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Ecosystem-driven karst carbon cycle and carbon sink effects

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Abstract: It is recognized that karst processes are actively involved in the current global carbon cycle based on twenty years research, and the carbon sink occurred in karst processes is possibly an important part of "missing sink" in global carbon cycle. In this paper, an overview is given on karst carbon cycle research, and influence factors, formed carbon pools (background carbon sink) and sink increase potentials of current karst carbon cycle are analyzed. Carbonate weathering could contribute to the imbalance item (B_{IM}) and land use change item (E_{LUC}) in the global carbon cycle model, owing to its uptake of both atmospheric CO_2 (carbon sink effect) and CO_2 produced by soil respiration (carbon source reduction effect). Karst carbon sink includes inorganic carbon sink resulted from hydrogeochemical process and organic carbon sink generated by aquatic photosynthetic DIC conversion, forming relatively stable river (reservoir) water body or sediment carbon sink. The sizes of both sinks are controlled by terrestrial ecosystems and aquatic ecosystems, respectively. Desertification rehabilitation and carbon sequestration by aquatic plants are two effective ways to increase the carbon sink in karst area. It is estimated that the rate of carbon sink is at least 381 000 t CO_2/a with vegetation restoration and afforestation in southwest China karst area, while the annual organic carbon sink generated by aquatic photosynthesis is about 84 200 t C in the Pearl River Basin. The development of a soil CO_2 based model for assessment of regional dissolution intensity will help to improve the estimation accuracy of carbon sink increase and potential, thus provide a more clear and efficient karst sink increase scheme and pathway to achieve the goals of "double carbon". With the deep investigation on karst carbon cycle, mechanism and carbon sink effect, and the improvement of watershed carbon sink measurement methods and regional sink increase evaluation approaches. Karst carbon sink is expected to be included in the list of atmospheric CO_2 sources/sinks of the global carbon budget in the near future.

Keywords: Karst carbon sink; Ecosystem; Sink-increase way; Carbon pool; Rock desertification rehabilitation; Aquatic photosynthetic carbon sequestration

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Introduction

The implementation of IGCP379 "Karst processes and the carbon cycle" (1995–1999), an UNESCO/IUGS sponsored International Geoscience Programme (IGCP) project, marked the beginning of correlation on carbonate weathering and karst dissolution rates in global scale (Yuan, 1998). More and more karstologists were involved in this newborn research field focusing on the role of karst processes in global carbon cycle and brought karst processes successfully into global change study (Yuan and Jiang, 2000; Yuan and Zhang, 2002). After that, the research work on karst carbon cycle and carbon sink effects were also included and emphasized in five successive karst IGCP projects: IGCP448 "Karst geology and relevant ecosystems" (2000–2004), IGCP513 "Karst aquifer and water resources"(2005–2009), IGCP598 "Environmental change and karst system sustainability" (2012–2016) and IGCP661 "The processes and functions of karst critical zones" (2017–2021). The relevant research topics have been expanded

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and enriched during the last twenty years, including carbonates weathering intensity and regional correlation (Yuan et al. 2002); environmental sensitivity of hydro-geochemical indexes (Merkel and Planer-Friedrich, 2005; Zhang et al. 2005; Ford and Williams, 2007; Liu et al. 2007; Guo et al. 2021; Zhang et al. 2022); karst carbon cycle and land uses impact (Zhang, 2011; Lan et al. 2013; Cao et al. 2018; Zhao et al. 2022; Yu and Ye, 2020); dissolved inorganic carbon (DIC) utilization and autogenic organic carbon (AOC) generation by aquatic photosynthesis and their converting effectiveness (Liu et al. 2008; Liu et al. 2004; Zhang et al. 2012), aerobic anoxygenic phototrophic bacteria (AAPB) and recalcitrant dissolved organic carbon (RDOC) (Xiao et al. 2020; He et al. 2022). One of the most important progresses achieved is the reveal of short-time scale effect of karst processes and their carbon sink stability mechanism, implying karst processes are actively involved in current global carbon cycle. The formed carbon sink is probably a significant constituents of "missing sink" in global carbon cycle model (Yuan and Zhang, 2002; Liu et al. 2007; Yuan, 2011; Jiang et al. 2012; Pu et al. 2015; Wang et al. 2022).

At present, karst carbon cycle and carbon sink research has developed to the stage of carbon cycle research in karst critical zones, where three main processes are emphasized in earth critical zones. They are the coupling study of hydrological process, bio-geochemical process and ecological process. It was found that karst carbon cycle presents multiple time-scale characteristics and is closely related to ecosystems. The relevant scientific results were recognized by the Intergovernmental Panel on Climate Change (IPCC) in the 5th Assessment Report (First Working Group Report), in which the time scale of carbon sink for karst processes (carbonate rock weathering) has been shorten to 10^3–10^4 years from 10^4–10^6 years, and the time scale for CO_2 removal pertains to 10^2–10^3 years (Regnier et al. 2013; Ciais et al. 2014).

