Biogeosciences

N$_2$O, NO and CH$_4$ exchange, and microbial N turnover over a Mediterranean pine forest soil

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Abstract. Trace gas exchange of N$_2$O, NO/NO$_2$ and 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 N$_2$O and CH$_4$ concentrations were determined. For both seasons a weak but significant N$_2$O uptake from the atmosphere into the soil was observed. During the unusually dry and hot spring mean N$_2$O uptake was $-4.32\,\mu$g N m^{-2} h^{-1}, whereas during the wet and mild autumn mean N$_2$O uptake was $-7.85\,\mu$g N m^{-2} h^{-1}. The observed N$_2$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 mg N kg^{-1} SDW d^{-1} in springtime to 2.68 mg N kg^{-1} SDW d^{-1} in autumn. Mean NO emission rates were significantly higher in springtime (9.94 μg N m^{-2} h^{-1}) than in autumn (1.43 μg N m^{-2} 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 NO$_2$ deposition was continuously higher than NO emission rates the examined forest soil functioned as a net NO$_x$ sink. Observed mean net CH$_4$ uptake rates were in spring significantly higher ($-73.34\,\mu$g C m^{-2} h^{-1}) than in autumn ($-59.67\,\mu$g C m^{-2} h^{-1}). Changes in CH$_4$ uptake rates were strongly negatively correlated with changes in soil moisture. The N$_2$O and CH$_4$ concentrations in different soil depths revealed the organic layer and the upper 0.1 m of mineral soil as the most important soil horizons for N$_2$O and CH$_4$ consumption.

1 Introduction

The atmospheric trace gases nitrous oxide (N$_2$O), nitric oxide (NO), nitrogen dioxide (NO$_2$) and methane (CH$_4$) have a major effect on the development of global climate. The global warming potential of N$_2$O is about 300 times higher than that of carbon dioxide (CO$_2$) 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$_2$O in the atmosphere is continuously increasing at a rate of approx. 0.25% yr^{-1} (IPCC, 2001). NO and NO$_2$ (NO$_x$) are secondary radiatively active trace gases, taking part in reactions eventually leading to the production of tropospheric ozone (O$_3$), a radiatively active greenhouse gas (Crutzen, 1995; Hall et al., 1996; Atkinson, 2000). N$_2$O as well as NO$_x$ 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$_2$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$_2$O and NO$_x$ between soils and the atmosphere.

CH$_4$ is next to H$_2$O and CO$_2$ 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$_4$, and it is estimated that CH$_4$ uptake activities of soils represent three to nine percent of the global atmospheric CH$_4$ sinks (Prather et al., 1995). Well aerated forest soils seem to play a major role in this context (Smith et al., 1994;

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King, 1997; Papen et al., 2001). Methane oxidation leading to a CH_4 uptake from the atmosphere into the soils is catalysed by soil microorganisms, most likely chemolithotrophic CH_4 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_4 oxidation has also been described (Segers, 1998).

While there is increasing knowledge about the role of agricultural soils and some natural ecosystems in N_2O, NO_x and CH_4 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 and 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 Thyrrenian 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 epignynous *Quercus ilex*. Only sparse ground vegetation can be found, mainly consisting of *Erica arborea, Phyllirea angustifolia, Rhamnus alaternus* and *Myrtus communis*.

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^{-1}. In the organic layer (thickness: $0.027 m \pm 0.004$) the pH value (0.01 M CaCl$_2$) is 4.4, the soil

organic carbon content (SOC) is 43.8% and the C/N ratio is 32.5. In the upper layer of the mineral soil (0–0.05 m) the pH value is 5.7. C content decreases from 13.9% (C/N ratio 30.0) in the uppermost 0.01 m to 1.0% (C/N ratio 13.5) in 0.1 m mineral soil depth. The soil texture of the uppermost 0.1 m of the mineral soil is: sand (93%), silt (3%) and clay (4%).

2.2 Measurements of N_2O, NO/NO_2 and CH_4 trace gas fluxes

Fluxes of the trace gases N_2O, NO/NO_2 and CH_4 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, soil/air temperature (soil depth: 0.03 m) and soil moisture (using TDR probes) was determined continuously at a climate station in close vicinity to the study site (50 m) using a tipping-bucket raingauge (Delta-T, Cambridge, Great Britain), Pt 1000 thermocouples (Thiess, Göttingen, Germany) and two TDR probes, respectively.

