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**N<sub>2</sub>O, NO and CH<sub>4</sub> exchange, and microbial N turnover**

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# N<sub>2</sub>O, NO and CH<sub>4</sub> exchange, and microbial N turnover over a Mediterranean pine forest soil

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## Abstract

Trace gas exchange of  $\text{N}_2\text{O}$ ,  $\text{NO}/\text{NO}_2$  and  $\text{CH}_4$  between soil and the atmosphere was measured in a typical Mediterranean pine (*Pinus pinaster*) forest during two intensive field campaigns in spring and autumn 2003. Furthermore, gross and net turnover rates of N mineralization and nitrification as well as soil profiles of  $\text{N}_2\text{O}$  and  $\text{CH}_4$  concentrations were determined. For both seasons a weak but significant  $\text{N}_2\text{O}$  uptake from the atmosphere into the soil was observed. During the unusually dry and hot spring mean  $\text{N}_2\text{O}$  uptake was  $-4.32 \mu\text{g N m}^{-2} \text{ h}^{-1}$ , whereas during the wet and mild autumn mean  $\text{N}_2\text{O}$  uptake was  $-7.8 \mu\text{g N m}^{-2} \text{ h}^{-1}$ . The observed  $\text{N}_2\text{O}$  uptake into the soil was linked to the very low availability of inorganic nitrogen at the study site. Organic layer gross N mineralization decreased from  $5.06 \text{ mg N kg}^{-1} \text{ SDW d}^{-1}$  in springtime to  $2.68 \text{ mg N kg}^{-1} \text{ SDW d}^{-1}$  in autumn. Mean NO emission rates were significantly higher in springtime ( $9.9 \mu\text{g N m}^{-2} \text{ h}^{-1}$ ) than in autumn ( $1.4 \mu\text{g N m}^{-2} \text{ h}^{-1}$ ). A significant positive correlation between NO emission rates and gross N mineralization as well as nitrification rates was found. The negative correlation between NO emissions and soil moisture was explained with a stimulation of aerobic NO uptake under N limiting conditions. Since  $\text{NO}_2$  deposition was continuously higher than NO emission rates the examined forest soil did function as a net  $\text{NO}_x$  sink. Observed mean net  $\text{CH}_4$  uptake rates were in spring significantly higher ( $-73.34 \mu\text{g C m}^{-2} \text{ h}^{-1}$ ) than in autumn ( $-59.67 \mu\text{g C m}^{-2} \text{ h}^{-1}$ ). Changes in  $\text{CH}_4$  uptake rates were strongly negatively correlated with changes in soil moisture. The  $\text{N}_2\text{O}$  and  $\text{CH}_4$  concentrations in different soil depths revealed the organic layer and the upper 10 cm of mineral soil as the most important soil horizons for  $\text{N}_2\text{O}$  and  $\text{CH}_4$  consumption.

## 1. Introduction

The atmospheric trace gases nitrous oxide ( $\text{N}_2\text{O}$ ), nitric oxide (NO), nitrogen dioxide ( $\text{NO}_2$ ) and methane ( $\text{CH}_4$ ) have a major effect on the development of global climate.

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The global warming potential of N<sub>2</sub>O is about 300 times higher than that of carbon dioxide (CO<sub>2</sub>) over a time horizon of 100 years (IPCC, 2001). In addition, it is involved in the destruction of stratospheric ozone (Crutzen, 1970; Davidson, 1991). The concentration of N<sub>2</sub>O in the atmosphere is continuously increasing at a rate of approx. 0.25% yr<sup>-1</sup> (IPCC, 2001). NO and NO<sub>2</sub> (NO<sub>x</sub>) are secondary radiatively active trace gases, taking part in reactions eventually leading to the production of tropospheric ozone (O<sub>3</sub>), a radiatively active greenhouse gas (Crutzen, 1995; Hall et al., 1996; Atkinson, 2000). N<sub>2</sub>O as well as NO<sub>x</sub> are facultative by-products of the major microbiological nitrogen cycling processes in soils, nitrification and denitrification (Butterbach-Bahl et al., 1997; Knowles, 2000). Forest soils have been identified to be significant sources for these N trace gases (Brumme and Beese, 1992; Skiba et al., 1994; Papen and Butterbach-Bahl, 1999; Gasche and Papen, 1999), but also net N<sub>2</sub>O or NO consumption by soils has been observed (Baumgärtner et al., 1996; Schiller and Hastie, 1996; Goossens et al., 2001; Papen et al., 2001). Soil aeration (Simojoki and Jaakkola, 2000; Vor et al., 2003), N availability (Bouwman, 1996; Del Grosso et al., 2000) and acidity (Granli and Bøckmann, 1994) have been identified to be key factors influencing exchange dynamics of N<sub>2</sub>O and NO<sub>x</sub> between soils and the atmosphere.

CH<sub>4</sub> is next to H<sub>2</sub>O and CO<sub>2</sub> the third most important greenhouse gas, and its atmospheric concentration is increasing constantly due to anthropogenic activities (IPCC, 2001). Soils have been identified as a significant sink for atmospheric CH<sub>4</sub>, and it is estimated that CH<sub>4</sub> uptake activities of soils represent three to nine percent of the global atmospheric CH<sub>4</sub> sinks (Prather et al., 1995). Well aerated forest soils seem to claim a major role in this context (Smith et al., 1994; King, 1997; Papen et al., 2001). Methane oxidation leading to a CH<sub>4</sub> uptake from the atmosphere into the soils is catalysed by soil microorganisms, most likely chemolithotrophic CH<sub>4</sub> oxidisers (King and Schnell, 1998; Dunfield et al., 1999), mainly localized in the uppermost layers of forest mineral soils (Steinkamp et al., 2001; Butterbach-Bahl and Papen, 2002). Methane oxidation generally occurs in well aerated soils, although an anaerobic pathway for CH<sub>4</sub> oxidation has also been described (Segers, 1998).

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While there is increasing knowledge about the role of agricultural soils and some natural ecosystems concerning N<sub>2</sub>O, NO<sub>x</sub> and CH<sub>4</sub> flux dynamics in the temperate and tropical zone, only little information exists about the exchange of these trace gases between forest soils of the Mediterranean climate zone and the atmosphere. In order to expand the applicability of process-oriented models, aiming to establish regional inventories of biogenic greenhouse gases from forest soils for a wider range of climatic zones, there is an urgent need for in situ trace gas exchange data in high temporal resolution, especially in the Mediterranean area (Butterbach-Bahl and Kiese, 2005).

