

Carbon dioxide partial pressure and its diffusion flux in karst surface aquatic ecosystems: a review

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Received: 8 May 2023 / Revised: 4 June 2023 / Accepted: 21 June 2023 / Published online: 7 July 2023

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Abstract Carbon dioxide (CO₂) emissions from aquatic ecosystems are an important component of the karst carbon cycle process and also a key indicator for assessing the effect of karst carbon sinks. This paper reviewed the CO₂ partial pressure (pCO₂) and its diffusion flux (FCO₂) in karst surface aquatic ecosystems, mainly rivers, lakes, and reservoirs, and their influencing factors summarized the methods for monitoring CO₂ emissions in karst aquatic ecosystems and discussed their adaptation conditions in karst areas. The pCO₂ and FCO₂ decreased in the order of rivers > reservoirs > lakes, and the values in karst lakes were eventually significantly lower than those in global lakes. The pCO₂ and FCO₂ of karst aquatic ecosystems had patterns of variation with diurnal, seasonal, water depth and hydrological cycles, and spatial and temporal heterogeneity. The sources of CO₂ in karst waters are influenced by both internal and external sources, and the key spatial and temporal factors affecting the CO₂ emissions from karst rivers, lakes, and reservoirs were determined in terms of physicochemical indicators, biological factors, and biogenic elements; additionally, the process of human activity interference on CO₂ emissions was discussed. Finally, a conceptual model illustrating the impacts of urban development, agriculture, mining, and dam construction on the CO₂ emissions at the karst surface aquatic ecosystem is

presented. Meanwhile, based on the disadvantages existing in current research, we proposed several important research fields related to CO₂ emissions from karst surface aquatic ecosystems.

Keywords Karst area · River · Lake · Reservoir · Partial pressure of CO₂ · CO₂ diffusion flux

1 Introduction

The carbon cycle, as the link between the Earth's biospheres, affects global climate change and plays an important role in maintaining the stability of biosphere structure and function (Battin et al. 2023; Tromboni et al. 2022). Therefore, quantifying the Earth's global carbon cycle is essential for a sustainable future because CO₂ has an active role in the Earth's energy budget (Smith et al. 2013). Inland aquatic ecosystems (rivers, lakes, and reservoirs) have become indisputable in the global carbon cycle as the most active sites of material cycling and energy exchange. Inland freshwater ecosystems generally have a high value of pCO₂, which makes the inland water column an important source of atmospheric CO₂ emissions (Borges et al. 2015; Holgersson and Raymond 2016; Li et al. 2018b; Ran et al. 2015; Tranvik et al. 2009), and in turn, affects the regional carbon balance. The global river (stream) and lake (reservoir) areas are 6.24×10^4 km² and 3×10^6 km², respectively, which account for only 0.47% and 2.2% of the global land area, but release approximately 1.8 Pg C/yr and 0.3 Pg C/yr (Raymond et al. 2013), respectively, and their combined release fluxes are comparable to the net uptake of 2.6 Pg C/yr by terrestrial ecosystems. However, the global account of CO₂ emissions from inland aquatic

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ecosystems is still largely unknown, and available estimates diverge greatly from one another. Cole et al. (2007) reported a global river CO₂ release flux of only 0.23 Pg C/yr. Lauerwald et al. (2015) estimated a global river CO₂ release flux of 0.65 Pg C/yr, Varis et al. (2012) showed a global reservoir CO₂ release of approximately 44.5 Tg C/yr, St. Louis et al. (2000) estimated CO₂ emissions from global reservoir of 272.7 Tg C/yr, and Deemer et al. (2016) estimated a reservoir CO₂ emissions of approximately 36.8 Tg C/yr. These results indicate that great uncertainty remains as to the contribution of these inland water bodies to the global carbon budget. Therefore, an accurate assessment of CO₂ emission fluxes from the inland water–air interface can not only improve understanding of the global carbon cycle but also provide a scientific database for the climate change management (Ran et al. 2021; Wang et al. 2021).