"Consolidation and strengthen of carbon sink capacity", as one of ten key tasks, has been listed in an action plan for peaking carbon dioxide emissions by 2030 in China, to consolidate carbon sequestration of ecosystem (including karst) and strengthen fundamental support of carbon sink. In karst carbon cycle and carbon sink, comprehensive treatment of rock desertification should be carried out to enhance the carbon sink capacity of karst ecosystem, as well as carbon sink background investigation, carbon storage assessment and potential analysis in karst areas. Carbon sequestration effects resulted from ecosystem protection and restoration will also be monitored and evaluated at the same time. China has announced the "double carbon" goals, namely, the country will strive to peak carbon dioxide emissions by 2030 and achieve carbon neutrality by 2060 proactively and steadily. Logically, carbon-input reduction (fossil fuels, land use changes and carbon storage, etc.) and carbon-uptake increase (forest vegetation, ocean, etc.) are two primary ways to achieve the "double carbon" goals. Carbonate rocks cover around 12% of continents globally, with an area of about 22×10^6 km^2 (Ford and Williams, 2007). Karst processes consume both atmospheric and soil CO_2. It has a negative feedback on global change (atmospheric CO_2 increase will stimulate carbonate rock dissolution and atmospheric CO_2 uptake) (Andrews and Schlesinger, 2001). Moreover, carbonate weathering is strictly controlled by ecosystem, it means that tree or grass land restoration would promote dissolution rates, since higher CO_2 production results from soil respiration, thus more soil CO_2 will be involved in underlying carbonate dissolution. Accordingly, karst processes can act as atmospheric CO_2 sink and have source reduction effect (retarding soil CO_2 release to atmosphere). In this paper, the research and progresses on karst carbon cycle are briefly reviewed first. Then the influence factors, formed carbon pools (background carbon sink) and sink increase potential of current karst carbon cycle are discussed and analyzed. It is expected that karst carbon sink can better serve the national "double carbon" goals.

1 Brief overview of karst carbon cycle

Karst carbon cycle is a key geochemical process in karst dynamics system. It is closely linked to global change owing to its uptake of atmospheric CO_2 and soil CO_2 and the formation of high resolution karst records (such as stalagmite and others). In this paper, karst carbon cycle refers to transport and transform processes of distinct carbon forms (CO_2, HCO_3^-, $CaCO_3$ and organic carbon, etc.) and their products in the five spheres of surface earth system. Karst carbon cycle has became a notable component in the current global carbon cycle due to its rapid kinetics of dissolution and sensitivity to environmental change. Both the atmospheric and soil CO_2 infiltrate into underlying carbonates aquifer via precipitation and can be involved in carbonate rock dissolution, thus act as atmospheric CO_2 sink or source reduction of soil CO_2 (release retarding effect of respiration produced CO_2), implying that carbonates weathering could contribute to the imbalance item (B_{IM}) and land use change item (E_{LUC}) in global carbon cycle model (Friedlingstein et al. 2020). In short, carbonates dissolution has both atmospheric CO_2 sink and source reduction effect. Based on existing estimates of CO_2 consumption resulted from karst processes in China or around the world, it may have high potential but underestimated in carbon sink (Yuan and Zhang, 2002; Li et al. 2018; Liu et al. 2018; Li et al. 2019).

The early studies on karst processes mainly calculated the carbonates dissolution rates by empirical formula or by using the standard limestone tablet test method (Pulina, 1974; Gams, 1981; Drogue et al. 1987). From 1990s to the beginning of this century, more comprehensive approaches were developed, emphasizing the combined influence of climate, hydrology, geology and other factors on karst processes, and introduced to the field of global change (Yuan, 1997) aiming to estimate regional (Jiang et al. 1999) and global carbon sink intensity. It was marked by the implementation of IGCP379 project "Karst processes and the Carbon Cycle" (1995–1999) (Yuan and Zhang, 2002).

The behavior differences of diverse karst dynamic systems are revealed after years of monitoring from typical karst experimental sites at home and abroad, especially their relationship with precipitation (particularly rainstorm events), vegetation and soil environment. It is found that carbonate rock matrix, the largest carbon pool in the world, is still very active in the global carbon cycle and may be an important part of the global "missing sink", thus opening up a new research field of karst geological process and carbon cycle and providing a new approach for the study of global change (Yuan, 2009). During this period, a global correlation study on the carbon cycle of surface karst dynamic systems was conducted, and a preliminary estimate of global carbon sink resulted from karst processes was 1.1–6.08 $\times 10^8$ t C/a, accounting for about 15%–30% of the missing sink (Yuan, 1997; Yoshimura et al. 1997; Liu and Zhao, 2000; Liu, 2000). In the present stage human activities are considered to have impacts on climate change, such as the impacts of land use change, especially the changes of vegetation conditions on karst carbon sinks. Typical studies and results from recent years show that vegetation restoration and increase of allogenic water in specific watershed can significantly promote carbonate rock dissolution (Ford and Williams, 2007; Zhang et al. 2008; Zhang, 2011). Under similar geological and hydrological conditions, carbon sink intensity in tropical karst area is 1.5–2.5 times than that in subtropical area (Zhang et al. 2016b). Experimental studies show that biological effects and soil carbonic anhydrase also promote carbonate rock dissolution to a certain extent (Li et al. 2004).

