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**N₂O, NO_x and CO₂
fluxes in a calcareous
mountain forest soil**

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Controls over N₂O, NO_x and CO₂ fluxes in a calcareous mountain forest soil

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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 12.1 kg nitrogen via wet and dry 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, additionally. For acquiring information on the effects of soil and meteorological conditions and of N-deposition on N-emissions we chose the autoregression 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 wet 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.

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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 N₂O, NO, and N₂ 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, N₂O and N₂ are influenced by various factors. These drivers are temperature, precipitation, total N, availability of O₂, 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 NH₃ 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 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, N₂O and N₂ (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, N₂O, CO₂, CH₄) 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. During a two-year sampling period of CO₂, N₂O and NO_x emissions, measurements were carried out in order (1) to investigate the trace gas exchange between a typical spruce-beech-fir forest soil in the limestone Alps and the atmosphere. Measurements

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were conducted in high temporal and spatial resolution (2) to get better estimates of annual emissions, (3) to study the relationships between N-trace gas emissions and meteorological factors and soil parameters, (4) to investigate if N-deposition affects N-emissions in these forest ecosystems and (5) to 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 Achenal 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 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. N₂O and CO₂ flux measurements

Gas measurements were carried out as described in Kitzler et al. (2005). Gas samples of four manually operated chambers (area: 1 m², volume: 80 l) were taken biweekly from April 2002 until July 2004. Duplicate air samples from the chambers were taken after 0, 1 and 2 h and injected into gas tight headspace vials (20 ml). 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

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by Kitzler et al. (2005) and has been shown to allow realistic N₂O emission estimates for forest soils (Zechmeister-Boltenstern et al., 2002). Gas samples were stored at 4°C until analysis. The time of automatic sampling was scheduled for 6 a.m. due to the fact that in a previous experiment highest emissions had been measured at morning dew.

5 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.

10 Emissions of N₂O ($\mu\text{g N m}^{-2} \text{h}^{-1}$) and CO₂ ($\text{mg C m}^{-2} \text{h}^{-1}$) were determined by the linear increase of the mixing ratio within the incubation period. Nitrous oxide and CO₂ fluxes were calculated as described in (IAEA, 1992).

A gas chromatograph (HP 5890 Series II) with a ⁶³Ni-electron-capture detector (ECD), connected to an automatic sample-injection system (DANI HSS 86.50, HEADSPACE-SAMPLER) was used for N₂O analysis. The oven, injector and detector temperatures were set at 120°C, 120°C and 330°C, respectively. A calibration gas of 5 $\mu\text{l l}^{-1}$ N₂O (Linde Gas) and N₂ in ECD-quality with a flow rate of 30 ml min⁻¹ served as carrier-gas. 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 CO₂ calibration gas contained 10 ml l⁻¹ CO₂ (Linde Gas).

2.3. NO flux measurements

25 Continuous measurements of NO/NO₂ were completed by a fully automated system (Holtermann, 1996), at an hourly frequency, throughout the vegetation periods of 2002 and 2003. NO and NO₂ were measured with a HORIBA APNA-360 chemoluminescence nitrogen oxide analyzer (detection limit: was 1 ppb; flow rate: 1 l min⁻¹). Calibration was conducted by using a HORIBA calibration unit (Transferstandard, ASGU-360, 0–600 ppb). To avoid reactions of NO and O₃ in the chambers, a filter cylinder, filled

with Purafil and activated charcoal, was used in 2002 as no ozone analyzer was available in this year. In year 2003 we used an ozone analyzer (HORIBA APOA-360) for measuring O₃ concentrations within the chambers. Thus, the chemical reaction between NO and O₃ could be considered. It has to be mentioned that the NO₂ measurements with the HORIBA is the sum of NO₂ (most likely the main component) and other nitrogen compounds (PAN, NH₃, HONO). Air samples were taken from 5 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 for 5 min within which steady state was reached. Fluxes were calculated as described by Schindlbacher et al. (2004) for 2002 fluxes and Butterbach-Bahl et al. (1997) for 2003 fluxes. For further details on analysis of gas samples and calculation of fluxes compare Kitzler et al. (2005). In view of the low concentrations and the spatial heterogeneity of NO_x fluxes the uncertainty coming from disregarding wall effects was assumed to be of minor importance (Ludwig, 1994).

2.4. Soil samples

Soil samples were taken approximately every two months. Extractable nitrogen was determined from litter layer (frame: 30×30 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 CaCl₂ solution using a glass electrode. Additionally to these analyses, an acetylene (C₂H₂) inhibition experiment was carried out twice (May 03 and August 03). Acetylene inhibits the reduction of N₂O to N₂ and is used to quantify the total N-loss (N₂O+N₂) that is produced via denitrification (Klemmedtsson et al., 1990).

