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Carbon sequestration potential and its eco-service function in the karst area, China

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Abstract: The karst critical zone is an essential component of the carbon (C) pool, constituting the global C cycle. It is referred to as one of the "residual land sink" that remains largely indeterminate. Karst area (2.2×10^7 km^2) comprises 15% of the world's land area, and karst area comprises 3.44×10^6 km^2 of area in China. Due to the complexity of karst structure and its considerable heterogeneity, C sequestration rate estimations contain large inaccuracies, especially in relation to the different methods used in calculations. Therefore, we reevaluated rock weathering-related C sink estimations in China (approximately 4.74 Tg C yr^{-1}), which we calibrated from previous studies. Additionally, we stipulated that more comprehensive research on rock-soil-biology-atmosphere continuum C migration is essential to better understand C conversion mechanisms based on uncertainty analyses of C sink estimations. Moreover, we stressed that a collective confirmation of chemical methods and simulated models through a combined research effort could at least partially eliminate such uncertainty. Furthermore, integrated C cycling research need a long-term observation of the carbon flux of multi-interfaces. The enhanced capacity of ecosystem C and soil C pools remains an effective way of increasing C sink. Karst ecosystem health and security is crucial to human social development, accordingly, it is critical that we understand thresholds or potential C sink capacities in karst critical zones now and in the future.

Keywords: karst; karst critical zone; carbon sink; carbon sequestration rate; China

1 Introduction

Carbon (C) is the core element in ecosystem matter and energy cycling, and C cycle is a key driving factor of global climate change. The World Climate Research Programme (WCRP), the Global Climate Project (GCP), and the International Geosphere-Biosphere Programme (IGBP) have greatly contributed to the evaluation of the global C cycle. Now, greater atten-

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tion is being paid to research on regional C sources and sinks and national C balances and their effect on global climate change (Pan *et al*., 2011; Gao *et al*., 2016). Uncertainty in the capacity of C sinks within the global C cycle is from 2 to 4 Pg C yr^{-1}, but these estimations have not considered all the C sources and sinks related to soil erosion and land-use changes (Schimel *et al*., 2001; Fang *et al*., 2004).

Global karst area is approximately 2.2×10^7 km^2, which is 15% of the planet's land area, and the "residual land sink" of C is 2.5 Pg C yr^{-1}, which was estimated by the Fifth Assessment Report (AR5) by the Intergovernmental Panel on Climate Change (IPCC) (Ciais *et al*., 2013; Pu *et al*., 2015). In contrast, net C uptake by terrestrial ecosystems is from 1.0 to 2.6 Pg C yr^{-1}, and the rock weathering C sink capacity is from 0.11 to 0.608 Pg C yr^{-1}, comprising from 4.4% to 24.3% of the residual land C sink (Liu and Zhao, 2000; Piao *et al*., 2009; Zhang, 2011). Karst processes do not only have a significant effect on terrestrial C uptake, but also have a strong effect on environmental quality and service functions of ecosystems on a regional scale (Piao *et al*., 2010; Jiang *et al*., 2013).

There has been profound discussion on how CO_3^{2-}-CO_2-H_2O mixed systems act as driving forces (e.g., pumps) in karst areas. The dynamic systems of karst areas are composed of this type of mixed system coupled with C cycling (Yuan and Zhang, 2008; Yan *et al*., 2011). Moreover, the capacity of karst areas to act as C sink is considered a significant factor for atmospheric carbon dioxide (CO_2) removal, and dissolved inorganic carbon (DIC) concentrations in karst water is a key parameter in C sink evaluations applying conventional methods (Liu, 2011a; Zhang, 2012).

The critical zone (CZ) concept put forward by the earth science community is highly consistent with ecosystem ecology (Richter and Billings, 2015). The CZ concept represents the complex interactions in the rock-soil-water-biology-atmosphere continuum within a heterogeneous soil surface environment, whose most intimate relationship with human survival determines resource allocation and social development demands (Lin, 2010). Furthermore, the CZ concept describes a vertical wholistic resource and environmental zone from the plant canopy to the bedrock aquifer. The concept of the karst CZ was put forward based on the strong consistency observed between ecosystems and the CZ to better understand the concept of "karstification" (Yuan, 2009). Not only does the coupling relationship between water, C, and nutrient cycling play a significant role in terrestrial ecosystems (Gao *et al*., 2013), but even greater relevant coupling relationships could occur within the karst CZ, which is widely believed to be an extremely unbalanced system.

