Short Communication δ¹³C Characteristics of Soil Organic Carbon in Hilly Karst Area

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Abstract

To understand the effects of geomorphology and environment on the ¹³C character of soil organic carbon (SOC) in a hilly karst area, 26 soil samples were collected in 2008 in Nanchuan, Chongqing, SW China. The results showed that the δ^{13} C-SOC values were between -18.66‰~-27.41‰, with the mean value of -23.3‰. The data firmly indicated that the modern soil organic carbon was the mixture of C3 and C4 plants and mainly originated from C3 plants rather than C4 plants. According to the sequence of δ^{13} C-SOC along the geomorphological change at this hilly karst area, it can be seen that the δ^{13} C-SOC values was the crest > brae > foot. Based on the results of correlation analysis, the positive correlation between the δ^{13} C-SOC values and their altitude is 0.432 (p=0.028), which reflects the land/soil degradation effects caused by the hilly geomorphology, especially in the water and soil erosion process.

Keywords: SOC, stable carbon isotope, karst area, geomorphological effect, Nanchuan Chongqing

Introduction

Heterogeneous soil organic carbon (SOC) plays an important role in soil structure and soil nutrients [1-3], which can be crucial indices of soil fertility and environmental quality [4]. The buried SOC is concerned with multitudinal processes that can potentially promote the δ value away from the original value reflecting the environmental effect [5, 6]. Therefore, SOC from a different site typically has a special δ^{13} C value that changes with environmental conditions [7]. Though the δ^{13} C values of SOC may undergo changes spatially [8], the C isotope variations are not large enough to mask the difference between the C3 and C4

plants ($\delta\Delta \sim 14\%$) [9, 10]. The δ^{13} C value of SOC as the important and powerful method was used to trace the biogeochemical process in the soil. The δ signature can document the shifts in community composition and distribution, the changes in ecosystem dynamics, the vegetation composition and structure, and C cycles along a gradient of precipitation while minimizing confounding effects of soil heterogeneity [7].

In the past, although characteristics of the distributions of soil organic carbon and their main components in the karst area have been discussed, there has been little study of the relationship between spatial δ^{13} C distribution characteristics of soil organic carbon and geomorphological effect [8, 11]. Moreover, in southwest China the karst ecosystem is fragile and the rock desertification is serious under the

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impact of anthropogenic activities, which leads to land/soil degradation resulting from soil and water erosion [12]. The purpose of this ongoing work focuses on the geomorphological effect and the δ^{13} C-SOC response to environmental changes, especially in the land/soil degradation karst region. Therefore, the distribution and equilibrium fractionation of δ^{13} C-SOC was discussed to reveal its geomorphological effect and their inner relationship in a hilly karst area in southwest China.

Materials and Methods

Description of Study Area

Nanping town (106°56'15"-107°0'30" E, 29°05'30"-29°0'10" N) is located in southwestern Nanchuan county, Chongqing province with an area of 10 km². The study area is characterized with a humid subtropical monsoon climate. Seasons alternate between humid springs, scorching summers with intense rainfall, dry autumns, and cold humid winters. The mean annual temperature is about 16°C and the average annual precipitation is 1,300 mm. The average annual sunshine is 1,273 h and global solar radiation is about 334,614 J/sq. The frost-free period is about 310 days. The rocky desertification at this site is very serious with a 34% soil erosion area [13]. The local people have to depend on rainfall for drinking and living due to the deep buried groundwater and the developed karst fracture [14]. Under bad conditions crops are irrigated by natural rainfall. The local people are almost under the living standard.

As a representative agriculture and rocky desertification county in a hilly karst area in China, more than 80% of the total area of Nanping town is used as cultivated land. The current fertilization and management style have prevailed for more than 50 years. In this area, single crops were replanted annually with continuous spring maize and sweet potatoes as the prevailing cropping system.

