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Dynamics of Organic Matter of Soil Profiles with Different Vegetation Conditions from the Chinese Loess Plateau: $\delta^{13}C$ and $\delta^{15}N$ Approaches

To cite this article: Long-Bo Li *et al* 2020 *IOP Conf. Ser.: Earth Environ. Sci.* **570** 022008

Dynamics of Organic Matter of Soil Profiles with Different Vegetation Conditions from the Chinese Loess Plateau: $\delta^{13}C$ and $\delta^{15}N$ Approaches

Long-Bo Li[1,2], Xiao-Dan Wang[3,*], Ping Zhang[3], Yao-Qiang Zhu[1], Ming-Qiang Ren[1], Da-Wei Cai[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, China
[3]College of Eco-Environmental Engineering, Guizhou Minzu University, Guiyang 550025, Guizhou, China

*Corresponding author's e-mail address: wangxiaodan@gzmu.edu.cn

Abstract. To understand the biogeochemical processes associated with soil organic matter (SOM) decomposition, we analyzed the SOM contents, the $\delta^{13}C$ and $\delta^{15}N$ values of the dominant species foliage, litter and SOM from soil samples for five soil profiles with different vegetation conditions in the Loess Plateau, Northwestern China. Results showed that the amounts of soil organic carbon (SOC) and total nitrogen (TN) mainly concentrated on the surface soil and differentiated according to the vegetation conditions in the following order: broad-leaved forest > coniferous woodland > shrub forest > grassland > wasteland. SOC and TN contents decreased with depth and varied in the ranges of 1.1–31.2 g/kg and 0.3–3.7 g/kg, respectively. Compared with the other regions, the ^{13}C and ^{15}N were enriched and the $\delta^{13}C$ and $\delta^{15}N$ values of topsoil SOM respectively increased in the ranges of 0.5‰–3.2‰ and 0.7‰–4.6‰ during litter degradation to SOM on the surface soil, which was controlled by SOM turnover rates. This result indicates that the effect of isotopic fractionation was obvious during the transformation of SOM from plant debris to SOM in topsoil, which resulted in great increments of SOM $\delta^{13}C$ and $\delta^{15}N$. Litter inputs lowered the surface soil $\delta^{13}C$ and $\delta^{15}N$ values while decomposition increased $\delta^{13}C$ and $\delta^{15}N$ values in deeper soil. Foliage and litter inputs averaged 1.0‰ and 1.3‰ $\delta^{15}N$ and -28.3‰ and -27.0‰ $\delta^{13}C$, respectively. The five soil profiles with different vegetation conditions had similar characteristics in variations of SOM $\delta^{13}C$ and $\delta^{15}N$ and increased with depth, respectively. However, the patterns of $\delta^{13}C$ in our sites were less pronounced than the patterns of $\delta^{15}N$ primarily because the discrimination against ^{13}C during organic matter decomposition is weaker than the discrimination against ^{15}N. Except for the shrub profiles, significant correlations were found between the two stable isotopes, ^{15}N and ^{13}C. Combined with information on SOM contents, the variations of the isotopic values of SOM showed a mixing process of litter inputs between different soil profiles. Two controls of soil isotopic compositions were established: new litter inputs and overall isotopic fractionation during decomposition. In conclusion, the overall isotopic fractionation during decomposition left residual soil N and C enriched in ^{15}N and ^{13}C, explaining the high $\delta^{15}N$ and $\delta^{13}C$ values observed in deeper soil.

1. Introduction

As a source of atmospheric CO_2, soil can release 68–75 Pg of carbon to the atmosphere every year [1]. Globally, soil organic carbon (SOC) is a major component of the terrestrial carbon pool, with the C amount in the soil being as much as two to three times more than that in living vegetation [2]. Plants can take in carbon from the atmosphere during photosynthesis. Part of the C is used by plants as a source of energy and then directly released through respiration, while another part is assimilated by the vegetation and then transferred to the soil as plant litter, where it becomes part of soil organic matter (SOM) [3]. Furthermore, changes in vegetation influence not only the carbon fluxes between the soil and the atmosphere but also the concentration of atmospheric CO_2 [4]. The Loess Plateau in northwestern China faces the worst soil erosion problems in the world. Its ecosystem has degraded at an alarming speed [5]. Soil degradation is the essence of land degradation [6]. As an important composition of soil nutrients, the essence of soil quality, and a major part of the terrestrial carbon reservoir, SOM plays a crucial role in soil degradation and in the global carbon cycle [6]. In addition, SOM is an important source of inorganic nutrients for plant growth in natural and artificial (or managed) ecosystems. SOM can affect the chemical and physical properties of the soil and its overall health. For instance, the SOM of the Chinese Loess Plateau is related to soil degradation and soil erosion. Therefore, changes in SOM characteristics with depth on the Loess Plateau need to be studied.

Stable carbon isotopic compositions have been widely used to study the changes in SOM characteristics with depth, investigate the biogeochemical processes in soils [7], assess the degree of decomposition [8], and to document vegetation changes [9]. However, a single isotope approach is insufficient to identify the biogeochemical processes associated with variations in SOM. Recently, the combined use of carbon and nitrogen stable isotopic ratios has been proven to be a successful multi-isotopic tracing approach for studying SOM characteristics [10], exploring C and N cycles in forests [11], and determining the characteristics of the overall C and N cycling at the ecosystem level [12].

The stable nitrogen isotopic composition is a powerful tool for evaluating N cycling because of its ability to integrate changes over space and time [13]. The natural abundance of ^{15}N has been used to evaluate the N losses and patterns of N mineralization [14,15], compare the N uptake patterns of plant species [16], and to determine the effects of land-use history on N cycles [17,18]. Eshetu and Högberg [17] concluded that disturbed sites have elevated soil ^{15}N signals, whereas the surface soil layers in less disturbed and natural forest ecosystems have depleted ^{15}N abundances relative to the lower horizons. Hence, changes in soil ^{15}N can be used as an indicator of the rehabilitation of soil degradation afforded by a forestation, as shown by Eshetu [18].

Many studies concerning the isotopic compositions of the SOM on the Chinese Loess Plateau have focused on reconstructing the paleovegetation and paleoclimate conditions by using a single isotopic approach ($\delta^{13}C$ or $\delta^{15}N$) [19,20], whereas few studies analyzed the characteristics of SOM with depth. A single isotope approach ($\delta^{13}C$ or $\delta^{15}N$) is insufficient to decipher comprehensively the characteristics of SOM with depth. In this study, based on the carbon and nitrogen isotopic compositions, five representative soil profiles with different vegetation conditions were selected as study sites on the Loess Plateau, northwestern China. The objectives of this study are as follows: (a) to determine the natural variability of SOC and total nitrogen (TN); (b) to explore the relationships between the $\delta^{13}C$ and $\delta^{15}N$ values of the dominant species of leaf, litter, and topsoil SOM; and (c) to study the spatial distribution of stable isotopes (^{13}C, ^{15}N) within the SOM and correlate these ^{13}C and ^{15}N values with different vegetation conditions.