Per sampling time 16 soil cores from the upper 7 cm mineral soil were incubated in airtight incubation cylinders (volume: 500 ml) and sealed with silicon grease. The headspace 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 N₂O production. Afterwards, acetylene was injected into the headspace exposing the soil

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core to 10 kPa acetylene. The incubation period lasted again for 4 h at 25°C. Nitrous oxide was analyzed as described in Sect. 2.2.

2.5. Meteorological data

Soil temperature (in °C, Vitel-thermistors) and soil moisture (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 temperature sensor at 2 m above ground. 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 deposition of NO₂ and NH₃ was captured by three passive diffusion tubes and three CEH ALPHA samplers, respectively (Tang et al., 2001), and were analysed by CEH Edinburgh. They were placed in the canopy at the investigation site and at an open site nearby, at a height of 1.5 m and were changed monthly. Dry deposition velocities were assumed to be 1.5 mm s⁻¹ for NO₂ and 3 mm s⁻¹ for NH₃ (Duyzer, pers. comm.). Wet deposition was collected biweekly using 15 crown throughfall collectors. Wet deposition was analysed for NH₄⁺ and NO₃⁻ (Dionex DX100 and Dionex 120).

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

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soil, meteorological or deposition data. A moving average of 2 or 3 was applied for deposition data.

As variables are autocorrelated in the course of time (Durbin-Watson statistic), the autoregression procedure – GARCH (p, q) 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. (2005). Variables that emerged to correlate best with N_2O 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 $138 \mu\text{g NH}_4^+\text{-N}$ and $80 \mu\text{g NO}_3^-\text{-N g}^{-1}$ dw (dry weight) in September 2002 (Fig. 1). Mean NH_4^+ and NO_3^- 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 $7.9 \mu\text{g NO}_3^-\text{-N g}^{-1}$ dw and up to $50 \mu\text{g NH}_4^+\text{-N g}^{-1}$ dw were reached in autumn 2002 and 2003, respectively. In 2003 considerably lower $\text{NH}_4^+\text{-N}$ 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 was ranging from 5.1–7.1.

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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 NO₃⁻:NH₄⁺ is 1.7:1. In general, N from throughfall had its maximum in spring/early summer. In 2003, however, the highest wet N-deposition was detected in autumn (Fig. 2). No relationship was found between precipitation rates and N-input. Dry deposition was measured from May 2002 to July 2003 and amounted to 1.52 kg N ha⁻¹ y⁻¹, thus amounting to a total of 12.1 kg N ha⁻¹ y⁻¹ through wet and dry deposition in the first year of sampling. NO₂ deposition was at its highest in winter, whereas concentration of NH₃ deposition was at its highest in spring and summer. The forest floor received 21.6 kg N per ha⁻¹ y⁻¹ (1999) through litterfall (Herman et al., 2002).

3.3. Gas fluxes

3.3.1. Carbon dioxide emissions

Maximum CO₂ emissions were recorded in the summer 2003 and 2004 (Table 4), following a seasonal course of air and soil temperature (Fig. 3a). In 2002 the summer peak was not as pronounced and summer emissions were significantly ($p < 0.01$) lower than in the following years. In late autumn emissions decreased steadily and reached a minimum in winter (0.0–0.4 mg CO₂-C m⁻² h⁻¹).

Mean annual CO₂ emission were 11.6±1.1 mg CO₂-C m⁻² h⁻¹ (year 1) and 19.7±2.0 mg CO₂-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 CO₂ production rate in year 2.

The most influencing parameters controlling CO₂ emissions (Table 6) were soil temperature at a soil depth of 3–25 cm ($r^2=0.86$) and air temperature ($r^2=0.70$). Furthermore, a positive correlation could be detected with N-deposition ($r^2=0.62$). A negative relationship was found between CO₂ emission and soil moisture in the upper 5 cm

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($r^2 = -0.59$). All correlations were highly significant ($p < 0.001$).

3.3.2. N₂O emissions

Nitrous oxide emissions were mostly dependent on air and soil temperature, as well as soil moisture. Figure 3b shows the high spatial and temporal variability during the field survey from May 2002 until July 2004. Spatial variation between the chambers was high (mean CV: 50%) and reached a maximum in winter (CV: 350%).

