Overview of 30 years of research on solubility trapping in Chinese karst

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ABSTRACT

Studies conducted over several decades have shown that solubility trapping in karst areas is an important component of the "missing carbon" in the global carbon cycle. Chinese researchers have taken advantage of their natural geography that includes numerous karst areas, representing approximately 1/7 of the global karst area, to conduct studies of solubility trapping. This paper reviews over 30 years of research progress on solubility trapping by China's researchers and summarizes the following five findings: (a) water plays an important role in the karst solubility trapping, regardless of its role as reactant or carrier; (b) the CO_2 concentration gradient in the soil environment, which contains biological activity, organic matter content, pH, and temperature, affects the karst solubility trapping; (c) transfer rules for CO_2 in the karst system are influenced by different land cover/land use; (d) relationships between biological metabolism and karst solubility trappings are analyzed; and (e) multiple models have been established to estimate the regional and global karst solubility trapping. This review concludes with proposals for future solubility trapping research.

Contents

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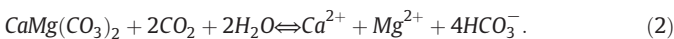 E-mail address: gzhou@glut.edu.cn (G. Zhou).

1. Background

In 1938, Callendar (1938) first revealed the imbalance between atmospheric carbon dioxide (CO_2) absorption and emission; however, his finding received little attention until Reiners (1973a,b) calculated the quantity of atmospheric CO_2 and determined that approximately 1–1.3 Gt (gigatons) of carbon was missing each year. Broecker et al. (1979) discussed that the fate of fossil-fuel-sourced carbon dioxide and the global carbon budget, and Keeling et al. (1995) demonstrated the interannual increases in the rate of rise of atmospheric carbon dioxide since 1980. Concurrently, other studies also discovered that the quantity of CO_2 produced by fossil fuel combustion, vegetation and soil degradation exceeded the sum of the ocean's absorption and increments of atmospheric CO_2. These findings further highlighted the difference between the absorption and emission of atmospheric CO_2. A difference regarded as the "*missing sink*" (Woodwell et al., 1983; Trabalka, 1985; Tans et al., 1990). Haughton (2009) later revealed that (a) global CO_2 emissions were approximately 9.2 Gt C/a; (b) the amount of CO_2 absorbed by the oceans was approximately 2.3 Gt C/a; and (c) the amount of CO_2 emissions into the atmosphere was approximately 4.1 Gt C/a, indicating that approximately 2.8 Gt C/a CO_2 was missing, which is approximately one-third of the global CO_2 emissions.

Thus, the question remains as to where the "missing sink" is located. Numerous researchers have maintained that the missing sink is located in the ocean system and forest vegetation system. After Tans et al. (1990) first proposed the idea that the "missing sink" might be located in a land system, particularly the Northern Hemisphere's karst systems, the majority of Chinese researchers came to believe that the karstification is one process causing solubility trappings of atmospheric CO_2 (Li and Yuan, 1996; Xu and Jiang, 1997). Until now, it has commonly been accepted that in the earth system, the biggest carbon pool is located at lithosphere where the quantity of the carbon in carbonate rocks is greater than 6.0×10^7 Gt, which is about 1500 times and 3.0×10^4 times greater than carbon in the ocean and terrestrial biosphere, respectively (Falkowski et al., 2000). The weathering processing can be expressed by the chemical equations below.

For limestone:

$$CaCO_3 + CO_2 + H_2O \Leftrightarrow Ca^{2+} + 2HCO_3^-. \qquad (1)$$

For dolomite:

$$CaMg(CO_3)_2 + 2CO_2 + 2H_2O \Leftrightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^-. \qquad (2)$$

Eqs. (1) and (2) demonstrate that (a) carbonate weathering consumes a significant amount of CO_2 from the atmosphere, the soil, or both; (b) dissolving 1.0 mol limestone consumes 1.0 mol CO_2; and (c) dissolving 1.0 mol dolomite consumes 2 mol CO_2. Therefore, CO_2 is transferred to water during carbonate weathering (Gilfillan et al., 2009).

Although it has widely been accepted that global carbonate weathering contributes to solubility trapping, the quantity and intensity and spatial distribution of absorption and factors that impact the terrestrial carbon sink remained unsolved. Thus, the "missing carbon" has been challenging the scientific community for 70 years. This paper provides a comprehensive overview of a 30-year research on China's karst solubility trapping, and details (1) the contribution of China's researchers over the past 30 years to the international research community with regard to missing carbon, and (2) the future research directions.

2. Retrospective 30 years of study on China's karst solubility trapping

2.1. Course of China's karst solubility trapping studies

China's karst area is approximately 3.44×10^6 km^2 and accounts for approximately 15.6% of the global karst area (22.0×10^6 km^2) and 27.9% of China's land area (Yuan and Zhang, 2002) (Fig. 1). Thus, China's

researchers have taken full advantage of these natural features to study karstification at a regional and global scale. Over 30 years, numerous efforts have been made to evaluate the intensity of the terrestrial ecosystem's carbon source/sink, investigate its spatial patterns and variation tendency in China, and reveal the environmental factors (including temperature, water, etc.) related to the function of the carbon sink. These efforts have significantly contributed to advancements in the international studies on the global carbon source/sink. Briefly, China's research has experienced three phases that are detailed below.

(1) Initial investigation: In 1987, a grant entitled "*The study on Eastern China karst geochemistry (1987–1990)*" was awarded by the Natural Science Foundation of China (NSFC), and it initiated the study of the karst solubility trapping. This research mainly investigated the karstification in Eastern China using geochemistry method. The research results from this investigation revealed the relationships between carbon, water and calcium in the karst system as well as the relationship of karstification dissolution or sedimentation with different karst rock types. The early work established a fundamental data set and foundation for further investigation and international collaboration;

(2) Wide investigation: From 1990 through 2009, China's researchers conducted four projects through the International Geoscience Programme (IGCP). The major investigation scope from the IGCP299 project, "*Geology, Climate, Hydrology and Karst formation*" (1990–1994), was an illustration of the karst formation mechanism through comparisons and analyses of the different physical, chemical and biological conditions in global karst areas, and it also indicated the karst formations in China and global karstification processes (Miu, 1996; Yuan and Liu, 1998). The major research scope from the IGCP379 project, "*Karstification and the carbon cycle*" (1995–1999), was the systematic evaluation of the carbon sink in relation to the effect of karstification on atmospheric CO_2, and such studies indicated that the amount of carbon trapped in water during karstification is greater than the carbon emissions. Further, the related studies estimated that the quantity of atmospheric CO_2 trapped by surface karstification is approximately 0.61 Gt C/year (Yuan and Jiang, 2000). With this project, Yuan and Zhang (2002) presented the karst dynamic system theory, which indicates that karst is a three-phase non-equilibrium system of water, carbonate, and CO_2. The IGCP448 project, "*The comparison between global karst geology and related ecosystems*" (2000–2004) mainly studied ecosystems in global karst areas. The related studies demonstrated that surface soil microorganisms can accelerate the dissolution rate of carbonate, and plant roots and soil microorganisms are two important sources of carbonic anhydrase (CA) (Yuan, 2000; Zhang and Yuan, 2001). The IGCP513 project, "*Global karst aquifer and water resources research*" (2005–2009), investigated the dissolution dynamics of carbonate rock; interaction processes among water, rock, and CO_2; and the influence of these factors on the global carbon cycle (Zhang et al., 2005; Lu, 2007; Yuan and Zhang, 2008; Guo et al., 2010);