2. Study Areas and Methods

2.1. Site description

The study was conducted in the Xiao-Zhang Zhao Village in Huan County, Qingyang City, Gansu Province, China and in the Lianjiabian forest farm in northern Ziwuling, Heshui County, Gansu, China (Figure 1). The study area has landforms typical of loess hilly topography and a mid-temperate continental monsoon climate [21]. Xiao-Zhang Zhao Village (107°22′E, 36°42′N) has an altitude of 1450 m and faces the worst soil erosion problems. The average annual precipitation is 407.3 mm, the average annual air temperature is 7.9°C, and the annual accumulated temperature ≥10°C is 3242.4 [22]. The entire Ziwuling area (107°30′–109°40′E, 33°50′–36°50′N) is located in the central–southwest part of the Loess Plateau, bordering Shaanxi and Gansu Province and covering a total area of 23,000 km^2. The Ziwuling area is one of the few places on the Loess Plateau containing relatively natural secondary forests. The region has an altitude of 1100–1756 m above sea level and a relative height difference of 200–400 m. The average annual precipitation is 587.6 mm, the average annual air temperature is 7.4°C, and the annual accumulated temperature ≥10°C is 2671.0 [23]. The soil in the region is calcareous "cinnamon soil" and forest Haplic Greyzem soil, which evolved from 50–100 m-deep primary or secondary loess [23]. The natural biomes are deciduous broad-leaf forests, and the climatic climax vegetation is a Quercus liaotungensis Koidz forest [24]. *Populus davidiana* Dode and *Betula platyphylla* Suk communities dominate the pioneer forests; *Sophora davidii* (Franch.) Skeels, *Hippophae rhamnoides* (Linn.), *Rosa xanthina* Lindl, and *Spiraea pubescens* Turcz are the main shrub species; and *Bothriochloa ischaemun* (Linn.) Keng, *Carex lanceolata* Boott, *Potentilla chinensis* (Ser), and *Stipa bungeana* Trin are the main herb species. Five soil profiles with different vegetation conditions were selected for sampling, including ZWL-II broad-leaf forest, ZWL-III coniferous woodland, ZWL-V grassland, ZWL-VII shrub forest, and HX-wasteland soil profiles. Detailed vegetation compositions were determined for each profile during the sampling (August 2010) and are summarized in Table 1.

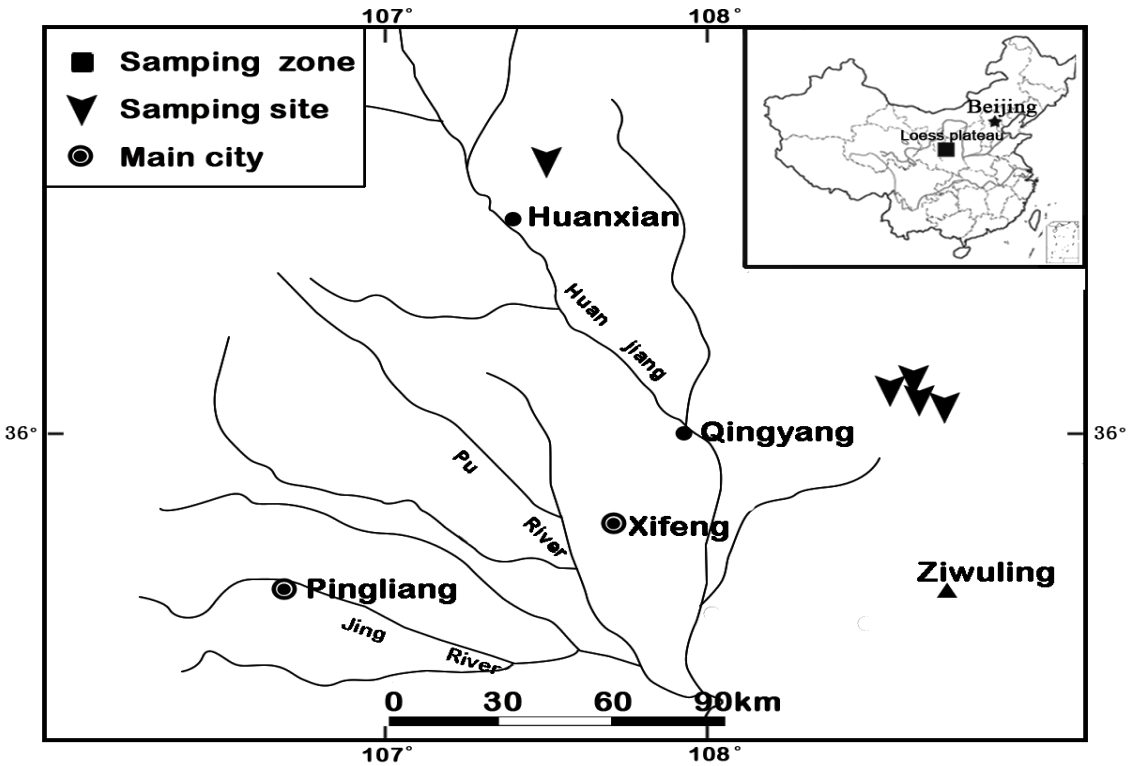

Figure 1. Location of the study areas.

Table 1. Basic features of the soil profiles.

Study area	Profile	Land-use type	Longitude	Latitude	Typical vegetation
Xiao-Zhang Zhao Village	HX	Wasteland	107°22′	36°42′	*Artemisia rubripes*
	ZWL-II	Broad-leaf forest	108°28′	36°06′	*Betula platyphylla Sulk.*
	ZWL-III	Coniferous woodland	108°28′	36°04′	*Festuca subulata trin, Pinus tabulaeformis Carr.*
Lianjiabian forest farm	ZWL-V	Grassland	108°28′	36°00′	*Artemisia lavandulaefolia DC, Bupleurum Chinese DC, Roegneria pendulina Nevski.*
	ZWL-VII	Shrub forest	108°28′	36°00′	*Syringa reticulata Hara var. mandshurica, Koelreuteria paniculata, Ailanthus altissima (Mill.) Swingle*

2.2. Soil sampling

Smaller horizons were removed before soil sampling. The soil samples were collected at the soil surface (0–5 cm depth) within the upper 50 cm, followed by sampling from the walls of the soil pits from 10 cm to about 140 cm deep in the lower horizon. Visible roots and organic residues were removed during sampling. The soil samples were air dried at ambient temperature, ground, and sieved through a 2 mm sieve. About 20 g soil sample was mixed with deionized water in a 100 mL glass beaker and stirred with a glass rod, and then the soil suspension was left to settle for 8 h. The material that suspended in the beaker after settling was removed using a Whatman filter. The precipitated soil in the beaker was dried at 40°C, which is Fraction 3 of the soil sample. This fraction will be referred to as mineral soil fraction. All three fractions were ground to 100 mesh using an agate mortar for analyses of nitrogen concentration and isotopic ratios.

Prior to soil sampling, litter was collected within a 4 m^2 area of each profile. Fresh foliage from the dominant trees, shrubs, and grass species of each major vegetation type was also sampled. The fresh foliage samples were cleaned with distilled water, and the litter samples were separated from any adhering oily material, dried at 60°C, and finely ground. The soil samples were treated with 2.0 M HCl at 25°C for 24 h to remove carbonates, washed with distilled water until neutral, centrifuged, dried at 60°C, pulverized, and then stored for carbon and isotopic analyses.

