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Karst carbon sink processes and effects: A review

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ABSTRACT

On shorter time scales, the karst carbon cycle coupled with photosynthesis, is a potential carbon sink. The surface water biological carbon pump (BCP) plays an important role by transforming dissolved inorganic carbon (DIC) to organic carbon (OC), forming a stable carbon sink through a series of biogeochemical processes on shorter timescales (i.e., years to thousands of years). A comprehensive understanding of the karst carbon sink (KCS) is important in understanding its role in the global carbon budget and carbon neutrality. In this paper, we review the current progress and prospect future research of KCS. The world is facing a quick change in climate and rapid variation in land-use, so the interaction mechanism between the above two and KCS needs to be further understood. Manual intervention to increase KCS also deserves attention. Meanwhile, due to the complexity of the karst system and karst carbon cycle, a comprehensive (water, rock, soil, atmosphere, biology) karst carbon cycle monitoring system needs to be established, integrating different types of carbon sink (e.g., soil, forest, karst) under a research framework. An in-depth understanding of these aspects will help KCS better serve the sustainable development of human society.

1. Introduction

Currently, global warming has increased extreme weather events such as heatwaves, cold waves, and droughts, which have significantly negatively impacted ecology and human social development (Senevirsatne, S.I. et al., 2021). The annual increase in emissions of CO_2 is one of the reasons for climate warming (Parrenin et al., 2013). In the study of the global carbon cycle, scientists have found that it is not entirely clear where anthropogenic CO_2 goes. A large amount of anthropogenic CO_2 (fossil fuel burning and land use changes) has significantly altered the global carbon cycle. Nearly 50% of anthropogenic CO_2 is trapped in the atmosphere, with the other being absorbed by the ocean and land (Melnikov and O'Neill, 2006). The terrestrial portion is the focus of debate because it is not clear exactly where the carbon, called the "missing sink" or "residual land sink", is going, which is estimated at 2.5 ± 1.3 Pg C yr^{-1} from 2002 to 2011 (Ciais, P. et al., 2013). To find this part of the carbon sink, researchers have made many efforts through terrestrial ecosystem simulation, forest carbon sequestration model, and an inverse method, but there is still a gap between the results and the missing sink (Fang et al., 2001; Gurney and Eckels, 2011; Liu et al., 2011; Pan et al., 2011; Regnier et al., 2013).

In 1997, Yuan (1997) proposed that karstification participates in the carbon cycle and has a carbon sink effect. The IGCP379 project (Karst Processes and the Carbon Cycles) established 18 karst dynamic system observation sites under different karst types and estimated the atmospheric CO_2 consumption of karstification in China based on field observation data (Yuan, 1999). Karstification is the process of carbonate rocks dissolution and precipitation by water, and it can be divided into epikarstification and deep-seated (geothermal) karstification. Deep-seated karstification could become a carbon source of atmospheric CO_2 because of the release of CO_2 from the deep earth, while epikarstification consumes atmospheric CO_2 and possesses a carbon sink effect (Becker et al., 2008; Gaillardet and Galy, 2008; Hren et al., 2007; Kerrick et al., 1995). In previous studies, there have been some controversies

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about the KCS, mainly because the atmospheric CO_2 consumed by carbonate weathering is easily returned to the atmosphere through the carbonate deposition (Berner et al., 1983; Curl, 2012; Zhang and Li, 2015). However, with the development of research, the KCS effect has been observed in many karst watersheds, and karstification-related carbon sinks have been gradually valued (Binet et al., 2022; Liu, 2012; Liu et al., 2018, 2021a, 2021b; Liu and Dreybrodt, 2015; Martin et al., 2013; Ulloa-Cedamanos et al., 2020; Yang et al., 2015).

Some researchers have paid more attention to the carbon sink caused by karstification in typical karst regions (carbonate outcrop areas) (Jiang and Yuan, 1999; Li et al., 2018; Suchet et al., 2003). Other researchers proposed that terrestrial carbonates all have such a carbon sink effect (Adams and Post, 1999; Liu et al., 2010, 2018; Zeng et al., 2019). The carbonate outcrop areas of the world are approximately 20 million km^2 (Ford and Williams, 2013; Suchet et al., 2003; Yuan, 1997), accounting for approximately 15% of the total land area (Fig. 1), and the area with carbonate distribution accounts for 50% of the whole land area (Liu et al., 2010). For countries with large karst areas, active research and full utilization of KCS will help to alleviate their emission reduction pressure and achieve carbon neutrality. Here, we will start with the KCS mechanism in the typical karst watershed, reviewing the research progress and prospecting future research.

2. Vertical structure and carbon cycle in a karst watershed

In recent years, surface earth science has focused on the study of the earth's critical zone, which is an area of interaction between the lithosphere, pedosphere, biosphere, hydrosphere, and atmosphere (Council, 2001). The critical zone is closely related to human activities, sensitive to environmental changes, and therefore closely related to the sustainable development of human society (Lin, 2010). Karst critical zone can be divided vertically into the epikarst zone and karst underground space (Fig. 2). The epikarst zone, with a strong cycle of the "carbon--water-calcium" cycle composed of the atmosphere – precipitation – vegetation – soil – fissure – bedrock – water, is a typical area with strong karstification in the upper part of the vadose zone; it is concerned with the transport of matter, the energy conversion, the dynamic mechanism, and the state of subsystems. Including karst pipelines, caves, underground rivers, and aquicludes, the karst underground space focuses on the movement, occurrence characteristics, and their inner relations with the upper critical zone of karst groundwater solutes (Z. Wu et al., 2019).

