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Variations and Indications of $\delta^{13}C_{SOC}$ and $\delta^{15}N_{SON}$ in Soil Profiles in Karst Critical Zone Observatory (CZO), Southwest China

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Abstract: Soil carbon and nitrogen storage and stabilization are the key to solving the problems of mitigation of global warming and maintaining of crop productivity. In this study, the contents of soil organic carbon (SOC) and soil organic nitrogen (SON) and their stable isotope compositions ($\delta^{13}C_{SOC}$ and $\delta^{15}N_{SON}$) in soil profiles were determined in two agricultural lands (including a farmland and an abandoned farmland) and four non-agricultural lands (including two shrub-grass lands and two shrub lands) in the karst critical zone observatory (CZO), Southwest China. The contents of SOC and SON were used for research on the effects of land use on SOC and SON storage, and the change of $\delta^{13}C_{SOC}$ and $\delta^{15}N_{SON}$ values in soil profiles were used to indicate SOC and SON stabilization. The results showed that agricultural activities reduced SOC and SON storage in the whole soil layers of farmland compared to non-agricultural lands, and farmland abandonment slightly increased SOC and SON storage. Crop rotation between peanut (C_3) and corn (C_4) affected the $\delta^{13}C_{SOC}$ in surface soils of agricultural lands (−21.6‰), which were intermediate between shrub lands (−22.7‰) and shrub-grass lands (−19.6‰). ^{15}N-depleted SON in surface soils in farmland compared to those soil in other lands possibly associated with synthetic N fertilizer application. In soil layers below 30 cm depth the $\delta^{13}C_{SOC}$ deceased with depth, while the $\delta^{15}N_{SON}$ displayed irregular fluctuation. The change in $\delta^{13}C_{SOC}$ and $\delta^{15}N_{SON}$ through soil profiles in karst soils were more intensive than those in semiarid grassland soils indicating the less stabilization of SOC and SON in karst soils.

Keywords: soil C and N cycling; stable C and N isotope; karst CZO; Southwest China

1. Introduction

Global population growth in the 21st century leads to an increasing pressure on agricultural productivity, such as food and fiber [1]. Soil organic carbon (SOC) and soil organic nitrogen (SON) contents are important indexes of soil fertility controlling agroecosystem productivity [2]. Previous studies have reported that agricultural activities, such as application of organic and inorganic fertilizers, irrigation, fallow, and intercultivation, affect SOC and SON storage, greenhouse gas emissions, loss of inorganic N, and soil structure [3–7]. However, these agricultural activities cause different kinds of feedback on SOC and SON dynamic due to the differences in climate, topography, and soil parent material in some studies [8–10]. Hence, it is necessary to further understand the soil C and N cycles associated with mitigation of global warming and maintaining of crop productivity [2].

Stable carbon isotope signature of soil is widely used to indicate the sources and turnover of SOC in agricultural ecosystem where there is a shift between C_3 and C_4 crop [11–15]. The ^{13}C compositions in surface soils inherit that of vegetation, and there were marked $\delta^{13}C$ discrepancies between C_3 (from −20‰ to −33‰) [16] and C_4 (from −17‰ to −9‰) vegetation [17]. However, the ^{13}C fractionation by soil microorganisms in the soil organic matter (SOM) decomposition process confuses the contribution to SOM from C_3 or C_4 plants, and further disturbs accurate indication of SOC sources and estimation of its turnover [18]. Since the vertical change of $\delta^{13}C_{SOC}$ with soil, depth is widely used for the indication of the rate of SOM decomposition [19]; the research of variation of $\delta^{13}C_{SOC}$ in soil profile is beneficial for more accurate interpretation of $\delta^{13}C_{SOC}$ as an indicator of C sources based on further understanding the ^{13}C fractionation in SOM decomposition process.

Synthetic N fertilizer can be fixed into SON through microbial immobilization and crop uptake, transformation and returning into soil as litter [20]. Therefore, the $\delta^{15}N_{SON}$ in cropland commonly decreases with the application of ^{15}N-depleted inorganic N fertilizers [21]. However, overuse of N fertilizer causes many forms of N loss, such us leaching of NO_3^- derived from nitrification, releasing of N_2 and nitrogen oxides (NO_X) after denitrification, and ammonia (NH_3) volatilization, and these N losses generally lead to ^{15}N enrichment in the remaining SON [21]. Thus, the $\delta^{15}N_{SON}$ is generally used as a coarse indicator of the N sources and loss processes in the agroecosystem [22,23]. Improved understanding of soil N processes is important for the coordination between fertilization availability and environmental influence in agricultural lands [24].

Soils are the most key part of Earth's critical zone, associated intimately with the sustainable development of mankind [25]. In the karst critical zone observatory (CZO) which is located in Puding county, Southwest China, we investigate the karst soil production and erosion processes, and the integrated geophysical–geochemical–ecological responses to anthropogenic perturbations and global climate change [26]. The karst soils are characterized by small capacity, uneven distribution, serious soil loss, and depletion, and these strongly threaten agricultural production [27]. Meanwhile, intensive agricultural activities lead to many environmental problems, such as karst rocky desertification and loss of water and soil [27]. SOC and SON play important roles in the maintenance of soil fertility and soil structure; therefore, the research of their biogeochemical cycling can provide guidance to solve the coordination problems between soil productivity and environmental sustainability in the karst CZO. The SOC and SON distribution, $\delta^{13}C_{SOC}$ and $\delta^{15}N_{SON}$ in soil profiles, were measured in agricultural region, karst CZO. The objectives of this study are: (1) To estimate the SOC and SON storage in agricultural lands and non-agricultural lands; (2) to identify the sources of SOC and SON in agricultural lands by using the SOC and SON contents and their stable isotope compositions; and (3) to illustrate the fractionation of C and N isotope and SOC and SON stabilization in karst soil according to the $\delta^{13}C_{SOC}$ and $\delta^{15}N_{SON}$ values in soil profiles. This research can perhaps provide fundamental information of soil nutrient element (C and N) dynamics to support the maintenance of agroecosystem productivity and protection of fragile soil resources in the karst CZO, Southwest China.