Mean annual N₂O emissions averaged $4.4 \pm 0.3 \mu\text{g N}_2\text{O-N m}^{-2} \text{h}^{-1}$ (Table 4). In the course of the year highest N₂O emissions were observed in summer 2003 ($40.6 \mu\text{g N}_2\text{O-N m}^{-2} \text{h}^{-1}$). Although we missed the summer peak with the manual chamber system in year 2002, we were able to observe high N₂O emissions by the AGPS (Fig. 3b). During winter, when the site was covered with snow, even a significant uptake of atmospheric N₂O (range: -0.3 to $-3.5 \mu\text{g N}_2\text{O-N m}^{-2} \text{h}^{-1}$) could be observed. Significant differences in the seasonality of N₂O emissions between both years could only be observed for August ($p < 0.01$).

Significant correlations could be found between C- and N-emissions, and soil, meteorological and N-input data (Table 6). Log-transformed N₂O emission rates 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 ($r^2 = 0.58$). A negative dependency was found with soil moisture ($r^2 = -0.52$). Correlation analysis between daily N₂O emissions from the AGPS system and soil temperature and soil moisture revealed weaker but significant relationships ($r^2 = 0.27$ and $r^2 = -0.32$, $p < 0.001$).

Nitrate and NH₄⁺ deposition via throughfall and NO₃⁻ concentration in the mineral soil showed significant positive effects on N₂O emission ($r^2 = 0.26$, $r^2 = 0.25$, $p < 0.001$ and $r^2 = 0.41$, $p < 0.05$), even higher correlation was found with NO₃⁻ concentration in the litter layer ($r^2 = 0.44$, $p < 0.01$).

Simple regression models were insufficient for revealing dependencies of emission

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data as residuals were correlated over time. Two GARCH models could be developed to predict N₂O 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 a soil depth of 3 cm. As an effect of N-deposition on N₂O emission was discovered while carrying out the correlation analysis (Table 6), we included the monthly sum of nitrogen input (NO₃⁻ and NH₄⁺) via throughfall within model 2 and achieved an improvement of modelled N₂O 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 N₂O emissions from the AGPS showed a high temporal variability. Moreover, correlations with soil parameters were lower compared to the N₂O 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 N₂O emissions are delayed by 8 days ($p < 0.001$, $r^2 = 0.43$).

3.3.3. NO_x emissions

NO and NO₂ flux rates from soil were measured from July 2002 until November 2003 (Fig. 3c) but not during the winter months. Mean NO emissions in the vegetation period were $0.7 \pm 0.04 \mu\text{g NO-N m}^{-2} \text{ h}^{-1}$ and hence significantly higher in year 2002 ($p < 0.001$) compared to the year 2003 ($0.5 \pm 0.07 \mu\text{g NO-N m}^{-2} \text{ h}^{-1}$) when low soil N concentrations were measured. Mean NO emissions were generally lower than N₂O emission rates. The ratio NO/N₂O was 1:3. A consistent seasonal trend could not be observed: In the year 2002 highest emissions occurred in autumn, whereas in year 2003 maximum emissions were measured in spring (Fig. 3c). Lowest NO emissions or even negative fluxes were observed in November 2003. NO₂ was deposited over the entire observation period with a mean of $-0.4 \pm 0.2 \mu\text{g NO m}^{-2} \text{ h}^{-1}$ (2002) and $-0.3 \pm 0.1 \mu\text{g NO}_2 \text{ m}^{-2} \text{ h}^{-1}$ (2003).

Correlation analysis (Table 6) revealed a weak positive relationship between mean daily NO fluxes and soil temperature at the soil depth of 5 cm ($r^2 = 0.19$, $p < 0.5$), whereas

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a highly significant positive dependency could be observed with soil moisture in 5 cm, ($r^2=0.55$, $p<0.001$). 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. Actylen inhibition

By using the C₂H₂ inhibition method the reduction of N₂O to N₂ is inhibited and total N-loss, which is produced via denitrification, can be measured. The increase of N₂O production in the Acetylene-treated samples, in comparison to the samples without added C₂H₂ was between 101% and 4200% with a median of 266%. The ratio of N₂O:N₂ was 1:6. Mean N₂ production of the two experiments (n=16) was $11.6\pm 1.4 \mu\text{g N}_2 \text{ m}^{-2} \text{ h}^{-1}$ and $19.1\pm 3.9 \mu\text{g N}_2 \text{ m}^{-2} \text{ h}^{-1}$.

4. Discussion

4.1. CO₂ emissions

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 CO₂ 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 showed also 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 O₂ deficiency in soil due to diffusion restrictions (Howard and Howard, 1993). Further significant relationships could be established between biweekly mean CO₂ emissions and biweekly N-deposition rates. The cumulative soil respiration rates at our site (1–1.6 t C ha⁻¹ y⁻¹) are lower than values for temperate coniferous forests reported by Raich and Schlesinger (1992).