(3) Deep investigation: The ongoing IGCP598 project, "*Environmental changes and karst system's sustainability*" (2011–2015), investigates the sustainability of karst systems and studies the interaction between karst systems and environmental changes under different temporal–spatial scales. For example, understanding the influence of carbonate rock dissolution by geo-biological processes and human activities will enable to better estimate the potential of the karst solubility trapping (Zhang et al., 2011, 2012).

Studies of the karst solubility trapping in China began with the study of the interaction between surface rock and near-surface atmospheric CO_2. Subsequently, the karst dynamic system was observed to be
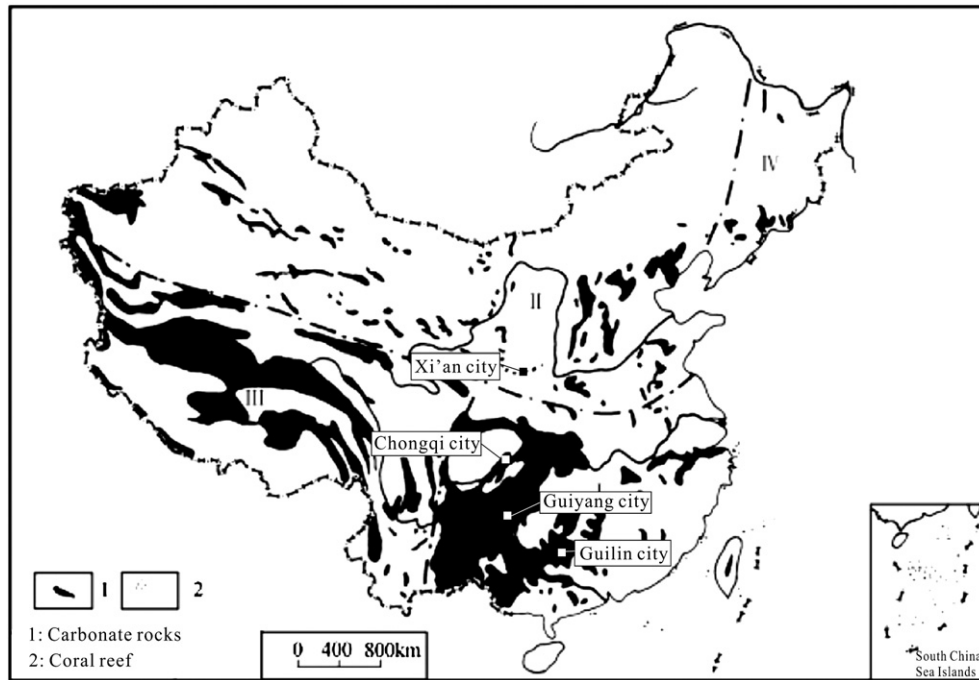
Fig. 1. The distribution of karst in China (Yuan and Zhang, 2002). I: Subtropical karst; II: Arid, semi-arid karst; III: High mountain karst; IV: Temperate semihumid karst.

sensitive to its surrounding environment, which represents the non-karst settings and they have immediate contact with karst areas. Furthermore, carbonate rock dissolution was found to be influenced by the transfer of CO_2 as well as by the soil and vegetation coverage. In addition, the interrelationship between the underground water cycle and carbon cycle was established. Overall, studies of the karst solubility trapping in China have four primary components: a) theoretical study of the karst mechanism, b) sensitivity of the karst system to environmental change (part of them are caused by karst hazards (Parise and Gunn, 2007, and Gutiérrez et al., 2014)), c) quantification of karst solubility trapping, and d) methodological study to provide estimations of the solubility trapping.

2.2. Theoretical study of sensitive factors related to solubility trapping

2.2.1. Water

As observed from Eqs. (1) and (2), water is the most important factor impacting solubility trapping in carbonate areas. In the early 1990s, researchers in the IGCP299 and IGCP379 projects explored reaction mechanisms and laws related to the "carbon dioxide–water–carbonate $(CO_2$–H_2O–$CO_3^{2-})$" system and concluded that water is not only the reactant of karstification but also the carrier that transports CO_2 and other substances. Therefore, water is the most important factor when calculating a solubility trapping rate (Dreybrodt et al., 1996; White, 2002; Ford and Williams, 2007; Zhai et al., 2007). Numerous investigators worldwide have also concluded that in the disequilibrium system of water (liquid), carbonate rocks (solid) and CO_2 (gas), carbon and water are coupled and greatly influence the global carbon budget (Ludwig et al., 1999; Gombert, 2002; Viles, 2003; Dreybrodt, 2004; Macpherson et al., 2008). Williams (1983) revealed the importance of subcutaneous storage in sustaining baseflow discharge at some sites and the contribution of subcutaneous water to flood hydrographs. He also presented the methods of estimating the volumes of subcutaneous and phreatic components of karst-spring flood hydrographs. And then, he gave a discussion of the significance of subcutaneous hydrologic processes for an understanding of karst geomorphology (Williams, 1983).

When investigating the reaction between carbonate rocks and atmospheric CO_2, water was observed to have differential impacts on carbon

trapping depending on the type of carbonate rock because of the different structural, physical and chemical characteristics of the rock (Yuan and Cai, 1988; Liu, 2000). Yuan and Cai (1988) revealed that the dissolution of limestone rock was affected by the rock structure, and the dissolution rate of the micritic component in limestone was nearly ten-fold that of the sparry calcite component. The detail discussions are listed as follows:

a) The thickness of diffusion boundary layer (DBL) is one of the most important factors for the dissolution rate. In the 1990s, Dreybrodt et al. (1996) and Liu and Dreybrodt (1997) noted that the carbonate rock dissolution rate was affected by both the thickness of DBL and the slow reaction of CO_2 in the boundary layer. Later, Yuan and Zhang (2002) revealed that the thickness of DBL changes with the temperature, and that CO_2 partial pressure influences the dissolution rate of calcite. When the DBL is between 5×10^{-3} cm and 10×10^{-3} cm, the dissolution rate decreases from 0.6×10^{-8} mmol/cm^2 s to 1.7×10^{-8} mmol/cm^2 s under constant temperature;