Although just 15% of the world's geographical area is covered by karst regions (Fig. 1), carbonate rocks make up 94% of the carbon pool (Xiong et al. 2022), and the carbon

sink effect formed by the karstification process $[(Ca_{1-x}Mg_x)CO_3 + CO_2 + H_2O \rightarrow (1-x)Ca^{2+} + xMg^{2+} + 2HCO_3^-]$ has become an important part of the global carbon cycle process at short time scales (Binet et al. 2022; Liu and Dreybrodt 2012; Martin 2017; Ulloa-Cedamano et al. 2020). It has been estimated that the global carbonate carbon sink is 0.89 ± 0.23 Pg C/yr, which amounts to 74.50% of the global net forest sink and accounts for 28.75% of the terrestrial sinks or 46.81% of the missing sink (Li et al. 2018a). However, according to the traditional view, the bicarbonates produced by karstification in solution will redeposit as calcite, and the associated CO₂ will be returned to the atmosphere, and thus, there will be no net sequestration of the CO₂ (Curl 2012). The calculation of the CO₂ exchange flux at the water–air interface in karst aquatic ecosystems is the key to accurately evaluating karst carbon flux and intensity, thus playing a crucial role in balancing the CO₂ budget in karst catchments. With the development of research, it was found that the dissolved inorganic carbon (DIC) produced by karstification can

