

Kandeler, E.: Ammonium and Nitrate, in: Methods of Soil Biology, edited by: Schinner, F., Öhlinger, T., Kandeler, E., and Margesin, R., Springer, Berlin, 406–410, 1995.

Kitzler, B., Zechmeister-Boltenstern, S., Holtermann, C., Skiba, U., and Butterbach-Bahl, K.: Nitrogen oxides emission from two beech forests subjected to different nitrogen loads, Biogeosciences, 3, 293-310, 2006,
http://www.biogeosciences.net/3/293/2006/.

Klemedtsson, L., Hanson, G., and Mosier, A.: The use of acetylene for the quantification of N$_2$ and N$_2$O production from biological processes in soils, in: Denitrification in soil and sediment, edited by: Sorensen, J. and Revsbech, N. P., Plenum Press, 167–180, 1990.

Li, C., Aber, J. D., Stange, F., Butterbach-Bahl, K., and Papen, H.: A process-oriented model of N$_2$O and NO emission from forest soils,1, Model development, J. Geophys. Res., 105(4) 4369–4384, 2000.

Lovett, G. M., Weathers, K. C., and Arthur, M. A.: Control of nitrogen loss from forested watersheds by soil carbon: Nitrogen ratio and tree species composition, Ecosys., 5, 712–718, 2002.

Ludwig, J.: Untersuchungen zum Austausch von NO und NO$_2$ zwischen Atmosphäre und Biosphäre, PhD Thesis, University of Bayreuth, 251, 1994.

Ludwig, J., Meixner, F. X., Vogel, B., and Förstner, J.: Soil-air exchange of nitric oxide: An overview of processes, environmental factors, and modeling studies, Biogeochemistry, 52, 225–257, 2001.

MacDonald, J., Skiba, U., Sheppard, L. J., Ball, B. C., Roberts, J. D., Smith, K. A., and Fowler, D.: The effect of nitrogen deposition and seasonal variability on methane oxidation and nitrous oxide emission rates in upland spruce plantation and moorland, Atmos. Environ., 31, 22, 3693–3706, 1997.

Meixner, F. X., Fickinger, T., Marufu, L., Serca, D., Nathaus, F.J., Makina, E., Mukurumbira, L., and Andreae, M. O.: Preliminary results on nitric oxide emissions from southern African savannah ecosystem, Nutr. Cycl. Agroecosys., 48, 123-138, 1997.

Merino, A., Pérez-Batallón, P., and Macías, F.: Responses of soil organic matter and greenhouse gas fluxes to soil management and land use changes in a humid temperate region of southern Europe, Soil Biol. Biochem., 36, 917–925, 2004.

Mogge, B., Kaiser, E.A. and Munch, J.C.: Nitrous oxide emissions and denitrification N-losses from forest soils in the Bornhöved lake region (Northern Germany), Soil Biol. Biochem., 30, 703–710, 1998.

Mutsch, F.: Bodenchemische Charakterisierung des Mühleggerköpfls im Rahmen einer Untersuchung über Stickstoff-Flüsse in den Norditoler Kalkalpen, FBVA Berichte, 116, Wien, 33–40, 2001.

NADP: National Atmospheric Deposition Program 2001 Summary, NADP Report, Illinois State Water Survey, Champaign, IL, 2002.

Papen, H. and Butterbach-Bahl, K.: A 3-year continuous record of N-trace gas fluxes from untreated and limed soil of a N-saturated spruce and beech forest ecosystem in Germany: I. N$_2$O-emissions, J. Geophys. Res., 104, 18 487–18 503, 1999.

Pilegaard, K., Hummelshoj, P., and Jensen, N. O.: Nitric oxide emission from a Norway spruce forest floor, J. Geophys. Res., 104, 3433–3445, 1999.

Raich, J. W. and Schlesinger, W. H.: The global carbon dioxide flux in soil respiration and its relationship to vegetation and climate, Tellus, 44B, 81–99, 1992.

Remde, A., Ludwig, J., Meixner, F. X., and Conrad, R.: A study to explain the emission of nitric oxide from a marsh soil, J. Atmos. Chem., 17, 249-275, 1993.

Rummel, U., Ammann, C., Gut, A., Meixner, F. X., and Andreae, M. O.: Eddy covariance measurements of nitric oxide flux within an Amazonian rain forest, J. Geophys. Res., 107(D20), 8050, doi:10.1029/2001JD000520, 2002.