Carbon transportation in karst critical zones is not only closely related to atmospheric, soil and rock carbon pools, but also related to hydrosphere and biosphere. The relationship between carbon cycle and the three processes in karst critical zones is sketched in Fig. 1. The left half represents the traditional karst process, which is mainly controlled by hydrological processes, while the right half represents the biogeochemical and ecological processes, which are controlled by photosynthesis/respiration. Due to the involvement of short-time scale biological processes, karst process becomes a relatively fast geological process, and the carbonate weathering rate is much higher than the silicate weathering rate (Plummer et al. 1978; Dreybrodt, 1988; Liu et al. 1997; Kump et al. 2000), resulting in relatively high specific conductivity and dissolved inorganic carbon (DIC) content in water in the karst watershed (Hèlie et al. 2002). Karst water with high DIC content provides abundant carbon sources for photosynthesis of aquatic plants, especially in tropical and subtropical karst areas, where intense aquatic photosynthesis converts DIC into organic carbon. Therefore, if the carbon pump effect of aquatic plants is considered, the carbon sink effect of karst processes is more significant (Liu et al. 2010; Montety et al. 2011).

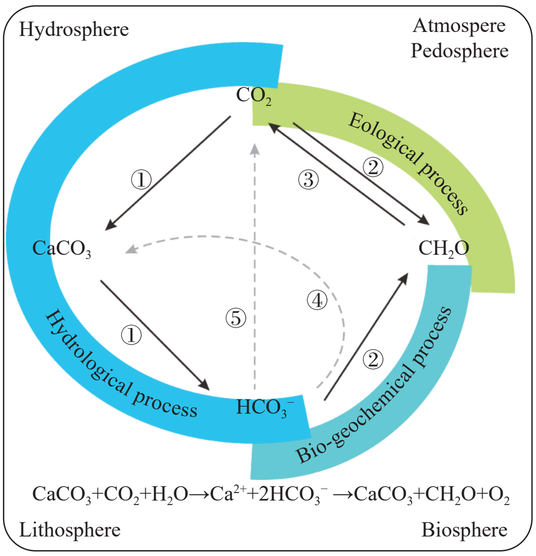

Fig. 1 The conceptual model of carbon cycle in karst critical zones

①Carbonate rock dissolution, ②Photosynthesis, ③Respiration, ④Organic calcification, ⑤Degassing

2 Influence factors on current karst carbon cycle

In tropical and subtropical karst areas of southern China, high resolution monitoring data of soil CO_2 and groundwater HCO_3^-, the two parameters closely related to karst processes in surface karst dynamics systems, exhibit remarkable seasonal and annual variations. An accordant relationship between soil CO_2 and groundwater HCO_3^- is observed, namely the increase of soil CO_2 will lead to carbonate rock dissolution, and produce higher HCO_3^- content accordingly. Karst region in Mediterranean climate zone has a similar phenomenon, where the driver of CO_2 is closely related to air temperature, precipitation regime (Zhang et al. 2022). It is proved that karst processes are very sensitive to environmental change and are basically synchronized with a variety of climate change (such as rainfall, temperature) and biological processes (such as fresh organic matter decomposition resulting in higher soil CO_2) without notable time lag. The environmental sensitivity of karst carbon cycle indicates that it is mainly controlled by ecosystems; water and temperature affect the carbon cycle through ecosystem regulation (Pan et al. 2000; Gaillardet et al. 2019).

Rapid biological processes involved in geochemical processes have important effects on the short-term geological carbon cycle. The karst resulted bicarbonate can be used as an inorganic carbon source for photosynthesis of aquatic plants and algae, thus be fixed in aquatic plants. Karst water with high concentration of HCO_3^- and Ca^{2+} helps to promote photosynthesis of aquatic plants, and converts inorganic carbon into organic carbon (Montety et al. 2011). The maximum conversion amount of bicarbonate in karst lake water is ~60% (Zhang, 2012). The amount of bicarbonate used by photosynthesis of aquatic plants in typical karst rivers in southwest China in summer is nearly 9 times higher than that in surface streams fed by karst springs in Florida, USA, suggesting that surface rivers in subtropical karst areas in south China have a higher carbon sink intensity generated by photosynthesis of aquatic plants (Zhang et al. 2016a). The positive vegetation succession has a significant promoting effect on karst carbon sink, and the amount of dissolution carbon sink in primary forest is 3 times of that in secondary forest and 9 times of that in shrub. Carbon sinks of terrestrial ecosystems increase with vegetation development or reforestation, and similar processes caused by karst dissolutional denudation can occur underground as well (Zhang, 2011).

