IOP Conference Series: Earth and Environmental Science

PAPER • **OPEN ACCESS**

Dynamics of organic matter in soils formed on limestone and sandstone in the karst area in southwestern China: δ^{13}C and δ^{15}N approaches

To cite this article: Long-Bo Li *et al* 2021 *IOP Conf. Ser.: Earth Environ. Sci.* **861** 062046

IOP Conf. Series: Earth and Environmental Science **861** (2021) 062046 doi:10.1088/1755-1315/861/6/062046

Dynamics of organic matter in soils formed on limestone and sandstone in the karst area in southwestern China: δ^{13}C and δ^{15}N approaches

Long-bo Li [1,2], Da-Wei Cai [1,*], Yao-Qiang Zhu [1], Ming-Qiang Ren [1]

1 Guizhou Institute of Geo-Environment Monitoring, 171th, Shilinxi Road, Guiyang 550081, Guizhou, China

2 State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, CAS, Guiyang 550081, Guizhou, China

*Corresponding author: Da-Wei Cai

Da-Wei Cai ORCID ：0000-0001-8828-050X

Abstract

To better understand biogeochemical processes associated with the dynamics of soil organic matter (SOM), the δ^{13}C and δ^{15}N values were analyzed in the SOM of limestone soil (developed on limestone) and sandstone soil (developed on sandstone), as well as in dominant plant species and litter samples collected on the studied soil profiles in karst areas of Southwest China. In general, the content of soil organic carbon (SOC) and soil organic nitrogen (SON) is highest in the surface soil layer and decreases downward in both types of soil profiles. In addition, the content of SOM (including both SOC and SON) in the limestone is much higher than in sandstone soil. The higher pH values, as well as the content of calcium, magnesium, and clay minerals, are probably the reasons for the higher SOM content in the limestone soil compared to the sandstone soil.

In the SOM of the upper layers of yellow sandstone and limestone soil δ^{13}C values range from 2.6‰ to 6.3‰ and δ^{15}N values from 5.1‰ to 8.1‰, which is larger than in litters. Yellow sandstone soils have smaller differences between δ^{13}C and δ^{15}N values of SOM from litter and topsoil than the limestone soil. The δ^{13}C and δ^{15}N values of SOM increase with depth in yellow sandstone soil profiles, but not in the limestone soil profiles. An increase in the values of δ^{13}C and δ^{15}N with a decrease in the SOM content in the yellow sandstone soil significantly substantiates the decomposition of SOM, which causes higher values of δ^{13}C and δ^{15}N values in the deeper soil horizons. By contrast, the limestone soil has complex depth profiles of δ^{13}C and δ^{15}N, which can be mainly attributed to land-use changes and organic and mineral interactions between soil accumulations.

Keywords: Soil organic matter; carbon isotope; nitrogen isotope; karst area; China

1 Introduction

The world's soils are an integral part of the global carbon (C) cycle and as a source of atmospheric CO_2 can release a large amount of C into the atmosphere every year [1]. SOC stocks in terrestrial ecosystems are almost three times greater than the storage of C in vegetation [2] and twice as large as the global atmospheric storage of C [3]. Due to the large amount stored in terrestrial ecosystems, a small change in SOC significantly affects the concentration of greenhouse gases in the atmosphere. Accordingly, concerns about global warming are increasing interest in quantifying the control of soil C dynamics and storage [4], [5]. Meanwhile, the issue of SOC is of growing concern as it is important for improving soil quality, sustaining food production and quality, and maintaining water quality [6]. Therefore, a better understanding of the mechanism and dynamics of SOC accumulation and storage is necessary to accurately quantify SOC stocks, study soil quality and productivity, and model the global C cycle.

Guizhou Province is located in the center of the karst zone of East Asia, which is one of the three largest karst areas in the world. The carbonate rocks outcrop in an area of 130000 km^2, which is 73% of the total land area of the province [7]. Regional rocky desertification is a serious ecological problem in the subtropical karst areas of Southwest China, which makes the residents poorer and poorer due to the loss of soil and water [8]. Rocky desertification is a process of land degradation that occurs due to the combined effect caused by the imposition of irrational anthropological activities on the vulnerable karst eco-geo-environment background [9].

With the continuation of rocky desertification, soils in karst areas undergo degradation, which leads to chemical and physical (decomposition and erosion) loss of SOM. Therefore, to protect soil quality, a better understanding of how SOM is decomposed and lost during land degradation in the karst area is needed.

The stable isotopic composition of C is widely used to study biogeochemical processes in soils [10], [11], [12] and to assess the degree of decomposition of SOM [13], [14], [15]. The natural amount of ^{15}N is used to access the loss of nitrogen (N) and the nature of N mineralization [16], [17], [18], [19], [20], [21], [22] to compare the patterns of N uptake by plant species [23], as well as to determine the impact of land-use history on N cycles [24], [25], [26]. Accordingly, in recent decades, many researchers have widely used the methods of dual stable isotopes (both ^{13}C and ^{15}N) to study the dynamics of SOM [27], [28], [29].

There are two main types of soils formed respectively on carbonate rocks and sandstones in the karst area in the Guizhou Province of Southwest China. In this study, we investigated variations in SOC and SON content, as well as variations in their $\delta^{13}C$ and $\delta^{15}N$ values in limestone soil and sandstone soil. The main objectives of this study are to characterize the content of SOC and SON, as well as the distributions of their $\delta^{13}C$ and $\delta^{15}N$ values in limestone and sandstone soils, as well as to study the factors controlling variations in the content of SOC, SON, and their $\delta^{13}C$ and $\delta^{15}N$ values in different soils, and, finally, to achieve a better understanding the dynamics of SOM and soil formation processes in karst areas.

2 Materials and methods

2.1 Study site

The investigated sites are located in Baiyi of Wudang and Wangjiazhai of Qingzhen, about 15 and 30 km, respectively, from Guiyang City (26°28′ 19″ N, 106°49′ 18″ E), the central region of Guizhou Province, China (Fig. 1), at an altitude of about 1300 m above sea level. The central region of Guizhou Province has a subtropical, monsoon, and humid climate, with an average annual temperature of 14.8 °C and an average annual rainfall of 1100 mm. Five soil profiles were selected: three soil profiles were sampled in Wangjiazhai of Qingzhen, which include two soil profiles formed on limestone (profiles QZ-I and QZ-II) and one profile formed on sandstone (QZ-III); two soil profiles were sampled in Baiyi of Wudang, which include one soil profile formed on limestone (BY-II) and the other on sandstone (BY-I). Soils formed on limestone are called limestone soil, classified as calcic Cambisol, and soils formed on sandstone are called yellow sandstone soil, classified as Ferralsol according to the FAO-UNESCO soil classification system [30]. Limestone soils can be further classified as black limestone soils (profiles QZ-I and QZ-II) and yellow limestone soil (soil profile BY-II) depending on their color (or SOM content). The main types of forests are the Masson pine forest, mixed broadleaf forest, and shrub. Detailed features of each soil profile during sampling are summarized in Table 1.

