Coupled nitrogen transformation and carbon sink in the karst aquatic system: a review

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ABSTRACT

Carbonate bedrock regions represent that 14% of Earth’s continental surface and carbon (C) sink in karst water plays an important role in the global C cycle due to the CO\textsubscript{2} consumption during carbonate mineral weathering. Intensive agriculture and urbanization have led to the excessive input of nitrogen (N) into aquatic systems, while the high concentrations of inorganic C in the karst water might affect the N cycle. This paper summarized the characteristics of water in karst regions and discussed the N transformation coupled with the C cycle in the condition of high Ca\textsuperscript{2+} content, high pH, and high C/N ratios. Carbonates can consume more atmospheric and pedologic CO\textsubscript{2} than non-carbonates because of their high solubility and high rate of dissolution, resulting in the higher average CO\textsubscript{2} sink in karst basins worldwide than that in non-karst basins. Therefore, carbonate mineral weathering and aquatic photosynthesis are the two dominant ways of CO\textsubscript{2} absorption, which are termed as coupled carbonate weathering. As the alkalinity and high C/N content of karst water inhibit the denitrification and mineralization processes, the karst aquatic environment is also served as the N sink.

Key words: atmospheric CO\textsubscript{2} sink, bicarbonate, carbonate weathering, karst water, nitrogen cycle

HIGHLIGHTS

- Karst aquatic systems contain high contents of DIC, Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, and high pH.
- C–N cycles in the karst aquatic systems are mainly related with DIC and NO\textsubscript{3}–.
- Enhanced nitrification and DIC can promote aquatic communities growth.
- Atmospheric CO\textsubscript{2} sink in carbonate area is high.

1. INTRODUCTION

1.1. Karst evolution and the urgency of carbon balance

The term ‘karst’ refers to regions that typically developed from carbonate rocks. These rocks mainly include mineral calcite (CaCO\textsubscript{3}) and mineral dolomite (CaMg(CO\textsubscript{3})\textsubscript{2}), containing limestone and dolomite rock or dolostone, respectively (Hartmann 2015). Carbonate bedrock regions represent 14% of Earth’s continental surface, including broad swaths of southwestern China. The southwestern China karst region is one of the largest globally continuous karst areas, covering ~540 × 10\textsuperscript{3} km\textsuperscript{2} over eight provinces (Zhang et al. 2020). Carbonate karst aquifers are severed as the drinking water source for about one-quarter of the global population (Ford & Williams 1989).

Stress on climate change due to carbon dioxide (CO\textsubscript{2}) emissions has increased significantly in recent decades, which is attributed to deforestation, the change of land-use type, and the use of fossil fuels (Melnikov & O’Neill 2006). Liu et al. (2015) estimated that China’s cumulative carbon (C) emission during 2000–2013 was nearly 2.9 gigatons, which was larger than China’s estimated total forest sink during 1990–2007 (2.66 gigatons of C). Moreover, this estimated C sink was still undervalued in terms of deserts and karst formations. In China, two considerable challenges for estimating C sink are the amount of CO\textsubscript{2} emitted and absorbed by the landscape.
As limestone degradation could be a substantial inorganic C sink, the C sink in the karst area might play an important role in the global C cycle and the balance of China’s C emission.

1.2. The important role of carbon sink in karst water
Water plays a critical role in the C cycle in the karst area, as it is a basic medium to transform derived organic and inorganic carbon, and C can also be exchanged with the atmosphere in the form of CO₂ across the water–air interface. Previous studies have shown that many non-karst (mainly silicate area) rivers are usually supersaturated with CO₂, then leading to the emissions of CO₂ (Butman & Raymond 2011; Wang et al. 2011; Rasilo et al. 2017). However, in karst water, such as rivers, lakes, and reservoirs, carbonate mineral weathering consumes CO₂ with a more rapid ratio and, therefore, increases the concentrations of dissolved inorganic carbon (DIC) (mainly HCO₃⁻/CO₃²⁻) (Berner 2003; Liu et al. 2011). As DIC can be consumed by aquatic phototrophs by photosynthesis and transformed to organic C in inland water, the absorption of CO₂ continues and forms karst C sink rapidly (Liu et al. 2011). Therefore, it is of great importance to understand the role of karst processes as a global C sink and the quantification of C fluxes.

1.3. Excessive input of nitrogen (N) in karst water
Intensive agriculture and urbanization have led to the excessive input of N into the soil and further increased the amount of nitrate (NO₃⁻) in water (Xin et al. 2019), as well as changed the N cycle process in the aquatic ecosystem. Human activities have delivered 64 Tg N/yr to rivers and streams in the 20th century, which doubled that in the 19th century (34 Tg N/yr) (Beusen et al. 2016). It has been shown that the cycling of C and N in karst aquatic systems is closely related to each other, as coupled C–N cycling is involved in the transformation of DIC into dissolved organic carbon (DOC) (Zhao et al. 2021). The increasing anthropogenic atmospheric CO₂ emissions result in a progressive increase in N limitation in plants. C sequestration and increased atmospheric CO₂ concentrations would lower terrestrial N availability and lead to decreases in N flux to the atmosphere and N deposition to aquatic ecosystems. As industrial and agricultural discharge drives a sharp increase in anthropogenic N emissions, the magnitude of N from this anthropogenic input will likely become large enough to sustain similar conditions of ecosystem N availability (McLauchlan et al. 2013). The elevated DIC concentrations in karst water may also enhance the aquatic photosynthetic uptake of DIC (Liu et al. 2010b, 2011) and then may promote N translation. However, the interactions between N translation and CO₂ absorption in karst aquatic ecosystems have not been well depicted.

1.4. Objectives
In this review, we provide an overview of the relevance of karst regions to the special water characteristics and discuss the impact on the N transformation due to these specific water characteristics. We (1) start with an introduction to the characteristics of karst water, (2) present an overview of N transformation in karst water systems, (3) discuss the processes related to carbon sink, and (4) show the challenges and new directions in karst water C/N balances.

2. CHARACTERISTICS OF KARST WATER
2.1. The characteristic of carbonate weathering
The carbonate weathering is formulated as CaCO₃ + CO₂ + H₂O ↔ HCO₃⁻ + Ca²⁺ and CaMg(CO₃)₂ + 2CO₂ + 2H₂O ↔ 4HCO₃⁻ + Ca²⁺ + Mg²⁺. CO₂ consumed during carbonates dissolution would finally be released to the atmosphere by the precipitation of carbonates in the oceans (Garrels 1983), and the kinetics of dissolution is much faster as compared to precipitation considering the ocean turnover time (timescales of <3 ka). Therefore, carbonate weathering is critical in global CO₂ balances (Van Cappellen & Qiu 1997; Kump et al. 2000).