4.2. N₂O emissions

At our site, seasonal variations in N₂O emissions followed mainly the annual changes in soil temperature, soil moisture and the availability of N in the soil. Highest 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 high emissions by the AGPS. Correlation analysis revealed that soil temperature was the most important factor controlling N₂O emissions followed by soil moisture. 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 that for the AK site a N₂O emission maximum for 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 N₂O emissions occurred at water 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 N₂O emissions could be predicted best using soil moisture and soil temperature as predictors ($r^2=0.89$).

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This analysis also revealed that past environmental conditions (up to 12 weeks) can significantly affect actual N₂O emissions. Within the model, soil moisture showed a highly significant effect ($p < 0.001$) whereas the effect of soil temperature was lower ($p < 0.01$). Furthermore, precipitation and air temperature showed a clear influence in daily (AGPS) N₂O emissions (model 3). Here a highly significant effect of conditions during the past 8 days were observed.

Highest emissions were observed in August 2003. There are various parameters that might have contributed to the N₂O 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 NO₃⁻ pool in the soil might have played an important role in the sudden release of N₂O (Davidson et al., 2000). Highest amounts in NO₃⁻ and NH₄⁺ via throughfall reached the forest floor in August. Although, throughout the study wet N-deposition accounted for up to 31% of the variation in N₂O emission (correlation analysis) only, a strong relationship was apparent between the two factors. This high N₂O peak coincided with significant larger available soil N concentrations, in particular soil NO₃⁻. Using model 2 the relationship between biweekly measured N₂O emissions and biweekly sum of nitrogen input (NO₃⁻ and NH₄⁺) via throughfall was found by a high model efficiency ($r^2 = 0.83$). The time series analysis revealed a highly significant ($p < 0.001$) lagged effect of wet N-deposition on N₂O emission for 2 weeks, but correlations are expected for a 3-month period.

The soil at the Mühleggerköpfl is, typically, moist (mean 55%) and denitrification may have been the main source of N₂O 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 N₂O emission. ¹⁵NO₃⁻ 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 Au-

gust/September that nitrate concentration increased and we suppose that the high N_2O peak in year 2003 is the product of nitrification.

At our site winter emissions were generally low and the site even functioned as a sink for N_2O . The AGPS system, in particular, was a useful means for detecting negative fluxes. Butterbach-Bahl et al. (2002) detected negative N_2O fluxes from pine forests with moderate N-deposition whereas a pine forest with high N-loads exclusively functioned as a source of N_2O during winter. On the other hand winter emissions, comparable to the ones from the rest of the year (January 2003; $4.3 \pm 1.3 \mu\text{g } N_2O\text{-N m}^{-2} \text{ h}^{-1}$), could be observed after freeze-thaw events. These high emissions were either a result of enhanced denitrification activity or could be due to the physical release of accumulated N_2O in the snow or in the soil (Teepe et al., 2001).

4.3. NO emissions

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). We found best correlations with soil moisture and only little dependency on soil temperature. The optimum soil temperature, as found in laboratory studies (20°C) by Schindlbacher et al. (2004), could not be confirmed in the field experiment, where highest NO emissions were found at $8\text{--}10^\circ\text{C}$ 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 highest NO emissions were found in autumn and in spring, when soil water content was between 45–50%. High spring emissions were detected in May, when soil was still moist and soil temperature increased. At our site soil moisture had a stronger impact on NO emission than soil temperature. With the GARCH procedure a relationship between NO emissions and soil moisture and soil temperature could be found with a model efficiency of r^2 of 0.77 (model 4). Autoregressive parameters were estimated for a time-lag of 2 days; i.e. soil moisture and soil temperature affected NO emission over a two days period at our site.

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Soil nitrogen content contributed to high NO emission in autumn, where highest NO₃⁻-N and NH₄⁺-N concentrations were measured. As in autumn 2003 the N-pool (especially extractable NH₄⁺-N) in the soil and the litter layer was low compared to concentrations measured in autumn 2002 no increase in NO emissions could be found.

5 The effect of rewetting the soil as it was found for N₂O emissions could not be seen for NO emissions.

Soil acidity is supposed to be an important factor promoting N-losses 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 N₂ (Simek and Cooper, 2002) but revealed an order of magnitude higher N₂O 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 HNO₂ and might, therefore, be responsible for low 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 (Zechmeister-Boltenstern, pers. comm.) could be a reason for low NO-fluxes. Results of PLFA studies of European soils by (Zechmeister-Boltenstern, pers. comm.) 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 higher NO and N₂O emissions. The assumption of a well-balanced microflora was supported by the acetylene inhibition and simulation runs with the Pnet-N-DNDC where high N₂ emissions were detected and a large portion of N was fully recycled (Butterbach-Bahl, pers. comm.).

