# **REGULAR ARTICLE**

# Soil-atmosphere exchange of $N_2O$ , $CO_2$ and $CH_4$ along a slope of an evergreen broad-leaved forest in southern China

Yunting Fang • Per Gundersen • Wei Zhang • Guoyi Zhou • Jesper Riis Christiansen • Jiangming Mo • Shaofeng Dong • Tao Zhang

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Abstract At most sites the magnitude of soil-atmosphere exchange of nitrous dioxide (N<sub>2</sub>O), carbon dioxide  $(CO_2)$  and methane  $(CH_4)$  was estimated based on a few chambers located in a limited area. Topography has been demonstrated to influence the production and consumption of these gases in temperate ecosystems, but this aspect has often been ignored in tropical areas. In this study, we investigated spatial variability of the net fluxes of these gases along a 100 m long slope of a evergreen broadleaved forest in southern China over a whole year. We expected that the lower part of slope would release more N<sub>2</sub>O and CO<sub>2</sub>, but take up less atmospheric CH<sub>4</sub> than the upper part due to different availability of water and nutrients. Our results showed that the soil moisture (Water Filled Pore Space, WFPS) decreased along the slope from bottom to top as we expected,

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Y. Fang (⊠) · W. Zhang · G. Zhou · J. Mo · S. Dong · T. Zhang South China Botanical Garden, The Chinese Academy of Sciences, Xingke Road No 723, Tianhe District, Guangzhou 510650, China e-mail: fangyt@scbg.ac.cn

P. Gundersen · J. R. Christiansen
Forest & Landscape Denmark, Faculty of Life Sciences, University of Copenhagen,
Hørsholm Kongevej 11,
2970 Hørsholm, Denmark but among the three gases only  $N_2O$  emissions followed this pattern. Annual means of WFPS ranged from 27.7% to 52.7% within the slope, and annual emissions of  $N_2O$  ranged from 2.0 to 4.4 kg N ha<sup>-1</sup> year<sup>-1</sup>, respectively. These two variables were highly and positively correlated across the slope. Neither potential rates of net N mineralization and nitrification, nor  $N_2O$  emissions in the laboratory incubated soils varied with slope positions. Soil CO<sub>2</sub> release and CH<sub>4</sub> uptake appeared to be independent on slope position in this study. Our results suggested that soil water content and associated N<sub>2</sub>O emissions are likely to be influenced by topography even in a short slope, which may need to be taken into account in field measurements and modelling.

Keywords Nitrous oxide · Carbon dioxide · Methane · Soil water content · Slope · Subtropical forest

## Introduction

Carbon dioxide (CO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O) and methane (CH<sub>4</sub>) are the three main greenhouse gases (GHG) contributing to global warming (IPCC 2001). The increases in their atmospheric concentrations are attributed mainly to anthropogenic activities, such as deforestation, agricultural practices, and fossil fuels combustion. Besides, a considerable amount of atmospheric GHG is produced and consumed through soil processes (IPCC 2001). However, the large temporal and spatial variability of soil processes makes the accurate estimation and prediction of landscape soil–atmosphere exchange of these gases challenging, especially in tropical forests where relatively few sites have been monitored (Breuer et al. 2000; Werner et al. 2007). Furthermore, at most sites the magnitude was estimated based on a few chambers located in a limited area (Breuer et al. 2000; Tang et al. 2006), which very likely causes potential error when estimating regional gas fluxes between land and atmosphere by scaling up from small sampling units over heterogeneous areas (Reiners et al. 1998).

A range of environmental factors, such temperature and moisture, and soil properties have been identified to be controls of soil C and N cycling processes (Davidson et al. 2000; Corre et al. 2002; Saiz et al. 2006; Tang et al. 2006; Mo et al. 2008). These controls are, in turn, influenced by topography, through the movements of surface and subsurface water, nutrients and dissolved soil organic matter (Hairston and Grigal 1994; Hirobe et al. 1998; Hishi et al. 2004). Nitrogen concentrations in living leaves, fresh litter, litter-layer and soil upper layers were shown to be lower in the valley plots than in both slope and plateau plots in a central Amazonian forest (Luizao et al. 2004). At the walker Branch forest watershed (Tennessee, USA), it was shown that valley floors had greater potential net nitrification, and greater microbial activities (Garten et al. 1994). Within a slope of a plantation in Shiga prefecture of Japan, net nitrification and percent nitrification were high in the lower part and very low in the upper part of the slope, although net N mineralization showed no clear gradient (Hirobe et al. 1998). Generally speaking, compared to upper slope well-drained soils, lower slope poorlydrained soils have higher microbial respiration, N mineralization, net nitrification, microbial biomass N, denitrification and lower N immobilization (see Corre et al. 2002). In addition, soil texture and vegetation, that influence soil C and N cycles, can also be affected by topography (Luizao et al. 2004). It can thus be predicted that the patterns of soil C and N processes along a slope will inevitably affect those of soil-atmosphere exchange of GHG. This has been demonstrated by a number of studies in temperate ecosystems (Corre et al. 1996, 2002; Ambus 1998; Holst et al. 2008; Jungkunst et al. 2008; Yu et al. 2008), but in tropics the spatial variability in GHG efflux appeared to be often ignored (Reiners et al. 1998). In some tropical areas with distinct dry and wet seasons, there may be a different spatial pattern of trace gas exchanges between soil and atmosphere along the slope in different seasons.

