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# Profile distribution and accumulation characteristics of organic carbon in a karst hillslope based on particle-size fractionation and stable isotope analysis

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# Abstract

Recent studies have highlighted tight coupling between soil aggregate fractions and soil organic carbon (SOC) turnover. However, large uncertainties remain and a mechanistic understanding of geomorphic and land use change effects on carbon storage in soil is still lacking. Taking typical slope of vegetation recovery in karst area as object, the present study analyzed organic carbon content and stable carbon isotope composition ( $\delta^{13}$ C value) of soil organic matter in bulk and particle size separates of soil on profiles at different topographic positions. The results showed that SOC content decreased gradually in downhill direction. Organic carbon content of sandy soil (50-2000µm) accounted above 50% in the upper slope positions but in the middle and lower slope soil profiles, organic carbon was mainly stored in silts (2~50 µm) and clays (<2 µm) which belonged to stable and highly humified SOC. The composition difference of  $\delta^{13}$ C values in soil profiles reflected the input of plant residues and accumulation characteristics. Organic matter was deposited in different soil particle sizes owing to different degrees of decomposition. Hence,  $\delta^{13}$ C value can help in identifying the storage and decomposition rates of soil organic matter.

**Key words** 

Karst area, Particle-size fractionation, Soil organic matter, Stable carbon isotope

#### Introduction

Southwest China is one of the three distribution centers of Karst in the world, in which peak-cluster depression and canyons are typical topographically features. As one of the most fragile ecosystems, the areas suffer from rugged and crumbled surface, steep slopes, significant dissolution and water erosions, slow soil formation from limestone, shallow and thin soil, incontinuous soil cover and week water-retaining ability. Especially, slopes are most prone to erosion (Yang et al., 2000; Wang et al., 2003).

The critical role of soil organic carbon in soil physics, chemistry and biology allows it to be a key index evaluating soil quality (Pan et al., 2009; Martin et al., 2011). Different particle-size fractions adsorb and adhere to organic carbon obviously differently because soil particles are highly dispersed. Therefore, the organic carbon therein significantly affects the cycling, transformation and availability of soil nutrients owing to

distinctively different interferences (Liao *et al.*, 2006; Von Lützow *et al.*, 2007). In other words, clarifying the distribution characteristics of organic carbon reservoir in different soil particles is crucial in revealing carbon cycling in soil. Besides, the stable carbon isotope composition ( $\delta^{19}$ C value) of soil organic matter is spotlighted in the studies on organic carbon cycling because it can effectively elucidate the migration and transformation of SOC storage and evaluate decomposition degree of soil organic matter (Wedin *et al.*, 1995; Bernoux *et al.*, 1998).

In the present study, organic carbon contents and stable carbon isotope composition of soil organic matter in bulk and particle size separates of soils profiles, at different topographic positions of a hillslope, was examined. The study aimed to assess the mechanism of SOC storage and changes in hillslope by determining SOC storage in soil physical fractions, clarify  $\delta^{\rm 13}C$  distribution pattern of organic matter residing in soil physical

fractions by estimating the source and degradation of SOC, and provide basic data for the studies on geo-biological-chemical circulation of soil organic matter in Karst ecosystems.

#### **Materials and Methods**

Study area: The study site located in Rencai village at the border of Southern Huanjiang County and Yizhou City, Guangxi is a representative of karst peak-cluster depression. This area was typical subtropical karst peak-cluster valley and the altitudes ranged from 272.0 to 647.2 m. The natural vegetation mainly included of shrubs, herbs and lianas. This area belonged to middle subtropical monsoon humid climate, with hot rainy season and a long frost-free period. The annual average temperature range from 16.5°C to 19.9°C with 1389 mm annual average rainfall, but rainfall was unevenly distributed and mainly concentrated during rainy season from April to September and was scarcely distributed during dry season from October to March. Soil in this area has mainly been developed from limestone parent materials. Soil cover was unevenly distributed and thickness of soil layers ranged from 10 to 160 cm. Vegetation was degraded and bedrocks were widely exposed due to human destructions.