2.3. Methods

The soil pH was measured using a glass electrode in a 1:2.5 soil to $CaCl_2$ solution suspension. The organic carbon and total nitrogen contents were analyzed by combustion in an elemental analyzer (PE2400, Perkin Elmer, USA). The analytical precision was ≤0.1%. Then, the C/N mass ratios were calculated from the organic carbon and total nitrogen contents. For the stable isotope analysis, a sample mass containing 0.5 mg of carbon was placed in a quartz tube with CuO, and then the sample tube was evacuated and flame-sealed. The organic carbon in the sample was oxidized into CO_2 at 850°C for 5 h. The CO_2 was collected and purified cryogenically in a vacuum extraction line. The quantity of CO_2 was measured manometrically before it was collected in a break-seal tube for subsequent mass spectrometric analysis [25]. The stable carbon isotopic ratios ($^{13}C/^{12}C$) were measured using a mass spectrometer (MAT-252, Finnigan MAT, USA) and are expressed in standard notation (‰ = per mil) relative to the Pee Dee Belemnite standard. The analytical precision, which was determined from the standard deviation of 35 replicates of laboratory reference IAEA C_3 cellulose, was ±0.1‰. The nitrogen isotopic ratios ($^{15}N/^{14}N$) were measured using a mass spectrometer (MAT-252, Finnigan MAT, USA). All of the $\delta^{15}N$ values are reported relative to the atmospheric N_2 isotopic standard. A soil standard with a known $\delta^{15}N$ value was measured daily to monitor the analytical accuracy. The standard deviation of the duplicate analyses was smaller than 0.3‰. The isotopic signatures are expressed using delta notation

$$\delta_x\ (‰) = 1000(R_{sample}/R_{standard} - 1),$$

where δ_x is the isotopic ratio of C or N in delta units relative to an international standard (Pee Dee Belemnite for C and atmospheric N_2 for N), and Rsample and Rstandard are the $^{13}C/^{12}C$ or $^{15}N/^{14}N$ ratios of the samples and standards, respectively. The internal precision was ≤0.1‰ for $\delta^{13}C$ and ≤0.15‰ for $\delta^{15}N$. The average standard deviations of the replicate analyses of an individual sample were ±0.1‰ for $\delta^{13}C$ and ±0.2‰ for $\delta^{15}N$.

3. Results

3.1. Soil properties

C/N ratios are commonly used as an indicator of decomposition and tend to decrease with increasing decomposition [26]. The C/N mass ratios of surface soils from the shrub forest, coniferous woodland, grassland, and wasteland were lower than those of surface soils from broad-leaf forest (Figure 2). In the shrub forest, coniferous woodland, and wasteland, the C/N mass ratios initially increased slightly and then decreased with soil depth, while the ratios of the surface soils from the other profiles decreased continuously with depth. However, the C/N mass ratios varied below 60 cm in the broad-leaf forest and shrub forest.

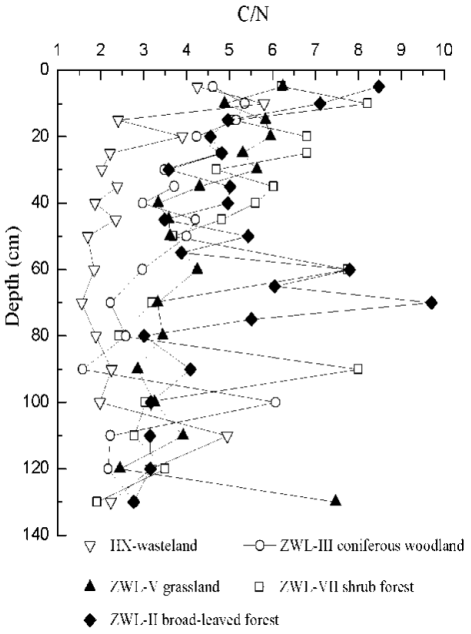

Figure 2. Changes in the soil C/N mass ratio with depth for the different soil profiles.

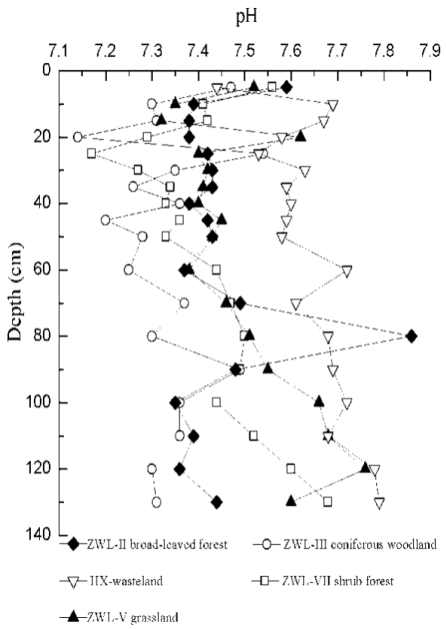

Figure 3. Changes in soil pH with depth for different soil profiles.

As shown in Figure 3, all of the soils were alkaline (pH-$CaCl_2$), ranging from 7.1 to 7.9 (mean of 7.5) in the profiles. The variation in pH with depth was similar within all of the sampling site profiles. According to the changes in vegetation conditions, the pH values can be organized as follows: wasteland > grassland > broad-leaf forest > shrub forest > coniferous woodland.

3.2. Soil organic carbon and nitrogen contents

As shown in Figure 4, in the soil profiles, the SOC content varied within the range of 1.1–31.2 g/kg. It decreased rapidly with depth near the surface, leveled off, and then approached a constant content in the deeper layers. All of the soil profiles shared this characteristic SOC distribution with depth. The SOC contents were mainly concentrated on the surface soils and can be differentiated according to the vegetation conditions in the following order: broad-leaf forest > coniferous woodland > shrub forest > grassland > wasteland. However, the rapid changes in the layers were different, and their corresponding layers were 10 cm thick in the broad-leaf forest and coniferous woodland, 20 cm thick

in the shrub forest and grassland, and 5 cm thick in the wasteland. The SOC contents decreased slowly below 60 cm in the soil profiles (Figure 4).

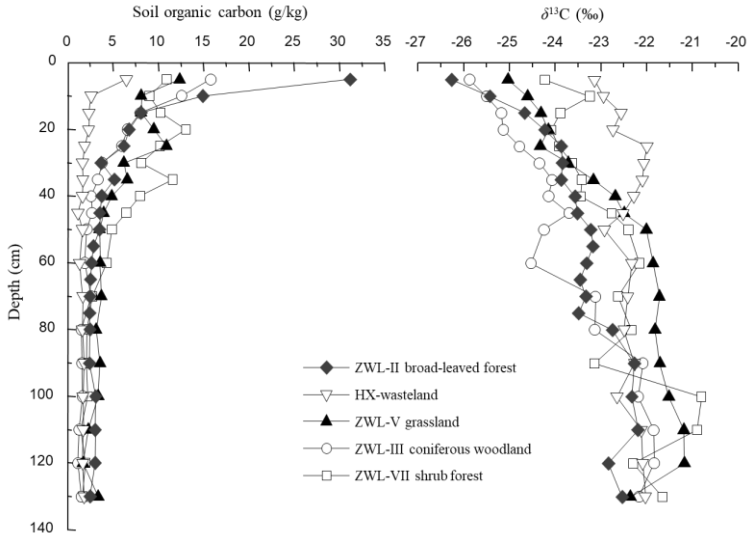

Figure 4. Variations in the SOC content and isotopic composition with depth for the different soil profiles.