Schimel, D. S. and Weintraub, M. N.: The implications fo exoenzyme activity on microbial carbon and nitrogen limitation in soil: a theoretical model, Soil Biol. Biochem., 35, 549–563, 2003.

Schindlbacher, A., Zechmeister-Boltenstern, S., and Butterbach-Bahl K.: Effects of soil moisture and temperature on NO, NO$_2$ and N$_2$O emissions from forest soils, J. Geophys. Res., 109, 1–12, 2004.

Sharma, S., Szele, Z., Schilling, R., Munch, J. C., and Schloter, M.: Influence of freeze-thaw on the structure and function of microbial communities and denitrifying population in soil, Appl. Environm. Microbiology, 72, 3, 2148–2154, doi:10.1128/AEM.72.3.2148-2154.2006, 2006.

Simek, M. and Cooper, J. E.: The influence of soil pH on denitrification: progress towards the understanding of this interaction over the last 50 years, Eur. J. Soil Sci., 53, 3, 345–354, 2002.

Skiba, U., Pitcairn, C. E. R., Sheppard, L. J., Kennedy, V. H., and Fowler, D.: The influence of atmospheric N deposition on nitrous oxide and nitric oxide fluxes and soil ammonium and nitrate concentrations, Water, Air Soil Poll., Focus 4, 37–43, 2004.

Smidt, S., Herman, F., Grill, D., and Guttenberger, H.: Studies of ecosystems in the Limestone Alps – "Achenkirch Altitude Profiles", Phyton, 36, Horn, Austria, 1996.

Smith, K. A. Ball, T., Conen, F., Dobbie, K. E., Massheder, J., and Rey, A.: Exchange of greenhouse gases between soil and atmosphere: interactions of soil physical factors and biological processes, Eur. J. Soil Science, 54, 4, 779–791, 2003.

Tang, Y. S., Cape, J. N., and Sutton, M. A.: Development and types of passive samplers for monitoring atmospheric NO$_2$ and NH$_3$ concentrations, The Scientific World, 1, 513–529, 2001.

Teepe, R., Brumme, R., and Beese, F.: Nitrous oxide emissions from soil during freezing and thawing period, Soil Biol.

Biochem., 33, 1269–1275, 2001.

Tietema, A. and van Dam, D.: Calculating microbial carbon and nitrogen transformations in acid forest litter with $^{15}$N enrichment and dynamic simulation modelling, Soil Biol. Biochem., 28, 953–965, 1996.

Van Cleemput, O. and Samater, A. H.: Nitrite in soils: accumulation and role in the formation of gaseous N compounds, Fertil. Res., 45, 81–89, 1996.

Van Dijk, S. M., Gut, A., Kirkman, G. A., Meixner, F. X., and Andreae, M. O.: Biogenic NO emissions from forest and pasture soils: Relating laboratory studies to field measurements, J. Geophys. Res., 107, 8058, doi:10.1029/2001JD000358, 2002.

Venterea, R. T., Groffman, P. M., Verchot, L. V., Magill, A. H., Aber, J. D., and Streudler, P. A.: Nitrogen oxide gas emissions from temperate forest soils receiving long-term nitrogen inputs, Global Change Biol., 9, 346–357, 2003.

Vermoesen, A., de Groot, C., Nollet, L., Boeckx, P., and Van Cleemput, O.: Effect of ammonium and nitrate application on the NO and N$_2$O emission out of different soils, Plant Soil, 181, 153–162, 1996.

WHO: Updating and revision of the air quality guidelines for Europe, Les Diablerets, 1995.

Williams, E. J., Hutchinson, G. L., and Fehsenfeld, F. C.: NO$_x$ and N$_2$O emissions from soil, Global Biogeochem. Cycl., 6, 351–388, 1992.

Wolf, I. and Brumme, R.: Dinitrogen and nitrous oxide formation in beech forest floor and mineral soils, Soil Sci. Soc. Amer. J., 67, 1862–1868, 2003.

Yamulki, S., Harrison, R. M., Goulding, K. W. T., and Webster, C. P.: N$_2$O, NO and NO$_2$ fluxes from a grassland: Effect of soil pH, Soil Biol. Biochem., 29, 1199–1208, 1997.

Zechmeister-Boltenstern, S., Hahn, M., Meger, S., and Jandl, R.: Nitrous oxide emissions and nitrate leaching in relation to microbial biomass dynamics in a beech forest soil, Soil Biol. Biochem., 34, 823–832, 2002.