CO₂ was absorbed by raindrops formed in the atmosphere, and of which the concentration would further increase after precipitation and infiltration in the soil due to vegetation and microbial processes. Furthermore, the CO₂ in soil water could dissolve the bedrock underlying soil, composed of carbonate rock, during percolation of soil moisture in the karst area. Previous research found that the contribution of carbonates, e.g. HCO₃⁻, to the total dissolved load in the lakes and rivers worldwide was up to 58% (Ferris et al. 1994).
2.2. High contents of HCO$_3^-$, Ca$^{2+}$, and Mg$^{2+}$ in alkaline karst water

The rapid process of carbonate weathering resulted in remarkably higher concentration of bicarbonate and calcium in water in carbonate terrains as compared to silicate terrains (Liu & Dreybrod 1997; Liu et al. 2007; Raymond et al. 2008). Therefore, the reaction between carbonate minerals and CO$_2$, which increases DIC (DIC = CO$_2$(aq) + HCO$_3^- + CO_3^{2-}$) concentrations, may impact the C cycle and represent a net sink of atmospheric CO$_2$ in a short time scale (Martin 2017).

Previous studies in Table 1 showed that the karst water pH values ranged from 6.45 to 9.7, with pH in most of the water samples higher than 7. Considering dissolved CO$_2$ is mainly present as HCO$_3^-$ (Liu et al. 2018) when the water pH varies from 6.5 to 10, the main form of DIC in karst water is HCO$_3^-$ and the conversion of HCO$_3^-$ to CO$_2$ is slow. While the HCO$_3^-$ concentration varies in different karst water samples, with the values ranging from 12.2 to 2,633 mg/L, the HCO$_3^-$ concentration in karst water is much higher than that in non-karst water of similar environmental parameters (e.g. temperature and precipitation). In addition, great variations of Ca$^{2+}$ and Mg$^{2+}$ concentrations were also observed. In terms of geographic locations, the concentrations of HCO$_3^-$, Ca$^{2+}$, and Mg$^{2+}$ in South China were higher than those in North China, which could be attributed to the differences in environmental parameters, such as temperature, lithology, and climate. As can be seen in Table 1, the concentrations of HCO$_3^-$, Ca$^{2+}$, and Mg$^{2+}$ in a typical karst catchment in Guangxi, China were about 10 times higher than that in the Yellow River. Therefore, it is summarized that karst water is typically with high contents of HCO$_3^-$, Ca$^{2+}$ and Mg$^{2+}$, and high pH.

2.3. C/N ratio in karst river and non-karst water

As shown in Table 2, the organic carbon (OC)/N ratio in karst water in the upstream of the Pearl River (11.8:1) is about twice compared to that in the Pearl River estuary (5.0:1) (Liu et al. 2020). While the organic carbon can be

| Locations | pH  | HCO$_3^-$ | Ca$^{2+}$ | Mg$^{2+}$ | References        |
|-----------|-----|-----------|----------|----------|-------------------|
| Karst water |     |           |          |          |                   |
| Groundwater, southwest China | 7.33–7.36 | 190.22–335.92 | 45.60–71.46 | 12.60–35.14 | Liu et al. (2007) |
| Reservoir water, Guizhou, China | 7.88 | 166.53 | 68.90 | – | Liu et al. (2021) |
| Spring water, southwest China | 7.08–7.52 | 184.04–273.84 | 62.72–93.87 | 0.27–2.34 | Liu et al. (2004) |
| Reservoir water, Guizhou, China | 7.25–9.18 | – | 24.74–74.09 | 5.54–19.01 | Ma et al. (2021) |
| Karst catchment, Guangxi, China | – | 270.00–2,633.00 | 122.00–1,382.00 | 20.00–176.00 | Sun et al. (2021a, 2021b) |
| Spring water, Guizhou, China | 7.50–9.7 | 90.1–255.30 | 24.30–61.00 | 9.10–21.60 | Chen et al. (2017) |
| Lijiang River Basin | 6.45–8.52 | 21.96–201.00 | 5.80–53.36 | 0.98–8.73 | Sun et al. (2019) |
| Guancun River, Guangxi, China | – | 173.90–289.04 | 71.14–86.04 | 4.81–14.37 | Cheng et al. (2012) |
| Karst spring-fed pool, Chongqing, China | – | – | 52.50–56.00 | 1.80–2.10 | Jiang et al. (2013) |
| Groundwater, Shandong, China | 7.57 | 263.78 | 158.59 | 26.06 | Wu et al. (2021) |
| Groundwater, Jianghan Plain, China | 6.60–7.50 | 439.00–748.00 | 85.00–140.00 | 20.00–43.00 | Zhou et al. (2015) |
| Groundwater, North China Plain | – | 12.20–1,879.50 | 2.40–1,622.20 | – | Zhang et al. (2013a) |
| Non-karst water |     |           |          |          |                   |
| River water, Guangdong, China | 7.73–7.95 | – | 37.67–131.36 | 6.57–276.97 | Chen et al. (2019) |
| Yellow River, China | 8.11–8.21 | 186.66–208.01 | 86–94 | 29.76–46.80 | Zhang et al. (1995) |
| Hanfeng Lake, Chongqing, China | 8.05–8.12 | 65.453–67.466 | – | – | Zhao et al. (2021) |
| Mixed water |     |           |          |          |                   |
| Tibetan lakes, China | 7.80–10.40 | ND–9,613.00 | 4.33–1,140.00 | 1.80–9,089.00 | Li et al. (2016) |
| Ichetucknee River water, USA | 7.48–8.06 | 2.86–2.95 | 1.34–1.40 | 0.29–0.30 | Montety et al. (2011) |

ND, not detected.
categorized into DOC and particulate organic carbon based on a size threshold of 0.2 \(\mu\text{m}\). A previous study showed that the DOC/N ratio in a karst reservoir in Guilin, China was 1.11:1 (Song et al. 2017), which is not consistent with aforementioned Liu et al.’s work. Moreover, the OC/N ratio values in karst soil were slightly lower than those in non-karst soil (Gu et al. 2018). In addition, Table 2 also shows that the DOC/N ratios in rivers of China are much lower than those in the Mississippi River estuary and Yenisei River, probably due to high precipitation and high organic matter (OM) inputs, indicating that the OM might be the key factor influencing the DOC/N ratio in rivers as riverine OM is with high DOC/N ratio (about 30:1) (Bauer et al. 2013).

Neither the data of the DIC/N ratio in the karst or the non-karst aquatic systems are available. The DIC contents in karst water are relatively higher as discussed before; therefore, it can be deduced that the total concentrations of carbon including DIC and DOC in karst water are also higher than those in non-karst water. As organisms translate DIC into total organic carbon (TOC) by photosynthesis, theoretically the total carbon (TC)/N ratios in karst water should also be higher. Considering the limited number of researches available currently, more researches are still required to figure out the differences of TC/N ratios between karst and non-karst water.