In this study, the soil organic nitrogen (SON) contents were not distributed evenly throughout the soil profiles, and the largest SON pools occurred in the top 20 cm of the soil horizon (Figure 5) because of the significant amount of organic matter stored in these layers. The SON decreased rapidly from the surface soils to 20 cm, decreased slowly from 20 cm to 60 cm, and then approached a constant content below 60 cm (Figure 5). In general, the SON contents varied within the range of 0.3–3.7 g/kg, and the amounts were distinctly different in the different soil profiles. In general, the SON contents of the soils can be differentiated according to the vegetation conditions in the following order: broad-leaf forest > coniferous woodland > shrub forest > grassland > wasteland.

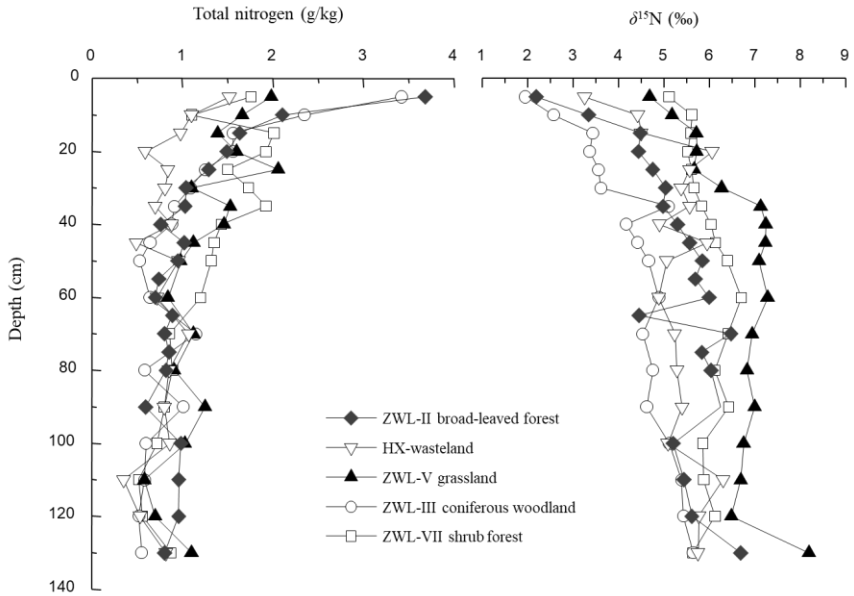

Figure 5. Variations in the TN contents and δ^{15}N values of SOM with depth for the different soil profiles.

3.3. $\delta^{13}C$ and $\delta^{15}N$ values of the dominant plant leaf, litter, and topsoil SOM

The dominant plants only refer to those with C_3 photosynthetic pathways and without C_4 photosynthetic pathways in our sampled sites. Figure 6 shows that ^{13}C gradually enriched from the dominant species foliage and litter to the topsoil SOM. The $\delta^{13}C_{SOC}$ in the wasteland, grassland, shrub forest, coniferous woodland, and broad-leaf forest increased by 3.2‰, 2.2‰, 2.2‰, 2.3‰, and 0.5‰, respectively, during the degradation of litter to SOM on the surface soil.

As shown in Figure 7, except for the wasteland soil profiles, ^{15}N increased from the dominant species foliage and litter to the topsoil SOM. The $\delta^{15}N$ values of the wasteland, grassland, shrub forest, coniferous woodland, and broad-leaf forest increased by 4.6‰, 2.5‰, 1.7‰, 1.1‰, and 0.7‰, respectively, during the degradation of litter to SOM on the surface soil.

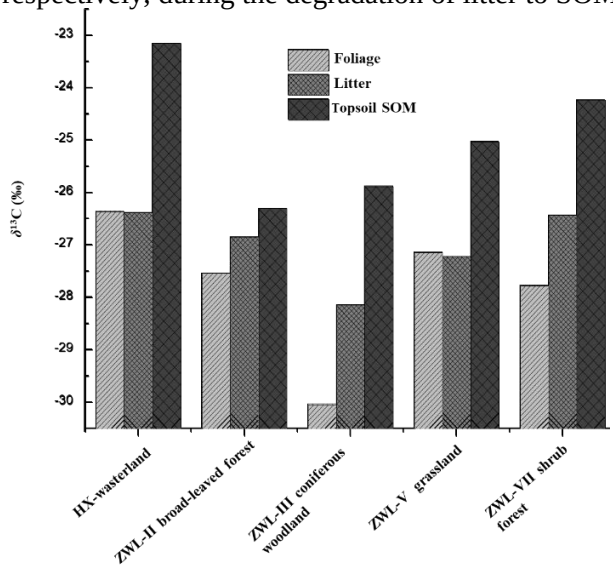

Figure 6. Average $\delta^{13}C$ values of the dominant species of leaf and litter and the topsoil SOM for the soil profiles.

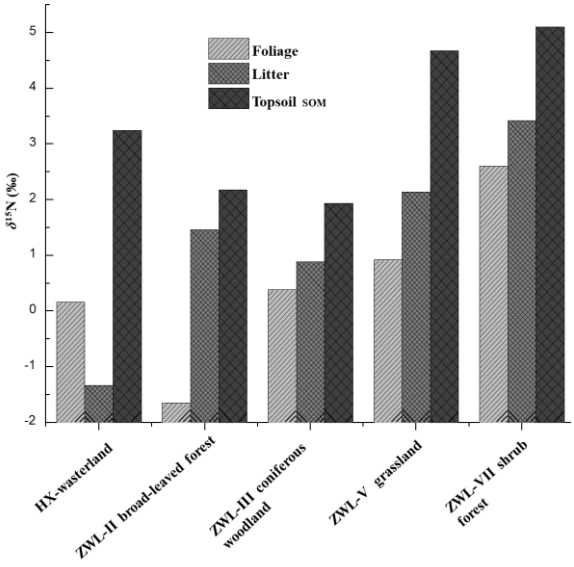

Figure 7. Average $\delta^{15}N$ values of the dominant species of leaf and litter and the topsoil SOM of the soil profiles.

3.4. $\delta^{13}C$ values of the SOC

The SOM $\delta^{13}C$ vs. depth curves showed that the $\delta^{13}C$ value of the SOM was typically the lowest at the surface and became richer in ^{13}C with depth (Figure 4). Compared with the SOC content (Figure 4), $\delta^{13}C$ changed more gradually with depth. The carbon isotopic profiles of the sampling sites (Figure 4) showed typical patterns of ^{13}C-enrichment with depth. The $\delta^{13}C$ values of the SOM ranged from −26.3‰ to −20.8‰, indicating that a distinct difference existed in the vertical patterns and that the carbon isotopic fractionation of the soil profiles with different vegetation conditions differed (Figure 4). In general, the ^{13}C fractionation in the different soil profiles decreased in the following order: broad-leaf forest > coniferous woodland > grassland > shrub forest > wasteland.