In southern China, forests are mainly distributed in mountains and hills, which exhibit a large landscape variability. The magnitude, temporal, and spatial patterns of soil-atmospheric exchanges of greenhouse gases in forests of this region are in particular highly uncertain (Tang et al. 2006; Werner et al. 2006). In an old-growth broadleaf forest of this region, Tang et al. (2006) found a high soil N<sub>2</sub>O emission rate of 4.7 kg N  $ha^{-1}$  year<sup>-1</sup>, which is well above the averages of 1.2-1.4 kg N ha<sup>-1</sup> year<sup>-1</sup> estimated for tropical forests (Stehfest and Bouwman 2006; Werner et al. 2007) and is far higher than the rate (0.5 kg N ha<sup>-1</sup> year<sup>-1</sup>) in a primary tropical forest in southwestern China (Werner et al. 2006). This high rate may be related to local high atmospheric N deposition (20-50 kg N ha<sup>-1</sup> year<sup>-1</sup>, Fang et al. 2008a). We have also found elevated N leaching in soil water below the main rooting zone  $(67 \text{ kg N ha}^{-1} \text{ year}^{-1} \text{ including organic N, Fang et al.}$ 2008a) in this forest. However, the N leaching in a small stream draining the catchment is much lower (17 kg N ha<sup>-1</sup> year<sup>-1</sup> including organic N, Fang et al. 2008b). We suspect that the reason for the reduction in N leaching from upslope soils to the stream would be due in part to denitrification (partially emitted as N<sub>2</sub>O) in the bottom of the catchment near the stream (Xiong et al. 2007; Ouyang et al. 2008).

In the present study, we investigated the spatial pattern of in situ soil–atmosphere exchange of  $N_2O$ ,  $CO_2$  and  $CH_4$  along a short and steep slope in an evergreen broadleaved forest in southern China over a whole year. At the end of field measurement, soils were taken to quantify the potential rates of net N mineralization and nitrification and these gas fluxes with laboratory incubation method. We hypothesized that soil water availability and soil N chemistry and thereby soil–atmosphere exchange of  $N_2O$ ,  $CO_2$ , and  $CH_4$  would change with slope position, i.e. the lower part of slope would release more  $N_2O$  and  $CO_2$ , but take up less  $CH_4$  than the upper part.

## Methods and materials

#### Site description

The study site is located in Dinghushan Biosphere Reserve (DHSBR) in the middle part of Guangdong province in southern China ( $112^{\circ}33'$  E and  $23^{\circ}10'$  N). This forest area is representative of the dominant landscape type of vast areas in the region. The climate is warm and humid. The mean annual rainfall of 1,927 mm has a distinct seasonal pattern, with 75% falling from March to August and only 6% from December to February (Huang and Fan 1982). Mean annual relative humidity is 80% and mean annual temperature is 21.0°C, with average temperatures in the coolest month (January) and the hottest month (July) of 12.6°C and 28.0°C, respectively (Huang and Fan 1982). These forests have been exposed to high atmospheric N deposition of 20–50 kg N ha<sup>-1</sup> year<sup>-1</sup> in the last 15 years (Fang et al. 2008a).

A short and steep slope was selected to conduct this study in a middle size forested catchment in August 2005. The slope is 100 m long from the stream to the ridge, and its slope is 15–35%, with an average of 29% (Fig. 1). This forest has been well protected since the establishment of the reserve in 1956. The major species are *Castanopsis chinensis*, *Machilus chinensis*, *Schima superba*, *Cryptocarya chinensis*, *Syzygium rehderianum* in the canopy and sub-canopy layers of this forest. The soil is lateritic red earth formed from sandstone (Oxisols). The pH value (H<sub>2</sub>O) in upper 10 cm mineral soil is 3.8 and the C/N ratio is 22 (Fang et al. 2008a).