### Table 2 | Organic C/N ratios reported in some world large rivers, modified based on Liu et al. (2020)

| Rivers/reservoirs      | DOC/N | References                          |
|------------------------|-------|-------------------------------------|
| **Karst water**        |       |                                     |
| Pearl River (pristine upstream) | 11.8:1 | Liu et al. (2020)                   |
| Longtan Reservoir, Tian’an, China | 7.13\textsuperscript{a} | Cao et al. (2019)                   |
| Wulixia Reservoir, Guilin, China | 1.11:1\textsuperscript{b} | Song et al. (2017)                  |
| Runoff in the Puding Country, China | 6–9\textsuperscript{c} | Song et al. (2019)                  |
| **Non-karst water**    |       |                                     |
| Superior Lake (Canada, Ontario) | 8.13:1 | Zigah et al. (2012)                 |
| Amazon River           | 29.1:1| Meybeck (1982)                      |
| Pearl River estuary    | 5:1   | Liu et al. (2020)                   |
| Yangtze River          | 6.2:1 | Wu et al. (2007)                    |
| Yellow River estuary   | 6.0:1 | Liu et al. (2012), Zhang et al. (2013b) |
| Mississippi River estuary | 20.4:1 | Dagg et al. (2005)                  |
| Yenisei River          | 43.1–52.4:1 | Holmes et al. (2012)            |

\textsuperscript{a}Dissolved inorganic carbon was used.  
\textsuperscript{b}TOC was used here.  
\textsuperscript{c}Dissolved carbon was used.

3. TRANSFORMATION OF NITROGEN IN KARST WATER

#### 3.1. Nitrogen emission in karst aquatic systems

As one of the most important cycles in water systems, the N cycle, including the conversion and flux of N, has received worldwide attention in recent years. Human activities, such as intensive agriculture and rapid urbanization, lead to excessive and repetitive N inputs, which significantly affect the natural cycle of N. In the 20th century alone, human activities have increased the amount of N delivering to rivers and streams from 34 to 64 Tg N/yr (Beusen et al. 2016). N pollution has become one of the most concerned and prevalent environmental problems, especially in karst areas. Karst areas are subjected to greater pressure of N pollution than other regions because karst aquifers are particularly sensitive and vulnerable to chemical pollution from human activities due to their developed networks of fractures, pipelines, and sinkholes (Jiang 2013).

In water systems, the two sources for N are natural and artificial activities. While biological N fixation was the only important process in Earth’s ecosystems producing reactive N to support C fixation into energy-rich OM (primary production) before the agricultural and industrial revolutions, human activities have been introducing large amounts of N into the environment through municipal sewage, industrial effluent, and agriculture since the agricultural and industrial revolutions (Wakida & Lerner 2005), especially the N fertilizer used in agriculture to promote crop growth and increase crop yield (Wang et al. 2019a, 2019b).
3.2. N cycle processes

In aquatic environments, N was composed by organic and inorganic N (Nie et al. 2018). The organic nitrogen is divided into dissolved organic nitrogen (DON) and particulate organic nitrogen (PON), depending on whether it can pass through a 0.2-μm filter (Jørgensen 2009). DON includes a variety of organic molecules and compounds, ranging from small molecules like urea and amino acids, to peptides and proteins, while PON includes both dead OM and living organisms that are larger than 0.2 μm (Jørgensen 2009). The inorganic nitrogen in aquatic ecosystems includes dissolved N₂ gas, oxidized ions such as nitrate (NO₃⁻), nitrite (NO₂⁻), ammonium ion (NH₄⁺), and ammonia gas (NH₃) (Howarth 2009). The most frequently detected mineral N fractions in water are NO₃⁻ and NH₄⁺, which are also the dominant components of N produced by human activities (Beusen et al. 2016).

In water systems, N would go through a variety of bacteria-mediated processes, mainly including nitrogen fixation, mineralization, nitrification, denitrification, dissimilated nitric acid reduction to ammonium, and ammonia oxidation (Figure 1). Most N on Earth is in the form of N₂, which becomes biologically significant after being fixed by bacteria, lightning, volcanic activity, and human activity. In aquatic environments, N fixation is mostly carried out by heterotrophic or autotrophic bacteria and cyanobacteria. NO₃⁻, NO₂⁻, NH₄⁺, and NH₃ are the active N in water. Algae, rooting plants, fungi, and bacteria absorb and reduce NO₃⁻ and NO₂⁻ to NH₃ in a process known as assimilative nitrate or nitrite reduction. NH₄⁺ could be catalytic-oxidized by nitrifying bacteria to NO₃⁻ in a process called nitrification, from which the nitrifying bacteria gain energy to fix CO₂ into new bacterial biomass. Plants, algae, and microorganisms use nitrates and ammonium to produce organic nitrogen-containing compounds, which could be further taken up by animals through the food chain, through one of the following processes: direct absorption, assimilation, and reduction. The organic N eaten by animals or decomposed by microorganisms is excreted as ammonium or as urea which is further rapidly hydrolyzed to ammonium. In addition, NO₃⁻ is also reduced by heterotrophic or autotrophic bacteria to NO₂⁻, which is further reduced to N₂ by a process known as traditional denitrification or dissimilated nitrate reduction. These processes that release of N from organic N back to the environment are called nitrogen mineralization. The other N cycle processes include denitrification based on chemosynthetic oxidation of sulfides or reduced iron (Howarth 2009), anaerobic oxidation of ammonia to N₂ (Anammox), dissimilatory reduction of NO₃⁻ to NH₄⁺ via NO₂⁻ (DNRA) (Medinets et al. 2015), and autohydrogenotrophic denitrification of NO₃⁻/NO₂⁻ to N₂ (Jiang et al. 2020). However, the relative importance of these newly discovered processes in water systems remains quite uncertain (Howarth 2009).

![Figure 1](http://iwaponline.com/bgs/article-pdf/doi/10.2166/bgs.2021.120/970920/bgs2021120.pdf)

**Figure 1** | The simplified N cycle in the karst water system (based on Howarth 2009). The plus sign suggests that alkaline karst water promotes the nitrification process. Minus signs indicate that the high C/N content and alkalinity in karst water inhibit the mineralization and denitrification processes.
3.3. N cycle characteristics in karst area

Due to the unique hydrochemistry of karst water (such as high Ca$^{2+}$ content, high pH, and high DIC concentrations), the N cycle characteristics in karst areas are different from those in non-karst areas. In the perspective of the N cycle, the alkalinity and high DIC contents in karst areas can inhibit the heterotrophic denitrification and mineralization processes, which determine the karst aquatic environment as an N sink. During nitrification, the oxidation of every ammonium ion produces two protons worth of acidity and makes the environment more acidic (Howarth 2009). Therefore, the alkaline environment in karst water is beneficial to neutralizing the acid generated by nitrification and further promotes nitrification. However, the denitrification process is opposite to nitrification. Every nitrate ion consumed during denitrification consumes one proton of acidity, and thus, this process tends to raise the pH of the environment (Howarth 2009). Consequently, the inherent alkalinity of karst water will inhibit the denitrification reaction. Furthermore, the high DIC/N ratios in karst water can inhibit the gross mineralization because microbes immobilize rather than mineralize N to maintain the stoichiometric ratio of DIC/N in their biomass (Xin et al. 2019).