b) Runoff also is another factor for rock erosion. Liu (2000) established the relationship between the dissolution rate of the rock and runoff. Studies in different river basins demonstrated that the capacity of the karst solubility trapping is positively correlated with runoff from river basins; the runoff in river basins increases after rainfall or during the wet season, decreasing the HCO_3^- concentration and thus increasing the karst reaction rate and karst solubility trapping (Table 1) (Tang et al., 2011);

c) The dissolution rate of carbonate rocks is also affected by the exogenous water. Here, the exogenous water represents the water from the land surface infiltrating into the karst system. When exogenous water flows into the karst system, the speed and intensity of carbonate dissolution is increasing due to greater aggressivity of mixing waters (Liu and Zhao, 2000; Gutiérrez et al., 2014). The erosion rate of carbonate rock blocks in exogenous water was accurately measured in Lijiadong, Chenzhou, Hunan Province in China (Liu et al., 2006). It is found that the highest dissolution rate of carbonate rock blocks is about 13.6 mm/a which is more than a hundred times that of carbonate rocks (0.09 mm/a) in Fengcong area, Guilin City (Zhang et al., 2006). Huang et al. (2011a,b) calculated the volume of exogenous

Table 1
The HCO_3^- flow and capacity of the karst solubility trapping at different times.

Region	Period	Flow (L/s)	HCO_3^- (m mol/L)	Carbon sink (gC/s)	References
Guilin Mao Village	2010-3-3 (dry season)	79.4	3.4	3.2	Tang et al. (2011)
	2010-6-13 (rainy season)	272	3.3	11	
Guijiang River	Drought period	4010	3.7	180	Huang et al. (2011b)
	Normal period	5740	3.6	250	
	Wet period	11,500	3.4	470	

water in upstream and the concentration of HCO_3^- at Xiaolongbei station (in the upstream) and Maocun station (in the downstream) in an underground water. The results show that the solubility trapping flux increased about 10 times (from 1.1×10^3 gC/day to 1.0×10^4 gC/day). Except for the CO_2 input related to precipitation, vegetation and land-use types, the mixed corrosion due to infiltration water plays a more important role in the increase of solubility trapping flux. Therefore, the influence of infiltration water on calculating solubility trapping cannot be ignored.

In addition, it is found that the amount of carbon trapped in water also depends on the types of carbonate rock, as they have different structural, physical and chemical characteristics (Yuan and Cai, 1988).

2.2.2. Soil

Eqs. (1) and (2) show that exposed carbonate rocks react directly with atmospheric CO_2 in the near-surface atmosphere under the action of water. However, the CO_2 concentration in the soil environment is several or even dozens of times greater than that in the near-surface atmosphere, indicating that carbonate buried beneath the ground has the potential to generate greater solubility trapping of exposed carbonate rocks. However, it is unclear if the buried carbonate rock has a greater sensitivity to CO_2 changes in the soil depending on the concentration in the atmosphere. Therefore, in the international scientific community, researchers have endeavored to explore the rules and established the relationship of the three-phase homeostasis system of CO_2–H_2O–CO_3^{2-} underground soil environments (e.g., Nakayama et al., 1994; Andrews and Schlesinger, 2001; Galdo et al., 2006).

Researchers pioneered such studies in the early 1990s (Liu and Dreybrodt, 1997; Liu et al., 1998; Tao et al., 1998), and published in the late 1990s through middle 2000s. The major accomplishments are listed below.

(1) Studying how the concentration of CO_2 is capable of controlling the dissolution rate of carbonate rocks for a given soil depth. For example, studies of the Maolan observatory station in 1993 showed that at soil depths of 20 cm from February to June, the CO_2 concentration changed from 800×10^{-6} to 7400×10^{-6} ppmv; the pH of the underlying karst springs decreased from 8.0 to 7.4; and the HCO_3^- concentration rose from 3.3 mmol/L to 4.7 mmol/L (Yuan, 2002). Similar results were also demonstrated by the observations from the Guilin observation station (Li et al., 2004a,b; Yang et al., 2007);

(2) Exploring how CO_2 concentrations in the soil at different depths impact the dissolution rate of carbonate rocks. The results showed that the CO_2 concentration in the soil profile increased with soil depth; however, the solubility of carbonate rock did not increase with depth. The research further determined that the CO_2 concentration gradient in the soil profile had an obvious relationship with soil depth. As shown in Fig. 2, a comparison of the HCO_3^- profile absolute concentration and concentration gradient at the Guilin Observation Station revealed that (a) "the CO_2 concentration gradients and CO_2 activity are positively correlated, although this is not a perfect relation in Fig. 2, as the highest CO_2 concentration is in August, and the highest CO_2 concentration gradient is in

October" (Yuan and Zhang, 2002); and (b) "it shows that when the CO_2 concentration gradient of CO_2 in soil increases, the content of HCO_3^- increases, too, which indicates that the dissolved CO_2 in the karst aquifer water relates to the CO_2 concentration gradient in the soil air" (Yuan and Zhang, 2002). These observations are fully consistent with those at the station of Shaanxi Zhenan Yudong's karst underground river (Yuan and Zhang, 2002). Further, we take Guilin Station as an example. The soil depth is over 3 m around S31 karst springs and the concentration of CO_2 was measured at various depths of soil from June, 1994 to December 1994. At a certain collecting time, the concentration of CO_2 is observed at various depths of soil. The absolute concentration of CO_2 is calculated by the average of these observations at the different depths. Dividing the concentration of CO_2 by the depth difference gives the CO_2 concentration gradient. At a certain collecting time, when you average the different CO_2 concentration gradient, you will get the final CO_2 concentration gradient. The comparison between the absolute concentration of HCO_3^- and CO_2, and CO_2 concentration gradient from Guilin Observation Station on S31 karst springs is represented in Fig. 2. The CO_2 absolute concentration reached the maximum in August from the depth profile of soil while HCO_3^- reached the maximum value in October. There is nearly two months interval. However, if we look at the concentration gradient of CO_2 instead of the concentration of CO_2, the changed trend is almost the same as the HCO_3^-, both reaching the maximum in October. With the observation station of S31 in Guilin, the results are consistent with the experience results at Zhennan Yudong in Shanxi Province (Yuan and Zhang, 2002) and reveal that it is difficult to describe the relationship between CO_2 dynamic change and karstification only using the absolute concentration of CO_2 in soil. By contrast, the driving force of karstification from CO_2 in soil is more likely dependent upon the concentration gradient of CO_2 (Yuan and Zhang, 2002);

(3) Determining that biological activity, organic matter content, pH, porosity, soil moisture and temperature all affect the dissolution
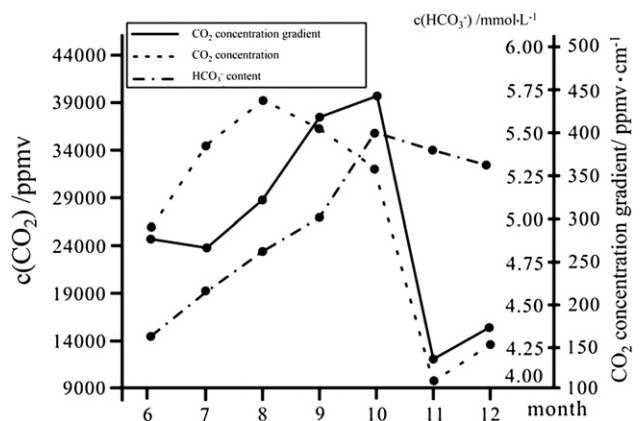

Fig. 2. The comparison between HCO_3^-, CO_2 absolute concentration and CO_2 concentration gradient from Guilin Observation Station on S31 karst springs. Yuan and Zhang (2002).