2. Materials and Methods

2.1. Study Area

The study area (Figure 1) is located in a small karst watershed (26°15.5′ N, 105°46.7′ E) which is one of the karst CZO sites, with an area of 1.54 km^2, Guizhou province, Southwest China. The land in the study area underwent serious soil degradation due to intensive tillage, and then the sloped arable lands were abandoned and recovered under the "Grain for Green Programme" (GGP) [26]. This study area is beneficial for research on SOC and SON dynamics response to land management. This region has a sub-tropical monsoonal climate; the average annual air temperature is 15.1 °C; the mean annual precipitation is 1315 mm, more than 80% of which occurs during the wet season (April to September) [28]. The altitude of this region ranges from 1310 m to 1524 m. The small karst watershed is surrounded by hills, the slope of which is generally more than 30° (~60%) [28]. Quaternary deposits are mainly located in the center of the depression in the watershed. Limestones are widely distributed on the hillsides, and many of them are exposed on the surface [28]. The calcareous soils developed from limestone are classified as Mollic Inceptisols according to United States Department of Agriculture (USDA) soil taxonomy [29]. The spatial distribution of soils is significantly discontinuous, with the thickness of soil layers ranging from 10 cm to 160 cm (average thickness is 30 cm) [30]. Ploughing using the moldboard plow in the 0–30 cm soil layer depths, crop rotation between peanut (C_3) and corn (C_4), fertilizer (urea and compound fertilizer) and pig manure application, and straw non-recycling are managed in farmland. Most of the farmlands are located in the low-lying center of the watershed, where the deposition region of erosive soil is derived from that of hillsides, thus the thickness of soil layers in farmlands is generally over 70 cm, which is enough for ploughing by moldboard plow. Paddy land accounted for 14.39% of total watershed area, 55.65% was dry land, 23.35% was shrubland, and 6.61% was secondary forest land in this study area before 2008 [31]; subsequently, many farmlands were abandoned and even evolved into shrublands or shrub-grass lands.

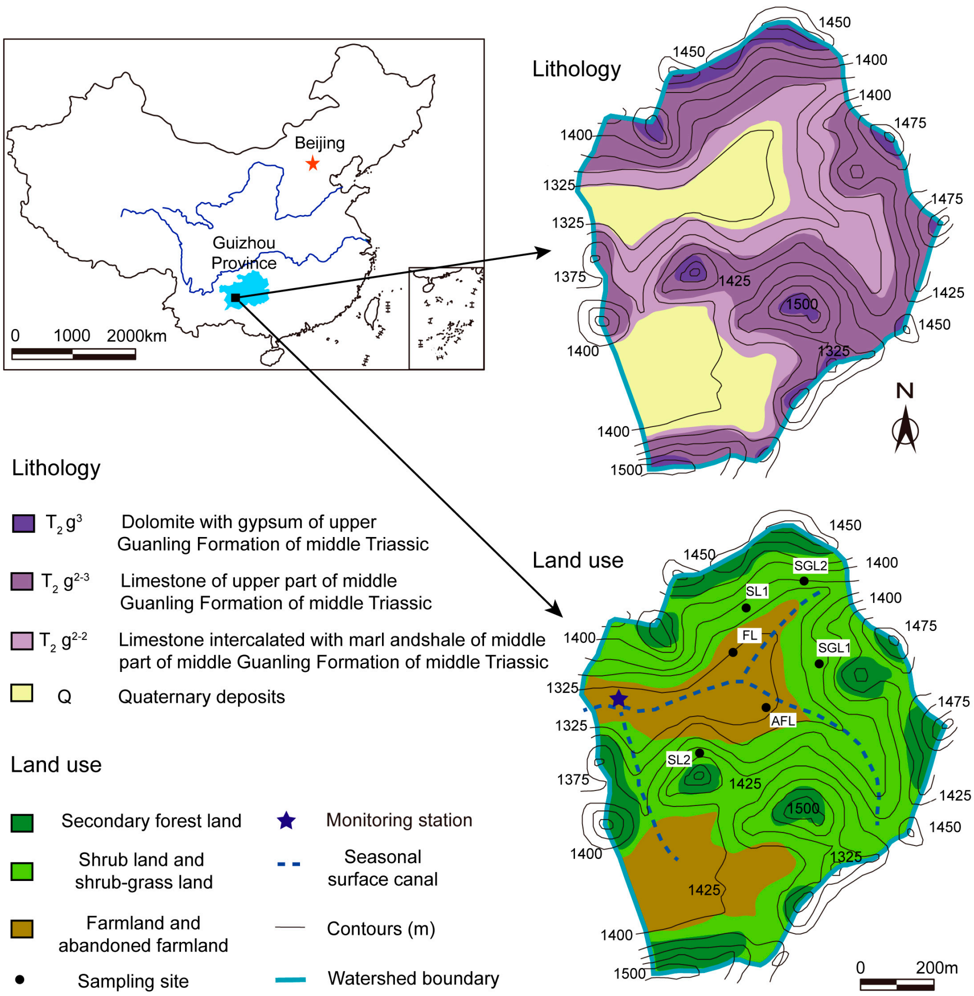

Figure 1. Location of study area and sampling sites.

2.2. Soil Sampling

Agricultural lands including farmland and abandoned farmland are located in center of the depression; non-agricultural lands including shrubland and shrub-grass land are mainly located in the middle slope of hills in study area (Figure 1). Six soil profiles were classified as farmland (FL), abandoned farmland (AFL), shrub-grass land (SGL1, SGL2), and shrubland (SL1, SL2). Three soil profiles of FL, SGL1, and SL2 were located in the north of the watershed; the other three soil profiles of AFL, SGL2, and SL1 were located in the middle of the watershed. The pictures of the six soil profiles are shown in Figure 2, and visible characteristics of these soil profiles are described carefully in Table 1.

All the soil profiles were chosen with a thickness over 70 cm, in order to compare the changes of SOC and SON contents and their stable isotope compositions with depth. Generally, SOM content in the soil layers profile is significantly changed in the soil layers of 0–30 cm soil depth, whereas it is slightly varied below 30 cm soil depth [30]. Thus, soil samples were collected with 10 cm interval in the soil layers 0–30 cm deep, and with 20 cm intervals in the soil layers below 30 cm deep in July, 2016. Descriptions about six soil profiles, thickness, dominant vegetations (or main crops), and δ^{13}C values of their leaf are given in Table 1.