#### Field measurements

Five sampling plots (5 m×10 m) were set at 15–25 m long intervals on the slope at the beginning of this study, and were designated as bottom, middle 1, middle 2, middle 3 and top, respectively (Fig. 1). In each plot, three replicate chambers 1–2.5 m apart at similar elevation were anchored 5 cm

into the soil permanently. Each chamber was a 25 cm diameter ring made of stainless-steel (Zhang et al. 2008a). In order to minimize the effect of tree distance (Butterbach-Bahl et al. 2002; Saiz et al. 2006), all chambers were at least 1.5 m away from stems. And plants inside ring were cut if any. At the beginning of this study, all living trees higher than 2 m within each plot were tagged, numbered, identified to species, and their height and diameter at breast height (DBH) were recorded.

Gases were collected monthly during the period from September 2005 to August 2006. During each flux measurement, a removable 35 cm high chamber top (made of stainless-steel) was attached to the ring. Gas samples were collected with 100 ml plastic syringes at 0 (time 0) and 30 min (time 1) after the chamber closure and analyzed for gas concentrations within 24 h using gas chromatography (Agilent 4890D, Agilent Co. USA, Tang et al. 2006) to calculate exchange rates (based on the difference in gas concentration between the time 0 and time 1). We did not sample gases in chamber at 10 min intervals during each measurement, as often found in other reports (Tang et al. 2006). This is because the previous study in an adjacent evergreen broadleaved forest showed air concentration in chambers at the same size as those we used, linearly increased within the first hour of field incubation (Tang et al. 2006).

The static chamber technique is known to underestimate gases production, like  $CO_2$  by about 10– 15%, because the rising concentration within the chamber headspace, reduces the diffusion gradient within the soil (Pumpanen et al. 2004). Since we here focused on the comparison between slope positions this underestimation is of minor importance. Soil

**Fig. 1** Schematic drawing of the designated slope position along the study slope in a subtropical evergreen broadleaved forest in DHSBR of southern China. The *arrows* indicated the locations of chamber



temperature and moisture at 5 cm below soil surface were recorded at each chamber at the beginning of each gas measurement. Soil temperature was measured using a digital thermometer. Volumetric soil moisture was measured simultaneously using a MPKit ((ICT, Australia). In this paper, these recorded soil moisture values were converted to WFPS (Water Filled Pore Space) by the following formula:

WFPS 
$$[\%] = Vol[\%] / (1 - SBD[g cm^{-3}] / 2.65 [g cm^{-3}])$$

Where SBD is soil bulk density, Vol is volumetric water moisture and 2.65 is the density of quartz.

#### Laboratory incubation

All organic layer (above the mineral soil) within each chamber were collected immediately by hand after the last field measurement (August 2006), and then the mineral soils (0–10 cm depth) were sampled for soil bulk density determination and laboratory incubations, using a stainless steel corer (3 cm diameter). In laboratory, organic layer was dried and weighed; the mineral soils from each chamber were mixed thoroughly by hand removing fine roots and stones, and then were passed through a 2 mm mesh sieve.

Of the sieved mineral soil, four sub-samples of about 10 g from each chamber were taken to measure soil water content, water holding capacity (WHC), pH value and extractable inorganic N ( $NH_4^+$  and  $NO_3^-$ ) concentration, respectively, and two replicate subsamples of 80 g were adjusted soil water content to 60% of WHC and were then put into 30 PVCcontainers of 1.2 L for further laboratory incubation. These containers were kept for 30 days in an airconditioned room at 20°C. The air in each container was sampled five times over the incubation period (0, 7, 14, 21, and 30 days). Prior to each air sampling, the containers were opened for an hour and then sealed with screw-caps fitted with plastic tubes for 12 h. Air from the headspace of the containers was drawn out with 100 ml nylon syringes to analyze concentrations of GHG, using the same method described above. Air samples from five blanks without soils were considered as the initial condition. After each sampling the containers were covered with gas-permeable polyethylene until the next sampling. The incubated soils were kept at constant gravimetric moisture content throughout the incubation period by regular additions of distilled water. At the end of the month-long incubation, extractable soil inorganic N concentration was measured for each incubated container.

For measurement of soil extractable inorganic N, one 10 g mineral soil from each chamber/ container was shaken for 1 h in 50 ml 1 mol L<sup>-1</sup> KCl, and filtered through pre-leached Whatman no.1 filters. The  $NH_4^+$  concentration in soil extracts was determined by the indophenol blue method followed by colorimetry, and the  $NO_3^-$  concentration was determined after cadmium reduction to  $NO_2^-$ , followed by sulfanilamide–NAD reaction (Liu et al. 1996). Soil pH was measured in deionized water suspension after shaking for 1 h at a ratio of 25 ml water to 10 g mineral soil, using a glass electrode (Liu et al. 1996).