Table 2
The relative erosion rate of karst rock samples (%) under four different conditions of indoor experiments (note: relative dissolution rate = (mass before erosion − mass after erosion) / mass after erosion) (Wang et al., 2007).

Time (day)	Water–rock system (%)	Water–rock–bacteria system (%)	Water–rock–actinomycete system(%)	Water–rock–epiphyte system (%)
5	2.5	3.6	5.0	6.7
15	2.0	2.8	4.0	5.7
30	1.6	2.3	3.4	5.0

of carbonate rocks. Details on these processes are listed as follows.

a) *Different biological activities can affect the dissolution rate of carbonate rock.* Wang et al. (2007) conducted indoor experiments of the carbonate rock dissolution rate under four different conditions: i) water rock system; ii) water–rock–bacteria system; iii) water–rock–actinomycete system, and iv) water–rock–epiphyte system. It was concluded that: i) the relative dissolution rate of epiphyte is the largest, the actinomycete's is the second, and the bacteria's is the smallest (see Table 2); ii) the morphologies of the dissolved carbonate rocks appear different. They have "comby morphology" in the water–rock–bacteria system (Fig. 3), "wirelike morphology" in the water–rock–actinomycete system (Fig. 4), and "flocculence morphology" in the water–rock–epiphyte system (Fig. 5);

b) *Dissolution rate under different land use patterns.* Yang et al. (2007) conducted the experiments below;
   i) The dissolution rate varies with different soil types under the same depth profiles, and it can be concluded that (see Table 3):
➢ At soil depth of 5 cm, the dissolution rate rank is: the bamboo land > woodland > grassland > shrub land > shrub-grassland;
➢ At soil depth of 20 cm, the dissolution rate rank is: the bamboo land > woodland > grassland > shrub land > shrub-grassland;
➢ At soil depth of 50 cm, the dissolution rate rank is: bamboo land > grassland > woodland > shrub land > shrub-grassland. Moreover, the dissolution rate difference between the largest area (in bamboo land) and the smallest area (shrub-grassland) is 15 times.
   ii) The dissolution rate varies from soil depth at the same soil types, and it can be concluded that (see Table 3):
➢ Dissolution rate of bamboo and grassland increases with depth, but decreases with depth for shrub land and shrub-grassland. However, dissolution rate increased 38 mg/m² d for woodland from 5 through 20 cm depth, but drastically reduced 110 mg/m² d from 20 through 50 cm depth;
➢ The average dissolution rate varies: bamboo land reaches the largest rate at 300 mg/m² d, shrub achieves the smallest at only 31 mg/m² d,

and their difference is nearly 10 times. The variation rule is bamboo ground > forest > grassland > shrub land > shrub-grassland.
(c) *The dissolution rate and soil CO_2 concentration, moisture and porosity are strongly, positively correlated.* Studies have shown that (Yang et al., 2007);
   ● The higher soil CO_2 concentration, the more water, and the greater the porosity, the higher dissolution rate (Fig. 6);
   ● CO_2 concentration is dynamic for water acting on carbonate karst dissolution, and the high CO_2 concentration is capable of producing dissolution rates as high as several tens of times faster than at low CO_2 concentration;
   ● Soil CO_2 dissolved in water forms carbonic acid, as shown in Eq. (1). Based on Eq. (1), the reaction will terminate when lacking of either CO_2 or water. Therefore, it is not proper to conclude that the higher the CO_2 concentration in soil, the greater the dissolution rate, without considering other controlling factors;
   ● Generally, the dissolution rate increases with the increasing CO_2 in the soil. However, the bamboo forest presents an anomaly, where lower soil CO_2 corresponds to faster carbonate dissolution rate.
d) *Dissolution rate is strongly, negatively correlated with soil pH.* This means that the dissolution rate decreases with increasing soil pH (Fig. 7). Thereby, the lower the pH and the higher the hydrogen ion concentration, the higher the dissolution rate of carbonate rocks. This suggests that when the CO_2 concentration and the organic contents are low in the soil, the soil pH value becomes a major controlling factor of dissolution rate. This phenomenon becomes obvious in the bamboo forestland;
e) *Dissolution rate is positively correlated with organic matter content.* It has been revealed that the organic carbon generated by hydrolysis of organic matter has acidic and chelating properties, i.e., the residual acid from inorganic fertilizers, such as nitric acid, sulfuric acid, phosphoric acid, and a small amount of organic acids from organic matter decomposition is capable of accelerating the dissolution of carbonate rocks in a soil environment. An exception is the forest land, where the highest organic matter content does not correspond to the highest dissolution rate (Fig. 7).

2.2.3. Vegetation

It is widely accepted that the uptake of CO_2 by vegetation decreases atmospheric CO_2 (Gorte, 2009). However, it is unclear how vegetation impacts the global carbon sink in karst areas. Studies of the international karst community have discovered that vegetation can alter the physical and chemical properties of the soil, modify rainfall patterns and affect the karst solubility trapping (Serrano et al., 2007; Breecker et al., 2012). Researchers in China have contributed to determining the effect
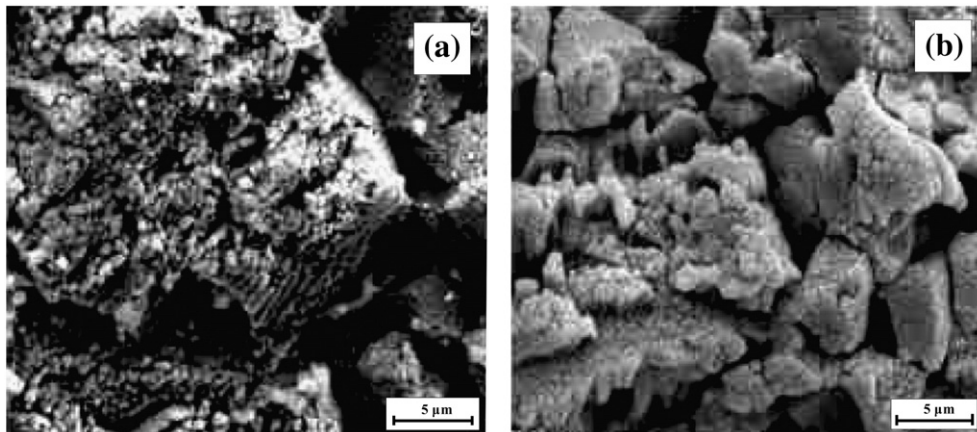

