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Nitrous oxide emissions from different land use patterns in a typical karst region, Southwest China

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Abstract Fluxes of nitrous oxide (N_2O) from different land use patterns (matured forest, secondary forest, grassland and cropland) in a subtropical karst region of Guizhou Province, Southwest China, were measured for one year with a closed static chamber technique and by gas chromatography. The results showed that soil under different land uses was a source of atmospheric N_2O. The cropland was a source with relatively high N_2O as compared to forest and grassland, but no significant differences were observed. N_2O emissions from soils varied with land use change and fertilizer application. There were two peaks of N_2O flux occurred following the combination of two obvious precipitation and fertilizer events in the cultivated land. Converting from the matured forest to secondary forest tended to increase annual emissions of N_2O (from 1.40 to 1.65 kg N ha^{-1} a^{-1}), while changing land use from secondary forest to scattered grassland tended to decrease annual emissions of N_2O slightly (from 1.65 to 1.45 kg N ha^{-1} a^{-1}). Our range of cumulative annual N_2O emission across different land uses (1.40–1.91 kg N ha^{-1} a^{-1}) in a karst region is in general agreement with previously published data in a non-karst region. However, in the maize field, N_2O emission factor (EF) was 0.34% for fertilizer application, which is about 71.2% lower than the IPCC default value. It is suggested that current IPCC (Intergovernmental Panel on Climate Change) EF methodology could overestimate N_2O emission from the karstic cropland. Anyway, the N_2O emission from cropland in the karst region would contribute significantly to the global N_2O budget, so reducing fertilization frequency during the crop growing season could lead to a decrease in N_2O emission in the whole year.

Key words karst region; N_2O emission; grassland; pine forest; maize field

1 Introduction

Climate change and global warming continue to be subject to considerable scientific debate and public concern. N_2O is of great interest from an environmental point of view because it plays an important part in the atmosphere. The potential of global warming of N_2O is 300 times higher than that of carbon dioxide (CO_2) on a 100-year time scale. Currently, its radiative forcing is about 10% higher than that of CO_2 and its atmospheric lifetime is estimated to be 120 years (Schindlbacher et al., 2004; Hofmann, 2006). Moreover, in the stratosphere, N_2O is transformed through photolysis to NO, which is responsible for stratospheric ozone destruction that is harmful to terrestrial organisms (Beauchamp, 1997). N_2O concentrations had increased from 270×10^{-9} in 1750 to 319×10^{-9} in 2005, and were estimated to account for approximately 6% of the predicted global warming (IPCC, 2007), but current estimates for total identified sources are less than those for the known sinks (Prather et al., 1995). Therefore, concern about the environmental consequences of increased N_2O in the atmosphere as well as the disparity between observed atmospheric increases and current source and sink estimates has stimulated interest in more accurately quantifying the intensity of N_2O release (Mummey et al., 2000).

Soil is the most important source of atmospheric N_2O, contributing about 70% to the total globally emitted N_2O (Bouwman, 1990). N_2O from soil is mainly produced as the byproduct of microbial nitri-

fication and denitrification. It has been discerned that anthropogenic disturbances (land use, tillage, fertilization, irrigation, etc.) to soil are mainly responsible for the increase of atmospheric N_2O (IPCC, 2001). Recently, a vast area of forests has been converted to farmland, plantation or pasture and so on. Land-use changes and land-use intensification are considered the important processes which have contributed greatly to the increasing concentrations of N_2O, and many scientists have shown great interest in the emissions of N_2O from various land uses and land cover changes (LUCC) including the conversion of forest land to farmland (Ishizuka et al., 2002; Lin Shan et al., 2010), and of forests to pastures (Keller et al., 1993; Melillo et al., 2001). However, there is a lack of qualitative and quantitative information about the emission of N_2O under the effects of LUCC, especially in karst regions. Karst ecosystems respond very quickly to changes in environmental conditions (Holl et al., 2005), so a greater LUCC in the future may induce greater changes in N_2O fluxes than in other regions. China is one of the countries featuring extensive karstification. The karstification area covers nearly 2.0×10^6 km^2, and accounts for about 23% of land area, covered by exposed and covered karst rocks, which are mainly concentrated in the southwest of China, including Guizhou, Yunnan, Guangxi, Sichuan, Hunan, Hubei provinces and Chongqing City (Zhang Baiping et al., 2006). Guizhou Province is located in the heart of the East Asia Karst Belt, one of the three largest almostly unbroken karst areas in the world (Bai Zhanguo and Wang Guojiang, 1998). Carbonate rocks in Guizhou occur as a 1.1×10^3–6.2×10^3 m sequence in depth, covering an area of 1.3×10^5 km^2 and accounting for about 73% of the total area (He Caihua et al., 1998; Zhu Shufa and Liu Congqiang, 2008). On the other hand, there is a large human population in the karst regions of Guizhou, with a population density as high as 185 persons per km^2. In contrast, karst regions in other areas of the world are slightly populated (Zhang Baiping et al., 2006). Therefore, a vast area of forest land has been converted to farmland in the mountainous areas of Guizhou because of the intensification of agricultural activities due to rapidly growing population in those karst regions. However, to our knowledge, effects of land use on changes in N_2O emissions from soils in the subtropical karst regions of Southwest China are poorly understood. Due to seasonal and spatial variations, N_2O emissions are difficult to quantify (Smith et al., 1994) and the estimation of annual N_2O emissions from a small number of observations may lead to considerable errors. Therefore, it is necessary to carefully study N_2O emissions from China's karst regions, so as to accurately estimate anthropogenic N_2O emissions.