Holding more than 6×10^7 Pg C, carbonate rocks are the largest carbon pool on Earth and account for over 99% of the total reserves (Falkowski et al., 2000). Karstification consumes CO_2, dissolves carbonate rock, and enters the hydrosphere in the form of dissolved inorganic carbon (DIC), which on the one hand plays a role in carbon shifting and on the other hand, has the potential of carbon sink. DIC transported by karstification remains in the hydrosphere partially, increasing the carbon turnover time (Downing et al., 1993; Semiletov, 1999). Some of them are collected as dissolved organic carbon (DOC) and sedimentary organic carbon (SOC) in inland waters, mainly lakes and reservoirs (Liu et al., 2021a). The rest will finally exist in the ocean carbon pool through biogeochemical processes (e.g., algae, shellfish) in the form of particulate organic carbon (POC), recalcitrant dissolved organic carbon (RDOC), etc. (Cavan et al., 2018; Jiao et al., 2010; Martini et al., 2022; Richardson, 2019; Ritschard, 1992; Siegenthaler and Sarmiento, 1993).

DIC is the total amount of inorganic carbon substances in environmental water, including CO_2 (aq), H_2CO_3, HCO_3^-, and CO_3^{2-}, which occurs mainly as HCO_3^- at $6.5 < pH < 10$ (Soetaert et al., 2007). Its generation, migration, and transformation in the karst watershed are shown as follows (Fig. 3):

First, the flowing water absorbs CO_2 through the soil and air, and the erosion is enhanced. After contact with carbonate rocks, the carbonate rocks are dissolved, and DIC is generated ($CaCO_3+CO_2+H_2O \rightarrow Ca^{2+}+2HCO_3^-$). The driving forces for this reaction are water and CO_2; the water is mainly from rainfall, while the CO_2 is mainly from atmospheric and soil respiration. Second, during the migration of DIC in the groundwater and surface water systems, some of them will degrade as CO_2 when the environmental conditions change, and part of the DIC redeposits as calcite (e.g., as travertine or speleothems). Finally, after converting from groundwater to surface water, the DIC-rich water is used by aquatic photosynthetic organisms to produce organic carbon (OC), which is a reaction with calcification ($Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + x\ (CO_2 \uparrow + H_2O) + (1-x)(CH_2O + O_2)$) because the protons needed for bicarbonate-based photosynthesis are derived largely from calcification (Li et al., 2005; Liu et al., 2018, 2021a; Liu and Dreybrodt, 2015; McConnaughey, 1998). There are three ways that OC can go, depositing in the watershed, degrading to CO_2 or CH_4, and discharging from the watershed with water flow.

3. Karst carbon sink effect and its stability

In the past, the carbon sink effect caused by karstification has been questioned for a long time (Berner et al., 1983; Curl, 2012; Zhang and Li, 2015). In the existing carbon cycle models, geological processes (including karstification) are 2-3 orders of magnitude smaller than biological and marine processes in setting carbon flux parameters (Mackenzie, 2010). Karstification is considered to have little or no contribution to current atmospheric CO_2 sources and sink. The reasons can be summarized in the following aspects: First, the karstification-driven carbon cycle does not produce carbon sinks on a long timescale. Weathering of limestone consumes CO_2 to form soluble

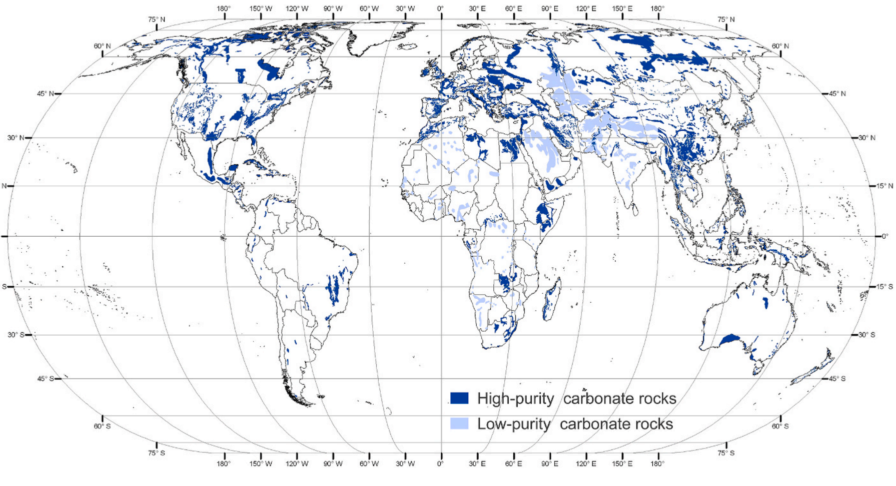

Fig. 1. Distribution of carbonate rocks at Earth's surface; modified from www.fos.auckland.ac.nz.