Fig. 3. Comparisons of carbonate rock before (a) and after (b) dissolution experiments in the water–rock–bacteria system (magnification, 10000×; Wang et al., 2007).
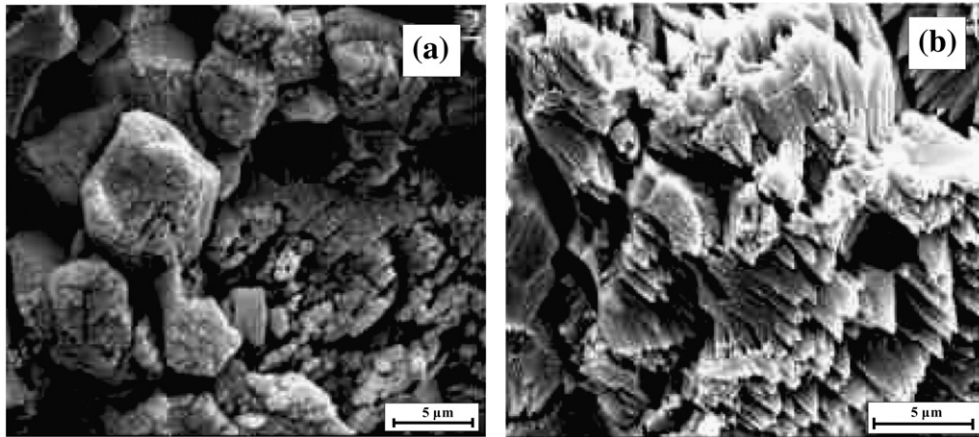
Fig. 4. Comparisons of carbonate rock before (a) and after (b) dissolution experiments in the water–rock–actinomycete system (magnification, 10000×; Wang et al., 2007).

of vegetation on the dissolution of carbonate rocks. The contributions can be summarized as follows.

(1) The karstification processes have sensitivity to different types of vegetation, as demonstrated by the following two examples. (a) Different types of vegetation result in different soil CO_2 concentrations, which produces different carbonate dissolution rates. Table 4 lists the effect of different types of vegetation on soil CO_2 concentrations in simulation experiments (Cao et al., 2004), watershed-scale studies (Li et al., 2004a,b), and regional studies (Lan et al., 2011). (b) Researchers have quantified the relationship between the vegetation types and karstification intensity by measuring dissolved Ca. For example, Zhang and Cao (2003) found that the spring water in a secondary-growth forest condition has a high electrical conductivity which ranges from 599 μs/cm to 603 μs/cm and the calcium ion concentration ranges from 73 mg/L to 90 mg/L, while the calcium ion concentration ranges from 52 mg/L to 83 mg/L in areas covered with brush;

(2) Different land-use patterns also affect the solubility trapping. Zhang et al. (2011) found that the amount of carbonate dissolution is greatest in grasslands, followed (in decreasing order) by woodlands, plowed land, fallow land, and shrub-covered land. The observations in different areas by Zhang (2011) and Luo et al. (2011) revealed that carbonate dissolution rates are significantly different under different land uses. Fig. 8 presents an analysis pertaining to the dissolution rate under different land uses.

Plant root exudates (e.g., organic acids and enzymes) are known to influence the soil carbon sink capacity (Yang et al., 1994; Li et al., 2011). Organic acids secreted by plant roots directly affect the generation and flow of the carbon sink, and they also indirectly affect the solubility trapping capacity of soil by influencing the effectiveness of soil nutrients and microbial activity (Zhao and Wu, 2011). However, carbonic anhydrase (CA) secreted by plant roots can effectively drive the action of karst solubility trapping through mutual conversion between CO_2 and HCO_3^- (Yu et al., 2004; Wu et al., 2008). The CA activities of the soil samples from different karst areas were measured. The results indicated that the CA activity could be detected both in surface (10–20 cm depth) soils of different karst ecosystems, and in the soil of sandy shale area. The comparative analysis showed that the CA activity varied obviously among the soils in different karst ecosystems. The mean CA activity of the soil in Misuga with poor vegetation cover is lowest while that in Jinfu Mountain and Nongla with good plant diversity is relatively high (Li et al., 2004a,b). The driving effects on the limestone corrosion by microbial CA from a strain numbered GLCa102 were studied in the laboratory under simulated karst conditions. The results show that microbial CA can enhance the total amount of conductible ions and Ca^{2+} concentration by 40% or more, which leads to a remarkable driving effect on the corrosion of limestone. This research indicates that microbial CA has an important role in karstification (Yu et al., 2004). Liu (2001) added CA to a carbonate rock reaction system and found that the calcite dissolution rate increased by approximately 2–10 fold when $CO_2 > 0.01$ atm. Li et al. (2011) also found that CA secreted by plant roots had higher activity than that secreted by mature leaves in
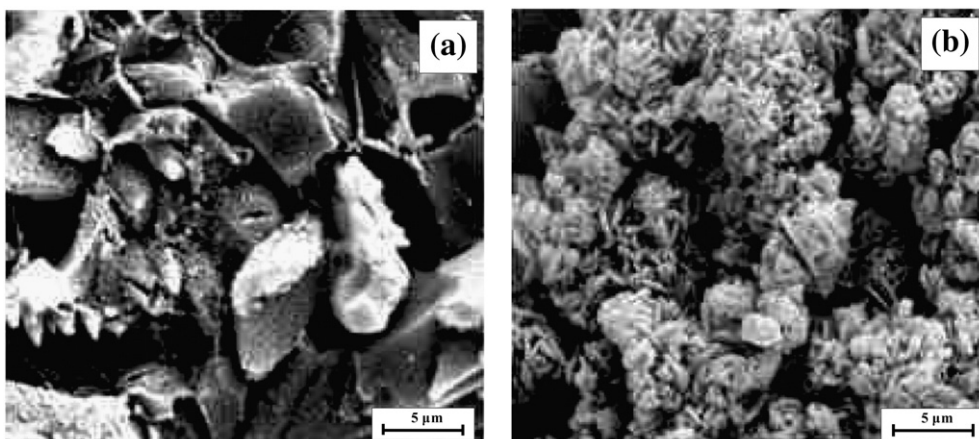

Fig. 5. Comparisons of carbonate rock before (a) and after (b) dissolution experiments in the water–rock–epiphyte system (magnification, 10000×; Wang et al., 2007).

Table 3
Dissolution rates of limestone tablets in different types of land uses from April–September, 2006 (unit: mg/m^2 d) (Yang et al., 2007).