Fully automated measuring systems were used to determine the rates of N_2O, NO/NO_2 and CH_4 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_2) and two-hourly resolution (N_2O/CH_4), respectively. The measuring system for determination of N_2O and CH_4 fluxes consisted of five static measuring chambers (side lengths: $0.7 m \times 0.7 m$; height: 0.3 m; all chambers where gas-tightly fixed on stainless steel frames which were driven approx. 0.15 m into the soil), an automated gas sampling device with sample air pump and flow controller and a gas chromatograph equipped with a FID for CH_4 analyses and a ^{63}Ni ECD for N_2O detection. Calibration of the gas chromatograph was performed automatically every two hours using a gas mixture containing 4020 ppbv CH_4 and 402 ppbv N_2O in synthetic air (Messer Griessheim, Munich, Germany). Static chambers were closed gas-tight for 60 min and than opened for another 60 min. Thus, a full measuring cycle was 120 min. The closing of the chambers was also checked by monitoring the increase in CO_2 concentrations in the sample air due to soil respiration. A pre-column filled with ascarite (Sigma Aldrich, Munich, Germany) was used to remove CO_2 and H_2O prior to N_2O analyses. Ascarite pre-columns were routinely changed on a weekly basis. Due to automated sample air injection we were able to detect even small changes in chamber air N_2O concentrations with time. Our detection limit for N_2O concentration changes in sample air at ambient atmospheric N_2O concentrations was approx. 3 ppbv N_2O h^{-1}, which is equivalent to a N_2O flux of 0.6 μg N_2O-N m^{-2} h^{-1}. Fluxes below this detection limit

or measurements for which the slope as derived from linear regression was not significantly different from zero were set to zero (approx. 10–15% of all measurements, see also Butterbach-Bahl et al., 1998). For further details of the measuring system see Butterbach-Bahl et al. (1997) and Breuer et al. (2000).

To determine the fluxes of NO/NO_2 five dynamic measurement chambers (side lengths: $0.5\,m \times 0.5\,m$; height: $0.3\,m$) and one dynamic reference chamber were used (Meixner et al., 1997; Butterbach-Bahl et al., 1997). 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^{-1}, a chemoluminescence detector (CLD 770 AL ppt, Ecophysics AG, Dürnten, Switzerland), a photolysis converter to allow the determination of NO_2 (PLC 760, Ecophysics AG, Dürnten, Switzerland) and an ozone analyzer (TE 49 C, Thermo-Environmental Instruments Inc., Franklin, MA, USA) in order to correct NO/NO_2 fluxes for reactions of NO with ambient O_3 (Butterbach-Bahl et al., 1997). Nine 2 cm wide round holes in the side wall of the dynamic chambers opposite to the gas outlet ensured a gas flux through the chamber during the measuring cycle without generating a significant pressure drop ($<0.02\,hPa$, PCLA 12X5D, Sensor Technics, Puchheim, Germany) within the chamber. However, it should be noted that even a small underpressure has been discussed to lead possibly to overestimations of NO_x fluxes (Davidson et al., 2002; Reichmann and Rolston, 2002). In each dynamic chamber two fans (EBM Papst 614, Farmington, USA) were installed conversely. Average wind speed in the chamber was $1.33\,m\,s^{-1}$ (range: 0.5–$5.25\,m$ s^{-1}). In addition to the air flow through the chamber generated by the air pump during the six-minute measuring cycle a complete turbulent mixing within the chamber was ensured. Furthermore the aerodynamic resistance inside the chamber was quantified by the KJ method as described by Ludwig (1994). By comparing chamber inlet and outlet O_3 concentrations and using potassium iodide (KI) solution as a perfect ozone absorber inside the chamber (Galbally and Roy, 1980; Meixner et al., 1997; Gut et al., 2002) and considering the flow through the chamber as well as the surface area of KJ solution the aerodynamic resistance was calculated to be $53\pm5\,s\,m^{-1}$. In an additional experiment using controlled continuous CO_2 addition to a blank chamber the leakage flux from inside chamber air through the entrance holes to the outside (ambient) air was determined to be $<8\%$. Considering also the given uncertainty of the concentration measurements during the leakage tests with CO_2 (2 ppm) fluxes may be underestimated by maximum 10%.

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_2 – Messer-Griesheim, Germany) with synthetic air (80% N_2, 20% O_2 – Messer-Griesheim, Germany) using a computer-

ized multi gas calibrator (Environics 100, Environics Inc., West-Wellington, USA). Efficiency of photolytic conversion of NO_2 into NO was determined weekly as described by Butterbach-Bahl et al. (1997). The detection limit of the NO_x measuring equipment was for NO 50 pptv, for NO_2 100 pptv and for ozone 100 pptv, equivalent to fluxes of 1 and $1.5\,\mu g$ N $m^{-2}\,h^{-1}$ for NO and NO_2, respectively (Gasche and Papen, 1999). The complete measuring system has been in use for NO, NO_2 and O_3 measurements for many years and was pre-conditioned with high O_3 concentrations prior to the first implementation. Nevertheless, we can not exclude an ozone loss within the system due to deposition of O_3 to the walls. However, as O_3 concentrations were mostly in excess of NO concentrations, an underestimation of ozone causes only minor changes of calculated average NO and NO_2 fluxes smaller than the detection limit. Detailed 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 (soil depths: $0.02\,m$, $0.05\,m$ and $0.15\,m$) and air temperature were directly recorded at the site with chamber measurements using the automated system.

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 with $20\,l\,m^{-2}$ day^{-1} during two three day periods within a three day break in-between (equalling 120 mm rainfall in total). For watering normal tap water was used (NH_4-N: $0.11\,mg\,l^{-1}$; NO_3-N: $1.71\,mg\,l^{-1}$). It should be mentioned that prior of watering no significant differences in fluxes of N_2O, NO, NO_2 or CH_4 existed between the individual chambers. Furthermore, for calculation of site specific mean fluxes results obtained for the watered chambers were excluded.