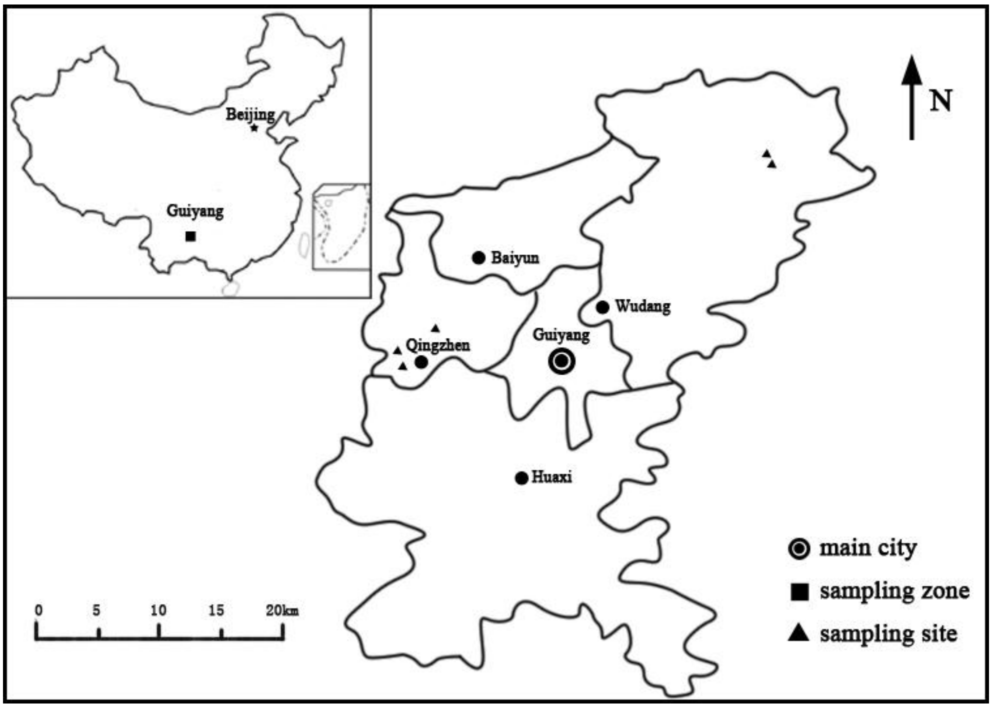

Fig.1. Map showing Guiyang Prefecture (including Guiyang urban area and surrounding areas) and sampling locations.

Table 1. The main features of the studied soil profiles.

Study area	Profiles	Soil type	Geographical coordinates	Altitude (m)	Landform	Dominant species
BaiYi of WuDang	BY-I	Yellow sandstone soil	26°47′ 3″ N, 107°01′ 16″ E	1214	Middle mountains	*Pinus massoniana Lam, Quercus alba L, Pterdium aquilinum var. Latiusculum, Qnercns glanca Thunb*
	BY-II	Yellow limestone soil	26°48′ 40″ N, 107°00′ 16″ E	1327	Low land	*Pterdium aquilinum var. Latiusculum, Castanea seguinii Dode, Quercus alba L, Pyracantha fortuneana*
WangJia Zhai of QingZhen	QZ-I	Black limestone soil	26°31′ 25″ N, 106°20′ 16″ E	1285	Middle mountains	*Caesalpinia vernalis Champ, Lonicera Japanica, Herba Artemisiae Annuals, Pterdium aquilinum var. latiusculum*
	QZ-II	Black limestone soil	26°31′ 41″ N, 106°20′ 18″ E	1291	Middle mountains	*Pachyrhizus erosus, Pterdium aquilinum var. latiusculum*
	QZ-III	Yellow sandstone soil	26°31′ 52″ N, 106°23′ 16″ E	1279	Hill	*Castanea seguinii Dode, Camellia Oleifera, Pterdium aquilinum var. latiusculum*

2.2 Soil sampling and laboratory analysis

The litter horizons were removed before soil sampling. Soil samples were taken from the soil surface (0–5 cm depth), followed by sampling from the pit walls from a depth of 5 cm to a depth of about 100 cm in the lower horizon. Visible roots and organic debris were removed during sampling. Soil samples containing about 1–2 mg of SOC were placed in 15 mL centrifuge tubes, and tubes without soil were used as controls; 10 mL of 2 mol L^{-1} KCl solution was added to the test tubes and shaken for 1 hour at 25 °C, and then centrifuged at 3000 r min^{-1} for 25 min, the supernatant was discarded, and then 10 mL of 0.1 mol L^{-1} HCl solution was added to the tubes and shaken for 24 hours at 25 °C and then centrifuged at 3000 r min^{-1} for 25 min, washed until neutral with distilled water, centrifuged and dried at 60 °C, then ground and kept for C and N isotopic analysis [31].

Before taking soil samples, litter was collected on an area of 4 m^2 for each profile. Samples of fresh foliage were also taken from the dominant tree, shrub, and grass species of each major vegetation type. Fresh foliage samples were cleaned with distilled water, and litter samples, separated from any adhering oil material, were dried at 60 °C and finely grounded.

The pH value of the soil was measured using a pH electrode (Orion) in a ratio of 1:2.5 (m/v) soil to deionized water. The content of organic C and N was analyzed by combustion in an Elemental Analyzer (PE2400 II, USA) with an analytical accuracy of 0.1%.

For the analysis of stable isotopes, a sample of mass giving 0.5 mg C was placed in a quartz tube with CuO, and then the sample tube was evacuated and sealed with a flame. The organic C in the sample was oxidized to CO_2 at 850 °C for 5 hours. CO_2 was collected and cryogenically purified in a vacuum extraction line, while the amount of CO_2 was measured by the manometric method before being collected in a test tube with a burst seal for subsequent mass spectrometric analysis [32]. Stable C isotope ratios ($^{13}C/^{12}C$) were measured on a Finnigan MAT 252 gas isotope mass spectrometer after purification with liquid nitrogen. The nitrogen isotopes in SON were measured by the Xiao method [31]. Analytical accuracy, defined as the standard deviation obtained over 35 replicates of the IAEA C3 laboratory cellulose standard. IAEA-C3 ($\delta^{13}C$ = −24.97‰, cellulose) was used as the standard for $\delta^{13}C$ and the analytical accuracy was ± 0.1‰. Analysis of the potassium nitrate standard (MOR2386-01, 1.92‰) provided by Shoko Co., Ltd. (Tokyo, Japan), gave the mean (± S.D.) $\delta^{15}N_{air}$ value 1.9 ± 0.2% (n = 5).

Isotope signatures are expressed by delta notation:

$$\delta x\ (‰) = 1000(R_{sample}/R_{standard} - 1)$$

where δx is the ratio of C or N isotopes in delta units relative to international standards (Pee Dee Belemnite for C and atmospheric N_2 for N) and R_{sample} and $R_{standard}$ are the $^{13}C/^{12}C$ or $^{15}N/^{14}N$ ratios for samples and standards, respectively. All experimental analyzes were carried out at the State Key Laboratory of Environmental Geochemistry of the Chinese Academy of Sciences.

3 Results

3.1 Soil pH values

Yellow sandstone soils have significantly lower pH values (from 4.0 to 4.8) than limestone soils, which range in pH from 4.8 to 7.0 (Fig. 2). Among limestone soils, yellow limestone soils (soil profile BY-II) show the lowest pH values. For all limestone soil profiles, the soil pH values increase with depth, while the soil pH values of the sandstone soil profiles change in different ways: the pH values remain nearly constant along the QZ-III soil profile, while the pH values in the BY-I soil profile first decrease to a depth of 30 cm and then increase from pH = 4.0 to pH = 4.7 in the lower part of the profile.