There is a view that carbonate rock dissolution has an important contribution to the uptake of atmospheric CO_2 at the geological historical scale, whereas it only shows "carbon shifted" rather than "carbon sequestration" in the current climate change scale, thus no carbon sink effects have happened (Curl, 2012). However, the "capture" of karst carbon cycle by ecosystem carbon transportation and conversion, and the discovery of karst carbon sink stability promoting mechanism such as carbon sequestration by aquatic vegetation photosynthesis as well as the formation of allogenic and recalcitrant organic carbon (Waterson and Canuel, 2008; Zhang et al. 2012; Yang et al. 2016; He et al. 2020; He et al. 2022), scientifically answered these questions on the rate and stability of karst carbon sink at home and abroad, and opened up a new research field of karst geological process and carbon cycle. The research results of karst processes and carbon cycle provided a scientific basis for China national assessment in the IPCC 5^{th} Report, and finally led to the recognition of geological carbon sinks in the revised IPCC 5^{th} Assessment Report (AR5) (Ciais et al. 2013; Pu et al. 2015).

Karst processes consume both atmospheric and soil CO_2, thus can mitigate soil CO_2 released into the atmosphere. At the catchment scale, karst carbon sink intensity and terrestrial ecosystem carbon sink are in the same order of magnitude, vegetation restoration increases the surface (vegetation) carbon sink and promotes the karst carbon sink as well, which has laid a good foundation for the study of geological carbon sinks in the field of climate change, also provides a new way to achieve the goals of national carbon emission reduction (Zhang et al. 2016b).

3 Waterbody carbon pool resulted from karst carbon cycle

Karst waterbody carbon pool is composed of inorganic and organic carbon. The former is dissolved inorganic carbon (DIC) (mainly in HCO_3^-), and the latter is autogenic organic carbon (AOC) formed by aquatic photosynthesis transformation of HCO_3^-. Their sizes are controlled by terrestrial ecosystems (forest vegetation, soil CO_2, soil moisture and temperature, etc.) and aquatic ecosystems (aquatic plants, algae, microbials, etc.), respectively.

3.1 Riverine inorganic carbon pool

The HCO_3^- generated by carbonate rock dissolution is drained with karst springs or underground rivers to form a dynamic carbon pool in surface water. Previous monitoring results showed that (Zhang et al. 2016a; Zhang and Xiao, 2021), CO_2 degassing at water-air interface mainly occurs in the early stage of groundwater resurgence. With the increase of flowpath, degassing greatly decreases, which results in relatively stable inorganic carbon pools in karst water.

Yuan (1999) preliminarily estimated the amount of atmospheric CO_2 uptake by surface karst processes as 0.22–0.608 Pg C/a globally, using standard limestone tablet method, hydrochemical-runoff method and diffusion boundary method, accounting for about 10%–25% of the global "missing sink". Li et al. (2018) estimated the global carbon sink by carbonates weathering to be 0.89±0.23 Pg C/a, accounting for 36% of the global "missed sink", using high-precision ecological, meteorological and hydrological raster data and field monitoring site data from 2004 to 2014.

There are four main types of karst in China, including southern karst, northern karst, the Tibet plateau karst and buried karst. Jiang et al. (2011) estimated the amount of inorganic carbon sink produced by karst processes is 10.09 Tg C/a according to years of hydrological data and DIC concentration in water from those four karst types. Li et al. (2019) estimated that carbonate karst carbon sink in China reached 11.37 Tg C/a based on ecological, meteorological, hydrological and monitoring data. Cao et al. (2011) established a regression equation based on limestone dissolution rate, precipitation, soil respiration rate and net primary productivity, and estimated that the karst carbon sink in the Pearl River Basin is 1.85 Tg C/a, considering the distribution of carbonate rock types as well. Qin et al. (2015) calculated that atmospheric CO_2 consumption caused by rock weathering in the Pearl River Basin is 1.30 Tg C/a through hydrochemistry and isotope analysis. By using the discharge and HCO_3^- concentration monitoring data, Pei et al. (2012) calculated that the annual carbon sequestration fluxes of Zhaidi underground river in Guilin of Guangxi, Da'an underground river in Huanjiang of Guangxi and Qingmuguan underground river in Beibei of Chongqing are 613 157 and 306 t C/a respectively.

It can be seen that the carbon sink estimations for various spatial scales by researchers are different in terms of methodology and the accuracy of data used, but there is little difference in the estimation results with about the same order of magnitude. The yearly magnitudes of karst carbon sink in the world, China, river basins and small watersheds are at the size of 100 million tons, 10 million tons, 1 million tons and 100 tons respectively.

3.2 River aquatic photosynthetic organic carbon pool

Recent studies have found that aquatic plants in karst water (underground rivers and reservoirs) utilize high concentration of HCO_3^- in water as carbon source for photosynthesis. The resulted organic carbon will be buried in solidified and deposited plant residues, forming a "biological carbon pump" effect (Yang et al. 2015; Liu and Dreybrodt, 2015). Typical studies show that about 47% of HCO_3^- in karst groundwater fed wetlands is sequestrated by photosynthesis of aquatic plants (Zhang et al. 2013; Li et al. 2015). The discovery of aquatic plants using inorganic carbon for photosynthesis in karst water implies there is an effective way to convert inorganic carbon into organic carbon in karst water, not only providing a strong evidence for karst carbon sink stability, but also assisting in the parameter determination in the carbon cycle model of karst critical zones (Chen et al. 2014).