2.3 Determination of N_2O and CH_4 concentrations at different soil depths

During the field campaign in autumn 2003, N_2O and 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[®] polypropylene tube (Membrana, Wuppertal, Germany) linked with a 1/8″ stainless 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 (5 ml) were drawn with a syringe 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 port (Breuer et al., 2000). The precision of N_2O measurements was ± 1.5 ppbv for N_2O and ± 5 ppbv for CH_4. For further details on the membrane tube technique for measurements of soil gas concentrations see Gut et al. (1998).

2.4 ^{15}N pool dilution technique for determination of gross N mineralization and gross nitrification rates

After removal of measuring chambers soil samples were taken 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}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 (0–0.05 m soil depth).

The soil samples were sieved (4 mm and 3.15 mm mesh width for organic layer and mineral soil, respectively) in order to homogenize them. The ammonium (NH_4^+) pool of the samples was marked using a $(NH_4)_2SO_4$ solution with 6% ^{15}N enrichment. For labelling 2 μg N dissolved in 3 ml H_2O was added per 100 g soil fresh weight of the soil sample. The moisture content was measured gravimetrically by oven drying soil samples at 105°C for 24 h. The average water content was approx. 25% w/w. Thus, water additions of 3 ml H_2O for labelling increased soil moisture of the sample only moderately by approx. 3% w/w. Each sample was subdivided into six equal portions. After a pre-incubation time of 16 h ($T_0=16$ 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 ($T_1=40$ 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_4^+ and NO_3^- 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_3 which was captured on a piece of ashless filter paper (Whatman No. 42, Springfield, Great Britain) acidified with 2.5 M $KHSO_4$. The $^{14/15}$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_3 solution with 6% ^{15}N enrichment. The experimental procedure to identify the $^{14/15}$N ratio followed the same laboratory series as described for gross N mineralization. Recovery rates for $^{15}NO_3$ were in a range of 77–96%. However, after MgO was added, KCl soil solutions were shaken for 20 hours until all NH_4^+ was exhausted. Afterwards 0.25 g Devarda alloy (50% Cu; 45% Al; 5% Zn) was added to reduce NO_3^- to NH_4^+ which was captured on filter papers and further analysed as described above.

Due to the rather low in-situ ammonium or nitrate concentrations in the soil (see Table 3) labelling resulted in a significant increase of the inorganic N pools. However, since by the ^{15}N pool dilution technique method the product and not the substrate pool of the investigated process is labelled, i.e. for ammonification the ammonium pool and for nitrification the nitrate pool, this should not have any effect on the magnitude of the rate itself.

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

Three replicates of soil samples were taken each measuring campaign for organic layer and mineral soil (0–0.05 m). 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, NH_4^+ and NO_3^- content were determined as described above (Sect. 2.4).

2.6 Statistics

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-normally 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 6.1 (Microcal Software, Northampton, USA).

3 Results

3.1 N_2O, NO/NO_2 and CH_4 trace gas fluxes

During almost the entire two measuring periods a net N_2O uptake from the atmosphere into the soil was observed. Mean N_2O uptake during the spring campaign with hot and dry weather conditions was significantly lower as compared to
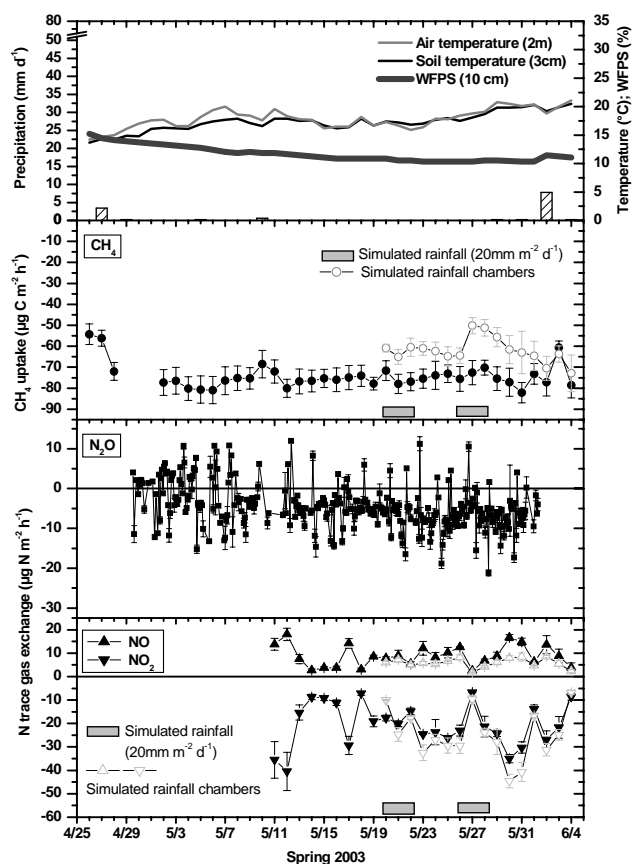
Fig. 1. Daily means for air and soil temperature, water filled pore space, CH$_4$ uptake ($\pm$SE; N=5 chambers) and NO$_x$ trace gas exchange ($\pm$SE; N = 5 chambers), two-hourly means of N$_2$O trace gas exchange ($\pm$SE; N=5 chambers) and daily precipitation during the spring field campaign (April to June 2003).