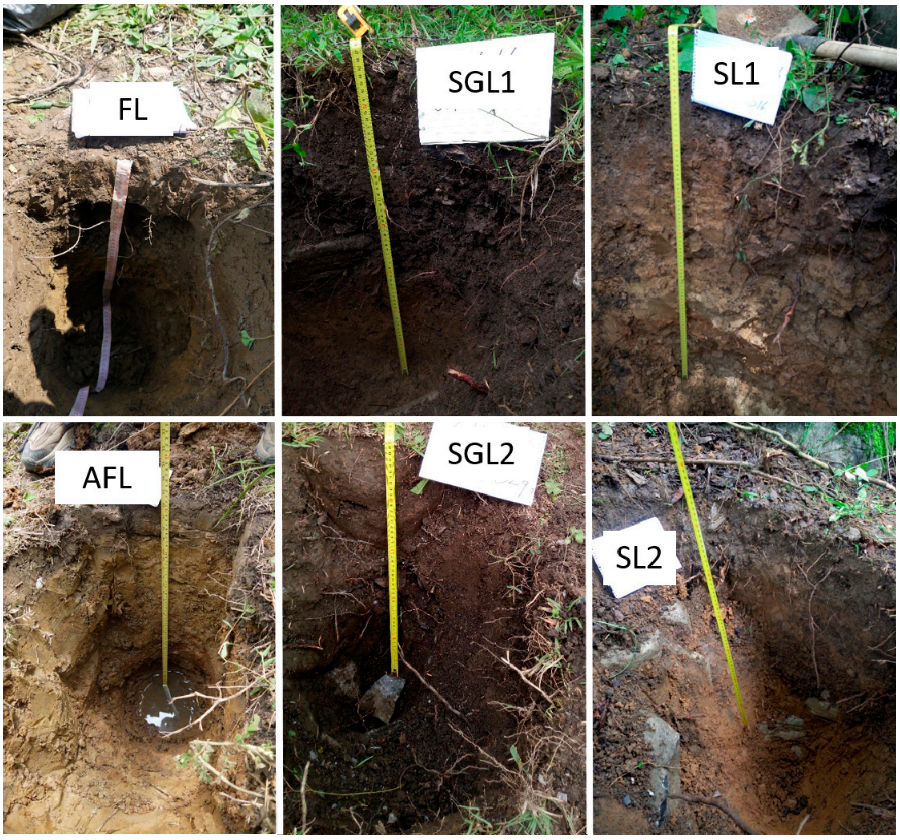

Figure 2. The pictures of the six soil sampling profiles. FL is farmland (cultivation over 50 years); AFL is abandoned farmland (farmland have be abandoned for two years, covered by weeds); SGL is shrub-grass land (SGL1: Farmland that has been abandoned for five years, and evolved to shrub-grass land; SGL2: Shrub-grass land with non-disturbance); SL is shrubland (SL1: Farmland that has been abandoned for eight years, and evolved to shrubland; SL2: Pear orchard that has been abandoned for eight years, and evolved to shrubland).

Table 1. Soil profile, profile thickness, visible characteristics, dominant vegetation species, and its $\delta^{13}C$ value in study area.

Profile	Thickness (cm)	Dominant vegetation species	$\delta^{13}C$ of leaf (‰)	Visible characteristics
			Agricultural land	
FL	70 cm	*Zea mays* (C_4) *Arachis hypogaea* (C_3)	−11.4‰ [a]	0–20 cm: brawn, block structure, tight, abundant plant roots and debris 20–70 cm: yellow, block structure, tight, no rootlet
AFL	70 cm	*Artemisia carvifolia* (C_3)	−28.4‰ [c]	0–6 cm: brawn, block structure, tight, abundant plant roots and debris 6–70 cm: yellow, block structure, tight, no rootlet
			Non-agricultural land	
SGL1	90 cm	*Miscanthus floridulus* (C_4) *Rubus biflorus* (C_3)	−12.3‰ [b] −28.7‰ [c]	0–22 cm: brawn, fine grained, loose, abundant plant roots 24–42 cm, Brawn, block structure, tight, few plant roots 42–90 cm: yellow, block structure, tight, no rootlet, merges to weathered crust below
SGL2	90 cm	*Miscanthus floridulus* (C_4) *Pyracantha fortuneana* (C_3)	−12.3‰ [b] −28.5‰ [c]	0–10 cm: black humus layer, fine grained, loose, abundant plant roots 10–35 cm: black brawn, block structure, tight, medium amount of plant roots 35–90 cm: red brawn, block structure, tight, no rootlet
SL1	90 cm	*Rubus biflorus* (C_3)	−28.7‰ [c]	0–15 cm: black humus layer, granular structure, loose, abundant plant roots and debris 15–40 cm: red, block structure, tight, few plant roots 40–90 cm: brawn, clayey, tight, no rootlet
SL2	70 cm	*Rhamnus davurica* (C_3) *Rubus biflorus* (C_3)	−28.4‰ [c] −28.7‰ [c]	0–10 cm: black humus layer, fine grained, loose, abundant plant roots 10–50 cm: brawn, block structure, tight, medium amount of plant roots 50–70 cm: red, clayey, tight, no rootlet

[a] Data are from Reference [32]; [b] Data are from Reference [33]; [c] Data are from Reference [34]. FL is farmland, AFL is abandoned farmland, SGL is shrub-grass land, and SL is shrubland.

2.3. Soil Analysis

Soil samples were dried with air (25 °C) and coarse roots and stones were removed. Subsamples separated by quartering were ground and passed through a 100-mesh sieve (<150 μm) for analysis of chemical properties. Soil pH (soil:water = 1:2.5) was measured using a pH meter [35], with a precision of ±0.05. Soil particle distribution was measured by a particle size analyzer (Malvern, Mastersizer 2000, England) and the results were shown as proportion of equivalent volume with a precision of ±1%. Carbonates in the powder samples (<150 μm) were removed using 0.5 mol L^{-1} diluted hydrochloric acid (HCl) for 24 h [36]. Inorganic N (including NH_4^+-N and NO_3^--N) were removed using 2 mol L^{-1} potassium chloride (KCl) for 24 h [37]. The treated samples were washed using deionized water until the supernatant liquid was neutral, dried at 55 °C until a constant weigh, ground, and passed through a 100-mesh sieve, used for analysis of the SOC and SON contents and their stable isotope ratios. The SOC and SON contents were calibrated due to loss of carbonate and inorganic N.