Soil Sample and Analysis of δ^{13} C-SOC

Soil samples were collected from Nanping using a push probe at $5 \sim 10$ cm from the surface layer to a depth of 20 cm,

which were mixed together. 26 samples at different topographic positions were collected randomly in 2008 (Fig. 1). Inorganic carbon-free samples (samples for δ^{13} C-SOC analysis were treated with 1mol·L⁻¹ HCl at 25°C for three days to remove carbonate C) were dispatched to Finnigan MAT DELTAPLUSXL isotopic ratio spectrometer (Bermen, Germany) under EAMS (element analyzer and mass spectrometer) conditions. The interface between the element analysis meter and the spectrometer is Conflow III (continuous flow III). Operation condition: oxidizing furnace temperature is 900°C, reducing furnace is 680°C, pillar temperature is 40°C. Standards consist of the Peedee Belemnite (PDB) formation from the institute of karst geology, CAGS, China. The results are expressed in δ^{13} C relative to the PDB standard in the conventional δ per mil notation as follows [15].

$$\delta^{13}C = [({}^{13}C/{}^{12}C)_{s}/({}^{13}C/{}^{12}C)_{sta} - 1] \times 1000$$

...where ${}^{13}C/{}^{12}C$ are the isotopic ratios of samples and PDB standard (sta). The overall (sample preparation plus analysis) analytical precision is $\pm 0.2\%$.

The Calculation of Percentages (%) from SOC₃ and SOC₄

Calculation is based on the following equation:

$$\delta = \delta_1 f + (1 - f) \delta_0$$

...where δ is the δ value of the soil, δ_1 is the δ value of the material derived from C4 plants (average δ^{13} C values of C4 plant is -12.5‰), δ_0 is the δ value of the material derived from C3 plants (average δ^{13} C values of C3 plant is -26.5‰), and f is the percentage of C4 plants as carbon source to soil organic carbon [16].

Statistical and Geostatistical Analysis

A semi-variogram is generated using the geostatistical method to quantify the spatial variation of a regionalized variable, which provides the input parameters for the spa-



Fig. 1. Sampling sites and numbers in Nanping town.

Table 1. The δ^{13} C values of or	rganic matter and the perc	centage of soil organic	carbon derived from C	C4 plants at Nanping town.
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Sample No.	Sample-feature	δ ¹³ C (PDB)‰	Altitude (m)	C3 plant (%)	C4 plant (%)
1	Pinewood field	-20.89	688.66	59.89	40.11
2	Camphor field	-23.27	702.88	76.87	23.13
3	Corn field	-19.66	738.97	51.11	48.89
4	Pricklyash peel field	-22.63	738.59	72.31	27.69
5	Jiufengyihao field	-22.75	735.2	73.16	26.84
6	Grassland	-18.66	740.66	43.97	56.03
7	Jackfruit field	-23.61	735.23	79.30	20.70
8	Lily magnolia field	-23.44	739.69	78.09	21.91
9	Jinfengyihao field	-23.14	724.94	75.95	24.05
10	Camphor field	-23.72	731.74	80.09	19.91
11	Lonicera macranthoides HandMazz. field	-23.85	733.85	81.01	18.99
12	Camphor	-24.24	708.82	83.80	16.20
15	Fructus evodiae field	-25.11	687.42	90.01	9.99
16	Wasteland	-21.52	671.21	64.38	35.62
17	Rice field	-22.83	682.11	73.73	26.27
18	Shrubbery	-23.02	716.32	75.09	24.91
19	Artificial reconstruct field	-27.41	663.85	106.42	-6.42
20	Rice field	-22.16	713.89	68.95	31.05
21	Pine field	-21.59	726.25	64.88	35.12
22	Grassland	-24.32	723.22	84.37	15.63
23	Forest field	-25.19	739.87	90.58	9.42
24	Artificial reconstruct field	-25.71	659.03	94.29	5.71
25	Rock desertification	-23.78	735.26	80.51	19.49
26	Cypress field	-23.83	676.24	80.87	19.13
27	Pricklyash peel field	-23.59	735.22	79.16	20.84
28	Grassland	-26.06	651.28	96.79	3.21
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tial interpolation method of kriging [17]. Kriging is chosen because it provides information about the spatial structure as well as the input parameters. In general, it provides a theoretical weighted moving average of the input parameter over the distance between sampling sites (lag distance).