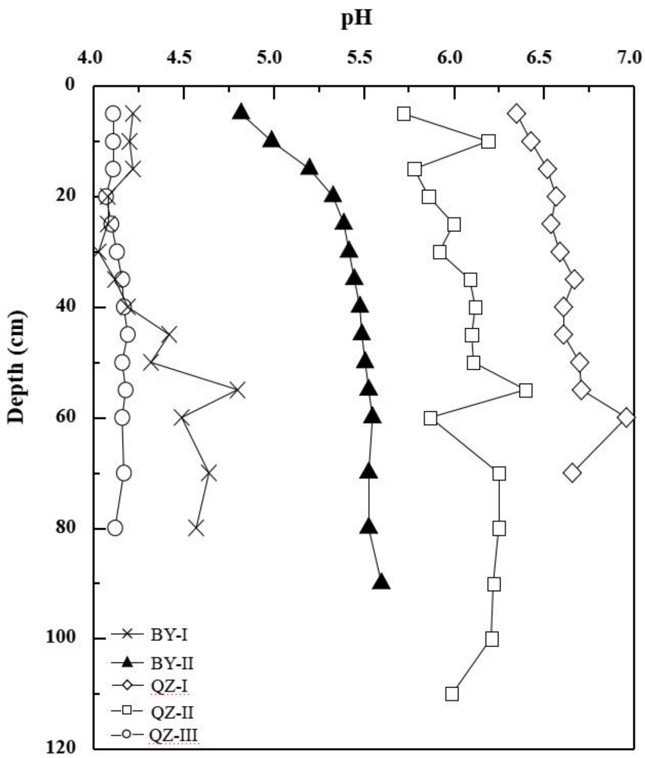

Fig. 2. Depth profiles of pH values in the studied soils.

3.2 Carbon and nitrogen content in the soil

As shown in Fig. 3a, SOC usually decreases with depth and is significantly higher in limestone soil than in yellow sandstone soil. SOC and SON are unevenly distributed over soil profiles, with the largest accumulations of SOC and SON occurring in the upper 20 cm of the soil horizon. Surface soils of profile QZ-III (yellow sandstone soil) show the lowest SOC content (20.6 g kg^{-1}), while surface soils of profile QZ-I (black limestone soil) show the highest SOC content (69.8 g kg^{-1}). For limestone soils, the SOC content exceeds 4.0 g kg^{-1}, with a maximum of 69.8 g kg^{-1} at the surface, while for yellow sandstone soils, the SOC content is in the range of 2.0–51.2 g kg^{-1}. This result is consistent with that reported by Zhu and Liu [33].

The SON content, like the SOC content, is highest in the surface layer of the soil and lowest at a certain depth in the soil (Fig. 3b) and is generally higher in limestone soil than in sandstone soil. Soils from the two black limestone profiles show distinctly high SON contents, especially for soils deeper than 60 cm. Another yellow limestone soil and two yellow sandstone soils demonstrate different styles of SON profile in depth, first decreasing from the topsoil to a depth of about 30 cm and then gradually increasing toward the bottom of the profiles.

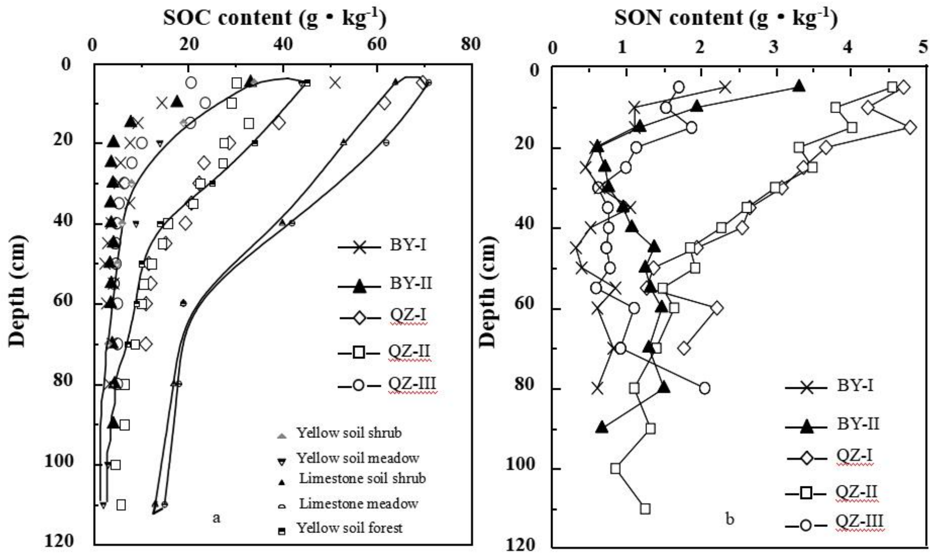

Fig. 3. Variations of soil organic carbon (SOC) (a) and soil organic nitrogen (SON) (b) contents with the yellow sandstone and limestone soil profiles. The limestone soil shrub, the limestone soil meadow, the yellow soil shrub, the yellow soil meadow, and the yellow soil forest originate from Zhu and Liu [33].

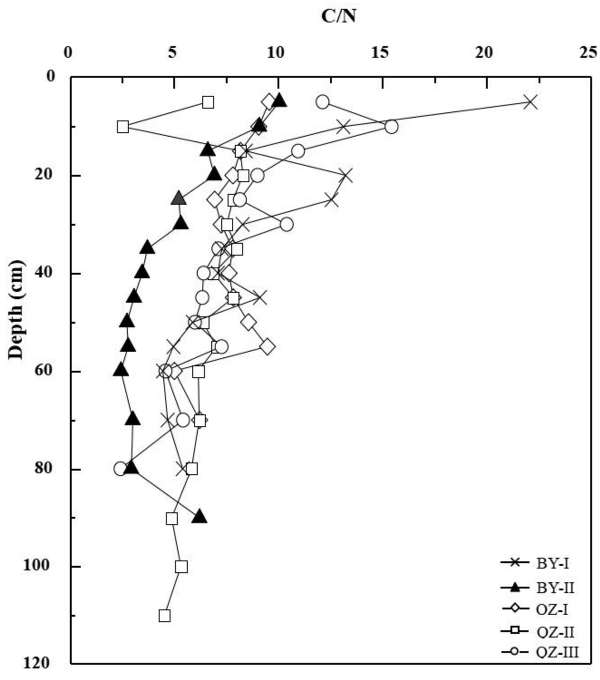

Fig. 4. Depth profiles of the mass ratios of organic carbon and nitrogen (C/N) in the studied soils.

As shown in Fig. 4, the mass ratio of organic carbon to nitrogen (C/N) in surface soils ranges from 6 to 22, with the highest value found in the surface layer of the yellow sandstone soil profile (BY-I) and the lowest value found in the surface layer of the black limestone soil profile (QZ-II). Except for the surface layer of the BY-I profile, the surface layers of soils of the other soil profiles display a range of C/N mass ratios from 6 to 15 and a range of C/N mass ratios from 2 to 10 at a depth of 60 cm, which shows an overall decrease from the top to the depth of the profile. There is no clear difference between the mass C/N ratios of limestone soil and sandstone soil.

3.3 $\delta^{13}C$ values of SOC

The yellow sandstone soils show different depth profiles of $\delta^{13}C_{SOC}$ from limestone soil profiles: the former shows a rapid increase in $\delta^{13}C_{SOC}$ from top to a depth of about 20 cm, and then maintains a constant or gradual increase downward, while the latter shows an overall increase in $\delta^{13}C_{SOC}$ within the first 20 cm from the soil surface, and then a decrease in $\delta^{13}C_{SOC}$ below about 20 cm to the depth at which the sample was taken (Fig. 5a). Maximum $\delta^{13}C_{SOC}$ values appear at depths of 25 and 15 cm, respectively, for the black limestone and yellow limestone soil profiles, maximum $\delta^{13}C_{SOC}$ values appear in soil samples at the bottom of sandstone soil profiles. The difference between the maximum and minimum $\delta^{13}C_{SOC}$ values ranges from 1.8‰ to 3.1‰ for the yellow sandstone soil profiles and from 1.3‰ to 1.4‰ for black limestone soil profiles. The profile of yellow limestone soil (BY-II) shows the largest difference (5.5‰) between the maximum and minimum $\delta^{13}C_{SOC}$ values.