The SOC and SON contents were analyzed using an elemental analyzer (Elementar, Vario TOC cube, Germany) with a precision of C ± 0.1% and N ± 0.02%, monitored with standard samples (low organic content soil OAS, CatNo B2152, C: 1.55% ± 0.04%; N: 0.13% ± 0.01%) in the Laboratory of Surficial Environment Geochemistry, China University of Geosciences (Beijing).

The stable carbon isotope ratio ($^{13}C/^{12}C$) of SOC and stable nitrogen isotope ratio ($^{15}N/^{14}N$) of SON were measured utilizing an isotope mass spectrometer (Thermo, MAT-253, USA) in the Center Laboratory for Physical and Chemical Analysis, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences. Measurements were normalized based on the measured values of standards material (Urea and L-glutamic acid, GBW04494, $\delta^{13}C_{VPDB}$: 45.6‰ ± 0.08‰; $\delta^{15}N_{Air}$: 0.24‰ ± 0.13‰), and expressed on standard δ ($\delta^{13}C$ and $\delta^{15}N$) notation (‰) relative to Vienna Pee Dee Belemnite (VPDB) and air, respectively, where:

$\delta^{13}C(‰) = [(R_{sample} - R_{VPDB})/R_{VPDB}] \times 1000$, where $R = {}^{13}C/{}^{12}C$

$\delta^{15}N(‰) = [(R_{sample} - R_{air})/R_{air}] \times 1000$, where $R = {}^{15}N/{}^{14}N$.

Reproducibility as determined through replicate measurements was better than 0.1‰ for $\delta^{13}C$, and better than 0.2‰ for $\delta^{15}N$.

2.4. Statistical Analysis

Statistical analysis was performed by SPSS 18.0 (SPSS Inc., Chicago, IL, USA) and SigmaPlot 12.5 (Systat Software GmbH, Erkrath, Germany) software package. The $\delta^{13}C_{SOC}$ values in the same layer were reported as the means ± standard errors for the middle sites (AFL, SGL2, and SL1) and the northern sites (FL, SGL1, and SL2). Least significant difference (LSD) test ($P < 0.05$) was used to examine the significance of $\delta^{13}C_{SOC}$ values in the same layer between middle sites and northern sites. The $\delta^{15}N_{SON}$ values in the same layer were reported as the means ± standard errors for agricultural lands (FL, AFL) and non-agricultural lands (SGL1, SGL2, SL1, and SL2). Least significant difference (LSD) test ($P < 0.05$) was used to examine the significance of $\delta^{15}N_{SON}$ values in the same layer between agricultural lands and non-agricultural lands.

3. Results

3.1. Soil Particle Distribution and Soil pH

The soils in all sampling sites were a silt loamy texture, with sand size proportion of 1.6–8.6% (mean: 4.1%) in the whole particle mass; silt size proportion of 70.4–79.5% (mean: 75.7%); and clay size proportion of 16.2–24.6% (mean: 20.2%) (Table 2).

Table 2. Soil particle distribution and soil pH in different soil depth.

Sampling site	Depth (cm)	Clay (%)	Silt (%)	Sand (%)	pH
FL	0–10	20.9	73.8	5.3	7.5
	10–20	20.6	73.6	5.8	7.4
	20–30	20.0	71.4	8.6	7.5
	30–50	19.2	73.1	7.8	7.3
	50–70	18.7	75.2	6.1	7.3
AFL	0–10	23.0	71.8	5.2	7.2
	10–20	24.6	70.4	5.0	7.4
	20–30	21.4	74.9	3.8	7.5
	30–50	21.1	73.9	5.0	7.4
	50–70	23.2	71.7	5.1	7.4
SGL1	0–10	21.9	74.2	3.9	6.8
	10–20	21.4	74.7	3.9	6.7
	20–30	20.2	76.7	3.1	6.7
	30–50	21.9	74.3	3.8	6.4
	50–70	20.6	75.3	3.8	6.4
	70–90	19.3	77.0	3.8	6.4
SGL2	0–10	19.8	76.9	3.3	7.7
	10–20	19.1	77.2	3.7	7.5
	20–30	19.4	77.4	3.1	7.7
	30–50	17.7	79.5	2.9	7.5
	50–70	20.2	78.3	1.5	7.4
	70–90	22.5	76.3	1.3	7.4
SL1	0–10	18.0	77.3	4.7	6.7
	10–20	19.7	76.9	3.4	6.8
	20–30	20.9	77.6	1.5	6.8
	30–50	20.3	78.2	1.5	6.8
	50–70	23.1	74.6	2.3	7.2
	70–90	23.6	74.4	2.0	7.5
SL2	0–10	18.0	77.3	4.7	7.0
	10–20	17.6	77.7	4.7	7.2
	20–30	16.5	79.1	4.4	7.3
	30–50	16.2	79.3	4.5	7.3
	50–70	16.6	78.6	4.8	7.4
Maximum		24.6	79.5	8.6	7.7
Minimum		16.2	70.4	1.3	6.4
Mean		20.2	75.7	4.1	7.2

Note: FL is farmland, AFL is abandoned farmland, SGL is shrub-grass land, and SL is shrubland.

Soil pH values in all samples ranged from 6.4 to 7.7 (mean: 7.2), which showed there were neutral and alkaline soils in the study area (Table 2).

3.2. SOC and SON Content and C/N Ratio

The SOC contents in all soil layers of six profiles ranged from 4.58 g kg^{-1} to 43.30 g kg^{-1}, and the SON contents ranged from 0.92 g kg^{-1} to 4.18 g kg^{-1} (Figure 3a,b). The SOC and SON contents in farmland soil were the lowest compared to non-agricultural land-use soils in the same-depth soil layer. Both the SOC and SON contents in six profiles generally decreased with increasing of soil depth. The SOC and SON contents in the most soil layers of abandoned farmland slightly increased compared to that in farmland in the same-depth soil layer, but those were still lower than in shrublands and shrub-grass lands.