A typical hillslope during vegetation recovery was selected within the site, which was naturally recovered by forest conservation. Soil and vegetation were distributed differently along the slope. The bedrocks were utterly exposed at the top slope, and the soil depth increased from the upper slope downhill. Vegetation comprised of naturally growing herbs and secondary shrubs during recovery. With vegetation succession, the species gradually changed from herbs (upslope) to shrubs dominantly (downslope).

**Soil sampling:** Soil profile of the slope were dug at the upper slope, middle slope and lower slope (Fig. 1). Soil samples were collected at an interval of 10 cm above the profile, which were

then seived through a 2 mm sieve, air-dried and stored.

**Physico-chemical analysis**: Soil pH was measured by a glass electrode. 10 g of treated sample was leached in CO<sub>2</sub>-free deionized water and pH was determined by mixing soil with water (I: 2.5). Analysis was repeated twice with error less than 0.1.

Particle-size fractionation was performed on materials (bulk soils) <2 mm that were fractionated into three sizes i.e., sand (53-2000  $\mu$ m), silt (2-53  $\mu$ m) and clay (<2  $\mu$ m) by combing wet sieving with centrifugation. Sand size fractions were isolated by wet sieving. The aggregates and soil suspension that were passed through sieve were transferred to measuring cylinders. After adequate settling times, fraction<2  $\mu$ m was determined by pipette. All fractionated samples were dried at 60°C before being ground for chemical analysis.

Particle-size samples were soaked in 0.5 mol  $\rm I^{-1}$  HCl for 24 hr to eliminate carbonates present in soil, washed to neutral by deionized water, dried at 60 °C and then grounded. Carbon concentration and isotope ratios were analyzed by Elemental Analyzer (PE2400, Perkin Elmer, USA) and CF-IRMS Continuous Flow Isotope Ratio Mass Spectrometer. Analyses were performed in duplicate.  $^{13}$ C results were expressed in relative  $\delta$  per thousand scale according to the following equation:

$$\delta^{13}$$
C‰=(R<sub>sample</sub>/R<sub>standard</sub>-1)×10<sup>3</sup>

where,  $R=^{15}C/^{12}C$ , was related to Pee Dee Belemnite (PDB).The analytical precisions for  $C_{org}$  and  $\delta^{13}C$  was 0.02 g  $C_{org}$  kg<sup>-1</sup> and 0.1‰, respectively.

#### **Results and Discussion**

Soil profile of hillslope gradually deepened downhill. As shown in Fig. 1, the upslope was mainly accumulated by recently weathered bedrocks and vegetation residues, consisting of laver

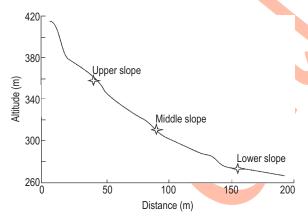
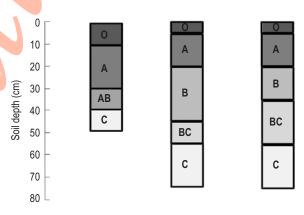


Fig. 1: Description of soil profiles at the four geomorphic positions



O and layer A other than layer B. In contrast, soil profile at the middle and lower slopes remained well-developed and layer-distribution integral. Table 1 shows that organic carbon content and C:N ratio of all soil profile decreased with increasing profile depth and downhill. However, organic carbon content (83.9 g·kg¹-113.2g·kg¹) and C:N ratio (14.3-15.5) of the upper-slope soil profile were apparently higher than those of the middle- and lower-slope ones.

The depth distribution characteristics of SOC were closely associated with input of litters and development of soil profiles (Chen et al., 2005). Well-developed profiles are generally rich in organic carbon owing to more significant organic matter input than decomposition, as topsoil are subject to accepting litters and contain considerable plant roots. The organ carbon content decreases exponentially and thereafter slowly from the top of soil profile downward corresponding to the dramatic reduction in number of microorganism and deceleration of organic matter cycling (Sollins et al., 1996). In the present study, unlike well-developed middle- and lower-slope profiles, the upper-slope had higher organic carbon content and C:N ratio due to low degradation degree of organic matter, originating from decomposition of surface plant residues.