A brief evaluation of karst distribution around the world has singled out the karst region of China for its significance, urgency, and enormous influence on sustainable agricultural development and ecological restoration. Accordingly, we amassed the numerous methods and models used in this research discipline to review C sink estimations and, by recalibrating previous estimations, provided a revaluation of the rock weathering C sink value in China. Following this, we discussed the key uncertainties according to the abundant available researches on integrated C cycling systems. Lastly, we provided scenarios related to potentially increasing C sink of the karst CZ in China.

2 Characteristics of geologic distribution and karst structure

Karst area is mainly distributed throughout East Asia, the Mediterranean coast, and the North American and Caribbean regions. However, between these three territories, karst area is concentrated mostly in East Asia (Durr *et al*., 2005). Karst area is approximately 344.7×10^4 km^2 and bare carbonate distribution area is 90.7×10^4 km^2, which comprises more than one-third and one-seventh of territorial area in China, respectively (Luo *et al*., 2014; Song *et al*., 2016). The southwestern karst zone of China is one of the most concentrated karst areas in the world, which primarily includes the provinces of Guizhou, Yunnan, and the Guangxi Zhuang Autonomous Region.

Multiple zoning methods are used to designate different karst areas in China, which are dependent on different factors. For example, tropical humid karst, subtropical humid karst, subtropical semi-humid karst, temperate arid karst, and plateau cold karst have been subdivided according to weather conditions, while bare karst, soddy karst, and buried karst have been subdivided based on their rock outcrop formations (Figure 1) (Wang *et al*., 2005; Bai *et al*., 2009; Jiang *et al*., 2011).

Distinctive karst landforms were mainly created from the dissolution of carbonite, principally limestone and dolomite. In karst areas, soil is considered a non-renewable resource on account of its slow pedogenesis and strong soil erosion (Long *et al*., 2005). Moreover, karst aquifers are extremely vulnerable to contamination due to the highly heterogeneous and anisotropic character by their springs, caves, and sinkholes. Weathered layers and corroded soil that result from the hydrological dynamic systems of karst formations exhibit discontinuous distribution characteristics in both vertical and horizontal horizons, which can also be described as soil mosaic distributions and rock outcrops. Subsurface flow moves rapidly due to highly developed underground conduits, and surface runoff coefficients are very low. On the whole, the soil structure and hydrological characteristics of the epikarst is defined as a three-dimensional dualistic structure (Figure 2).