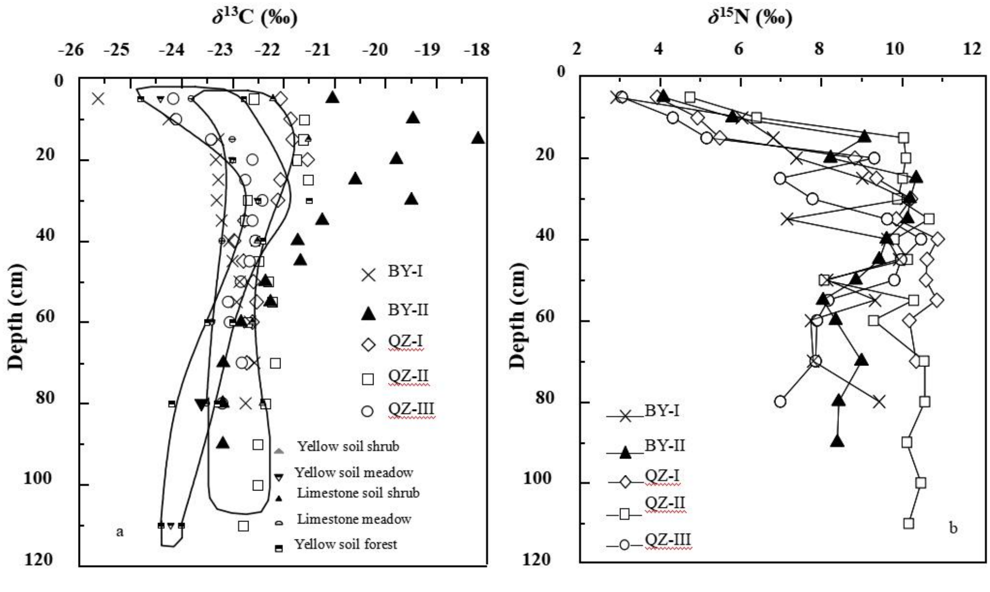

Fig. 5. Variations of $\delta^{13}C$ (a) and $\delta^{15}N$ (b) values depending on the soil profile from yellow sandstone and limestone soil profiles. The limestone soil shrub, the limestone soil meadow, the yellow soil shrub, the yellow soil meadow, and the yellow soil forest originate from Zhu and Liu [33].

3.4 $\delta^{15}N$ values of SON

The depth profiles of $\delta^{15}N$ values ($\delta^{15}N_{SON}$) for the soil samples are shown in Fig. 5b. On all profiles, the $\delta^{15}N_{SON}$ values increase from about +2.9‰ in the surface layer of the soil to about +10.9‰ in the soil at a depth of about 20 cm. Starting from a depth of 20 cm and below, the profiles of black limestone show constant $\delta^{15}N_{SON}$ values, while the profiles of yellow sandstone and yellow limestone show that $\delta^{15}N_{SON}$ values decrease with depth. In addition, at a depth of 20 to 60 cm, the $\delta^{15}N$ values change a lot and differ greatly depending on the soil profile.

3.5 $\delta^{13}C$ and $\delta^{15}N$ values for leaves of dominant plants and the litters

The values of $\delta^{13}C$ and $\delta^{15}N$ measured for the leaves of dominant plant species and litter samples collected from different soil profiles are shown in Table 2. The leaves of dominant plants grown on yellow sandstone soil have $\delta^{13}C$ values ranging from −29.6‰ to −27.4‰, and those grown on limestone soil have $\delta^{13}C$ values ranging from −30.0‰ to −26.9‰ (Table 2). The value of $\delta^{15}N$ measured for the plant leaves in yellow sandstone soil profiles are from −2.1‰ to +0.8‰, and for the plant leaves in limestone soil profiles are from −1.9‰ to +3.9‰.

Litter samples have values of $\delta^{13}C$ −28.2‰ and −27.1‰ for the yellow sandstone soil profiles BY-I and QZ-III, respectively, and −27.3‰, −27.8‰, and −28.1‰ for yellow limestone soil profile BY-II and black limestone soil profiles QZ-I and QZ-II, respectively. The values of $\delta^{15}N$ measured for corresponding litter samples are −2.2‰ and −2.3‰ for yellow sandstone soil profiles BY-I and QZ-III, respectively, and −2.4‰, −3.3‰, and −3.3‰ for yellow limestone soil profile BY-II and black limestone soil profiles QZ-I and QZ-II, respectively.

Table 2. Values of $\delta^{13}C$ and $\delta^{15}N$ for leaves of dominant species, litters, and topsoil SOM.

Profiles	Soil type	Dominant species	$\delta^{13}C_{leaf}$	$\delta^{15}N_{leaf}$	$\delta^{13}C_{litter}$	$\delta^{15}N_{litter}$	$\delta^{13}C$ value of topsoil SOM	$\delta^{15}N$ value of topsoil SOM
BY-I	Yellow sandstone soil	*Pinus massoniana Lam.*	-28.4	-0.9	-28.2	-2.2	-25.6	2.9
		Quercus alba L.	-29.5	-0.7				
		Pterdium aquilinum var. latiusculum	-29.7	-0.2				
		Qnercns glanca Thunb	-29.5	0.8				
BY-II	Yellow limestone soil	*Pterdium aquilinum var. latiusculum*	-27.7	-0.6	-27.3	-2.4	-21.0	4.1
		Castanea seguinii Dode	-29.1	1.6				
		Quercus alba L	-27.6	1.7				
		Pyracantha fortuneana	-29.6	1.5				
QZ-I	Black limestone soil	*Caesalpinia vernalis Champ*	-28.6	-0.1	-27.8	-3.3	-22.1	3.9
		Lonicera Japanica	-30.0	-1.1				
		Herba Artemisiae Annuals	-28.7	1.6				
		Pterdium aquilinum var. latiusculum	-26.9	0.6				
QZ-II	Black limestone soil	*Pachyrhizus erosus*	-27.6	3.9	-28.1	-3.3	-22.6	4.8
		Pterdium aquilinum var. latiusculum	-29.1	-1.9				
QZ-III	Yellow sandstone soil	*Castanea seguinii Dode*	-28.6	0.6	-27.1	-2.3	-24.1	3.1
		Camellia Oleifera	-28.0	-2.1				
		Pterdium aquilinum var. latiusculum	-27.4	-0.3				

4 Discussion

4.1 Lithological control of SOM in soils

Heckman et al [4] recently conducted a systematic study of geological control of soil C cycling and microbial dynamics in temperate coniferous forests and demonstrated that the mechanisms of carbon stabilization differ in various soils formed from different parent rocks. They concluded that the change in the mechanism of carbon stabilization could be directly related to the control of parent material over soil pH and mineral complex. There is a clear difference in SOC and SON content between yellow sandstone and limestone soils, and their content in limestone soils is higher than in yellow sandstone soils. As shown in Fig. 6, black limestone soils have both high SOC and high pH values, while yellow sandstone soils have both low SOC and low pH values, indicating pH control of SOM in soils.

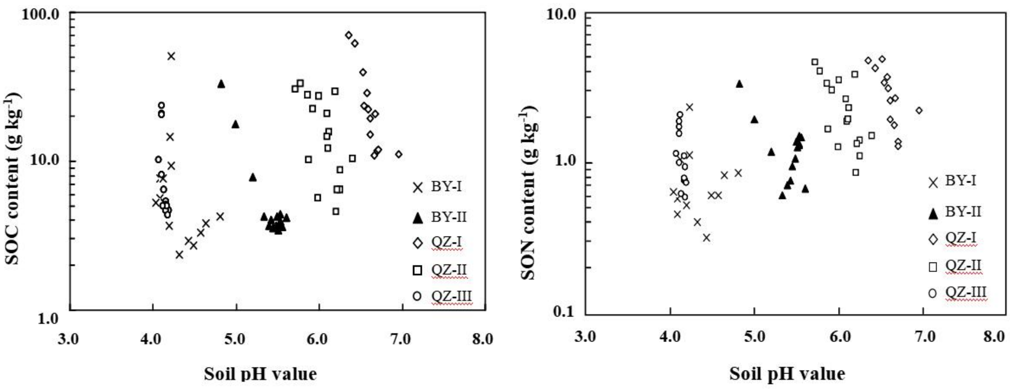

Fig. 6. Changes in soil organic carbon (SOC) and soil organic nitrogen (SON) content with soil pH values.

