N₂O and CH₄ fluxes in undisturbed and burned holm oak, scots pine and pyrenean oak forests in central Spain

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Abstract We investigated N_2O and CH_4 fluxes from soils of *Quercus ilex, Quercus pyrenaica* and *Pinus sylvestris* stands located in the surrounding area of Madrid (Spain). The fluxes were measured for 18 months from both mature stands and post fire stands using the static chamber technique. Simultaneously with gas fluxes, soil temperature, soil water content, soil C and soil N were measured in the stands. Nitrous oxide fluxes ranged from -11.43 to 8.34 µg $N_2O–N$ m^{-2} h^{-1} in *Q.ilex*, -7.74 to 13.52 µg $N_2O–N$ m^{-2} h^{-1} in *Q. pyrenaica* and -28.17 to 21.89 µg $N_2O–N$ m^{-2} h^{-1} in *P. sylvestris*. Fluxes of CH_4 ranged from -8.12 to 4.11 µg $CH_4–C$ m^{-2} h^{-1} in *Q.ilex*, -7.74 to 3.0 µg $CH_4–C$ m^{-2} h^{-1} in *Q. pyrenaica* and -24.46 to 6.07 µg $CH_4–C$ m^{-2} h^{-1} in *P. sylvestris*. Seasonal differences were detected; N_2O fluxes being higher in wet months whereas N_2O fluxes declined in dry months. Net consumption of N_2O was related to low N availability, high soil C contents, high soil temperatures and low moisture content. Fire decreased N_2O fluxes in spring. N_2O emissions were closely correlated with previous day's rainfall and soil moisture. Our ecosystems generally were a sink for methane in the dry season and a source of CH_4 during wet months. The available water in the soil influenced the observed seasonal trend. The burned sites showed higher CH_4 oxidation rates in *Q. ilex*, and lower rates in *P. sylvestris*. Overall, the data suggest that fire alters both N_2O and CH_4 fluxes. However, the magnitude of such variation depends on the site, soil characteristics and seasonal climatic conditions.

Keywords Greenhouse flux · Fire · Soil water content · Soil temperature · *Quercus pyrenaica* · *Pinus sylvestris* · *Quercus ilex*

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Introduction

Nitrous oxide (N_2O) and methane (CH_4) are greenhouse gases (GHG) that interact with long-wave (infrared) solar radiation and, as a result, contribute to 'greenhouse warming'. Global atmospheric

concentrations of N_2O and CH_4 have increased markedly as a result of human activities since 1750 and now far exceed pre-industrial values (from 270 to 320 ppb N_2O and from 700 to 1782 ppb CH_4 in 2006). The observed increase in N_2O is largely attributed to agricultural activity. Increased livestock production and fossil fuel use are the main reasons for the atmospheric increase in CH_4 (IPCC 2007).

Although less abundant than CO_2, the Global Warming Potential of N_2O and CH_4 are about 310 and 21 times respectively, greater than CO_2 (IPCC 2007); and together they are responsible for more than 21% of the radiative forcing of Earth's energy balance (IPCC 1992). N_2O is also involved in the destruction of the stratospheric ozone layer (Cicerone 1979).

Soils play a key role in the global budget of N_2O and CH_4, as both gases are biologically produced and consumed by soil microorganisms (Conrad et al. 1989; Firestone and Davidson 1989; Chapuis-Lardy et al. 2007). Soils are usually considered as net sources of atmospheric N_2O. Total annual emissions from natural soils have been estimated to be 6.0 Tg N–N_2O year^{-1} and 3.5 Tg N–N_2O year^{-1} from agricultural soils (IPCC 2007), but with large uncertainties. The principal sources of N_2O in soils are microbial nitrification, nitrifier denitrification and denitrification, with the latter ones also being able to consume N_2O (Granli and Bøckman 1994; Schmidt et al. 2004). Nitrifying microbes convert soil ammonium (NH_4^+) to nitrate (NO_3^-) under aerobic conditions. Anaerobic denitrifiers reduce nitrogen oxides to nitric oxide (NO), N_2O and finally N_2, when there is sufficient carbon (C) and available NO_3^-; incomplete conversion results in the emission of N_2O. These microbial processes can occur simultaneously in adjacent anaerobic and aerobic micro-sites within the soil profile (Firestone and Davidson 1989; Potter et al. 1996b). There are some indications that soils may also function as significant sinks for atmospheric N_2O and that the soil N_2O reduction has decreased over recent decades (Chapuis-Lardy et al. 2007; Goldberg and Gebauer 2009). The main environmental factors controlling N_2O production in forest soils are soil nitrogen (N) status, soil moisture, precipitation, aeration, pH, atmospheric nitrogen deposition, temperature and tree species composition (Butterbach-Bahl et al. 2002; Schindlbacher et al. 2004; Kitzler et al. 2006; Skiba et al. 2004; Skiba et al. 2009; Weslien et al. 2009; Pilegaard et al. 2006).

CH_4 is produced by groups of anaerobic *Archea,* which require a low redox potential (Philippot et al. 2009). Therefore, high CH_4 fluxes are typical of wetlands, rice paddies or environments where anoxic fermentation is favoured. The impact of these sources is only partly balanced by removal processes in upland soils (Houghton et al. 1996). The extent of CH_4 removal by terrestrial oxidation is uncertain, with best estimates between 20 and 51 Tg CH_4 year^{-1} (Potter et al. 1996a; Smith et al. 2000). Soils have been identified as a significant biological sink for atmospheric CH_4 due to the oxidation of CH_4 to methanol (CH_3OH) for energy by methanotrophic bacteria, generally in well-drained, aerobic soils (Mosier et al. 1991; Papen et al. 2001). Forests are generally recognized as the largest sinks for CH_4, while CH_4 uptake by disturbed soils tends to be small (Smith et al. 2000). The diffusivity of CH_4 through the soil profile is the primary limiting factor upon CH_4 oxidation and this is influenced by soil moisture and bulk density. Furthermore, soil N status can limit CH_4 oxidation directly by inhibiting/competing with the monooxygenase enzyme of methanotrophs (Castro et al. 1995).

An important scientific priority of terrestrial trace gas studies is to create data bases of trace gas fluxes for different ecosystems, which could be used to parameterize and validate biogeochemical models (Potter et al. 1996a, b; Parton et al. 2001). However, much of the experimental data currently available has been collected in temperate regions (Smith et al. 2000), boreal forests, prairies, agricultural areas and tropical forest. Less information is available on seasonally-dry ecosystems, which are potentially able to act as efficient sinks for atmospheric CH_4 and significant sources of N_2O (Potter et al. 1996a, b; Castaldi et al. 2004, 2006; Wolf et al. 2010). This knowledge is particularly evident for Mediterranean type ecosystems. Trace gas emissions from Spanish forest soils have rarely been studied (Merino et al. 2004), and therefore there is a little understanding of the spatial and temporal variability of N_2O and CH_4 exchange in Spanish forest soils or the soil parameters that control this exchange. The importance of forest type or tree species and the effects of land disturbances are also poorly understood. A high level of uncertainty exists as to the contribution (source or sink) of Spanish forests to the regional, continental, and global N_2O and CH_4 balance.

Fire is among the most relevant form of ecosystem disturbance affecting nutrient cycling in Mediterranean forest ecosystems (Johnson et al. 2005), significantly affecting the soil-plant system (Wienhold and Klemmedson 1992).

Over the last few decades, the number of wildfires has increased in this region destroying thousands of hectares every year. Interest in the effects of fire on forest soil fertility and soil-atmosphere exchange of N_2O and CH_4 has recently heightened due to the concern that climate change may increase fire frequency and intensity (Westerling et al. 2006).

The short term effects of fires on forest soils have been widely studied (Rodríguez et al. 2009; Poth et al. 1995; Castaldi and Fierro 2005; Certini 2005; Neary et al. 1999; Castaldi and Aragosa 2002; Inclán et al. 2010). However, less information is available on the long-term effects of wildfires (Wan et al. 2001; Johnson et al. 2009; Durán et al. 2009). Wildfires may lead to soil degradation, including deterioration of structure as well as losses of soil organic matter and nutrients (Giovannini et al. 1988; Gillon et al. 1995; Prieto-Fernández et al. 1998; Inclán et al. 2010). The abovementioned effects of fire along with its impact on soil microbial populations can significantly alter soil C and N transformation rates and ultimately the C and N cycles of forest ecosystems (Johnson et al. 2009). Fire can have substantial long-term effects on ecosystem C and N by causing changes in vegetation, often through the facilitation of occupancy of the burned site by N-fixing vegetation, which in turn can indirectly cause long-term increases in ecosystem C capital in N-limited ecosystems (Johnson et al. 2005).

Immediately after burning, nitrification and denitrification can be significantly reduced, probably as a direct effect of fire on soil microorganisms (Castaldi and Aragosa 2002). The capacity of the soil to retain water can decrease after fire, as both water holding capacity and the ability to resist evaporation may be reduced in burned soil, slowing down nitrification and denitrification processes. Increases in N mineralization and microbial activity have been reported after initial post-fire stages as an effect of transient increases in temperature, water content and labile sources of C and N for microbes (Rutigliano et al. 2007). These initial increases are short-lived and 10 years after the last fire, significant decreases in net mineralization rates were observed indicating slow

recovery of N turnover (Durán et al. 2009). It was expected that increasing NH_4^+ content in the soil would reduce methanotrophic activity, since it has been hypothesized that NH_3 can act as a competitive substrate for methane monooxygenase (Bédard and Knowles 1989). Nitrite, formed during NH_4^+ oxidation by methanotrophs, may also have a role in the inhibiting effect of NH_4^+ addition on soil CH_4 oxidation capacity. Soil NH_4^+ levels often increase following fire because of heat-induced decomposition of organic N in soil and possibly by inorganic N inputs from ash (Certini 2005; Neary et al. 1999). Post-fire concentrations of NH_4^+ were found to decrease in the long-term (Durán et al. 2009). Hence, fluxes of N_2O and CH_4 may increase or decrease in forest soils after fire depending on the time elapsed since the disturbance. As a consequence of the strong seasonality of rainfall, opposite situations might occur such as the inability of microbes to exploit the increased mineral N content, due to summer drought, or significant N losses by denitrification and leaching during winter months, in which more significant precipitation events are concentrated. Greater differences between burned and unburned plots might be expected on spring sampling dates in comparison to winter sampling dates due to higher soil temperatures (Gallardo and Schlesinger 1994).

The aim of this work was to study the long-term effect of wildfires on N_2O and CH_4 soil-atmosphere exchange in three typical Mediterranean type forest ecosystems in the surrounding area of Madrid (Spain). We hypothesized that the effects of fire-induced type conversion from forest to grass-shrub mosaic on N_2O and soil CH_4 flux depends on forest site, soil characteristics and seasonal climatic conditions.

Materials and methods

Study sites and experimental design

The research was conducted in three forest stands (Table 1) near Madrid (Spain): A Holm oak stand (*Quercus ilex* subsp. *Ballota;* hereafter QI); a Pyrenean Oak forest stand (*Quercus pyrenaica* Willd.; hereafter QP); and a Scots pine forest stand (*Pinus sylvestris* L.; hereafter PS). All the stands are located within protected areas that have been managed in the

past. Oaks have been coppiced for centuries to provide firewood, charcoal and grazing for domestic livestock. In the last 50 years, the use of fossil fuels has led to a drop in the value of firewood and the near abandonment of coppice management systems. Consequently, many of these forests currently exhibit very high densities and are more susceptible to fire. PS stands have been managed in a relatively consistent, systematic manner; harvesting trees through successive uniform thinning interventions, with a cycle of around 120 years and a regeneration period of 20 years. Today, forests are managed using ecologically sustainable methods aimed at reducing the fuel potential for forest fires and increasing the resilience of forests to possible future fires through selective clearing, pruning, cutting and removal.

The forest understory in QI consists of shrub-type vegetation and grasses, including *Cistus ladanifer*, *Lavandula stoechas*, *Rosmarinus officinalis*, *Crataegus monogyna*, *Stipa tenacísima*, *Lygeum spartum*.

In QP, other species present include scattered *Fraxinus angustifolia*, *Cytisus scoparius*, *Genista florida*, *Rubus ulmifolius*, *Crataegus monogyna*, *Prunus spinosa*, *Lonicera peryclimenum* and *Tamus communis.* In PS, the understory is dominated by shrubs (*Genista cinerea*, *Adenocarpus hispanicus*, *Rosa canina*, *Santolina rosmarinifolia*) and grasses (*Pteridium aquilinum*, *Rumex scutatus*, *Stipa gigantean*).

The forests are located on granitic bedrock. Soils are Haplic Umbrisols (FAO 1998). The main properties of these soils are shown in Table 1.