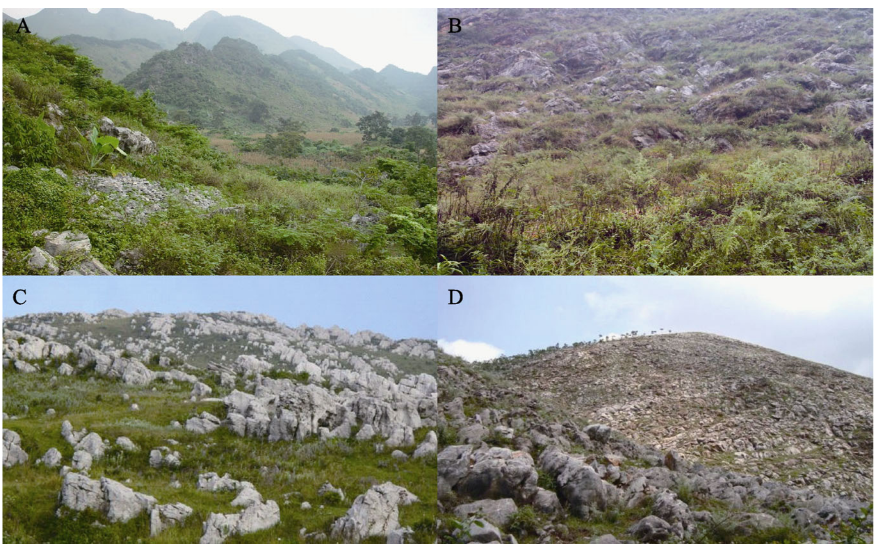


Figure 1 Different erosion degrees of karst topography

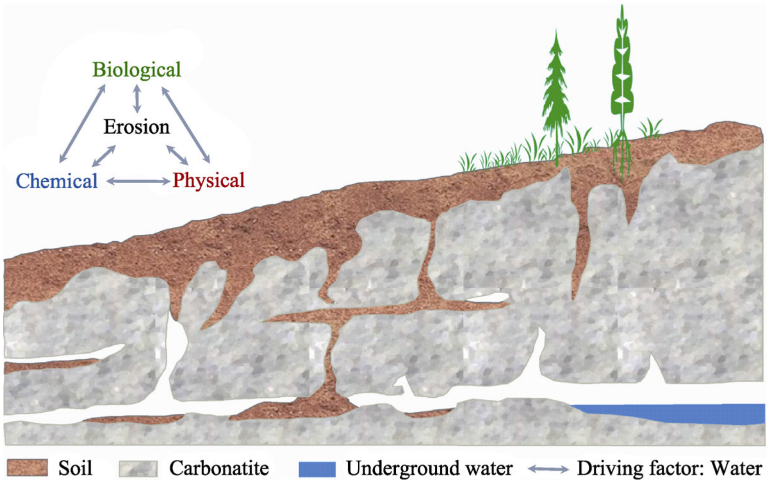


Figure 2 Karst structure controlled by soil erosion and rock weathering

3 Estimating rock-weathering carbon sink

3.1 Estimated methods

The C sequestration rate is a parameter used in C sink evaluations; however, various calculation methods are used and significant uncertainties remained. The reverse approach and forward modeling are two popular C sink estimation methods used in karst areas. Estimations using the reverse approach are suitable for small watersheds where rock types are clearly known, and hydrochemical relationships between river and rock weathering products are conducted on the basis (Hartmann, 2009). Forward modeling derives from the Temperate Stream Model, which is based on relationships between rock types, rock-weathering rates, and runoff effects (Meybeck, 1987; Suchet and Probst, 1993; Suchet and Probst, 1995; Velbel and Price, 2007). According to numerous studies, the following equation expresses an existing global empirical model on C uptake rates:

$$F_1 = a\sum_{n-1}^{12}(q_s + q_u) \tag{1}$$

where F_1 represents C sequestration in a karst area; q_s and q_u represent the monthly mean flux of surface water and underground water, respectively; a is the empirical parameter dependent on the rock type; and a is 0.0294 g C mm^{-1}, estimated by Bluth (Bluth and Kump, 1994), and 0.0383 g C mm^{-1}, estimated by Suchet (Suchet and Probst, 1993). By applying this empirical equation to the Houzhai River basin in southwest China, Yan *et al*. (2011) estimated the value of C sequestration at 22.3 g C m^{-2} yr^{-1} and 29.0 g C m^{-2} yr^{-1}, respectively (Yan *et al*., 2011). This result is inconsistent with other estimated values, primarily because both parameters lack data support in China.

Popular methods used in China are the solute load method, the carbonate-rock-tablet test, the diffusion boundary layer (DBL) theory, model simulations, and the inverse modeling method as well as other methods that derive from the above methods (Liu and Zhao, 2000; Liu *et al*., 2010; Liu, 2011b; Yan *et al*., 2011). The solute load method is suitable for C sink estimations of closed and complete drainage basins on a macro scale. This method, however, demands a large amount of hydrochemical data and strict conditions. Nevertheless, mixed C forms can still be released from the Earth's interior as well as from exogenous acid effects (Lerman *et al.*, 2007; Gaillardet and Galy, 2008; Hurwitz *et al.*, 2010; Zhang and Li, 2012). Bicarbonate concentrations in surface runoff, groundwater, and water discharge are essential parameters used in estimating C sequestration rates. Moreover, new monitoring technologies, such as eddy covariance, remote sensing, stable isotope tracers, and GIS-based spatial analysis, are combined in global C cycling observation systems (Cao *et al.*, 2004; Yu *et al.*, 2011). The current challenge remains to combine observational data with multiple models for estimating or forecasting.

Chemical weathering reactions of limestone and dolomite differ as follows:

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^- \quad (2)$$

$$CaMg(CO_3)_2 + 2CO_2 + 2H_2O \rightleftharpoons Ca^{2+} + Mg^{2+} + 4HCO_3^- \quad (3)$$

The two chemical equations above show that 1 or 2 mols of CO_2 would be needed when 1 mol of $CaCO_3$ or $CaMg(CO_3)_2$ dissolved. Although the CO_2 required for rock weathering does not directly derive from the atmosphere (deriving partly from soil), rock weathering C uptake processes could still be considered an atmospheric CO_2 sink because the CO_2 released from the soil to the atmosphere will decrease in conjunction with C uptake rock weathering processes.