Similar variation patterns were found for the broad-leaf forest and coniferous woodland soil profiles (Figure 4). The $\delta^{13}C$ of the SOM of these two profiles rapidly increased from the surface to 40 cm, exhibited smaller variation ranges below 40 cm, and then reached a constant value (Figure 4). The $\Delta^{13}C$ ($\delta^{13}C_{max}$-$\delta^{13}C_{min}$) values of the SOM were 4.1‰ for the broad-leaf forest and 4.0‰ for the coniferous woodland. However, the $\delta^{13}C$ values of the SOM in the shrub forest showed distinctly different variation patterns than the two woodland profiles (Figure 4). The $\delta^{13}C$ SOM values increased from the surface to 15 cm depths, decreased from 15cm to 20 cm, and increased from 20 cm to 40 cm. The values of the SOM varied over a smaller range below 40 cm and finally reached a constant value (Figure 4). The $\Delta^{13}C$ ($\delta^{13}C_{max}$-$\delta^{13}C_{min}$) value of the SOM was 3.4‰ for the shrub forest.

Moreover, the $\delta^{13}C$ values of the SOM in the grassland profiles were higher than those of the broad-leaf and coniferous woodland, and they showed the same variation trends as those of the two

woodland profiles (Figure 4). The $\Delta^{13}C$ ($\delta^{13}C_{max}$-$\delta^{13}C_{min}$) value of the SOM was 3.9‰ for the grassland profiles. Compared with the other profiles, the wasteland profiles showed higher topsoil SOM $\delta^{13}C$ values and varied from -22.0‰ to -23.2‰ (Figure 4). The $\Delta^{13}C$ ($\delta^{13}C_{max}$-$\delta^{13}C_{min}$) value of the SOM was 1.2‰ for the wasteland profiles. In addition, the $\delta^{13}C$ values of the SOM varied over a smaller range below 60 cm (Figure 4). This result is mainly attributed to the fact that they have the same parent soil material and are less affected by the vegetation conditions of the soil profiles.

3.5. $\delta^{15}N$ values of SON

Compared with the increase in $\delta^{13}C$ of the organic matter with depth, the increase in $\delta^{15}N$ with depth was much larger (Figure 5). By contrast, the soil profiles exhibited continuous decreases in TN content from 3.7 g/kg to 0.3 g/kg with soil depth (Figure 5). The $\delta^{15}N$ values of the SOM ranged from 1.9‰ to 8.2‰, indicating that a distinct difference existed in their vertical variation patterns, and the variation ranges differed for the different soil profiles (Figure 5). In this study, the ^{15}N fractionation of the different soil profiles decreased in the following order: broad-leaf forest > coniferous woodland > grassland > wasteland > shrub forest.

In addition, the $\delta^{15}N$ values of the SOM showed a similar variation trend in all of the soil profiles (Figure 5). From the topsoil to 40 cm, the $\delta^{15}N$ values of the SOM increased rapidly with depth, decreased slowly, and then reached a constant value (Figure 5). Compared with the other profiles, the coniferous woodland had lower topsoil SOM $\delta^{15}N$ values and ranged from 1.9‰ to 5.6‰. The grassland profiles showed higher topsoil SOM $\delta^{15}N$ values and ranged from 4.7‰ to 8.2‰ (Figure 5). The differences between the maximum and minimum SOM $\delta^{15}N$ were 3.7‰ for the coniferous woodland profiles and 3.5‰ for the grassland profiles. However, the differences between the maximum and minimum SOM $\delta^{15}N$ were 1.6‰ for the shrub forest profiles, 4.5‰ for the broad-leaf forest profiles, and 3.1‰ for the wasteland profiles.

4. Discussion

4.1. Links between the isotopic compositions of the dominant plant leaves and litter and the topsoil SOM

This study shows that the $\delta^{13}C$ values gradually increased from the dominant plant foliage and litter to the topsoil SOM (Figure 6), suggesting that isotopic fractionation occurred during the formation of the SOM from the decomposition and mineralization of plant debris, resulting in considerable enrichment in the $\delta^{13}C$ of the topsoil SOM. These results are similar to those reported by Hobbie [27], which report that during foliage senescence and fall, the decomposition of litter and the formation of SOM can lead to a distinct ^{13}C enrichment relative to that of the foliage based on their carbon isotopic composition and independent of vegetation type. Compared with the other profiles, the $\delta^{13}C$ values of the dominant species foliage in the wasteland profiles are similar to those of their corresponding litter (Figure 6), which is presumably due to the discrepancy in the turnover of plan debris between the different species of vegetation and may also be due to the differential break down of the plant debris in the profiles. Different plant species produce organic matter compounds, which vary in abundance and nature as a function of species [28]. In addition, during foliage senescence, translocation processes can lead to changes in the $\delta^{13}C$ values of the foliage. An enrichment factor of 0.12‰ has been incorporated into some of the carbon balance models to account for the differences in the $\delta^{13}C$ values of the leaves and litter [29]. However, this shift may be less important than the isotopic changes observed during the later stages of leaf decomposition [30].

Many investigations [11,31] have shown that the $\delta^{13}C$ difference between the vegetation and the surface soil varies from 0.5‰ to 2.5‰. We obtained similar results for the five soil profiles from the Chinese Loess Plateau. These results indicate that ^{13}C was enriched and $\delta^{13}C$ SOC increased within the range of 0.5‰–3.2‰ during the degradation of litter into the SOM on the surface soil. Typically, the $\delta^{13}C$ of the litter on the forest floor is approximately 0.5‰ higher than that of the foliage input [32]. If this enrichment is considered, the $\delta^{13}C$ difference between the soil and vegetation would be 2.0‰–3.5‰

for the surface soil. The aboveground vegetation litter is a major source of topsoil SOM. The study of Balesdent [11] suggests that in well-aerated soils covered by C_3 vegetation, the topsoil SOM has higher $\delta^{13}C$ values than the litter. The main mechanism for these changes is the biological and biochemical transformations occurring during humification, leading to ^{13}C enrichment of the residual organic carbon in the SOM [33]. For example, the $\delta^{13}C$ values of lignin are about 2.0‰–6.0‰ lower than those of the whole plant tissue. Hence, during humification, the decomposition of organic structures, such as the lignin in the soil, can promote ^{13}C enrichment of the SOM on the surface soils compared with the original plant material [34]. Microbial respiration and fermentation lead to ^{13}C enrichment of the microbial biomass carbon compared with the released CO_2 [35]. The second mechanism is predominantly controlled by the turnover rate of the topsoil SOM [36]. In the present study, the $\delta^{13}C_{soc}$ of the wasteland profiles increased by 3.2% and was distinctly higher than that of the other soil profiles during the degradation of litter into the SOM on the surface soil. This phenomenon is likely due to the fact that the wasteland profiles have higher pH values, higher microbe activity, and less litter input than the other profiles. Therefore, the SOM turnover rate increases, resulting in the large carbon isotopic fractionation of the wasteland profiles.