Therefore, the results from trace gas flux measurements in a typical Mediterranean forest ecosystem obtained during the two seasons, which are characteristic for the Mediterranean climate zone (spring/early summer and autumn) are presented in this paper. Furthermore gross and net rates of microbiological N turnover processes – here N mineralization, nitrification – either directly or indirectly involved in N trace gas production were determined, and trace gas concentrations in different soil depths were measured.

## 2. Study site and methods

### 2.1. Site description

The study site is located in the region of Tuscany in Italy, which belongs to the Mediterranean climate type. It is located inside the regional park San Rossore which ranges along the Tyrrhenian Sea between the cities of Viareggio and Livorno. The experimental area is located 800 m east from seashore in a 600 m wide strip of *Pinus pinaster* forest. The exact coordinates are 10°17'3" east and 43°43'58" north.

The pines were planted on the sandy calcareous regosoil in 1964 and since then developed to a very homogeneous 20 m high stand with only few added *Pinus pinea* and some epigynous *Quercus ilex*. Only sparse ground vegetation can be found, mainly consisting of *Erica arborea*, *Phyllirea angustifolia*, *Rhamnus alaternus* and *Myrtus com-*

*munis.*

Mean annual air temperature is 14.1 °C and annual mean precipitation is 918 mm with a typical Mediterranean seasonality over the year, characterized by a wet and mild winter as well as an arid and hot summer. The annual N deposition is about 12 kg N ha<sup>-1</sup>. In the organic layer the pH value (0.01 m CaCl<sub>2</sub>) is 4.4 and the C/N ratio is 32.5, in the upper layer of the mineral soil (0–5 cm) the pH value is 5.7 and the C/N ratio is 30.0.

## 2.2. Measurements of N<sub>2</sub>O, NO/NO<sub>2</sub> and CH<sub>4</sub> trace gas fluxes

Fluxes of the trace gases N<sub>2</sub>O, NO/NO<sub>2</sub> and CH<sub>4</sub> were monitored during two field campaigns in 2003, proceeding from the end of April until the beginning of June and from the end of October until the beginning of December, respectively, thus covering the two seasons of the Mediterranean zone during which the highest stimulation of soil microbial activity can be expected due to sufficient soil moisture and sufficiently high soil temperatures. Precipitation and soil/air temperature was continuously determined in close vicinity to the study site (50 m) using a tipping-bucket rain gauge (Delta-T, Cambridge, Great Britain) and Pt 1000 thermocouples (Thiess, Göttingen, Germany), respectively.

Fully automated measuring systems were used to determine the rates of N<sub>2</sub>O, NO/NO<sub>2</sub> and CH<sub>4</sub> exchange between the soil of the study site and the atmosphere (Butterbach-Bahl et al., 1997). The trace gas fluxes were determined in hourly (NO/NO<sub>2</sub>) and two-hourly resolution (N<sub>2</sub>O/CH<sub>4</sub>), respectively. The measuring system for determination of N<sub>2</sub>O and CH<sub>4</sub> fluxes consisted of five static measuring chambers (side lengths: 0.7 m × 0.7 m; height: 0.3 m), an automated gas sampling device with sample air pump and flow controller and a gas chromatograph equipped with a FID for CH<sub>4</sub> analyses and a <sup>63</sup>Ni ECD for N<sub>2</sub>O detection. Calibration of the gas chromatograph was performed automatically every 2 h using a gas mixture containing 4020 ppbv CH<sub>4</sub> and 402 ppbv N<sub>2</sub>O in synthetic air (Messer Griesheim, Munich, Germany). For further details of the measuring system see Butterbach-Bahl et al. (1997) and Breuer et

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al. (2000).

To determine the fluxes of NO/NO<sub>2</sub> five dynamic measurement chambers (side lengths: 0.5 m×0.5 m; height: 0.3 m) and one dynamic reference chamber were used. In contrast to the measuring chambers, the reference chamber had a gas tight bottom made of perspex. Furthermore, the system consisted of an automated sampling device, a sample air pump and flow controller to achieve a sample air flow of approximately 130 l min<sup>-1</sup>, a chemoluminescence detector (CLD 770 AL ppt, Ecophys AG, Dürnten, Switzerland), a photolysis converter to allow the determination of NO<sub>2</sub> (PLC 760, Ecophys AG, Dürnten, Switzerland) and an ozone analyzer (TE 49 C, Thermo-Environmental Instruments Inc., Franklin, MA, USA) in order to correct NO/NO<sub>2</sub> fluxes for reactions of NO with ambient O<sub>3</sub> (Butterbach-Bahl et al., 1997). Calibration of the chemoluminescence detector was performed at least weekly using 10 ppb NO in synthetic air produced by dilution of standard gas (0.997 ppm NO in N<sub>2</sub>, Messer-Griesheim, Germany) with synthetic air (80% N<sub>2</sub>, 20 % O<sub>2</sub>, Messer-Griesheim, Germany) using a computerized multi gas calibrator (Enviroics 100, Enviroics Inc., West-Wellington, USA). Efficiency of photolytic conversion of NO<sub>2</sub> into NO was determined weekly as described by Butterbach Bahl et al. (1997). Exact descriptions of the automated measuring systems including design of chambers, gas chromatographic conditions and modes of calculation of flux rates can be found in detail in previous publications (Butterbach-Bahl et al., 1997, 1998; Gasche and Papen, 1999; Steinkamp et al., 2001).

Beside trace gas fluxes environmental parameters as soil temperature in different depths and air temperature were recorded.

The ten measuring chambers were installed in five pairs of one dynamic and one static chamber close to each other. These pairs were distributed randomly over the experimental area. At latest after 14 days the position of each chamber was changed to ensure a representative monitoring of the study site and to minimize the influence of the chambers on soil conditions.

At the end of the measuring campaign in spring 2003 an artificial rainfall experiment was implemented. Three static and three dynamic chambers where watered

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with  $201\text{ m}^{-2}\text{ day}^{-1}$  during two three day periods within a three day break in-between (equalling 120 mm rainfall in total).

### 2.3. Determination of $\text{N}_2\text{O}$ and $\text{CH}_4$ concentrations at different soil depths

During the field campaign in autumn 2004,  $\text{N}_2\text{O}$  and  $\text{CH}_4$  concentrations were measured in triplicate at four different soil depths (0, 10, 20 and 30 cm). The 0 cm depth thereby represented exactly the transition between the organic layer and the mineral soil. For installation of the sampling tubes a 40 cm deep manhole was dug, from which holes with the same diameter as the sampling tubes were drilled approx. 0.3 m horizontally into the soil profile. After installation the manhole was refilled with soil. A sampling unit consisted of a 0.3 m long (diameter 5 mm) gas permeable but hydrophobic Accurel<sup>®</sup> polypropylene tube (Membrana, Wuppertal, Germany) linked with a 1/8" (3 mm diameter) steel pipe leading vertically to the surface. The end of the steel pipe was closed with a rubber septum, thus gas samples could be taken with a 10 ml gas tight syringe (Baton Rouge, Louisiana, USA). Soil air samples were drawn every three days (eleven sampling days during autumn field campaign in total) and analysed immediately with the gas chromatograph described before using a manual injection unit (Breuer et al., 2000).