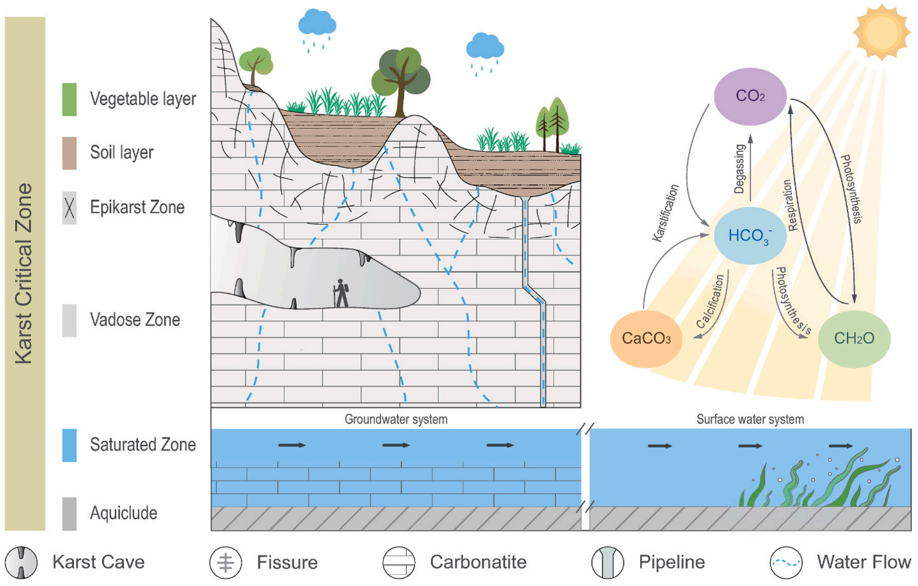

Fig. 2. Sectional structure of a typical karst area.

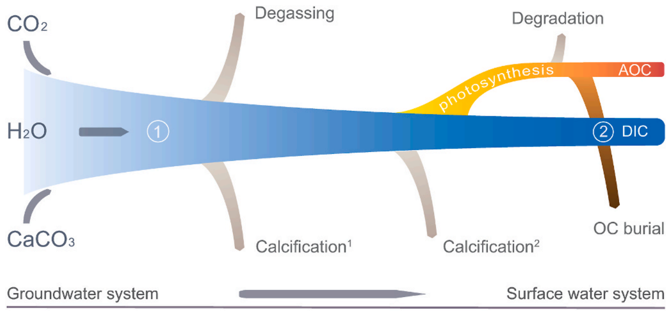

Fig. 3. Simplified process of the carbon cycle in a karst watershed. Notes: 1. “Degassing” includes degassing under the conditions of cave water dripping and karst groundwater coming out of the surface, and the carbonate deposition in these processes (e.g., as travertine or speleothems) is represented by “Calcification^1”. 2. “Calcification^2” refers to calcification during photosynthesis using bicarbonate. 3. “Degradation” — Under the action of microorganisms, some of the active organic carbon is degraded, producing CO_2 or CH_4. 4. Autochthonous organic carbon(AOC), DIC, and OC burial at the end together constitute the potential karst carbon sink flux (KCSF) of a watershed. 3. ① and ② indicate the results from different estimation methods (refer to 5.3).

bicarbonate in solution. If redeposited as calcite (e.g., as travertine or speleothems) or sequestered as shells or reefs when it is carried into the oceans, the associated CO_2 from the atmosphere will be released again, so there will be no net sequestration of CO_2 but rather a transfer from land to the oceans, where it will equilibrate over time with the atmosphere (Curl, 2012). Second, due to the traditional concept of time scale, all geological processes are regarded as slow processes of ten thousand years or more, while ecological processes are classified as fast processes of century-scale (Wigley, 2005). Therefore, when people pay attention to climate change and the carbon cycle in the past or future century, they often ignore the impact of karstification and the relationship between karstification and biological processes. However, with a deeper understanding of the karst carbon cycle, the KCS effect has been taken seriously.

3.1. *Rapid kinetic properties of carbonate rocks dissolution*

Karstification is a rapid dynamic process under the condition of an open system; when the soil CO_2 volume fraction is 1%, the time for calcite to reach dissolution equilibrium is 6 h (Merkel and Planer-Friedrich, 2005). Meanwhile, a large number of monitoring and research results in typical karst areas in Southwest China show that karstic intensity is highly correlated with rainfall, diurnal temperature change, vegetation conditions, and other factors and is closely linked with the atmosphere, hydrosphere and biosphere, with an obvious short time scale characteristics (Liu, 2000a; Pan et al., 2001; Zeng et al., 2016; Zhang, 2010; Zhao et al., 2010; M. Zhao et al., 2015). This means that the carbonate rocks dissolution process can quickly capture large amounts of CO_2 and transform to DIC, which can play an important role in regulating atmospheric CO_2 on short-time scales.

3.2. *Biological carbon pump (BCP)*

Previous studies suggest that TOC in river sediments is mostly derived from allochthonous organic carbon in eroded soils or rocks (Meybeck, 1993). However, for most watersheds, autochthonous organic carbon (from aquatic photosynthesis) is likely to dominate. Tao et al. (2004) showed that in the Zengjiang River (Southern China), approximately 70% of OC in suspended sediment came from algae (autochthonous carbon), while allochthonous organic carbon accounted for only 26.5% of the total. Additionally, in America, approximately half of the TOC in sediments in the Mississippi River watershed is autochthonous organic carbon (Waterson and Canuel, 2008). Moreover, many studies support this idea (Cole et al., 2007; Einsele et al., 2001; Sun et al., 2019). It has been confirmed that a large number of aquatic organisms can directly use HCO- 3 in water as a carbon source for photosynthesis, including submerged plants, algae, photosynthetic bacteria, etc. (Bulthuis, 1983; Chen et al., 2021; Liu et al., 2018, 2021a; Liu and Dreybrodt, 2015; McConnaughey, 1998; Waidner and Kirchman, 2007; Yang et al., 2020; Yue et al., 2003; Zhao et al., 2022), and the photosynthetic rate increases with rising of the concentration of DIC (Maberly, 1985). Therefore, DIC generated by karstification is converted to OC through aquatic photosynthesis, which enhanced the KCS effect.