3.4. Cycling of C and N in karst area

The cycling of C and N in aquatic environments is closely related, with coupled control of organic carbon concentrations through aquatic biological processes of assimilation or denitrification (Gruber & Galloway 2008; Zeng et al. 2019). Although there are few studies on the C–N coupling cycle in karst water systems, some studies have found that excessive nitrogen emissions from human activities lead to the C–N coupling cycle participating in the carbonate weathering process, resulting in the increase of DIC flux in karst water systems (Raymond et al. 2008; Jiang 2013; Zhao et al. 2020). Most biological processes in water systems are C-limited processes, but this is not the case in karst aquatic environments. As shown in Figure 2, in karst water systems, higher DIC and increased NO$_3^-$ concentration due to the enhanced nitrification and human activities can promote the growth of aquatic communities (Liu et al. 2018; Zeng et al. 2019). The growing amount of algae and microorganisms in water increases the consumption of DIC and NO$_3^-$ through photosynthesis, as the conversion of DIC to OC by photosynthesis induces the consumption of NO$_3^-$, and therefore, reduces the NO$_3^-$ concentration (Pedersen et al. 2013; Nõges et al. 2016; Liu et al. 2018). In addition, during this process, DIC and NO$_3^-$ are converted to OM and O$_2$ is released, which contrasts with the traditional knowledge that CO$_2$ is released during carbonate precipitation (Jiang 2013). It has been shown that in the Lijiang River water, the consumption of DIC and NO$_3^-$ by aquatic photosynthesis was in a ratio of 9:1 (mol/mol) to produce autochthonous DOC (Zhao et al. 2021). To sum up, the C–N cycle coupled with DIC and NO$_3^-$ promotes the generation of in-situ DOC in karst aquatic environments, which constitutes the relatively long-term natural C and N sinks in karst water systems, as shown in Figure 2.

![Figure 2](http://iwaponline.com/bgs/article-pdf/doi/10.2166/bgs.2021.120/970920/bgs2021120.pdf)
4. THE PROCESSES RELATED TO CARBON SINK IN KARST WATER

4.1. The global carbon budget and carbonate CO2 sink volume

Five major components in the global C budget are fossil CO2 emissions ($E_{FOS}$), emissions from land-use change ($E_{LUC}$) (mainly deforestation), atmospheric CO2 ($G_{ATM}$), ocean CO2 sink ($S_{OCEAN}$), and terrestrial CO2 sink ($S_{LAND}$). Over the last decade (2010–2019), $E_{FOS}$ and $E_{LUC}$ were 9.6 ± 0.5 and 1.6 ± 0.7 Pg C/yr, respectively, $G_{ATM}$ was 5.1 ± 0.02 Pg C/yr, $S_{OCEAN}$ and $S_{LAND}$ were 2.5 ± 0.6 and 3.4 ± 0.9 Pg C/yr, respectively, and the imbalance budget ($B_{IM}$) was –0.1 Pg C/yr (Friedlingstein et al. 2020). The accepted values for $S_{LAND}$ at present range from 1.8 to 3.4 Pg C/yr in the global C budget (Melnikov & O’Neill 2006; Lal 2008; Friedlingstein et al. 2020). Similarly, another research indicated that $S_{LAND}$ was calculated at 2.6 Pg C/yr, while CO2 sink due to photosynthesis and CO2 emissions from plant respiration were 14.1 and 11.6 Pg C/yr, respectively (Yuan & Liu 2003).

A large C sink is missing from the global carbon cycle with the value of 1.7–2.5 Pg C/yr (Cao et al. 2011). CO2 sink from carbonate might be an important component missed in previous studies; however, the volume of CO2 sink by carbonate weathering on continents varied greatly in different researches, with its volume ranging from 0.018 to 0.6 Pg C/yr worldwide, which is about 7–36% of the missing C sink (Yuan 1997; Gaillardet et al. 1999; Gombert 2002; Liu et al. 2010b). Liu et al. (2011) found that carbonate weathering contributed about 94% to the atmospheric CO2 sink, while only 6% resulted from silicate weathering. More researches on CO2 absorption experiments using more accurate calculation methods are still needed to estimate the atmospheric CO2 sink by carbonate weathering.

4.2. Carbonate-related atmospheric CO2 sinks

Two primary processes related to global sinks of atmospheric CO2 are the transformation of CO2 to HCO3− in water due to rock weathering (Li et al. 2011) and the assimilation of CO2 by photosynthesis to organic C (Sabine et al. 2004; Zeebe & Caldeira 2008). There are three sources of HCO3−, including carbonate weathering by carbonic acid, carbonic weathering by sulfuric and/or nitric acids, and silicate weathering. Carbonates can consume more atmospheric and petrologic CO2 because of their high solubility and high dissolution rate (Liu et al. 2010b), resulting in aquatic photosynthesis being the main process for CO2 absorption in silicate terrains, the roles of both carbonate mineral weathering and aquatic photosynthesis, termed as coupled carbonate weathering, are significant in karst areas (Liu et al. 2018). In addition, Sun et al. (2021a, 2021b) also observed that the average contributions made by silicate weathering to the CO2 sink in the Lijiang River basin ranged from only 2.3 to 14.8%, which indicated that carbonate weathering was the main source of HCO3− in this basin although carbonate rock area (3,832 km2) is smaller than silicate rock area (5,482 km2).

DIC is mainly consumed by phototrophs in aquatic ecosystems such as rivers, lakes, and the oceans (Dean & Gorham 1998; Cassar et al. 2004; Tortell et al. 2008). During this process, DIC is transformed in the water to OC and pCO2 is reduced, which results in the continuous uptake of atmospheric CO2 (Liu et al. 2010b). The biological productivity of aquatic phototrophs has been found to be associated with the supply of DIC from rock weathering. For instance, the utilization of HCO3− by Oocystis solitaria Witt in karst water was 4.6-fold higher than that in non-karst water (Liu et al. 2010a).

Previous researches concluded that the atmospheric CO2 consumed by carbonate weathering was compensated by a CO2 released from marine carbonate precipitation over a relatively short time. However, this conclusion neglected the large amount of atmospheric CO2 uptake during aquatic photosynthesis (Liu et al. 2010b). Moreover, Liu et al. (2018) also observed that the increased DIC concentration controlled by carbonate weathering in the karst area might enhance aquatic photosynthesis, promoting the consumption of atmospheric carbon. Therefore, the amount of CO2 absorbed by the C sink in the karst area was larger as compared to other areas.

4.3. High carbon sink rate in carbonate area

As shown in Table 3, the range of carbon sink rate in carbonate area was 1.54–73 tC/km2/yr, while in silicate area the range of this value was 0.02–8.0 tC/km2/yr. The annual average C sequestration flux of limestone weathering in China was estimated to be 4.28–5.02 tC/km2/yr (Li et al. 2019). The C sinks produced by carbonate weathering and the ‘biological C pump’ in the Li River basin were 12.17 and 2.24 tC/km2/yr, respectively (Sun et al. 2021a, 2021b). The average amount of CO2 consumed by C sinks in karst basins around the world (8.5 tC/km2/yr) was about three times higher than that in non-karst basins (2.86 tC/km2/yr). In karst water, the C sink is enhanced by...
N translation, as the concentration of dissolved CO$_2$ was decreased dramatically (about 75%) due to the increase of NO$_3^-$/C0$_2$ in the Yangtze River (Wang et al. 2007). Therefore, in the karst basin, the transformation of C and N by aquatic phototrophs was coupled.