However, at the surface, the $\delta^{15}N$ values of the organic matter gradually became similar to or slightly greater than the values for plant litter, and they increased from the plant litter to the topsoil SOM (Figure 7) as the input plant material progressively decomposed. These results indicate that the nitrogen isotopic values of the SOM, foliage, and plant litter significantly correlate with one another. Thus, SOM inherits the isotopic composition of the foliage and litter. In this study, ^{15}N is found to be enriched during the degradation of litter into the SOM on the surface soil. One explanation for ^{15}N enrichment from decomposition is that respiration preferentially uses organic matter enriched in ^{15}N [13].

Compared with the data from Mount Kinabalu, Borneo (range: 3.0‰–6.0‰) [37], our SOM $\delta^{15}N$ values ranged from 1.9‰ to 8.2‰ and had a larger mean and a greater variation range. The environmental conditions of our sample sites are possibly more complex. Mount Kinabalu, Borneo is a tropical mountainous region with a warm climate and no marked seasonal difference between the dry and wet seasons. On the Loess Plateau, humidity varies significantly seasonally. The degree of decomposition may also affect the $\delta^{15}N$ difference between the plants and soil, but further investigations are needed to confirm this interpretation.

Basing from the above-described results, we conclude that the isotopic values of the topsoil SOM are higher than those of the corresponding litter (Figures 6 and 7). This result may indicate that new litter inputs and overall isotopic fractionation during decomposition are the major factors controlling the ^{13}C and ^{15}N enrichment during the degradation of litter into the SOM on the surface soil. Furthermore, the differences in the $\delta^{13}C$ and $\delta^{15}N$ values are predominantly controlled by the turnover rate of the topsoil SOM. The greater the turnover rate, the larger the difference [38]. Soil fauna plays a key role in SOM turnover. For instance, earthworms, which produce intestinal mucus rich in energetic and easily metabolizable compounds, induce a priming effect that stimulates SOM decomposition [39]. The pH values of the soil profiles ranged from 7.1 to 7.9 (mean = 7.5) (Figure 2), indicating high fauna and microbiological activity and decomposition rates for the topsoil SOM. Thus, compared with the research results for other regions, the isotopic values of the topsoil SOM of our soil profiles increased more significantly than those of the litter during the degradation of litter into the SOM on the surface soil.

4.2. Variations in the SOM $\delta^{13}C$ values due to SOM decomposition

The SOC content and $\delta^{13}C$ of the soil profiles showed highly different characteristics (Figure 4). The variation in SOC content with depth was very similar for all of the profiles from the sampling sites (Figure 4), which are similar to the thousands of reported SOC distributions of soil profiles. Typically, SOC content decreases rapidly from the surface to certain soil layers and then decreases more slowly in the deeper soil layers. These results are attributed to SOM decomposition with depth and the main loss of SOM as CO_2. On the basis of the SOC content profile, limited soil processes occur at depth.

Compared with the SOC content, the SOM $\delta^{13}C$ profile exhibited relatively rapid changes near the surface (although less so than the SOC content), but the ^{13}C enrichment continued in the deeper layers (Figure 4). This finding indicates that most of the SOM are decomposed and lost gradually as CO_2, and the remaining C are concentrated in areas with high $\delta^{13}C$ values. These results are consistent with the results of other studies conducted in different climatic zones [11,27,40]. They also suggest that even slow decomposition of resistant organic matter is associated with ^{13}C enrichment.

Several mechanisms have been proposed to account for the ^{13}C enrichment of SOM with depth. The first mechanism is isotopic fractionation during decomposition. The most important processes are microbial respiration and fermentation, which lead to ^{13}C enrichment of the microbial products compared to the organic substrate [35]. This mechanism is considered to be the main reason for the observed ^{13}C enrichment between the litter and vegetation and with increasing soil depth. The second mechanism involves the different decay rates of the various components of the organic matter having different $\delta^{13}C$ values. These effects also significantly alter the total $\delta^{13}C$, but the expected magnitude and direction depend on the relative proportions of the components, and they are not completely known (Feng, 2002). The third mechanism is related to the belowground biomass (roots) being enriched in ^{13}C compared with the aboveground biomass (leaves) [30].

Our results show different changes and the increasing tendency, maximum value, and corresponding depth of the $\delta^{13}C$ values of the SOM from one of the soil profiles differ, resulting from the different vegetation conditions and the type of organic matter input predominantly from leaf and stem derived litter at the surface and belowground litter derived from roots. Vegetation is more important than microclimate, soil, successional processes, slope, aspect, and elevation in controlling the SOC in an ecosystem [41]. Vegetation directly influences soil carbon accumulation and soil development through aboveground and belowground net primary production [42]. The developing status of aboveground vegetation directly influences the natural properties of soil profiles [43]. Aboveground vegetation species and vegetation composition are dominant factors influencing the SOM content and its distribution with depth [38]. Therefore, topography, aboveground vegetation species, and vegetation composition are the dominant factors controlling the variations in SOM $\delta^{13}C$ with depth on the Chinese Loess Plateau. Compared with the other soil profiles, the SOM $\Delta^{13}C$ ($\Delta^{13}C = \delta^{13}C_{max}$-$\delta^{13}C_{min}$) values of the broad-leaf forest soil profiles were significantly different. The $\Delta\delta^{13}C$ values of the SOM in the soil profiles were as follows: 4.0‰ for the coniferous woodland, 3.9‰ for the grassland, 3.4‰ for the shrub forest, 1.2‰ for the wasteland profile, and 4.1‰ for the broad-leaf forest (Figure 4). This result may be ascribed to the abundant litter material (e.g., leaf fall) in broad-leaf forests and the more active microbial action in its soil that increase the carbon isotopic fractionation of organic matter. The wasteland has sparse vegetation cover, and the litter input to the topsoil is small, resulting in less fractionation of the SOC. In addition, Chen [36] concluded that the evolution of soil profiles can significantly affect the distribution of SOM with depth. Although the five studied soil profiles exhibited different degrees of development with large soil thickness, they had different absolute ages. For similar terrain conditions, the soil environments (such as climate and biology) of the different soil layers were different. Thus, distinct differences existed between the degrees of decomposition of the SOM, which may be another factor controlling the trends in ^{13}C abundance with depth in the SOM in the soil profiles.

4.3. Variation in SOM $\delta^{15}N$ with depth

The N isotopic compositions of the SOM are reported in Figure 5. The $\delta^{15}N$ values of the SOM ranged from 1.9‰ to 8.2‰ and increased with soil depth, which corresponds to a decrease in TN content from 3.7 to 0.3 g/kg (Figure 5). This variation trend is consistent with the results of other studies [44]. This result suggests that low $\delta^{15}N$ values persist on the surface soil because most of the N taken up from the soil by the forest trees is tightly cycled and eventually return as inputs to the upper soil layers via litter fall and root death. Furthermore, the stable nitrogen isotopic depth profiles may indicate that isotopic fractionation occurs during N loss because of the faster reaction rate of ^{14}N compared with ^{15}N. The differences between the maximum and minimum SOM $\delta^{15}N$ values were 3.7‰ for the coniferous

woodland profiles and 3.5‰ for the grassland profiles. However, the differences between the maximum and minimum SOM $\delta^{15}N$ were 1.6‰ for the shrub forest profiles, 4.5‰ for the broad-leaf forest profiles, and 3.1‰ for the wasteland profiles. These results are similar to the range of 1.5‰–4.8‰ reported by Nadelhoffer and Fry [45]. The enrichment of the residual N in ^{15}N is presumably due to the combined effects of multiple processes, including the differential preservation of ^{15}N enriched materials, the illuviation of ^{15}N enriched materials from shallower to deeper soil layers, and decomposition [45].