In order to understand the characteristics of N_2O variaiton under different land use systems in the karst areas of Southwest China, we carried out this measurement. In this paper we addressed the following questions: (1) how to determine the effects of land use changes on N_2O emissions; (2) how to comparatively analyze N_2O emissions between karst and non-karst regions; and (3) how to assess annually soil-transformed N_2O from fertilizer application in the cropland.

2 Materials and methods

2.1 Site description

The study area (26°32′N; 106°46′E) is located in the Longdongbao district of Guiyang, the capital city of Guizhou Province, a typical karst region in Southwest China (Fig. 1), which is about 1200 m above the sea level and situated in a subtropical monsoon climate zone. The mean annual temperature is 14.8℃ with the lowest mean temperature in January at 3.9℃ and the highest mean temperature in July at 23.2℃. The mean annual precipitation is recorded to be 1118 mm with the lowest mean precipitation in December at 21.4 mm and the highest mean precipitation in July at 203.1 mm, and most rainfall (more than 86%) is concentrated in the wet season (from April to October).

The landscape is characterized by cultivated land, forests, patchy grassland and fast expanding cities and towns. Four land use patterns were chosen for this study. They are matured forest, secondary forest, grassland and cropland, which are the typical land use patterns in the karst region. The forest land is composed of Pinus massoniana trees (*Pinus L.*), about 50 years old. The stand density of the pine forest is 2000 trees ha^{-1}, and the average DBH (diameter at breast height) and height are 15 cm and 13 m, respectively. The forest floor is covered by shrubby vegetations including Camellia oleifera and Itea yunnanensis, and some low-rise herbs (*Artemisia SP.*) under the shrub layer. The privet trees (*Ligustrum L.*) are an important constructive and dominant species of the secondary forest, which was planted about 8 years ago. The sedge grassland (*Cyperus L.*) is newly developed in the year of experiment after a wild fire the year before, and the cultivated land is an upland maize (*Zea L.*) field.

2.2 Experimental

Fluxes of N_2O were measured by the closed static chamber technique during June, 2008 to May, 2009. The chamber was made of transparent polyvinyl chloride (PVC) (30 cm×30 cm×50 cm), and was used with a stainless steel base (30 cm×30 cm×10 cm)

with a U-shaped groove at the top edge. The base was installed permanently in the soil once the experiment was begun. After the chamber was placed onto the base, the groove was filled with water so as to make the chamber airtight. The chamber was equipped with a vent (diameter: 3 cm) for gas mixing. A series of samples were taken with a 30 mL plastic syringe fitted with a three-way stopcock at 0, 5, 10, 15 and 20 minutes following the closure of the chamber and transferred subsequently to the glass bottles previously vacuumized to 0.04 millibar. Three polyvinyl chambers were randomly installed on the surface of soil under each of different land uses.

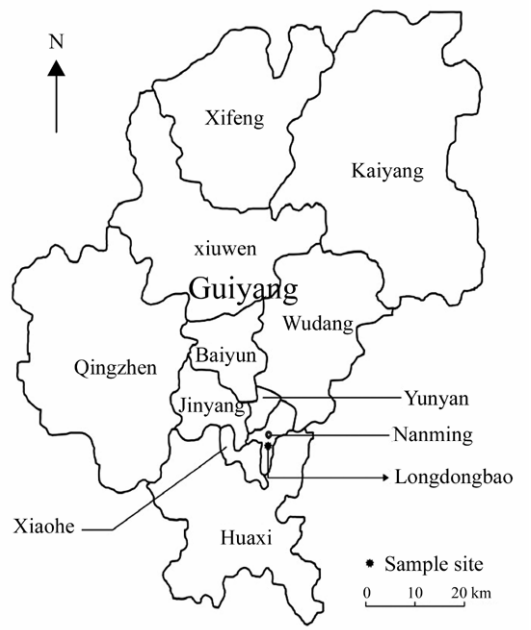

Fig. 1. The study area and its adjacent districts in the city of Guiyang, Guizhou Province.

2.3 Soil properties

Soil samples were taken approximately every 15 days and soils (0–10 cm) were collected from each sampling site at the time of gas flux measurement. The soil samples used for C and N analysis were dried at 70℃ for 48 hours and then milled in a Tecator 1093 Cyclotec Sample Mill, using a 0–5 mm screen, and then determined by means of an elemental analyzer (Model: PE 2400Ⅱ, Perkin Elmer, USA). Soil NH_4^+-N and NO_3^--N concentrations were determined by extracting mineral N in the soils with 2 M KCl solution (1:5 soil to KCl solution), the suspension was shaken for 1 hour and filtered with Watmann #42 filter paper. NH_4^+-N and NO_3^--N concentrations in the extracts were analyzed on a UV-VIS spectrophotometer. Soil pH was measured in 1:2.5 soil/water solution using a pH meter with a glass electrode. The gravimetric water content was measured by drying a sample at 105℃ for 24 hours to constant weight, which was converted to WFPS: WFPS=gravimetric water content × bulk density/(1-bulk density/2.65).

2.4 Gas flux rate determination

N_2O concentrations were analyzed by a HP 6890 gas chromatograph (GC) in the laboratory within 24 hours following sampling. The GC was equipped with a Poropak-Q column (mesh: 80/100) and ECD detector. The temperatures of the column, injector and detector were 60, 100 and 250℃, respectively. The carrier gas was N_2 with the purity of 99.999%, and the flow rate was set as 20 mL min^{-1}. In order to ensure there was no instrument drift, multiple gas standards were run every 10–12 samples and a full set of standards were run again at the end of the day. Repeatability of gas standards was typically represented by a coefficient of variation of less than 5%. The calculation of N_2O flux followed the description of Yan Yuping et al. (2008). Negative flux values represent N_2O uptakes from the atmosphere, and positive flux values indicate N_2O emissions to the atmosphere.