Zhang (2012), using the carbon isotope model, calculated that 58.8% of DIC generated by karstification in the Caohai River watershed (Southwestern China) was utilized by aquatic plants. Li et al. (2015) show that the proportion of hydrophytes using HCO- 3 as an inorganic carbon source for photosynthesis was 47.84% on average. Sun et al. (2021) conducted a detailed survey of the KCS in the Lijiang River watershed (Southwestern China), and the result considering biological processes was approximately 17% higher than the carbon sink considering DIC only. Although the utilization rate of DIC by aquatic photosynthesis is different due to the differences in climate, geology, hydrology, and other conditions in the different study areas, its contribution to KCS cannot be ignored.

3.3. *Carbon budget in a karst river*

Adamczyk et al. (2009) showed that the pKa of carbonic acid (~3.45) is much lower than previously understood (~6.35), indicating that the H_2CO_3 in water prefers to deprotonate rather than decomposition into CO_2 and H_2O. Many studies have focused on the degassing process of rivers in karst areas; studies have shown that rivers in karst areas usually have obvious degassing in the upstream (high slope) (Drysdale et al., 2002; Hoffer-French and Herman, 1989; Lan et al., 2021), but the effect tends to balance quickly with the river flow (C. Zhang et al., 2021). In Lan et al.(2021) monitoring of streams in karst areas, they found that, even in the initial reach, the obvious CO_2 degassing could offset about 29% of the atmospheric CO_2 absorbed by karstification at most, while in the relatively low and moderate terrain, the degassing had little effect on the KCS. C. Zhang et al. (2021) have studied CO_2 degassing of a high-level karst river (Southwest China); the results show that only 1.7% of DIC in the monitored reach is returned to the atmosphere through degassing, implying that the DIC in the water still has a certain stability and will not be converted into a large amount of CO_2 back to the atmosphere. Studies about the carbon budget in some karst watersheds show that the CO_2 flux in the water surface is positive, which means that the water absorbs CO_2 from the air (carbon sink), further supporting the KCS effect (Liu et al., 2015, 2021b; Yang et al., 2015). This phenomenon is contrary to that observed in the Yangtze River and the Santa Fe River (carbon source) (Zhai et al., 2007; Khadka et al., 2014). Liu et al. (2021b) think the reason is as follows: Driven by karstification, the unique water chemistry of the karst watershed promoted the growth of aquatic plants through the DIC fertilization effect (high biomass), which on the one hand inhibited CO_2 degassing and on the other hand promoted the conversion of more DIC to OC by photosynthesis.

In summary, on a short time scale, the karst carbon cycle driven by karstification coupled with BCP has the potential to act as a carbon sink. Pu et al. (2015) declared that the KCS effect is stable on the century-scale to the millennial-scale and can be felt by human beings. Liu et al. (2018) assessed carbonate mineral weathering as a potential sink of atmospheric CO_2 on a short time scale (years to thousands of years) that could respond to rapid disturbances in the global carbon cycle. In addition, groundwater and seawater cycles occur on centennial and millennial time scales (Oki et al., 2004). Therefore, the KCS effect should not be negligible when we are seriously concerned about the carbon cycle on the century-scale.

4. Factors influencing the karst carbon sink effect

From the above discussion, it can be seen that the KCS effect is produced by geological processes (karstification) and biological processes. Runoff output (Zhang and Schilling, 2006) and DIC concentration (Kardjilov et al., 2006) are the main factors affecting the carbon sink intensity (Zeng et al., 2017), and they are controlled by many environmental factors. Here, we divide the environmental factors into five basic categories: geological, climatic, biological, hydrological, and soil conditions (Fig. 4).

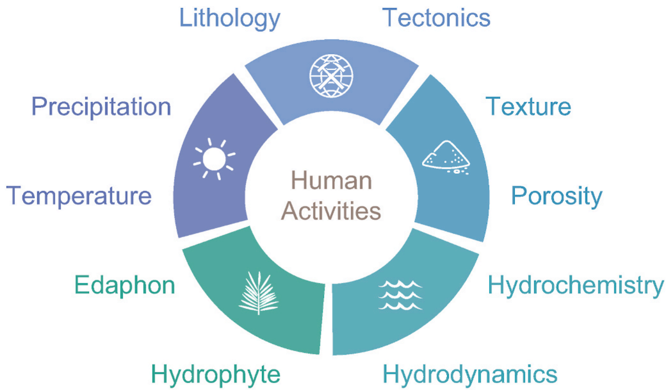

Fig. 4. Influencing factors of KCS. From the top clockwise, these are some representative factors of geology, soil, hydrology, biology and climate. Human activities act on the KCS effect indirectly through these factors.