## Statistical analysis

Repeated measures ANOVA (RMANOVA) with Turkey's HSD test was performed to examine the difference in soil temperature, soil moisture and gas fluxes among five slope positions for the study period from September 2005 to August 2006. Oneway ANOVA was also performed for each sampling occasion. In order to examine the difference in spatial pattern of these variables along the slope between in dry season and wet season, we designated the period from October 2005 to February 2006 as dry-cool season and the rest of year as humid-warm season (Fig. 2) and performed two-way ANOVA (sampling date and slope position as main factors) for these two seasons separately. For soil variables (for in situ, annual means only) both one-way ANOVA and ANOVA with increasing distance from the bottom of the slope (broken down into orthogonal polynomial components) was used to identify the spatial pattern on the slope. Single correlation analysis was used to examine the relations between soil variables. For the relationship between in situ gas fluxes, soil temperature and soil moisture, both linear and nonlinear regression models (Tang et al. 2006; Mo et al. 2008) were further examined and the best-fitted regressions were chosen in terms of correlation coefficients. All analyses were conducted using SPSS 10.0 for Windows. Statistical significant differences were set at P values <0.05 unless otherwise stated.



Fig. 2 Seasonal patterns of precipitation, air temperature, soil temperature, moisture (WFPS) and fluxes of N<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> at different slope position from the stream. *Error bars* represented standard errors (n=3). *Asterisks* indicated significant differences between slope positions at P<0.05

### Results

Precipitation and air temperature

The data from the weather station in the reserve showed that there was a prolonged drought from October to December 2005 during the measuring campaign (Fig. 2), but annual precipitation (1,880 mm) was close to the long-term average of 1,927 mm (Huang and Fan 1982). Only 118 mm or 6% of annual precipitation fell in the dry-cool season (October 2005 to February 2006). Also the annual mean temperature 21.7°C, as well as the monthly temperature range from 12.1°C (December 2005) to 28.9°C (July 2006) (Fig. 2), were close to the long-term averages (Huang and Fan 1982).

## Stand characteristics

The density was on average 1,580 stems  $ha^{-1}$  for the trees with height over 2 m (Table 1). The mean height was 6.9–10.5 m, and mean DBH was 10.6 to 19.2 cm. The basal area at breast height varied greatly from 20 to 62 m<sup>2</sup> ha<sup>-1</sup> within the slope, with a total mean of 38 m<sup>2</sup> ha<sup>-1</sup>. There were no clear gradients for these measurements along the slope. However, the amount of organic soil layer, ranging from 2.6 to 4.3 Mg ha<sup>-1</sup>, appeared to increase with the slope from bottom to top (Table 1).

## Soil characteristics

Soil temperature and moisture exhibited clear seasonal courses, and generally followed those of air temperature and precipitation (Fig. 2). Mean soil temperature across the slope ranged from 14.5°C to

Slope position	Distance <sup>a</sup> (m)	Elevation <sup>b</sup> (m)	Density (stems ha <sup>-1</sup> )	Height (m)		DBH (cm)		Basal area	Floor litter
				Range	Mean	Range	Mean	$(m^2 ha^{-1})$	$(Mg ha^{-1})$
Bottom	1.5	0.5	800	2.6-19.5	7.4	3.0-43.2	10.6	19.5	2.6
Middle 1	25	7	1,800	3.6-19.5	10.5	3.0-47.0	19.2	61.7	3.1
Middle 2	50	13	2,200	2.7-13.6	6.9	3.0-36.3	11.2	28	3.5
Middle 3	75	20	1,200	3.3-22.6	8.7	3.1-48.2	12.1	35.8	3.9
Тор	90	25	1,900	2.2-18.6	7.7	3.1–38.7	12.7	46.4	4.3

Table 1 Stand characteristics along the slope (10 m×15 m plots)

<sup>a</sup> The distance from the stream (Fig. 1)

<sup>b</sup> The elevation above the stream

30.3°C, and mean soil moisture (WFPS) ranged from 18.4% to 70.9%. The soil temperature varied significantly between slope positions across the observation period, although the absolute differences were very small (Fig. 2). The differences were statistically significant at most sampling dates and thus also on the seasonal means and annual means (Fig. 2 and Table 2). Soil moisture was significantly different by the slope positions almost throughout the whole year (Fig. 2). Annual mean moisture over the study period ranged from 27.7% to 52.7% on the slope, which was within that of seasonal variation (18.4% to 70.9%). The highest moisture was not located in the lowest part of the slope, but in the middle part, although they were not statistically significant (Figs. 2 and 3). The driest part was observed in the top of the slope as expected (Fig. 3). Soil moisture differed with slope position stronger in the dry-cool season than the humid-warm season (Fig. 3).