The metabolic activities of aquatic plants can affect the carbon cycle and the chemical characteristics of carbonate water. Photosynthesis and respiration drive diurnal variation of dissolved CO_2 content in water, resulting in the daily cycle of pH (Simonsen and Harremoes, 1978; Langmuir, 1997), thus affecting the dissolution and deposition of carbonate minerals. Photosynthesis during daytime promotes carbonate deposition, resulting in reduction of dissolved inorganic carbon (DIC) and Ca content in water (Spiro and Pentecost, 1991; Hartley et al. 1996; Guasch et al. 1998; Liu, 2008). In contrast, CO_2 produced by plant respiration at night promotes dissolution of carbonate and the return of DIC and Ca to the water body (Cicerone et al. 1999; Liu, 2008). Results from a travertine stream in the United Kingdom further showed that the diurnal DIC loss and Ca deposition caused by photosynthesis were significantly higher than those released by degassing (Spiro and Pentecost, 1991).

High-resolution monitoring results from a karst spring fed stream in Florida, USA showed that DIC (mainly HCO_3^-) and Ca concentrations along Ichetucknee river decreased by 0.5 g/m/d and 0.8 g/m/d, respectively. The daily loss of DIC in 5.4 km long monitoring reach is 2.6 kg, 88% of which is generated by photosynthesis of aquatic plants, and the daily deposition of Ca is 4.3 kg (Montety et al. 2011). It suggests that karst process is no longer a purely inorganic geological process in the traditional sense due to the involvement of biological processes, and the rate is greatly accelerated featured by Ca and HCO_3^- enriched groundwater. After water resurgence as underground rivers or springs, on the other hand, the in-situ deposition of Ca and HCO_3^- (by aquatic plants photosynthesis uptake) in stream acts as a real carbon sink, thus could contribute to carbon storage and provide a potential pathway for carbon emission reduction.

The monitoring data of a spring fed stream during summer in Guancun, Guangxi, China showed that both the DIC concentration and its diurnal variation range are much larger than that in Ichetucknee River. Taken the average HCO_3^- concentration (4.4 mmol/L) at the outlet of Guancun spring as the input value and using mean discharge rate of 149 L/s, the estimated daily HCO_3^- loss along the 1.35 km long flowpath is 94.9 kg, i.e. 1 152 mmol/day/m, accounting for 4.7% of the input DIC at the outlet (Zhang et al. 2012; Wang et al. 2015), whereas the HCO_3^- loss in Ichetucknee river is only 130 mmol/d/m. It suggests that the carbon sink generated by photosynthesis of aquatic plants in small surface rivers in subtropical karst area of south China in summer is much higher, and has potentially greater carbon sequestration capacity. The results revealed that riverine allogenic organic carbon sink are formed by converting inorganic carbon to organic carbon, which is controlled by aquatic photosynthesis and calcification of organisms.

The results from in-situ microbial culture experiments showed that the average concentration of recalcitrant dissolved organic carbon (RDOC) in Lijiang River, Guilin, China is 2.42 mg/L, accounting for 78.06% of the average value of DOC. RDOC fluxes at Guilin and Yangshuo hydrological station are 0.75×10^7 kg·a^{-1} and 1.3×10^7 kg·a^{-1} respectively, suggesting that RDOC flux increases along with the flowpath and the organic carbon formed by aquatic photosynthesis converting process is stable in general (Xiao et al. 2020; He et al. 2022). Moreover, the RDOC flux is about 5%–10% of the inorganic carbon sink, thus should be counted in the karst carbon sink.

Microorganisms in karst processes can not only promote the dissolution of carbonate rocks, but also sequestrate the carbon sink by absorbing inorganic carbon (Zhang et al. 2011), suggesting that HCO_3^- in karst groundwater or karst spring fed streams can be taken up by photosynthetic microorganisms and part of HCO_3^- may be utilized by non-photosynthetic microorganisms (Lian et al. 2011), through which the stability of karst carbon sink is improved.

One of the most critical challenges in the current carbon cycle is the global CO_2 budget imbalance. Namely, there is a remarkable "missing sink" of total CO_2 emissions after deducting atmospheric CO_2 increase and ocean carbon sink, which is 1.8 to 3.4 PgC/a (Melnikov and O' Neill, 2006; Lal, 2008; Le Quere et al. 2012; Le Quere et al. 2014). In the Fifth Assessment Report (AR5) of Climate Change released by IPCC, this value is up to 2.5 PgC/a (Ciais et al. 2013).