Researchers have proposed various direct (e.g., loss of ^{15}N depleted nitrate) and indirect (e.g., climate) controls on the $\delta^{15}N$ patterns of soil horizons. The indirect controls influence the $\delta^{15}N$ patterns by affecting the factors directly controlling $\delta^{15}N$. Partitioning of ^{15}N within soil profiles, compound classes, or organisms only influences the $\delta^{15}N$ patterns of soil horizons if the ^{15}N enriched or ^{15}N depleted nitrogen can preferentially move up or down within the soil profile [46]. In the present study, ^{15}N fractionation in soil profiles with different vegetation conditions decreased in the following order: broad-leaf forest > coniferous woodland > grassland > wasteland > shrub forest. This result is attributed to the abundant litter material input (e.g., leaf fall) in broad-leaf forests and the more active microbial action (e.g., soil fauna, soil food webs, bioturbation) in their soils that increase the carbon isotopic fractionation of organic matter. Högberg [47] demonstrated that the input of ^{15}N depleted foliar litter to the surface soil and the input of ^{15}N depleted root litter and ^{15}N enriched mycorrhizal fungi at depth could result in the deep soil horizons being substantially enriched in ^{15}N relative to the surface litter. The degree of ^{15}N enrichment should in part reflect the relative importance of roots vs. mycorrhizal fungi as the source of SON in stable organic matter. In addition, soil fauna processes large quantities of soil N [48,49], and the cycling of N through soil food webs could potentially influence soil $\delta^{15}N$ patterns. Although N can be released from litter directly during fungal or bacterial mediated decomposition, much of the N release from soils depends on the grazing of primary decomposers by high trophic levels, such as nematodes and amoebae. $\delta^{15}N$ values increase 3.4% per trophic level during N transfer from litter to detritivores to predators. Haubert [50] found similar ^{15}N enrichment during the trophic transfer of N in soil microinvertebrates (2.9% ± 2.1%). If ^{15}N enriched nitrogen from soil fauna is preferentially preserved and the ^{15}N depleted excretion products are preferentially removed, then faunal processing of soil N could contribute to ^{15}N enrichment with increasing soil depth if the net N flux increases down the soil profile. However, compared with the other soil profiles, the $\delta^{15}N$ values of the SOM in the shrub forest profiles vary over a smaller range, and the $\delta^{15}N$ values of the SOM range from 5.1‰ to 6.7‰ with higher $\delta^{15}N$ values for the topsoil SOM.

Several researchers have pointed out that the average $\delta^{15}N$ value of tropical foliage is 3.7‰ ± 3.5‰ ($n = 73$), which is greater ($p < 0.01$) than the temperate forest value of −2.8‰ ± 2.0‰ ($n = 90$) [51]. In tropical forests, the $\delta^{15}N$ values of 2.0‰–23.0‰ have been reported for soils [51]. $\delta^{15}N$ values for temperate forest soil profiles range from -8.0‰ on the forest floor to 8.0‰ in the mineral soil [47,51]. The $\delta^{15}N$ values of soils from arid and semi-arid areas in northwestern China are significantly lower than those reported for tropical forests, indicating that climatic factors are strongly correlated with soil $\delta^{15}N$ and/or foliar $\delta^{15}N$. However, in our study, they did not correlate with ^{15}N enrichment with soil depth. This finding suggests that the processes controlling foliar and soil $\delta^{15}N$ on large scales differ from the processes controlling the development of the $\delta^{15}N$ patterns within the soil profiles and that the nitrogen dynamics within the soil profiles are not primarily controlled by climate factors. Furthermore, they did not significantly differ from those of temperate forests. Natural $\delta^{15}N$ abundances (3.1‰–6.3‰) in mineral soils significantly differ from those of plant samples. Soils are ^{15}N enriched relative to plants and are ^{15}N enriched at depth relative to the surface. The causes of ^{15}N enrichment and of decreases in N with increasing soil depth have been discussed in detail in previous studies [12,13].

4.4. Correlations and the link between the $\delta^{13}C$ and $\delta^{15}N$ of the soils

In the present study, the $\delta^{13}C$ and $\delta^{15}N$ values of SOM were the lowest at the surface and became richer in ^{13}C and ^{15}N with depth (Figures 4 and 5). This is because the N and C isotopic compositions

of the surface soil appear to be controlled by the mixing of new litter inputs, which are depleted in ^{15}N and ^{13}C, with older, more highly decomposed SOM, which is relatively enriched in ^{15}N and ^{13}C. The stable carbon and nitrogen isotopic depth profiles are consistent with the results of other studies on forest soils [11,45]. Nadelhoffer and Fry [45] demonstrated that four main mechanisms can lead to ^{15}N and ^{13}C enrichment with increasing soil depth. These mechanisms are (1) the overall isotopic fractionation during decomposition and (2) the differential preservation of the SOM or litter fractions. The preservation of litter components enriched in ^{15}N and ^{13}C could potentially account for the patterns of heavy isotopic enrichment with soil depth. Our results (Figure 6 and 7) support this idea. For N, all of the litter components had $\delta^{15}N$ values slightly higher or similar to those of whole foliage, and all of the litter fractions were depleted in ^{15}N relative to the soil. For C, ^{13}C was enriched and increased by 0.5‰–3.2‰ during the degradation of litter into the SOC on the surface soil. Other mechanisms are (3) the litter source changes and (4) the illuviation of ^{15}N or ^{13}C enriched dissolved organic matter. Our findings show that $\delta^{13}C$ and $\delta^{15}N$ do not evenly increase within a given horizon. Compared with the other soil profiles, the wasteland soils were depleted in ^{13}C and ^{15}N from 20 cm to 40 cm.

As shown in Table 2, significant correlations were found between ^{15}N and ^{13}C. The latter was linked to the accumulation of SOM from surface litter. The top soils at the sampling site were up to 1.9‰ lighter than the lower soil horizons, indicating ^{14}N depletion during SOM build up because of litter-fall decomposition at the sampling site. The correlation coefficients are as follows: broad-leaf forest (r^2 = 0.856; $p < 0.01$) (*p value* means significant value, $p < 0.01$ indicates a significant correlation), wasteland (r^2 = 0.641; $p < 0.01$), grassland (r^2 = 0.747; $p < 0.01$), and coniferous woodland (r^2 = 0.851; $p < 0.01$) (Table 2). However, no correlation was found between $\delta^{13}C$ and $\delta^{15}N$ for the shrub soil profiles (Table 2), which can be attributed to the fact that the $\delta^{15}N$ values of the SOM in the shrublands vary over a smaller range and have higher topsoil SOM $\delta^{15}N$ values than those of the other soil profiles. In addition, the $\delta^{15}N$ values of the SOM ranged from 5.1‰ to 6.7‰. However, the $\delta^{13}C$ values of the SOM in shrublands increased with depth, except from 0 to 20 cm. These results indicate that the C isotopic composition patterns are less pronounced than the N isotopic composition patterns primarily because discrimination against ^{13}C during organic matter decomposition is weaker than discrimination against ^{15}N.