Aggregate stability is used as an indicator of soil structure (Six *et al.*, 2000). However, aggregation is based on the composition of soil particle. The particle size distribution range of profiles differed significantly downhill (Table 1). Sand content ( $50\sim2000~\mu m$ ) in topsoil of each profile ranged from 51.1% on the upper slope to 2.82% on the lower slope, whereas clay content showed opposite trend (upper and lower slopes: 5.87% and 48.1%). In addition, silt content ( $2\sim50~\mu m$ ) range

slightly between 42.7% and 55.8%. From topsoil downwards, sand content increased in profile on the upper slope, and that of clay sand silt content decreased. Besides, clay and silt dominated the soil profile on the middle and lower slopes, whereas sand only accounted for 6.3% and 2.8%, respectively. It has been reported that variability of particles in hillslope soil profile is mainly attributed to microtopography, soil erosion and soil development (Honeycutt et al., 1990; Norton et al., 2003). High sand content in soil profile on the upper slope mainly results due to accumulation of weathered bedrocks, dominant herb vegetation, as well as vulnerability of surface to weathering and that of fine particles to erosion. However, the profiles on the middle and lower slopes were shielded from the clay soil and surface vegetation.

As exhibited in Fig. 2, the average organic carbon content of sand (50~2000 μm) was highest followed by silt (2~50 μm) and clay (<2 µm). Accumulation of newly input C was emphasized in light and sand fractions (Shang and Tiessen, 2000; Li et al., 2005; Lima et al., 2006). By calculating the proportion of organic carbon in each particle fraction can imply the enrichment degree (Garten et al., 1999). Fig. 3 shows that sand accounted for over 50% of organic carbon in soil profile on the upper slope, while silt and clay dominated on downslopes. We commonly ascribe particulate organic carbon (POC) to highly humified and sand-binding (<0.05 mm) organic carbon, which was unprotected and subject to erosion. On contrary the organic carbon binding silt and clay was relatively stable (Galantini et al., 2000; Jia et al., 2006; Li et al., 2006). Therefore, organic matter was rapidly accumulated on the upslope soil, allowing the obvious increase in organic carbon, which was however easy-to-lost in sand soil. On the contrary, organic carbon in downslope soil profile was more stable than that

Table 1: Properties of soil profile at different slope positions in study area

Geographical positions  Upperslope	Soil depth (cm)	<b>pH</b> 7.5	SOC C:N (g kg <sup>-1</sup> ) ratio		Particle size								
					sand (53~2000 μm) (%) SOC / (g kg <sup>-1</sup> ) C:N			silt (2~53 μm) (%) SOC / (g kg <sup>-1</sup> ) C:N			clay (<2 μm) (%) SOC / (g kg <sup>-1</sup> ) C:N		
				10-20	7.5	100.4	15.5	44.5	124.1	46.8	43.4	97.6	27.9
	20-30	7.6	96.8	15.1	49.8	123.3	47.4	36.4	86.3	26.4	13.7	36.1	6.6
	30-40	7.7	83.9	14.3	50.3	107.8	41.1	35.9	77.8	21.8	14.8	34.5	6.4
Middle slope	0-10	7.1	62.8	11.5	6.3	98.1	15.4	55.8	77.9	12.2	37.6	31.3	6.8
	10-20	7.1	48.5	10.7	4.8	87.4	13.7	52.5	62.3	11.3	42.7	30.5	6.5
	20-30	7.2	37.8	10.5	3.9	66.2	13.2	49.1	47.8	9.74	46.8	27.5	6.2
	30-40	7.0	29.4	9.4	2.1	54.3	12.7	48.3	35.5	8.3	49.5	21.3	5.8
	40-50	7.3	25.8	8.6	2.7	38.2	10.3	46.9	32.7	8.1	50.3	19.7	5.7
	50-60	7.2	18.4	8.4	1.9	35.9	9.9	42.4	27.9	7.3	55.6	12.6	6.1
Lowerslope	0-10	6.9	44.3	11.4	2.8	65.1	10.2	48.7	51.6	10.8	48.4	34.4	6.7
	10-20	7.0	34.7	11.3	2.6	58.7	9.6	46.2	47.4	11.7	52.1	22.3	7.1
	20-30	7.1	29.1	9.1	2.3	42.9	8.8	42.1	41.1	9.4	54.5	19.7	7.2
	30-40	7.1	24.5	8.8	2.1	35.3	6.4	39.4	37.4	10.1	58.4	16.3	6.4
	40-50	7.0	16.8	7.7	1.8	20.3	5.7	31.9	19.9	9.4	66.2	14.9	6.1
	50-60	7.2	13.6	7.4	1.2	22.1	5.2	21.1	16.3	8.4	77.6	12.8	5.8