The climate is continental Mediterranean in QP and QI and mountain-Mediterranean in PS, which is situated at higher altitude. The continental Mediterranean climate is characterized by extreme temperatures: very hot in the summer and very cold in winter. Rainfall is scarce, especially in summer and is concentrated in spring and autumn. During the winter, this precipitation is usually in the form of snow. In general, rainfall remains below 900 mm per

Table 1 Site characteristics of the different studied forest in Madrid, Spain

	Non burned	Burned	Non burned	Burned	Non burned	Burned
Vegetation	*Quercus ilex*	*Quercus ilex*	*Quercus pyrenaica*	*Quercus pyrenaica*	*Pinus sylvestris*	*Pinus sylvestris*
Location	N40°35′39.3″	N40°35′39.7″	N40°34′07.8″	N40°34′06.3″	N40°43′21.2″	N40°44′08.5″
	W3°55′30.5″	W3°55′31.7″	W4°08′54.8″	W4°08′55.2″	W4°07′20.1″	W4°06′21.9″
Stand age (year)	40	–	50	–	120	–
Mean precipitation (mm)[a]	655	655	788	788	895	895
Mean air temperature(°C)[a]	14	14	13	13	8	8
Elevation (m.a.s.l)	985	986	1020	1017	1409	1397
Slope (%)	0	0	0	0	40	25
Aspect (°)	–	–	–	110°ESE	SE	E
Tree height (m)	3.1	–	7.5	–	16	–
DBH (cm)	14	–	18	–	27	–
pH Ca Cl$_2$	5.9a	5.8ab	5.8ab	5.4b	4.1c	3.7c
C (g/kg)	20.9c	18.6c	34.3bc	37.0b	73.4a	64.1a
N (g/kg)	1.3c	1.3c	2.4bc	2.6b	4.0a	4.8a
C/N	16.1b	14.1c	14.1c	14.0cd	17.5a	13.2d
Soil type	Haplic umbrisol	Haplic umbrisol	Haplic umbrisol	Haplic umbrisol	Haplic umbrisol	Haplic umbrisol
Clays (%; <2 μm)	20ab	15ab	28a	12b	11b	19a
Silt + Sand (%; >2 μm)	80a	85a	72b	88a	89a	81a

Different letters in each line indicate significant statistical differences ($p < 0.05$)

[a] Average rainfall and temperature from 1999 to 2009 Spanish National Meteorological Service (http://www.aemet.es/es/portada)

year (Table 1). The mountain-Mediterranean climate tends to be cold and damp. The mean annual minimum and maximum temperatures at the different locations vary between 2.4 and 24.1°C in QI, 2.6 and 23.1°C in QP and −2.9 and 7.5°C in PS.

Wildfires have occurred in these forests at different times in the past. QI suffered a fire in August 2004, affecting approximately 12 ha; in QP the fire occurred in August 2002, affecting around 10 ha; and around 71 ha of forest were burned in PS in August 2001. The intensity and severity of the fire was assessed according to the amount and height of bark charring on tree stems. Based on this data as well as on information provided by local environmental agencies, all the fires at the plots were classified as crown fires.

In each forest stand we selected two (50 m × 50 m) plots: one affected by fire (burned, B) and the other unaffected (unburned-control, NB). The B and NB plots at each forest site are similar in terms of slope/aspect. The burned area in each stand is devoid of trees and the vegetation mainly comprises the previously described understory shrub species associated with each ecosystem. In the burned plots located in QI and QP, the understory is sparse whereas in PS, the vegetation cover is dominated by the leguminous *Adenocarpus hispanicus*, which is endemic of the Sistema Central (Spain) and is capable of fixing atmospheric N due to a symbiotic relationship with *Rizobium* bacteria.

N_2O and CH_4 flux measurements

Fluxes of N_2O and CH_4 between the soil and the atmosphere were measured using the closed chamber technique. Measurements were taken approximately on a monthly basis from December 2007 until September 2009. Gas measurements were carried out as described in Kitzler et al. (2006). Gas emissions were measured using four manual chambers installed randomly in each plot.

A manual chamber consists of an aluminium frame (1 × 1 × 0.05 m). A single-wall rigid polyethylene light-dome (volume: 70 l) with a compressible seal at the bottom was fixed onto the frame by means of two elastics bands fixed to the soil. Large chambers were chosen to account for small scale variability.

Air samples from the chambers were taken using 100 ml gas-tight syringes at intervals of 0, 0.5 and 1 h after the closure of the chamber in order to measure the increase or the decrease in concentration inside the chamber. These samples, which were taken between 9.00 and 13.00 GMT, were then injected into gas tight head-space vials (20 ml). The linearity of the emission was tested and additional measurements every 0.5 h showed that the increase in CH_4 and N_2O concentrations remained linear for up to 2 h.

The vials with the gas samples were transported to the laboratory and analysed using a gas chromatograph (HP-6890) equipped with a headspace autoanalyzer (HT3). HP-Plot Q capillary columns transported gas samples from the injector to a [63]Ni electron-capture detector to measure N_2O and to a flame ionization detector (FID) fitted with a methanizer to measure CH_4. N_2 served as carried gas with a flow rate of 30 ml/min[−1]. The gas-chromatograph was cross-calibrated with standard gases. The temperatures of the injector, oven and detector were 50, 50, and 300°C, respectively.

Emissions of N_2O (μg N_2O–N m^{−2}h[−1]) and CH_4 (μg CH_4–C m^{−2}h[−1]) were determined from the rate of change in the concentration in the air inside the chambers during the 1-h sampling period. This was estimated as the slope of the linear regression between concentration and time (after corrections for temperature) and from the ratio between chamber volume and soil surface area. Annual emissions for each plot (kg N_2O–N ha^{−1} year^{−1}, kg CH_4–C ha^{−1} year^{−1}) were calculated by integrating monthly losses over time.

Meteorological data

Soil moisture or water content (%) was measured continuously by capacitance (ECH_2O, Decagon Devices, Inc., USA); and soil temperature (°C) by thermocouples (TMCx-HD, Onset Computer Corporation) at soil depth of 10 cm in each plot. Data were stored at intervals of 0.5 h in the data logger (HOBO® H8, Onset Computer Corporation).

During each gas flux sampling, soil moisture content and soil temperature in the top 10 cm of soil were measured next to each gas measurement chamber using a time-domain reflectometry system (TRIMEGM, IMKO GmbH, Ettlingen, Germany) and a thermocouple sensor (Omega Engineering, Stamford, CT).

Air temperature (°C) and daily precipitation (l/m^2) in each forest stand was taken from the nearest meteorological stations belonging to the Spanish National Meteorological Service.

Soil samples

Three square 2×2 m^2 plots were marked out in close proximity to the chambers. In every season (winter, January 2008, March 2009; spring, June 2008; summer, August 2008; autumn, October 2008) three samples of the mineral soil were taken from each square plot, pooled and sieved through a 2-mm sieve (using a metal cylinder 10 cm high and 8 cm in diameter). Soil samples from each of the square plots (n = 3) were analysed for soil mineral N (total N, NO$_3^-$ and NH$_4^+$), total dissolved organic carbon (DOC), total carbon (C) and water-filled pore space (WFPS).

The chemical and physical properties over the whole soil profile (0–100 cm) were characterized at the beginning of the experiment at each study site. The soil characteristics from the fist layer of the profile are shown in Table 1.

Nitrate, NH$_4^+$ and DOC were extracted from the soil samples. To measure soluble nitrate an aliquot of the homogenized moist soil (2 g) was shaken for one hour with 20 ml of Milli-Q water at room temperature. The supernatant was filtered through 0.45 μm Millipore filter and the extraction solution was analyzed. To measure the ammonium, an aliquot of the homogenized moist soil (10 g) was shaken for 1 h with 20 ml of 1 M KCl solution at room temperature. The supernatant was filtered through 0.45 μm Millipore filter and the extraction solution was analyzed. For DOC analysis 30 ml of MILLI-Q water was added to 3 g moist-soil. The tubes were then extracted at room temperature (25°C) for 30 min in a shaker at 30 rpm, centrifuged (20 min, 3500 rpm) and the supernatant was filtered through 0.45 μm pore size Millipore filter. The water sample was first acidified to a pH value of 2. In this way, the carbonates and hydrogen carbonates are transformed into carbon dioxide. The CO$_2$ is then removed by sparging with carrier gas. What remains is a solution of non-volatile organic carbon.

The total amounts of C and N in the soils were determined using a LECO TRUSPEC analyzer (LECO Corp., St. Joseph, USA). DOC was analyzed using Shimadzu's TOC-V (SHIMADZU, Shimadzu Scientific Instruments, Kyoto, Japan). Nitrate was determined using a Dionex ICS-200 Ion Chromatography System (Dionex Corp., Sunnyvale, USA). Ammonium was determined using an Orion Research 901 Micro-Ionalyzer. The pH of the soils was potentiometrically measured in the supernatant suspension of a 1:5 soil: CaCl$_2$ liquid (v/v) mixture by means of an ORION 720A pH-meter. Soil mineralogy (0–10 cm) was determined by X-ray diffraction (Philips X'Pert-MPD) and Infrared spectroscopy (Nicolet 6700).

WFPS was calculated by dividing volumetric water content by total porosity. Volumetric water contents were calculated by multiplying gravimetric water content by bulk dry density. Total porosity was calculated as ((1-(bulk dry density/particle density)) × 100%, using a particle density of 2.65 g cm^{-3}.

Statistical analysis

Prior to analysis, the data were checked for homogeneity of variances and for normal distribution. Whenever necessary, data were transformed as logx or log (x + n). Differences in soil emissions, soil temperature, soil moisture, and soil chemistry data were evaluated using a three-way "repeated measures" analysis of variance (ANOVA) considering site type (ecosystem), time (month) and states (fire). Post-hoc comparisons were tested using Tukey's HSD test.

Differences between the cumulative fluxes of the different states (B and NB) in each forest stand were carried out using the t-test.

The relationships between fluxes and soil and meteorological data were investigated using Pearson correlation. All tests were performed at the 5% probability level. All statistical evaluation of the data was performed using the Statistica 6.0 software package (StatSoft. Inc., Tulsa. USA).

Results

Environmental conditions

The amount of precipitation recorded at each site during the study period (December 2007–September 2009) was: 923 mm in the QI stand, 1049 mm in the
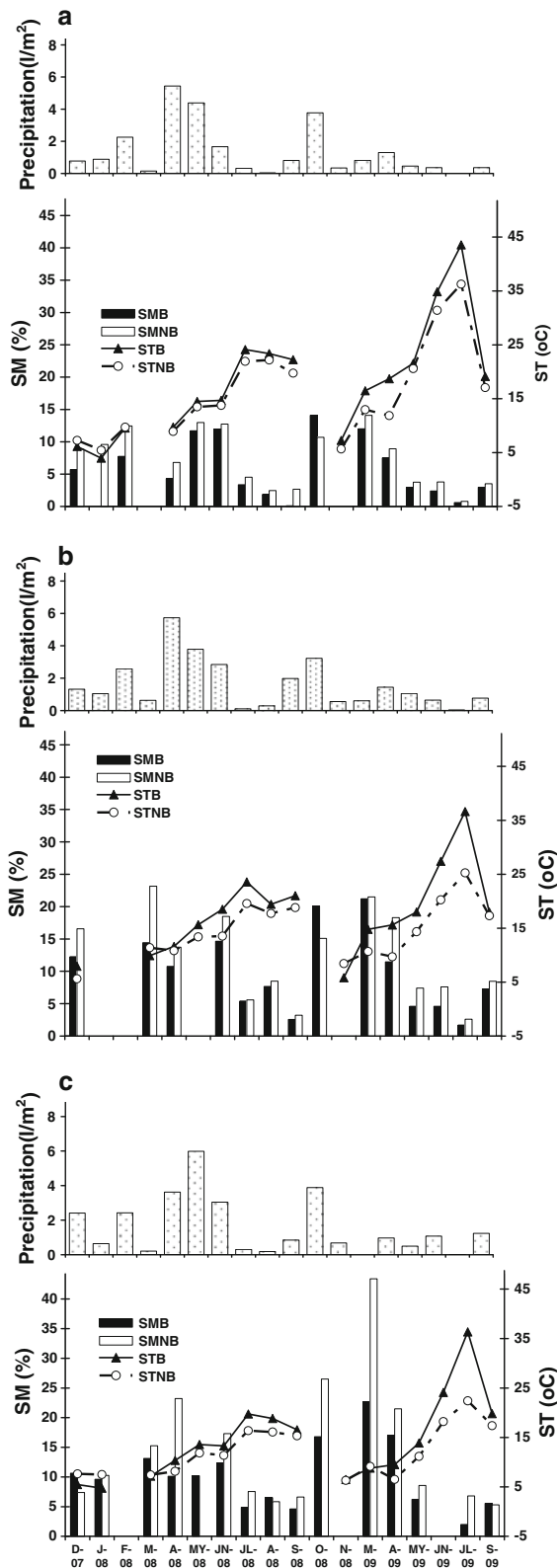
QP stand and 940 mm in the PS stand. Historical mean precipitations at each site, averaged over a period of 10 years (1999–2009) are shown in Table 1. Rainfall was concentrated in the winter, spring and autumn months, with the PS stand receiving the highest amount of rainfall (Fig. 1).