Geostatistical analysis is carried out using GS+ (5.1), and the map of δ^{13} C-SOC spatial distribution pattern is produced by using the Arcview (5.3) and its extension module of spatial analysis (version 2.0).

Correlation analyses are done using the Pearson correlation method with significance defined at P<0.05. Statistical analysis is performed using SPSS 13.0 software for Windows XP.

Results and Discussion

The δ^{13} C of Soil Organic Carbon

In our study area, the δ^{13} C-SOC is in the range of -18.66‰~-27.41‰, with the mean value of -23.3‰ (Table 1). In sample 3, as a 50-year maize field, the δ^{13} C-SOC is much lower than that of 18-year-old maize soil, which ranged from -13.2‰ to -14.2‰ [18].

The δ^{13} C technique to determine the sources of SOC was based on the difference in isotopic ¹³C signatures of C4 plants and C3 plants during photosynthesis [5, 19]. The δ^{13} C values from plants with C3 photosynthesis such as wheat typically range from -40 to -23‰ with a mean of -26.5‰,



Fig. 2. Spatial distribution of δ^{13} C-SOC at Nanping town

while δ^{13} C values with C4 photosynthesis such as maize range from -19 to -9‰, with a mean of -12.5‰ [16, 19]. When vegetation becomes compositionally stable for a long time, the δ^{13} C values of SOC in the plough layer (0-20 cm) can approach the values of the plant community [20, 21], because only slight isotope fractionation may occur during early stages of organic matter decomposition in soils [22]. According to the δ^{13} C-derived data of No. 3, it can be inferred that the SOC sample of No. 3 was the mixture of C3 and C4 withered vegetation (the mixed organic matter from spring maize and sweet potato) and had the light δ^{13} C-SOC value.

Percentages (%) of SOC₃ and SOC₄

Based on the calculated percentage of soil organic carbon derived from C4 plants, no more than 50% carbon from C4 sources would be incorporated into the modern organic carbon pool, respectively (Table 1). Though the prevailing cropping system is spring maize, the data firmly indicated that modern soil organic carbon mainly originated from C3 plants rather than C4 plants, as revealed by the percentage of soil organic carbon.

As to sample 19, the result can't be explained by the inner interaction of soil respiration, microorganism respiration, and mineralization of the soil. By comparing the altitudes of sample 16, 19, and 25, it can be found that sample 19 was just at the sunken place. The soil with δ^{12} C will be accumulated at this site, especially during the land/soil degradation process from the strong water and soil erosion. Most of SOC_{4 plant} disappeared from the high site during the storm period accompanied by water and soil erosion [10, 23]. So the percentage of soil organic carbon derived from C4 plants in No. 19 has a negative result. Moreover, the result also indicate that the strong interaction between hydrology, plant community characteristics, topographic position, and soil texture may be other important factors to affect the δ^{13} C-SOC values.

Geomorphological Effects

According to previous studies [6, 8, 23], soil organic carbon from vegetation changes in the surface soil with good drainage, usually shows 1‰~2‰ of the rapid increase[16, 24]. Soil carbon isotopic fractionation inherent

in the process can only make the soil δ^{13} C values ranged in between 1‰~3‰ [21]. If the $\Delta\delta$ exceeds 3‰, the input of organic matter in soil is from the mixture of C3 and C4 plants [7, 21]. By comparing the δ^{13} C-SOC values, it can be seen that the sequence of δ^{13} C-SOC is crest > brae > foot in the study area with the range between -18.66‰~-27.41‰ and the $\Delta\delta$ exceeds 3‰ (Table 1 and Fig. 2). In order to evaluate geomorphological effects during the land/soil degradation process to δ^{13} C-SOC, the correlative coefficient between the δ^{13} C-SOC values and the altitude is calculated. The positive correlation ratio is 0.432 (p=0.028).