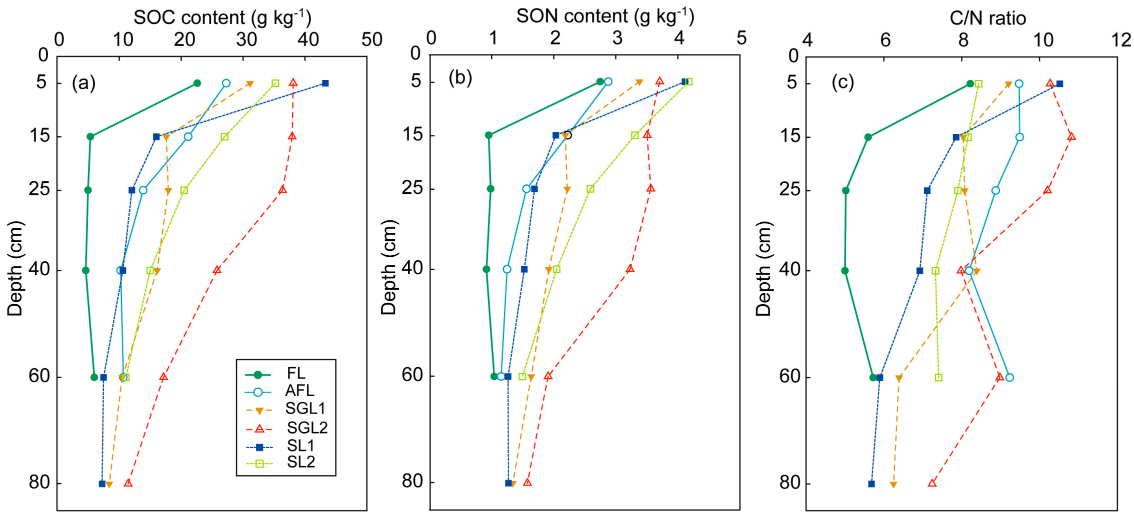

Figure 3. Variation of soil organic carbon (SOC) in and soil organic nitrogen (SON) content and C/N ratio in soil profiles. (**a**) SOC in soil profiles; (**b**) SON in soil profiles and (**c**) C/N ratio in soil profiles. FL is farmland, AFL is abandoned farmland, SGL is shrub-grass land, and SL is shrubland.

The C/N ratios of SOM in the 0–10-cm-deep soil layer of six profiles varied from 8.22 to 10.52 (Figure 3c), and most of them obviously decreased with increases in soil depth in soil profiles. The C/N ratios in all soil layers of farmland were lower than those soils in other land uses in the same depth, especially the significantly low value (5.00–5.60) in the 10–50 cm soil layer depths.

3.3. $\delta^{13}C_{SOC}$ and $\delta^{15}N_{SON}$ in Soil Profiles

In the 0–10 cm soil layer depth, the $\delta^{13}C_{SOC}$ was near −21.6‰ in farmland (FL) and abandoned farmland (AFL) soils, near −19.6‰ in shrub-grass land (SGL1 and SGL2) soils, and near −22.7‰ in shrubland (SL1 and SL2) soils (Figure 4a). In the 10–30 cm soil layer depth, the $\delta^{13}C_{SOC}$ focused on −22.0‰ in soil profiles from northern sites (FL, SGL1, and SL2), while close to −19.1‰ in soil profiles from middle sites (AFL, SGL2, and SL1). The $\delta^{13}C_{SOC}$ values in six profiles all decreased by 1.1–2.4‰ from the 30 cm depth to the bottom of the soil profiles. In the 10–90 cm soil layer depth, the mean $\delta^{13}C_{SOC}$ in soil profiles from middle sites was 2.6–3.4‰ higher than the mean $\delta^{13}C_{SOC}$ in soil profiles from northern sites in the same-depth soil layer (Figure 5a). Mean $\delta^{13}C_{SOC}$ values in soil profiles from both northern and middle sites decreased by 1.6‰ from the 10 cm depth to the bottom in the soil profiles, contrasting with increases in $\delta^{13}C_{SOC}$ (increased by 0.4–1.0‰) as increasing soil depth in northern semiarid grassland (the data were from Reference [38]).

In the 0–10 cm soil layer depth, the $\delta^{15}N_{SON}$ values from six soil profiles were slightly varied from 2.9‰ to 4.3‰ (Figure 4b). The $\delta^{15}N_{SON}$ in non-agricultural land remarkably increased in the 10–20 cm soil layer depth compared to that in 0–10 cm depth (increased by 2.3–3.6‰). In most soil layer depths, the $\delta^{15}N_{SON}$ values in farmland were lower than those soils in other lands. Especially, in the 10–20 cm soil layer depth, the $\delta^{15}N_{SON}$ values in agricultural lands (~3.9‰) were significantly lower than in non-agricultural lands (5.5–7.9‰). The $\delta^{15}N_{SON}$ through soil profiles fluctuated more strongly in karst soils (2.4–4.1‰) compared to that in northern semiarid grassland (1.0–1.6‰) (Figure 5b).