In natural environments, these factors are closely intertwined and controlled by climate and land cover (Beaulieu et al., 2012; Berg et al., 2021). For a specific watershed, its geological processes are basically stable, so the intensity of KCS mainly depends on the climate and land cover/land use (soil, biology, etc.) (Gaillardet et al., 2019; Hagedorn and Cartwright, 2009; Moosdorf et al., 2011; White and Blum, 1995; Zeng et al., 2019). The HCO_3^- concentration and groundwater CO_2 storage of a karst aquifer in the Konza Prairie (central United States) have increased synchronously over the past 26.5 years, which was attributed to long-term changes in temperature and land use in the region (Macpherson et al., 2019). Raymond et al. (2008) found that in the Mississippi River basin, the increased rainfall, higher proportion of cultivated land, water conservancy construction, and the use of lime fertilization has markedly enhanced the HCO_3^- export flux, almost increasing by +50% in recent decades. Considering the importance of climate change to future human survival and the rapid changes in global land use/land cover change caused by human activities, we will discuss them separately after introducing five basic factors.

4.1. *Geological processes*

Carbonate rocks can be divided into two types: limestone and dolomite; their karstic reaction formula is as follows:

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- (\text{limestone}) \tag{1}$$

$$CaMg(CO_3)_2 + 2CO_2 + 2H_2O \leftrightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- (\text{dolomite}) \tag{2}$$

For limestone, the dissolution of 1 mol calcium carbonate will absorb 1 mol CO_2 from the atmosphere, but for dolomite, this result will be 2 mol CO_2 from the atmosphere. In practice, the corrosion of dolomite and limestone mainly depends on the chemical composition of rocks, the structure of rocks and minerals, the proportion of different mineral components, seepage conditions, and other factors (Gu and Liu, 2022). The corrosion test of two lithologies shows that the specific corrodibility of limestone is generally higher than that of dolomite (Zhu, 1997; Chen et al., 2001; X. Wu et al., 2019), and it is observed that the underground pipeline in a limestone area is better developed (Nie, 1994). It is also found that the effect of the presence of gypsum (or anhydrite) on the dissolution of dolomite is positive when the temperature is below 75 °C and pressure is below 20 MPa (Huang et al., 1996).

Moreover, if there are strong tectonic activities in the watershed and a large number of faults, fissures, and joints are developed, water-rock interaction will be strengthened, and the karstification intensity will be improved (Chen et al., 2016).

4.2. *Climatic factors*

Precipitation is the main driving force of karstification, which directly affects the condition of hydrology and runoff and thus changes the intensity. The effect of temperature on KCS is largely realized by changing biological activities. Higher temperatures can promote biological effects, increase the soil CO_2 concentration, and accelerate its migration but also reduce the stability of CO_2 in water and the solubility of the carbonates (Huang et al., 2014). Gaillardet et al. (2019) examined three global databases of rivers and springs draining carbonate regions under various climate conditions; they found that carbonate weathering intensity depends upon land temperature according to a boomerang-type relationship, with maximum dissolution between 10 and 15 °C.

4.3. Biological processes

Direct corrosion: The growth of organisms on carbonate rocks directly corrodes carbonate. Cao and Wang.(1998) found that crustose lichens' growth on the surface of carbonate rocks can increase the carbonate corrosion rate by 26%–64%. Due to the thin soil, many trees grow directly on rocks in karst areas, and their roots corrode carbonate rocks. The observation results of the Maolan karst forest in southern China show that the amount of direct corrosion of carbonate rocks by plant roots accounts for 40% of the total chemical corrosion in the region (Cao et al., 2001).

Indirect corrosion: The metabolism of organisms changes the surrounding microenvironment and then affects karstification. Field experimental data show that the erosion rate of carbonate karst under the soil is much higher than that on the surface and in the air because the activities of plant roots and soil microorganisms make the CO_2 concentration in soil dozens to hundreds of times higher than that in the air (Cao et al., 2008). In addition, researchers also found that carbonic anhydrase (CA) secreted by plant roots and microorganisms had a significant enzymatic dissolution effect on limestone fields(Yu et al., 2004; Shen et al., 2017; Wang et al., 2018).

Biological carbon pump: A suitable climate and channel environment can promote the growth and reproduction of aquatic phototrophs, thus enhancing the BCP effect, converting more DIC into OC, and finally enhancing the carbon sink effect (refer to 3.2).

4.4. Hydrological processes

The hydrological processes include two aspects, hydrodynamics, and hydrochemistry. There is a diffusion boundary layer (DBL) between the solid carbonate rock and the water interface. With the increase in flow velocity and hydraulic gradient, the DBL becomes thinner, and the dissolution rate of carbonate rocks accelerates (Dreybrodt and Buhmann, 1991; Liu and Dreybrodt, 1998). Hydrochemical conditions determine the erosive ability of water to carbonate rocks, and water from non-karst areas with low hardness and pH has a stronger erosive ability than karst water (carbonate is nearly saturated or even supersaturated) (Liu, 2000b). Sulfuric acid or nitric acid emitted by humans enters karst systems, which can also dissolve carbonate rocks and generate DIC; since this process does not consume atmospheric CO_2, it needs to be excluded in the estimation of the carbon sink; otherwise, the KCS will be overestimated (Meyer et al., 2009).

4.5. Soil properties

Soil thickness, porosity, pH, humidity, texture, and so on can affect the KCS effect (R. Zhao et al., 2015). Taking porosity as an example, on the one hand, by controlling the infiltration of water, the activated carbon and nutrients on the surface are transported to the depth of the soil, which increases the activity of microorganisms and the soil CO_2 concentration (Le Bissonnais, 2016); on the other hand, it also restricts soil CO_2 migration. When soil porosity is low and gas exchange is slow, soil CO_2 can be more easily dissolved in water and participate in the karstification (Weisskopf et al., 2010).