Both soil temperature and moisture content varied according to the season. Maximum soil temperatures coincided with minimum soil moisture during the summer, and minimum soil temperatures were recorded in winter when soil moisture was highest. Average daily surface soil temperatures ranged from 4.0 to 43.6°C in the QI stand, from 5.6 to 36.6°C in the QP stand, and from 4.7 to 36.3°C in the PS stand (Fig. 1). Soil temperature was often greater ($p < 0.05$) at the burned sites than at the undisturbed site (Fig. 1). Soil temperature in summer was highest in QI stands.

Average daily soil moisture ranged from 0.1 to 14% in the QI stand, from 2 to 23% in the QP stand, and from 2 to 43% in the PS stand (Fig. 1). Soil moisture in the surface soil was generally lower ($p < 0.05$) at the burned sites. Soil moisture presented the highest values in the QP plots followed by the PS and finally by the QI plots.

Surface soil WFPS varied seasonally in response to rainfall (data not shown). Soil WFPS ranged from 1.1 to 43.5% in the QI stand, from 3.6 to 48% in the QP stand and from 4.2 to 50.1% in the PS. The highest WFPS values were recorded in October 2008, June 2008 and March 2009. The QI stand had the lowest WFPS values ($p = 0.01$).

Soil parameters

The mean total soil C values in the PS stands were higher than in the QP and QI stands (Table 1). Nitrogen values among the forest stands follow the same pattern as C, with PS and QP exhibiting the highest values. The C/N ratio was lower in burned plots located in QI and PS stands. The soil pH values

were lower in the PS stands. The clay content of the soil was higher in PSB and QPNB. The Silt + Sand content of the soil was lower in QPNB.

The concentration of DOC in soil water varied seasonally ($p = 0.006$), being high in June 2008 and declining in August 2008 (Fig. 2). Soil DOC was greater in PS and QP stands as well as in undisturbed stands from these forest species. The site x states (fire) interaction in the ANOVA analysis showed that in the case of soils in the QI stands ($p = 0.04$) there were no differences in the DOC values between

Fig. 2 Soil nitrate (NO_3^-), ammonium (NH_4^+), dissolved organic C (DOC), over time at the three forest stands at Madrid, Spain (2008–2009). Values represent means of three replicates (μg/g). *QIB Quercus ilex* burned, *QINB Quercus ilex* unburned, *PSB Pinus sylvestris* burned, *PSNB Pinus sylvestris* unburned, *QPB Quercus pyrenaica* burned, *QPNB Quercus pyrenaica* unburned

burned and unburned plots. In the deciduous oak QP stands, DOC concentrations were lower in January 2008 and March 2009 when there were no leaves on the trees.

Soil NH_4^+ and NO_3^- concentrations in the surface soil varied seasonally ($p < 0.05$) (Fig. 2). Soil NO_3^- concentrations were highest in June 2008 and lowest in October 2008 in PS and QP stands. In the QI stands, the highest NO_3^- values were found in August 2008.

Soil NH_4^+ concentrations were greatest in March 2009 with the exception of PS stands, which peaked in August 2008.

Burned stands exhibited higher NO_3^- values than the unburned stands in June 2008 and lower values in August 2008, with the exception of the QP stands in August 2008 where burned soils presented higher NO_3^- values than unburned soils. Soil NH_4^+ concentrations ($p = 0.09$) tended to be lower in October 2008 and March 2009 in burned stands compared to control stands. The highest NO_3^- and NH_4^+ values were found in PS and QP stands.

Soil pH was negatively correlated with total soil C ($r = -0.93$, $p = 0.0$) and total soil N ($r = -0.95$, $p = 0.0$). Soil NH_4^+ was positively correlated with soil moisture ($r = 0.79$, $p = 0.05$), WFPS ($r = 0.84$, $p = 0.03$), DOC ($r = 0.81$, $p = 0.04$), total soil C ($r = 0.77, p = 0.05$), total soil N ($r = 0.71, p = 0.05$), and previous day's rainfall ($r = 0.85, p = 0.02$).

Soil DOC was negatively correlated with soil temperature ($r = -0.89$, $p = 0.01$), and positively correlated with soil moisture ($r = 0.95$, $p = 0.003$).
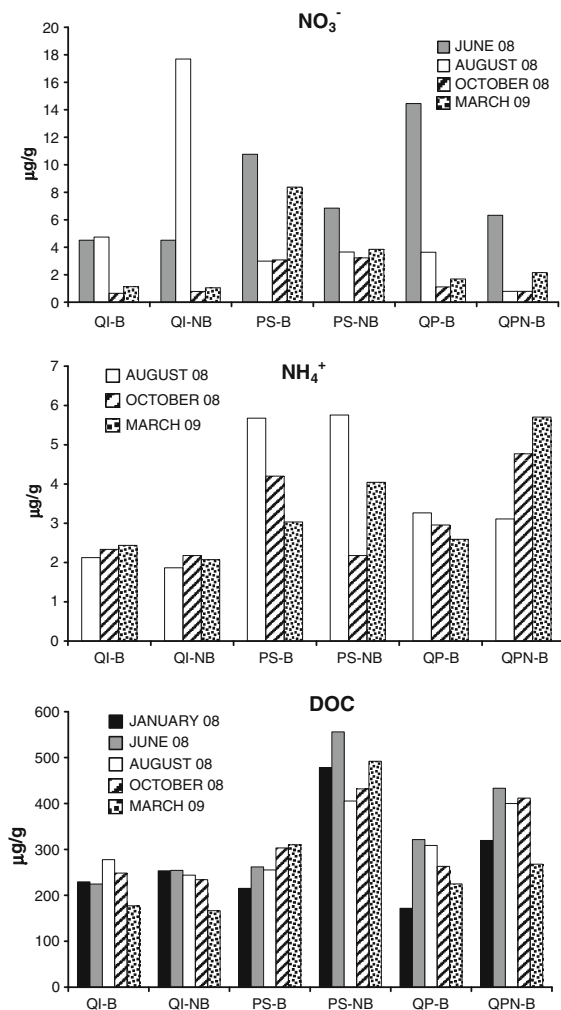
N₂O fluxes

Nitrous oxide fluxes ranged from -11.43 to 8.34 μg N₂O–N m⁻² h⁻¹ in QI stands, -7.74 to 13.52 μg N₂O–N m⁻² h⁻¹ in QP stands and -28.17 to 21.89 μg N₂O–N m⁻² h⁻¹ in PS stands (Fig. 3). A significant time effect on N₂O fluxes was observed, whereas the effects of site and fire were not statistically significant (Table 2). The emissions of N₂O from the soils of QI stands were the lowest. In unburned stands, minimum values were recorded in July 2008, September 2008, October 2008, April 2009 and July 2009. The maximum values were found in February 2008, April 2008, June 2008 and June 2009. In burned stands, the minimum values were recorded in June 2008, July 2008 and August 2008.

Fig. 3 Nitrous oxide flux (N_2O–N µg m^{-2}h^{-1}) over time at a *Quercus ilex* stand (**a**), a *Quercus pyrenaica* (**b**) and a *Pinus sylvestris* stand (**c**) in Madrid, Spain (December 2007– September 2009). Gas flux values represent means (±SE) of four replicates. *B* burned site, *NB* unburned site
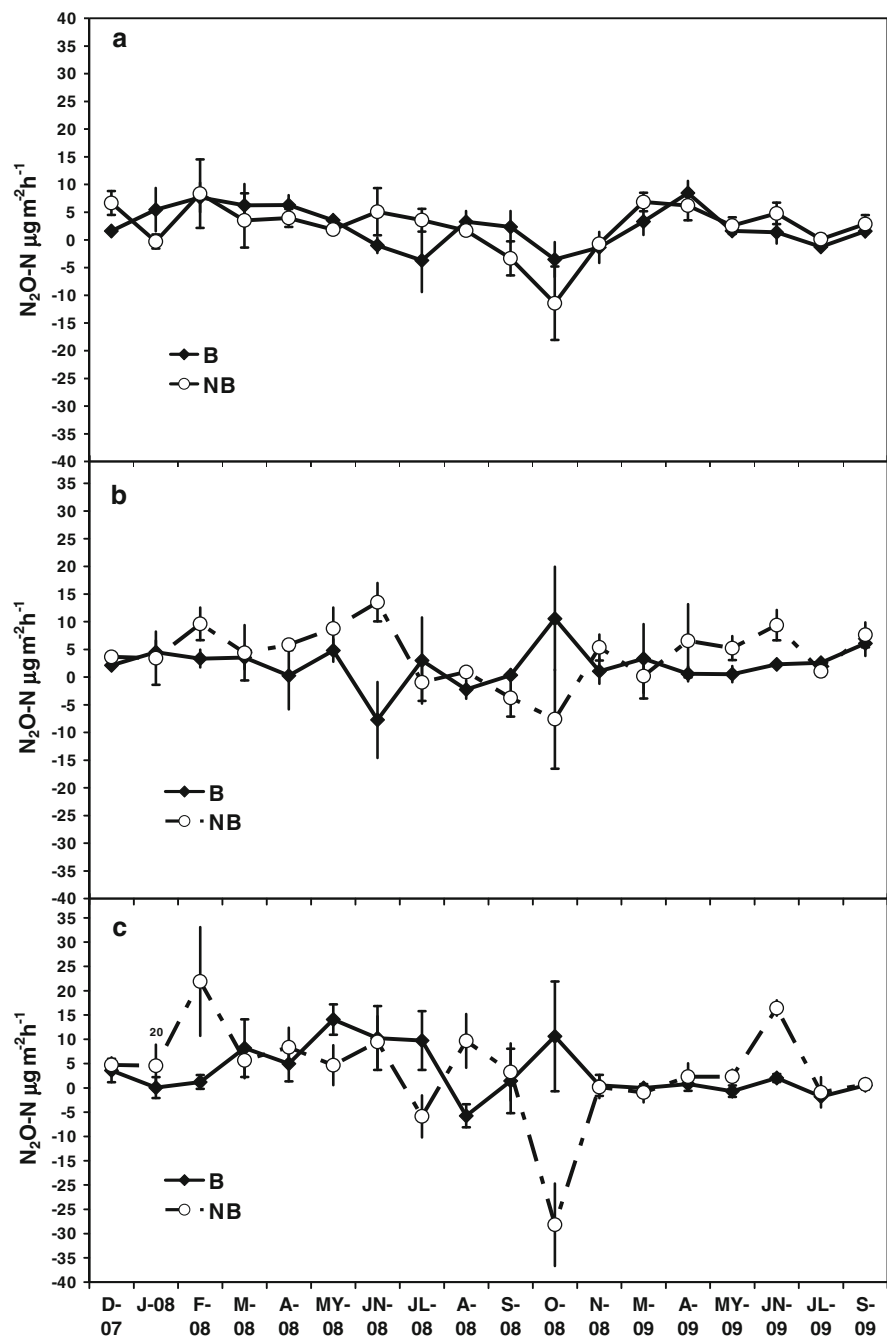
In QP stands, the time x site x fire interaction ($p = 0.01$) (Fig. 3b, Table 2) revealed that fire reduced N_2O emissions in February 2008, June 2008, May 2009 and June 2009.

In PS stands (Fig. 3c), fire reduced N_2O emissions in February 2008, April 2008 and June 2009. However we observed an increase in N_2O emissions

from burned soils in May 2008, July 2008 and October 2008.