4.4. Annual N-losses

25 In both years N released in form of N₂O was between 0.3 and 0.4 kg N₂O-N ha⁻¹ y⁻¹, and 0.03 kg NO-N ha⁻¹ (Table 5). These values correspond to a yearly release of actual N input of 2.5–3.5% in form of N₂O and 0.2% in form of NO and are located in the lower

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reported percentage of deposited N which is 0–16% (N₂O) and 0–10% (NO) (Skiba et al., 2004). Through the acetylene inhibition we calculated a N₂/N₂O ratio of 6.0 and concluded a rough estimation of 2.2 kg N ha⁻¹ of annual N₂ loss. Simulated mean N₂ production by the model PnetNDNDC for years 1998–2001 (Zechmeister-Boltenstern, unpublished) was 14 kg, which would mean that more than 18% of the deposited N were lost by the complete pathway of microbial soil processes as N₂. As the acetylene inhibition was only conducted twice within the investigation period this value has to be interpreted with caution. However, it can be hypothesized that the deposited N from the atmosphere is mainly emitted as N₂ at this limestone site.

The magnitude of N₂O emissions from our site are 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). Considerable higher fluxes were measured in more acidic spruce forests, where high loads of N was deposited (Papen and Butterbach-Bahl, 1999; Butterbach-Bahl et al., 2002) and in deciduous forest ecosystems with low pH (Brumme and Beese, 1992; Borken and Brumme, 1997).

Nitric oxide emission measured in our study are low in comparison to other published NO fluxes from temperate coniferous forests. But our rates are in accordance with studies by (Johansson, 1984) who reported annual NO emissions of 0.04 kg NO-N ha⁻¹ from an unfertilized coniferous forest soil in Sweden. The majority of studies, however, revealed significantly higher values. Pilegaard et al. (1999) and Butterbach-Bahl et al. (2002) found in moderately N-affected spruce forests annual NO losses of 3.15 kg NO-N ha⁻¹ and 3.1 μg 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 higher in more acidic soils compared to N₂O fluxes (Yamulki et al., 1997).

Nitrogen oxide emissions could be predicted with high efficiencies. Nitrous oxide emissions measured by manual chambers revealed an r² of 0.89 (model 1) and an r² of 0.83 (model 2). Through model 2, where N-deposition is the only independent

variable, annual emission rates could be estimated better than with model 1, where soil moisture and soil temperature were the crucial parameters. Especially in year 2003, where high emissions were detected in August, the predicted emissions with model 2 revealed a better accuracy as model 1. High variations in N₂O emissions measured by the AGPS led to an overestimation of N₂O emissions through model 3 (21–27%). Nitric oxide emissions predicted with model 4 could be predicted with an r² of 0.77 and annual simulated fluxes were in accordance with measured annual NO emissions.

It can be concluded that with time series analysis lagged effects of the controlling factors soil moisture, soil temperature and N-deposition on N₂O and NO emissions could be revealed. In particular significant two weeks delayed response of N₂O emission to N-deposition was observed. Nitric oxide emissions were three times lower compared to N₂O emissions and total losses 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 N₂.

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Table 1. Site and soil characteristics of the investigation site AK.

Location	47°34′50″ N 11°38′21″ E
Vegetation	<i>Aposerido-Fagetum caricetosum albae</i> – <i>Carici albae-Fagetum</i> ^{a)}
Stand age [y]	127
Exposition, elevation [m]	N, 895 m a sl.
Tree height [m]	19.1
Basal area [m ² ha ⁻¹]	40
Soil type	Rendzic Leptosols / Chromic Cambisol
Soil texture	loam
Soil acidity 0-7cm (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)	0.3
N _{tot} (mg g ⁻¹)	9 ^{c)}
C _{org} (mg g ⁻¹)	150 ^{c)}

^{a)}Englisch and Starlinger 1995, ^{b)} Mean of years 1998-2003, ^{c)} Mutsch 2001.

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Table 2. Mean soil nitrogen [$\mu\text{g N g}^{-1} \text{ dw}$] and pH (CaCl_2) in the litter layer and in the upper 7 cm mineral soil in year 1 and year 2 at AK.

	year 1	year 2
Litter layer		
NH ₄ ⁺	65.8 (8.5)	43.1 (4.0)
NO ₃ ⁻	31.4 (4.4)	18.3 (2.2)
pH (CaCl ₂)	6.1 (0.1)	5.8 (0.1)
Mineral soil		
NH ₄ ⁺	21.0 (3.0)	8.8 (1.2)
NO ₃ ⁻	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.