### 2.4. $^{15}\text{N}$ pool dilution technique for determination of gross N mineralization and gross nitrification rates

After removal of measuring chambers soil samples were taken precisely from the soil area covered by the individual chambers. The soil samples were used to determine the gross N mineralization and gross nitrification rates applying the  $^{15}\text{N}$  pool dilution technique. During the field campaign in springtime gross N mineralization and gross nitrification were determined for the organic layer, in autumn gross N mineralization for both, organic layer and mineral soil (0–5 cm soil depth).

The soil samples were sieved (4 mm and 3.15 mm mesh width for organic layer and

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mineral soil, respectively) in order to homogenize them. The ammonium (NH<sub>4</sub><sup>+</sup>) pool of the samples was marked using a (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution with 6 % <sup>15</sup>N enrichment. The moisture content was measured gravimetrically by oven drying soil samples at 105 °C for 24 h. Each sample was subdivided into six equal portions. After a pre-incubation time of 16 h the first half of the sub samples was extracted with 1 M KCl, the second half after an additional incubation time of 24 h under in situ conditions. KCl soil mixtures were shaken 30 min and filtered through glass microfibre filters (Whatman GF/A, Springfield, Great Britain). NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> content of the KCl soil extracts was determined colorimetrically by a commercial laboratory (Dr. Janssen, Gillersheim, Germany) following the VD LUFA Method A 6141 (Hoffmann, 1991). 0.25 g of MgO were added to 30 ml of the KCl extracts to release NH<sub>3</sub> which was captured on a piece of ashless filter paper (Whatman No. 42, Springfield, Great Britain) acidified with 2.5 M KHSO<sub>4</sub>. The <sup>14/15</sup>N-isotope ratio of the nitrogen captured by the dried filter paper was analysed at the Risø National Laboratory (Roskilde, Denmark) using an elemental analyser (EA 1110, Carlo Erba Instruments, Milan, Italy) and a mass spectrometer (MAT Delta Plus, Thermo Finnigan, Bremen, Germany).

For determination of gross nitrification rates the soil nitrate pool was marked using a KNO<sub>3</sub> solution with 6% <sup>15</sup>N enrichment. The experimental procedure to identify the <sup>14/15</sup>N ratio followed the same laboratory series as described for gross N mineralization. However, after MgO was added, KCl soil solutions were shaken until all NH<sub>4</sub><sup>+</sup> was exhausted. Afterwards 0.25 g Devarda alloy (50% Cu; 45% Al; 5% Zn) was added to reduce NO<sub>3</sub><sup>-</sup> to NH<sub>4</sub><sup>+</sup> which was captured on filter papers and further analysed as described above.

## 2.5. Buried bag incubations to determine net N-mineralization and nitrification rates

Tripled replicates of soil samples were taken each measuring campaign for organic layer and mineral soil (0–5 cm). One half was analysed immediately, the other half was incubated in buried bags on the study site to be analysed at the end of the measuring



campaign. Soil was sieved and moisture content was detected gravimetrically. KCl soil extracts were gained and both,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  content were determined as described above (Sect. 2.4).

## 2.6. Statistics

5 For analyzing the normal distribution of the data the Kolmogorov-Smirnov test was performed. For normally distributed data the t-test was applied to identify significant differences between data sets. As N and C trace gas fluxes were non-normal distributed the non-parametric Mann-Whitney test was performed here instead. Statistical analyses were calculated using SPSS 8.0 and SigmaPlot 2000 (SPSS Inc., Chicago, USA). Regressions and correlations were fitted and computed using Microcal Origin  
10 6.1 (Microcal Software, Northampton, USA).

## 3. Results

### 3.1. $\text{N}_2\text{O}$ , $\text{NO}/\text{NO}_2$ and $\text{CH}_4$ trace gas fluxes

15 During almost the entire two measuring periods an  $\text{N}_2\text{O}$  uptake from the atmosphere into the soil was observed. Mean  $\text{N}_2\text{O}$  uptake during the spring campaign with hot and dry weather conditions was significantly lower as compared to the field campaign in autumn when mild and wet weather prevailed (Figs. 1 and 2; Table 1). The mean water content ( $\pm\text{SE}$ ) of the organic layer in spring was  $57.6\pm 6.3\%$  (SDW=Soil Dry Weight), whereas in autumn it was significantly higher ( $123.5\pm 9.1\%$ ) due to wetter  
20 weather conditions. Simulated rainfall during the spring campaign did not result in significant changes of the magnitude or direction of  $\text{N}_2\text{O}$  fluxes. However, the mean water content of the organic layer in the watered chambers seven days after the last simulated rainfall event was significantly higher ( $84.7\pm 8.1\%$ ) than in the non-watered control chambers ( $29.8\pm 5.2\%$ ). Also the magnitude of  $\text{NO}_x$  fluxes was rather low (Figs. 1 and

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2; Table 1). Mean NO emissions dropped significantly from  $9.9 \mu\text{g N m}^{-2} \text{h}^{-1}$  in spring-time to  $1.4 \mu\text{g N m}^{-2} \text{h}^{-1}$  in autumn. Mean NO<sub>2</sub> deposition was in a range of  $-23$  to  $-24 \mu\text{g N m}^{-2} \text{h}^{-1}$  and showed only a slight seasonal variation, which, however, was not significantly different. Since NO<sub>2</sub> deposition was continuously higher than NO emissions, the forest soils were net sinks for NO<sub>x</sub>, during both measuring campaigns. For a few days in autumn even an uptake of NO by the soil was observed (Fig. 2). Like for N<sub>2</sub>O fluxes, no significant positive or negative effects of simulated rainfall on NO<sub>2</sub> fluxes could be demonstrated. However, NO emissions were significantly lower in watered chambers than in non-watered chambers (Fig. 1).

10 CH<sub>4</sub> uptake rates differed significantly between spring and autumn measurements. Mean methane uptake rates from the atmosphere into the soil were significantly higher in springtime ( $-73.3 \pm 2.7 \mu\text{g C m}^{-2} \text{h}^{-1}$ ) than in autumn ( $-59.7 \pm 2.3 \mu\text{g C m}^{-2} \text{h}^{-1}$ ) (see also Figs. 1 and 2; Table 1). This result is underlined by the watering experiment during the spring field campaign. Here, simulated rainfall led to a significant decrease of CH<sub>4</sub> uptake rates, while during the following dry period CH<sub>4</sub> uptake increased again (Fig. 1).