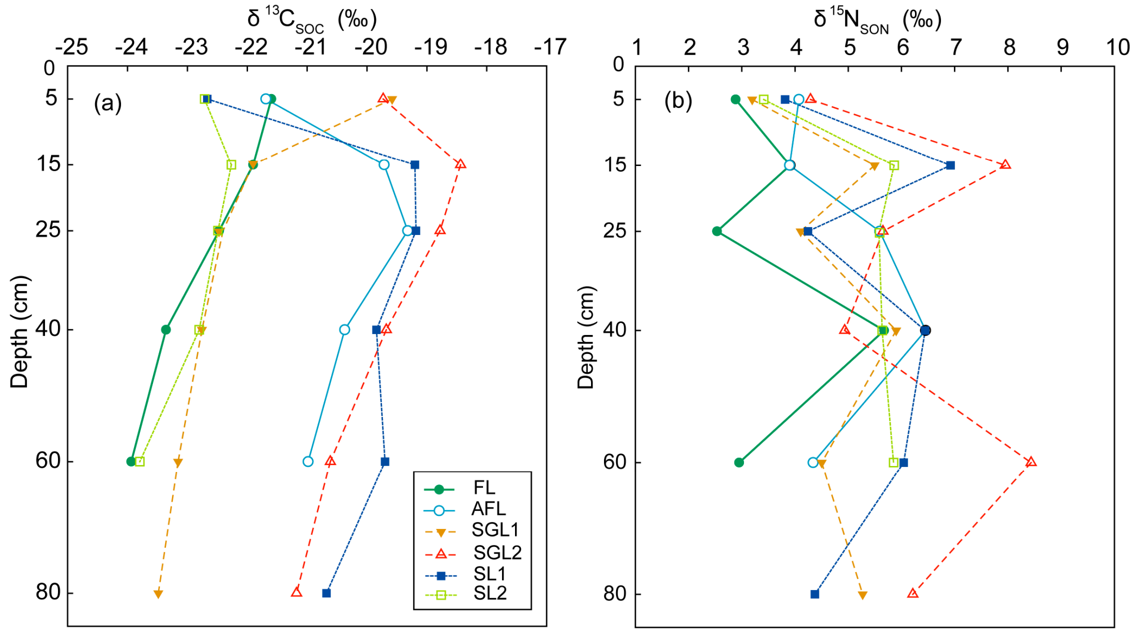

Figure 4. Variation of $\delta^{13}C_{SOC}$, $\delta^{15}N_{SON}$ in soil profiles. (**a**) $\delta^{13}C_{SOC}$ in soil profiles and (**b**) $\delta^{15}N_{SON}$ in soil profiles. FL is farmland, AFL is abandoned farmland, SGL is shrub-grass land, and SL is shrubland.

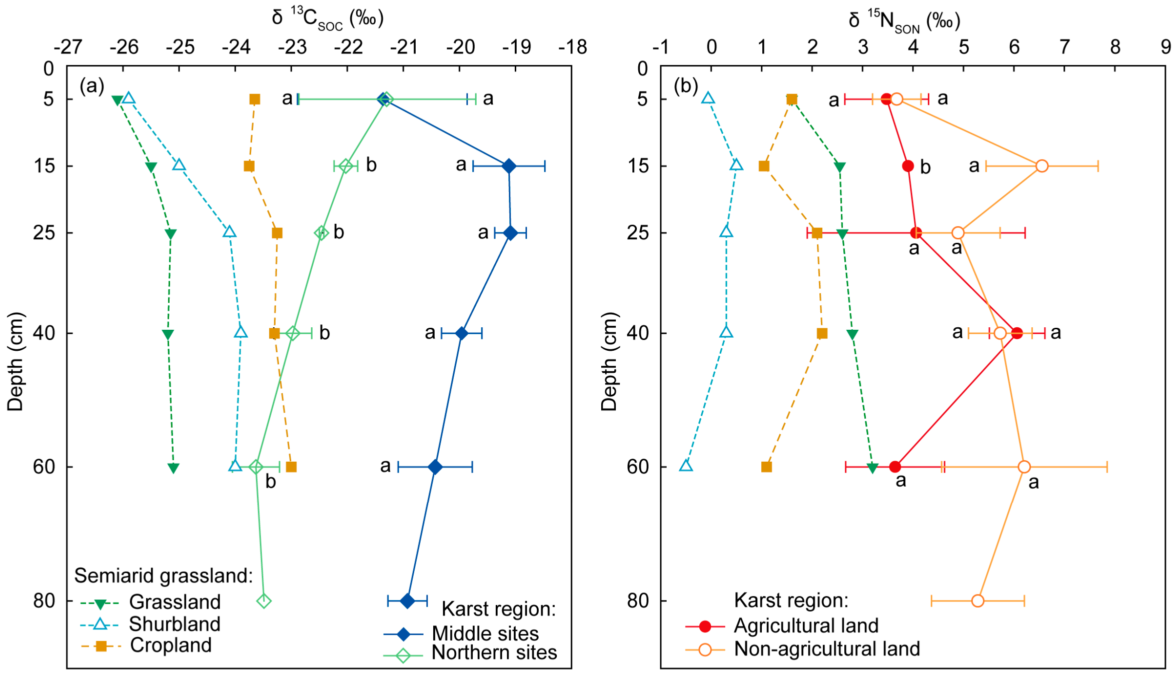

Figure 5. Contrastive variations of $\delta^{13}C_{SOC}$, $\delta^{15}N_{SON}$ in soil profiles between southwestern karst region and northern semiarid grassland in China. (**a**) Contrastive $\delta^{13}C_{SOC}$ in soil profiles and (**b**) contrastive $\delta^{15}N_{SON}$ in soil profiles. Different lowercase letters indicate significant differences of $\delta^{13}C_{SOC}$ in same soil layer between middle sites (AFL, SGL2, and SL1) and northern sites (FL, SGL1, and SL2) in (**a**), and significant differences of $\delta^{15}N_{SON}$ in same soil layer between agricultural land and non-agricultural land in (**b**), at $P < 0.05$ based on the least significant difference (LSD) test. The $\delta^{13}C_{SOC}$ and $\delta^{15}N_{SON}$ data in grassland, shrubland, and cropland in northern semiarid grassland are from Reference [38]. FL is farmland, AFL is abandoned farmland, SGL is shrub-grass land, and SL is shrubland.

4. Discussion

4.1. Indication of Agricultural Activity, C and N Sources in Agricultural Land

The SOC content and its spatial distribution mainly depend on input of surface vegetation including litters, secretions, and residues of roots [39,40]. In the study area, straw non-recycling led to decreased input of organic matter in farmland [41]. Thus, the SOC contents in agricultural land soils were lower than in non-agricultural land in all soil layers, as shown in Figure 3a. Furthermore, intensive tillage in farmland increases the rate of SOC decomposition associated with disturbance of protected-SOC within macro-aggregates [14,42], since aggregate protection for SOC is generally benefit for SOC storage through reduction in the SOM turnover [13]. Continuous input of new C provides abundant SOM and strongly affects the $\delta^{13}C_{SOC}$ in the topsoil, while resistant old C mostly determines the $\delta^{13}C_{SOC}$ in deeper soil layers [43]. The $\delta^{13}C_{SOC}$ value in topsoil is inherited from the stable C isotope composition of surface vegetation [44]. There was no doubt that the $\delta^{13}C_{SOC}$ values in the 0–10 cm soil layer depth were reformed by present vegetation composition (or crops), in which they had an alteration of land use. In the 0–10 cm soil layer depth, the $\delta^{13}C_{SOC}$ in shrub-grass land (−19.6‰) was higher than in shrubland (−22.7‰), which contributed to additional input from C4 vegetation (Table 1); while in the 0–10 cm soil layer depth of agricultural land, the $\delta^{13}C_{SOC}$ (−21.6‰) reflected the rotation between peanut (C_3) and corn (C_4). Although the abandoned farmland (AFL) had been covered by C_3 weed, the $\delta^{13}C_{SOC}$ in the 0–10 cm soil layer depth was similar to that in farmland, resulting from short abandonment time (two years) and decomposition of new C [45]. In the 10–30 cm soil layer depth, the $\delta^{13}C_{SOC}$ showed obvious difference between northern sites (mean: −22.0‰) and middle sites (mean: –19.1‰), indicating the $\delta^{13}C_{SOC}$ in subsurface soils were mainly determined by old C the since effect of present vegetation should not reach this depth in a few years. Furthermore, we speculated that the historical vegetation composition in middle sites and in northern sites had a significant difference in $\delta^{13}C$. Since the $\delta^{13}C_{SOC}$ in middle sites remained 2.9–3.4‰ higher than that in northern sites in the 10–70 cm soil layer depth (Figure 5a), we also speculated that the historical vegetation composition did not chang for a long time.