Fig. 2. Daily means for air and soil temperature, water filled pore space, CH$_4$ uptake ($\pm$SE; N=5 chambers) and NO$_x$ trace gas exchange ($\pm$SE; N=5 chambers), two-hourly means of N$_2$O trace gas exchange ($\pm$SE; N=5 chambers) and daily precipitation during the autumn field campaign (October to December 2003).

the field campaign in autumn when mild and wet weather prevailed (Figs. 1 and 2; Table 1). The mean water content ($\pm$ 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$9.1%) due to wetter weather conditions. Simulated rainfall during the spring campaign did not result in significant changes of the magnitude or direction of N$_2$O fluxes. However, the mean water content of the organic layer in the watered chambers seven days after the last simulated rainfall event was significantly higher (84.7$\pm$8.1%) than in the non-watered control chambers (29.8$\pm$5.2%). Also the magnitude of NO$_x$ fluxes was rather low (Figs. 1 and 2; Table 1). Mean NO emissions dropped significantly from 9.9 μg N m^{-2} h^{-1} in springtime to 1.4 μg N m^{-2} h^{-1} in autumn. Mean NO$_2$ deposition was in a range of -23 to -24 μg N m^{-2} h^{-1} and showed only a slight seasonal variation, which, however, was not significantly different. Since NO$_2$ deposition was continuously higher than NO emissions, the forest soils were net sinks for NO$_x$ during both measuring campaigns. For a few days in autumn even an uptake of NO
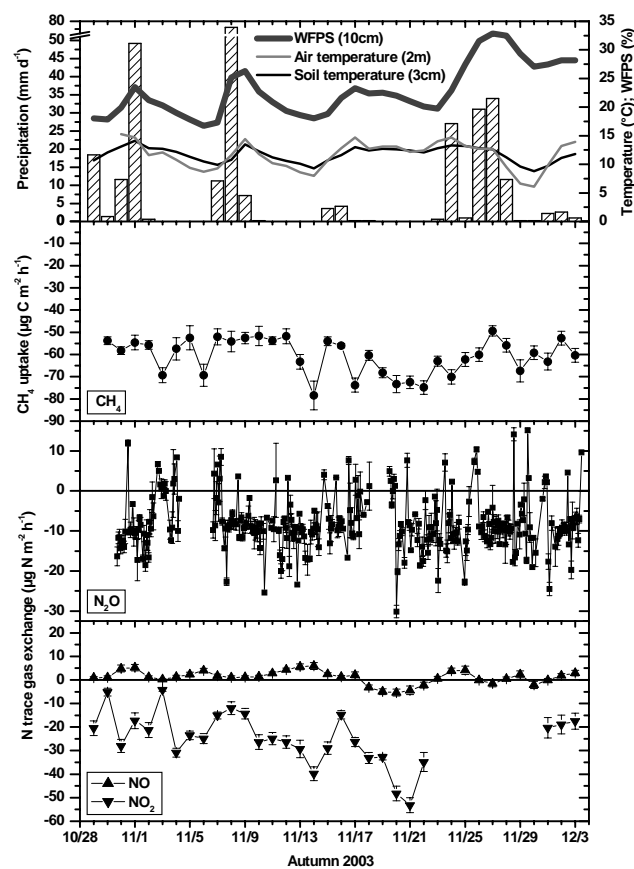
by the soil was observed (Fig. 2). Like for N$_2$O fluxes, no significant positive or negative effects of simulated rainfall on NO$_2$ fluxes could be demonstrated. However, NO emissions were significantly lower in watered chambers than in non-watered chambers (Fig. 1).

CH$_4$ 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 ± 2.7 μg C m^{-2} h^{-1}) than in autumn (-59.7 ± 2.3 μg C m^{-2} 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$_4$ uptake rates, while during the following dry period CH$_4$ uptake increased again (Fig. 1).

3.2 N$_2$O and CH$_4$ concentrations at different soil depths

The observation of a net uptake of atmospheric N$_2$O and CH$_4$ by the soil is further supported by measurements of N$_2$O and CH$_4$ gas concentrations in different soil depths.

Table 1. Mean (±SE) fluxes, and maximum and minimum fluxes for measuring chamber positions of N_2O, NO, NO_2 (μg N m^{-2} h^{-1}) and CH_4 (μg C m^{-2} h^{-1}) as observed during the two field campaigns; N: number of measuring chamber positions; C_v: coefficient of variation (%).