2.5 Statistical methods

Differences in N_2O fluxes among different land use patterns were compared using a two-way ANOVA followed by the least significant difference (LSD) test, relationships between N_2O fluxes and soil properties (N availability and C/N, etc.) were analyzed using linear regression models fitting. R^2 of the model parameters was used to determine the goodness of fit. All statistical considerations were based on $p<0.05$ significant level. Statistical analyses were conducted using SPSS 13.0 software package (SPSS Inc., Chicago, USA).

3 Results

3.1 General soil characteristics

The physical and chemical characteristics of the surface soils under different land use patterns are summarized in Table 1. Organic C and total N were high in the grassland (sedge), low in the cropland (maize), and intermediate in the matured forest (pine) and secondary forest (privet). Despite these differences, the C/N ratios were similar under different land use systems (from 13.2±0.9 to 14.3±1.3). Soil pH was 7.2 in the cropland and lower than 7.0 in the forests and grassland. NH_4^+-N was high in the grassland, low in the cropland, and intermediate in the matured and secondary forests. The content of NO_3^--N in the soil was opposite to that of NH_4^+-N, with the highest content occurring in the cropland. The ratio of NO_3^--N to

the sum of (NO_3^--N and NH_4^+-N) was the indicator of soil N availability, which was about 4–8 times higher in the cropland than in the other three land use patterns.

3.2 N_2O emissions from different land use systems

All the soils are characterized by emissions of N_2O in every month and seasonal N_2O emission patterns under different land uses were similar during one year measurement (Fig. 2). Temporal variations in N_2O fluxes for three uncultivated lands are presented in Fig. 2b and they show exactly similar tendencies, with the maximum difference of less than 20%. However, they are nearly 30% lower than the fluxes of N_2O in the cropland. The N_2O emissions of the pine matured forest, privet secondary forest and sedge scattered grassland vary within the ranges of 3.0–41.8, 2.0–45.7 and 11.9–22.3 μg N m^{-2} h^{-1} with the average values of 16.0±13.0, 18.8±14.0 and 16.5±3.2 μg N m^{-2} h^{-1} (n=24), respectively (Table 2, Fig. 2b). Temporal variations in N_2O emissions are naturally large in soils under different land use systems because of significant differences in soil moisture and temperature around the year. During the sampling period, two peaks of N_2O flux occurred following the two obvious precipitation events which happened in July, 2008 and April in 2009, respectively. However, the peaks N_2O flux (monthly average) from the privet secondary forest and pine matured forest were 45.7 and 41.8 μg N m^{-2} h^{-1}, respectively, which were extremely greater than that of sedge grassland (22.3 μg N m^{-2} h^{-1}). Moreover, interesting N_2O fluxes of three uncultivated lands were relatively high during early spring, but temperatures were only 8–10°C above zero (Fig. 2a). That is because the microbial processes (both nitrification and denitrification) may have been stimulated by higher availabilities of organic carbon and nitrogen due to thawing of the frozen soil. A similar phenomenon was also observed by Christensen and Tiedje (1990).

Fig. 2c shows a large range of seasonal variations in N_2O fluxes in the maize field. Seasonal N_2O emissions followed the order of spring (March–May) (28.0 μg N m^{-2} h^{-1}), summer (June–August) (26.8 μg N m^{-2} h^{-1}), autumn (September–November) (17.5 μg N m^{-2} h^{-1}) and winter (December–next February) (14.8 μg N m^{-2} h^{-1}), respectively. N_2O emission rates varied from 9.0 to 36.0 μg N m^{-2} h^{-1} with the annual average of 21.8±8.5 μg N m^{-2} h^{-1} in the cropland (n=24), which was almost 1.5 times higher in the cropland than what was detected in the matured forest (Table 2). During planting maize, 11445 kg ha^{-1} of cattle manure, 385 kg ha^{-1} of compound fertilizer and 290 kg ha^{-1} of chemical nitrogen fertilizer were applied to the field, and soil moisture in the meantime was kept high to facilitate plant growth. Hence, N_2O emissions were stimulated by fertilizer application (Fig. 2c). However, during the fertilizer application period, only two apparent peaks of N_2O flux occurred following the two obvious precipitation events (205 and 275 mm, respectively), which happened in April and July (Fig. 2a). Our results have confirmed that the magnitude of N_2O fluxes may strongly be influenced by the amount and distribution of rainfall during crop growing period after fertilizer application, similar phenomena were observed in other croplands (Smith et al., 1998; Ruser et al., 2001).

3.3 Correlations of N_2O fluxes and soil C/N ratios, N availability

Surface soils in forests have larger C/N ratios than those in the grassland and cropland (Table 1), and a close negative correlation between soil C/N ratios and N_2O emissions was observed (r^2=0.786, n=4), indicating that soils with large C/N ratios have lower N_2O fluxes. Moreover, changes in land use patterns from the matured forest to cropland tended to a slight increase in N_2O emission (from 16.0 to 21.8 μg N m^{-2} h^{-1}), which was consistent with changes in soil N availability (10.9%, 90.0% in the pine forest and maize field, respectively) (Tables 1–2). Meanwhile, correlation analysis was conducted between N_2O emissions and N availability under different land use systems and the correlation coefficient (R^2) was found to be as high as up to 0.776 (n=4), indicating that the N_2O emission had a positive correlation with the soil N availability, and a similar correlation pattern between them was also observed in a pasture chronosequence in central Amazonia, Brazil (Wick et al., 2005).