### 3.2. N<sub>2</sub>O and CH<sub>4</sub> concentrations at different soil depths

The observation of a net uptake of atmospheric N<sub>2</sub>O and CH<sub>4</sub> by the soil is further supported by measurements of N<sub>2</sub>O and CH<sub>4</sub> gas concentrations in different soil depths. N<sub>2</sub>O concentrations measured in 0–20 cm soil depth were approx. 1–2% lower than atmospheric N<sub>2</sub>O concentrations. In 30 cm soil depth soil air N<sub>2</sub>O concentrations increased to values slightly above atmospheric N<sub>2</sub>O concentrations (Table 2), thus indicating that N<sub>2</sub>O production in this soil depth exceeds N<sub>2</sub>O consumption (Table 2). CH<sub>4</sub> concentrations decreased continuously with increasing soil depth to values as low as 0.35 ppmv CH<sub>4</sub> in 30 cm soil depth. However, the decline in CH<sub>4</sub> concentration was strongest between 0–10 cm soil depth, where the CH<sub>4</sub> concentration reached only 40% of the ambient air value.

### 3.3. Inorganic N content and microbial N turnover rates

Soil ammonium and nitrate concentrations in the organic layer and mineral soil were significantly higher in spring than in autumn (Table 3). In both campaigns ammonium as well as nitrate concentrations were approx. 3–12 times higher in the organic layer as compared to the mineral soil. The same trend was also found with regard to gross N mineralization. Highest gross N mineralization rates were again found in spring with  $5.06 \pm 0.68 \text{ mg N kg}^{-1} \text{ SDW d}^{-1}$  in the organic layer of the forest soil, whereas gross N mineralization rates in autumn were approx. a factor of two lower. Gross N mineralization in the mineral soil was only determined during the autumn measuring campaign and rates for the mineral soil were found to be approx. 5 times lower ( $0.43 \pm 0.05 \text{ mg N kg}^{-1} \text{ SDW d}^{-1}$ ) than in the organic layer. Gross nitrification rates in the organic layer were measured only during the spring measuring campaign and were identified to be about seven times lower ( $0.73 \pm 0.26 \text{ mg N kg}^{-1} \text{ SDW d}^{-1}$ ) than corresponding gross N mineralization rates. Net N mineralization rates were up to five fold lower than gross rates. Compared to net N mineralization rates net nitrification rates were at least two to three magnitudes lower and close to the detection limit (Table 3).

### 3.4. Relation between trace gas fluxes, gross N turnover rates, $\text{NO}_3^-$ concentrations and organic layer water content

There was only a weak and insignificant relationship between chamber  $\text{N}_2\text{O}$  fluxes and corresponding organic layer gross N turnover rates and  $\text{NO}_3^-$  and water contents (Figs. 3A and 3B; Table 4). However, for NO fluxes a significant positive correlation with gross N mineralization rates, gross nitrification rates as well as with  $\text{NO}_3^-$  content was found. For chambers with high NO emission rates also high gross N turnover rates and elevated  $\text{NO}_3^-$  concentrations in the soil were detected (Figs. 3C and 3D; Table 4). Furthermore, NO emission rates were negatively correlated with organic layer water content. As  $\text{NO}_2$  deposition rates are strongly affected by NO emission rates, high N turnover rates also led indirectly to a significant increase of  $\text{NO}_2$  deposition rates.

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Chamber CH<sub>4</sub> uptake rates correlated significantly as well with corresponding organic layer gross N mineralization rates as with NO<sub>3</sub><sup>-</sup> and water contents. No significant relationship was found between CH<sub>4</sub> uptake and gross nitrification rates, which were determined only during the spring field campaign (Table 4). Despite the lack of data for gross nitrification during the autumn field campaign still a significantly positive linear relationship between organic layer gross nitrification rates and water content was found. High NO<sub>3</sub><sup>-</sup> values during the dry conditions of the spring field campaign and low NO<sub>3</sub><sup>-</sup> concentrations during the wet conditions of the autumn field campaign yielded a significant relationship between organic layer NO<sub>3</sub><sup>-</sup> and water content (Table 4).

#### 4. Discussion

The N<sub>2</sub>O fluxes presented in this paper are among the first determined in high temporal and spatial resolution for forest ecosystems in the Mediterranean climate zone (see also Butterbach-Bahl and Kiese, 2005). Previous studies showed that Mediterranean forest soils are mostly weak N<sub>2</sub>O emitters (<10 μg N m<sup>-2</sup> h<sup>-1</sup>) or even temporarily sinks for atmospheric N<sub>2</sub>O (Fenn et al., 1996; Musacchio et al., 1996; Bernal et al., 2003; Butterbach-Bahl and Kiese, 2005). However, our study is the first which demonstrates that Mediterranean forest soils can act as a weak but significant sink for atmospheric N<sub>2</sub>O over longer time periods. The mean annual N<sub>2</sub>O uptake for the pine forest at San Rossore was estimated to be approx. 0.5 kg N ha<sup>-1</sup> yr<sup>-1</sup>.

Up to now the only microbial process known to consume N<sub>2</sub>O is denitrification, which mainly occurs under prevailing anoxic conditions (Conrad, 2002). For that reason one should assume that rainfall may increase N<sub>2</sub>O consumption, since increased soil moisture should increase anaerobiosis in soils. As a matter of fact, in our experiments significantly higher N<sub>2</sub>O uptake rates were found at higher water contents in autumn as compared to spring at very low soil water contents. However, in our simulated rainfall experiments no positive effect of simulated rainfall on N<sub>2</sub>O uptake could be demonstrated. Moreover, there was no significant relationship between mean chamber values