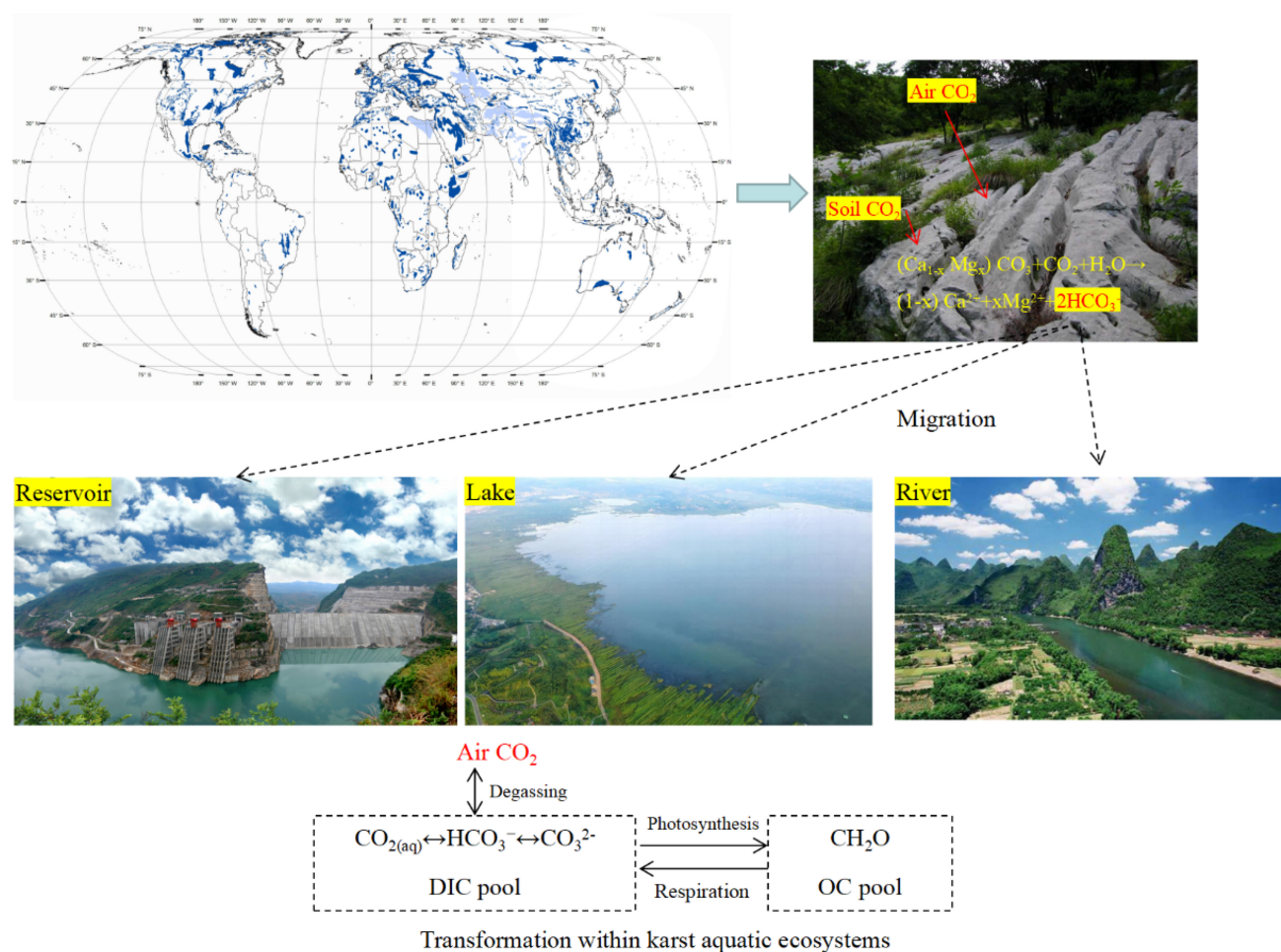


Fig. 1 Distribution of carbonate rocks at Earth's surface and the effect of surface aquatic ecosystems on the DIC produced by dissolved carbonate rocks

provide a sufficient carbon source for photosynthetic organisms in karst surface aquatic environments (Fig. 1), and DIC is transformed into relatively stable organic carbon (OC) under the effect of the biological carbon pump (BCP), thus enhancing the stability of karst carbon sinks (Liu 2022; Liu et al. 2018b); this process can also reduce the $p\text{CO}_2$ in surface water (He et al. 2022). Moreover, some studies have stated that carbonate dissolution is one of the key factors driving the release of CO_2 from more than half of the world's lakes (Marcé et al. 2015); however, the proportion of CO_2 outgassing flux accounts for only less than 10% of the weathering carbon sink of carbonate rock in the catchment (Lv 2018; Zhang 2018). In addition, compared with non-karst areas, rivers in karst areas generally have a relatively high pH due to the weathering of carbonate rocks, which makes the rivers in this area have relatively low $p\text{CO}_2$ and FCO_2 (Liu and Han 2021). Thus, the DIC produced by karstification is not all returned to the atmosphere as CO_2 . Moreover, the existing research shows that the CO_2 emissions from the surface water in different karst regions show significant spatial and temporal heterogeneities, and these changes are controlled by complex biological, chemical, and physical factors, and are even sensitive to anthropogenic activities.

The chemical weathering of carbonates coupled with photosynthesis is an important part of the ecosystem carbon sink at short timescales (Chen et al. 2023). The inland aquatic ecosystem plays an important role in the karst carbon cycle, and the CO_2 exchange process across the water–air interface in karst water is the key process to evaluate the stability of karst carbon sequestration (Liu et al. 2018a; Zhang et al. 2023). This paper summarizes the current monitoring methods and their adaptability for $p\text{CO}_2$ and its diffusion flux in karst surface water environments; additionally, it analyzes the key factors affecting CO_2 emissions, especially the disturbance process of human activities. The outcomes of the study help to deepen the understanding of carbon cycle processes in karst aquatic ecosystems.

2 CO_2 partial pressure and its diffusion flux calculation method

Currently, two methods, the thin boundary layer method (TBL) and the closed static chamber method (CSC), are commonly used to measure the CO_2 emissions from karst surface water (Tables 1, 2).

The estimation method of the TBL model is based on the gas transfer coefficient (k) value of CO_2 and the difference in the CO_2 concentration at the water–air interface. The concentration of dissolved CO_2 in water can be calculated by the carbonate equilibrium method (Zhang et al. 2020a).

Generally, after the parameters such as alkalinity, temperature, pH, and ion compositions of the samples are measured, the $p\text{CO}_2$ of the water samples can be calculated by using CO_2 SYS, PHREEQC, and WATSPEC software (Li et al. 2022b; Liu et al. 2008b; Yang et al. 2021), or the CO_2 concentration in water can be measured based on the headspace equilibrium method (Miao et al. 2022). The gas transport rate k is a key parameter for quantifying and predicting the CO_2 gas exchange process and flux across the water–air interface of the water column. Most studies use the mathematical empirical formula established by Jähne et al. (1989) to determine the k value or the SF_6 gas tracer method can be used to measure the k value in the field. However, previous research shows that the average k value of karst surface streams (~ 3.5 m wide) obtained by the empirical formula was 42.12 cm/h, while the average k value obtained by the SF_6 tracer experiment was 19.03 cm/h. This result indicates that the k values obtained by different methods in the process of karst groundwater transformation into surface water are quite different and have obvious temporal and spatial variation characteristics (Wu 2018). This high spatiotemporal variability makes the estimation of CO_2 emission capacity based on empirical formula biased, requiring multiple field verifications. However, for the Lijiang River (~ 220 m wide) with an open water surface, the average k values obtained by formula calculation and SF_6 tracer experiment were 14.88 cm/h and 16.52 cm/h, respectively, and the difference between them was small (Zhang 2018). In addition, the pH value, wind speed, water temperature and other indicators have significant influences on the results of the TBL estimation method (Yao et al. 2015).