Table 1 Soil characteristics of different land use patterns at the 10-cm depth

Land use pattern	Organic C (%)	Total N (%)	C/N (Molar)	NH_4^+-N (mg kg^{-1})	NO_3^--N (mg kg^{-1})	N availability (%)	WFPS (%)	pH (H_2O)	Sample size (N)
Matured forest	3.6±0.6	0.29±0.03	14.3±1.3	22.9±16.0	2.8±1.0	10.9	76.0±7.2	6.0±0.4	24
Secondary forest	4.7±0.7	0.41±0.05	13.2±0.9	23.1±15.0	4.1±3.0	15.1	61.1±16.7	6.5±0.6	24
Grassland	5.1±0.6	0.42±0.06	14.2±0.6	26.2±19.6	7.6±8.5	22.5	60.1±15.1	6.7±0.2	24
Cropland	3.2±0.3	0.28±0.04	13.2±1.2	2.1±1.3	19.0±11.3	90.0	48.9±14.6	7.2±0.4	24

Mean ± standard deviation. Nitrogen fertilizer applications in the cropland: 75.5 kg N ha^{-1} on April 15, 57.5 kg N ha^{-1} on May 20, 133 kg N ha^{-1} on July 10.

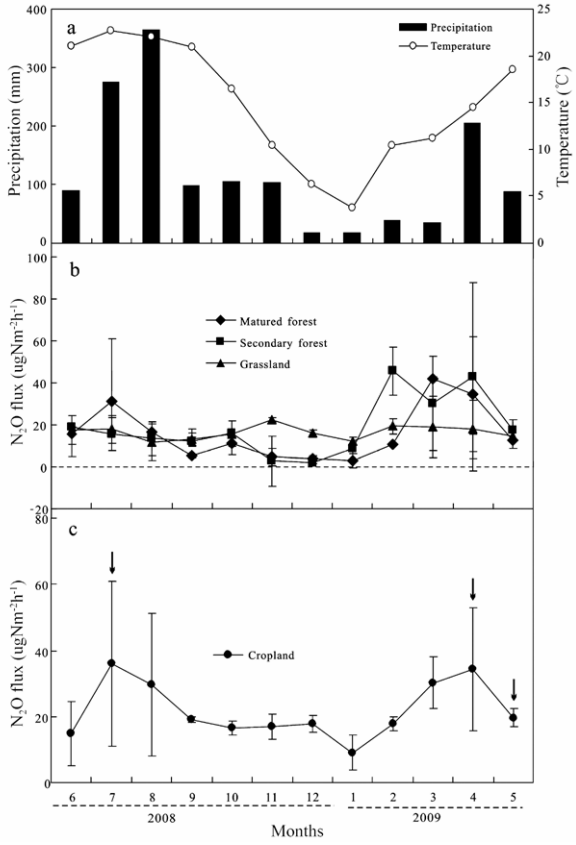

Fig. 2. Seasonal variations in N_2O fluxes from different land use systems in comparison with mean monthly temperature and precipitation during the study period. Error bars represent standard deviations. Arrows indicate time of fertilizer application in the cropland (maize field).

4 Discussion

4.1 Effect of seasonal changes on N_2O fluxes

As for all the four land use systems, seasonal N_2O emission patterns are similar during one year measurement. The N_2O fluxes are high in spring and summer seasons, and low in autumn and winter seasons. When emissions are high, variations in emission rates are also greatest (Fig. 2b, c). Seasonal changes in soil N_2O flux display a seasonal weather pattern, with high N_2O emission rates in the rainy-hot seasons and low rates in the dry-cool seasons (Fig. 2), which is in agreement with the findings in other studies (Lin Shan et al., 2010; Liu Juan et al., 2011). Temperature and precipitation can regulate the N_2O emission of soils through its influence on microbial activity. The relatively high temperature and rainfall in summer seasons are beneficial for microbial activity, as the mineralization of organic N is likely to have contributed significantly to the potential for N_2O loss by nitrification and denitrification, which can explain why N_2O fluxes for all these four land use systems varied seasonally with high emissions during this period (Liu Juan et al., 2011). Although the rainfall is relatively low in spring seasons, there are also high N_2O emissions under four different land use patterns. This might be that microbial processes (nitrification and denitrification) may have been stimulated by higher availability of organic carbon and inorganic nitrogen due to thawing of the frozen soil through a long winter. Once in September, temperature and precipitation began to decrease. The activity of soil microbes was also lower and might even be in the dormancy state in winter, with low N_2O emissions under different land use patterns in autumn and winter seasons.

4.2 Comparison with the results of other studies in non-karst regions

Our range of cumulative annual N_2O emissions from different land use patterns (1.40–1.91 kg N ha^{-1} a^{-1}, Table 2) in karst regions is in general agreement with previously published data for the same systems in non-karst regions (summarized in Table 3). Annual mean soil N_2O-N emissions are 1.40 and 1.65 kg N ha^{-1} a^{-1} for the matured and secondary forests, respectively. Some far higher values were found, such as 2.6 kg N ha^{-1} a^{-1} for a tropical seasonal rain forest in Southwest China (Yan Yuping et al., 2008), 3.4 kg N ha^{-1} a^{-1} for a gradient of elevation forest in the coastal Brazilian Atlantic (Neto et al., 2011), but higher than 0.8 kg N ha^{-1} a^{-1} for a 23-year old secondary forest (Palm et al., 2002) and 0.9 kg N ha^{-1} a^{-1} for a spruce forest in Wildmooswald, Germany (Jungkunst et al., 2004) (Table 3). However, the values are within the range of annual estimates for some other forests worldwide (between 1 and 2 kg N ha^{-1} a^{-1}) (Brumme et al., 1999; Lamers et al., 2007). Therefore, the N_2O emissions from forest soils worldwide are greatly different under the conditions of different climates, various types of soils and vegetations, etc.