The SON content was significantly correlated with the SOC content due to primary source SOM [46]; thus, the SON distribution was also affected by straw non-recycling and tillage practices. Extraneous inorganic N, synthetic N fertilizer, and atmospheric N deposition can also be transformed into SON through uptake and transformation by plants and microbes [20]. In farmland (FL), markedly lower C/N rations in the 10–50-cm-deep soil layer likely resulted from biological immobilization of nitrogenous fertilizer. Since SOM decomposition by microbes loses C as CO_2 while N is reserved, the C/N ratios gradually deceased in this process. The decreased C/N ratios with increases in soil depth indicated the accumulation of old organic matter in Figure 3c. However, significantly lower ratios might have indicated extraneous inorganic N input. The $\delta^{15}N$ values of synthetic N fertilizers (~0‰) are lower than that of organic N derived from the litters and microbes, due to negligible fractionation in chemical fixation of N_2 [21]. Choi et al. [21] reported that various synthetic N fertilizer (mean $\delta^{15}N$: -0.3 ± 0.2‰) were significantly more ^{15}N-depleted than raw or composted livestock manure (mean $\delta^{15}N$: 7.8 ± 0.6‰). The synthetic N fertilizer in agroecosystem is the largest N source [47]. The low $\delta^{15}N_{SON}$ in the 0–30 cm soil layer depth, which is strongly affected by agricultural activity (Figure 4b), possibly resulted from application of ^{15}N-depleted N fertilizer. In non-agricultural land, the pathway that plant organic debris enter the soil is of great importance for influencing the $\delta^{15}N_{SON}$ in the surface soils [48]. The $\delta^{15}N$ of plants is also affected by soil $\delta^{15}N$, resulting in intimate feedbacks between soil N and vegetation N in the ecosystem [44]. The $\delta^{15}N_{SON}$ values in the 0–10 cm soil layer depth were higher in karst soil (2.9–4.3‰) than that in semiarid grassland soil (−0.1–1.6‰) (Figure 5b). Firstly, the difference in $\delta^{15}N_{SON}$ may have resulted from the discrepancy of foliar $\delta^{15}N$ of vegetations in the two regions, which depend on many factors, for example precipitation, temperature, species, foliar N concentration, N availability, and degree of N_2 fixation [49]. Secondly, the $\delta^{15}N_{SON}$ values in the two regions were affected by atmospheric deposition, for example wet deposition ($\delta^{15}N$ of NO_3^- is

2‰, $\delta^{15}N$ of NH_4^+ is −12‰) in Southwest China [50] and dry deposition (10–15‰) in England [51]. The climatic difference between southwestern karst region and northern semiarid region results in the different types of atmospheric N deposition.

4.2. Fractionation of C and N Isotopic in Decomposition, Transformation, and Translocation Processes

The $\delta^{13}C_{SOC}$ values through soil profiles commonly increase with increases in soil depth [19], resulting from the following processes: (a) The Suess effect (^{13}C-depleted CO_2 in modern atmosphere since the industrial revolution); (b) the change of environment factors, such as water and light, affect the efficiency of CO_2 conservation in photosynthesis; (c) preferential utilization of ^{13}C-depleted plant compounds and accumulation of ^{13}C-enriched microbial biomass; (d) downward translocation of ^{13}C-enriched dissolved organic carbon (DOC) through profiles [18]. However, the $\delta^{13}C_{SOC}$ can decline with increases in soil depth when (e) recalcitrant and ^{13}C-depleted lignin, lipid, and cellulose are accumulated at depth in the decomposition process of C_4 plant debris [52]. One or more of these processes are dominant in different ecosystems, resulting in various changes in $\delta^{13}C_{SOC}$ through soil profiles [44]. The $\delta^{13}C_{SOC}$ values decreased from the intermediate layer to the bottom in the soil profiles (Figure 4a) and analogues were widely reported in other regions of Southwest China [53,54]. Accumulation of ^{13}C-depleted lignin can likely respond to declined $\delta^{13}C_{SOC}$ with depth in karst soils [53]. But van Bergen et al. [55] stated that lignin accounts for a significant fraction of SOM in the topsoil, while markedly decreased in the deeper soils. Furthermore, the $\delta^{13}C_{SOC}$ values in the soil layer below 30-cm deep decreased from −22.5‰ to −23.6‰ with increases in soil depth in northern sites, and decreased from −19.1‰ to −20.9‰ in middle sites; both of them exceeded the range of C_4 vegetation (from −17‰ to −9‰). Thus, it was disputable that accumulation of ^{13}C-depleted lignin in the decomposition process of C_4 plant debris led to the decrease in $\delta^{13}C_{SOC}$ with depth. Remaining SOC was ^{13}C-depleted at depth, for which ^{13}C-enriched carbonaceous matter could left from original materials; for example, CO_2 released in SOM decomposition or CH_4 released in methane fermentation processes and translocated DOC. However, soil-released CO_2 and CH_4 were commonly ^{13}C-depleted compared to organic substrate [56]. In this small karst watershed, the permeable soils with high permeation are convenient for DOC leaching in a well-drained watershed [57]. A more reasonable assumption, that ^{13}C-enriched DOC was translocated from its original site into underground water, was proposed in this paper. Liu et al. [58] reported that DOC/SOC ratios increased from 0.2% to 1.1% with depth, and $\delta^{13}C_{DOC}$ increased by 3–6‰ with depth in some soil profiles of karst soils. Anyhow, the ^{13}C fractionation of SOC at depth should be further researched in karst soils.