Soil pH can be an important comprehensive control of SOC dynamics, although there is no direct correlation between pH and SOC [4]. Soil pH can play an important role in affecting SOM by controlling mineral and microbial variables [34], [35], as well as mineral dissolution and metal speciation [36]. For example, at higher soil pH, Fe is less soluble, and sorption reactions between the negatively charged surfaces of Fe-oxyhydroxide and SOC are preferable to the formation of metal-humus complexes [37]. High pH values of black limestone soils contribute to the preservation of mobile cations and traces of metals due to the sorption of minerals, which can stabilize SOC due to the formation of a calcium-humus complex and sorption of carbon [4]. On the other hand, yellow sandstone soils tend to have pH values below 5.0, therefore more calcium and magnesium are lost through leaching from the soil, and poor calcium enrichment by an organism leads to a lower SOM content than those in limestone soil.

As observed by many researchers [38], [39], there is a positive correlation between the SOC content and the clay content in the soil. According to Zhu and Liu [33], the limestone soils have high clay content and show a clear enrichment of clay from top to bottom soil. Clay minerals have a high specific surface area and carry a charge that allows them to bind and thus chemically stabilize organic matter. Clay aggregates also provide micropores for the physical protection of the SOM [40]. These two types of protective effects may be another important reason why limestone soils maintain a higher SOC content than yellow soils.

The clay content in the soil is the main factor affecting the change in $\delta^{13}C$ in SOM with depth in the profile [38]. Limestone soil profiles have a high clay content and show an obvious enrichment in clay from top to bottom soil [33]. The chemical and/or physical protection provided by clay minerals reduces the rate of decomposition of SOM and leads to the fractionation of a small C isotope. This may explain why the degree of ^{13}C enrichment in the SOM of limestone profiles is lower than in yellow soil profiles. At the same time, high content of clay in the soil can lead to a decrease in the supply of oxygen to the deep layers of the soil, so that most aerobes that can decompose SOM exist only in the upper layer of the soil. As a result, the corresponding soil depth at which the maximum ^{13}C values of SOM appears is distinctly small in limestone soil. The specific reasons require further study in the future.

4.2 Relationships of isotopic compositions between leaves of dominant plants, litters, and topsoil SOM

The chemical composition of plant resources is considered important for predicting the rate of decomposition of litter in forest soils [41], [42], [43]. However, much is unknown about how litter quality affects the amount and chemical nature of C stored in the long term as SOM [44]. The dual-isotope approach was chosen for separate tracking of C and N retention and transformation, as stable isotope markers (^{13}C, ^{15}N) combined with the SOM fractionation approach can be used to directly measure stabilization rates and pathways of specific substrates among defined SOM pools on shorter time scales [38], [45].

It was observed that the dominant plant species usually have the lowest $\delta^{13}C$ values, followed by litter and finally the SOM of topsoil, which is consistent with previous studies [46], [47], [48]. However, we note that, in contrast to the $\delta^{13}C$ value, the average $\delta^{15}N$ values of plant litter are lower than those of the plant leaf and SOM of the upper soil layers for both types of soil profiles (Table 2). The differences in the values of $\delta^{13}C$ and $\delta^{15}N$ between the dominant plant species and litter are much smaller than between the litter and SOM of the topsoil. SOM in the upper layer of soil of yellow sandstone and limestone soil profiles has a value of $\delta^{13}C$ by 2.6–3.0‰ and 5.5–6.3‰, respectively, larger than litter. The same case is that SOM in topsoils of yellow sandstone and limestone soil profiles has a value of $\delta^{15}N$ by 5.1–5.4‰ and 6.5–8.1‰, respectively, larger than litter. This indicates that the differences between the values of $\delta^{13}C$ and $\delta^{15}N$ of litter and topsoil SOM in yellow sandstone soil are much smaller than the differences between the litter and topsoil SOM in limestone soil.

Biological and biochemical transformations that occur during humification processes lead to the enrichment of ^{13}C in residual organic C in SOM [49]. For example, the value of $\delta^{13}C$ of lignin is approximately 2.0–6.0‰ lower than in whole plant tissues, and therefore the decomposition of organic structures such as lignin in the soil may contribute to the enrichment of ^{13}C of SOM in the surface soils during the humification process as compared with the original plant material [49]. The most important processes are microbial respiration and fermentation, leading to an enrichment of ^{13}C in microbial biomass carbon compared to the emitted CO_2. The second mechanism is mainly controlled by the rate of SOM turnover in the upper soil layer. The higher the turnover rate, the greater the increment [50].

As indicated above, in contrast to the $\delta^{13}C$ value, the average $\delta^{15}N$ value of plant litter is 1–3‰ lower than that of plant leaves for both types of soils. It is unclear why litters have clearly lower $\delta^{15}N$ values than the current leaves of the plant since the decomposition of organic matter usually leads to enrichment with heavier isotopes in the residual materials. There are probably several reasons for the interpretation. First, the different plant species at the same area have different $\delta^{15}N$ values; the difference in $\delta^{15}N$ values can reach several ‰. The litter, if it consists of different plant tissues of different plant species, has on average a lower or different $\delta^{15}N$ value than the current plant leaf. Second, at the initial stage of decomposition, the residual litter is enriched in ^{14}N (a decrease in $\delta^{15}N$ from 2‰ to 3‰) [51]. Finally, exotic materials can enter the litter during their decomposition above the soil, as an example of this is that the introduction of atmospheric NH_4^+ into the litter reduces the value of $\delta^{15}N$ of litter, because NH_4^+ is the main form of atmospheric deposition and it shows a value of $\delta^{15}N$ on average −12.3 ± 6.7‰ around the sampling sites [52].

Like the $\delta^{13}C$ values, the $\delta^{15}N$ values increase from the litter to topsoil SOM by about 5.0‰ in yellow sandstone soil profiles and by about 7.0‰ in limestone soil profiles. One of the explanations for this enrichment in ^{15}N and ^{13}C due to SOM decay is that respiration preferentially uses organic matter enriched in ^{14}N and ^{12}C [46]. The differences in $\delta^{13}C$ and $\delta^{15}N$ values between litter and SOM in the topsoil of the limestone soil are greater, or, in other words, SOM in the topsoil of limestone soil profiles is more enriched in ^{13}C and ^{15}N than litter compared litter in yellow sandstone soil profiles. This suggests that the rate of decomposition or degree of decomposition of SOM in the topsoil of limestone soil profiles is higher than in topsoil of yellow sandstone, or that the SOM in the upper layer of limestone soil was derived from old vegetation different from the current vegetation cover. The latter interpretation is more reasonable since the degradation of SOM is usually faster or more intense in yellow sandstone soil with a lower pH than in limestone soil with a higher pH.

4.3 Degradation of SOM

Previous studies have shown that there are significant correlations between SOC and SON content, and these correlations are indicative of the main plant-derived N in soils [53]. As shown in Fig. 7a, the SOC and SON contents are largely correlated, which indicates that plants provide the main nitrogen supply to the soils of the karst area.