The following equation describes the solute load method:

$$F_2 = 0.5 \times c \times q \times \frac{M_c}{M_{HCO_3}} \quad (4)$$

where F_2 is the C sequestration rate; c is the HCO_3^-concentration in karst runoff; q is water discharge; M_c and M_{HCO_3} are the relative molecular mass of C and HCO_3^-, respectively. Yan (2011) calculated the C sequestration rate in the Houzhai River basin within the southwestern karst zone in China using this formula. The result, which derived from surface and subsurface water data from 1986 to 2007, was 20.7 g C m^{-2} yr^{-1}, being much higher than the 8.6 g C m^{-2} yr^{-1} estimated by Jiang (Jiang and Yuan, 1999; Liu and Zhao, 2000; Yan *et al.*, 2011).

The carbonate-rock-tablet test is suitable for karst areas where no carbonatite overlies soil. This mature method has been widely used for its simple operation and short duration period. At the same time, however, it has limitations, such as representativeness and scale conversions, and this is on account of the vast heterogeneity of karst soil and the diversity in runoff erosion (Liu, 2011b; Zeng *et al.*, 2014). All these issues could cause great differences in final estimations. One hydrologic year is generally required to test weight decreases in the tablet, which is the key information required to calculate C sequestration.

$$F = 365 \times 10^4 \times (W_1 - W_2) \times R \times \frac{M_c}{M_{CaCO_3} ST} \quad (5)$$

where F is the C sequestration rate (g C m^{-2} yr^{-1}); $W_1 - W_2$ is the absolute quality of carbonatite corrosion (g); R is the relative content percentage of $CaCO_3$ in the tablet; S is the superficial area of the tablet (cm^2); T is burial time (d). Using this method, Zhang *et al.* determined the sequestration rate in an order of magnitude from farmland>woodland> cultivated land>fallow land>bush fallow land (Zhang *et al.*, 2006).

3.2 Carbon sink evaluation in the karst zone, China

The global C sink is 0.8242 Pg C yr^{-1}, of which the net C sink is 0.7052 Pg C yr^{-1}, which was estimated by Liu *et al*., who took accounted of carbonatite weathering and aquatic organism (Liu *et al*., 2010). Using the multiple estimation method, the terrestrial ecosystem C sequestration rate was from 0.19 to 0.26 Pg C yr^{-1}, which converts to 0.26 Pg C yr^{-1} using the inverse modeling method (Piao *et al*., 2009). According to mean bicarbonate ion concentrations and runoff modulus, the C sink in the karst area of China is 10.09 Tg C yr^{-1}, estimated using the solute load method (Jiang *et al*., 2011). However, there exists some deviation in this estimation that must be recalculated (Zhang, 2012; Jiang *et al*., 2013). Jiang *et al*. (2013) divided China karst area into four regions, which were the southern karst region, the northern karst region, the Tibetan Plateau karst region, and the buried karst region, and their occupied areas were 5.648×10^5 km^2, 3.258×10^5 km^2, 5.560×10^5 km^2, and 2.001×10^6 km^2, respectively (Figure 3 and Table 1). We reevaluated C sink in the karst zone in China by remedying the data of the northern karst and buried karst regions, and we used a correction coefficient (a=0.65) to eliminate interference from sulfuric acid and nitric acid caused by carbonatite dissolution. As Tables 1 and 2 show, the total C sink in the karst zone of China is 4.74 Tg C yr^{-1}, which is roughly approximate with the estimation reported by Jiang (2013).