The δ^{13} C decreased from the high place to the low site, along the topographic positions which reflected the land use type with the low land-cover, the single species, and the low metabolism rate [13]. Under the impact of anthropogenic activities, the rocky desertification area has the serious problem of water and soil erosion, which can accumulate the SOC with the δ^{12} C at the low-lying site [8]. So, the δ^{13} C-SOC is different from the routine results. From the primary results, it can be found that when the δ^{13} C-SOC was used to indicate the environmental conditions, the land/soil degradation process with water and soil erosion and the mixture of C3 and C4 plants can't be ignored, which can produce the complex results. Considering the carbon isotope fractionation relating to the soil environment and the plant community characteristics, more investigation must be enforced in the future to explain the spatial structure of variables related to soil carbon cycling, which can provide new perspectives to guide the relationship of soil erosion and rocky desertification [20].

Conclusions

According to the data from this hilly karst area, it can be found that δ^{13} C-SOC values are between -18.66‰~-27.41‰, with the mean value of -23.3 ‰.The change in δ^{13} C of soil organic carbon reflected that the SOC was the intermixture of the C3 and C4 plants with their typical δ^{13} C values. The sequence of δ^{13} C-SOC derives from crest > brae > foot with positive correlation between the δ^{13} C-SOC values and their altitude results (r=0.432, p=0.028), which reflects the geomorphological effects during the land/soil degradation process. The δ^{12} C-SOC will be transferred along the landform conditions and accumulated at the depression site, especially in the storm period in a hilly karst area. So in the future, if the δ^{13} C values in soil organic carbon were used to trace the biogeochemical process in a hilly karst area, the mixture condition of C3 and C4 plants and geomorphological effects must be taken into account.

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References

- ESWARAN H., VANDENBERG E., REICH P. Organic C in soils of the world. Soil Sci. Soc. Am. J. 57, 192, 1993.
- BLANCO-CANQUI H. and LAL R. Soil structure and organic carbon relationships following 10 years of wheat straw management in no-till. Soil Till. Res. 95, (1-2), 240, 2007.
- ANDRE B., JOB K., BERNARD V., BOAZ W., JOSEPH K. Soil organic carbon dynamics, functions and management in West African agro-ecosystems. Agr. Syst. 94, (1), 13, 2007.
- WANG L.X., GREGORY O., KELLY C.C., STEPHEN A.M. Spatial heterogeneity and sources of soil carbon in southern African savannas. Geoderma. 149, (3-4), 402, 2009.
- BAI E., BOUTTON T.W., WU X.B., LIU F., ARCHER S.T. Landscape-scale vegetation dynamics inferred from spatial patterns of soil δ¹³C in a subtropical savanna parkland. J. Geophys. Res. 114, (G01019), 1, 2009.
- KRULL E.S., BESTLAND E.A., GATES W.P. Soil organic matter decomposition and turnover in a tropical Ultisol: evidence from δ¹³C, δ¹⁵N and geochemistry. Radiocabon. 44, (1), 93, 2002.
- WANG G., FENG X., HAN J., ZHOU L., TAN W., SU F. Paleovegetation reconstruction using δ¹³C of soil organic matter. Biogeosciences. 5, 1325, 2008.
- LIU T. Z., LIU C. Q., ZHANG W. Spatial distribution characteristics of soil organic carbon and difference in stable carbon isotope composition in slopes of karst areas. J. Soil Water Conserv. 22, (5), 115, 2008.
- MARIE B. Detection of dietary changes by intra-tooth carbon and nitrogen isotopic analysis: An experimental study of dentine collagen of Cattle (Bos taurus). J. Archaeo. Sci. 28, 235, 2001.
- RAO Z.G, CHEN F.H., ZHANG X., XU Y.B., XUE Q., ZHANG P.Y. Spatial and temporal variations of C3/C4 rela-

tive abundance in global terrestrial ecosystem since the last glacial and its possible driving mechanisms. Chinese Science Bulletin. **57**, (31), 4024, **2012**.