The principle of the CSC method is to design a chamber of appropriate volume and fix it on a floating device (foam board, tire, etc.), by monitoring the change in the CO_2 concentration in the box for a long time to determine its emission flux. The CO_2 concentration in the chamber is usually measured by gas chromatography after a gas sample is taken by an aluminum foil sampling bag (Li et al. 2015a), or the chamber is directly connected to a portable analyzer (equipment produced by PP Systems, LGR, Picarro, Vaisala, etc.) to realize the continuous measurement of the CO_2 concentration in the chamber (Chen 2019; Li et al. 2016; Wu 2018). The CSC method is also susceptible to pressure disturbance in the chamber caused by the flow of water below, which affects the diffusion of gas molecules in the chamber and can cause deviations in the observation results.

In karst areas, there is a significant positive correlation between the results obtained by the two methods, but the flux obtained by the TBL method is usually higher than that obtained by the CSC method (Wu 2018; Zhang 2018). It has also been shown that the CSC results are higher than the TBL results due to the effect of turbulence on the river

Table 1 Comparison of pCO₂ and CO₂ fluxes from rivers in different karst regions

River's name	Flux calculation method	Annual average temperature (°C)	Water temperature (°C)	pH	pCO ₂ /μatm	FCO ₂ /mmol (m ² d) ⁻¹	References
Xijiang (Mainstream)	TBL	14.0~22.0	16.4 ± 2.2	7.97 ± 0.23	1591 ± 698	190.7 ± 40.4	Liu and Han (2021)
Xijiang (Tributaries)	TBL	14.0~22.0	16.4 ± 1.0	7.51 ± 0.24	2548 ± 1084	574.8 ± 288.4	
Guancun	CSC	19.7	14.8~24.9	7.22~8.28	2751.7~8818.4	9.0~613.8	Pu et al. (2019)
Guancun outlet	CSC	19.7	20.8 ± 0.4	7.43 ± 0.16	10,073.2 ± 3464.5	248.6(76.1~485.9)	Li et al. (2016)
Guancun downstream	CSC	19.7	21.1 ± 3.2	8.03 ± 0.17	1282.6 ± 5576.9	87.3(9.0~460.5)	
Li River (DM and PY section)	TBL	19.0	11.9~29.9	7.15~8.85	–	102.6 (– 76.5~499.5)	Zhang (2018)
	CSC	19.0	11.9~29.9	7.15~8.85	–	52.5 (– 21.8~423.4)	
Guijiang (Summer)	TBL	35.1	28.1 ± 1.7	8.40 ± 0.42	1944.3 ± 1158.6	127.8 ± 134.7	Zhang et al. (2019)
Guijiang (Winter)	TBL	21.8	16.7 ± 1.5	7.17 ± 0.08	650.9 ± 691.5	28.4 ± 91.4	
Danling	TBL	17.5	16.1 ± 4.2	8.21 ± 0.29	1198.2 ± 1122.9	329.8 ± 470.2	Ni et al. (2019)
Pengxi	CSC	17.7 ± 0.4	21.5 ± 1.9	–	–	17.04 ± 11.04	Li et al. (2013c)
Qijiang	TBL	–	–	–	620.3 ± 1028.7	154.3 ± 772.6	Ni and Li (2022)
Xiangxi	CSC	21.0 ± 9.6	19.7 ± 5.5	8.41 ± 0.43	–	21.4 ± 8.9	Huang et al. (2015)
Chiwuxi	TBL	15.5	13.2 ± 1.1~17.2 ± 1.5	8.47 ± 0.09~8.50 ± 0.10	460.5~567.8	26.09~70.39 ^b	Ding et al. (2022)
Yoyu	TBL	21.6 ± 6.6	15.9 ± 4.9	7.86 ± 0.30	3894.5 (455.4~2949.6)	239.9 ± 216.1	Chen (2019)
Baiyan	TBL	22.9 ± 6.8	16.7 ± 4.9	8.09 ± 0.26	2613.8 (508.5~57,804.8)	125.0 ± 139.3	
Jinzhong	TBL	29.7 ± 7.6	20.9 ± 4.8	8.00 ± 0.26	3066.8 (414.8~6099.6)	376.8 ± 378.9	
Furong	TBL	13.8 ± 2.6	^a	7.78 ± 0.50	3733.4 ± 4832.7	534.5 ± 801.4	Liu et al. (2021a)
Liuchong	TBL	–	17.2 ± 4.9	8.30 ± 0.10	684 ± 195	6.8 ± 4.4	Peng et al. (2013)
Gedangzhai	TBL	–	17.2 ± 3.2	7.57 ± 1.14	3685.8 ± 6275.1	89.2 ± 162.8	Zhou (2022)
Gubing	TBL	–	16.4 ± 2.5	7.27 ± 1.16	3562.3 ± 3694.4	141.4 ± 165.1	
Sancha	TBL	14.0	–	7.40~8.21	3100	248~466.6	Qian et al. (2017)