During early summer (June 2008), elevated N_2O emissions coincided with elevated soil moisture content, surface soil temperatures (Fig. 1), previous day's rainfall, and soil mineral N concentrations (Fig. 2). In October 2008, lower NO_3^- coincided

Table 2 Results of three-way repeated measures analysis of variance on N_2O flux from the three studied sites

Factors	Sum of squares	Degr. of freedom	Mean square	F	p
Intercept	1894.11	1	1894.11	32.39252	**0.00**
Forest species (S)	24.69	2	12.34	0.21108	0.81
Fire (F)	1.98	1	1.98	0.03389	0.85
S × F	277.83	2	138.91	2.37565	0.13
Error	760.16	13	58.47		
Time (Month M)	2957.30	17	173.95	2.70881	**0.00**
M × S	1438.22	34	42.30	0.65869	0.92
M × F	3044.42	17	179.08	2.78861	**0.00**
M × F × S	3761.83	34	110.64	1.72287	**0.01**
Error	14192.55	221	64.22		

Bold numbers indicate significant differences at $p < 0.05$ level

Table 3 Pearson correlation coefficients between real-time fluxes and soil parameters for the period 2007–2009 in each of the forest stands

	N_2O Quercus ilex		N_2O Quercus pyrenaica		N_2O Pinus sylvestris		CH_4 Quercus ilex		CH_4 Quercus pyrenaica		CH_4 Pinus sylvestris	
	Non burned	Burned	Non burned	Burned	Non burned	Burned	Non burned	Burned	Non burned	Burned	Non burned	Burned
Soil temperature[a]	−0.20	−0.38*	−0.25	0.00	0.00	−0.19	−0.06	−0.25	−0.18	0.00	−0.17	0.00
Soil moisture[a]	0.46*	0.06	0.37*	−0.10	0.13	0.08	−0.07	−0.06	−0.16	−0.13	0.14	−0.16
WFPS	0.26	0.01	0.10	−0.20	−0.12	0.40	0.45*	−0.06	0.15	−0.23	0.00	−0.36
P1DB	0.04	0.22	**0.56**	**−0.62**	0.23	0.42*	−0.19	0.00	−0.27	**−0.61**	−0.11	−0.08
MP4DB	0.35	0.17	**0.44**	−0.23	0.32	**0.53**	−0.23	−0.30	−0.03	**−0.46**	0.00	0.00
DOC	−0.71*	−0.07	0.66*	**−0.89**	−0.73*	0.44	0.37	−0.20	−0.10	−0.40	0.32	0.17
NO_3^-	−0.22	0.13	0.84*	−0.93*	0.57	0.81*	−0.11	−0.66	−0.29	**−0.96**	−0.23	0.57
NH_4+	−0.12	−0.18	0.02	−0.98*	0.80	−0.86	−0.28	0.80	**−0.99**	0.64	0.95*	−0.76

[a] At 10 cm

WFPS water-filled pore space, *P1DB* precipitation 1 day before gas sample measurements, *MP4DB* mean precipitation of 4 days before gas sample measurements

* Asterisk indicates tendencies (* $p = 0.05$–0.1)

Bolded values refer to significant differences ($p < 0.05$)

with lower NH_4^+ and lower N_2O fluxes (Figs. 2 and 3). N_2O sinks were observed during dry months.

In the QI burned plots (Table 3), mean N_2O flux was best correlated with soil temperature (r = −0.38). In non-burned plots, N_2O flux was correlated with DOC (r = −0.71) and soil moisture (r = 0.46). In burned QP soils, the N_2O flux was correlated with DOC (r = −0.89) and previous day's rainfall (r = −0.62). N_2O fluxes from unburned soils were correlated with

previous day's rainfall (r = 0.56 and 0.44). In PS burned soils, mean N_2O flux was best correlated with the previous day's rainfall (r = 0.53). In non-burned PS plots, the best fitting was found with DOC (r = −0.73).

The N_2O emissions from all ecosystems (Table 4), were positively correlated with previous day's rainfall (r = 0.23, 0.32) and soil moisture (r = 0.19), and negatively correlated with soil temperature (r = −0.20).

Table 4 Pearson correlation coefficients between real-time fluxes and soil parameters for the period 2007–2009 in all forest stands

	N_2O	$logN_2O$	CH_4	[a]Soil temperature	[a]Soil moisture	WFPS	P1DB	MP4DB	NO_3^-	NH_4^+	pH
N_2O											
$logN_2O$	−0.02										
CH_4	−0.16*	−0.07									
[a]Soil temperature	**−0.20**	−0.18*	−0.09								
[a]Soil moisture	0.19*	**0.21**	−0.05	**−0.66**							
WFPS	0.05	0.19*	−0.04	**−0.63**	**0.85**						
P1DB	**0.23**	0.00	−0.17*	−0.05	0.19*	**0.26**					
MP4DB	**0.32**	0.02	−0.10	−0.11	**0.22**	**0.26**	**0.72**				
NO_3^-	−0.04	−0.27	0.01	**0.58**	**−0.55**	**−0.59**	0.00	−0.02			
NH_4^+	−0.01	−0.31	−0.07	−0.03	−0.01	−0.07	−	**0.63**	−0.17		
pH	−0.17	0.11	0.25*	0.22	−0.18	0.11	−0.33*	−0.24*	0.22	−0.49	

[a] At 10 cm

WFPS water-filled pore space, *P1DB* precipitation 1 day before gas sample measurements, *MP4DB* mean precipitation of 4 days before gas sample measurements

* Asterisk indicates tendencies (* $p = 0.05$–0.1)

Bolded values refer to significant differences ($p < 0.05$)

Mean annual N_2O emissions were related with mean annual values of soil parameters (Fig. 4). Mean annual N_2O emissions were negatively related with soil pH (r = −0.30; ns), and positively correlated with soil DOC (r = 0.79, $p = 0.06$), soil NH_4^+ (r = 0.90, $p = 0.01$), WFPS (r = 0.67, $p = 0.1$). Log-transformed N_2O fluxes were negatively correlated with the C/N-ratio (r = −0.84; $p = 0.03$) and positively correlated with soil clay content (r = 0.83; $p = 0.03$).

Mean N_2O emissions averaged over the entire experimental period were identical in all the plots (Table 5). The N_2O cumulative fluxes (kg N_2O–N ha^{-1} year^{-1}) were significantly ($p < 0.05$) higher in unburned plots (6.4 kg N_2O–N ha^{-1} year^{-1}) than in burned plots (3.4 kg N_2O–N ha^{-1} year^{-1}) in the QP stands. The annual N_2O fluxes in the PS plots were 5.1–5.2 kg N_2O–N ha^{-1} year^{-1}. In the QI stand no significant differences were found between burned plots (3.7 kg N_2O–N ha^{-1} year^{-1}) compared to nonburned plots (3.7 kg N_2O–N ha^{-1} year^{-1}).

CH_4 fluxes

Fluxes of CH_4 ranged from −8.12 to 4.11 µg CH_4–C m^{-2} h^{-1} in QI stands, −7.74 to 3.0 µg CH_4–C m^{-2} h^{-1} in QP stands, and −24.46 to 6.07 µg CH_4–C m^{-2} h^{-1} in PS stands (Fig. 5). Differences in CH_4 fluxes among sites were significant ($p < 0.05$)

and PS and QP stands were found to absorb more CH_4 than QI stands.

Soil CH_4 flux varied over the measurement period (Table 6). CH_4 uptake was highest in dry months (June, July) and February 2008. A net source of CH_4 was found during wet months. Differences between burned and unburned stands in relation to CH_4 fluxes were identified in soils under QI. Fire increased CH_4 uptake in June 2008, May 2009 and July 2009 (Fig. 5a). In burned QP stands (Fig. 5b), CH_4 uptake was higher than at the unburned stand during June 2008 and July 2008 (not significant). However, in June 2009, July 2009 and September 2009, the unburned stand showed more CH_4 consumption.

In PS stands, CH_4 uptake was higher in undisturbed soil than in burned soil in February 2008 and June 2009 (Fig. 5c). Mean CH_4 fluxes (Table 3) were correlated with WFPS (r = 0.45) in unburned QI soils. In burned QP soils, mean CH_4 flux was correlated with previous day's rainfall (r = −0.61, −0.46) and NO_3^- (r = −0.96). CH_4 fluxes were correlated with NH_4^+ (r = −0.99) in unburned soils. No significant correlation was found between mean CH_4 flux and the studied parameters in PS stands. No significant correlations were found between mean CH_4 flux from all ecosystems (Table 4) and the studied soil parameters.

Fig. 4 Relationship between average annual N$_2$O fluxes (N$_2$O–N μg m^{-2}h^{-1}) versus average mean soil parameters. *QIB Quercus ilex* burned, *QINB Quercus ilex* unburned, *PSB Pinus sylvestris* burned, *PSNB Pinus sylvestris* unburned, *QPB Quercus pyrenaica* burned, *QPNB Quercus pyrenaica* unburned
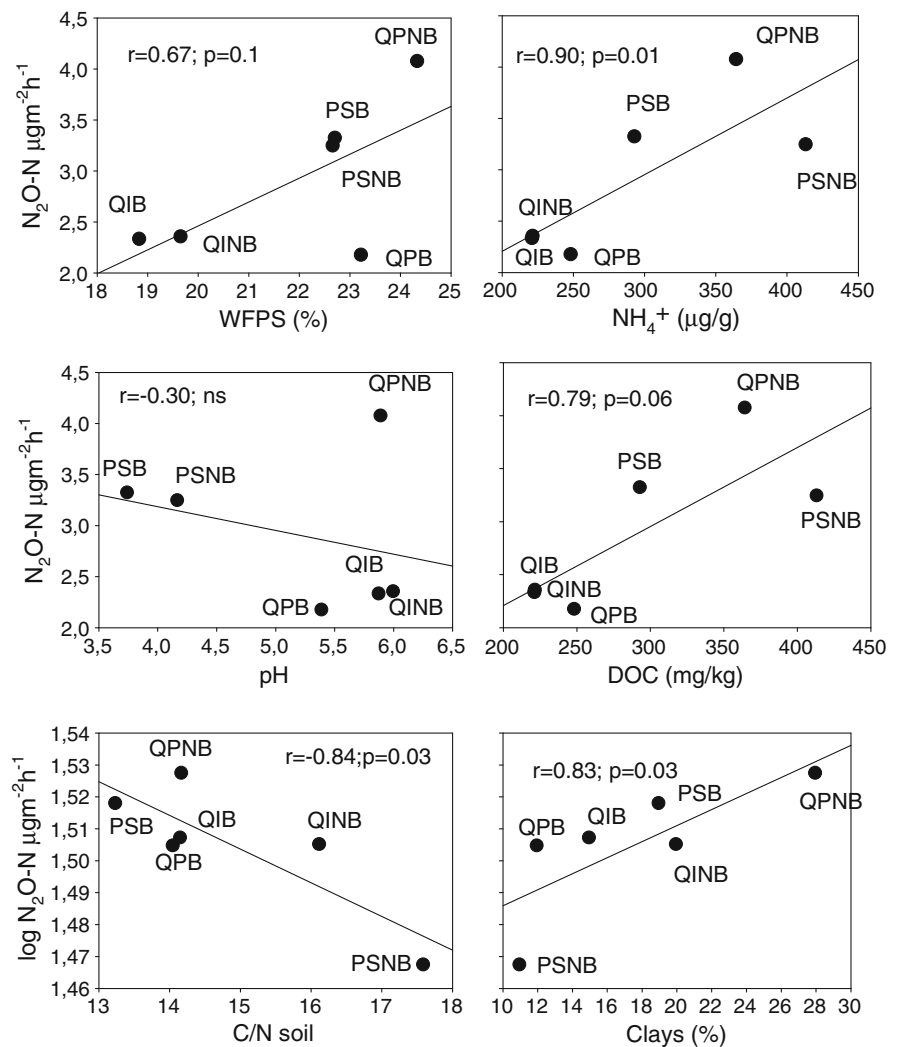

Table 5 Estimated annual mean and cumulative annual emission of N$_2$O and CH$_4$ across forest sites in Madrid

	N$_2$O–N mean (μg m^{-2} h^{-1})[a]		Annual N$_2$O–N (kg ha^{-1})[b]		CH$_4$–C mean (μg m^{-2} h^{-1})[a]		Annual CH$_4$ (kg ha^{-1})[b]	
	Non burned	Burned	Non burned	Burned	Non burned	Burned	Non burned	Burned
Quercus ilex	2.2	2.3	3.7	3.7	−0.6	−2.1	−0.9	−3.3
Quercus pyrenaica	4.1	2.2	6.4	3.4	−2.2	−2.5	−3.4	−3.9
Pinus sylvestris	3.2	3.3	5.1	5.2	−3.5	−0.9	−5.5	−1.4

[a] Estimated annual mean

[b] Cumulative annual emission

Mean annual CH$_4$ fluxes were related with mean annual values of soil parameters (Fig. 6). Mean annual CH$_4$ flux were positively related with soil clay content (r = 0.62, p = 0.1), and negatively correlated with

soil DOC (r = −0.61, p = 0.1), soil NH$_4^+$ (r = −0.30, ns) and soil moisture (r = −0.61, p = 0.1).