4.6. Land-use and climate change

Many studies have shown that land-use and cover change will affect karstification in three ways: soil CO_2, runoff, and exogenous acids (Andrews and Schlesinger, 2001; Ahearn et al., 2005; Perrin et al., 2008; Zeng and Jiang, 2016). First, land with good ecological conditions has high productivity, biomass, and strong soil respiration, leading to high soil CO_2 concentrations (Frank et al., 2006). Andrews and Schlesinger. (2001) designed a field experiment and proved that the increase in the soil CO_2 concentration enhanced carbonate rock weathering. Second, land use and cover change significantly changed the surface conditions, resulting in corresponding changes in surface hydrological processes (evapotranspiration, soil moisture, soil infiltration rate, etc.), which restricted the runoff output of the watershed. For instance, the roots of crops are relatively shallow, so compared with natural cover, the intensity of evapotranspiration on farmland is weak (Scanlon et al., 2005). Third, anthropogenic land-use change may bring about exogenous acids such as sulfuric acid and nitric acid, which may interfere with natural karstification. Perrin et al. (2008) studied the effects of nitrogen fertilizer on carbonate rock corrosion in agricultural areas in southeastern France and found that the resulting nitric acid can reduce the amount of atmospheric CO_2 consumption by carbonate weathering by approximately 7%–17%. In addition, the effect of land-cover on karstification may be bidirectional; forest restoration can enhance the KCS effect by increasing soil CO_2 concentration on the one hand and negatively affect it because runoff has been weakened by forest crown interception on the other hand (Jackson et al., 2005).

In the foreseeable future, the global climate will experience a continuous rise in temperature, an increase in atmospheric CO_2 concentration, an intensification of the global water cycle, and an intensification of runoff. There is an optimal temperature range for the carbonate weathering (Gaillardet et al., 2019), which means climate warming will enhance the KCS effect in high-latitude areas and weaken the effect in low-latitude areas(Zeng et al., 2021). Binet et al. (2022) found that rising temperatures can increase carbonate weathering by encouraging bacteria to oxidize organic matter (OM); protons produced by OM oxidation can alter the calcium-carbon balance and dissolve carbonate rocks, which can occur even if the saturation of the calcite is reached. The increase in atmospheric CO_2 concentration not only directly increased the soil CO_2 concentration but also enhanced soil respiration and promoted BCP through the fertilization effect (Romero-Mujalli et al., 2019). The promotion of precipitation increase on KCS is also obvious. For example, the amount of carbon sequestration produced by karstification in the Pearl River watershed in wet years is 3 times that in dry years (Huang et al., 2014).

A Forty-year survey in a karst watershed shows that, in the context of global warming and hydroclimatic fluctuations, DIC concentrations presented a significant rising trend (Ulloa-Cedamanos et al., 2020). By using the model, Liu et al. (2010) predict that until 2100, global warming will increase the global carbonate weathering carbon sink by 20%. Zeng et al. (2019) inferred that there is likely to be a widespread and consistent increase in the global carbonate weathering carbon-sink flux (CCSF) over the period 1950–2100, ranging from +9.8% (RCP4.5) to + 17.1% (RCP8.5). Even though these conclusions need to be confirmed by further studies, they still indicate that the potential of KCS in the context of climate perturbance and anthropogenic land-use change is worthy of attention, and its negative feedback effect on global warming may play an important role in the future.

5. Estimation of karst carbon sink

5.1. Methods

Many researchers have tried to evaluate KCS from different angles. According to different principles, the methods can be categorized as follows.

5.1.1. Dynamic method

The dynamical method obtains data on the reaction rate, activation energy, and pre-exponential factors by analyzing the relationship between the concentration of reactants or products in karstification and the time spent. The main models include the diffusion boundary layer model (Dreybrodt and Buhmann, 1991) and the PWP model (Plummer et al., 1978). However, this kind of method mainly built models for pure carbonate rocks (such as calcite) from a microscopic point of view, and it is difficult to explain the differences in the dissolution of different types of carbonate rocks (Qian et al., 2010). Meanwhile, the method does not consider the influence of the stress environment on the dissolution characteristics, and the solubility and its rate of rock minerals under different stress environments have certain differences (Bosworth, 1981; Tang et al., 2008). Therefore, it is rarely used in the research of karst geology or engineering problems (Qiu et al., 2004; Qian et al., 2010).

5.1.2. Thermodynamic method

This method was established by White (1984). It is also known as the maximum potential dissolution method (MPD). The method assumes that the water discharged from the watershed reaches carbonate equilibrium concerning local temperature and CO_2 conditions and establishes the relationship. As long as basic climatic data, such as temperature, precipitation, and evapotranspiration, are known, the theoretical maximum of carbonate rock dissolution in the area can be calculated. It does not require a long time of on-site monitoring and sampling, and the required data can be easily obtained. It should be noted that this method calculated the theoretical maximum dissolution amount (potential) under given climatic and geological conditions, and could not reflect the actual amount of CO_2 consumed by karstification in the region. Zeng et al.(2016, 2019) adopted an improved MPD and discussed the impact of climate change on the KCS in southwestern China and the sensitivity of global carbonate weathering carbon sink flux to climate and land-use changes.