**724** T. Liu et al.

on the upslope due to stable clay and silt therein despite of lower organic carbon contents.

The C:N ratio of soil organic matter, which indicates nutritional balance between C and N, generally decreases with

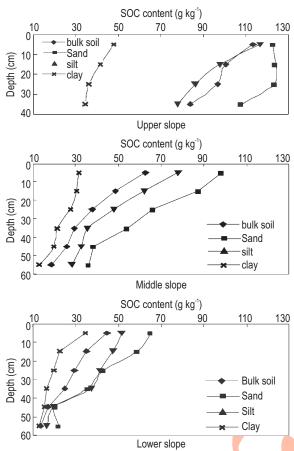


Fig. 2: Variation of SOC in each soil profile with depth

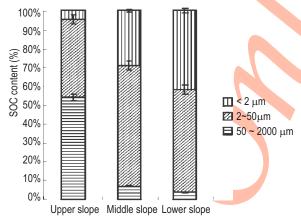


Fig. 3: Proportion of organic carbon of different fraction in soil profiles

enhancing decomposition. The C:N ratio of particle-size fractions followed descending order of clay>silt>sand (Table 1), suggesting that soil organic matter was less prone to decomposition with reducing particle size. Nevertheless, dependence of C:N ratio on profile depth differed remarkably in three particles. The C:N ratio of clay fluctuated minimally on each profile and at each depth because they were of low size, high adsorption ability, tight binding and little air contact for microbial decomposition, thereby stabilizing the organic matter more effectively (Tom et al., 1997). The results suggest that soil organic matter of clay was decomposed into stable humified compounds. Differently, the C:N ratio of clay and silt on the upper-slope profile raised with increasing depth, which could essentially be attributed to more fresh organic matter input by soil below profile due to late deposited organic matter, thin soil layers, entrance of surface litters and numerous dead plant roots and particularly augmented herbs roots. Reduction of C:N ratio on the middle and lower slopes, along the profile downwards, can mainly be ascribed to appropriate development, thick soil layers and thorough decomposition of organic matter.

The mechanism by which isotopic fractionation occurs during photosynthesis in plant is well known and  $^{13}$ C value of plant biomass and its degradation products of two plants ( $C_3$ ,  $C_4$ ) differ. In  $C_3$  plants photosynthesis has average  $\delta^{13}$ C value of about - 27‰, while in  $C_4$  plants photosynthesis show higher average  $\delta^{13}$ C value of about - 13‰ (Farquhar *et al.*, 1989; Boutton *et al.*, 1998).