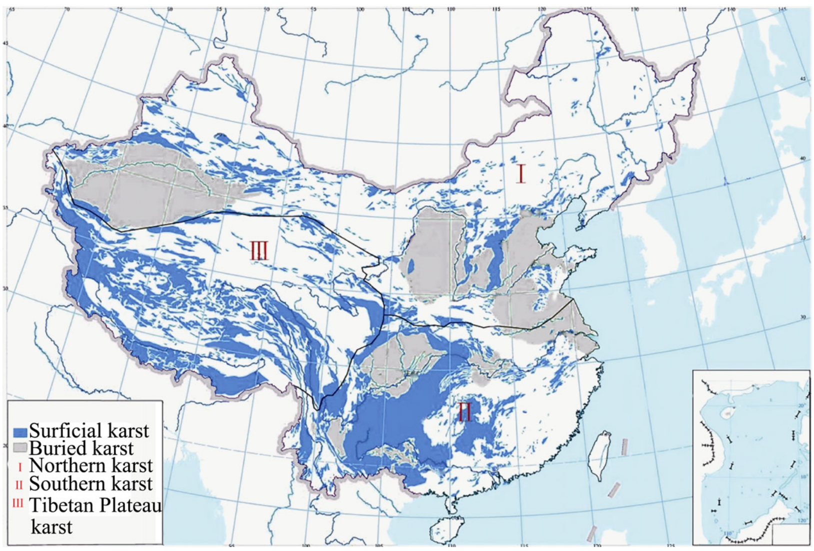


Figure 3 Regions divided of karst type in China

Table 1 CO_2 sink estimated result in each karst region, China

Karst regions	Area (10^4 km^2)	HCO_3^- (g L^{-1})	Runoff modulus (10^7 L km^{-2} yr^{-1})	Correction coefficient	CO_2 sink (10^4 t yr^{-1})
Southern karst	56.48	0.23	40.59	0.65	1241.5
Northern karst	32.58	0.25	6.31	0.65	118.1
Tibetan Plateau karst	55.60	0.15	19.95	0.65	377.0
Buried karst	200.01	0.23	0.01	0.65	1.1
Total	344.67				1737.6

Table 2 C sequestration rate of Chinese karst by using different methods

Estimation method	Study area*	Average C sequestration/ ($Tg C yr^{-1}$)	Global average C sequestration/ ($Pg C yr^{-1}$)	Data source
Solute load method	Bare karst in China	12	—	Yan *et al*., 2011
Solute load method	Bare karst in China	4.8	—	Jiang and Yuan, 1999
Carbonate-rock-tablet test	Bare karst in China	3.2	—	Jiang and Yuan, 1999
DBL theory (potential C sink)	China	64.2	0.41	Liu and Zhao, 2000
Solute load method	China	17.9	0.11	Liu and Zhao, 2000
Carbonate-rock-tablet test	China	17.5	0.11	Liu and Zhao, 2000
Carbonate-rock-tablet test	China	3.21	—	Jiang *et al*., 2013
Solute load method	China	4.84	—	Jiang *et al*., 2013
Simple accumulate method (By province)	China	5.07	—	Jiang *et al*., 2013
GIS-based carbonate-rock-tablet test	China	3.88	—	Jiang *et al*., 2013
$GEM-CO_2$ Model	China	14.1	—	Qiu *et al*., 2004
Solute load method	China	10.09	—	Li *et al*., 2014
Comprehensive method	—	—	0.7052	Liu *et al*., 2010
Solute load method	China	4.74	—	This research

*Bare karst area in China is 0.907×10^6 km^2; Total karst area in China is 3.44×10^6 km^2