In all soil types, the content of SOC and SON decreases with increasing depth of soil profiles, which is consistent with what has been observed in many studies [53], [54], [55], [56], [57]. However, the extent of this reduction in SOC concentration varies between different soil profiles (Fig. 3a). Compared to SOC in the 0–20 cm soil horizon, the amount of SOC from 20 cm to the bottom depth, on average, decreases by 7.1% in limestone soil and by 31.5% in yellow sandstone soil. SOC and SON content is mainly concentrated in the surface layer of the soil, which can be attributed to more litter in the surface layers of the soil and more accumulation of organic matter.

SOC stabilization is controlled by a combination of three interacting factors: chemical protection, physical protection, and inherent structural resistance to degradation [58]. SOC can be chemically protected by organo-mineral complexes with silt and clay particles, which limit the effects of enzymes that destroy SOC [59]. Physical protection occurs when SOC is contained in stable soil aggregates, limiting the diffusion of water and oxygen and reducing the physical access of degrading organisms [60]. In addition, depending on the type of microorganisms present in the soil, biochar, and the forms of lignin, tannins, and aliphatic substances, SOC is more resistant to degradation and exhibits an inherently slower decomposition rate [61], [62]. These factors help to determine the overall biogeochemical stability of microbial and plant SOC, although the dominant mechanisms will vary depending on interactions between microbes, available substrates, and abiotic driving variables.

Significant correlations were found between $\delta^{15}N$ and $\delta^{13}C$ in yellow sandstone soil profiles but not in limestone soil profiles (Fig. 7b). The depth profiles of the $\delta^{13}C_{SOC}$ and $\delta^{15}N_{SON}$ in yellow sandstone soil and limestone soil vary in different styles: the former shows a rapid increase in $\delta^{13}C_{SOC}$ and $\delta^{15}N_{SON}$ values from topsoil to a depth of about 20–30 cm, and then remains almost constant or increases relatively slow downward, while the latter shows an increase from the topsoil to about 20 cm and then decrease downward, with the $\delta^{13}C_{SOC}$ values in the topsoil being almost the same or even higher than those of the soil at its deepest depth. The depth profiles of the $\delta^{13}C_{SOC}$ and $\delta^{15}N_{SON}$ values for yellow sandstone soils can be attributed to the decomposition of SOM by origin. In contrast, the depth profiles of the $\delta^{13}C_{SOC}$ values for limestone soils indicate a more complex origin or pedogenesis of limestone soil, which will be discussed in more detail later.

During the decomposition of SOM, kinetic fractionation of both $^{13}C/^{12}C$ and $^{15}N/^{14}N$ occurs in an open system, which leads to the concentration of ^{13}C and ^{15}N in the residual organic matter retained in the soil. The ^{13}C enrichment follows a Rayleigh distillation process, according to which the $^{13}C/^{12}C$ ratio is a function of the natural logarithm of the fraction of remaining SOC, resulting in the SOC being enriched with ^{13}C to 6‰ compared to the original biomass [63], [64]. Fig. 8 shows the variations in $\delta^{13}C_{SOC}$ and $\delta^{15}N_{SON}$ values with the natural logarithm of SOC and SON (Fig. 8a and 8b) in yellow sandstone soil profiles, which suggests the Rayleigh distillation process responsible for the ^{13}C and ^{15}N enrichment in the remaining SOM in deep soil horizons. In contrast, the depth profiles of both $\delta^{13}C_{SOC}$ and $\delta^{15}N_{SON}$ values for limestone soils are more complex, and there is no relationship between the $\delta^{13}C_{SOC}$ or $\delta^{15}N_{SON}$ values and the natural logarithm of SOC and SON, indicating that the depth profiles of both $\delta^{13}C_{SOC}$ or $\delta^{15}N_{SON}$ values were not simply derivatives from the decay of SOM.

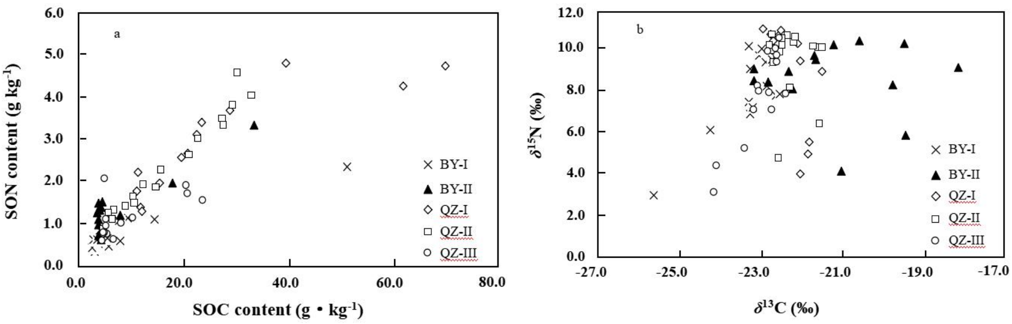

Fig.7. Correlation between soil organic nitrogen (SON) and soil organic carbon (SOC) (a), and between $\delta^{13}C$ and $\delta^{15}N$ (b) in soils.

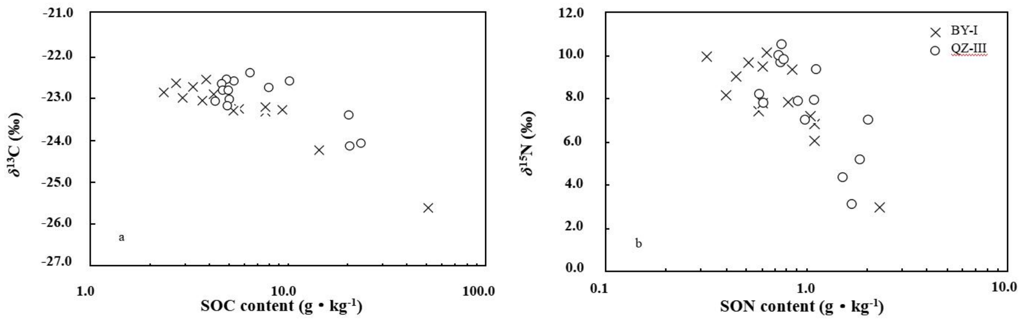

Fig.8. Variation of $\delta^{13}C$ (a) and $\delta^{15}N$ (b) depending on soil organic matter (SOM) in yellow sandstone soil profiles.

4.4 Implications for land-use change in limestone soils

The distribution of limestone soils in the karst landform is not continuous and is uneven in the depth of the soil. The depth of the soil varies from an average depth of about 20 cm on the hillside to more than 1 m at the foot of the hill. In addition, the geochemical and pedological characteristics of limestone soil are heterogeneous, changing significantly even in a limited area. Sandstone soil profiles usually show a simple tendency to increase the depth of $\delta^{13}C$, but the depth profiles of $\delta^{13}C$ in limestone soil are complex, with the higher value of $\delta^{13}C$ in the topsoil than in deep soil. This phenomenon was also observed earlier by Zhu and Liu [33] for two limestone soil profiles. Accordingly, the pedogenesis of limestone soils distributed over a wide area in southwestern China is complex.