### Table 3 | The carbon sink rates (in tC/km$^2$/yr) in the different basins

| Location                  | C sink rate | Silicate weathering | Carbonate weathering | References           |
|---------------------------|-------------|---------------------|----------------------|----------------------|
| Lijiang river, China      | 14.41       | 12.17               |                      | Sun et al. (2021a, 2021b) |
| Guancun Underground Stream, China | 73.00        |                      | Pu et al. (2017)    |
| Guancun Underground Stream, China | 12.34       |                      | Guo et al. (2011)   |
| Mumei Underground Stream, China | 31.44       |                      | Guo et al. (2011)   |
| Banzhai Underground Stream, China | 11.80       |                      | Guo et al. (2011)   |
| Pearl River basin, China  | 11.68       |                      | Cao et al. (2011)   |
| China (2000–2014)         | 4.28        |                      | Li et al. (2019)    |
| Taiwan, China             | 27.15       |                      | Li et al. (2019)    |
| Karst zone, Southeastern China | 8.56        |                      | Jiang et al. (2011) |
| Karst zone, North China   | 1.54        |                      | Jiang et al. (2011) |
| Karst zone, Qinghai-Tibetan plateau, China | 2.20        |                      | Jiang et al. (2011) |
| Pearl River, China        | 7.40        |                      | Qin et al. (2015)   |
| Pearl River basin, China  | 35.98       |                      | Wei (2003)          |
| Yangtze River, China      | 11.27       |                      | Zhang et al. (2016) |
| Yangtze River, China      | 10.07       |                      | Li et al. (2019)    |
| Yellow River, China       | 5.74        |                      | Li & Zhang (2003)   |
| Yellow River, China       | 2.65        |                      | Li et al. (2019)    |
| Xijiang River, China      | 11.06       |                      | Yang et al. (2020)  |
| Russia                    | 0.08        |                      | Zhang et al. (2021) |
| Canada                    | 0.18        |                      | Zhang et al. (2021) |
| United States             | 0.49        |                      | Zhang et al. (2021) |
| Round the world           | 0.02–8.00   |                      | Gaillardet et al. (1999) |

N translation, as the concentration of dissolved CO$_2$ was decreased dramatically (about 75%) due to the increase of NO$_3^-$/C0$_2$ in the Yangtze River (Wang et al. 2007). Therefore, in the karst basin, the transformation of C and N by aquatic phototrophs was coupled.

### 5. CONCLUSIONS AND OUTLOOKS

Carbonate bedrock regions represent 14% of the continental surface of the Earth and provide drinking water resources for about 25% of the global population. C sink in karst water plays an important role in the global C cycle due to the CO$_2$ consumption during carbonate mineral weathering. This review highlights the consumption of CO$_2$ during carbonate weathering and the relevance of the N and C cycles in karst regions. Existing concentrations of HCO$_3^-$, Ca$^{2+}$, Mg$^{2+}$, and C/N ratios are presented, followed by a review of previous studies.

Here we show that,

1. Karst aquatic systems are characterized by high contents of HCO$_3^-$, Ca$^{2+}$, Mg$^{2+}$, high pH, and high C/N ratios.
2. The cycling of C and N in karst aquatic environments is closely related and the high content of DIC in karst systems will increase the nitrogen sink. Also, the growth of aquatic communities was promoted by higher concentration of DIC and the increase of NO$_3^-$ due to the enhanced nitrification and human activities.
3. The budget of CO$_2$ sink from carbonate ranged from 0.018 to 0.6 Pg·C/yr (about 7–36% of the missing carbon sink), which indicated that carbonate weathering was an important component neglected in previous studies.
4. The range of C sink rates in carbonate area was 1.54–73.00 tC/km$^2$/yr, while in silicate area the range of this value was 0.02–8.00 tC/km$^2$/yr.

The N input in karst areas worldwide would increase due to continuous population growth, industrial activities expansion, and lifestyles improvement. This necessitates the collection of sufficient information about the C and N sinks in karst systems to provide reliable projections of C and N balances. As few studies are available
specifically focusing on the impact of karst characteristics on the C sink as well as the N cycle, more field observations targeting the relationships between C and N cycles in karst aquatic systems are urgently needed to figure out the mechanism of N sink in karst water with high abundance of DIC.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Bauer, J. E., Cai, W.-J., Raymond, P. A., Bianchi, T. S., Hopkinson, C. S. & Regnier, P. A. G. 2013 The changing carbon cycle of the coastal ocean. Nature 504, 61–70. https://doi.org/10.1038/nature12857.

Berner, R. A. 2003 The long-term carbon cycle, fossil fuels and atmospheric composition. Nature 426, 323–326. https://doi.org/10.1038/nature02131.

Beusen, A. H., Bouwman, A. F., Van Beek, L. P., Mogollón, J. M. & Middelburg, J. J. 2016 Global riverine N and P transport to ocean increased during the 20th century despite increased retention along the aquatic continuum. Biogeoosciences 15, 2441–2451.

Butman, D. & Raymond, P. A. 2011 Significant efflux of carbon dioxide from streams and rivers in the United States. Nature Geoscience 4, 839–842. https://doi.org/10.1038/ngeo1294.

Cao, J., Yang, H. & Kang, Z. 2011 Preliminary regional estimation of carbon sink flux by carbonate rock corrosion: a case study of the Pearl River Basin. Chinese Science Bulletin 56, 5766–5773. https://doi.org/10.1016/j.sci.2011.04.005.

Cao, Y., Yuan, R., Jiao, S., Zhang, Q. & Deng, F. 2019 Spatial distribution patterns of dissolved carbon and nitrogen based on semi-variation in Longtan Reservoir. Yellow River 41, 94–99.

Cassar, N., Laws, E. A., Bidigare, R. R. & Popp, B. N. 2004 Bicarbonate uptake by Southern Ocean phytoplankton. Global Biogeochemical Cycles 18. https://doi.org/10.1029/2003GB002116.

Chen, B., Yang, R., Liu, Z., Sun, H., Yan, H., Zeng, Q., Zeng, S., Zeng, C. & Zhao, M. 2017 Coupled control of land uses and aquatic biological processes on the diurnal hydrochemical variations in the five ponds at the Shawan Karst Test Site, China: implications for the carbonate weathering-related carbon sink. Chemical Geology 456, 58–71. https://doi.org/10.1016/j.chemgeo.2017.03.006.

Dean, W. E. & Gorham, E. 1998 Magnitude and significance of carbon burial in lakes, reservoirs, and peatlands. Geology 26, 535–538. https://doi.org/10.1130/0091-7613(1998)026<0535:MAASC>2.3.CO;2.

de Montety, V., Martin, J. B., Cohen, M. J., Foster, C. & Kurz, M. J. 2011 Influence of diel biogeochemical cycles on carbonate weathering in a karst river. Chemical Geology 283, 31–43. https://doi.org/10.1016/j.chemgeo.2010.12.025.