At the end of the field measurement campaign, the upper 10 cm mineral soil from all chambers was collected for property analysis. The results showed that soil bulk density was not significantly different by the slope position (Table 3). The soils were strongly acidic, with pH values being 3.63– 3.82. The highest pH value was found in the bottom of the slope. Concentrations of total extractable inorganic N (NH<sub>4</sub><sup>+</sup>+NO<sub>3</sub><sup>-</sup>) were similar between the slope positions. However, extractable NH<sub>4</sub><sup>+</sup> concentration was highest in the top of the slope and lowest in the bottom, and it increased significantly with the distance from the slope bottom to top (Table 3). The reverse was observed for extractable NO<sub>3</sub><sup>-</sup> concentration (Table 3). In situ soil–atmosphere exchange of  $N_2O$ ,  $CO_2$ , and  $CH_4$ 

Emission rates of N<sub>2</sub>O and CO<sub>2</sub> were significantly lower in the dry-cool season where there was a 3month long drought period, than in the humid-warm season (Figs. 2 and 3). Over the slope, emission rates of N<sub>2</sub>O and CO<sub>2</sub> were 68% and 98% higher in humidwarm season, respectively (Fig. 3). These patterns well agreed with those of soil temperature and moisture, as evidenced by significant correlations between these variables across the slope (all P <0.001, n=180, Fig. 4). Higher emission rates occurred in soils with temperature 25–30°C and with WFPS 35–65% (Fig. 4). At most sampling times, CH<sub>4</sub> was consumed by the soil, but no obvious seasonal trend and thereby no dependency on soil temperature and moisture were found (Figs. 2 and 3).

Soil N<sub>2</sub>O emissions (4.4–111.7  $\mu g$  N m<sup>-2</sup> h<sup>-1</sup>) were significantly affected by slope position on three out of 12 sampling dates (Fig. 2), and RMANOVA over the study period showed that soil N<sub>2</sub>O emissions were significantly different by slope position (P=0.005). The effect of slope position on N<sub>2</sub>O emissions was smaller in the dry-cool months than in the humidwarm months (Figs. 2 and 3). Soil N<sub>2</sub>O emissions exhibited a substantial spatial variability with a range from 22.6 to 50.6  $\mu$ g N m<sup>-2</sup> h<sup>-1</sup> over the study period. This range was slightly narrower than the temporal variation of 12.1 to 69.9  $\mu$ g N m<sup>-2</sup> h<sup>-1</sup>. The highest emission rate was not located in the bottom of the slope. The spatial pattern of N<sub>2</sub>O emission rates along the slope followed that of soil moisture from bottom to top (Fig. 3, Table 2).

	ANOVA (individual position)			ANOVA (increasing slope)		
	df	F	Р	F	P<0.05	Orthogonals
Temperature (°C)	4	17.1	< 0.001	65.2	< 0.001	Linear
WFPS (%)	4	5.8	0.01	12.8	0.001	Quadratic
$N_2O (\mu g N m^{-2} h^{-1})$	4	7.5	0.005	8.4	0.005	Quadratic
$CO_2 (mg C m^{-2} h^{-1})$	4	1.9	0.19	2.6	0.13	n.s.
$CH_4 (\mu g C m^{-2} h^{-1})$	4	1.2	0.35	0.29	0.75	n.s.

**Table 2** Analyses of variance (ANOVA) on the effects of individual slope position and of increasing distance from the slope bottom (broken down into orthogonal polynomial components) on annual mean soil temperature, moisture, and fluxes of  $N_2O$ ,  $CO_2$  and  $CH_4$ 

n.s. not significant

Fig. 3 Seasonal and annual means of soil temperature and moisture (WFPS), and fluxes of N<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> along the slope. *Error* bars represented standard errors (n=3). Values with the same letter indicated no significant differences between slope positions at P < 0.05



Table 3 Mineral soil properties (0–10 cm depth) at the last sampling occasion (Aug 2006), which also were initial conditions for the laboratory incubation