Table 1 continued

River's name	Flux calculation method	Annual average temperature (°C)	Water temperature (°C)	pH	pCO ₂ /μatm	FCO ₂ /mmol (m ² d) ⁻¹	References
Maling	TBL	15.0~18.0	28.5	7.70–8.16	2367.1	12.7	Cao et al. (2018)
Nanming	TBL	15.3	17.0 ± 2.0	8.20 ± 0.29	1056.1 ± 804.5	118.8 ± 169.9	Li et al. (2023)
Lower Santa Fe	CSC	20.4	17.4 ± 7.0~26.7 ± 0.9	4.70 ± 0.50~7.20 ± 0.90	8492 ± 8102~36,890 ± 6095	85.2 ± 65.1~167.1 ± 88.8	Khadka et al. (2014)
Wiesent River	TBL	9.1	9.6 ± 3.3	8.04 ± 0.36	4620 ± 6610	450 (230~5680)	van Geldern et al. (2015)
Yellow River					2810 ± 1985	856 ± 409	Ran et al. (2015)
Yangtze network					2662 ± 1240	–	Ran et al. (2017)
Mississippi River					1335 ± 129	1182 ± 390	Dubois et al. (2010)
Mekong River					1090	195	Li et al. (2013b)
China Rivers					–	179.7 ± 149.4	Wang et al. (2023)
Global Rivers					2400	359.4	Lauerwald et al. (2015)

^a“–” indicates that relevant data in the literature were not obtained

^bOnly the mean values are available in the table, since the standard deviation values of relevant indicators were not provided in references