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of N<sub>2</sub>O fluxes and corresponding organic layer moisture. Furthermore, the sandy soil found at the San Rossore study site should be very well aerated even under wet conditions (max. 200% water content for the organic layer). To explain these observations one may consider the findings by Robertson et al. (1989, 1995) who described that common heterotrophic nitrifying bacteria like *Alcaligenes faecalis* and *Thiosphaera pantotropha* are often able to denitrify under aerobic conditions. Wrage et al. (2001) hypothesized that aerobic denitrification by heterotrophic nitrifiers mainly occurs at high soil O<sub>2</sub> concentration, low soil N but high soil C contents. This parameter combination is in perfect agreement with the site properties found at San Rossore and therefore may explain our observation of prevailing net atmospheric N<sub>2</sub>O uptake. Furthermore, the measurements of N<sub>2</sub>O soil air concentration profiles at the San Rossore site showed that N<sub>2</sub>O concentrations below the C rich organic layer and in uppermost mineral soil were slightly lower than atmospheric N<sub>2</sub>O concentrations. This finding is also in-line with the hypothesis of Wrage et al. (2001), indicating that N<sub>2</sub>O uptake may be mainly associated with the uppermost C rich soil layers. In the case of shortage in nitrate supply denitrifying bacteria might use atmospheric N<sub>2</sub>O as an alternative electron acceptor to nitrate. This assumption is reinforced by seasonal variations of N<sub>2</sub>O fluxes, soil N content and microbial N turnover rates. During the autumn field campaign significantly more atmospheric N<sub>2</sub>O was consumed than in springtime. This corresponded with significantly lower nitrate concentrations in both soil layers in autumn as compared to the spring field campaign. Seasonal variations of microbial N turnover rates showed the same pattern, i.e. gross mineralization rates were significantly higher in spring than in autumn, although the correlation of chamber values of gross N turnover rates and NO<sub>3</sub><sup>-</sup> concentrations with corresponding N<sub>2</sub>O fluxes was not significant.

This means that the N<sub>2</sub>O uptake from the atmosphere into the soil observed at San Rossore is most likely linked to the very low nitrogen availability in the soil, where NO<sub>3</sub><sup>-</sup> concentrations in the organic layer as well as in the upper mineral soil were <1 mg N kg<sup>-1</sup> SDW, and NH<sub>4</sub><sup>+</sup> concentrations were <2 mg N kg<sup>-1</sup> SDW which is in accordance with the extremely low net ammonification and nitrification rates observed. Thus, both

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values (ammonium and nitrate concentrations) are significantly lower as found for many other forest sites across Europe. Bernal et al. (2003) determined NO<sub>3</sub><sup>-</sup> concentrations between 1–11 mg N kg<sup>-1</sup> SDW and NH<sub>4</sub><sup>+</sup> concentrations in the range of 1.5–4.5 mg N kg<sup>-1</sup> SDW in the upper 10 cm of mineral soil of a Mediterranean riparian forest in north-eastern Spain. Nitrate concentrations of the upper mineral soil of temperate European forests tend to be in the range of 1–30 mg N kg<sup>-1</sup> SDW, whilst ammonium concentrations are in most cases in the range of 2 to 200 mg N kg<sup>-1</sup> SDW (Priha et al, 1999; Herman et al., 2002; Wang and Ineson, 2003; Aubert et al., 2005). Steinkamp et al. (2001) even detected for the organic layer of an N limited spruce forest in Germany NH<sub>4</sub><sup>+</sup> concentrations of 21.6 mg N kg<sup>-1</sup> SDW, i.e. a value which is approx. one magnitude higher as the NH<sub>4</sub><sup>+</sup> concentrations we observed for San Rossore.

Also the N turnover rates observed in the present work were low in comparison with previous studies involving forest soils. Tietema (1998) determined gross N mineralization rates of 15.9 mg N kg<sup>-1</sup> SDW d<sup>-1</sup> and net mineralization rates of 6.6 mg N kg<sup>-1</sup> SDW d<sup>-1</sup> in the organic layer of a spruce forest in Sweden. Though the site of Tietema received a comparable atmospheric nitrogen input as our study site, rates of gross mineralization were at least five times higher than at San Rossore. Similarly Pedersen et al. (1999) found gross N mineralization rates of 13.2 mg N kg<sup>-1</sup> SDW d<sup>-1</sup> in the organic layer and 2.4 mg N kg<sup>-1</sup> SDW d<sup>-1</sup> in the mineral soil of a mixed conifer forest in California. Gross nitrification rates determined in the present study were also at the lower end of reported values for temperate forests, which are in the range of 0.2–7.6 mg N kg<sup>-1</sup> SDW d<sup>-1</sup> for the organic layer (Tietema, 1988; Hart et al., 1997; Verchot et al., 2001; Vervaet et al., 2004). We hypothesize that the low rates of microbial N turnover at the San Rossore site as compared to other forest sites are mainly due to moisture limitations, which are caused by the climatic conditions and the light textured soil.

Like for N<sub>2</sub>O, also NO<sub>x</sub> measurements in such high temporal and spatial resolution in a Mediterranean forest have never been reported before. The magnitude of the observed NO release in our study is in the range of reported NO emissions for temperate,

nitrogen limited forest soils (Rondón, et al, 1993; Skiba et al, 1994; Butterbach-Bahl et al., 2002). For a mixed coniferous forest growing under Mediterranean climate conditions Fenn et al. (1996) reported NO emissions in the range of 2 to 22  $\mu\text{g N m}^{-2} \text{h}^{-1}$ . However, in contrast to our study Fenn et al. (1996) measured higher NO emissions under more humid compared to dry soil conditions. In our study NO emissions were negatively correlated with soil moisture. This was demonstrated by the simulated rainfall experiment, where NO emissions in the watered chambers were significantly lower than in the non-watered chambers. Furthermore during the wet autumn field campaign significantly less NO was released than during the dry spring period. As NO emissions are supposed to be mainly due to nitrification activity rather than to denitrification activity (Davidson, 1992), the increasing water content may have led to unfavourable nitrification conditions, resulting in decreasing NO emissions. However, this is very unlikely to occur for the sandy soil at the San Rossore site. Furthermore, Breuer et al. (2002) showed that nitrification activity can even increase with increasing soil water contents. The latter observation is in accordance with our results, i.e. higher rates of gross nitrification in chambers with higher soil water content in the organic layer. Our observation of a decrease of NO emissions with increasing soil moisture, may be explained with a pronounced increase in aerobic NO consumption by heterotrophic nitrifiers (Baumgärtner et al., 2001), which would be in accordance with our explanation of the mechanism of N<sub>2</sub>O uptake at the San Rossore site. However, if this is true we need to question ourselves why we see mostly net NO emissions and not net NO uptake as observed for N<sub>2</sub>O. This can only be explained if NO formation is directly occurring in the uppermost centimetres of the soil surface, so that once formed NO can directly escape to the atmosphere before it is consumed. Wetting of the organic layer would then increase the residence time of NO in the uppermost organic layer, so that the likeliness of aerobic NO consumption by nitrification or by aerobic denitrification would sharply increase.

Because NO<sub>2</sub> deposition was continuously higher than NO emission the San Rossore forest constituted a net NO<sub>x</sub> sink with a potential magnitude of about 1.5 g

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$\text{N ha}^{-1} \text{ yr}^{-1}$ . Although  $\text{NO}_2$  deposition correlated significantly with NO emission rates, there was neither a significant influence of simulated rainfall nor significant differences between the two seasons.