5.1.3. Tablet test method

Carbonate standard tablets are placed at different depths in the air, surface, and soil layers of the target area. After a period of time (usually one hydrological year), they are removed and weighed to assess the intensity of karstification based on weight changes of the tablet (Chevalier, 1953; Gams, 1985; Krklec et al., 2021). The advantage of this method is that it is simple and easy to carry out a comparative analysis of the factors that affect the carbonate karst erosion rate, such as climate, lithology, hydrology, and land use, without considering the watershed boundary. However, the disadvantages are also very obvious; it is mostly a question of authenticity and representation. First, the dissolution amount obtained by this method is a potential dissolution capacity under man-made conditions, rather than the real dissolution amount, because it is difficult to reproduce the real dissolution situation in the natural state (Z. Zhang, 2012). Second, if there are more primary and secondary carbonate rocks in the overlying soil layer of the test tablet, rainwater will react with the first. When the water reaches the position of the test tablet, its proximity has been greatly weakened, so that the results obtained are small, and it may even obtain negative values due to the oversaturation of the rainwater (Plan, 2005). In addition, due to the strong spatial heterogeneity of the karst area, it is difficult to evaluate and realize the regional representativeness of test tablets.

5.1.4. Hydrogeochemistry method

By measuring the runoff and the concentration of solutes (e.g., HCO_3^-, K^+, Na^+, and Ca^{2+}) in the outflow of watersheds, the rate of various types of rock weathering was calculated based on the distribution of rocks in the watershed, and the mass of carbon consumed by weathering was estimated. Hydrogeochemical methods mainly include (Zhou et al., 2020): the river chemistry method, solute load method, GEM-CO_2, and SiB algorithm; among them, the solute load method and GEM-CO_2 model are widely used.

The solute load method estimates the atmospheric CO_2 consumed by carbonate weathering based on the DIC concentration, runoff, and watershed area at the outlet of the watershed. The traditional formula (3) assumes that half of the DIC generated comes from atmospheric CO_2 and a half from carbonate rocks, so the coefficient n is 0.5 generally (Liu et al., 2010). Liu et al. (2018) considered the role of the BCP and proposed an improved runoff method formula (4). Results calculated by this method are closer to the real value than previous methods because it takes into account biological processes. Due to the relatively new time when the theory was proposed, the actual monitoring studies using this method are few and limited to the southwest China (He et al., 2020; Sun et al., 2019, 2021; Yang et al., 2020, 2022). Therefore, more relevant studies need to be carried out on a larger scale to test it.

$$\mathrm{CSF} = \mathrm{n} \times \mathrm{Q} \times [\mathrm{DIC}] / \mathrm{A} \tag{3}$$

$$\mathrm{CSF} = \mathrm{Q} \times (\mathrm{n}[\mathrm{DIC}] + [\mathrm{AOC}]) / \mathrm{A} + \mathrm{F}_{\mathrm{AOC(s)}} \tag{4}$$

where CSF is the carbon sink flux; Q is the runoff discharge; [DIC] is the concentration of DIC (dissolved inorganic carbon) at the outlet of the river watershed; [AOC] is the concentration of AOC (autochthonous organic carbon) at the outlet of the river watershed; $F_{AOC(s)}$ is the sedimentary flux of AOC in the surface water system; A is the watershed area; and n is the proportion of [DIC] from atmospheric CO_2.

The solute load method relies on accurate Q and DIC concentration, which requires extensive field investigation, sampling, and monitoring in the study area. In addition, when using this method to calculate the carbon sink, attention should be given to disturbances such as weathering of silicate rocks (Liu et al., 2011), CO_2 release from deep earth (Hurwitz et al., 2010), and exogenous acids (Perrin et al., 2008; Li et al., 2010). Otherwise, the results will be biased.

The GEM-CO_2 model was created by Suchet and Probst. (1993a). Based on the data of surface runoff and major dissolved elements in 232 lithologically single watersheds in France (Meybeck, 1987), they established an empirical relationship model, which could estimate the atmospheric CO_2 consumption from weathering of different rocks in the region requiring only lithology, temperature, and precipitation data. The model has been applied in many regions (Qiu et al., 2004; Suchet and Probst, 1993b, 1995; Zhou et al., 2017). However, since the model is based on the situation in France, the coefficients of the model may not be applicable in some regions (Zhou et al., 2020).

5.2. Comparisons of global estimation

Here, we show the global karst carbon sink flux (KCSF) calculated by different researchers (Table 1). The global KCSF ranges from 0.2 to 0.9 Pg C/a, with an average of 0.453 Pg C/a. It should be noted that although some studies have made pathbreaking contributions to the estimation of KCS, they use limited point data from field sites, which increases the uncertainty of the results and leads to poor space-time representation and expansibility of the estimation, e.g., Yuan (1997), Liu and Zhao, (2000).

5.3. Limitations

Top-down evaluation methods (e.g., MPD model, tablet test) tend to overestimate KCSF (Fig. 3, ①) because they focus on the amount of atmospheric CO_2 consumed by karstification, but not all of these CO_2 turns into a stable carbon sink. Bottom-up methods (e.g., solute load method, GEM model) directly calculate the carbon sink part. However, due to the lack of understanding of the karst carbon cycle, it is difficult to consider thoroughly, and it may lead to low results (Fig. 3, ②). Apparently, most of the existing methods are relatively old, and the majority consider only geological processes and neglect biological processes. To meet the needs of the development of KCS research, it is urgent to explore improvements or establish new effective evaluation methods.