3.3 Models used for C sink estimations

There are great differences in the mechanisms, operations, and purposes of terrestrial ecosystem models now. Given that few models have been specifically developed for karst areas, such models face significant challenges and uncertainty. Even the Community Land Model (CLM), one of the most highly developed terrestrial system models, established by the National Center for Atmospheric Research (NCAR) of the United States of America, performed poorly in Tibetan Plateau, China (Luo *et al*., 2013). Various types of models have been applied in China, such as the Atmosphere-Vegetation Interaction Model (AVIM2); the Carbon Exchange in the Vegetation-Soil-Atmosphere model (CEVSA); the Geoscience Knowledge Integration Protocol (GeoPro) based on C, nitrogen (N), and water coupling system; the Global Erosion Model for CO_2 fluxes model ($GEM-CO_2$) based on different weathering coefficients of rocks; the Global Production Efficiency Model (GLO-PEM), Carnegie-Ames-Stanford Approach (CASA), and GEOLUE models based on the efficiency of photosynthesis and autotrophic respiration; and the Terrestrial Ecosystem Model (TEM) based on eco-models (Suchet and Probst, 1993; Suchet and Probst, 1995; Qiu et al., 2004). Net primary productivity (NPP) of the Tibetan Plateau is 302.44 $Tg C yr^{-1}$, which was estimated using TEM (Zhou *et al*., 2004). The 50-year mean Net Ecosystem Productivity (NEP) of Guizhou Province, China, dominated by karst landforms under a semitropical climate, is 23.9 $g C m^{-2} yr^{-1}$, which was estimated using AVIM2 (Ma *et al*., 2013). Moreover, this result was roughly one-fifth of the non-karst area in the Qilian Mountains, Qinghai Province, China, which was also estimated using AVIM2. Additionally, $GEM-CO_2$ has been used to estimate rock weathering C sink in a karst region in China (Liu *et al*., 2015). Rock weathering C sink flux is 14.1 $Tg C yr^{-1}$ in China, which was estimated using $GEM-CO_2$, and contributions of carbonatite and silicate rocks were 52.65% and 47.35%, respectively (Qiu *et al*., 2004). However, there is much work to be done to increase model applicability in karst areas. The combination and mutual authentication of ecosystem C cycle models, regional scale inversion models, and remote sensing observation systems will provide strong support and greater accuracy in C sink estimations in karst areas. Discovering how to optimize terrestrial ecosystem models for application in karst ecosystems by adding correction coefficients or redefining model parameters would be a significant step forward.

4 Uncertainty analysis

4.1 Exogenous acids effect on carbonatite corrosions

Bicarbonate ions can be generated from reactions of nitric acid with carbonatite, and sulfuric acid with carbonatite as well (the exception of carbon acid). As a result, bicarbonate ion concentrations are rather high in karst water. As shown in Eqs. (6) and (7), neither atmospheric CO_2 nor soil participated in such reactions. Both the chemical mass balance model and stable isotope analysis confirmed that these processes had a nonnegligible effect on C sink estimations.

$$(Ca_{(1-x)}Mg_x)CO_3+HNO_3 \rightleftharpoons (1-x)Ca^{2+}+xMg^{2+}+NO_3^-+HCO_3^- \tag{6}$$

$$2(Ca_{(1-x)}Mg_x)CO_3+H_2SO_4 \rightleftharpoons 2(1-x)Ca^{2+}+2xMg^{2+}+SO_4^{2-}+2HCO_3^- \tag{7}$$

Yan (2011) found that Ca^{2+}, Mg^{2+}, HCO_3^-, and SO_4^{2-} accounted for 96% of the total dissolved solids, and the proportion of negative ions from SO_4^{2-} was second only to HCO_3^-. Moreover, SO_4^{2-} concentrations in water have a direct relationship with its contribution to rock weathering (Yan *et al*., 2011). Liu (2008) estimated that CO_2 released from sulfuric acid-driven carbonatite weathering in southwestern China was 4.4 Tg yr^{-1}; therefore, it was calculated that 28 Tg yr^{-1} was the CO_2 flux released from karst areas in China, which accounted for 33% of rock weathering C sink (Liu, 2008). On a smaller scale, results from an agriculture dominant karst catchment within the Qingmuguan subterranean watershed area in Chongqing City, China, showed that DIC produced by sulfuric and nitric acids accounted for 33.8% of the total DIC in subterranean water, which took up almost the same percentage (Zhang *et al*., 2012). Additionally, other carbonatite areas showed a slightly smaller influence from sulfuric and nitric acids. In the Yalong River, that drains into the eastern Tibetan Plateau, China, approximately 13% of DIC originated from sulfuric and nitric acid-driven carbonate weathering (Li *et al*., 2014). In another small drainage basin of the Qinhe River in northern China, CO_2 released from sulfuric acid-driven carbonate weathering was 0.63×10^5 mol km^{-2} yr^{-1}, which accounted for 44% of CO_2 released by carbonate weathering (Zhang *et al*., 2015). Thus, applying a 0.35 calibration factor is scientifically-based and appropriate for use in the above reevaluation.

Furthermore, water from non-karst catchments will also directly result in deviations in uncertainty during C sink evaluations. However, given that the dilution effect is difficult to quantify, this has seldom been considered before. Moreover, spatial scale conversions are one of the most difficult and recurrent problems which cause immeasurable uncertainty in C sink estimations.