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Table 3. Wet and dry deposition [$\text{kg N ha}^{-1} \text{y}^{-1}$], precipitation via throughfall, soil nitrogen and pH (CaCl_2) in study year 1 and study year 2 at AK.

	year 1	year 2
Precipitation [mm]	1416	1067
N-input by wet deposition/throughfall		
NH ₄ ⁺	3.5	4.6
NO ₃ ⁻	7.1	7.3
Sum of wet deposition	10.6	11.9
N-input by dry deposition		
NH ₃	0.56	n.d.
NO ₂	0.96	n.d.
deposition	1.52	n.d.

n.d. = not determined.

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Table 4. Mean annual CO₂-C, N₂O-N and mean NO-N losses in the vegetation period, minimum and maximum values and number of observations at AK for the two investigation years.

		CO ₂ -C [mg C m ⁻² h ⁻¹]	N ₂ O [μg N m ⁻² h ⁻¹]	NO
year 1	mean	11.6	4.5	0.7
	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
	min-max	(0.2-83.0)	(-2.9-40.6)	(-0.1-7.6)
	N	96	288	145

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Table 5. Measured and predicted annual CO₂-C, N₂O-N losses (± S.E) from the manual chambers for the two investigation years at the site AK; N₂O-N (AGPS) and NO-N losses are calculated for June–November 2002 (year 1) and May–November 2003 (year 2).

	CO ₂ kg C ha ⁻¹ y ⁻¹		N ₂ O-manual		N ₂ O-AGPS kg N ha ⁻¹ y ⁻¹		NO	
	measured	measured	predicted ¹⁾²⁾	measured	predicted ³⁾	measured	predicted ⁴⁾	
year 1	1020±241	0.30±0.11	0.36±0.04 0.33±0.03	0.22±0.02	0.28±0.01	0.03±0.002	0.03±0.001	
year 2	1636±283	0.41±0.09	0.26±0.04 0.38±0.04	0.19±0.02	0.23±0.01	0.03±0.004	0.03±0.004	

^{1)–4)} Model 1 - Model 4.

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Table 6. Matrix of Pearson correlation coefficients for significant relationships of mean C- and N-emissions (M=manual chambers, A=AGPS) and soil-, meteorological- and N-input data at the site AK. Total N-deposition (Total N_{dep}) is calculated from the first investigation year when dry deposition was measured.

	lnCO ₂	lnN ₂ O M	lnN ₂ O A	lnNO
CO ₂		0.58 ***		
N ₂ O	0.58 ***			
NO				
Air temperature	0.70 ***	0.58 ***	0.16 *	
Soil temperature	0.86 ***	0.64 ***	0.27 ***	0.19 **
Soil moisture	-0.59 ***	-0.52 ***	-0.32 ***	0.55 ***
NO ₃ ⁻ litter layer	0.39 *	0.44 **		
NO ₃ ⁻ mineral soil		0.41 *		
TF NO ₃ ⁻	0.43 ***	0.26 ***		
TF NH ₄ ⁺	0.21 **	0.25 ***		
TF sumN	0.46 ***	0.31 ***		
DRY_NO ₂	-0.66 *	-0.37 **		
DRY_NH ₃	0.71 ***	0.37 **		
Total N_{dep}	0.62 ***	0.33 *		

TF = throughfall, DRY = dry deposition. A moving average of 2 was applied to deposition data. Asterisk indicates the statistic significance (* p<0.05, **p<0.01, ***p<0.001).

Table 7. Parameter estimation for the autoregression models 1 to 4 to predict N₂O and NO emissions from the study site, AK. Independent variables (x_1) and (x_2) for the individual models are shown in the table (regression coefficients). Sample period is from April 2002–May 2004.

<i>Model</i>		1	2	3	4
<i>independent variable (y_t):</i>		N ₂ O	N ₂ O	N ₂ O	NO
<i>Intercept: β₀</i>		-12.9481 **	1.9971 ***	7.0895 ***	1.0429 ***
<i>regression coefficients of the independent variables (x₁) and (x₂) with significance level:</i>					
<i>β₁</i>	(<i>x₁</i>) soil moist.	0.2885 ***			-0.0034 *
	(<i>x₁</i>) wet N dep.		-0.4061 *		
	(<i>x₁</i>) precip.			0.0851 ***	
<i>β₂</i>	(<i>x₂</i>) soil temp.	0.4753 **			-0.0308 *
	(<i>x₂</i>) air temp.			-0.1992 *	
<i>total R²:</i>		0.89	0.83	0.43	0.77
<i>n</i>		147	213	260	217

Regression coefficients and model parameters are statistically significant at the * p<0.05, ** p<0.01, *** p<0.001 level.