The mean fluxes (μg CH$_4$–C m^{-2} h^{-1}) averaged over the experimental period were not significantly different

Fig. 5 Methane flux (CH$_4$–C µg m^{-2}h^{-1}) over time at a *Quercus ilex* stand (**a**), a *Quercus pyrenaica* (**b**) and a *Pinus sylvestris* stand (**c**) in Madrid, Spain (December 2007–September 2009). Gas flux values represent means (±SE) of four replicates. *B* burned site, *NB* unburned site
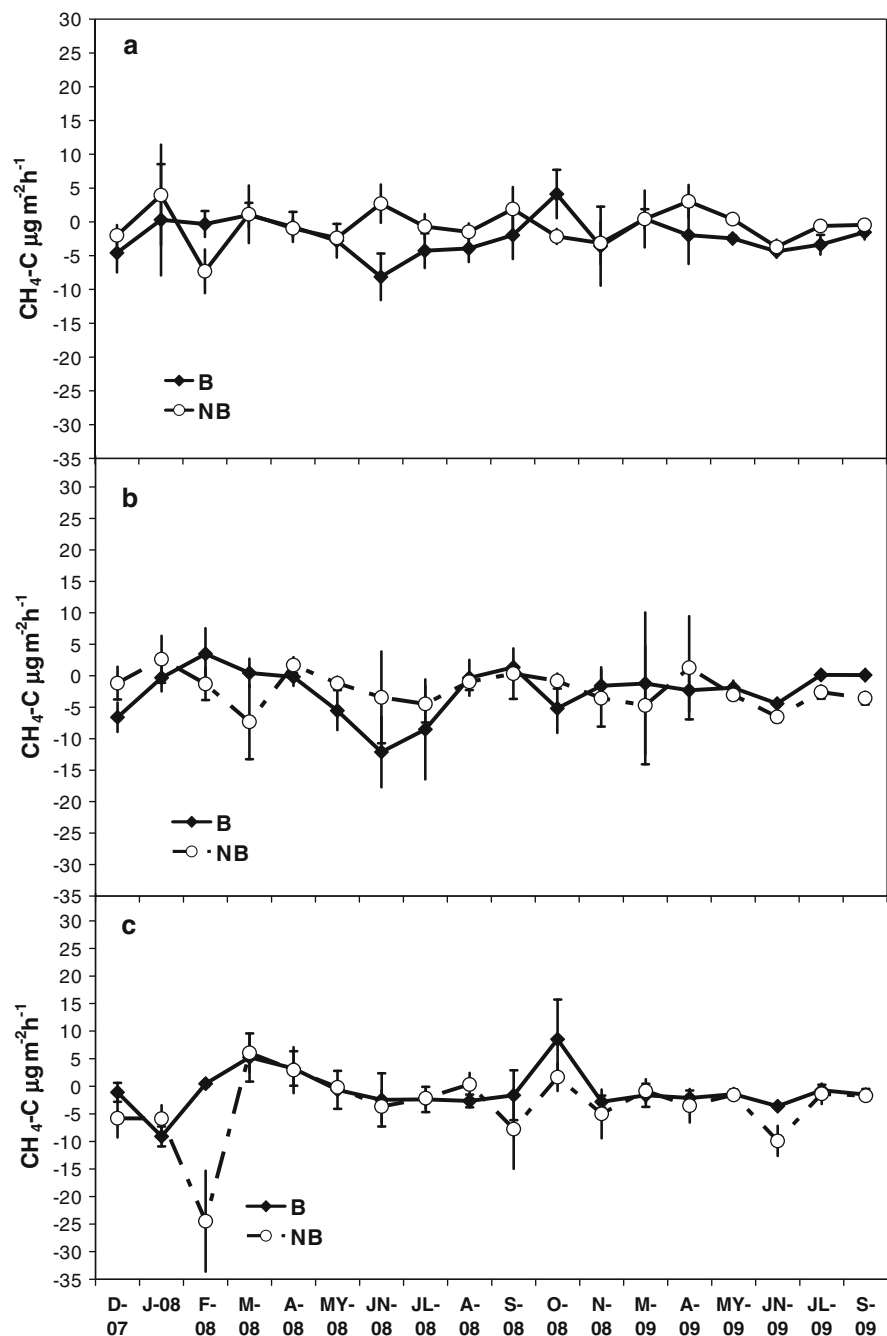
(Table 5). Fire increased CH$_4$ uptake cumulative fluxes (kg CH$_4$–C ha^{-1} year^{-1}) for QI (B = −3.3 kg CH$_4$–C ha^{-1} year^{-1}; NB = −0.9 kg CH$_4$–C ha^{-1} year^{-1}). In PS plots, fire reduced CH$_4$ uptake (B = −1.4 kg CH$_4$–C ha^{-1} year^{-1}; NB = −5.5 CH$_4$–C ha^{-1} year^{-1}). In QP no clear differences were found between burned and un-burned plots (B = −3.9 kg CH$_4$–C ha^{-1} year^{-1}; NB = −3.4 kg CH$_4$–C ha^{-1} year^{-1}).

Discussion

Nitrous oxide fluxes

Seasonal variation

Our soils are weak N$_2$O emitters and temporary sinks for atmospheric N$_2$O fluxes. The low N$_2$O fluxes

Table 6 Results of three-way repeated measures analysis of variance on CH_4 flux from the three studied sites

Factors	Sum of squares	Degr. of freedom	Mean square	F	p
Intercept	4144.63	1	4144.62	10.48556	**0.00**
Forest species (S)	2985.13	2	1492.56	3.77606	**0.05**
Fire (F)	832.98	1	832.98	2.10737	0.17
S × F	2102.32	2	1051.16	2.65935	0.11
Error	4743.24	12	395.27		
Time (month M)	20179.60	17	1187.03	2.89059	**0.00**
M × S	34538.99	34	1015.85	2.47374	**0.00**
M × F	19202.66	17	1129.56	2.75065	**0.00**
M × F × S	33643.98	34	989.52	2.40964	**0.00**
Error	83773.59	204	410.65		

Bold numbers indicate significant differences at p<0.05 level

presented in this work were also reported in previous studies concerning Mediterranean forest soils (Castaldi et al. 2006; Rosenkranz et al. 2006; Pilegaard et al. 2006). N_2O fluxes were temporally variable. Seasonal differences indicated that in wet months N_2O fluxes were high and in dry months N_2O fluxes declined. The parameters that best explain the seasonal variation in N_2O flux in all the forest ecosystems are soil temperature, soil moisture and previous day's rainfall. Production of N_2O in soils is primarily driven by microbial processes such nitrification and denitrification (Firestone and Davidson 1989), therefore soil temperature is a key variable affecting the emission rates of both gases. Emissions of N_2O increase with increasing soil temperatures (Skiba et al. 1998) due to the fact that rates of enzymatic processes generally increase with temperature as long as other factors (e.g., substrate or moisture) are not limiting. Soil water acts as a transport medium for NO_3^- and NH_4^+ and influences the rate of O_2 supply and thereby controls whether aerobic processes such nitrification or anaerobic processes such as denitrification dominate within the soil. In our case the relationship between hourly N_2O fluxes in all ecosystems are negatively correlated with soil temperature and positively correlated with soil moisture. This pattern is typical in seasonally dry ecosystems, revealing the fact that soil water content is a limiting factor in N_2O fluxes. Most of the temporal variation observed within a given site was explained by precipitation.

In general, dry and warm summer soils can be affected by drought, which favours soil aeration and is thus thought to make conditions unfavourable for N_2O production by denitrification (Castaldi 2000) or nitrifier denitrification. Furthermore, drought limits the overall activity of soil microorganisms, reducing the amount of N cycled in the ecosystem.

Therefore, lack of available N together with the low water content could contribute to a limitation of the N_2O production in the dry season. In Mediterranean ecosystems, total N tends to be low (Rovira and Vallejo 1997); and mineralization rates are generally low as a consequence of allelopathic compounds leached from plants and the quality of the sclerophyllous leaf, typical of such ecosystems (Gallardo and Merino 1992). This might result in low availability of mineral N in the soil, which could limit the rate of both nitrification and denitrification.

During the dry period many microorganisms and plants die, thereby increasing the concentrations of labile N and C available in the soil. The first rainfall on dry soil produces pulses of N_2O (Davidson 1993). The initial fluxes are thought to be caused by the accumulation of inorganic N in dry soils and the reactivation of water-stressed bacteria upon wetting, which then metabolize the available inorganic N (Davidson 1993). The significant increase in N_2O fluxes in wet months observed in our study may be explained at least in part by the positive correlation found between N_2O fluxes and the previous day's rainfall.

The significant increase in N_2O emissions in the wet months could be due to a combined effect of increased soil water content and mineralization. N_2O production improves as soil water content increases and aeration becomes restricted, with optimum values around 60%WFPS (Davidson 1991; Castaldi 2000).

Fig. 6 Relationship between average annual CH$_4$ fluxes (CH$_4$–C µg m^{-2}h^{-1}) versus average annual soil parameters. *QIB Quercus ilex burned, QINB Quercus ilex unburned, PSB Pinus sylvestris burned, PSNB Pinus sylvestris unburned, QPB Quercus pyrenaica burned, QPNB Quercus pyrenaica unburned*
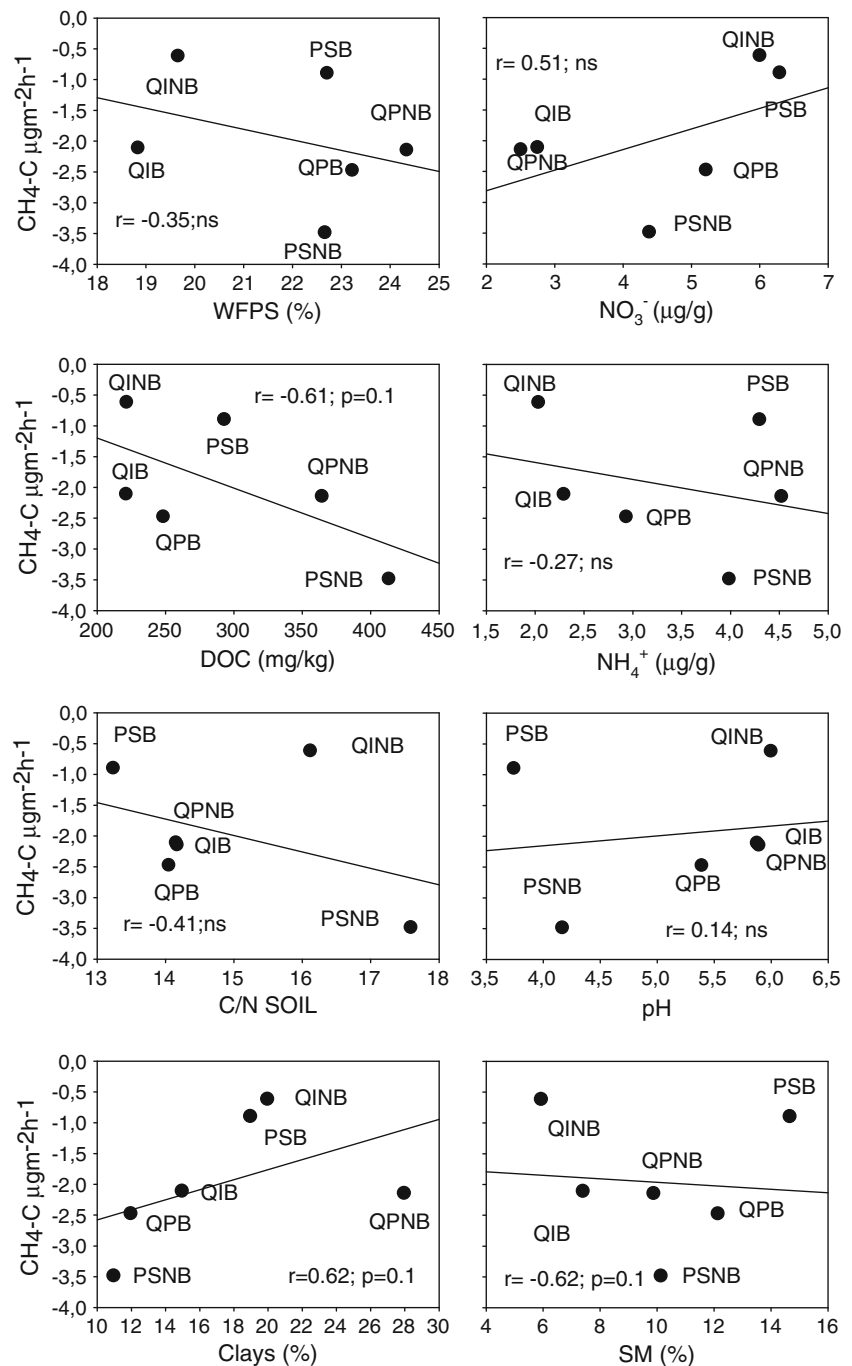
Maximum N$_2$O emissions were measured between 80 and 95% WFPS in a laboratory experiment with soil cores from different forests in Europe (Schindlbacher et al. 2004). The correlation between N$_2$O and WFPS is a well-known relationship associated with both nitrification and denitrification (Davidson 1992). In the case of this field data, WFPS was not a significant parameter affecting N$_2$O emission; a logarithmic transformation of N$_2$O emission improved the significance of the correlation, and N$_2$O fluxes tend to increase with monthly mean values of WFPS although the relationship stated is not significant.