Depth (cm)	Bamboo land	Woodland	Grassland	Shrub land	Shrub-grassland
5	270	210	110	79	43
20	310	250	170	30	30
50	320	140	230	30	21
Average	300	200	170	47	31

the karst ecosystem and it is capable of catalyzing soil CO_2 and H_2O to HCO_3^- and H^+ and promoting the dissolution of carbonates (Li et al., 2004a,b, 2011).

2.2.4. Biological metabolism

In addition to considering factors such as water, soil and vegetation, researchers have determined that biological activity plays an important role in karst solubility trapping because organisms can impact their surrounding environment through their own metabolism and community networks to participate in the process of karstification. The major accomplishments of such studies are listed below.

(1) Algae, mosses, and lichens contribute to the dissolution rate of carbonate rock through the transfer of atmospheric CO_2 to carbonate rock, which occurs through changes to the physical and chemical characteristics of the surroundings induced by the organisms, thus forming a biological microenvironment (Zhang, 1993a,b; Zhang et al., 1996);

(2) The metabolites and enzymes contributed through the respiration and secretions of microorganisms in the soil can also contribute to the dissolution of the underlying rock (Xiao et al., 2012). Moreover, the impact of different microorganisms on karstification varies in intensity: fungi has the strongest impact, while actinomycetes are also strong and bacteria is weak

(Table 5), where actinomycetes lie between bacteria and fungi, have characteristics linking them to both groups, and are soil microorganisms. Further studies have shown that microbes live on rock surfaces and in crevices, which increases the effect of microbial metabolites and enzymes on karstification (Zhao and Wu, 2011). This phenomenon can accelerate the weathering of carbonate rocks and impact the solubility trapping.

2.2.5. Other effects

Carbonate dissolution is affected by environmental temperature as well (Huang and Song, 1987; Wu et al., 2013). From the results of the experiment in static state under different temperatures, the dissolution speed of carbonate rocks may be indicated as Buxiniesike's recession function of CO_2. Its attenuation coefficient increases with the temperature and decreases with the increase of reaction time. That is, the reaction between CO_2 and carbonate becomes stronger as temperature increases and, as such, the dissolution speed of carbonates increases. However, when temperature is too high, it results in escape of CO_2, which reduces carbonate dissolution (Huang and Song, 1987).

The effect of temperature on carbonate dissolution is also related to the types of carbonate rocks. Four temperatures were tested: low (0.5 °C, 0.7 °C), normal (25 °C), moderate (40–60 °C) and high (80 °C). The dissolution speed of limestone is much faster than that of dolomite at low, normal, and moderate temperatures. However, at high temperature condition, the dissolution speed of these two types of carbonate rocks is similar. The dissolution experiments show that low and high temperatures are not optimal for dissolution of carbonates, and only moderate temperatures may be the best for karstification (Huang and Song, 1987).

In addition, acid rain can accelerate the dissolution rate of carbonate and increase the release of CO_2 (Lan, 1997; Yu et al., 2012). The results of simulation experiments indicate that the dissolution rate of carbonate under acid-rain pH of 2 is up to ten times faster than under normal rain pH (Lan, 1997).
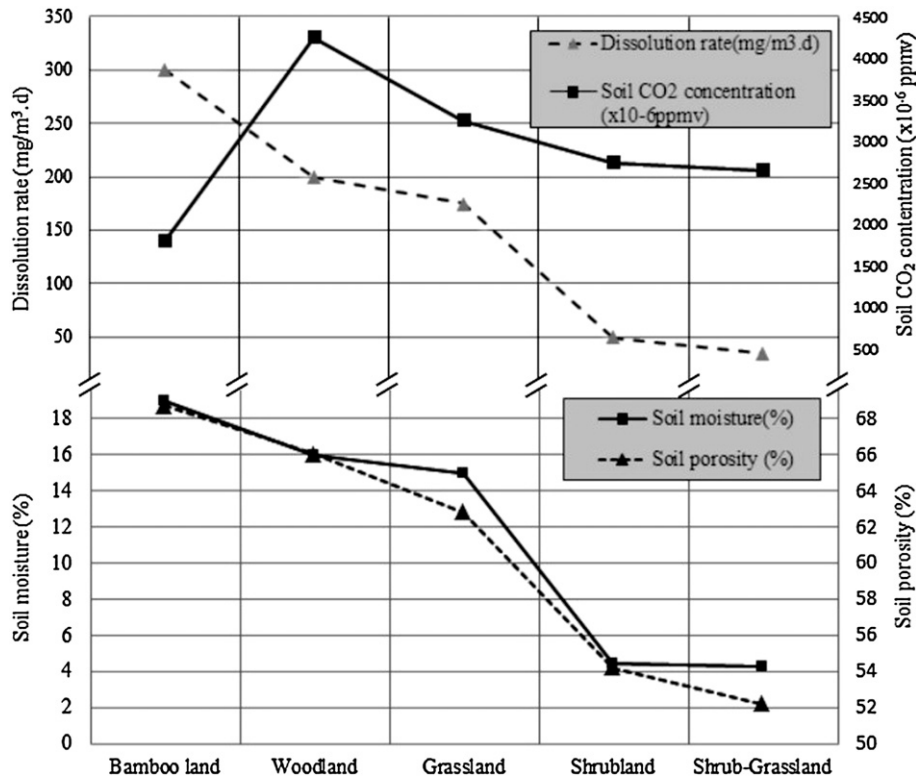

Fig. 6. Effects of soil CO_2 concentration, moisture and porosity in soil and their dissolution rate. Yang et al. (2007).
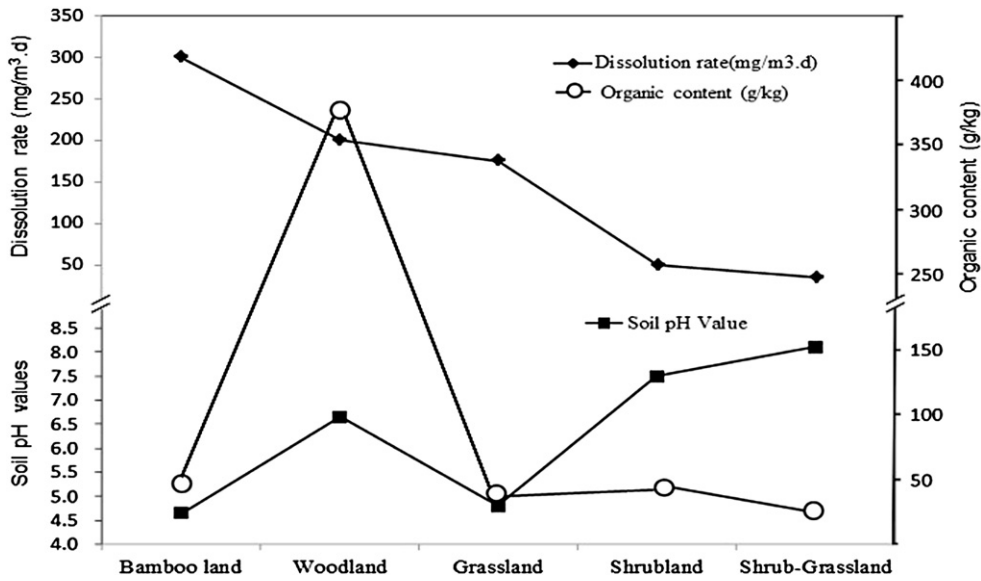
Fig. 7. Effects of the pH and organic matter content in soil and their dissolution rates.
Yang et al. (2007).