6. Summary and perspectives

KCS has been paid more and more attention by researchers, and some important research findings have been achieved (Li et al., 2018; Liu

Table 1
Estimates of global CSF from different studies.

Reference	Method	Details	Magnitude (Pg C/a)
Yuan (1997)	Solute load method	Based on case studies of 13 monitoring sites in China and then extrapolated from similar global data set.	0.61
Liu and Zhao (2000)	Tablet test	Calculate the CSF of China based on an area ratio and extrapolated estimated rates to global outcrop of bare karst terrains only	0.41
	Solute load method	China's CCS is calculated based on the observation data of China's stations, and the global CCS is calculated based on the proportion of karst areas in China and the world.	0.42
Gombert (2002)	MPD	Based on global meteorological station data.	0.3
Suchet et al. (2003)	GEM-CO_2	Global mapping of lithology, coupled with watershed composition.	0.21
Liu et al. (2018)	Solute load method	Coupled carbonate weathering (CCW), DIC concentration in precipitation in different regions of the World, compilation of site data,	0.5
Li et al. (2018)	MPD	Thermodynamic equilibrium estimates based on global high spatial resolution hydrological, meteorological and geochemical data, coupled with a machine learning algorithm.	0.89
Li et al. (2019)	Solute load method	Based on the multi-year average monitoring data of major river watersheds over 100,000 km^2 provided by GEMS-GLORI Global River Database.	0.28
Average			0.453

et al., 2018; Suchet et al., 2003; Ulloa-Cedamanos et al., 2020; Zeng et al., 2021). The contribution of KCS at the global scale needs to be further studied, but the carbon sink effect is evident in many karst regions (Liu et al., 2015, 2021b; Sun et al., 2021; Yang et al., 2022, 2015; C. Zhang et al., 2021). Further study of the KCS will help solve the problem of the missing sink and improve the global carbon cycle model. For countries with large karst areas, active research and full utilization of KCS will help to alleviate their emission reduction pressure and achieve carbon neutrality. In addition, ecological restoration and reconstruction in karst areas can not only increase the KCS but also improve the soil, ecosystem diversity, and regional economy. As the country with the largest karst area in the world, China has actively explored this research karst ecological reconstruction and utilization of the KCS (Lan et al., 2016; Zeng et al., 2018), which is a positive beginning and a good demonstration to the world. However, due to the complexity of the karst system and karst carbon cycle, much research needs to be carried out.

6.1. The influence of climate change and land-use change

Karstification is sensitive to climate perturbance and land-use change (Pan et al., 2001; Probst et al., 1994; Zeng et al., 2019; M. Zhao et al., 2015). In the future, KSCF will be expected to become a considerable carbon sink that is against the rising atmospheric CO_2 concentration and has the potential to act as negative feedback to global warming. At present, most of the research on KCS in the world is concentrated in the middle and low latitudes but few in the high latitudes. In the future, we need to pay more attention to the KCS effect located in different karst types and under different climates. It is quite important to clarify the regulatory potential of climate and land-use on KCS, which will provide a scientific basis for the sustainable development of society and economy under the background of global change and the formulation of measures to cope with climate change.

6.2. Manual intervention to increase KCS

Based on the occurrence mechanism of the KCS, some studies have explored increasing the carbon sink through manual intervention to help achieve the goal of carbon neutrality. The existing methods include ground vegetation restoration (Cheng, 2011; Lan et al., 2016), soil improvement (Zhou et al., 2002; Lan et al., 2016; Zeng et al., 2018), exogenous water irrigation (Bughio et al., 2016; Schindlbacher et al., 2019; Kim et al., 2020), aquatic community structure optimization (C.-L. Zhang et al., 2021), etc. However, there is still a lack of systematic experimental and demonstration areas for artificial intervention to increase carbon sinks, so carbon neutrality evaluations cannot be conducted systematically from the perspective of the carbon budget. Relevant research platforms need to be established to carry out more detailed research (C.-L. Zhang et al., 2021).

6.3. Systematic study on the karst carbon cycle

Recently, some studies have attempted to enrich the meaning of the KCS (Wu and Wu, 2022; Zhang et al., 2022). To understand KCS accurately, the karst carbon cycle needs more and more studies on all aspects. Research on KCS needs to be fully connected with terrestrial ecosystem carbon flux observation and groundwater monitoring systems, establishing a comprehensive (water, rock, soil, atmosphere, biology) karst carbon cycle monitoring system. Various types of carbon sinks, such as soil, forest, karst, and so on, need to be integrated under a research framework, which will be beneficial to macro control of the overall carbon cycle and carbon sink of the system and will help to find a more efficient and reliable method of carbon sequestration (Kang et al., 2020). In addition, the effects of aquatic photosynthesis have been partially considered by studies of ocean and lake carbon pools (Walsh, 1991; Ritschard, 1992; Siegenthaler and Sarmiento, 1993; Jiao et al., 2010). Therefore, it is necessary to clarify whether the coupled KCS has repeated calculations with other terrestrial carbon sinks.

Data availability

All data for this review article was published, please see the original references.

CRediT authorship contribution statement

Lvfan Chen: Conceptualization, Investigation, Writing – original draft, Writing – review & editing. **Liangcheng Tan:** Conceptualization, Writing – review & editing, Supervision, Project administration. **Min Zhao:** Conceptualization, Writing – review & editing. **Ashish Sinha:** Writing – review & editing. **Tianli Wang:** Writing – review & editing. **Yongli Gao:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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