Ehleringer et al [14] and Balesdent et al (1993) [27] reviewed some hypotheses that have been developed over the past few decades to explain the commonly observed $\delta^{13}C_{SOC}$ profiles enriched with depth in well-drained mineral soils. In a discussion by Wynn et al [65], these hypotheses were grouped into 3 categories: (1) hypotheses involving the mixing of SOM with different ^{13}C content, (2) hypotheses involving the predominant decomposition of SOM components with different ^{13}C content, and (3) hypotheses concerning the kinetic fractionation of C isotopes during SOM maturation. The lowest values of $\delta^{13}C_{SOC}$ in the profiles of limestone soils are observed for the deepest soil, similar to the values in sandstone soil at the same depth. From bottom to top, the $\delta^{13}C_{SOC}$ values of the profiles of limestone soils increase and reach a maximum value at a soil depth of about 20 cm, and then decrease to the soil surface. From a depth of 20 cm and below, the profiles of limestone soils show a tendency to decrease in depth, which is most likely due to changes in vegetation types with increasing participation of C4 plants. From a depth of 20 cm and above, soil profiles are likely to receive more carbon from C3 plants than from C4 plants. Limestone soil profiles were collected from the slopes of the hills, which are suspected to have left the soil and been eroded. Soil erosion removes SOC-enriched surface soil and ^{13}C-enriched soil residue. As the vegetation recovers, the abandoned soil becomes rich in SOM, and the $\delta^{13}C_{SOC}$ value decreases due to an increase in the introduction of C3 plants. Thus, the depth profiles of $\delta^{13}C_{SOC}$ for limestone soil mainly indicate a history of land-use change, a history of deforestation, land cultivation, land abandonment, and vegetation restoration.

5 Conclusions

The amounts of SOC and SON are mainly concentrated in the surface layer of the soil, and decrease with increasing depth and appear in different amounts in different types of soils, with the SOM in limestone soil being significantly higher than in the yellow sandstone soil. The higher SOM content in limestone soil can be attributed to soil mineralogy, higher pH, and more Ca ions than in yellow sandstone soil.

The dominant plant species usually have the lowest δ^{13}C values, followed by litter and, finally, the SOM of topsoil. However, in contrast to the δ^{13}C value, the average δ^{15}N values of the plant litter are lower than those of the plant leaves and SOM of the upper soil layer for both types of soil profiles. SOM in topsoils of yellow sandstone and limestone soil profiles has δ^{13}C values, respectively, from 2.6‰ to 3.0‰ and from 5.5‰ to 6.3‰, and δ^{15}N values, respectively, from 5.1‰ to 5.4‰ and from 6.5‰ to 8.1‰, which is more than in litters. The differences between the δ^{13}C and δ^{15}N values of the litter and SOM of topsoil in yellow sandstone soil are significantly less than in limestone soil.

The δ^{13}C and δ^{15}N values of SOM increase with depth in yellow sandstone soil profiles, which indicate that SOM degradation becomes more intense with increasing soil depth. The relationship that an increase in the values of δ^{13}C and δ^{15}N with a decrease in SOM content in the yellow sandstone soil significantly justifies the decomposition of SOM and, therefore, causes an increase in the values of δ^{13}C and δ^{15}N in deeper soil horizons of yellow sandstone soil profiles. However, the δ^{13}C and δ^{15}N values of SOM in limestone soil profiles have a complex tendency to change with increasing soil depth and SOM content, which can be mainly attributed to changes in land use and soil accumulation. Compared to yellow sandstone soil profiles, limestone soil profiles have less variation in δ^{13}C and δ^{15}N values, mainly due to soil pH value, clay content, and higher amounts of calcium and magnesium elements present in limestone soil profiles.

Acknowledgments

Financial support for this research came from the Study supported by Bureau of Geology and Mineral Exploration and Development Guizhou Province (NO. [2021].11), the Key Laboratory of Karst Environment and Geohazard, Ministry of Land and Resources (NO.2018K02), the Study on the Migration Mechanism of Trace Elements in the Process of Emeishan Basalt in Guizhou Province (NO. [2018].32), the geochemical survey and evaluation of plough quality in Guizhou Province (NO. [2017].04), the Mountain Geohazard Prevention R&D Center of Guizhou Province, China (NO. [2017]5402). We thank Ms.Yunchao Lang, QilianWang, and Mr. Jiayi Feng for their assistance during the sample collection. We also thank anonymous reviewers for giving comments and suggestions.

References

[1] Lorenz K, Lal R, Preston C M, Nierop K G J 2007 Strengthening the soil organic carbon pool by increasing contributions from recalcitrant aliphatic bio (macro) molecules *Geoderma* **142** 1-10

[2] Schlesinger W H, 1990 Evidence from chronosequence studies for a low carbon-storage potential of soils *Nature* **348** 232-234

[3] Lal R, 2004 Soil carbon sequestration to mitigate climate change *Geoderma* **123** 1-22

[4] Heckman K, Welty-Bernard A Rasmussen C, Schwartz E 2009 Geologic controls of soil carbon cycling and microbial dynamics in temperate conifer forests *Chem Geol* **267** 12-23

[5] Schlesinger, W H, 1997 Carbon balance in terrestrial detritus *Annu Rev Ecol Syst* **8** 51-81

[6] Singh K P, Suman A, Singh P N, Srivastava T K 2007 Improving quality of sugarcane-growing soils by organic amendments under subtropical climatic conditions of India *Biol Fertil Soils* **44** 367-376

[7] Han Z J, Jin Z S 1996 Hydrogeology of Guizhou Province China *Seismic Publication Beijing*

[8] Yuan D X, 1997 Rock desertification in the subtropical karst of South China Z *Geomorphol* 108 81-90

[9] Yuan D X 1997 The carbon cycle in the karst Z *Geomorphol* **108** 91-102

[10] Canadell J G, Mooney H A, Baldocchi D D, et al, 2000 Carbon metabolism of the terrestrial biosphere: A multitechnique approach for improved understanding *Ecosystems* **3** 115-130

[11] Malhi Y, Baldocchi D D, Jarvis P G, 1999 The carbon balances of tropical temperate and boreal forests *Plant Cell Environ* **22** 715-740

[12] Schimel D S, House J I, Hibbard K A, et al, 2001 Recent patterns and mechanisms of carbon exchange by terrestrial ecosystems *Nature* **414** 169-172

[13] Connin S L, Feng X, Virginia R A 2001 Isotopic discrimination during long-term decomposition in an arid land ecosystem *Soil Biol Biochem* **33** 41-51

[14] Ehleringer J R, Buchmann N, Flanagan L B 2000 Carbon isotope ratios in below ground carbon cycle processes *Ecol Appl* **10** 412-422

[15] Wedin D A, Tieszen L L, Dewey B, Pastor J 1995 Carbon isotope dynamics during grass decomposition and soil organic matter formation *Ecology* **76** 1383-1392

[16] Austin A T, Vitousek P M 1998 Nutrient dynamics on a precipitation gradient in Hawaii *Oecologia* **113** 519-529

[17] Emmett B A, Kjonaas O J, Gundersen P, Koopmans C, Tietema A, Sleep D 1998 Natural abundance of ^{15}N in forests across a nitrogen deposition gradient *For Ecol Manage* **101** 9 -18

[18] Garten C T 1993 Variations in foliar ^{15}N abundance and the availability of soil nitrogen on walker branch watershed *Ecology* **74** 2098-2113

[19] Högberg P 1993 ^{15}N abundance of forests is correlated with losses of nitrogen *Plant and Soil* **157** 147-150

[20] Johanisson C, Högberg P 1994 ^{15}N abundance of soils and plants along and experimentally induced forest nitrogen supply gradient *Oecologia* **97** 322-325

[21] Kramer M G, Sollins P, Sletten R S, Swart P K 2003 N isotope fractionation and measures of organic matter alteration during decomposition *Ecology* **84** 2021-2025

[22] Pardo L H, Hemond H F, Montoya J P, Pett-Ridge J 2007 Natural abundance ^{15}N in soil and litter across a nitrate-output gradient in New Hampshire *For Ecol Manag* **251** 217-230

[23] Nadelhoffer K J, Shaver G, Fry B, Giblin A, et al, 1996 ^{15}N natural abundances and N use by tundra plants *Oecologia* **107** 386-394

[24] Eshetu Z 2004 Natural ^{15}N abundance in soils under young-growth forests in Ethiopia *For Ecol Manage* **187** 139-147