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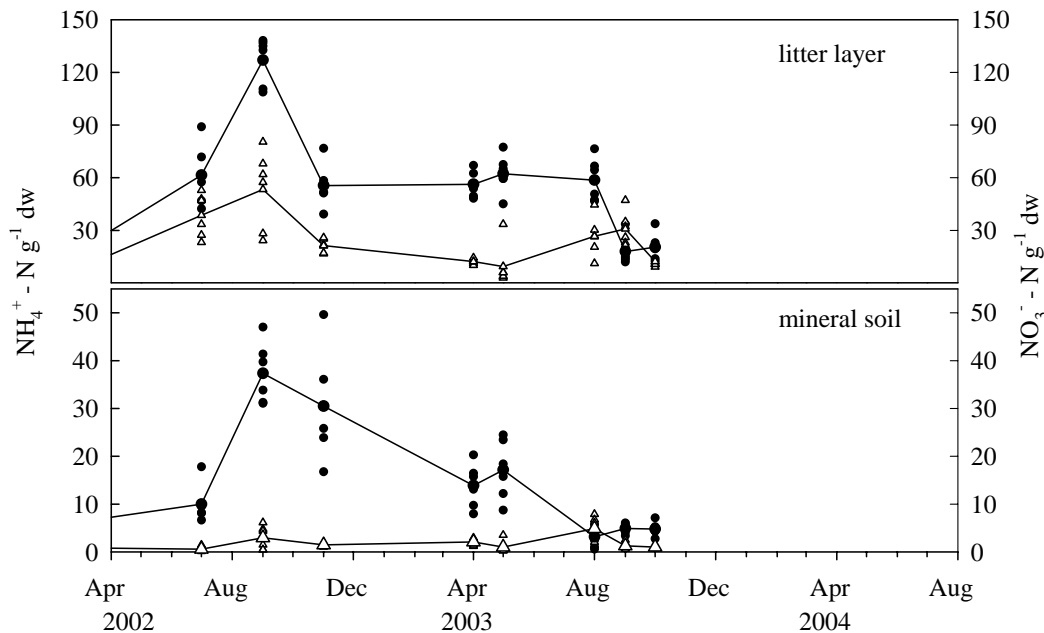


Fig. 1. Extractable NH₄⁺ (circles) and NO₃⁻ (triangles) in the litter layer and in the mineral soil at AK in the investigation years. Pooled samples (n=4) were taken from around the individual chambers.

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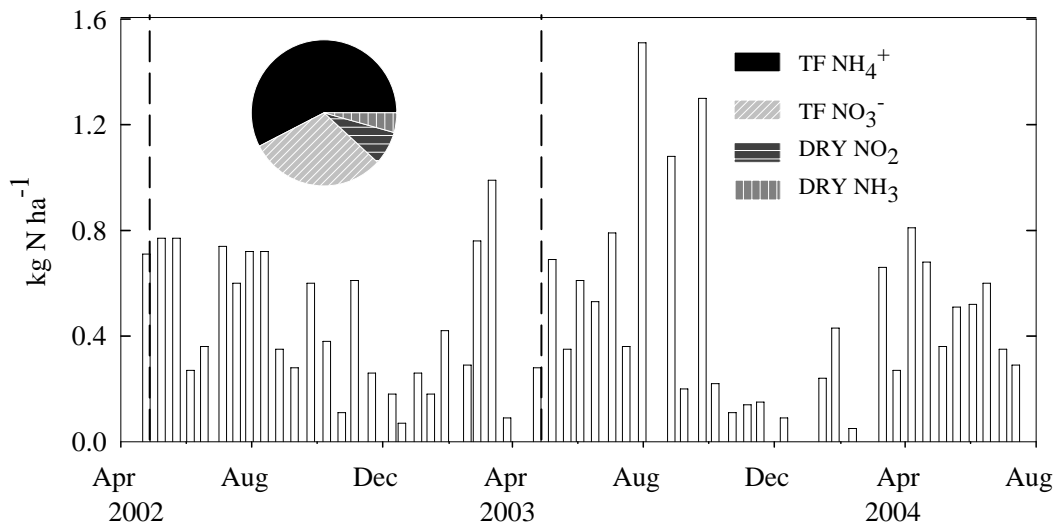


Fig. 2. Bar chart: Biweekly N-input (kg N ha⁻¹) at AK measured in the two investigation years. Note: Dry deposition was measured only in the first year. Pie chart: Portion of throughfall (TF NH₄⁺, TF NO₃⁻) and dry deposition (DRY NO₂, DRY NH₃) on annual N-input (kg N ha⁻¹) in the first investigation year.