Annual mean soil N_2O-N emission is 1.45 kg N ha^{-1} a^{-1} from the scattered grassland in the karst region, Southwest China. The result presented here falls within the range of soil N_2O-N emission rates reported in a number of similar studies worldwide (Mosier et al., 1997; Tilsner et al., 2003). It is lower than 2.8 kg N ha^{-1} a^{-1} from an experimental grassland farm "Karkendamm" of the Kiel University, northern Germany (Lampe et al., 2006) and 3.0 kg N ha^{-1} a^{-1} from grazed pasture soils in the humid tropics of Costa Rica (Veldkamp et al., 1998), but higher than 0.2 kg N ha^{-1} a^{-1} from different fertilized grasslands in southern Germany (Glatzel and Stahr, 2001) and 0.3–0.6 kg N ha^{-1} a^{-1} from grassland ecosystems in Inner Mongolia, China (Chen Guanxiong et al., 2000) (Table 3). The result showed that N_2O emissions from the warm-wet

grasslands are higher than those from the cold-dry grasslands. For example, in northern China, the mass of grasslands are located in semi-arid and arid regions, which are assorted to ecologically fragile zones. The poor soils and low precipitation can limit N_2O emissions due to the depressed processes of nitrification and denitrification (Zhang Feng et al., 2010).

Cropland is a major source of atmospheric N_2O. Our study showed that soil from the maize field in the karst region released N_2O with an annual mean N_2O flux of 1.91 kg N ha^{-1} a^{-1}, which is higher than 0.8–1.0 kg N ha^{-1} a^{-1} in three arable soils in the UK (Webb et al., 2000), and 1 kg N ha^{-1} a^{-1} in the cultivation of energy crops on sandy soils (Hellebrand et al., 2003), but lower than 4.4 kg N ha^{-1} a^{-1} in the fertilized and manured maize fields (Cates and Keeney, 1987) and 2.6 kg N ha^{-1} a^{-1} in humid tropical agricultural soils (Weitz et al., 2001) (Table 3). However, our result is comparable with some N_2O emissions, such as 1.8 kg N ha^{-1} a^{-1} in a fine-loamy soil and 2.1 kg N ha^{-1} a^{-1} in a maize field, north of Munich in southern Germany (Ruser et al., 2001; Sehy et al., 2003). These results showed the great variations in soil N_2O emission and complexity of the controlling factors (especially in fertilizer) in the cropland, which must be thoroughly studied.

4.3 Fertilizer-derived N_2O emission from the cropland

Fertilizer is not only necessary for crop growth, but also provides a substrate for N_2O formation under both aerobic and anaerobic conditions (Bremner and Blackmer, 1978). It is believed that large N_2O emissions observed above are in part due to the influence of the added organic and chemical nitrogen fertilizers. Using the definition by IPCC (2006), we calculated the N_2O emission factor (EF) by $EF=(E-E_0)/N\times100\%$. Here, E and E_0 indicate N_2O-N emissions from the fields with and without nitrogen fertilizer application, respectively. Due to a lack of measurement in the non-fertilized maize field, we used the N_2O basic emission value of 1 kg N_2O-N ha^{-1} a^{-1} in the non-fertilized cropland (Bouwman, 1996) to calculate the EF in the whole year. In the maize field, fertilizers were applied at an average rate of 266 kg N ha^{-1} a^{-1}. When using the mean annual N_2O emission from the cropland in a karst region (1.91 kg N ha^{-1} a^{-1}), the calculated chemical nitrogen fertilizer-derived N_2O emission in the whole year was 0.34% or 3.40 g N_2O-N (kg N a)$^{-1}$.

Our result is comparable to the results of Chu Haiyan et al. (2007) who observed a loss of 0.35%–0.52% of nitrogen fertilizer from a winter barley cultivated under Japanese Andisol and the fertilizer-transformed N_2O-N from the rape field accounted for 0.31%–0.55% of the applied nitrogen in central China (Lin Shan et al., 2011). It is lower than the calculated (by McSwiney and Robertson, 2005) fertilizer induced emission factors of 2%–7% at fertilizer rates of 134–291 kg N ha^{-1} a^{-1} and 1.09%–1.63% of the chemical fertilizer-transformed N_2O-N from a vegetable field (Cao Bing et al., 2006), but higher than the values of 0.16%–0.18% observed in the North China Plain (Ding Weixin et al., 2007) and 0.13% for fertilizer treatment in a sandy soil for maize (van Groenigen et al., 2004). The above results showed a very wide range of N_2O EF, revealing inconsistency amongst the available studies. Fertilizer application history, variations in nitrogen input sources, soil types as well as dynamic soil-plant interactions in the systems receiving a superoptimal level of nitrogen addition could partly account for this sufficient EF variability, and extremely high EF values would occur when soil mineral nitrogen availability exceeds the capacities of plant and soil nitrogen uptake (McSwiney and Robertson, 2005).

Following IPCC guidelines, default EF for both soils and all nitrogen application rates and types would be estimated at 1.25%. However, our result shows that the EF value is not higher than 0.5% for chemical and traditional manure applications, the default EF defined by IPCC could overestimate N_2O emissions from the nitrogen fertilizers applied to soils, at least for conditions such as those in the karst regions, Southwest China. Brown et al. (2001) and Ding Weixin et al. (2007) also confirmed that the IPCC methodology overestimated N_2O emissions in the U.K. and North China, respectively. The collective evidence supports the critical need for perfecting the existing N_2O estimation methodology for superior accuracy of both field-specific and global budget N_2O calculations (Kim and Hernandez-Ramires, 2010).