According to the AR5, the global carbon sink of rock weathering is about 0.4 PgC/a. This value reaches about 0.6 PgC/a after considering the allogenic organic carbon sink (about 0.23 PgC/a) formed by the utilization of DIC in water by aquatic photosynthetic organisms (Cole et al. 2007), probably contributes significantly to balancing the global carbon budget. The AR5 report improved and discriminated the time scales of rock weathering carbon sinks, which were reported as 10^4–10^6 years for silicate rocks and 10^3–10^4 years for carbonate rocks. The AR5 report listed rock weathering carbon sink as one of the four methods for CO_2 removal, and accepts that carbon sink time scale of carbonate weathering ranges from 100 years to 1 000 years. The AR5 report presented some new insights, but continued to maintain that the rate of carbon sequestration by rock weathering is still too slow to be included in global carbon budget model. Currently, more attentions are paid to the accurate evaluation of intensity of carbon source/sink in global and regional scale (Yu, 2014), the cause of this dilemma lies mainly in the uncertainty of ecosystem carbon sequestration, model calculation and less consideration of relevant geological factors. On the other hand, it is associated with the basic concept used for establishing global carbon cycle model. All those models tend to ignore the related geological processes, such as rock weathering carbon sinks (including karst processes), which has been underestimated in the global carbon budget due to the time scale, chemical reaction rates and stability issues.

4 Analysis of karst sink potential based on "double carbon" goals

4.1 Carbon sinks by rocky desertification rehabilitation and land use control

The change of land use and the positive succession of vegetation can promote karst processes and increase carbon sink. The size of carbon sink gradually increases from grassland to forest land in terrestrial ecosystems. Typical studies show that the carbon sink generated by karst processes also increases with vegetation recovery, this includes the surface sink generated by vegetation photosynthesis as well as the underground sink increase (Zhang, 2011).

Due to the heterogeneity of karst processes, the amount of atmospheric/soil CO_2 uptake by karst processes varies greatly with different land uses. The monitoring data of typical peak-cluster karst area in Nongla, Guangxi and karst terrace in Jinfo mountain, Chongqing showed that the carbon sinks generated by karst processes are primary woodland, grassland, secondary forest land, shrub land and cultivated land in descending order. The maximum carbon sink is 7.62 tC/km^2·a in primary forest, 4.8 tC/km^2·a in grassland, 2.4 tC/km^2·a in secondary forest, 0.84 tC/km^2·a in shrub and 0.48 tC/km^2·a in cultivated land respectively. The karst carbon sink of secondary forest in Bitan spring watershed is about 3 times of that in degraded shrub land nearby and 5 times of that in cultivated land (Zhang, 2011). The value in primary forest is three times of that in secondary forest (Table 1). In other words, the karst carbon sink will increase by 1.56–1.92 tC/km^2·a from cropland or shrub to secondary forest, and increases by 6.82–7.14 tC/km^2·a if evolved into primary forest. The above data also indicates that the dissolution rate varies significantly with different land uses. Therefore, land use types must also be considered in regional estimation of karst carbon sink, in addition to climate (temperature and precipitation), hydrological (runoff, allogenic water) conditions and geological settings.

The CO_2 consumed by subsoil karst processes comes from atmosphere or soil respiration. Soil respiration is an important part of terrestrial carbon cycle, and the accuracy of its evaluation directly affects the estimate of terrestrial carbon source/sink (Zhou et al. 2008). Part of the CO_2 generated by soil respiration in karst areas may be consumed by karst processes (Zhang et al. 2022). A large number of studies have shown that biogenic CO_2 can accelerate carbonate rock dissolution with a rate from several times to nearly 20 times (Hinsinger et al. 2001; Gulley et al. 2015). The proportions of soil CO_2 uptake by dissolution to total respiration produced CO_2 ranges from 5% in temperate zone (Schindlbacher et al. 2015) to 29% in subtropical zone (Dong et al. 2018). Accordingly, the impact of karst processes on emission item of land use change (E_{LUC}) in the global carbon cycle should be considered in the assessment of carbon cycle potential in karst areas.

Forests are the largest carbon pool of terrestrial ecosystems, and the total carbon sequestration of forests in China is 5.9 Pg C. From the perspective of vegetation carbon sequestration, forest has the largest carbon sequestration, followed by grassland and wetland, while crops rank the lowest (Fang et al. 2007). Karst carbon sink has a similar change pattern with different land uses, indicating that forest can significantly promote karst processes.

The subsoil dissolution rates under different land uses in tropical peak-cluster valleys of Kanchanaburi Province, Thailand are 29.0–72.8 t/km^2·a which decreases from bamboo land to sparse forest land, barren grass land, and to artificial woodland. The amount of subsoil dissolution at different depths in rainy season accounts for 57.2%–87.9% of the annual total with an average of 76.5%. Generally, the subsoil dissolution rate in Kanchanaburi is higher than that in peak-cluster depression of subtropical area of southwest China under similar lithological and hydrogeological conditions and same land use (forest), which is about 1.5–2.5 times of that in subtropical karst area (southwest

Table 1 Carbon sink of karst processes with different land uses in typical subtropical karst areas of southern China

Site	Land use	Dissolution rate (t/km^2·a)	CO_2 consumption (t/km^2·a)	Carbon sink (tC/km^2·a)
Nongla, Mashan county, Guangxi	Tilled land, Nongtuan	4.02	1.77	0.48
	Secondary forest, Landiantang	19.97	8.79	2.40
	Orchard land, Landiantang	32.97	14.51	3.96
Jinfo mountain, Nanchuan county, Chongqing	Rock desertification land	10.38	4.57	1.25
	Secondary forest, Bitan spring	20.00	8.80	2.40
	Shrub land, Bitan spring	7.00	3.08	0.84
	Primary forest, Shuifang spring	63.50	27.94	7.62
	Grass land, Shuifang spring	40.00	17.60	4.80

China) (Zhang et al. 2014; Zhang et al. 2016b).