	Spring 2003	Autumn 2003
N_2O fluxes		
Mean	-4.32 ± 0.43^a	-7.85 ± 0.51^b
Maximum	-1.29	-5.17
Minimum	-7.42	-10.87
N	20	15
C_v	44.86	25.15
NO fluxes		
Mean	9.94 ± 1.72^a	1.43 ± 0.43^b
Maximum	28.14	3.75
Minimum	4.97	-1.81
N	13	15
C_v	62.42	116.68
NO_2 fluxes		
Mean	-23.78 ± 4.75	-24.83 ± 1.96
Maximum	-8.43	-12.73
Minimum	-71.49	-38.63
N	13	15
C_v	71.98	30.54
CH_4 fluxes		
Mean	-73.34 ± 2.65^a	-59.67 ± 2.25^b
Maximum	-49.33	-49.19
Minimum	-90.97	-74.2
N	23	15
C_v	17.32	10.94

Different letters indicate significant differences between seasons (P<0.05).

N_2O concentrations measured in 0–20 cm soil depth were approx. 1–2% lower than atmospheric N_2O concentrations. In 30 cm soil depth soil air N_2O concentrations increased to values slightly above atmospheric N_2O concentrations (Table 2), thus indicating that N_2O production in this soil depth exceeds N_2O consumption (Table 2). CH_4 concentrations decreased continuously with increasing soil depth to values as low as 0.35 ppmv CH_4 in 30 cm soil depth. However, the decline in CH_4 concentration was strongest between 0–10 cm soil depth, where the CH_4 concentration was already only 40% of the ambient air value.

3.3 Inorganic N content and microbial N turnover rates

Soil nitrate concentrations in the organic layer and mineral soil were significantly higher in spring than in autumn (Table 3). The same trend was found for soil ammonium concentrations with a significant difference between the two field campaigns in the mineral soil. In both campaigns ammonium as well as nitrate concentrations were approx. 3–5 times

Table 2. Relative concentrations of N_2O and CH_4 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_2O	$99.1\%\pm0.8^a$	$98.8\%\pm1.9^a$	$98.9\%\pm0.6^a$	$101.0\%\pm1.6^a$
CH_4	$78.3\%\pm1.8^a$	$39.9\%\pm4.0^b$	$32.3\%\pm2.0^c$	$18.4\%\pm0.4^d$

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

higher in the organic layer than in 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 ± 0.68 mg N kg^{-1} SDW d^{-1} in the organic layer of the forest soil, whereas gross N mineralization rates in autumn were lower by approx. a factor of two. 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 on a dry weight basis (0.43 ± 0.05 mg N kg^{-1} 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 ± 0.26 mg N kg^{-1} SDW d^{-1}) than the 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, NO_3^- concentrations and organic layer water content

There was only a weak and insignificant relationship between chamber N_2O fluxes and corresponding organic layer gross N turnover rates and NO_3^- and water contents (Fig. 3A and B; Table 4). However, for NO fluxes a significant positive correlation with gross N mineralization rates, gross nitrification rates as well as with NO_3^- content was found. For chambers with high NO emission rates also high gross N turnover rates and elevated NO_3^- concentrations in the soil were detected (Fig. 3C and D; Table 4). Furthermore, NO emission rates were negatively correlated with organic layer water content. As NO_2 deposition rates are strongly affected by NO emission rates, high N turnover rates also led indirectly to a significant increase of NO_2 deposition rates. Chamber CH_4 uptake rates correlated significantly both with corresponding organic layer gross N mineralization rates and with NO_3^- as well as water contents. No significant relationship was found between CH_4 uptake and gross nitrification rates, which were determined only during the spring field campaign (Table 4). Despite the lack of data for gross nitrification

Table 3. Mean (±SE) inorganic soil nitrogen content (mg N kg^{-1} SDW, N=3), microbial nitrogen gross turnover rates (mg N kg^{-1} SDW d^{-1}) and nitrogen net turnover rates (mg N kg^{-1} SDW 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$_4^+$ concentration	1.84±1.32^{Aab}	0.35±0.13^{Aab}	0.72±0.15^{Aa}	0.21±0.06^{Ab}
NO$_3^-$ concentration	0.52±0.06^{Aa}	0.2±0.02^{Ab}	0.17±0.02^{Bb}	0.04±0.0^{Bc}
Gross N mineralization	5.06±0.68^{Aa}		2.68±0.2^{b}	0.43±0.05^{c}
N	39		30	30
Gross nitrification	0.73±0.26^{B}			
N	40			
Net N mineralization	1.25±0.59^{Aab}	0.14±0.06^{Aab}	0.56±0.2^{Aa}	0.05±0.21^{Ab}
Net nitrification	0.0019±0.002^{Aa}	0.0021±0.0022^{Aa}	0.0032±0.0015^{Aa}	0.0007±0.0002^{Ba}

Lower case letters indicate significant differences (P<0.05) for a given parameter in dependence of samping depth (organic layer or mineral soil) and/or sampling periods (spring or autumn). Capital letters indicate significant differences (P<0.05) between NH$_4^+$ and NO$_3^-$ concentrations, gross N mineralization and gross nitrification or net N mineralization and net nitrification for a given layer and a given sampling period.

during the autumn field campaign still a significantly positive linear relationship between organic layer gross nitrification rates and water content was found. High NO$_3^-$ values during the dry conditions of the spring field campaign and low NO$_3^-$ concentrations during the wet conditions of the autumn field campaign yielded a significant relationship between organic layer NO$_3^-$ and water content (Table 4).