Table 4
CO_2 concentrations at different soil depths (unit: $\times 10^3$ mg/m^3).

Region	Vegetation types	Depth			Reference
		−20 cm	−30 cm	−50 cm	
Nonggang Station (in July)	Brush	21	/	30	Li et al. (2004a,b)
	Grass	18	/	41	
Yangshuo Station (in August)	Brush	75	/	73	
	Grass	100	/	120	
Guijiang Station	Grass	7.2–20	12–30	15–29	Lan et al. (2011)
	Brush	11–23	12–27	9.4–40	
	Woodland	5.4–15	9–30	9.6–35	
Guilin Station	Tree box	28	/	/	Cao et al. (2004)
	Grass box	16	/	/	
	Soil box	11	/	/	

2.3. Estimating solubility trapping of CO_2 in Chinese karst

2.3.1. Methods for estimating the karst solubility trapping

Different methods have been proposed to estimate the karst solubility trapping and each method has established its own model by considering the proper controlling factors and corresponding data sources.

These methods can be categorized into three types: carbonate-rock-tablet-test method, hydrochem-discharge and DBL theory. Table 6 summarizes the characteristics of the three types of methods and indicates that the controlling factors considered in the estimation of solubility trappings include rainfall, runoff, dissolution rate, and soil respiration. From previous investigations, the following common characteristics can be summarized.

(a) All the types of methods have considered runoff to be a controlling factor for karst weathering and dissolution. Moreover, watershed runoff is positively correlated with greater amounts of runoff, producing a faster karstification rate. To evaluate the sensitivity of the karst solubility trapping to changes in runoff, Liu (2000) established an estimation model;

(b) The carbonate-rock-tablet-test method was first applied in the IGCP299 project (1990–1994). In the IGCP379 project, "*Karst processes and the carbon cycle*" (1995–1999), the method provided preliminary estimates of the Chinese and global karst solubility trapping. The method has many advantages; for example, it does not require long-term monitoring and is relatively simple. Moreover, it is the most effective for directly obtaining
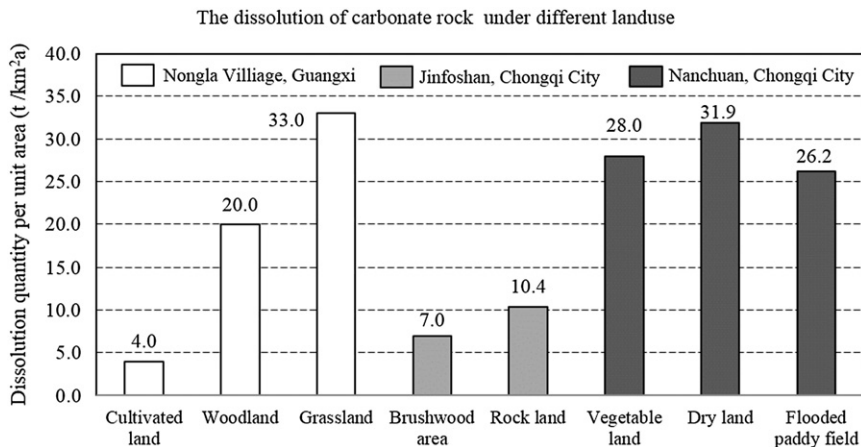

Fig. 8. Dissolution rates of carbonate rock under different land uses.

Table 5
The relative dissolution rate of calcite chips (%) (Wang et al., 2007) (Note: relative dissolution rate = (sample quality before dissolution − sample quality after dissolution) / sample quality after dissolution).

Dissolution time (d)	No microorganisms	Bacteria	Actinomycetes	Fungi
5	2.5	3.5	5.0	6.7
15	2.0	2.8	4.0	5.7
30	1.6	2.3	3.4	5.0

real data in a karst area. However, it also has some disadvantages; for example, it does not account for the diversity of different regional climates, vegetation, and lithology; therefore, errors may occur when estimating the regional or national karst solubility trapping by the dissolution rate. Another possible error in the tablet method is that it assumes that only the limestone is dissolving. In some studies, carbonate-laden dust may be a significant contribution to the Sr and Ca in karst water, so the tablet overestimates the limestone dissolution (Capo and Oliver, 1999; Wood and Macpherson, 2005);

(c) The TDS-discharge method only considers the contribution of carbonate and does not consider the contribution from silicate rock and HCO_3^- ions. Silicate rock weathering is also important, and the consumption of carbon during silicate rock weathering provides a net solubility trapping over a long time scale. Therefore, the solubility trapping caused by silicate rock weathering should be considered as well;

(d) The dynamic method usually considers the average reaction rate under natural conditions as representative of the national and global reaction rate, i.e., this method does not analyze the rate under different natural conditions. However, the estimation accuracy of the solubility trapping by this method is considerable.

2.3.2. Comparison of the CO_2 solubility trapping estimates in China

In recent decades, scholars have quantitatively evaluated the annual flux of CO_2 from the karst reaction using different methods to estimate the value of the karst solubility trapping. Table 7 lists the values of the karst solubility trapping using three methods as applied to nine different sites or experiments. Except for the hydrochem-discharge-combined-with-remote-sensing-technology method, proposed by Zhou et al. (2013), the other methods are all based on a fixed-point observation station, i.e., called as *point data*. The point data are first interpolated into area data, and then the latter are used to compute the solubility trapping. With the fixed-point observation data, the karst solubility trapping was estimated, and the results are listed in Table 7, which shows that the values estimated by these methods provide an approximate quantity of the solubility trapping at the 10^7 level. For example, Xu and Jiang (1997) estimated the solubility trapping at approximately 1.8×10^7 t/a in China by a TDS-discharge method. Further estimates showed that the global karst solubility trapping was approximately 6.1×10^8 t/a (Yuan, 1999), which accounted for approximately 1/3 of the global "missing carbon". This finding has not only driven

Table 6
Methods for estimating karst solubility trappings.