However log-transformed data correlated with soil water content. Smith et al. (1998) also found that emission increases with increasing water content. Castaldi et al. (2004) found no significant correlation between N_2O fluxes and WFPS in savanna ecosystems. The coarse texture and the low water retention capacity of these soils limit the likelihood of anaerobic microsites developing in which N_2O production could take place (Firestone and Davidson 1989; Smith 1990). In our study sites, WFPS was always below 60%; the value at which O_2 diffusion is sufficiently reduced to allow for a sharp increase in N_2O production (Davidson 1991).

Soil emissions of N_2O are often positively correlated with inorganic N availability (Skiba et al. 2009). However, no clear relationship could be established between N_2O fluxes and soil NO_3^- in the present study. The possible existence of nitrification processes in these well-drained soils may explain the lack of correlation between N_2O fluxes and NO_3^- content since the nitrification process (NO_3^- production) is opposed to denitrification process.

In seasonally dry ecosystems, the nitrification rate is controlled by low water contents during part of the year (Bate 1981), and by allelopatic compounds (Gallardo and Merino 1992). In this type of ecosystems, soil C and N cycling may be also affected by the timing of plant biomass turnover relative to seasonal patterns of temperature and soil moisture. As the summer dry-season develops, perennial plants reduce growth rates and increase litterfall. The annual grasses senesce with the onset of the summer. In these soils, soil availability would be expected to increase during the early-summer due to the pulse of high C/N leaf and root litter inputs. The highest DOC values in our study were found in June 2008 (early summer) as was expected. In warm and dry areas, the highest concentrations of inorganic N were found in winter and spring or early-summer, when moisture favours mineralization, and the lowest concentrations were found during the summer, after the period of maximum plant growth and uptake. In our case, the highest soil NO_3^- content was observed in June 2008 (late spring-early summer) in all forest types, and also in March 2009 (winter) in the case of PS stands. This increment in NO_3^- might explain the increases observed in N_2O fluxes during these months.

We also found a peak in NO_3^- and NH_4^+ in PS and QINB plots, in August 2008. Surface soils of semiarid ecosystems tend to accumulate NO_3^- during the summer (Davidson et al. 1990). This NO_3^- accumulation suggests that microbial N immobilization is limited by C availability, which is inconsistent with the expectation that plant detrital inputs during the summer stimulate soil C availability. One explanation for this inconsistency is that by the time annual grasses senesce in late spring (May–June), the soil may already be too dry for microbes to colonize the newly released detritus.

The highest N_2O emissions were observed in February 2008, June 2008 and June 2009, in QPNB and PSNB plots. There are various parameters that might have contributed to the N_2O peak. The increase in soil moisture after rainfall, may have caused an increase in microbial activity. On the other hand, the level of N-deposition and the NO_3^- in the soil might have played an important role in the sudden release of N_2O (Davidson et al. 2000). The highest amounts of NO_3^- and NH_4^+ via throughfall reached the forest floor during these months (data not shown). A correlation was identified between N_2O flux and throughfall NO_3^- deposition. This N_2O peak coincided with higher concentrations of available inorganic N in the soil. Clear relationships between input of nitrogen to the forest and N_2O emissions have been reported previously (Butterbach-Bahl et al. 2002; Kitzler et al. 2006).

Net consumption of N_2O has been reported in forests (Fenn et al. 1996; Rosenkranz et al. 2006; Kitzler et al. 2006; Goldberg and Gebauer 2009). Net negative N_2O fluxes reported in the literature vary widely, from -0.0014 to -484 µg N_2O–N m^{-2}h^{-1} (Chapuis-Lardy et al. 2007). The net negative N_2O fluxes measured in our study fall within this range. Most N_2O uptake has been reported to occur under conditions of low mineral nitrogen availability and high soil moisture (Chapuis-Lardy et al. 2007), during denitrifying processes, which mainly occur under prevailing anoxic conditions. These conditions favour microbial N_2O consumption, because NO_3^- is preferred as an electron acceptor over N_2O, and high soil moisture may support the reduction of N_2O to N_2 due to anaerobic conditions. One difference between the two periods in which a sink effect was observed in our study was the WFPS, which was lower in summer (July 2008, August 2008) than in spring and fall (June 2008, October 2008). The negative fluxes observed in October 2008 in QPNB, QIB, QINB and

PSNB plots may be explained by the low soil NO_3^- content observed and the high soil moisture.

In summer, the sink effect observed may have been produced by a different pathway.

There are few reports in the literature that point to a soil N_2O sink function under dry conditions (Rosenkranz et al. 2006, Goldberg and Gebauer 2009) but underlying reasons have not yet been identified. Rosenkranz et al. (2006) linked negative fluxes in Mediterranean forest soils to very low N availability and high soil C content. They considered aerobic denitrification by heterotrophic nitrifiers as a possible pathway. Yamulki et al. (1995) linked low emission rates, as well as net negative fluxes, to high temperatures and low soil moisture content. An increase in soil temperature positively influences microbiological activity and gas diffusion, while it negatively affects the solubility of N_2O. This parameter combination coincides with our site properties and may explain our observation of net atmospheric N_2O uptake. In July 2008 and August 2008, the N_2O sink may be related to high DOC content and high soil temperature, combined with low levels of soil moisture and nitrogen.

Effects of forest type

The differences identified between the N_2O emissions from the different forest soils studied can most likely be explained by differences in soil properties and soil moisture. Differences among species were also identified as regards the quantity of C and N on the forest floor, which can be explained by interspecific differences in litter production and quality (Finzi et al. 1998; Pilegaard et al. 2006).

Soil nitrogen and C concentrations, as well as soil moisture were higher in PS and QP stands. DOC, total C and NH_4^+ were positively correlated with soil moisture and negatively correlated with soil temperature. Total mean N_2O emissions were positively correlated with soil moisture, WFPS, DOC and NH_4^+, and negatively correlated with soil temperature.

Among the different sites, the QI stands showed the lowest N_2O fluxes. Low soil N_2O fluxes have previously been documented in similar type ecosystems (Castaldi et al. 2006). This type of ecosystem is characterized by acidic, porous soils with rapid drainage and poor water retention capacity. Furthermore, due to the limited amount of substrate (C and

N) that can be used by microbes, N_2O emissions decrease (Firestone and Davidson 1989). The precipitation and soil moisture levels in the stands of this forest were lower than in the other studied stands, while soil temperatures were higher. Castaldi et al. (2006) reviewed published data regarding N_2O fluxes from soils of savannas and seasonally-dry ecosystems and concluded that N_2O fluxes were strongly limited by soil characteristics.

Under QP and PS, the higher organic matter input on the forest floor increases the nutrient content and improves soil structure. Moreover, the shading of soil surfaces, due to the higher vegetation cover, reduces the tendency of the surface to dry. This could explain the differences in N_2O fluxes from QI stands. Another reason for the difference in N-oxide emission between QI stands and the others forest stands, is the differences in N-deposition. In PS stands, N deposition in throughfall was 12 kg ha^{-1} $year^{-1}$ while in QI stands it was 2 kg ha^{-1} $year^{-1}$.

Shifts in the dominant vegetation type may alter soil C availability through differences in the quantity and quality of plant detritus inputs (Carrera et al. 2003), particularly in semiarid ecosystems where soil organic C and N pools are small. Increased C inputs, through differences in foliage and root turnover among different vegetation types, may increase microbial N demand and reduce N available for plant uptake. By contrast, increased quality of plant detritus inputs (i.e. lower litter C/N ratios) may result in greater N availability due to decreased microbial demand for inorganic N per unit organic C consumed (Carrera et al. 2003). This study revealed a negative correlation between log-N_2O total mean emission and the C/N ratio. This is in accordance with the findings of Ambus et al. (2006) and Pilegaard et al. (2006). A similar negative relationship has been identified between net nitrification and C/N ratio in forests throughout Europe (Persson et al. 2000). Klemedtsson et al. (2005) found that where C/N ratios are low (below 15–20), other parameters such as climate and pH increase in importance as predictors for N_2O emission.

In PS stands where N_2O fluxes were higher, the pH values were low. There was a (non significant) negative correlation between N_2O flux and pH. The negative correlation between N_2O and soil pH is a well-known relationship (Weslien et al. 2009). Di-nitrogenoxide reductase is inhibited by acidic pH, thus enhancing N_2O emissions (Firestone and

Davidson 1989; Skiba et al. 1993). Similar results have been found in Dutch forest soils (Martikainen and de Boer 1993) where acidic conditions favour N_2O production from both autotrophic and heterotrophic nitrifiers. In contrast, it has been demonstrated that pH values below 5 decrease N_2O production (Granli and Bøckman 1994).

There was a negative correlation (non significant) between pH and NH_4^+ in soil, which could be due to the acidifying effect of NH_4^+ in soil. The sites with high N_2O emission also consistently exhibited low pH (PS). Soil pH was negatively correlated with total soil C ($r = -0.93$, $p = 0.0$) and total soil N ($r = -0.95$, $p = 0.0$), which may be the result of differences in humic acid concentration and or types.

The observed variations in N_2O fluxes were positively related to variations in clay content. In QPNB plots, the N_2O emissions might be related to higher clay content and higher mean pH values, which provide favourable conditions for N_2O production by denitrification. N_2O production by denitrification and nitrification improves as soil water content increases and aeration becomes restricted, with optimum values reached at around 60%WFPS (Davidson 1991; Castaldi 2000). In this case, with WFPS values at around 30%, the higher proportion of fine soil particles improves the capacity of the soil to retain water, as well as the amount of soil micropores (as opposed to macropores) where O_2 limitation might occur more easily, thus favouring N_2O production.

Effects of fire

As stated in our first hypothesis the effect of fire on soil N_2O flux depends on forest site, soil characteristics and seasonal climatic conditions. The N_2O cumulative fluxes were higher in unburned plots (6.4 kg N_2O–N ha^{-1} year^{-1}) than in burned plots (3.4 kg N_2O–N ha^{-1} year^{-1}) in the QP stands. In the QI and PS stands no significant differences were found between burned compared to non-burned plots (QI = 3.7 kg N_2O–N ha^{-1} year^{-1}; PS = 5.2 kg N_2O–N ha^{-1} year^{-1}). When N_2O cumulative fluxes were compared between burned plots in the different forest stands, we found that PS had the highest values.

In QP, the decrease in cumulative fluxes in burned plots compared to non-burned may be explained by the different characteristics of each stand. In QPNB, vegetation cover in conjunction with the presence of

higher clay content in the soil, protects the soil from desiccation. The higher soil moisture content in this plot over the entire experimental period could explain the higher N_2O fluxes.

In QI, the absence of differences in N_2O cumulative fluxes might be explained by the time elapsed since the wildfire. In this forest, the wildfire was the most recent of those studied (August 2004); 4 years prior to the experimental period. The temporal transient increase in N content following the fire may explain the absence of differences in N_2O fluxes between burned and un-burned plots. Fire usually causes an immediate increase in available N pools. By way of explanation for the increase in mineral-N, most authors point to the rapid decomposition of organic-N compounds produced by the combustion of organic matter (Certini 2005).

However in the PS plots, where the fire occurred at an earlier date (2001), we expected a decrease in soil N content and N_2O fluxes since this effect is often observed in the long-term. The absence of differences in N_2O fluxes between burned and unburned plots in this case might be explained by the invasion of the burned plot by the N-fixing leguminous plant *Adenocarpus hispanicus*. This plant is a pioneer species which is particularly invasive following fire activity since it is especially adapted to fire. *Adenocarpus hispanicus* seeds which have lain dormant in forest litter for many years are activated by fire and winter weather, resulting in prolific germination following a wildfire. Nitrogen fixing plants can increase soil N content as well as cycling rates (Rothe et al. 2002). Consequently in PSB stands, lost N may be replaced by inputs from N fixers following a fire. In other forest and woodland soils, the presence of N fixing vegetation has been shown to increase soil N_2O production (Angoa-Perez et al. 2004, Benedikt et al. 2009). However, significant differences in total N were not detected between burned and un-burned plots in our forest stands.

We observed different patterns in N_2O fluxes between burned and un-burned stands over the course of the year. We expected that on the spring sampling dates (June 2008), the differences in inorganic N and N_2O levels between burned and unburned plots would be greater than on the winter sampling dates due to higher soil temperature and moisture levels, which would promote higher microbial activity (Gallardo and Schlesinger 1994). However, this pattern was only observed in QP stands.

In burned soils, N_2O fluxes were low in wet and hot months (spring). A possible explanation for this is that the water retention capacity of the soil as well as its ability to resist evaporation might be negatively affected when this ecosystem is disturbed by wildfire, further slowing the processes of nitrification and denitrification. A significant decrease in net mineralization rates in comparison to unburned plots was still observed in a *Pinus* forest in Spain 17 years after a fire (Durán et al. 2009), indicating slow recovery of N turnover in these forests. Another reason for the low N_2O fluxes could be the competition between microbes and plants for N during the vegetative growth period.