In our study gross N turnover rates and  $\text{NO}_3^-$  concentrations correlated significantly positive with the corresponding NO fluxes. This indicates that besides the soil moisture content also nitrogen availability determines seasonality of NO fluxes, which is in accordance with findings by e.g. Venterea et al. (2004).

Well aerated soils are known to be significant sinks for atmospheric  $\text{CH}_4$  (Dobbie and Smith, 1996; Brumme and Borken, 1999). Until now there are no publications about  $\text{CH}_4$  exchange between Mediterranean forest soils and the atmosphere to compare with the results of our study. The magnitude of the observed net  $\text{CH}_4$  uptake at San Rossore is in the range of reported  $\text{CH}_4$  uptake rates by temperate nitrogen limited forest soils (Butterbach-Bahl et al., 1998; Butterbach-Bahl et al., 2002; Papen et al., 2001; Steinkamp et al., 2001). For a Mediterranean shrub land Castaldi et al. (2005) observed  $\text{CH}_4$  fluxes between  $-16$  and  $-250 \mu\text{g C m}^{-2} \text{ h}^{-1}$  with the same seasonal variations as observed in this work. Castaldi et al. (2005) determined highest  $\text{CH}_4$  oxidation rates during dry and warm periods. As high availability of inorganic nitrogen is supposed to reduce microbial oxidation of atmospheric  $\text{CH}_4$  (Butterbach-Bahl and Papen, 2002; Gullledge et al., 2004), the low  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations found in the San Rossore soil favour its sink strength for atmospheric  $\text{CH}_4$ . Furthermore,  $\text{CH}_4$  uptake is supposed to be strongly affected by soil texture (Born et al., 1990; Dörr et al., 1993) and soil moisture (Borken et al., 2000) due to their effects on diffusion velocities of  $\text{CH}_4$  and  $\text{O}_2$  (Potter et al., 1996). At San Rossore a high sand fraction (93% in the upper 5 cm mineral soil) supports good soil aeration. The influence of soil moisture was confirmed as simulated rainfall led to a significant decrease of  $\text{CH}_4$  oxidation. Moreover,  $\text{CH}_4$  uptake was apparently influenced by precipitation events during the measuring periods. There was also found a strong significant correlation between chamber  $\text{CH}_4$  flux values and corresponding organic layer water content, with  $\text{CH}_4$  uptake being significantly higher under dry soil conditions.

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In contrast to previous studies in which an inhibitory influence of inorganic nitrogen concentrations on methane oxidation was demonstrated (Bedard and Knowles, 1989; King and Schnell, 1994; Schnell and King, 1994; Butterbach-Bahl et al., 2002; Wang and Ineson, 2003), in the present work methane consumption was higher in chambers with high gross N mineralization rates and high nitrate concentrations. One reason for this contradictory result could be the very low nitrogen availability at San Rossore where even at the upper range of soil nitrogen content was probably still too low to inhibit CH<sub>4</sub> oxidation. Another explanation could be that the methanotrophic community at San Rossore was even nitrogen limited, as Bodelier and Laanbroek (2004) showed in their review on methane oxidation in soils. The soil air CH<sub>4</sub> concentration profile measurements underlines the strong sink function of San Rossore forest soil for atmospheric methane. The decreasing concentration gradient suggests that CH<sub>4</sub> oxidation is strongest in the upper mineral soil layer between 0 and 10 cm soil depth but continues down to at least 30 cm soil depth. This is in accordance with previous findings for CH<sub>4</sub> oxidation activities in temperate forest soils (Steinkamp et al., 2001; Butterbach-Bahl and Papen, 2002). This deep reaching CH<sub>4</sub> uptake is giving more evidence for the extraordinary aeration of the sandy soil at San Rossore even under the wet conditions during the autumn field campaign.

## 5. Conclusions

Our work demonstrates that our understanding of C and N trace gas exchange at Mediterranean forest sites is still limited. We have shown that such forests can act over longer time periods as a weak but significant sink for atmospheric N<sub>2</sub>O. It still remains unclear if this is of significance with regard to the global budget of this trace gas. However, it is evident that in process oriented models simulating the biosphere-atmosphere exchange of N<sub>2</sub>O uptake mechanisms should be implemented. In our work we hypothesize that N<sub>2</sub>O uptake at our study site was mainly related to aerobic denitrification of heterotrophic nitrifiers in well aerated and nitrogen limited soil.

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**Table 1.** Mean ( $\pm$  SE), minimum, maximum flux rates of N<sub>2</sub>O, NO, NO<sub>2</sub> ( $\mu\text{g N m}^{-2} \text{h}^{-1}$ ) and CH<sub>4</sub> ( $\mu\text{g C m}^{-2} \text{h}^{-1}$ ) as observed during the two field campaigns; N: number of measurements; C<sub>v</sub>: coefficient of variation (%).

|                              | Spring 2003                    | Autumn 2003                    |
|------------------------------|--------------------------------|--------------------------------|
| <b>N<sub>2</sub>O fluxes</b> |                                |                                |
| Mean                         | -4.32 $\pm$ 0.43 <sup>a</sup>  | -7.85 $\pm$ 0.51 <sup>b</sup>  |
| Maximum                      | -7.42                          | -5.17                          |
| Minimum                      | -1.29                          | -10.87                         |
| N                            | 20                             | 15                             |
| C <sub>v</sub>               | 44.86                          | 25.15                          |
| <b>NO fluxes</b>             |                                |                                |
| Mean                         | 9.94 $\pm$ 1.72 <sup>a</sup>   | 1.43 $\pm$ 0.43 <sup>b</sup>   |
| Maximum                      | 28.14                          | 3.75                           |
| Minimum                      | 4.97                           | -1.81                          |
| N                            | 13                             | 15                             |
| C <sub>v</sub>               | 62.42                          | 116.68                         |
| <b>NO<sub>2</sub> fluxes</b> |                                |                                |
| Mean                         | -23.78 $\pm$ 4.75              | -24.83 $\pm$ 1.96              |
| Maximum                      | -8.43                          | -12.73                         |
| Minimum                      | -71.49                         | -38.63                         |
| N                            | 13                             | 15                             |
| C <sub>v</sub>               | 71.98                          | 30.54                          |
| <b>CH<sub>4</sub> fluxes</b> |                                |                                |
| Mean                         | -73.34 $\pm$ 2.65 <sup>a</sup> | -59.67 $\pm$ 2.25 <sup>b</sup> |
| Maximum                      | -49.33                         | -49.19                         |
| Minimum                      | -90.97                         | -74.2                          |
| N                            | 23                             | 15                             |
| C <sub>v</sub>               | 17.32                          | 10.94                          |

Different letters indicate significant differences between flux rates ( $P < 0.05$ ).