[25] Eshetu Z, Högberg P 2000 Effect of land-use on ^{15}N natural abundance of soils in Ethiopian

foliar ^{15}N and ^{13}C abundance to evaluate effects of microbiotic crust on nitrogen and water utilization in Pinus assonant in deteriorated pine stands of south China *Ecol Res* **18** 279-286

[26] Piccolo M C, Neill C, Cerri C 1994 Natural abundance of ^{15}N in soils along forest-to-pasture chronose-quences in the western Brazilian Amazon Basin *Oecologia* **99** 112-117

[27] Balesdent J, Girardin C, Mariotti A 1993 Site-related ^{13}C of tree leaves and soil organic matter in a temperate forest *Ecology* **74** 1713-1721

[28] Högberg P 1997 ^{15}N natural abundance in soil-plant systems *New Phytol* **137** 179-203

[29] Tiunov A V 2007 Stable isotopes of carbon and nitrogen in soil ecological studies *Biol Bull* **34** 395-407

[30] FAO/UNESCO 1974 Soil Map of the World (1:5 000 000) vol l, Legend *Unesco Paris*

[31] Xiao H Y 2002 Nitrogen biogeochemical cycles in a seasonally anoxic lake Doctoral thesis Institute of Geochemistry *Chinese Academy of Sciences* Guiyang Guizhou China (in Chinese)

[32] Boutton T W, Wong W W, Hachey D L, et al, 1983 Comparison of quartz and Pyrex tubes for combustion of organic samples for stable carbon isotope analysis *Anal Chem* 55 1832-1833

[33] Zhu S F, Liu C Q 2006 Vertical patterns of stable carbon isotope in soils and particle-size fractions of karst areas Southwest China *Environ Geol* **27** 1119-1127

[34] Fierer N, Jackson R B 2006 The diversity and biogeography of soil bacterial communities *Proc Natl Acad Sci* U S A **103** 626-631

[35] Schnittler M, Stephenson S L 2000 Myxomycete biodiversity in four different forest types in Costa Rica *Mycologia* **92** 626-637

[36] Rai D, Kittrick J A 1989 Mineral equilibria and the soil system in: Dixon J B Weed S B (Eds) Minerals in soil environments *Soil Sci Soc* Am J Madison USA, pp 161-198

[37] Tipping E, Castro C R, Bryan S E, Taytor J H 2002 Al (III) and Fe (III) binding by humic substances in freshwaters and implications for trace metal speciation *Geochim Cosmochim Acta* **66** 3211-3224

[38] Bird M I, Kracht O, Derrien D, Zhou Y 2003 The effect of soil texture and roots on the carbon isotope composition of soil organic carbon *Aust J Soil Res* **41** 77-94

[39] Ladd J N, Foster R C, Nannipieri P, Oades J M 1996 Soil Structure and Biological Activity in: Stotzky G Bollag J M (Eds) *Soil biochemistry* vol 9 Dekker New York, pp 23-28

[40] Wattel-Koekkoek E J W, van Genuchten P P L, Buurman P, Lagen B 2001 Amount and composition of clay-associated soil organic matter in a range of kaolinitic and smectitic soils *Geoderma* **99** 27-49

[41] Aerts R 1997 Climate leaf litter chemistry and leaf litter decomposition in terrestrial ecosystems: a triangular relationship *Oikos* **79** 439-449

[42] Aber J D, Melillo J M, McClaugherty C A 1990 Predicting long-term patterns of mass loss nitrogen dynamics and soil organic matter formation from initial fine litter chemistry in temperate forest ecosystems *Can J Bot* **68** 2201-2208

[43] Silver W L, Miya R K 2001 Global patterns in root decomposition: comparisons of climate and litter quality effects *Oecologia* **129** 407-419

[44] Kögel-Knabner I 2002 The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter *Soil Biol Biochem* **34** 139-162

[45] Swanston C W, Torn M S, Hanson P J, et al, 2005 Initial characterization of processes of soil carbon stabilization using forest stand-level radiocarbon enrichment *Geoderma* **128** 52-62

[46] Nadelhoffer K J, Fry B 1994 Nitrogen isotope studies in forest ecosystems, in: Lajtha K,

Michener R H (Eds) Stable isotopes in ecology and environmental science *Cambridge: Blackwell*, pp 281-304

[47] Torn M S, Lapenis A G, Timofeev A, et al, 2002 Organic carbon and car-bon isotopes in modern and 100-year-old-soil archives of the Russian steppe *Globl Change Biol* **8** 941-953

[48] Wang G A, Feng X H, Han J M, et al, 2008 Paleovegetation reconstruction using δ^{13}C of soil organic matter *Biogeosciences* **5** 1325-1337

[49] Solomon D, Fritzsche F, Lehmann J, Tekalign M, Zech W 2002 Soil organic matter dynamics in the subhumid agroecosystems of the Ethiopian highlands: Evidence from natural ^{13}C abundance and particle-size fractionation *Soil Sci Soc Am J* **66** 969-978

[50] Chen Q Q, Sun Y M, Shen C D, et al, 2002 Organic matter turnover rates and CO_2 flux from organic matter decomposition of mountain soil profiles in the subtropical area south China *Catena* **49** 217-229

[51] Melillo J M, Aber J D, Linkins A E, et al, 1989 Carbon and nitrogen dynamics along the decay continuum: plant litter to soil organic matter *Plant and Soil* **115** 189-198

[52] Xiao H Y, Liu C Q 2002 Sources of nitrogen and sulfur in wet deposition at Guiyang Southwest China *Atmos Environ* **36** 5121-5130

[53] Jiang C L, Zhang X S 2009 N isotopes and N cycle in the TieShanPing subtropical forest ecosystem Southwestern China *Environ Monit Asscess* **154** 301-308

[54] Cheng P N, Wang G A, Han J M, et al, 2010 δ^{13}C difference between plants and soil organic matter along the eastern slope of Mount Gongga *Chin Sci Bull* **55** 55-62

[55] Hobbie E A, Ouimette A P 2009 Controls of nitrogen isotope patterns in soil profiles *Biogeochemistry* **95** 355-371

[56] Krull E S, Skjemstad J O 2003 δ^{13}C and δ^{15}N profiles in ^{14}C-dated Oxisol and Vertisols as a function of soil chemistry and mineralogy *Geoderma* **112** 1-29

[57] Lv Y Z, Zhang F R, Sun D F 2005 Altitudinal distribution of soil organic matter in soils on BaiHua Mountains *Soils* **37** 277-283, in Chinese

[58] Sollins P, Homann P, Caldwell B A 1996 Stabilization and destabilization of soil organic matter: mechanisms and controls *Geoderma* **74** 65-105

[59] Hassink J 1997 The capacity of soils to preserve organic C and N by their association with clay and silt particles *Plant and Soil* **191** 77-87

[60] Jastrow J D 1996 Soil aggregate formation and the accrual of particulate and mineral-associated organic matter Soil Biol *Biochem* **28** 665-676

[61] Derenne S, Largeau C A 2001 A review of some important families of refractory macromolecules: composition origin and fate in soils and sediments *Soil Sci* **166** 833-847

[62] Kalbitz K, Schwesig D, Schmerwitz J, et al, 2003 Changes in properties of soil-derived dissolved organic matter induced by biodegradation *Soil Biol Biochem* **35** 1129-1142

[63] Macko S A, Estep M L F 1984 Microbial alteration of stable nitrogen and carbon isotopic compositions of organic matter *Org Geochem* **6** 787-790

[64] Poage M A, Feng X H 2004 A theoretical analysis of steady state δ^{13}C profiles of soil organic matter *Global Biogeochem Cycles* **16** 1-11

[65] Wynn J G, Harden J W, Fries T L 2006 Stable carbon isotope depth profiles and soil organic carbon dynamics in the lower Mississippi Basin *Geoderma* **131** 89-109