Table 2 N_2O fluxes in different land use patterns

Land use pattern	Range of fluxes (μg N m^{-2} h^{-1})	Mean±SD (μg N m^{-2} h^{-1})	CV (%)	Total N_2O emission (kg N ha^{-1} a^{-1})	Sample size (N)
Matured forest	3.0－41.8	16.0±13.0	81.8	1.40	24
Secondary forest	2.0－45.7	18.8±14.0	74.6	1.65	24
Grassland	11.9－22.3	16.5±3.2	19.4	1.45	24
Cropland	9.0－36.0	21.8±8.5	39.2	1.91	24

Note: SD indicates the standard deviation; CV indicates the coefficient of variation.

Table 3 Comparison with annual N_2O-N emissions in non-karst regions

Land use pattern	Duration (year)	SOC (g kg^{-1})	TN (g kg^{-1})	N fertilizer (kg N_2O-N ha^{-1} a^{-1})	N_2O (kg N ha^{-1} a^{-1})	Reference
Forest	1	36–47	2.9–4.1	0–0	1.40–1.65	1
	2	128–295	6–12.5	0–0	1.37–1.69	2
	1	34	n.d.	0–0	1.3	3
	2	11	n.d.	0–0	0.8	4
	2.5	299–319	15–16	0–0	0.9	5
	1	21.7	1.4	0–0	2.6	6
	1	31.8–45.9	2.4–3.4	0–0	3.4	7
Grassland	1	51	4.2	0–0	1.45	1
	2	8.9–9.5	0.9–1.1	0–0	1.4	8
	1	17.8	n.d.	0–0	1.6	9
	1.6	34.5	3.5	0–0	0.2	10
	1	19.7–33.6	1.3–2.1	0–0	0.3–0.6	11
	1	41	2.3	0–0	2.8	12
	2	n.d.	n.d.	0–0	3	13
Cropland	1	32.0	2.8	266	1.91	1
	2	9.4	1.1	110	1.8	14
	1	12.1	1.0	319	2.1	15
	3	32.5	0.7	40–250	0.8–1	16
	1	9.0	n.d.	0–150	1	17
	2	50.4	5.3	122	2.63	18
	1	1.2	n.d.	181–237	4.4	19

Note: 1. This study; 2. Lamers et al., 2007; 3. Brumme et al., 1999; 4. Palm et al., 2002; 5. Jungkunst et al., 2004; 6. Yan Yuping et al., 2008; 7. Neto et al., 2011; 8. Mosier et al., 1997; 9. Ruser et al., 2001; 10. Glatzel and Stahr, 2001; 11. Chen Guanxiong et al., 2000; 12. Lampe et al., 2006; 13. Veldkamp et al., 1998; 14. Tilsner et al., 2003; 15. Sehy et al., 2003; 16. Webb et al., 2000; 17. Hellebrand et al., 2003; 18. Weitz et al., 2001; 19. Cates and Keeney, 1987.

5 Conclusions

Land use change and fertilizer application have a great effect on N_2O fluxes in the subtropical karst region, Southwest China. N_2O fluxes follow the order: cropland (1.91 kg N ha^{-1} a^{-1}), secondary forest (1.65 kg N ha^{-1} a^{-1}), grassland (1.45 kg N ha^{-1} a^{-1}) and matured forest (1.40 kg N ha^{-1} a^{-1}). Changing land use pattern from forest and grassland to cropland will increase N_2O production, but changing land use pattern from the secondary forest to matured forest will decrease N_2O emission. It is suggested that the cultivated land is a relatively higher N_2O source than forest and grassland in the karst region.

Large N_2O emissions observed in the maize field are in part due to the influence of the added fertilizers, and the N_2O EF value is 0.34% of fertilizer applied, which is about 71.2% lower than the IPCC default value. It is suggested that the current IPCC EF methodology could overestimate N_2O emissions from the karstic cropland.

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References

Bai Zhanguo and Wang Guojiang (1998) Variability of aquatic chemistry in central Guizhou karst region, China [J]. *Chinese Journal of Geochemistry*. **17**, 241−248.

Beauchamp E.G. (1997) Nitrous oxide emission from agriculture soils [J]. *Canadian Journal of Soil Science*. **77**, 113–123.

Bouwman A.F. (1990) *Soils and the Greenhouse Effect* [M]. John Wiley and Sons, New York.

Bouwman A.F. (1996) Direct emission of nitrous oxide from agricultural soils [J]. *Nutrient Cycling in Agroecosystems.* **46**, 53–70.

Bremner J.M. and Blackmer A.M. (1978) Nitrous oxide: Emission from soils during nitrification of fertilizer nitrogen [J]. *Science*. **199**, 295–296.

Brown L., Brow S.A., Jarvis S.C., Syed B., Goulding K.W.T., Phillips V.R., Sneath R.W., and Pain B.F. (2001) An inventory of nitrous oxide emissions from agriculture in the UK using the IPCC methodology: emission estimate, uncertainty and sensitivity analysis [J]. *Atmospheric Environment.* **35**, 1439–1449.

Brumme R., Borken W., and Finke S. (1999) Hierarchical control on nitrous oxide emission in forest ecosystems [J]. *Global Biogeochemical Cy-*

cles. **13**, 1137–1148.

Cao Bing, He Fa Yun, Xu Qiuming, Yin Bin, and Cai Guixin (2006) Denitrification losses and N_2O emissions from nitrogen fertilizer applied to a vegetable field [J]. *Pedosphere.* **16**, 390–397.

Cates R.L. and Keeney D.R. (1987) Nitrous oxide production throughout the year from fertilized and manured maize fields [J]. *Journal of Environmental Quality.* **16**, 443–447.

Chen Guanxiong, Huang Bin, Xu Hui, Zhang Ying, Huang Guohong, Yu Kewei, Hou Aixin, Du Rui, Han Shijie, and VanCleemput O. (2000) Nitrous oxide emissions from terrestrial ecosystems in China [J]. *Chemosphere.* **2**, 373–378.