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**Table 2.** Relative concentrations of N<sub>2</sub>O and CH<sub>4</sub> in different soil layers (100%=ambient air concentration) as observed during the autumn field campaign.

| Soil depth       | 0 cm                   | 10 cm                  | 20 cm                  | 30 cm                  |
|------------------|------------------------|------------------------|------------------------|------------------------|
| N <sub>2</sub> O | 99.1%±0.8              | 98.8%±1.9              | 98.9%±0.6              | 101.0%±1.6             |
| CH <sub>4</sub>  | 78.3%±1.8 <sup>a</sup> | 39.9%±4.0 <sup>b</sup> | 32.3%±2.0 <sup>c</sup> | 18.4%±0.4 <sup>d</sup> |

Mean±SE (N=3). Different letters indicate significant differences between soil depths ( $P<0.05$ ).

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**Table 3.** Mean ( $\pm$  SE) inorganic soil nitrogen content ( $\text{mg N kg}^{-1}$  SDW,  $N=3$ ), microbial nitrogen gross turnover rates ( $\text{mg N kg}^{-1}$  SDW  $\text{d}^{-1}$ ) and nitrogen net turnover rates ( $\text{mg N kg}^{-1}$  SDW  $\text{d}^{-1}$ ,  $N=3$ ) as observed during the two measuring campaigns; N: number of measurements.

|  | Spring 2003                         |                                      | Autumn 2003                          |                                      |
|--|-------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
|  | Organic layer                       | Mineral soil                         | Organic layer                        | Mineral soil                         |
| NH <sub>4</sub> <sup>+</sup> concentration | 1.84 $\pm$ 1.32 <sup>Aa</sup>       | 0.35 $\pm$ 0.13 <sup>Aa</sup>        | 0.72 $\pm$ 0.15 <sup>Aa</sup>        | 0.05 $\pm$ 0.01 <sup>Aa</sup>        |
| NO <sub>3</sub> <sup>-</sup> concentration | 0.52 $\pm$ 0.06 <sup>Aa</sup>       | 0.2 $\pm$ 0.02 <sup>Ab</sup>         | 0.17 $\pm$ 0.02 <sup>Ab</sup>        | 0.04 $\pm$ 0.0 <sup>Ac</sup>         |
| Gross N mineralization                     | 5.06 $\pm$ 0.68 <sup>Aa</sup>       |                                      | 2.68 $\pm$ 0.2 <sup>Bb</sup>         | 0.43 $\pm$ 0.05 <sup>Cc</sup>        |
| N  | 39                                  |                                      | 30                                   | 30                                   |
| Gross nitrification                        | 0.73 $\pm$ 0.26 <sup>B</sup>        |                                      |                                      |                                      |
| N  | 40                                  |                                      |                                      |                                      |
| Net N mineralization                       | 1.25 $\pm$ 0.59 <sup>Aa</sup>       | 0.14 $\pm$ 0.06 <sup>Aa</sup>        | 0.56 $\pm$ 0.2 <sup>Aa</sup>         | 0.05 $\pm$ 0.21 <sup>Aa</sup>        |
| Net nitrification                          | 0.0019<br>$\pm$ 0.002 <sup>Aa</sup> | 0.0021<br>$\pm$ 0.0022 <sup>Aa</sup> | 0.0032<br>$\pm$ 0.0015 <sup>Aa</sup> | 0.0007<br>$\pm$ 0.0002 <sup>Ba</sup> |

Different letters indicate significant differences ( $P<0.05$ ) between a) organic layer and mineral soil and/or sampling periods (lower case letters) or b) NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> concentrations, gross N mineralization and gross nitrification or net N mineralization and net nitrification for a given layer and a given sampling period.

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**Table 4.** Results of linear correlation analysis between mean chamber values of N<sub>2</sub>O, CH<sub>4</sub>, NO and NO<sub>2</sub> fluxes during the last 48 h prior to the determination of organic layer N turnover rates as well as organic layer NO<sub>3</sub><sup>-</sup> and water contents.

| N <sub>2</sub> O | NO | NO <sub>2</sub> | Gross N mineralization | Gross nitrification | NO <sub>3</sub> <sup>-</sup> content | Water content |                                      |
|------------------|----|-----------------|------------------------|---------------------|--------------------------------------|---------------|--------------------------------------|
| -0.239           |    |                 | -0.453 **              | 0.528               | -0.429 *                             | 0.588 ***     | CH <sub>4</sub>                      |
|                  |    |                 | 0.220                  | -0.111              | 0.192                                | -0.332        | N <sub>2</sub> O                     |
|                  |    | -0.779 ***      | 0.822 ***              | 0.934 **            | 0.425 *                              | -0.472 *      | NO                                   |
|                  |    |                 | -0.760 ***             | -0.883 **           | 0.030                                | 0.083         | NO <sub>2</sub>                      |
|                  |    |                 |                        | -0.292              | 0.040                                | -0.233        | Gross N mineralization               |
|                  |    |                 |                        |                     | -0.058                               | 0.510 *       | Gross nitrification                  |
|                  |    |                 |                        |                     |                                      | -0.544 ***    | NO <sub>3</sub> <sup>-</sup> content |

Asterix' indicate a significant correlation (\*=*P*<0.05; \*\*=*P*<0.01; \*\*\*=*P*<0.001).

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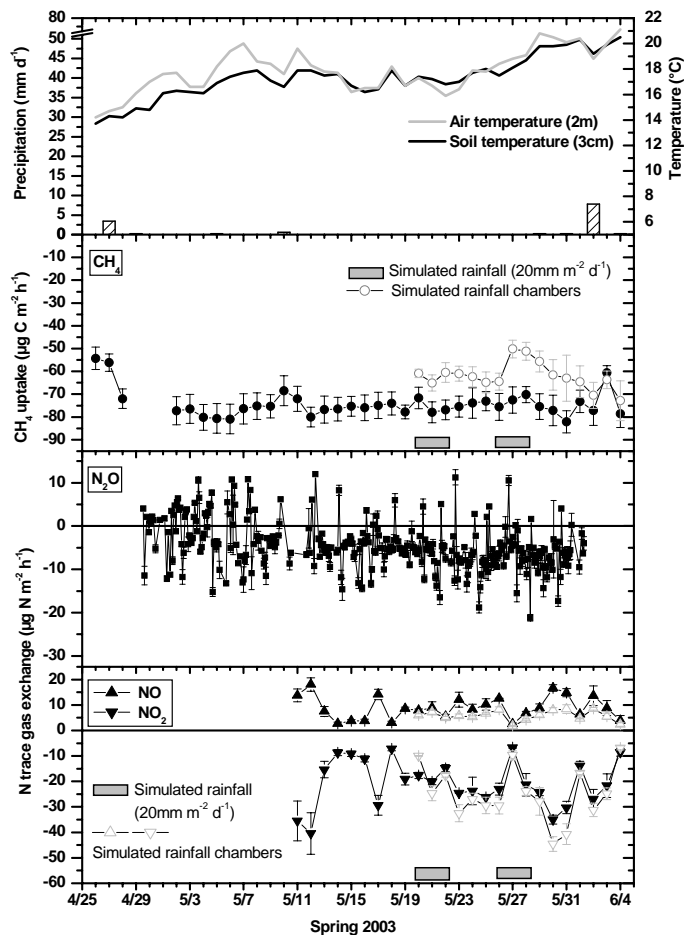
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**Fig. 1.** Daily means for soil and air temperature, CH<sub>4</sub> uptake ( $\pm$ SE; N=5) and NO<sub>x</sub> trace gas exchange ( $\pm$ SE; N=5), two-hourly means of N<sub>2</sub>O trace gas exchange ( $\pm$ SE; N=5) and daily precipitation during the spring field campaign (April to June 2003).