Ferris, F. G., Wiese, R. G. & Fyfe, W. S. 1994 Precipitation of carbonate minerals by microorganisms: implications for silicate weathering and the global carbon dioxide budget. Geomicrobiology Journal 12, 1–13. https://doi.org/10.1080/01490549409377966.

Ford, D. & Williams, P. W. 1989 Karst Geomorphology and Hydrology. Chapman&Hall, London.
Gaillardet, J., Dupré, B., Louvat, P. & Allègre, C. J. 1999 Global silicate weathering and CO2 consumption rates deduced from the chemistry of large rivers. Chemical Geology 159, 3–30. https://doi.org/10.1016/S0009-2541(99)00051-5.

Garrels, R. 1983 The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. American Journal of Science.

Gombert, P. 2002 Role of karstic dissolution in global carbon cycle. Global and Planetary Change 33, 177–184. https://doi.org/10.1016/S0921-8181(02)00069-3.

Gruber, N. & Galloway, J. N. 2008 An earth-system perspective of the global nitrogen cycle. Nature 451, 293–296.

Gu, J., Yang, Q., Jiang, Z., Luo, W., Zeng, H., Qin, X. & Lan, F. 2018 Spatial variation analysis of soil carbon, nitrogen and phosphorus eco-stoichiometric ratios in karst and non-karst areas of Guangan country, Yunnan, China. Carsologica Sinica 37, 761–769.

Guo, F., Jiang, G. & Kang, Z. 2011 Study on carbon sink effect in typical sub-tropical karst water system. Carsologica Sinica 30, 403–409.

Hartmann, A. 2015 Karst water resources in a changing world: review of hydrological modeling approaches. Reviews of Geophysics, 218–242.

Holmes, R. M., McClelland, J. W., Peterson, B. J., Tank, S. E., Bulygina, E., Eglinton, T. I., Gordeev, V. V., Gurtovaya, T. Y., Raymond, P. A., Repeta, D. J., Staples, R., Striegl, R. G., Zhulidov, A. V. & Zimov, S. A. 2012 Seasonal and annual fluxes of nutrients and organic matter from large rivers to the Arctic ocean and surrounding seas. Estuaries and Coasts 35, 569–382. https://doi.org/10.1007/s12237-011-9386-6.

Howarth, R. 2009 Nitrogen. In: Encyclopedia of Inland Waters (Likens, G. E., eds). Academic Press, Oxford, pp. 57–64. https://doi.org/10.1016/B978-012370626-3.00098-3.

Jiang, Z., Qin, X., Cao, J., Jiang, X., He, S. & Luo, W. 2011 Calculation of atmospheric CO2 sink formed in karst progresses of the karst divided regions in China. Carsologica Sinica 30, 363–367.

Jiang, Y. 2013 The contribution of human activities to dissolved inorganic carbon fluxes in a karst underground river system: evidence from major elements and δ13CDIC in Nandong, Southwest China. Journal of Contaminant Hydrology 152, 1–11.

Jiang, Y., Hu, Y. & Schirmer, M. 2013 Biogeochemical controls on daily cycling of hydrochemistry and δ13C of dissolved inorganic carbon in a karst spring-fed pool. Journal of Hydrology 478, 157–168. https://doi.org/10.1016/j.jhydrol.2012.12.001.

Jørgensen, N. O. G. 2009 Organic nitrogen. In: Encyclopedia of Inland Waters (Likens, G. E., eds). Academic Press, Oxford, pp. 852–851. https://doi.org/10.1016/B978-012370626-3.00119-8.

Kump, L. R., Brantley, S. L. & Arthur, M. A. 2000 Chemical weathering, atmospheric CO2, and climate. Annual Review of Earth and Planetary Sciences 28, 611–667. https://doi.org/10.1146/annurev.earth.28.1.611.

Lai, R. 2008 Carbon sequestration. Philosophical Transactions of the Royal Society B: Biological Sciences 363, 815–830. https://doi.org/10.1098/rstb.2007.2185.

Li, J. & Zhang, J. 2005 Chemical weathering processes and atmospheric CO2 consumption in the Yellow River drainage basin. Marine Geology & Quaternary Geology, 43–49.

Li, Q., He, Y., Cao, J., Liang, J. & Zhu, M. 2011 The plant carbonic anhydrase at karst area and its ecological effects. Ecology and Environmental Sciences 20, 1867–1871.

Li, C., Kang, S., Liu, Y., Hou, J., Guo, J., Liu, X., Cong, Z. & Zhang, Q. 2016 Distribution of major ions in waters and their response to regional climatic change in large rivers. Science China Earth Science 66, 974–991. https://doi.org/10.1007/s11430-018-9324-2.

Liu, Z. & Dreybrod, W. 1997 Dissolution kinetics of calcium carbonate minerals in H2O-CO2 solutions in turbulent flow: the role of the diffusion boundary layer and the slow reaction H2O + CO2 → H+ + HCO3-. Geochimica et Cosmochimica Acta 61, 2879–2898. https://doi.org/10.1016/S0016-7037(97)00143-9.

Liu, Z., Groves, C., Yuan, D., Meiman, J., Jiang, G., He, S. & Li, Q. 2004 Hydrochemical variations during flood pulses in the south-west China peak cluster karst: impacts of CaCO3–H2O–CO2 interactions. Hydrological Processes 18, 2423–2437. https://doi.org/10.1002/hyp.1472.

Liu, Z., Li, Q., Sun, H. & Wang, J. 2007 Seasonal and storm-scale hydrochemical variations of typical epikarst springs in subtropical karst areas of SW China: soil CO2 and dilution effects. Journal of Hydrology 337, 207–223. https://doi.org/10.1016/j.jhydrol.2007.01.034.

Liu, Y., Zhang, J., He, Y., Sun, H. & Liu, Z. 2010a The utilization of dissolved inorganic carbon by Oocystic solitaria Wittr and its influence on the precipitation of calcium carbonate. Geochimica 39, 191–196.

Liu, Z., Dreybrod, W. & Wang, H. 2010b A new direction in effective accounting for the atmospheric CO2 budget: considering the combined action of carbonate dissolution, the global water cycle and photosynthetic uptake of DIC by aquatic organisms. Earth-Science Reviews 99, 162–172. https://doi.org/10.1016/j.earscirev.2010.03.001.

Liu, Z., Dreybrod, W. & Liu, H. 2011 Atmospheric CO2 sink: Silicate weathering or carbonate weathering? In: Applied Geochemistry, Ninth International Symposium on the Geochemistry of the Earth’s Surface (GES-9) 26. pp. S292–S294. https://doi.org/10.1016/j.apgeochem.2011.05.085.

Liu, S. M., Li, L. W., Zhang, G. L., Liu, Z., Yu, Z. & Ren, J. L. 2012 Impacts of human activities on nutrient transports in the Huangye (Yellow River) estuary. Journal of Hydrology 430–431, 103–110. https://doi.org/10.1016/j.jhydrol.2012.02.005.