However this argument can not be used to explain the increase in N_2O flux in burned soils under PS (May 2008, June 2008, October 2008) and QI (May 2008). In these months, higher soil temperatures and moistures measured in these plots might increase the rate of decomposition during this period. Higher temperatures were recorded in burned plots, probably as a consequence of the reduced plant canopy which leads to higher levels of irradiance reaching the soil surface. In PS stands, leguminous plants might have increased the inorganic nitrogen content in the soil during this period. Moreover, the PS burned stands exhibited higher NO_3^- values than the unburned stands in June 2008.

In August 2008, the N_2O flux in PSB plots was lower than in unburned plots. Soil NO_3^- values in PSB were also lower. This may be explained again by the presence of *Adenocarpus hispanicus*. Leguminous plants require a higher concentration of N than plants of other families, which is not dependent on the assimilation methods of individual plants. Thus, when atmospheric-N fixation is not possible, such as during decreased water availability in summer, leguminous plants must increase N uptake from the soil (Peoples and Craswell 1992). Water stress affects the N-fixing process more significantly than N assimilation and uptake. Consequently, the lower water content may have diminished soil mineralization and N-fixation rates more than N uptake, resulting in a decrease in soil N. In winter (March 2009), NO_3^- is higher in PSB plots. A higher concentration of N-rich organic matter from litterfall beneath the legume canopy may explain the higher NO_3^- in the soil (Jones et al. 2005). However, there were no differences in soil N_2O flux, probably due to the lower soil moisture content in the burned stand during this month.

Methane fluxes

Seasonal variation

In general, our ecosystems appeared to act as methane sinks. However during wet months, they could also be a net source of CH_4. The magnitude of the observed net CH_4 uptake is in the range of that reported for Mediterranean and temperate nitrogen limited forest ecosystems (Merino et al. 2004; Rosenkranz et al. 2006; Castaldi and Fierro 2005; Castaldi et al. 2006). Well aerated soils are known to be significant sinks for atmospheric CH_4. Castaldi and Fierro (2005) also observed higher CH_4 oxidation rates during dry, warm periods in a *Q. ilex* stand in Italy.

The observed seasonal trend was influenced by soil water availability. However, no significant correlations were found between soil water content and CH_4. The observed seasonal trend is consistent with other studies (Butterbach-Bahl and Papen 2002; Castaldi and Fierro 2005, Castaldi et al. 2006; Sullivan et al. 2008) in which CH_4 oxidation rates increased during the drier season. During the wet season, when soils were wetter, net CH_4 emissions have been reported (Butterbach-Bahl and Papen 2002).

The shift from CH_4 sink to CH_4 source in well-aerated soils has been related to the formation of anaerobic microsites where CH_4 production could occur. Verchot et al. (2000), found that CH_4 flux variability was predicted by a linear combination of WFPS and soil respiration, so that net CH_4 emissions corresponded to the periods of higher soil respiration and water content. Thus, although CH_4 emissions are typically associated with heavy textured and water saturated soils, the development of anaerobic microsites in which CH_4 production might take place, might also be hypothesized to occur in medium and light textured soil (Verchot et al. 2000). The mechanism might be similar to that proposed by Smith (1990) to explain N_2O production and denitrification in aerobic soils. Zones of intense microbial activity might develop in association with easily decomposable fresh organic matter, and if the water content in the soil is sufficiently high to result in O_2 consumption by respiration at a faster rate than O_2 diffusion from the surrounding areas, then anaerobic conditions

might be reached and CH_4 produced. This is consistent with the observed increase in net CH_4 production reported in this study, when the increase in soil water content also corresponds with the growing season, which implies higher root and microbial respiration rates (data not shown).

Effects of forest type

PS and QP stands absorb more CH_4 than QI stands. CH_4 uptake is supposed to be strongly affected by soil texture (Born et al. 1990) and soil moisture (Borken et al. 2000) due to their effect on the diffusion velocities of CH_4 and O_2 (Potter et al. 1996a).

CH_4 absorption increases with soil DOC content and C/N ratio. There is a relationship between clay content and CH_4 consumption. The forest plot with the highest clay content exhibited lower CH_4 uptake. This may be due to a reduced diffusion rate of atmospheric CH_4 into the soil. Boeckx and Van Cleemput (1996) found a lower CH_4 consumption rate in fine-textured soils than coarse-textured soils.

The optimum pH for CH_4 oxidation was 5.5. In our case we observed CH_4 oxidation at pH values below this threshold (3.5–5). Acidophilic methanotrophos and others can be active in soils at pH 4 (Dedysh et al. 2000; Radajewski et al. 2002). This may explain why CH_4 oxidation appeared to be independent of pH in forest soils, in accordance with reports review by Borken and Brumme (1997).

Increasing NH_4^+ and NO_3^- concentrations were associated with decreasing CH_4 consumption rates. NH_4^+ production appears to have an inhibitory effect on CH_4 oxidation because ammonium mono-oxidase and methane mono-oxidase enzymes are linked in methanotrophs (Bédard and Knowles 1989). However, NO_3^- inhibition on CH_4 oxidation is less likely.

Effects of fire

Fire increases CH_4 uptake cumulative fluxes in QI (B = −3.3 kg CH_4–C ha^{-1} $year^{-1}$; NB = −0.9 kg CH_4–C ha^{-1} $year^{-1}$). This suggests no direct effect of fire on soil capacity to oxidize CH_4 or that the microbial population recovers within 4 years after fire. The amount of soil heating would only be enough to destroy a small fraction of the total soil microorganism population within the greater soil profile. Poth et al. (1995) found that soil CH_4 uptake

significantly increases after fire in savanna soils burned 30 days earlier. They hypothized that burning might increase the diffusion of CH_4 into the soil, and hence CH_4 oxidation by opening root channels and removing litter layers.

In QP stands, no clear differences were found between burned and unburned plots (B = −3.9 kg CH_4–C ha^{-1} $year^{-1}$; NB = −3.4 kg CH_4–C ha^{-1} $year^{-1}$).

In PS stands, fire decreases CH_4 uptake (B = −1.4 kg CH_4–C ha^{-1} $year^{-1}$; NB = −5.5 kg CH_4–C ha^{-1} $year^{-1}$). This may be due to the increasing inorganic N in the soil as a consequence of the N-fixing species present in this plot. Increasing NH_4^+ content in the soil should lead to a reduction in methanotrophic activity because NH_3 might be a competitive substrate for methane monooxygenase (Castaldi and Fierro 2005). Another explanation is the combination of higher temperature, less structured soil and smaller quantity of soil nutrients that could be detrimental to the methanotrophic population of these soils and their CH_4 oxidation capacity.

Low CH_4 oxidation values in PSB may also be explained by the low pH values observed in this plot. Negative effects of pH on CH_4 oxidation were noted by Hütsch et al. (1994). The probable explanation in their case was that acid precipitation had caused a release of heavy metals, such as aluminium, iron, manganese and cadmium. This may also explain the results obtained in our study, in which we have detected an increase in exchangeable acidity (EA), the release of exchangeable Al^{3+} from organic matter and the diminution of Ca^{2+}, Mg^+, K^+ and Na^+.

Conclusions

The forest soils in the surrounding area of Madrid were mostly weak N_2O emitters and significant sinks for atmospheric CH_4. The nutrient status in forest soils had an effect on the fluxes of N_2O and CH_4. Mean fluxes of N_2O and CH_4 were highest in Scots Pine and Pyrenean oak stands. A weak N_2O uptake from the atmosphere into the soil was observed in fall and summer. The shift from CH_4 sink to CH_4 source was observed in wet months.

N_2O and CH_4 seasonal variation were mainly related to soil water availability.

The impact of fire on the fluxes of N_2O and CH_4 differed from one ecosystem to another, and from one season to another. The burned sites showed higher CH_4 oxidation in *Q.ilex* stands, and lower oxidation rates in *P. sylvestris* stands. Fire decreases N_2O fluxes in *Q. pyrenaica* stands.

Thus, the results confirm the hypothesis that was being tested: that the impact of fire on CH_4 and N_2O flux might strongly depend on the climatic seasonal patterns, ecosystem type and main soil characteristics.

Due to the lack of information on fluxes in Mediterranean ecosystems, it is difficult to compare their contribution to the local, regional and global flux of N_2O and CH_4. This emphasizes the necessity for better estimates of atmospheric CH_4 and N_2O fluxes, which can only be achieved through an improved understanding of the underlying processes and supplementary field data.

References

Ambus P, Zechmeister-Boltenstern S, Butterbach-Bahl K (2006) Relationship between nitrous oxide production and nitrogen cycling in European forests. Biogeosciences 3:135–145

Angoa-Perez MV, Castaneda JG, Frias-Hernandez JT, Franco-Hernandez O, Van Cleemput O, Dendooven L, Olalde V (2004) Trace gas emissions from soil of the central highlands of Mexico as affected by natural vegetation: laboratory study. Biol Fertil Soils 40(4):252–259

Bate GC (1981) Nitrogen cycling in savanna ecosystems. In: Clark FE, Rosswall T (eds) Terrestrial nitrogen cycles. Swedish National Science Research Council, Stockholm, Sweden, pp 463–475

Bédard C, Knowles R (1989) Physiology, biochemistry, and specific inhibitors of CH_4, NH_4^+, and CO oxidation by methanotrophs and nitrifiers. Microbiol Mol Biol Rev 53:68–84

Benedikt JF, Livesley SJ, Drösler M, Van Gorsel E, Arndt SK (2009) Soil-atmosphere greenhouse gas exchange in a cool, temperate *Eucalyptus delegatensis* forest in south-eastern Australia. Agr Forest Meteorol 149:393–406

Boeckx P, Van Cleemput O (1996) Methane oxidation in neutral landfill cover soil: influence of moisture content, temperature and nitrogen-turnover. J Environ Qual 25:178–183

Borken W, Brumme R (1997) Liming practice in temperate forest ecosystems and the effects on CO_2, N_2O and CH_4 fluxes. Soil Use Manage 13:251–257

Borken W, Brumme R, Xu YJ (2000) Effects of prolonged soil drought on CH_4 oxidation in a temperate spruce forest. J Geophys Res 105:7079–7088

Born M, Dörr H, Levin I (1990) Methane consumption in aerated soils of the temperate zone. Tellus 42B:2–8

Butterbach-Bahl K, Papen H (2002) Four years continuous record of CH_4 exchange between the atmosphere and untreated and limed soil of a N-saturated spruce and beech forest ecosystem in Germany. Plant Soil 240:77–90

Butterbach-Bahl K, Breuer L, Gasche R, Willibald G, Papen H (2002) Exchange of trace gases between soils and the atmosphere in Scots pine forest ecosystems of the northeastern German lowlands 1. Fluxes of N_2O, NO/NO_2 and CH_4 at forest sites with different N-deposition. For Ecol Manage 167:123–134

Carrera AL, Bertiller MB, Sain CK, Mazzarino MJ (2003) Relationship between plant nitrogen conservation strategies and the dynamics of soil nitrogen in the arid Patagonian Monte, Argentina. Plant Soil 255:595–604

Castaldi S (2000) Responses of nitrous oxide, dinitrogen and carbon dioxide production and oxygen consumption to temperature in forest and agricultural light-textured soils determined by model experiment. Biol Fert Soils 36:67–72

Castaldi S, Aragosa D (2002) Factors influencing nitrification and denitrification variability in a natural and fire-disturbed Mediterranean shrubland. Biol Fert Soils 36:418–425

Castaldi S, Fierro A (2005) Soil–atmosphere methane exchange in undisturbed and burned Mediterranean Shrubland of southern Italy. Ecosystems 8:182–190

Castaldi S, De Pascale RA, Grace J, Nokonova N, Montes R, San José J (2004) Nitrous oxide and methane fluxes from soils of the Orinoco savanna under different land uses. Glob Chang Biol 10:1947–1960

Castaldi S, Ermice A, Strumia S (2006) Fluxes of N_2O and CH_4 from soils of savannas and seasonally-dry ecosystems. J Biogeogr 33:401–415

Castro MS, Steuler PA, Melillo JM (1995) Factors controlling atmospheric methane consumption by temperate forest soils. Global Biogeochem Cycles 9:1–10

Certini G (2005) Effects of fire on properties of forest soils: a review. Oecologia 143:1–10

Chapuis-Lardy L, Matay A, Chotte JL, Berboux (2007) Soils, a sink for N_2O? A review. Glob Chang Biol 13:1–17

Cicerone RJ (1979) Changes in stratospheric ozone. Science 21:35–42

Conrad R, Andreae MO, Schimel DS (1989) Control of methane production in terrestrial ecosystems. In: Andreae MO, Schimel DS (eds) Exchange of trace gases between terrestrial ecosystems and the atmosphere. Wiley, New York, pp 39–58