As shown in Fig 4, the organic carbon δ<sup>13</sup>C values in topsoil of all profiles lowered downhill from -14.2% to -20.7%. The upslope was covered by C<sub>4</sub> herbs, while the downslope was covered by mixed C<sub>4</sub> herbs and C<sub>3</sub> shrubs, indicating that the changes of δ<sup>13</sup>C were closely associated with vegetation succession. The  $\delta^{13}$ C values on the upper layer soil at the upper, middle and lower slopes all rose and then decreased by 3.3%, 3% and 2.6%, respectively, which mainly resulted from differed decomposition of organic matter in soil and highly mixed vegetation. Commonly, well-drained topsoil managed to drastically elevate initial δ<sup>13</sup>C value of litters by 1‰-2‰. However, the δ<sup>13</sup>C value can only be elevated by over 3% via input of organic matter stemming from mixed C<sub>3</sub> and C<sub>4</sub> plants rather than fractionation of intrinsic carbon isotope (1%-3%) (Farquhar et al., 1989; Boutton et al., 1998; Buchmann et al., 1997). Moreover, the δ<sup>13</sup>C values of organic matter in various soil profiles also increased differently and peaked at different positions. The δ<sup>13</sup>C values of organic matter on the upper and middle slopes peaked at 10-20 cm, whereas that on the lower slope peaked at 20-30 cm. The results are related with selective absorption of microorganisms at threshold of organic matte input (Krull et al., 2002; Zhu et al., 2007). The lower position of maximum  $\delta^{13}$ C value on lower slope may be attributed to decelerated organic matter decomposition due to protection of carbon isotope from fractionation by highly contented clays (Powers et al., 2002; Chen et al., 2005). The δ<sup>13</sup>C values showed subtle decrease in deeper

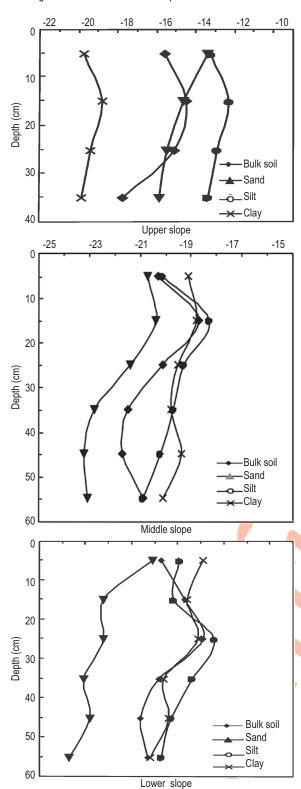


Fig. 4: Variation of  $\delta^{13}$ C value with depth in each soil profile

soil layer on the middle- and lower-slope positions. Which may be attributed to surface vegetation transition or soil-forming environmental alterations. The results also indicated similar origin of organic matter in previously deposited soil and slight variation in surface vegetation.

Fig 4 shows δ<sup>13</sup>C values of sand fluctuation in different soil profiles, which were -13.1% and -21.1% on the upper- and lowerslope surfaces in accordance with vegetation changes. The δ<sup>13</sup>C values of sand decreased sharply with increasing depth (upper slope: 2.5%; middle slope: 2.8%; lower slope: 3.8%), which may be relevant to considerably mixed growing C<sub>3</sub> and C<sub>4</sub> plants, complex resources of soil organic matter and selective utilization of microorganisms in the midst of decomposition (Ehleringer et al., 2000). Besides, the  $\delta^{13}$ C values of sand were obviously higher than those of other particles on the middle and lower slopes probably due to differed decomposition-resisting capabilities of plant residues entering soils. For example, Wedin et al. (1995) found that wood fiber organisms decomposed more slowly in soil than non-wood-fiber ones, thus leading to more negative δ<sup>13</sup>C values of the former. Lesser fluctuation of clay δ<sup>13</sup>C values than those of sand and silt ones are essentially ascribed to effectively hindered carbon isotope fractionation resulting from augmented organic matter humification and decomposition-resisting ability (Chen et al., 2005; Bird et al., 2003). Notably, the  $\delta^{13}$ C values of clay on the upper slope were remarkably negative than those of bulk soil and other particles. The upper-slope profile is an accumulative one aged younger, which failed to reserve organic matter and decelerate decomposition due to resultant low clay content.

Thus it can be concluded, vegetation recovery allowed increase in SOC of degraded hillslope in karst area. Although higher content of organic carbon was discerned in most severely eroded upslope soil, and was unstably stored as coarse particle organic matter. The  $\delta^{13}C$  values of sand revealed that input organic matter decomposed slowly or got deposited merely for a short time period, while those of silts and clays indicate more thorough decomposition of organic matter. In other words,  $\delta^{13}C$  values can accurately evaluate the decomposition rate and degree of organic matter in soils. However, studies on  $\delta^{13}C$  values and prone to surface vegetation types, soil-forming environments and etc., needs to be investigated.

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