4.2 Instability of carbonatite weathering C sequestration

Many studies have also proposed that carbonate weathering may not lead to a stable C sink, but silicate weathering can absorb atmospheric CO_2 as a net C sink on a geological timescale (Gaillardet *et al*., 1999; Larson, 2011; Curl, 2012; Groves *et al*., 2012). Because the chemical equations (Eqs. (2) and (3)) are reversible, an equal quantity of CO_2 will be released when subterranean karst water returns to the surface. Thus, silicate weathering is considered the only way for C sequestration to occur in these studies.

$$2CO_2 + 3H_2O + CaSiO_3 = Ca^{2+} + 2HCO_3^- + H_4SiO_4 \quad (8)$$

Like Eq. (8) shows, CO_2 sequestrated by silicate weathering could be transported into oceans and then settle as carbonate, which results in stable, long-term C sequestration storage in the duration of millions of years (Berner *et al*., 1983). CO_2 consumption rates of global silicate weathering are from 9.86 to 14.01×10^{12} mol yr^{-1}, which was deduced through the chemistry of large rivers (Gaillardet *et al*., 1999; Moon *et al*., 2014).

At the same time, other studies have shown that HCO_3^- will not deliver all CO_2 back to the atmosphere. Biological cycling could increase both rates and the stability of rock weathering C sequestration. Moreover, biological behavior can participate in carbonate weathering processes both directly and indirectly. Carbonatite dissolution can be raised one order of magnitude by means of carbonic anhydrase. Additionally, 88% of C uptake from photosynthetic processes of aquatic plants derives from water; and particulate organic carbon (POC) uptake by aquatic organisms is also an important means of C sequestration (Liu, 2001; Lian *et al*., 2011; de Montety *et al*., 2011). Liu (2010) estimated that the terrestrial aquatic ecosystem contributes 0.2334 Pg C yr^{-1} or 33.1% of the net sink of carbonate dissolution, the global water cycle, and photosynthetic uptake by aquatic organisms (Liu *et al*., 2010). Therefore, C emission from rock weathering can be sequestrated by multiple means.

5 Karst critical zone service functions

5.1 Potential increases in C sink processes

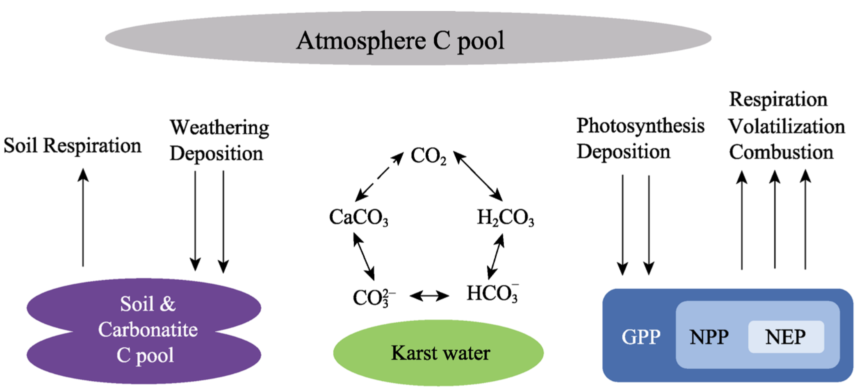
With the exception of rock weathering C sink, many other processes could also result in CO_2 fixation in the karst critical zone. Unlike non-karst areas, both soil-plant organic processes and biological pump processes, under a precondition of high DIC concentrations in karst water, could result in significant differences.

In conjunction with global climate change, the C sink from carbonatite weathering is predicted to increase by 21% to 0.18 Pg C yr^{-1} (Liu *et al*., 2010). However, not only feedback mechanisms of global ecosystems but also anthropogenic activities can provide means for C sink management. In the past 50 years, for example, a large bicarbonate flux increased in the Mississippi River, the United States of America, mainly due to land-use changes and management (Raymond *et al*., 2008). At the same time, it has also been demonstrated that groundwater is a CO_2 sink because limestone weathering has caused a 20% increase in groundwater CO_2 concentrations (Macpherson *et al*., 2008).