Vast area in southwest China is covered by karst as one of the largest areal distributions of karst in the world. Supported by China Geological Survey, a program titled "the Research of Geologic Carbon Sequestration Potential of China" was implemented from 2005 to 2015, in which four projects were related to karst carbon cycle and carbon sink effect, including mechanism study, process investigation, catchment carbon sink monitoring and potential assessment. 54 100 km^2 of rocky desertification has been rehabilitated in China by 2020 (The State Council Information Office, 2021), and the cumulative increase of karst carbon sink generated by rocky desertification control is estimated to be 2.74 million tCO_2. Average restoration rate of rocky desertification is about 3 300 km^2/a in Year 2016–2020. Based on this value, the estimated increase of carbon sink will grow at a rate of 381 000 tCO_2/a at least in the future. The implementation of the comprehensive control of rocky desertification has great potential to increase karst sink, thus help to achieve the national "double carbon" goals and enhance the role of the geological communities in the field of climate change.

4.2 Organic carbon sink potential resulting from aquatic photosynthetic DIC converting

The carbon sequestration of aquatic plants in karst water could be interpreted as the carbon enhancement effect of rocky desertification control (vegetation restoration). Considering the carbon sequestration of aquatic plants, the carbon sink generated by the CO_2 uptake will be more substantial and relatively stable.

Chaotian river, a tributary of Lijiang river in Guilin, is a medium-sized river. 75%–80% of DIC in Chaotian river comes from karst groundwater annually (Zhang et al. 2017). Daily monitoring data in summer season show that the amount of DIC converted by aquatic photosynthesis is about 997 kg/d, equivalent to 0.62 t/(km·d), accounting for 4% of the total DIC input. The amount of converted DIC is about 5–6 times of that in the spring fed streams in the karst regions of southwest China (Zhang et al. 2021).

Lijiang river in Guilin is a larger river. Daily monitoring data in the middle reaches in summer presents that the amount of DIC converted by aquatic photosynthesis is 30.96 t/d, equivalent to 2.06 t/km·d, accounting for about 6% of the DIC input in the upper reaches. This value is about 3–4 times of that in Chaotian tributary. DIC consumed by photosynthesis and calcium precipitation accounts for about 70% of the total converted DIC, and is stored in the riverbed in forms of organic carbon or $CaCO_3$, thus can be counted as a component of karst carbon sink (Zhang and Xiao, 2021).

Monitoring and research results from rivers of different orders show that the indirect HCO_3^- use by aquatic photosynthesis during summer days together with calcium deposition result in the decrease of HCO_3^-, Ca concentrations and CO_2 partial pressure in water body. Combined the results from Lijiang river and its tributary, an average of about 5% of DIC produced by karst processes is utilized by aquatic photosynthetic and converted into organic carbon. The higher the river order is, the larger the allogenic organic carbon sink is. It also suggests that aquatic photosynthesis can restrain CO_2 degassing at the water-air interface. Taking the Pearl river basin as an example, the annual karst inorganic carbon sink is about 1.6 million tC, and if a conversion rate of 5% is used, the annual organic carbon sink generated by aquatic photosynthesis is about 84 200 tC.

The remarkable effect of aquatic photosynthesis on carbon sequestration in karst rivers suggests that the screening of aquatic plants or algae with high HCO_3^- utilization efficiency can be used for artificial intervention. It means that aquatic photosynthesis may be a potential and effective technological approach to increase karst sink, furthermore provides scientific evidence for the inclusion of karst carbon sink in the source/sink list of greenhouse CO_2.

The fluxes of dissolved inorganic carbon in rivers are mainly controlled by carbonate dissolution, organic matter decomposition, aquatic photosynthesis and water-air interface exchange. The last can be significantly influenced by aquatic photosynthesis. The estimated DIC flux of Sava River in Slovenia shows that CO_2 exchange between water and air interface accounts for only 1% of DIC flux under the condition of low temperature and less rainfall in spring, 7% with high temperature at the end of summer and 5% with low temperature in rainy winter, respectively. The proportion of organic matter decomposition increased from 11% in spring to 17% at the end of summer (Kanduč et al. 2007). A reasonable explanation for the significant increase of degassing in summer could be the weak aquatic photosynthesis in Sava River. In summer with high temperature, no aquatic plants or algae act as an agency to convert HCO_3^- into organic carbon through photosynthesis to reduce CO_2 partial pressure and retards the release of CO_2 in water in this case.

As mentioned above, the proportion of DIC utilization by aquatic photosynthesis in Lijiang river, Guilin, developed in subtropical karst areas, is 6% in summer. Compared with the Sava river, this part of DIC could be released back to atmosphere during CO_2 degassing if no aquatic photosynthetic occurs. It can be concluded that the DIC utilization in aquatic photosynthetic would reduce the CO_2 partial pressure effectively and retard the degassing process, also form allogenic organic carbon, which is a stable component of karst carbon sink.