4 Discussion

The N$_2$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$_2$O emitters (<10 μg N m^{-2} h^{-1}) or even temporarily sinks for atmospheric N$_2$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$_2$O over longer time periods. The mean annual N$_2$O uptake for the pine forest at San Rossore – as calculated from the mean value of both measuring campaigns – was estimated to be approx. 0.5 kg N ha^{-1}. However, caution is advised here, since our measurements cover in total only approx. a two month period. Nevertheless, short periods with high N$_2$O emissions can significantly bias annual estimates of N$_2$O fluxes, as has been shown for temperate forests for N$_2$O emissions during short-term freezing-thawing events (Papen and Butterbach-Bal, 1999). Therefore, annual estimates should be based on year-round measurements.

It should be emphasized that the observed N$_2$O fluxes at the soil surface are always the result of simultaneously occurring production and consumption processes (Conrad, 1996, 2002). In accordance with the compensation point concept (Conrad, 1996) our data demonstrate that uptake of N$_2$O can dominate over N$_2$O production in the soil.

Up to now the only microbial process known to consume N$_2$O is denitrification, which mainly occurs under prevailing anoxic conditions (Conrad, 1996, 2002). For that reason one should assume that rainfall may increase N$_2$O consumption, since increased soil moisture should increase anaerobiosis in soils. As a matter of fact, in our experiments significantly higher net N$_2$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 net N$_2$O uptake could be demonstrated. This can be interpreted in such a way, that increases in soil moisture stimulated N$_2$O production but simultaneously also increased N$_2$O consumption, so that the net-effect – as measured at the soil surface as N$_2$O flux – was zero. To further study the effect of soil moistening on N$_2$O exchange a separation of in-situ production and consumption processes is needed. This may be done by the use inhibitors, e.g. low concentrations of C$_2$H$_2$ (0.01%), which mainly affect nitrification rather than denitrification (Conrad, 2002). Moreover, there was no significant relationship between mean chamber values of N$_2$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)
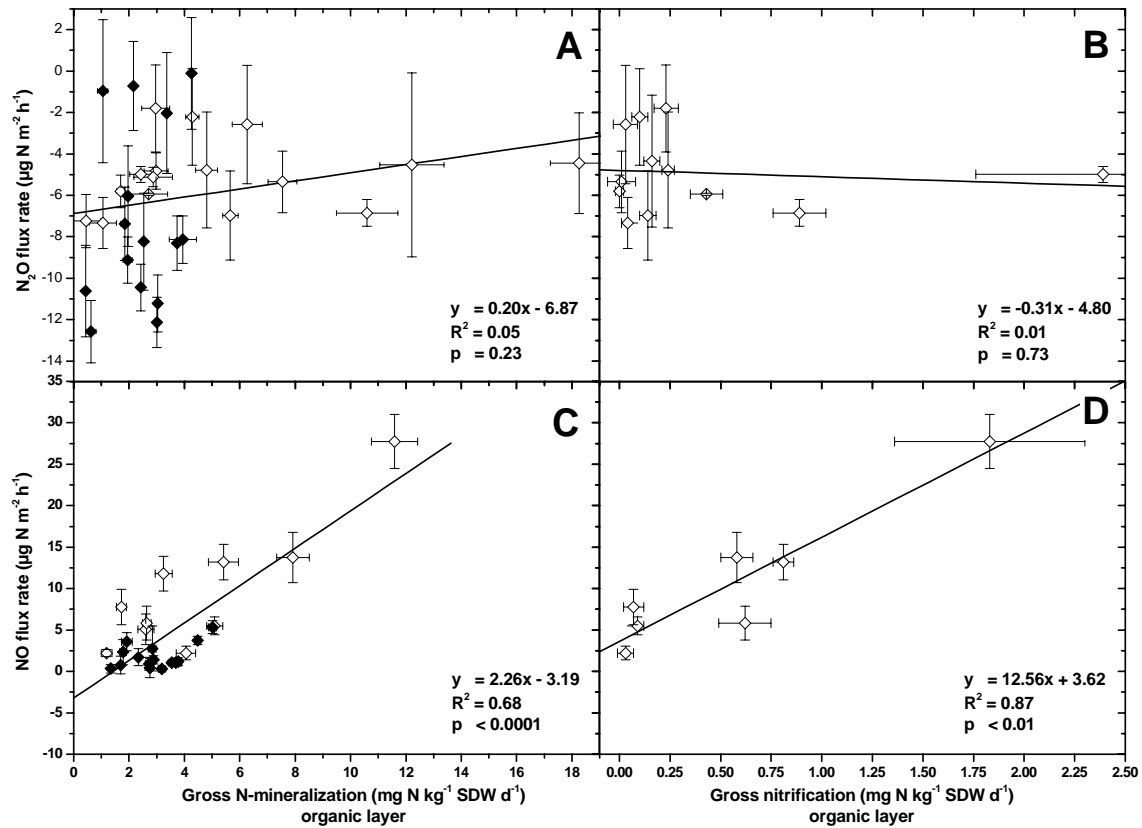
Fig. 3. Dependency of N_2O and NO trace gas exchange on gross rates of N mineralization and nitrification (organic layer). Shown are mean hourly (NO_x) and two-hourly (N_2O) values ($\pm$SE), respectively, of each chamber for the last 48 h prior to determination of gross N turnover rates, for spring ($\diamond$) and autumn ($\blacklozenge$) field campaigns.