- LI L.B., LIU T.A., LI X.D., LIU W.J., LIU C.Q. Vertical distribution patterns of organic carbon and its isotopic composition in typical soil types in Guizhou karst areas of Southwest China. Chinese J. Ecol. 31, (2), 241, 2012 [In Chinese with English abstract].
- 12. YUAN D.X. On the karst ecosystem. Acta Geologica Sinica. **75**, (3), 336, **2001**.
- WEI X.P., YUAN D.X., XIE S.Y. Relationship between soil erosion and rocky desertification in Southwest China karst region – A case in Nanchuan karst area, Chongqing. Carsologica Sinica. 29, (1), 20, 2010 [In Chinese with English abstract].
- LI Q., LIANG J.H., HE Y.Y., HU Q.J., YU S. Effect of land use on soil enzyme activities at karst area in Nanchuan, Chongqing, Southwest China. Plant Soil Environ. 60, (1), 15, 2014.
- CAO J.H., SONG L.H., JIANG G.H., XIE Y.Q., YOU S.Y. Diurnal Dynamics of Soil Respiration and Carbon Stable Isotope in Lunan Stone Forest, Yunnan Province. Carsologica Sinica. 24, (1), 27, 2005 [In Chinese with English abstract].
- DIELS J., VANLAUWE B., SANGINGA N., COOLEN E., MERCKX R. Temporal variations in plant δ¹³C values and implications for using the δ¹³C technique in long-term soil organic matter studies. Soil Biol. Biochem. 33, (9), 1245, 2001.
- ZHANG C., LI Z., GU M., DENG C., LIU M., LI L. Spatial and vertical distribution and pollution assessment of soil fluorine in a lead-zinc mining area in the Karst region of Guangxi, China. Plant Soil Environ. 56, (6), 282, 2010.
- CHRISTENSEN B.T., OLESEN J.E., HANSEN E.M. Annual variation in δ¹³C values of maize and wheat: Effect on estimates of decadal scale soil carbon turnover. Soil Biol. Biochem. 43, (9), 1961, 2011.
- WITTMER M., AUERSWALD K., BAI Y.F., SCHAUFELE R., SCHNYDER H., AUERSWALD K. Changes in the abundance of C3/C4 species of Inner Mongolia grassland: evidence from isotopic composition of soil and vegetation. Global Change Biol. 16, (2), 605, 2010.
- TODD E.D., STEFANIA M., AGNETA H.P., PAMELA H.T., KEVIN P.T. Stable isotopes in plant ecology. Annu. Rev. Ecol. Syst. 33, 507, 2002.
- STILL C.J., BERRY J.A., COLLATZ G.J., DEFRIES R.S. Global distribution of C3 and C4 vegetation: carbon cycle implications. Global Biogeochem. Cy. 17, (1), 1006, 2003.
- 22. BIRD M.I., VEENENDAAL E.M., LLOYD J.J. Soil carbon inventories and δ^{13} C along a moisture gradient in Botswana. Global Change Biol. **10**, (3), 342, **2004**.
- CHEN Q.Q., SHEN C.D., SUN Y.M., PENG S.L., YI W.X., LI Z.A., JIANG M.T. Spatial and temporal distribution of carbon isotopes in soil organic matter at the Dinghushan Biosphere Reserve, South China. Plant Soil. 273, (1-2), 115, 2005.
- SUN Z.G., MOU X.J., LI X.H., WANG L.L., SONG H.L., JIANG H.H. Application of stable isotope techniques in studies of carbon and nitrogen biogeochemical cycles of ecosystem. Chinese Geogr. Sci. 21, (2), 129, 2011.