Table 2. Correlation between the SOM $\delta^{13}C$ and $\delta^{15}N$ values observed in soil profiles with different vegetation conditions.

Study area	Profile	Land-use type	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	Correlation between SOM $\delta^{13}C$ and $\delta^{15}N$
Xiao-Zhang Zhao Village	HX	Wasteland	−23.1 to −22.0	3.2–6.3	0.641**
Lianjiabian forest farm	ZWL-II	Broad-leaf forest	−26.3 to −22.2	2.2–6.7	0.856**
	ZWL-III	Coniferous woodland	−25.9 to −21.8	1.9–5.6	0.851**
	ZWL-V	Grassland	−25.0 to −21.2	4.7–8.2	0.747**
	ZWL-VII	Shrub forest	−20.8 to −24.2	5.1–6.7	0.425

Note: "**" indicates a significant correlation at $p < 0.01$

Previous studies demonstrated the importance of ^{15}N measurements of plants and soils as an ecosystem indicator when considering the regulatory effect of N availability on soil C dynamics. Reviews of multiple studies demonstrated that N fertilization generally increases forest soil C stocks [52] through increased inputs and decreased losses of SOM. In addition, several studies of soil N availability gradients indicated that annual leaf litter production increases with annual net soil N mineralization [45]. Greater soil N availability also increases fine root production and turnover in forests [53]. Increased leaf litter production and fine root turnover can directly contribute to increased soil C inputs in N rich forests.

The present study showed that the differences in $\delta^{15}N$ values with depth were greater than the differences in $\delta^{13}C$ values with depth, even though soil N concentrations decreased less with depth

than soil C concentrations. This result suggests that despite the tight links between the cycling of N and C [40], a large $\delta^{15}N$ gradient can develop faster than a $\delta^{13}C$ gradient. The most important cause of the $\delta^{15}N$ gradient is the deposition of ^{15}N depleted litter on the surface soil [12], but the accumulation of recalcitrant, ^{15}N enriched microbially derived N with increasing soil depth may contribute to this pattern [12]. The accumulation of ^{15}N enriched microbially derived N would be consistent with the increased contribution of ^{13}C enriched microbially derived material with soil depth. The present study also indicated that the heavy isotopic enrichment patterns of the SOM from the Chinese Loess Plateau sites resulted from the combination of the following factors: (1) new litter inputs that decrease the $\delta^{15}N$ and $\delta^{13}C$ values of the surface soil and (2) overall isotopic fractionation during organic matter decomposition that increases these values with depth. These results are similar to those reported by Nadelhoffer and Fry [45]. Furthermore, the isotopic composition of the organic matter on the surface soil was higher than that of the plant litter because isotopic fractionation occurs during the degradation of litter into the SOM on the surface soil. As ^{15}N and ^{13}C depleted inorganic N and C were released into soil solution and into the atmosphere via decomposition reactions, the organic matter particles gradually decreased in size and in C/N [54] and became relatively enriched in ^{15}N and ^{13}C. Nadelhoffer and Fry [45] demonstrated that these smaller, more decomposed, more refractory, and isotopically enriched particles migrate gradually downward as a result of the physical mixing of soil during SOM decomposition. Although C is released more rapidly than N during organic matter decay and although the C/N mass ratios decrease with increasing soil depth, the $\delta^{15}N$ values increase more than the $\delta^{13}C$ values. This result is due to the fact that the overall discrimination against heavy isotopes during decomposition is greater for ^{15}N than for ^{13}C. Thus, the N isotopic fractionation within our soil profiles is higher than the C isotopic fractionation.

5. Conclusion

The soil properties and $\delta^{13}C$ and $\delta^{15}N$ values of the dominant species of foliage and litter and the SOM were analyzed to study the characteristics of SOM with depth on the Loess Plateau, northwestern China. The geochemical data analyzed in this study indicate that the amounts of SOC and TN are mainly concentrated on the surface soil and decrease with depth. The SOM contents are differentiated according to the vegetation conditions in the following order: broad-leaf forest > coniferous woodland > shrub forest > grassland > wasteland. This variation trend is similar to the vegetation succession in natural ecosystems. Therefore, in the hills of the Chinese Loess Plateau, converting wasteland to forestland and grassland is a good way of improving the soil nutrient conditions.

^{13}C and ^{15}N are gradually enriched from the dominant species foliage and litter to the topsoil SOM. In addition, the $\delta^{13}C$ and $\delta^{15}N$ values increase more significantly during the degradation of litter into the SOM on the surface soil compared with the other regions. This finding suggests that the effect of isotopic fractionation is significant during the transformation of SOM from plant debris to topsoil SOM, which results in significant increases in the $\delta^{13}C$ and $\delta^{15}N$ of the SOM. Litter inputs lower the $\delta^{13}C$ and $\delta^{15}N$ values of the surface soil, while decomposition increases the $\delta^{13}C$ and $\delta^{15}N$ values of the deeper soil. The $\delta^{13}C$ and $\delta^{15}N$ values of the SOM increase with increasing depth in the studied soil profiles, suggesting that the degree of degradation of the SOM is more significant with depth on the Loess Plateau. The ^{13}C fractionation of the different soil profiles decreases in the following order: broad-leaf forest > coniferous woodland > grassland > shrub forest > wasteland. The ^{15}N fractionation decreases in the following order: broad-leaf forest > coniferous woodland > grassland > wasteland > shrub forest. The difference in ^{13}C and ^{15}N fractionation is ascribed to the vegetation conditions and different soil-forming environments (such as climate and biology) of the different soil layers.

Except for the shrubs profiles, significant correlations were found between the two stable isotopes, ^{15}N and ^{13}C. The latter is linked to the accumulation of the SOM from the surface litter. Although C is released more rapidly than N during organic matter decay and although the C/N mass ratios decrease with depth, the $\delta^{15}N$ values increase more than the $\delta^{13}C$ values. Therefore, the heavy isotopic enrichment patterns of the SOM from the Chinese Loess Plateau sites result from a combination of the following: (1) new litter inputs that decrease the $\delta^{15}N$ and $\delta^{13}C$ values of the soil surface and (2)

overall isotopic fractionation during decomposition that increases these values with depth. Compared with the results of studies of other regions, the vertical variation patterns of the stable isotopic composition of the SOM from the Loess Plateau have a distinct regional characteristic. This in-depth study using a dual-isotope approach ($\delta^{13}C$ and $\delta^{15}N$) increases our understanding of the SOM characteristics of the Chinese Loess Plateau.

Acknowledgments
This work was jointly supported by the National Natural Science Foundation of China (NO. 41803022); the Science and Technique Foundation of Education department of Guizhou Province, China (NO. [2018]139); the Key Laboratory of Karst Environment and Geohazard, Ministry of Land and Resources (NO. 2018K02); and the Mountain Geohazard Prevention R&D Center of Guizhou Province, China (NO. [2017]5402).

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