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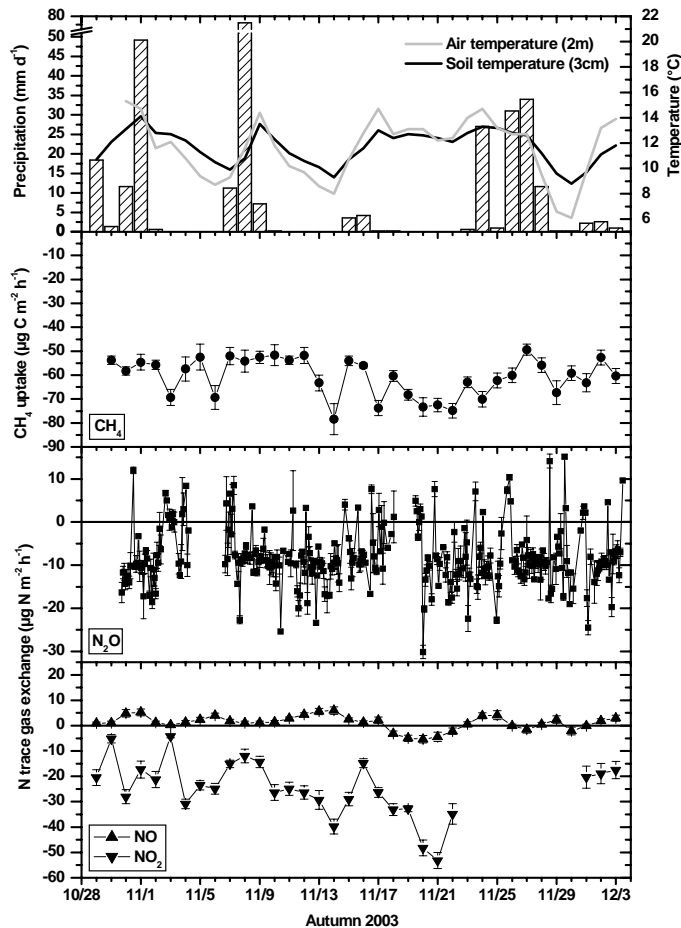
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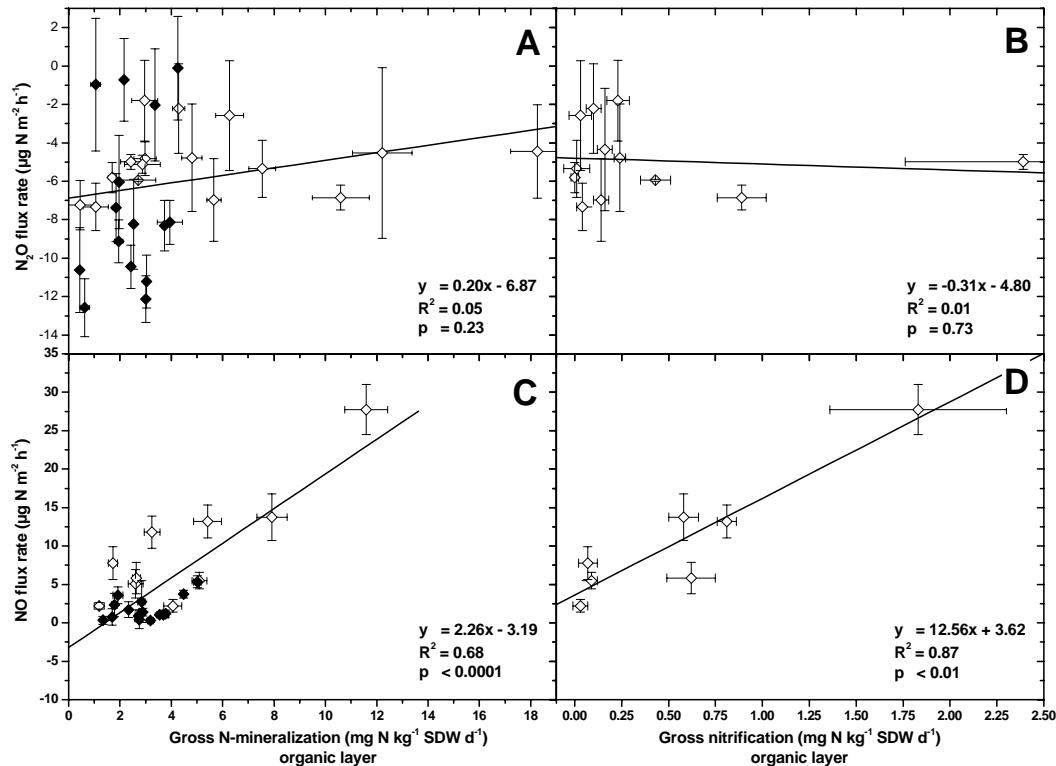
**Fig. 2.** Daily means for soil and air temperature, CH<sub>4</sub> uptake ( $\pm$ SE; N=5) and NO<sub>x</sub> trace gas exchange ( $\pm$ SE; N=5), two-hourly means of N<sub>2</sub>O trace gas exchange ( $\pm$ SE; N=5) and daily precipitation during the autumn field campaign (October to December 2003).

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**Fig. 3.** Dependency of N<sub>2</sub>O and NO trace gas exchange on gross rates of N mineralization and nitrification (organic layer). Shown are mean hourly (NO<sub>x</sub>) and two-hourly (N<sub>2</sub>O) values (±SE), respectively, of each chamber for the last 48 h prior to determination of gross N turnover rates, for spring (◇) and autumn (◆) field campaigns.

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