Table 2 continued

Names (Sampling time/year)	Flux calculation method	Annual average temperature/°C	Water temperature/°C	Altitude/m	Surface area/km ²	Year of construction	pH	pCO ₂ /μatm	FCO ₂ /mmol (m ² d) ⁻¹	References
Wanfeng (2017)	TBL	20.0	19.75	780	176	1998	7.97	2486.5	65.2	Zhang et al. (2020a)
Hongfeng (2007–2008)	TBL	14.9	–	1321	57.2	1958	7.99 ± 0.75	38–3300	15	Wang et al. (2011)
Baihua (2007–2008)	TBL	14.5	–	1190	14.5	1960	7.89 ± 0.71		24	
Xiwen (2007–2008)	TBL	14.4	–	1161	0.114	1960	7.75 ± 0.37		47	
Hongyan (2007–2008)	TBL	14.4	–	884	0.304	1971	8.06 ± 0.66		22.4	
Hongjiadu (2006–2007)	TBL	15.2	19.69 ± 6.3	1071	80.5	2001	8.36 ± 0.30	598	6.14	Yu et al. (2008)
Aha (2017–2018)	TBL	17.6	23.19 ± 9.8	1108	8	1958	8.15 ± 0.33	1712.5	8.5 ± 11.6	Chen (2019)
Aha (2021)	TBL	15.3	19.9 ± 0.6	1108	8	1958	7.99 ± 0.22	861.6 ± 462.8	6.2 ± 9.6	Li et al. (2022b)
SongBaishan (2021)	TBL	14.4	22.3 ± 1.1	1176	2.3	1987	8.77 ± 0.25	223.6 ± 213.1	– 5.9 ± 5.3	
Baihua (2021)	TBL	15.3	22.1 ± 0.7	1190	14.5	1966	8.70 ± 0.14	139.3 ± 63.6	– 8.6 ± 1.0	
Hongfeng (2021)	TBL	15.3	23.1 ± 1.72	1240	57.2	1958	8.80 ± 0.15	126.2 ± 50.9	– 7.6 ± 1.1	
Hongjiadu (2011–2012)	TBL	14.1	18.5 ± 5.6	1071	80.5	2001	8.20 ± 0.20	884 ± 484	4.7 ± 7.6	Peng et al. (2013)
Hongfeng (2011–2012)	TBL	15.3	18.1 ± 6.3	1240	57.2	1958	8.40 ± 0.40	592 ± 596	11.2 ± 18.0	
Wujiangdu (2017)	TBL	16.2	18.5 ± 3.5	760	47.5	1980	7.32 ~ 8.54	3087 ± 1487	38.2 ± 32.2	Wang et al. (2019)
Hongjiadu (2017)	TBL	15.2	16.73 ± 3.77	1093	80.5	2001	7.83 ± 0.27	3080 ± 1580	56.8	Wang et al. (2021)
Dongfeng (2017)	TBL	17.4	16.95 ± 3.52	965	19.1	1994	7.93 ± 0.29	2780 ± 1510	67.4	
Suofengying (2017)	TBL	17.4	17.20 ± 2.67	850	5.7	2002	7.76 ± 0.78	3210 ± 1890	167.2	
Wujiangdu (2017)	TBL	17.2	18.40 ± 3.63	760	47.8	1979	7.85 ± 0.25	3090 ± 1490	105.6	
Silin (2017)	TBL	20.3	19.10 ± 3.64	457	38.4	2006	8.15 ± 0.47	4880 ± 2870	240.5	
Pengshui (2017)	TBL	20.6	18.84 ± 2.77	336	15.3	2003	7.81 ± 0.15	2860 ± 1010	222.5	
Yingpan (2017)	TBL	20.2	18.95 ± 2.89	285	11.4	2007	7.82 ± 0.16	2680 ± 1030	210.6	
Hongfeng (2017)	TBL	14.9	17.73 ± 5.40	1230	57.2	1958	8.17 ± 0.38	2230 ± 1730	42.5	
Pingzhai (2020)	TBL	11.0	13.60 ~ 20.7	1331	15	2018	8.40–8.80	459.4	– 0.53	Liu (2021)
Three Gorges Reservoir								–	89.1 ± 64.1	Yang et al. (2013)
China Reservoirs								–	9.4 ± 13.6	Wang et al. (2023)
Global Reservoir								–	27.8	Deemer et al. (2016)

^a “–” indicates that relevant data in the literature were not obtained^b Only the mean values are available in the table, since the standard deviation values of relevant indicators were not provided in references

surface (Chen 2019). In summary, although both the flux-box method and the model method have certain errors, none of the existing methods can provide an accurate estimation of the CO_2 potential from the karst surface water. Generally, the TBL method can be used due to its wide range and low cost, and this method is suitable for streams, rivers, and lakes, while the CSC method is more suitable for lentic water ecosystems (lakes, reservoirs, etc.) or rivers with open water surfaces based on section monitoring; however, the CSC method requires a larger sampling frequency. Therefore, it is necessary to adopt an appropriate estimation method based on the requirement of the study and financial availability.

3 Source analysis of CO_2

Since CO_2 is an important component of DIC in water, the equilibrium among the ions ($\text{CO}_2 \leftrightarrow \text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-}$) contained in DIC is rapid (Johnson 1982), which gives rise to the rapid exchange of CO_2 between the water–gas interface in an equilibrium state. Generally, the stable ($\delta^{13}\text{C}$) and radiocarbon isotopes ($\Delta^{14}\text{C}$) of DIC can be analyzed to reveal the source of CO_2 in karst water and the influence of biogeochemistry, which can also reveal the effect of exogenous carbon-containing substances on the cycle of DIC in karst water (Huang et al. 2017; Wang et al. 2019; Cao et al. 2022; Li et al. 2022a, b).