The favorable succession order of karst vegetation is bare rock with sparse grass > grassland > scrub-grassland > scrub > liana-scrubland > broad deciduous forests > climax community. However, the path of succession could be more complex in consideration of different conditions of soil, climate, species reproduction strategies, internal community environments, and anthropogenic interference. Saltational evolution could occur under artificial restoration, and reverse succession could occur under anthropogenic disturbances. Previous studies have shown that ecological restoration and land-use pattern conversions could enhance the capacity of C sinks in karst areas. Dissolution rates of different land utilization types showed significant differences, and subterranean C sinks of primary forests were three times greater than that of secondary forests and nine times greater than that of scrubland. After conversion from cultivated land and scrubland to secondary forests, C sinks can increase by 5.71–7.02 g C m^{-2} yr^{-1} after conversion from cultivated land and scrubland to secondary forests, and will increase by 24.86–26.17 g C m^{-2} yr^{-1} if those lands could develop into primary forests (Zhang, 2011).

Therefore, based on the discussion above, land-use strategy optimization and ecosystem restoration are efficient ways to increase C sink in the karst critical zone. To increase karst C sink under an integrate framework, it is indispensable that researchers get a comprehensive understanding of the rock-soil-biology-atmosphere continuum. In China, a series of policies, such as afforestation, which converts farmland back to forests, and ecomigration have been applied for karst critical zone restoration. However, NPP is considered only a short-term solution for C sequestration in terrestrial ecosystems, and there are limitations in increasing C sink in a fragile karst system due to the equilibrium of the carbon-nitrogen- water coupling relationship (Tao *et al*., 2001; Tao *et al*., 2003; Gao *et al*., 2014). To date, an increase in biomass remains an efficient C sink strategy under vegetation degradation in the karst critical zone. However, this will cause a significant and undefined issue, that is, the determination of the actual C sink threshold.

Another way to increase C sink capacities is reducing soil loss. However, due to its thin and spare soil layer, C sequestration in karst soil is smaller than in non-karst soil. At the same time, reducing soil loss can foster forward vegetation succession, which may promote a virtuous cycle (Figure 4).



Weathering: Carbonatite and silicate weathering; Respiration: Plant, animal & microorganism;
Combustion: Burning inorganic carbonaceous gas; Volatilization: Biogenic volatile organic compound (VOC);
Deposition: Dissolved carbon, particulate carbon

Figure 4 Carbon translation during pools of karst area

5.2 Eco-service functions of karst critical zone

The critical zone (CZ) is a holistic framework for integrated studies of water in conjunction with soil, rocks, air, and biotic resources in near-surface terrestrial environments (Lin, 2010). Karst CZ focuses on the rock-soil-biology-atmosphere continuum, which is characterized by three-dimensional and dualistic structures. The soil ecosystem is the core of the karst CZ, which interacts with the surface crust (vegetation, bedrock, and groundwater) through rock weathering and runoff erosion.

Karst areas have developed conduit systems include natural rock fractures, cenotes, and funnels at macroscopic scale, and soil pore and vascular bundle at microcosmic scale. Matter and energy transport through karst conduit systems are mainly in the form of solute transport. In terms of soil-atmosphere interfacial processes, interaction and feedback mechanisms between photosynthesis and transpiration are mainly dominated by stomatal behavior, which is sensitive to available soil water content. In terms of the soil-root system interface, how rhizospheric microorganisms obtain C depends on root exudates and degradable organic matter in surface soil.

Furthermore, NPP is the core assessment index of ecosystem service functions and vegetation activity. Ecosystem C cycle is a representation of the close correlation between biology and abiotic systems. Gao *et al*. (2013) reported that the carbon-nitrogen-water coupling cycle relationship dominates the C thresholds and balances of soil ecosystems. According to the C mass balance model, this relationship may cause excessive C uptake by karst ecosystem during rock weathering process, and surplus C loss will occur via soil erosion or other ecological processes.

6 Prospective

Accurately and synthetically estimating C sinks in karst areas is an issue on the frontier of our knowledge and is also an obstacle in C cycling research in terrestrial ecosystems. From the perspective of karst ecosystems, research on C sequestration pathways and biological mechanisms remains a fundamental task that is far from completed. Of which, DIC uptake efficiency by aquatic organisms via photosynthetic processes (also referred to as the "biological pump") plays an important role in C sequestration in the karst critical zone. From a research standpoint based on quantification, a number of methods should be combined or performed simultaneously to mutually confirm and thereby generate accurate results. Moreover, the threshold or potential C sink capacity of the karst CZ also needs to be quantified for ecosystem health and security.

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