Davidson EA (1991) Fluxes of nitrous oxide and nitric oxide from terrestrial ecosystems. In: Rogers JE, Whitman WB (eds) Microbial production and consumption of greenhouse gases: methane, nitrogen oxides and halomethanes. American Society of Microbiology, Washington DC, pp 219–235

Davidson EA (1992) Pulses of nitric oxide and nitrous oxide flux following wetting and dry soil: an assessment of probable sources and importance relative to annual fluxes. Ecol Bull 42:149–155

Davidson EA (1993) Soil water content and the ratio of nitrous oxide to nitric oxide emitted from soil. In: Oremland RS (ed) Biogeochemistry of global change. Chapman and Hall, New York, pp 369–386

Davidson EA, Stark JM, Firestone MK (1990) Microbial production and consumption of nitrate in an annual grassland. Ecology 71:1968–1975

Davidson EA, Keller M, Erickson HE, Verchot LV, Veldkamp E (2000) Testing a conceptual model of soil emissions of nitrous and nitric oxides. Bioscience 50:667–680

Dedysh SN, Liesack W, Khmelenina VN, Suzina NE, Trotsenko YA, Semraum JD et al (2000) Methylocella palustris gen.nov.s sp nov., a new methane-oxidizing acidophilic bacterium from peat bogs; representing a novel subtype of serine-pathway methanotrophs. Int J Syst Evol Micr 50: 955–969

Durán J, Rodríguez A, Fernández-Palacios JM, Gallardo A (2009) Changes in net mineralization rates and soil N and P pools in pine forest wildfire chronosequence. Biol Fertil Soils 45:781–788

FAO (1998) World reference base for soil resources, food and agriculture. Organization of the United Nations, Rome

Fenn ME, Poth MA, Johnson DW (1996) Evidence for nitrogen saturation in the San Bernardino Mountains in southern California. Forest Ecol Manag 82:211–230

Finzi A, Van Breemen N, Canham CD (1998) Canopy tree-soil interactions within temperate forest: species effects on soil carbon and nitrogen. Ecol Appl 8:440–446

Firestone MK, Davidson EA (1989) Microbiological basis of NO and N_2O production and consumption in soil. In: Andreae MO, Schimel DS (eds) Exchange of trace gases between terrestrial ecosystems and the atmosphere. Wiley, New York, pp 7–21

Gallardo A, Merino J (1992) Nitrogen inmobilization in leaf litter at two Mediterranean ecosystems of SW Spain. Biogeochemistry 15:213–228

Gallardo A, Schlesinger WH (1994) Factors limiting microbial biomass in the mineral soil and forest floor of a warm-temperate forest. Soil Biol Biochem 26:1409–1415

Gillon D, Gomendy V, Houssard C, Marechal J, Valette JC (1995) Combustion and nutrient losses during laboratory burns. Int J Wildland Fire 5:1–12

Giovannini G, Lucchesi S, Giachetti M (1988) Effect of heating on some physical and chemical parameters related to soil aggregation and erodibility. Soil Sci 146: 255–261

Goldberg SD, Gebauer G (2009) Drought turns a central European Norway spruce forest soil from an N_2O source to a transient N_2O sink. Glob Chang Biol 15:850–860

Granli T, Bøckman OC (1994) Nitrous oxide from agriculture. Norw J Agr Sci 12(suppl):1–128

Houghton JT, Meira F, Callander IG, Harris BA, Kattenberg N, Maskell K (1996) Climate change 1995: the science of climate change. Cambridge University Press, New York

Hütsch BW, Webster CP, Powlson DS (1994) Methane oxidation in soil as affected by land use, soil pH and N fertilization. Soil Biol Biochem 26:1613–1622

Inclán R, Uribe C, De la Torre D et al (2010) Carbon dioxide fluxes across the Sierra de Guadarrama, Spain. Eur J Forest Res 129:93–100

IPCC (1992) Greenhose gases and aerosols. In: Houghton JT, Callander BA, Varney SK (eds) Climate change 1992. The supplementary report to the IPCC scientific assessment, Cambridge University Press, Cambridge

IPCC (2007) Climate change 2007: the physical science basis. Contribution of working group I to the fourth assessment report of the intergovernmental panel on climate change. Cambridge University Press, Cambridge

Johnson DM, Murphy JD, Susfalk RB, Caldwell TG, Miller WW, Walker RF (2005) The effects of wildfire, salvage logging, and post-fire N fixation on the nutrient budgets of a Sierran forest. For Ecol Manag 220:155–165

Johnson DW, Fenn ME, Watkins WM, Hunsaker CF (2009) Fire effects on carbon and nitrogen cycling in forests of the Sierra Nevada. In: Bytnerowicz A, Arbaugh A, Riebau A, Andersen C (eds) Developments in environmental science, vol 8. Elsevier BV, San Diego, pp 405–423

Jones DL, Healey JR, Willett VB et al (2005) Dissolved organic nitrogen uptake by plants-an important N uptake pathway? Soil Biol Biochem 37:413–423

Kitzler B, Zechmeister-Boltenstern S, Holtermann CL et al (2006) Nitrogen oxides emission from two beech forests subjected to different nitrogen loads. Biogeosciences 3:310–393

Klemedtsson L, Von Arnold K, Weslien P, Gundersen P (2005) Soil CN ratio as a scalar parameter to predict nitrous oxide emissions. Glob Chang Biol 11:1142–1147

Martikainen PJ, de Boer W (1993) Nitrous oxide production and nitrification in acidic soil from a Dutch coniferous forest. Soil Biol Biochem 25:343–347

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

Mosier AR, Schimel DS, Valentine D, Bronson K, Parton WJ (1991) Methane and nitrous oxide fluxes in native, fertilized and cultivated grasslands. Nature 350:330–332

Neary DG, Klopatek CC, DeBano LF, Ffolliott PF (1999) Fire effects on belowground sustainability: a review and synthesis. Forest Ecol Manag 122:51–71

Papen H, Dunkin KA, Firestone MK (2001) N_2O and CH_4 flux soils of an N-limited and N-fertilized spruce forest ecosystem of temperate zone. J Appl Bot 75:159–163

Parton WJ, Holland EA, Del Grosso SJ et al (2001) Generalized model for NO_x and N_2O emissions from soils. J Geophys Res 106:17403–17419

Peoples MB, Craswell ET (1992) Biological nitrogen fixation: investments, expectations and actual contributions to agriculture. Plant Soil 141:13–39

Persson T, Rudebeck A, Jussy JH, Colin-Belgrand M, Priemé A, Dambrine E, Karlsson PS, Sjöberg RM (2000) Soil nitrogen turnover: mineralisation, nitrification and denitrification in European forest soil. In: Schulze ED (ed) Carbon and nitrogen cycling in European forest ecosystems. Springer-Verlag, Berlin, pp 297–340

Philippot L, Hallin S, Börjesson G, Baggs EM (2009) Biochemical cycling in the rhizosphere having an impact on global change. Plant Soil (special) 321:61–81

Pilegaard K, Skiba U, Ambus P, Beier N et al (2006) Factor controlling regional differences in forest soil emission of nitrogen oxides (NO and N$_2$O). Biogeosciences 3: 651–661

Poth M, Anderson IC, Miranda HS, Miranda AC, Riggan PG (1995) The magnitude and persistence of soil NO, N$_2$O, CH$_4$ and CO$_2$ fluxes from burned tropical savanna in Brazil. Global Biogeochem Cycles 9:503–513

Potter CS, Davidson EA, Verchot LV (1996a) Estimation of global biogeochemical controls and seasonality in soil methane consumption. Chemosphere 32:2219–2246

Potter CS, Matson PA, Vitousek PM et al (1996b) Process modeling of controls on nitrogen gas emissions from soils worldwide. J Geophys Res 101:1361–1477

Prieto-Fernández A, Acea MJ, Carballas T (1998) Soil microbial and extractable C and N after wildfire. Biol Fertil Soils 27:132–142

Radajewski S, Webster G, Reay DS, Morris SA, Ineson P, Nedwell DB et al (2002) Identification of active methylotroph populations in an acidic forest soil by stable isotope probing. Microbiol-SGM 148:2331–2342

Rodríguez A, Durán J, Fernández-Palacios JM, Gallardo A (2009) Spatial pattern and scale of soil N and P fractions under the influence of a leguminous shrub in a *Pinus canariensis* forest. Geoderma 51:303–310

Rosenkranz P, Brüggemann N, Papen H, Xu Z, Seufert G, Butterbach-Bahl K (2006) N$_2$O, NO and CH$_4$ exchange, and microbial N turnover over a Mediterranean pine forest soil. Biogeosciences 3:121–133

Rothe A, Cromack K Jr, Resch SC, Makineri E, Son Y (2002) Soil carbon and nitrogen changes under Douglas-fir with and without red alder. Soil Sci Soc Am J 66:1988–1995

Rovira P, Vallejo VR (1997) Organic carbon and nitrogen mineralization under Mediterranean climatic conditions: the effects of incubation depth. Soil Biol Biochem 29: 1509–1520

Rutigliano FA, De Marco A, Dáscolo CS, Gentile A, Virzo De Santo A (2007) Impact of fire on fungal abundance and microbial efficiency in C assimilation and mineralization in a Mediterranean maquis soil. Biol Fertil Soils 44:371–377

Schindlbacher A, Zechmeister-Boltenstern S, Butterbach-Bahl K (2004) Effects of soil moisture and temperature on NO, NO$_2$ and N$_2$O emission from European forest soils. J Geophys Res 109, D17302:1–2

Schmidt I, Van Spanning RJM, Jetten MSM (2004) Denitrification and ammonia oxidation by *Nitrosomonas europaea* wild-type, and NirK- and Nor-deficient mutants. Microbiology 150:4107–4114

Skiba U, Smith KA, Fowler D (1993) Nitrification and denitrification as sources of nitric oxide and nitrous oxide in a sandy loam soil. Soil Biol Biochem 25:1527–1536

Skiba U, Sheppard LJ, MacDonald J, Fowler D (1998) Some key environmental variables controlling nitrous oxide emissions from agricultural and semi-natural soils in Scotland. Atmos Environ 32:3311–3320

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

Skiba U, Drewer J, Tang YS et al (2009) Biosphere-atmosphere exchange of reactive nitrogen and greenhouse gases at the NitroEurope core flux measurement sites: measurement strategy and first data sets. Agr Ecosyst Environ 133:139–149

Smith KA (1990) Anaerobic zones and denitrification in soil: modellling and measurements. In: Revsboech NP, Sørensen J (eds) Denitrification in soil and sediments. Plenum Press, New York, pp 228–240

Smith KA, Thomson PE, Clayton PE, McTaggart IP, Conen F (1998) Effects of temperature, water content and nitrogen fertilization on emissions of nitrous oxide by soils. Atmos Environ 32:3301–3309

Smith KA, Dobbie KE, Ball BC, Bakken LR, Sitaula BK, Hansens S, Brumme R, Borken WB, Christensen S, Priemé A, Fowler D, MacDonald A, Skiba U, Klemedtsson L, Kasimir-Klemedtsson A, Derorska A, Orlanski P (2000) Oxidation of atmospheric methane in Northern European soils, comparison with other ecosystem, and uncertainties in the global terrestrial sink. Glob Chang Biol 6:791–803

Sullivan BW, Kolb TE, Hart SC, Kaye JP, Dore S, Montes-Helu M (2008) Thinning reduces soil carbon dioxide but not methane flux from southwestern USA ponderosa pine forest. Forest Ecol Manag 255:4047–4055

Verchot LV, Davidson EA, Cattânio JH et al (2000) Land use change and biogeochemical controls of methane fluxes in soils of Eastern Amazonia. Ecosystems 3:41–56

Wan S, Hui D, Luo Y (2001) Fire-effects on nitrogen pools and dynamics in terrestrial ecosystems: a meta-analysis. Ecol Appl 11:1349–1365

Weslien P, Kasimir Klemedtsson A, Börjesson G, Klemedtsson L (2009) Strong pH influence on N$_2$O and CH$_4$ fluxes from forested organic soils. Eur J Soil Sci 60: 311–320

Westerling AL, Hidalgo HG, Cayan DR, Swetnam TW (2006) Warming and earlier spring increase western U.S. forest wildfire activity. Science 313:940–943

Wienhold BJ, Klemmedson JO (1992) Effect of prescribed fire on nitrogen and phosphorus in Arizona chaparral soil-plant systems. Arid Soil Res Rehabil 6:285–296

Wolf B, Zheng X, Brüggemann N, Chen W, Dannenmann M, Han X, Sutton MA, Wu H, Yao Z, Butterbach-Bahl K (2010) Grazing-induced reduction of natural nitrous oxide release from continental steppe. Nature 464:881–884

Yamulki S, Goulding KWT, Webster CP, Harrison RM (1995) Studies on NO and N$_2$O fluxes from wheat field. Atmos Environ 14:1627–1635