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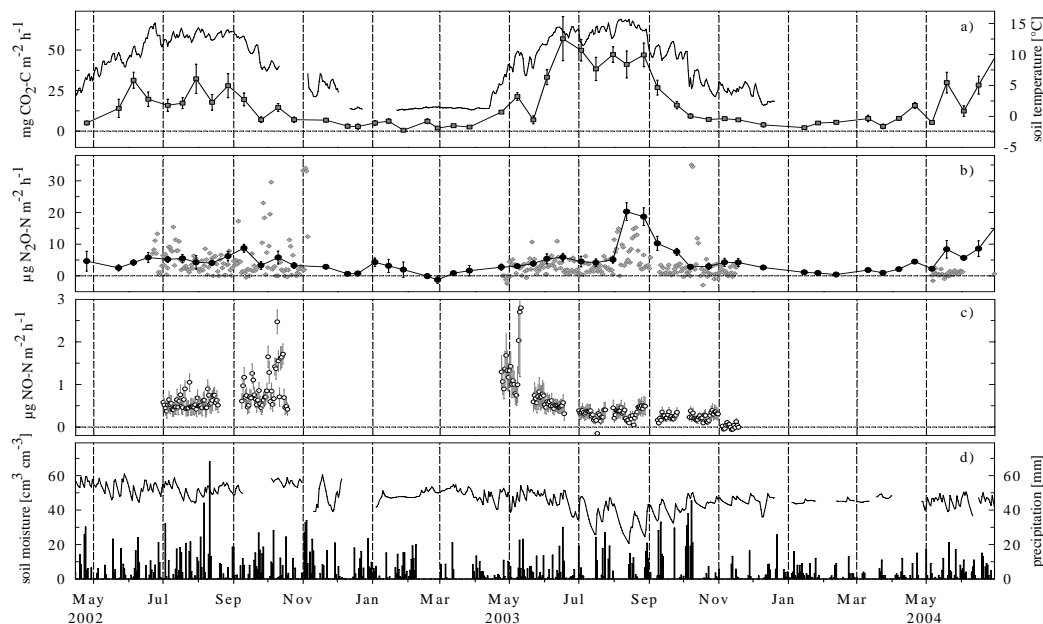


Fig. 3. (a) Mean CO₂ emissions (squares ± S.E.) measured with the manual chambers and soil temperature [5 cm] (black line), (b) mean N₂O emissions from manual (circles ± S.E.) and automatic (diamonds) chambers, (c) mean NO emissions (± S.E.) and, (d) daily precipitation and soil moisture [5 cm] at the study site AK from May 2002 to July 2004.

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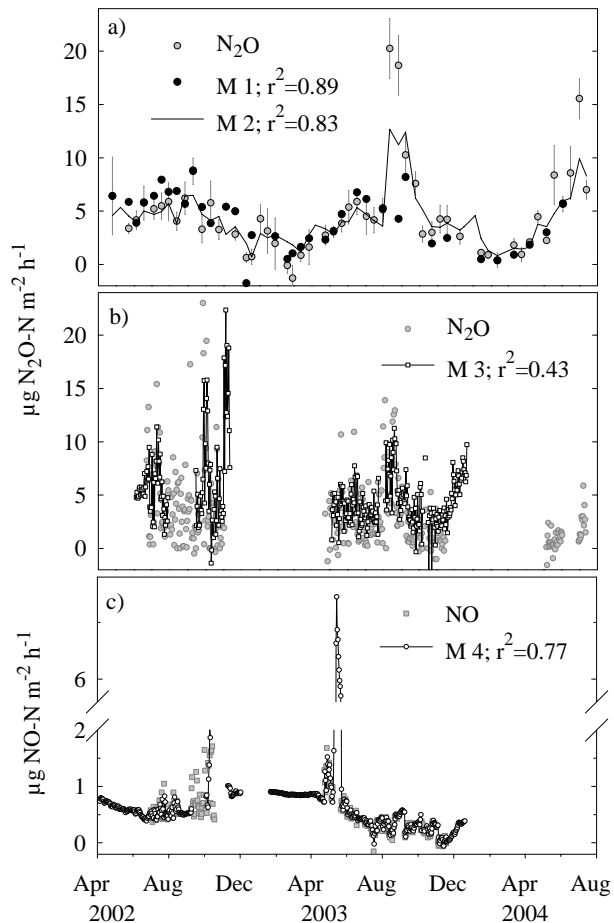


Fig. 4. Predicted versus measured N₂O and NO emissions at AK between April 2002 and July 2004. Independent variables are soil moisture and soil temperature for model 1 (M 1) and model 4 (M 4); N-deposition (NH₄⁺ and NO₃⁻) for model 2 (M 2) and, precipitation and air temperature for model 3 (M 3).

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