Christensen S. and Tiedje J.M. (1990) Brief and vigorous N_2O production by soil at spring thaw [J]. *Journal of Soil Science.* **41**, 1–4.

Chu Haiyan, Hosen Y., and Yagi K. (2007) NO, N_2O, CH_4 and CO_2 fluxes in winter barley field of Japanese Andisol as affected by N fertilizer management [J]. *Soil Biology and Biochemistry.* **39**, 330–339.

Ding Weixin, Cai Yan, Cai Zucong, Yagi K., and Zheng Xunhua (2007) Nitrous oxide emissions from an intensively cultivated maize-wheat rotation soil in the North China Plain [J]. *Science of the Total Environment.* **373**, 501–511.

Glatzel S. and Stahr K. (2001) Methane and nitrous oxide exchange in differently fertilised grassland in southern Germany [J]. *Plant and Soil.* **231**, 21–35.

He Caihua, Xiong Kangning, Li Xiaoling, and Cheng Xing (1998) Karst geomorphology and its agricultural implications in Guizhou, China [J]. *Supplements of Geografia Fisica Dinama Quaternaria Volume III.* **4**, 121–125.

Hellebrand H.J., Kern J., and Scholz V. (2003) Long-term studies on greenhouse gas fluxes during cultivation of energy crops on sandy soils [J]. *Atmospheric Environment.* **37**, 1635–1644.

Hofmann D.J., Butler J.H., Dlugokencky E.J., Elkins J.W., Masarie K., Montzka S.A., and Tans P. (2006) The role of carbon dioxide in climate forcing from 1979 to 2004: Introduction of the Annual Greenhouse Gas Index [J]. *Tellus*. **58**, 614–619.

Holl B.S., Jungkunst H.F., Fiedler S., and Stahr K. (2005) Indirect nitrous oxide emission from a nitrogen saturated spruce forest and general accuracy of IPCC methodology [J]. *Atmospheric Environment.* **39**, 5959–5970.

IPCC (2001) *Climate Change 2001: The Scientific Basis, Summary for Policymakers. Contribution of Working Group 1 to the Third Assessment Report of the Intergovernmental Panel on Climate Change* [M]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

IPCC (2006) *2006 IPCC Guidelines for National Greenhouse Gas Inventories, Prepared by the National Greenhouse Gas Inventories Programme* (eds. Eggleston H.S., Buendia L., Miwa K., Ngara T., and Tanabe K.) [M]. Published: IGES, Japan.

IPCC (2007) Summary for Policymakers. In *Climate Change 2007: The physical Science Basis. Contribution of Working Group 1 to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [M]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Ishizuka S., Tsuruta H., and Murdiyarso D. (2002) An intensive field study on CO_2, CH_4, and N_2O emissions from soils at four land use types in Sumatra, Indonesia [J]. *Global Biogeochemical Cycles.* **16**, doi: 10.1029/2001GB001614.

Jungkunst H.F., Fiedler S., and Stahr K. (2004) N_2O emissions of a mature Norway spruce (*Picea abies*) stand in the Black Forest (Southwest Germany) as differentiated by the soil pattern [J]. *Journal of Geophysical Research.* **109**, doi:10.1029/2003JD004344.

Keller M., Veldkamp E., Weitz A.M., and Reiners W.A. (1993) Effect of pasture age on soil trace-gas emissions from a deforested area of Costa Rica [J]. *Nature.* **365**, 244–246.

Kim D.G. and Hernandez Ramirez G. (2010) Dependency of nitrous oxide emission factors on nitrogen input rates: a meta-analysis. In *Proceedings 19th World Congress of Soil Science. Greenhouse Gases from Soils, IUSS, Brisbane, Congress Symposium* (eds. Gilkes R.J. and Prakongkep) [C]. **4**, 40–43 (Published on DVD).

Lamers M., Ingwersen J., and Streck T. (2007) Nitrous oxide emissions from mineral and organic soils of a Norway spruce stand in South-West Germany [J]. *Atmospheric Environment*. **41**, 1681–1688.

Lampe C., Dittert K., Sattelmacher B., Wachendorf M., Loges R., and Taube F. (2006) Sources and rates of nitrous oxide emissions from grazed grassland after application of N-labelled mineral fertilizer and slurry [J]. *Soil Biology and Biochemistry.* **38**, 2602–2613.

Lin Shan, Lqbal J., Hu Ronggui, and Feng Minglei (2010) N_2O emissions from different land uses in mid-subtropical China [J]. *Agriculture Ecosystems and Environment.* **136**, 40–48.

Lin Shan, Iqbal J., Hu Ronggui, Wu Jinshui, Zhao Jinsong, Ruan Leilei, and Malghani S. (2011) Nitrous oxide emissions from rape field as affected by nitrogen fertilizer management: A case study in central China [J]. *Atmospheric Environment.* **45**, 1775–1779.

Liu Juan, Jiang Peikun, Li Yongfu, Zhou Guomo, Wu Jiasen, and Yang Fang (2011) Responses of N_2O flux from forest soils to land use change in subtropical China [J]. *Botanical Review.* **77**, 320–325.

McSwiney C. and Robertson G.P. (2005) Nonlinear response of N_2O flux to incremental fertilizer addition in a continuous maize (Zea mays L.) cropping system [J]. *Global Change Biology.* **11**, 1712–1719.

Melillo J.M., Steudler P.A., Feigl B.J., Neill C., Garcia D., Piccolo M.C., Cerri C.C., and Tian H. (2001) Nitrous oxide emissions from forests and pastures of various ages in the Brazilian Amazon [J]. *Journal of Geophysical Research.* **106**, 34179–34188.

Mosier A.R., Parton W.J., Valentine D.W., Ojima D.S., Schimel D.S., and Heinemeyer O. (1997) CH_4 and N_2O fluxes in the Colorado shortgrass steppe. 2. Long-term impact of land use change [J]. *Global Biogeochemical Cycles.* **11**, 29–42.