HCO_3^- can be converted to autogenic organic carbon (AOC) by aquatic photosynthesis. This carbon sink effect has been proved by studies in large rivers or lakes in recent years. For example, AOC in Mississippi River, USA accounts for 20%–57% of total organic carbon (Waterson and Canuel, 2008). This ratio in Pearl River, China is as high as ~65% (Yang et al. 2016). In Fuxian Lake, a deep-water lake in Yunnan, China, particulate AOC accounts for 61% of total organic carbon (Chen, et al. 2018), which is even higher in sediments (60%–80%) (He et al. 2020).

Due to the rapid kinetics of carbonate rock dissolution and its sensitivity to environment, the DIC concentration in rivers generated by dissolution is high in summer, in accordance with the high temperature and high soil CO_2 content in recharge area. For example, Sava River, a typical river developed in karst area, has an average DIC concentration of 3 mM (2.63–4.79 mM) (Kanduč et al. 2007), which is much higher than that of European rivers with an average DIC concentration of 1.5 mM (Kempe et al. 1991). The annual average DIC flux was 4×10^7 g C/($km^2 \cdot a$) in Sava River (Kanduč et al. 2007), equivalent to 10 times that of Mississippi River and 13 times the average of global river (Amiotte and Probst 1993). It is suggested that carbonate karst dissolution has a great potential to increase carbon sink with afforestation or vegetation restoration and a strong regulation (source reduction) effect on soil respiration produced CO_2.

5 Conclusions and perspective

In the field of karst carbon cycle, formation mechanism and carbon sink effect study using the concept of earth critical zone have been the new research direction. Extensive monitoring and research reveal that karst process is a special geological process that is extremely sensitive to environmental changes and closely related to the ecosystems, suggesting that it is actively involved in the current global carbon cycle. In other words, the modern karst carbon cycle is an important part of the global carbon cycle. The carbon sinks formed during the karst process may contribute to the "missing sinks" of the global carbon budget imbalance. Karst carbon sink includes inorganic carbon sink (background karst carbon sink) produced from hydrogeochemical process and organic carbon sink generated by DIC conversion through aquatic photosynthesis, forming relatively stable river (reservoir) water body or sediment carbon sink. Desertification control and carbon sequestration by aquatic plants are two effective ways to increase the carbon sink in karst area. With more intensive monitoring on karst carbon cycle, comprehensive research on mechanism and carbon sink effect, and the improvement of watershed and regional carbon sink evaluation methods, karst carbon sink is expected to be included in the list of atmospheric CO_2 sources/sinks of the global carbon budget in the near future.

The intensity and potential of karst carbon cycle are mainly controlled by ecosystems and climatic zones, which determine the sizes and variations of soil CO_2, the key driving force of carbonates dissolution. CO_2 produced by soil respiration infiltrates with rainwater into underlying karst aquifer and is further involved in the dissolution process, suggesting that karst process can mitigate the release of soil CO_2 to the atmosphere. Namely, it can reduce the item "land use change" (E_{LUC}) in the global carbon budget. The amount of karst carbon sink is usually estimated by using watershed hydrochemistry and runoff, but it is not possible to distinguish the effects of land use change. If the regional dissolution is evaluated by using annual soil CO_2 combined with hydrochemistry, the increase of carbon sink caused by land use change could be predicted as well as the background carbon sink, which can be used to estimate the annual karst carbon sinks. This will require us to make changes and adjustments in investigation and monitoring.

Firstly, the influence of gradient factors (such as elevation, climate and lithology) on the dissolution rate of carbonate rocks in large watershed scale should be built into the dissolution rate gradient factor model. Secondly, comparative study can be developed in a smaller watershed with same or similar land uses (such as forest, shrub, grassland or rock desertification land) by monitoring soil temperature, moisture and CO_2 annually, analyzing seasonal and diurnal soil CO_2 variations and their response to air temperature and precipitation events. These will help to establish soil CO_2 variability equation based on soil temperature and moisture and to evaluate the proportion of CO_2 consumed by dissolution in total soil respiration CO_2. Simultaneous monitoring of changes in water chemistry and runoff should also be conducted, in main springs, underground stream outlets and karst water fed surface rivers in the watershed, to reveal internal relations between HCO_3^- and Ca^{2+} concentrations from watershed and soil CO_2 variations, and finally to develop a soil CO_2 based model (reverse model) for assessment of dissolution intensity. In this way, reverse model together with gradient factor model and CO_2 variability equation, can be used to estimate the annual carbon sink fluxes in different regions, and to evaluate annual carbon sink increment and potential as well. This research strategy will help to uncover the role of carbonates dissolution in reducing the land use change (E_{LUC}) item in the global carbon budget. This new approach to evaluate watershed or regional karst carbon cycle will provide a more evident and efficient karst sink increase scheme and pathway to achieve the "double carbon" goals.

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