Liu, Z., Guan, D., Wei, W., Davis, S. J., Ciais, P., Bai, J., Peng, S., Zhang, Q., Hubacek, K., Marland, G., Andres, R. J., Crawford-Brown, D., Lin, J., Zhao, H., Hong, C., Boden, T. A., Feng, K., Peters, G. P., Xi, F., Liu, J., Li, Y., Zhao, Y., Zeng, N. & He, K.
2015 Reduced carbon emission estimates from fossil fuel combustion and cement production in China. *Nature* 524, 335-338. https://doi.org/10.1038/nature14677.

Liu, Z., Macpherson, G., Groves, C., Martin, J. B., Yuan, D. & Zeng, S. 2018 Large and active CO2 uptake by coupled carbonate weathering. *Earth Science Reviews* 182, 42-49.

Liu, Q., Liang, Y., Cai, W.-J., Wang, K., Wang, J. & Yin, K. 2020 Changing riverine organic C:N ratios along the Pearl River: implications for estuarine and coastal carbon cycles. *Science of the Total Environment* 709, 136052. https://doi.org/10.1016/j.scitotenv.2019.136052.

Liu, X., Zhou, Z., Zhang, H., Dan, Y. & Jiang, Y. 2021 Changes of hydrochemistry and dissolved inorganic carbon during thermal stratification in Pingzhi Reservoir. *Resources and Environment in the Yangtze Basin* 50, 936-945.

Ma, S., Wei, Y., Han, C., Yan, H., Liu, Z., Sun, H. & Bao, Q. 2021 Hydrochemical characteristics in karst reservoir and its implication for inorganic carbon deposition fluxes. *Journal of Lake Sciences*, 1-14.

Martin, J. B. 2017 Carbonate minerals in the global carbon cycle. *Chemical Geology* 449, 58-72. https://doi.org/10.1016/j.chemgeo.2016.11.029.

McLauchlan, K. K., Williams, J. J., Craine, J. M. & Jeffers, E. S. 2013 Changes in global nitrogen cycling during the Holocene epoch. *Nature* 495, 352-355. https://doi.org/10.1038/nature11916.

Medinet, S., Skiba, U., Rennenberg, H. & Butterbach-Bahl, K. 2015 A review of soil NO transformation: associated processes and possible physiological significance on organisms. *Soil Biology and Biochemistry* 80, 92-117.

Melnikov, N. B. & O’Neill, B. C. 2006 Learning about the carbon cycle from global budget data. *Geophysical Research Letters* 33, L02705. https://doi.org/10.1029/2005GL023935.

Meybeck, M. 1982 Carbon, nitrogen, and phosphorus transport by world rivers. *American Journal of Science* 282.

Nie, S., Zhao, L., Lei, X., Sarfraz, R. & Xing, S. 2018 Dissolved organic nitrogen distribution in differently fertilized paddy soil profiles: implications for its potential loss. *Agriculture, Ecosystems & Environment* 262, 58-64.

Nõges, P., Cremona, F., Laas, A., Martma, T., Rõõm, E.-I., Tömm, K., Vilk, M., Vilbaste, S. & Nõges, T. 2016 Role of a productive lake carbon sequestration within a calcareous catchment. *Science of the Total Environment* 530, 225-230.

Pedersen, O., Colmer, T. D. & Sand-Jensen, K. 2013 Underwater photosynthesis of submerged plants—recent advances and methods. *Frontiers in Plant Science* 4, 140.

Pu, J., Li, J., Khadka, M. B., Martin, J. B., Zhang, T., Yu, S. & Yuan, D. 2017 In-stream metabolism and atmospheric carbon sequestration in a groundwater-fed karst stream. *Science of the Total Environment* 579, 1543–1555. https://doi.org/10.1016/j.scitotenv.2016.11.132.

Qin, X., Jiang, Z., Zhang, L., Huang, Q. & Liu, P. 2015 The difference of the weathering rate between carbonate rocks and silicate rocks and its effects on the atmospheric CO2 consumption in the Pearl River Basin. *Geological Bulletin of China* 34, 1749-1757.

Rasilo, T., Hutchins, R. H. S., Ruiz-González, C. & del Gorgio, P. A. 2017 Transport and transformation of soil-derived CO2, CH4, and DOC sustain CO2 supersaturation in small boreal streams. *Science of the Total Environment* 579, 902–912. https://doi.org/10.1016/j.scitotenv.2016.10.187.

Raymond, P. A., Oh, N.-H., Turner, R. E. & Broussard, W. 2008 Anthropogenically enhanced fluxes of water and carbon from the Mississippi River. *Nature* 451, 449–452. https://doi.org/10.1038/nature06505.

Sabine, C. L., Feely, R. A., Gruber, N., Key, R. M., Lee, K., Bullister, J. L., Wanninkhof, R., Wong, C. S., Wallace, D. W. R., Tilbrook, B., Millero, F. J., Peng, T.-H., Kozyr, A., Ono, T. & Rios, A. F. 2004 The oceanic sink for anthropogenic CO2. *Science* 305, 367–371. https://doi.org/10.1126/science.1097403.

Song, A., Peng, W., He, R., Jin, Z., Lu, X., Fang, J., Huang, B. & Li, Q. 2017 Hydrochemistry characteristics in front of the Wulixia Reservoir Dam associated with feedback from aerobic anoxygenic phototrophic bacteria. *Rock and Mineral Analysis* 36, 171–179.

Song, X., Gao, Y., Green, S. M., Wen, X., Dungait, J. A. J., Xiong, B., Quine, T. A. & He, N. 2019 Rainfall driven transport of carbon and nitrogen along karst slopes and associative interaction characteristic. *Journal of Hydrology* 573, 246-254. https://doi.org/10.1016/j.jhydrol.2019.03.083.

Sun, P., He, S., Yuan, Y., Yu, S. & Zhang, C. 2019 Effects of aquatic phototrophs on seasonal hydrochemical, inorganic, and organic carbon variations in a typical karst basin, Southwest China. *Environmental Science and Pollution Research* 26, 32836–32851. https://doi.org/10.1007/s11356-019-06374-6.

Sun, P., He, S., Yu, S., Pu, J., Yuan, Y. & Zhang, C. 2021a Dynamics in riverine inorganic and organic carbon based on carbonate weathering coupled with aquatic photosynthesis in a karst catchment, Southwest China. *Water Research* 189, 116658. https://doi.org/10.1016/j.watres.2020.116658.

Sun, P., He, S., Yu, S., Pu, J., Yuan, Y. & Zhang, C. 2021b Dynamics in riverine inorganic and organic carbon based on carbonate weathering coupled with aquatic photosynthesis in a karst catchment, Southwest China. *Water Research* 189, 116658. https://doi.org/10.1016/j.watres.2020.116658.

Tortell, P. D., Payne, C., Gueguen, C., Strzepek, R. F., Boyd, P. W. & Rost, B. 2008 Inorganic carbon uptake by Southern Ocean phytoplankton. *Limnology and Oceanography* 53, 1266–1278. https://doi.org/10.4319/lo.2008.53.4.1266.

Van Cappellen, P. & Qiu, L. 1997 Biogenic silica dissolution in sediments of the Southern Ocean. II. Kinetics. *Deep Sea Research Part II: Topical Studies in Oceanography* 44, 1129–1149. https://doi.org/10.1016/S0967-0645(96)00112-9.