Mummey D.L., Smith J.L., and Bluhm G. (2000) Estimation of nitrous oxide emissions from US grasslands [J]. *Environmental Management.* **25**, 169−175.

Neto E.S., Carmo J.B., Keller M., Martins S.C., Alves L.F., Vieira S.A., Piccolo M.C., Camargo P., Couto H.T.Z, Joly C.A., and Martinelli L.A. (2011) Soil-atmosphere exchange of nitrous oxide, methane and carbon dioxide in a gradient of elevation in the coastal Brazilian Atlantic forest [J]. *Biogeosciences.* **8**, 733–742.

Palm C.A., Alegre J.C., Arevalo L., Mutuo P.K., Mosier A.R., and Coe R. (2002) Nitrous oxide and methane fluxes in six different land use systems in the Peruvian Amazon [J]. *Global Biogeochemical Cycles*. **16**, doi:10.1029/2001GB001855.

Prather M., Derwent R., Ehhalt D., Fraser P., Sanhueza E., and Zhou X. (1995) Other trace gases and atmospheric chemistry. In *Climate Change 1994. Radiative Forcing of Climate Change and an Evaluation of the IPCC IS92 Emission Scenarios* (eds. Hougughton J.T.,

Meira Filho L.G., Bruce J., Hoesung Lee, Callander B.A., Haires E., Harris N., and Maskell K.) [M]. pp.75–126. Cambridge, Cambridge University Press.

Ruser R., Flessa H., Schilling R., Beese E., and Munch J.C. (2001) Effect of crop-specific field management and N fertilization on N_2O emissions from a fine-loamy soil [J]. *Nutrient Cycling in Agroecosystems.* **59**, 177–191.

Schindlbacher A., Zechmeister-Boltenstern S., and Butterbach-Bahl K. (2004) Effects of soil moisture and temperature on NO, NO_2, and N_2O emissions from European forest soils [J]. *Journal of Geophysical Research.* **109**, doi:10.1029/2004JD004590.

Sehy U., Ruser R., and Munch J.C. (2003) Nitrous oxide fluxes from maize fields: relationship to yield, site-specific fertilization, and soil condition [J]. *Agriculture Ecosystems and Environment.* **99**, 97–111.

Smith K.A., Clayton H., Arah J.R.M., Christensen S., Ambus P., Fowler D., Hargreaves K.J., Skiba U., Harris G.W., Wienhold F.G., Klemedtsson L., and Galle B. (1994) Micrometeorological and chamber methods for measurement of nitrous oxide fluxes between soils and the atmosphere: Overview and conclusions [J]. *Journal of Geophysical Research.* **99**, 16541–16548.

Smith K.A., McTaggart I.P., Dobbie K.E., and Conen F. (1998) Emissions of N_2O from Scottish agricultural soils, as a function of fertilizer N [J]. *Nutrient Cycling in Agroecosystems.* **52**, 123–130.

Tilsner J., Wrage N., Lauf J., and Gebauer G. (2003) Emission of gaseous nitrogen oxides from an extensively managed grassland in NE Bavaria, Germany. I. Annual budgets of N_2O and NO_X emissions [J]. *Biogeochemistry.* **63**, 229–247.

van Groenigen J.W., Kasper G.J., Velthof G.L., van den Pol-van Dasselaar A., and Kuikman P.J. (2004) Nitrous oxide emissions from silage maize fields under different mineral nitrogen fertilizer and slurry applications [J]. *Plant and Soil*. **263**, 101–111.

Veldkamp E., Keller M., and Nunez M. (1998) Effects of pasture management on N_2O and NO emissions from soils in the humid tropics of Costa Rica [J]. *Global Biogeochemical Cycles.* **12**, 71–79.

Webb J., Harrison R., and Ellis S. (2000) Nitrogen fluxes in three arable soils in the UK [J]. *European Journal of Agronomy.* **13**, 207–223.

Weitz A.M., Linder E., Frolking S., Crill P.M., and Keller M. (2001) N_2O emissions from humid tropical agricultural soils: Effects of soil moisture, texture and nitrogen availability [J]. *Soil Biology and Biochemistry.* **33**, 1077–1093.

Wick B., Veldkamp E., de Mello W.Z., Keller M., and Crill P. (2005) Nitrous oxide fluxes and nitrogen cycling along a pasture chronosequence in Central Amazonia, Brazil [J]. *Biogeosciences* **2**, 175–187.

Yan Yuping, Sha Liqing, Cao Min, Zheng Zheng, Tang Jianwei, Wang Yinghong, Zhang Yiping, Wang Rui, Liu Guanren, Wang Yuesi, and Sun Yang (2008) Fluxes of CH_4 and N_2O from soil under a tropical seasonal rain forest in Xishuangbanna, Southwest China [J]. *Journal of Environmental Sciences.* **20**, 207–215.

Zhang Baiping, Xiao Fei, Wu Hongzhi, Mo Shengguo, Zhu Shouqian, Yu Lifei, Xiong Kangning, and Lan Aanjun (2006) Combating the fragile karst environment in Guizhou, China [J]. *AMBIO: A Journal of the Human Environment.* **35**, 94–97.

Zhang Feng, Qi Jiaguo, Li Fengmin, Li Changshen, and Li Changbin (2010) Quantifying nitrous oxide emissions from Chinese grasslands with a process-based model [J]. *Biogeosciences.* **7**, 2039–2050.

Zhu Shufa and Liu Congqiang (2008) Stable carbon isotopic composition of soil organic matter in the karst areas of Southwest China [J]. *Chinese Journal of Geochemistry*. **27**, 171−177.