Method	Basic concept	Factors considered	Factors not considered	Scope of application	Advantages and disadvantages	Example of models	Reference
Carbonate-rock-tablet-test method	Standard limestone specimens are subject to different conditions, such as climate, geomorphology and vegetation. The consumption of CO_2 by the rock dissolution is measured to estimate the absorption of CO_2 and reaction rate of the rock	Climate Geomorphology Vegetation Rainfall.	The effect of rock type	Can be applied to regional karst solubility trapping capacity estimations within the same geological conditions	It can directly obtain real data in the study area and has revealed that multiple factors affect the karst solubility trapping rate. This method only applied to the karstification of limestone specimens, but there are many different types of rocks in nature. If standard specimens are used to represent all carbonate rocks, an error will result in the solubility trapping capacity estimation.		Yuan (1997), Liu (2000), Cao et al. (2011)
Dynamic method (DBL-model)	The reaction rate, activation energy and other factors are obtained from the reactants of karstification as well as the relationship between the reactant concentration and time.	Solid–liquid diffusion boundary layer	Environmental conditions, Seasons	Can be applied to microcosmic research of the karst solubility trapping	It has high precision but is difficult to use for large-scale estimations of solubility trapping capacity.	• PWP model • DBL model • Step-Kink model	Wigley et al. (1978), Dreybrodt and Buhmann (1991), Liu and Dreybrodt (1998)
Hydrochem-discharge method	Relationship between the total ion content of the surface runoff and rivers and rock distribution is analyzed, and the rock weather velocity is then calculated. Finally, the carbon consumption of weathering is estimated.	Lithology Runoff Temperature	Landform Vegetation Soil	Can be applied to solubility trapping capacity estimations over a large karst area	It can manage large-scale estimates and is easily combined with advanced technology, such as remote sensing (RS) and geographic information systems (GIS). The model does not consider the effect of different environmental factors and subsurface rock types on the solubility trapping capacity, and its estimation accuracy is low.	• Water-chemical-runoff method, • GEM-CO_2 model, • SiB algorithm	Corbel (1959), Liu and Zhao (2000)

Table 7
Quantity of the estimated solubility trapping obtained by the different methods in China.

Methods	Sink of CO_2 (t/a)	References
Carbonate rock tablet test method	1.2×10^7	Xu and Jiang (1997)
	6.4×10^7	Liu and Zhao (2000)
	1.4×10^{7a}	Jiang et al. (2000)
Dynamic method	2.4×10^8	Liu and Zhao (2000)
TDS-discharge method	1.8×10^7	Xu and Jiang (1997)
	6.6×10^7	Liu and Zhao (2000)
	5.2×10^7	Yuan and Zhang (2002)
	4.7×10^7	Qiu et al. (2004)
	3.7×10^7	Jiang et al. (2011)
	$6.1 \times 10^{7\#}$	Zhou et al. (2013)

[a] Specimen method + GIS.
[#] TDS-discharge method + remote sensing.

further research on karst dynamics theory but also increased our understanding of how karst solubility trapping impacts changes in the global climate.

3. Future work in CO_2 solubility trapping in karst systems

Although significant efforts have been made to determine the contribution of global carbonate weathering as a carbon sink, an evaluation of karst solubility trapping, including its spatial patterns and variation tendencies, controlling factors, etc., has proved to be a challenge to the scientific community for the past 70 years. Thus, research efforts are still required in the near future.

3.1. Theoretical study of the solubility trapping mechanism

Although the factors that impact the karst solubility trapping mechanism have been investigated, research gaps still remain (Gruber et al., 2004; Liu et al., 2010; Shi et al., 2014). For example, although efforts have been made to determine the effect of water on carbonate and significant improvements have been made to our understanding of the karst dynamic system of CO_2, water, and carbonate, little research has been devoted to the quantitative relationship between underground water and solubility trappings, despite underground rivers being widely distributed in karst area. Second, the investigations have been performed to determine the contributions of soil CO_2 environments at different depths to the solubility trapping; however, further research is required on the effect of soil carbon on the karst reaction to understand carbon transfer in the soil. Third, additional research is required to determine the effect of different vegetation coverages on the karst solubility trapping, especially on the effects of root secretions. Fourth, further investigations are required to determine the contributions of biological metabolism to solubility trapping and the methods by which microbes living on rock surfaces and in crevices form microbial metabolites that impact karstification. (e) In addition to the factors listed above, studies must be performed to determine how temperature, topography, geological structure, rock type, acid rain and human activities impact the dissolution of carbonate rock. Both natural and anthropogenic factors cause severe environmental changes, which may have significant effects on carbonate dissolution (Parise and Gunn, 2007, and Gutiérrez et al., 2014).

3.2. Model and data with improved estimations of the karst solubility trapping

Different methods have been proposed to estimate karst solubility trapping, and each method has established its own model by considering the proper controlling factors and corresponding data sources (Amiotte and Probst, 1995); controlling factors include rainfall, runoff, dissolution rate, and soil respiration. However, additional studies on the development of estimation models for karst solubility trapping are

required, and they should integrate the effects of rainfall, net primary productivity (NPP), and soil respiration on carbonate dissolution rates.

Except for the method proposed by Zhou et al. (2013), eight applications for estimation of solubility trapping are based on the fixed-point observation station. Karst carbon sink of a certain area is estimated by only interpolating the resulting point data, resulting in inaccuracy due to lack of enough sampling data. In order to overcome this shortcoming, Zhou et al. (2013) proposed combination of TDS-discharge method and remote sensing satellite data to estimate solubility trapping. There are several advantages for applying remote sensing data. First, land use/land cover data over large areas can be obtained using image classification methods; second, different types of rocks can also be obtained through classifications of remotely sensed satellite images; and third soil moisture can be detected from remotely sensed satellite images. Hence, we can obtain data related to karst carbon sinks by combining with remotely sensed data.

4. Conclusions

This paper first presents the progress of 30 years of research on China's karst solubility trapping, including the history and research achievements, and described our vision for studies in the near future on the karst solubility trapping.

There are five major research achievements on karst solubility trapping by China's researchers in the past 30 years. (1) Water plays an important role in the karst solubility trapping regardless of its role as reactant or carrier because such roles are coupled. Additionally, the karst solubility trapping is directly or indirectly affected by the solid–liquid boundary layer, runoff, and exogenous water. (2) The karst solubility trapping is affected by the CO_2 concentration gradient in the soil environment, which, in turn, is affected by biological activity, organic matter, pH, and temperature. (3) The transfer rules for CO_2 in the karst system are influenced by different land covers/land uses, including land-use patterns and vegetation types. (4) The relationship between biological metabolism and karst solubility trapping has been analyzed. (5) Multiple karst solubility trapping estimation models have been established to estimate regional and global solubility trappings.

Although many accomplishments have been achieved, additional research is required on topics that include the following: (1) the quantitative relationship between underground water and solubility trapping, (2) effect of soil carbon on the karst reaction, (3) effect of vegetation root secretions on the karst solubility trapping, (4) impact of microbial metabolites on karstification, (5) impact of temperature, topography, geological structure, rock types, acid rain, and human activities on the dissolution of carbonate rock, (6) establishment of methods and models that can provide exact estimations of karst solubility trapping according to different environmental conditions in different areas, and (7) collection of high accuracy spatial data in addition to fixed-point observation station data.

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