In non-agricultural lands, the largest N source for plant and microbe uptake and loss from system derive from mineralization of SON [59]. Rapid decomposition of SON leads to ^{15}N enrichment in the remaining SOM and mycorrhizal fungi [60]. Therefore, the SON in non-agricultural lands showed an obvious ^{15}N enrichment in the 10–20 cm soil layer depth compared to that in the 0–10 cm soil layer depth (Figure 4b). The SON content generally decreases with increases in depth with downward water translocation, while the proportion of the inorganic N in total N increases [20]. Therefore, soil N processes are commonly dominated by SON ammonification and mineralization in the surface layers, while dominated by inorganic N transformation processes, such as nitrification and denitrification, in the intermediate and bottom soil layers [20]. The leaching of ^{15}N-depleted NO_3^- derived from nitrification and releasing of ^{15}N-depleted N_2 and N_2O derived from denitrification result in ^{15}N enrichment in the remaining SON, which are commonly used for explanation of abnormally high $\delta^{15}N_{SON}$ in the intermediate soil layer [60]. The $\delta^{15}N_{SON}$ in the soil layer below 30 cm deep strongly fluctuated with depth in karst watershed (Figure 4b), which likely responded to intensive nitrification and denitrification. We also assumed that soil water processes controlled the change in $\delta^{15}N_{SON}$ through soil profiles. On the one hand, loss of the dissolved organic nitrogen (DON) as water transported affected $\delta^{15}N_{SON}$ in soil profile [20]. On the other hand, soil water processes affected redox environment, which was of great importance to control the occurrence and scope of nitrification and denitrification [61]. Furthermore, in the small karst watershed, special environmental conditions, such as monsoon climate, large terrain gradient, and uneven distribution of soil, led to uneven distribution of soil water in temporal and spatial [62]. Further, the nonuniformity of soil water complicated the processes of nitrification and denitrification. For example, Hefting et al. [63] found that the N transformation process was dominated by ammonification, where the water table level was less than 10 cm, by denitrification where it was 10–30 cm, and by nitrification where it was over than 30 cm, respectively. Sogbedji et al. [64,65] found that the paths of soil N loss were dominated by denitrification and gaseous emission in waterlogged soils, while by nitrification and NO_3^- leaching under well-drained aerobic condition. Thus, soil water processes may control the strongly fluctuated $\delta^{15}N_{SON}$ through soil profiles in the karst soils.

4.3. The Impacts of the Soil Organic C and N Isotopic Fractionation on Source Identification in the Karst Soil

The variations of $\delta^{13}C_{SOC}$ and $\delta^{15}N_{SON}$ through soil profiles in karst soils compared with that in semiarid grassland soils of northern China [38], as shown in Figure 5. In the soil layers below 10 cm deep, the change of $\delta^{13}C_{SOC}$ in karst soils (~1.6‰) were larger than that in semiarid grassland soils (0.4%–1.0‰) and showed an opposite trend with depth. The $\delta^{13}C_{SOC}$ increased with depth through soil profiles in semiarid grassland soils, which was the same as that in other studies [18,19,44]. Although the ^{13}C fractionation of SOC at depth was not clear in karst soils, the direction and magnitude of change in $\delta^{13}C_{SOC}$ with depth were significantly different compared to that in semiarid grassland soils. The fractionation of ^{13}C of SOC in subsurface soils should be considered adequately, which also indicate the lower stabilization of SOC in karst soils.

The $\delta^{15}N_{SON}$ in the soil organic layer can indicate the relative rate of soil N cycling due to significant correlation between $\delta^{15}N$ and mineralization and nitrification rate [66]. The $\delta^{15}N_{SON}$ values in the 0–10 cm soil layer depth in karst soils (2.4–4.1‰) were higher than those in semiarid grassland soils (−0.1–1.6‰) (Figure 5b), possibly indicating more rapid soil N cycling in karst soils. In non-agricultural land, the $\delta^{15}N_{SON}$ in the 10–20 cm soil layer depth was 2.9‰ larger than that in the 0–10 cm soil layer depth in karst soils, while increased by 0.6–0.9‰ in 10–20 cm depth layers of semiarid grassland soils (Figure 5b), showing more ^{15}N enrichment in remaining SON and mycorrhizal fungi in karst soils. In karst soils, the more ^{15}N-enriched SON in the 0–10 and 10–20 cm soil layer depths indicated the stronger microbial activity and SOM decomposition, attributed to intensive microbial activities in a wetter and hotter environment. The low terrain gradient and dry climate in semiarid grassland determined the more stable soil water processes. The $\delta^{15}N_{SON}$ values in intermediate layers of soil profiles strongly fluctuated in karst soils compared to that in semiarid grassland soil (Figure 5b), resulting from strong spatial dynamics of soil water processes and their controlled redox environment associated with nitrification and denitrification. On the other hand, intensive soil water dynamics in the karst region intensify the N losses into other ecosystems. Inorganic N migrates more easily than organic N; therefore, application of organic fertilizer is beneficial for the controlling of agricultural nitrogen pollution in the agroecosystem, especially soils.

5. Conclusions

The vertical distribution of the SOC and SON contents, $\delta^{13}C_{SOC}$ and $\delta^{15}N_{SON}$ values, from six soil profiles revealed storage and stabilization of SOC and SON under agricultural lands and non-agricultural lands in the karst CZO, Southwest China. SOC and SON storage reduced in all soil layers of agricultural lands compared to those in non-agricultural lands. Agricultural activities, such as crop rotation and fertilizer application, affected $\delta^{13}C_{SOC}$ and $\delta^{15}N_{SON}$ in the surface soils. The more intensive changes in $\delta^{13}C_{SOC}$ and $\delta^{15}N_{SON}$ through soil profiles in karst soils compared to those in semiarid grassland soils indicated the lower stabilization of SOC and SON in karst soils. This study suggests the application of organic fertilizer is of great importance to coordinate the relationship between soil productivity and environmental sustainability in the karst CZO.

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