Table 4. Results of linear correlation analysis between mean chamber values of N_2O, CH_4, NO and NO_2 fluxes during the last 48 h prior to the determination of organic layer N turnover rates as well as organic layer NO_3^- and water contents.

N_2O	NO	NO_2	Gross N mineralization	Gross nitrification	NO_3^- content	Water content	
−0.239			−0.453 **	0.528	−0.429 *	0.588 ***	CH_4
			0.220	−0.111	0.192	−0.332	N_2O
		−0.779 ***	0.822 ***	0.934 **	0.425 *	−0.472 *	NO
			−0.760 ***	−0.883 **	0.030	0.083	NO_2
				−0.292	0.040	−0.233	Gross N mineralization
					−0.058	0.510 *	Gross nitrification
						−0.544 ***	NO_3^- content

Asterisks indicate a significant correlation (* = P<0.05; ** = P<0.01; *** = P<0.001)

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_2 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_2O uptake. Furthermore, the measurements of N_2O soil air concentration profiles at the San Rossore site showed that N_2O concentrations below the C rich organic layer and in uppermost mineral soil were slightly lower than atmospheric N_2O concentrations. This finding is also in-line with the hypothesis of Wrage et

al. (2001), indicating that N_2O 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_2O as an alternative electron acceptor to nitrate. This assumption is reinforced by seasonal variations of N_2O fluxes, soil N content and microbial N turnover rates. During the autumn field campaign significantly more atmospheric N_2O 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_3^- concentrations with corresponding N_2O fluxes was not significant.

This means that the N_2O 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_3^- concentrations in the organic layer as well as in the upper mineral soil were <1 mg N kg^{-1} SDW, and NH_4^+ concentrations were <2 mg N kg^{-1} SDW which is in accordance with the extremely low net ammonification and nitrification rates observed. Thus, both values (ammonium and nitrate concentrations) are significantly lower than those found for many other forest sites across Europe, and one can assume that e.g. nitrate leaching is negligible at the San Rossore site. Bernal et al. (2003) determined NO_3^- concentrations between 1–11 mg N kg^{-1} SDW and NH_4^+ concentrations in the range of 1.5–4.5 mg N kg^{-1} 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^{-1} SDW, whilst ammonium concentrations are in most cases in the range of 2 to 200 mg N kg^{-1} 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_4^+ concentrations of 21.6 mg N kg^{-1} SDW, i.e. a value which is approx. one magnitude higher than the NH_4^+ 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^{-1} SDW d^{-1} and net mineralization rates of 6.6 mg N kg^{-1} SDW d^{-1} 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^{-1} SDW d^{-1} in the organic layer and 2.4 mg N kg^{-1} SDW d^{-1} 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^{-1} SDW d^{-1} 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_2O, also NO_x 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). Using the mean value from the spring and autumn measuring campaign as a proxy the annual NO emission at our site would amount to 0.5 kg NO-N ha^{-1} yr^{-1}.

For a mixed coniferous forest growing under Mediterranean climate conditions Fenn et al. (1996) reported NO emissions in the range of 2 to 22 μg N m^{-2} 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. Earlier studies have demonstrated that NO emissions from soils have their maximum at WFPS$<60\%$ (e.g. Davidson, 1994; Gasche and Papen, 1999). In a laboratory study involving a sandy forest soil from a Mediterranean site Schindlbacher et al. (2004) even found an optimum of NO production at 15% WFPS, which is close to the value we observed in our study (optimum between 10 and 13% WFPS). Our findings are also supported by a laboratory study performed by van Dijk and Meixner (2001) investigating a sandy tropical forest soil, in which a soil moisture optimum for NO release at a water content of 27% WFPS was demonstrated. As NO emissions are supposed to be mainly due to nitrification activity rather than to denitrification activity (Davidson, 1992), increasing soil water content may induce 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_2O 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_2O. 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_2 deposition was continuously higher than NO emission, the San Rossore forest constituted a net NO_x sink with a potential magnitude of about $1.5\,kg\,N\,ha^{-1}\,yr^{-1}$. Although NO_2 deposition correlated significantly with NO emission rates there was neither a significant influence of simulated rainfall on NO_2 fluxes nor significant differences between the seasons. The converse correlation between NO and NO_2 fluxes can be partly explained by fast oxidation of NO with O_3 to NO_2 within the forest stand (Gut et al., 2002). In this context it has to be mentioned, that the degree of NO oxidation will depend on the magnitude of turbulent mixing of below canopy air masses. However, as NO_2 deposition was continuously higher than soil NO emissions, the major share of NO_2 deposition has to originate from a net NO_2 influx to the forest stand. From our measurements we can not exclude that NO emissions from the soil surface may at least partly be stimulated due to NO_2 deposition to the soil surface.