Wakida, F. T. & Lerner, D. N. 2005 Non-agricultural sources of groundwater nitrate: a review and case study. *Water Research* 39, 3–16.
Wang, F., Wang, Y., Zhang, J., Xu, H. & Wei, X. 2007 Human impact on the historical change of CO₂ degassing flux in River Changjiang. *Geochemical Transactions* 8, 7. https://doi.org/10.1186/1467-4866-8-7.

Wang, F., Wang, B., Liu, C.-Q., Wang, Y., Guan, J., Liu, X. & Yu, Y. 2011 Carbon dioxide emission from surface water in cascade reservoirs-river system on the Maotiao River, southwestern China. *Atmospheric Environment* 45, 3827–3834. https://doi.org/10.1016/j.atmosenv.2011.04.014.

Wang, Q., Ma, M., Jiang, X., Guan, D., Wei, D., Zhao, B., Chen, S., Cao, F., Li, L. & Yang, X. 2019a Impact of 36 years of nitrogen fertilization on microbial community composition and soil carbon cycling-related enzyme activities in rhizospheres and bulk soils in northeast China. *Applied Soil Ecology* 136, 148–157.

Wang, Y., Ying, H., Yin, Y., Zheng, H. & Cui, Z. 2019b Estimating soil nitrate leaching of nitrogen fertilizer from global meta-analysis. *Science of the Total Environment* 657, 96–102.

Wei, X. 2005 *The Fluxes of Carbon and Erosion in Pearl River Delta*. PhD, Graduate School of Chinese Academy of Sciences.

Wu, Y., Zhang, J., Liu, S. M., Zhang, Z. F., Yao, Q. Z., Hong, G. H. & Cooper, L. 2007 Sources and distribution of carbon within the Yangtze River system. *Estuarine, Coastal and Shelf Science* 71, 13–25. https://doi.org/10.1016/j.ecss.2006.08.016.

Wu, X., Song, Y., Wang, J., Gao, H., Liu, C. & Li, B. 2021 Groundwater hydrogeochemical characteristics in the up reaches of Chaiwen River, Shandong Province. *Environmental Chemistry*, 1–10.

Xin, J., Liu, Y., Chen, F., Duan, Y., Wei, G., Zheng, X. & Li, M. 2019 The missing nitrogen pieces: a critical review on the distribution, transformation, and budget of nitrogen in the vadose zone-groundwater system. *Water Research* 165, 114977. https://doi.org/10.1016/j.watres.2019.114977.

Yang, R., Sun, H., Chen, B., Yang, M., Zeng, Q., Zeng, C., Huang, J., Luo, H. & Lin, D. 2020 Temporal variations in riverine hydrochemistry and estimation of the carbon sink produced by coupled carbonate weathering with aquatic photosynthesis on land: an example from the Xijiang River, a large subtropical karst-dominated river in China. *Environmental Science and Pollution Research* 27, 13142–13154. https://doi.org/10.1007/s11356-020-07872-8.

Yuan, D. 1997 Modern karstology and global change study. *Earth Science Frontiers*, 21–29.

Yuan, D. & Liu, Z. 2003 *Carbon Cycle and Karst Geological Environment*. Sciences Press, Beijing.

Zeebe, R. E. & Caldeira, K. 2008 Close mass balance of long-term carbon fluxes from ice-core CO₂ and ocean chemistry records. *Nature Geoscience* 1, 312–315. https://doi.org/10.1038/ngeo185.

Zeng, S., Liu, H., Liu, Z., Kaufmann, G., Zeng, Q. & Chen, B. 2019 Seasonal and diurnal variations in DIC, NO₃⁻ and TOC concentrations in spring-pond ecosystems under different land-uses at the Shawan Karst Test Site, SW China: carbon limitation of aquatic photosynthesis. *Journal of Hydrology* 574, 811–821. https://doi.org/10.1016/j.jhydrol.2019.04.090.

Zhang, J., Huang, W. W., Létolle, R. & Jusserand, C. 1995 Major element chemistry of the Huanghe (Yellow River), China – weathering processes and chemical fluxes. *Journal of Hydrology* 168, 173–203. https://doi.org/10.1016/0022-1694(94)02635-O.

Zhang, E., Wang, Y., Qian, Y., Ma, T., Zhang, D., Zhan, H., Zhang, Z., Fei, Y. & Wang, S. 2015a Isotope in groundwater of the North China Plain: spatial patterns and hydrogeochemical processes of enrichment. *Journal of Geochemical Exploration* 135, 40–55. https://doi.org/10.1016/j.jgeoexp.2012.11.016.

Zhang, L. J., Wang, L., Cai, W.-J., Liu, D. M. & Yu, Z. G. 2013b Impact of human activities on organic carbon transport in the Yellow River. *Biogeoosciences* 10, 2513–2524. https://doi.org/10.5194/bg-10-2513-2013.

Zhang, L., Qin, X., Liu, P. & Huang, Q. 2016 Chemical denudation rate and atmospheric CO₂ consumption by H₂CO₃ and H₂SO₄ in the Yangtze River Catchment. *Acta Geologica Sinica* 90, 1933–1944.

Zhang, Z., Chen, X., Cheng, Q., Li, S., Yue, F., Peng, T., Waldron, S., Oliver, D. M. & Soulsby, C. 2020 Coupled hydrological and biogeochemical modelling of nitrogen transport in the karst critical zone. *Science of The Total Environment* 732, 138902. https://doi.org/10.1016/j.scitotenv.2020.138902.

Zhang, S., Bai, X., Zhao, C., Tan, Q., Luo, G., Wang, J., Li, Q., Wu, L., Chen, F., Li, C., Deng, Y., Yang, Y. & Xi, H. 2021 Global CO₂ consumption by silicate rock chemical weathering: its past and future. *Earth’s Future* 9. https://doi.org/10.1029/2020EF001938.

Zhao, H., Xiao, Q., Miao, Y., Wang, Z. & Wang, Q. 2020 Sources and transformations of nitrate constrained by nitrate isotopes and Bayesian model in karst surface water, Guilin, Southwest China. *Environmental Science and Pollution Research* 27, 21299–21310.

Zhao, H., Jiang, Y., Xiao, Q., Zhang, C. & Behzad, H. M. 2021 Coupled carbon-nitrogen cycling controls the transformation of dissolved inorganic carbon into dissolved organic carbon in karst aquatic systems. *Journal of Hydrology* 592, 125764.

Zhou, Y., Wang, Y., Li, Y., Zwahlen, F. & Boillat, J. 2015 Hydrogeochemical characteristics of central Jianghan Plain, China. *Environmental Earth Sciences* 68, 765–778. https://doi.org/10.1007/s12665-012-1778-9.

Zigah, P. K., Minor, E. C. & Werne, J. P. 2012 Radiocarbon and stable-isotope geochemistry of organic and inorganic carbon in Lake Superior. *Global Biogeochemical Cycles* 26. https://doi.org/10.1029/2011GB004132.

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