Slope position	SBD (g $cm^{-3}$ )	WFPS (%)	pH (H <sub>2</sub> O)	$\mathrm{NH_4^+} \ (\mathrm{mg} \ \mathrm{N} \ \mathrm{kg}^{-1})$	$\mathrm{NO_3}^- (\mathrm{mg} \ \mathrm{N} \ \mathrm{kg}^{-1})$	$NH_4^+ + NO_3^- (mg \ N \ kg^{-1})$
Bottom	0.95 (0.13)	46.9 (5.4)	3.8 (0.04)a	2.7 (0.3)ab	6.3 (1.0)a	9.0 (0.8)
Middle 1	0.92 (0.05)	40.3 (5.0)	3.6 (0.05)b	2.2 (0.6)b	6.6 (0.6)a	8.9 (0.9)
Middle 2	0.98 (0.03)	41.8 (2.3)	3.6 (0.01)b	3.5 (0.4)ab	4.3 (0.3)ab	7.7 (0.6)
Middle 3	1.03 (0.06)	42.6 (3.5)	3.7 (0.01)ab	4.7 (0.5)ab	2.8 (0.2)b	7.5 (0.6)
Тор	1.06 (0.04)	34.6 (3.0)	3.6 (0.05)b	5.7 (1.3)a	3.2 (0.8)b	8.9 (1.9)
<i>P</i> 1	0.64	0.35	0.01	0.032	0.005	0.76
P2	0.12	0.11	0.20	0.002	< 0.001	0.67

SE in parentheses. P1 and P2 denote the P values obtained from the effect of individual slope position (one-way ANOVA) and obtained from ANOVA on the effect of increasing distance from the bottom of the slope, respectively. Values within columns sharing the same letter were not significantly different (one-way ANOVA with Tukey's HSD; P < 0.05)

Fig. 4 Relationships between fluxes of N<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> and soil temperature and moisture (WFPS) across the slope and across the study period. n=180, P<0.001



The topographic influence on soil CO<sub>2</sub> emissions was not clear in humid-warm season, but significant lowest values were observed on the top position in dry-cool season (Fig. 3). Over the study period, RMANOVA showed the topographic influence was not significant (Fig. 3 and Table 2). The difference of maximum and minimum soil CO<sub>2</sub> emissions on the slope was similar between the two seasons (Fig. 3). No significant difference in CH<sub>4</sub> uptake was found among slope position, in any season or over the whole study year (Fig. 3 and Table 2), but soils appeared to take up more atmospheric CH<sub>4</sub> in dry-cool season than in humid-warm season (Fig. 3).

When linking annual fluxes of three gases to annual means of soil temperature and moisture across the entire slope, we found that annual N<sub>2</sub>O emissions were correlated significantly (P=0.01) with soil temperature and marginally (P=0.08) with soil moisture (Fig. 5). But no such correlations were found for either soil CO<sub>2</sub> emissions or CH<sub>4</sub> uptake.

The pH and concentrations of extractable  $NH_4^+$ – N and  $NO_3^-$ –N in the top 10 cm mineral soil, were measured on the last sampling date. We related these variables to in situ soil N<sub>2</sub>O and CO<sub>2</sub> emission and CH<sub>4</sub> uptake on that sampling date, and found that soil N<sub>2</sub>O emissions were marginally correlated with concentrations of extractable  $NO_3^-$ –N (positively,

P=0.06) and  $NH_4^+-N$  (negatively, P=0.08). Soil  $N_2O$  emissions were not correlated with soil temperature or moisture on that sampling date. Soil  $CO_2$ emissions were significantly (P=0.02) correlated with soil pH values only. Soil  $CH_4$  uptake was not influenced by any soil variable.

Potential rates of soil N transformations and fluxes of  $N_2O$ ,  $CO_2$ , and  $CH_4$ 

Monthly rate of potential net N mineralization ranged from 15.5 to 21.1 mg N kg dry soil<sup>-1</sup> and all mineralized N was nitrified (Table 4). Neither potential net N mineralization nor nitrification was found to be different by the slope position (Table 4). Nor were accumulative emissions of N<sub>2</sub>O or CO<sub>2</sub> from incubated soils in laboratory. In contrast, the ability to oxide CH<sub>4</sub> appeared to decrease from the bottom to the top (Table 4). There were no significant correlations between mean in situ and potential fluxes for any of the three gases. Potential N<sub>2</sub>O emission or CH<sub>4</sub> uptake showed no significant correlations with soil extractable N or with N mineralization and nitrification in the laboratory incubation (Table 4). However, we found good relationships between potential CO<sub>2</sub> fluxes and N mineralization and nitrification (P=0.029 and 0.012, respectively).

Fig. 5 Relationships between annual fluxes of N<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> and mean soil temperature and moisture (WFPS) across the slope. n=15



# Discussion

Annual soil N<sub>2</sub>O emissions from this study forest are 2.0–4.4 kg N ha<sup>-1</sup> year<sup>-1</sup>, with a mean of 3.0 kg N ha<sup>-1</sup> year<sup>-1</sup>, and annual CO<sub>2</sub> are 5.4–9.0 Mg C ha<sup>-1</sup> year<sup>-1</sup>, with a mean of 6.2 Mg C ha<sup>-1</sup> year<sup>-1</sup> across the slope (Fig. 5). These values are somewhat smaller than the observations from the nearby broadleaved forests which have been protected for more than 400 years (on average, 4.7 kg N ha<sup>-1</sup> year<sup>-1</sup> and 9.9 Mg C ha<sup>-1</sup> year<sup>-1</sup>, Tang et al. 2006). Likewise, the soil CH<sub>4</sub> uptake is smaller in our study forest (-4.3–0.4 kg C ha<sup>-1</sup> year<sup>-1</sup>, on average -1.9 kg C ha<sup>-1</sup> year<sup>-1</sup>, than in that old forest (-7.8 kg C ha<sup>-1</sup> year<sup>-1</sup>).