In our study gross N turnover rates and NO_3^- concentrations correlated significantly positively with the corresponding NO fluxes. This indicates that besides the soil moisture content also nitrogen availability determines the seasonality of NO fluxes, which is in accordance with findings by e.g. Venterea et al. (2004).

Due to the low net N_2O and NO exchange rates, in addition to the detection limit of the gas analysis devices (see Sect. 2.2) other possible sources of errors need to be discussed. Keller et al. (2000) investigated the effect of soil disturbance by installation of measuring chambers. For tropical soils a possible stimulation of nitrogen oxide emissions over a time period up to one month was reported and interpreted to be caused by cutting of roots during installation of measuring chambers. In contrast to the strongly rooted upper soil layers of a tropical soil, at the experimental site of San Rossore only few roots are found in the upper soil layers due to taproots of pine trees and sparse ground vegetation. As we observed net N_2O uptake, cutting of roots would lead in our case to an underestimation of N_2O uptake, as mineralization of the severed roots and reduced root assimilation would increase the nitrogen pools and thus should depress N_2O consumption. However, root cutting might have stimulated NO emissions, but fluxes are rather low. Another possible error could be the chamber volume used for flux calculations. Rayment (2000) demonstrated for CO_2 measurements, that soil pore volume might cause an underestimation of fluxes using static chamber systems. This error decreases with increasing chamber

height. Due to sandy soil conditions at the San Rossore experimental site a good aeration of soil is given. Following the approach of Rayment (2000) it has to be stated that determined flux rates might be underestimated up to 50%, considering soil pore volume of the upper 0.3 m of the mineral soil. This would mean in the case of N_2O, that even higher uptake rates than determined can be assumed. Finally it has to be mentioned, that, because chambers are closed half of the time, only 50% of precipitation could reach the forest floor covered by a chamber. However, this error was minimized by frequent position changes of the measuring chambers (see Sect. 2.2).

Well aerated soils are known to be significant sinks for atmospheric CH_4 (Dobbie and Smith, 1996; Brumme and Borken, 1999). Until now there are no publications about CH_4 exchange between Mediterranean forest soils and the atmosphere to compare with the results of our study. The magnitude of the observed net CH_4 uptake at San Rossore is in the range of reported CH_4 uptake rates by temperate nitrogen limited forest soils (Butterbach-Bahl et al., 1998, 2002; Papen et al., 2001; Steinkamp et al., 2001). Total annual CH_4 uptake at our site was estimated to be $5.83\,kg\,C\,ha^{-1}\,yr^{-1}$ (as calculated from the mean value of both measuring campaigns).

For a Mediterranean shrub land Castaldi et al. (2005) observed CH_4 fluxes between -16 and $-250\,\mu g\,C\,m^{-2}\,h^{-1}$ with the same seasonal variations as observed in this work. Castaldi et al. (2005) determined highest CH_4 oxidation rates during dry and warm periods. As high availability of inorganic nitrogen is supposed to reduce microbial oxidation of atmospheric CH_4 (Butterbach-Bahl and Papen, 2002; Gulledge et at., 2004), the low NH_4^+ and NO_3^- concentrations found in the San Rossore soil favour its sink strength for atmospheric CH_4. Furthermore, 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 CH_4 and O_2 (Potter et al., 1996). At San Rossore a high sand fraction (93% in the upper 0.05 m mineral soil) supports good soil aeration. The influence of soil moisture was confirmed as simulated rainfall led to a significant decrease of CH_4 oxidation. Moreover, CH_4 uptake was apparently influenced by precipitation events during the measuring periods. A strong significant correlation was also found between chamber CH_4 flux values and corresponding organic layer water content, with CH_4 uptake being significantly higher under dry soil conditions.

In contrast to previous studies in which an inhibitory influence of inorganic nitrogen concentrations (mainly ammonium) 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_4 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_4 concentration profile measurements underlines the strong sink function of San Rossore forest soil for atmospheric methane. The decreasing concentration gradient suggests that CH_4 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_4 oxidation activities in temperate forest soils (Steinkamp et al., 2001; Butterbach-Bahl and Papen, 2002). This deep reaching CH_4 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_2O while further experiments favored under controlled laboratory conditions have to be done to improve the understanding of the mechanisms. It still remains unclear if these findings are 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_2O uptake mechanisms should be implemented. In our work we hypothesize that N_2O uptake at our study site was mainly related to aerobic denitrification of heterotrophic nitrifiers in well aerated and nitrogen limited soil. Furthermore we showed that the site investigated in this study was a net sink for NO_x as well as for CH_4. With regard to NO_x we demonstrated that NO_2 deposition dominated over the rather weak NO emission.

Edited by: F. X. Meixner

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