Tang et al. 2006). This could be because we studied a young forest (50 years old), where a stronger N utilization by vegetation and soil organisms are expected than in that old forest. However, our results are slightly higher than those in the adjacent mixed and the pine forests, where N<sub>2</sub>O emissions were measured to be 2.1–2.7 kg N ha<sup>-1</sup> year<sup>-1</sup> (Tang et al. 2006; Zhang et al. 2008a). On the other hand, the seasonal pattern of soil variables were observed in the study (Figs. 2 and 3) similarly as the previous reports (Tang et al. 2006; Mo et al. 2008; Zhang et al. 2008a, b).

Riparian zone or wetland area situated at the interface of terrestrial and aquatic environment, have long been identified to be "hotspots" of  $N_2O$ 

Slope position	N mineralization (mg N kg $^{-1}$ mo $^{-1}$ )	Nitrification (mg N kg <sup><math>-1</math></sup> mo <sup><math>-1</math></sup> )	$\begin{array}{c} N_2O~(\mu g~N\\ kg^{-1}~mo^{-1}) \end{array}$	$\begin{array}{c} \mathrm{CO}_2 \ (\mathrm{mg} \ \mathrm{C} \\ \mathrm{kg}^{-1} \ \mathrm{mo}^{-1} ) \end{array}$	$CH_4 (\mu g C kg^{-1} mo^{-1})$
Bottom	17.8 (2.2)	18.6 (2.4)	138 (88)	237 (36)	-135 (38)b
Middle 1	15.9 (3.0)	16.4 (2.8)	42 (48)	211 (36)	-122 (7)ab
Middle 2	15.5 (2.4)	17.6 (2.0)	61 (10)	210 (11)	-51 (35)ab
Middle 3	17.5 (4.2)	17.7 (3.4)	50 (6)	208 (30)	-95 (41)ab
Тор	21.1 (3.8)	21.2 (3.5)	89 (16)	269 (7)	10 (8)a
P1	0.75	0.81	0.49	0.48	0.04
P2	0.43	0.48	0.49	0.56	0.01

Table 4 Potential rates of N transformation and cumulative amounts of N<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> over the incubation of 1 month

SE in parentheses. P1 and P2 denote the P values obtained from the effect of individual slope position (one-way ANOVA) and obtained from ANOVA on the effect of increasing distance from the bottom of the slope, respectively. Values within columns sharing the same letter were not significantly different (one-way ANOVA with Tukey's HSD; P < 0.05)

production in the landscape (Groffman et al. 1998; Hefting et al. 2006). In the present study, the bottom position which was 1.5 m away from the stream, can also be considered to be such a kind of area. Our results did show an increase in N2O emission rates in this part of the slope (Fig. 3), the soil N<sub>2</sub>O emission rate at the bottom position (6.7–77.9  $\mu$ g N m<sup>-2</sup> h<sup>-1</sup>, Fig. 2) is, however, much smaller than those reported for temperate riparian forest soils (up to 9,000 µg N  $m^{-2}$  h<sup>-1</sup>, Hefting et al. 2006). This could be due in part to our bottom position locating by a periodically stream within a small catchment (<10 ha) and low soil water content (SWFP on average 45%, Fig. 3). Similarly, this absolute increase (top to bottom difference 2.2 kg N ha<sup>-1</sup> year<sup>-1</sup>) is too small to explain the observed difference in the leaching N flux below the main rooting zone (67 kg N  $ha^{-1}$  year<sup>-1</sup>. Fang et al. 2008a) and in streamwater (17 kg N  $ha^{-1}$ year<sup>-1</sup>, Fang et al. 2008b). On the other hand, this result suggests that other mechanisms, such as plant uptake, sorption, desorption, and microbial decomposition in deeper soil layers (Fang et al. 2008b), the emissions of NO (Li et al. 2007) and N<sub>2</sub>, might be of importance in the reduction in N leaching from upslope to the stream. Additional N removal, like N uptake and denitrification in stream water might also occur after the water exported from soils but before was sampled for chemical analysis.

Soil moisture varied greatly with the slope position, and it decreased in the upper part of the slope as we expected. But the wettest area was not located in the bottom of the slope (the lowest part), and soil water content showed quadratic relationship with slope position over the study year with being more pronounced in dry-cool season (Fig. 3). Among the three gases we investigated, however, only N<sub>2</sub>O emissions followed the pattern of soil moisture along the slope (Fig. 3). Soil N<sub>2</sub>O emissions exhibited a substantial spatial variability, with a range being slightly narrower than the temporal variation. This result indicates that the effect of slope position and associated soil moisture on soil N2O emissions is comparable to that of season in the study forest. However, we observed decreased soil N2O emissions on the middle 2 position where the soils were the wettest. One of explanations is that high denitrification activity occurred on this position, by which a large fraction of N<sub>2</sub>O produced was reduced to N<sub>2</sub> or NO. This is consistent with the fact that higher N<sub>2</sub>O emission rate take place in soils with WFPS of 35– 65%, not over 70% (Fig. 4). Low root and/or microbial activity indicated by low soil respiration can also in part account for the decreased  $N_2O$ emission therein (Fig. 3). Both nitrification and denitrification can produce  $N_2O$ , but the present study does not allow us to distinguish their respective contribution. Thus further research need to address which process is the main source of  $N_2O$  in the study soil and if it varies with slope position.

The measurement of extractable NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> in the upper 10 cm mineral soil at the end of sampling period can provide a snap-shot index of the relative sized of N availability and N processes as shaped by topographic conditions within the slope. Extractable  $NO_3^{-}$  concentration was significantly higher in the lower part of the slope than in the upper, and the reverse was true for extractable  $NH_4^+$  concentration (Table 3). The percentage of  $NO_3^-$  of the total extractable inorganic N decreased from 61-82% in the bottom and middle 1 of the slope to 24-46% in the top (Table 3). The soil  $N_2O$  emissions on the same sampling date were found to positively relate to the concurrent extractable  $NO_3^-$  concentration (P=0.06). These results indicated that the soils might have a stronger nitrification process in the lower part than in the upper part, during which N<sub>2</sub>O was produced. More  $NO_3^{-}$  concentration in the lower part also meant that there was more  $NO_3^-$  source therein to fuel the denitrifier and thereby promote denitrification in combination with higher soil water content (lower oxygen concentration).

There were no differences in the potential rates of net N mineralization and nitrification, and cumulative N<sub>2</sub>O emissions as well, across the slope position in the laboratory incubation where moisture was kept constant. The vegetation was not shown to differ significantly along this short and steep slope either (Table 1). Soil temperature decreased from the top to the bottom of the slope, but the difference was very small (Fig. 3). The observed negative correlation between soil temperature and N<sub>2</sub>O emissions (Fig. 5), opposite to the normal effect of temperature on microbial processes, was due to the covariant soil temperature and moisture over the gradient. We can therefore conclude that the difference in in situ soil N<sub>2</sub>O emissions along the slope may mainly result from the environmental control, soil water availability in field.

In this study, no clear gradient along the slope was found for soil CO<sub>2</sub> emission over the whole study year, although slope position has a significant influence in dry-cool season (Fig. 3). It indicated that soil CO<sub>2</sub> emissions might be influenced by other factors in addition to soil water, such as amount of organic materials on the floor (Table 1), root biomass and soil depth (the latter two were not measured in this study). In situ soil CH<sub>4</sub> uptake was not significantly influenced by slope position either (Figs. 2 and 3), despite that the ability to oxide atmosphere CH<sub>4</sub> in the laboratory incubation appeared to be stronger in the soil from the lower part compared to that from upper part (Table 4).

The wettest part was not observed in the bottom of the slope in our study. This might be related to soil texture, bedrock depth, water flow pattern and organic matter content. At the bottom of the slope close to the stream, the soil was well drained, because the stream channel was about 0.5 m deep. Some organic materials, a key component holding moisture and providing fuels for microbes including nitrifying and denitrifying bacteria, in this part of the slope is likely to be taken away by seasonal floodings, which may also explain partially why the amount of organic layer was the lowest in this part of the slope (Table 1). Similar trend of soil moisture was found in a 108 m long slope in a Japanese forest (Hirobe et al. 1998).

In conclusion, this study demonstrated that soil water content and  $N_2O$  emission rates were significantly different by slope position even within a short and steep slope. Annual soil  $N_2O$  emission was highly related to mean soil moisture across the slope. No clear trends were observed for soil  $CO_2$  release and  $CH_4$  uptake in this study. Our results nonetheless indicated that soil water content and associated soil  $N_2O$  emissions are likely to be influenced by topography, with the spatial variation by slope positions being comparable to the temporal variation by seasons. This may need to be taken into account in field measurements and modelling.

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