DIC in karst freshwater is mainly influenced by a combination of internal and external sources (Fig. 2). The endogenous sources are mainly biological anaerobic/aerobic respiration or photochemical degradation of organic matter within the river (Duan and Huang 2021), while the exogenous sources under natural conditions are mainly DIC contributed by carbonate karst dissolution, terrestrial

organic matter, soil, and atmospheric CO_2 input (Zhang 2018), usually because the river pCO_2 is higher than atmospheric pCO_2 ; thus, the DIC exchange of atmospheric CO_2 to the river water surface can be neglected, but when karst surface waters have a pCO_2 less than the atmospheric pCO_2 under the influence of photosynthesis, the contribution of atmospheric CO_2 to the DIC of karst water needs to be considered. Overall, the carbonate weathering and biochemistry processes were the predominant factors controlling the spatial distributions of the DIC concentrations in the karst area (Chen et al. 2021; Zavadlav et al. 2013).

In addition, anthropogenic wastewater contains a large amount of inorganic and organic carbon-bearing substances, which can directly affect the pCO_2 and its release flux from the receiving water; furthermore, the large amount of exogenous acids (nitric acid and sulfuric acid) produced by human activities intensifies the dissolution of carbonate rocks in the watershed (Lyu et al. 2018; Xu et al. 2021; Zhang 2017), which also increases the discharge flux of DIC into karst surface water. Therefore, in the future, with a relatively high urbanization rate and developed industrial and commercial activities, it is necessary to further research on CO_2 source identification, clarify the contribution of different types of human activities to the CO_2 in the water of lakes, reservoirs, and rivers in karst areas, and then improve the accuracy of CO_2 flux estimation.

4 Spatial and temporal characteristics of CO_2 partial pressure and its emission

4.1 The overall distribution characteristics

As can be seen in Tables 1 and 2, the minimum and maximum values of pCO_2 in river (stream) water were

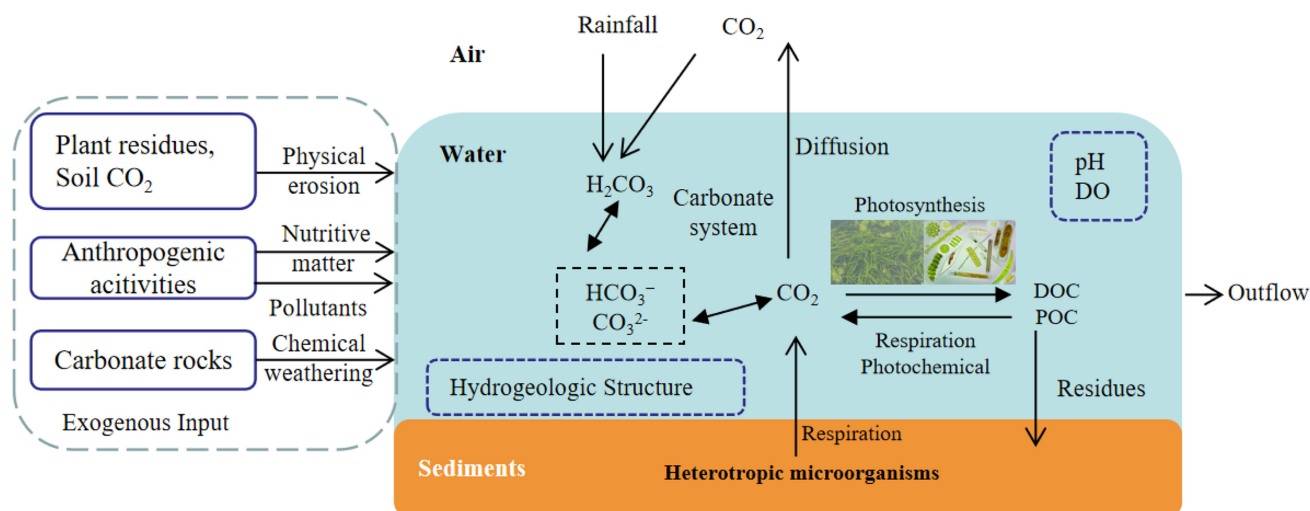


Fig. 2 Schematic diagram of the carbon cycle in the karst aquatic ecosystem

$650.9 \pm 691.5 \text{ } \mu\text{atm}$ and $10,073.2 \pm 3464.5 \text{ } \mu\text{atm}$, respectively, and the minimum and maximum values of the FCO_2 diffusion flux were $6.8 \pm 4.4 \text{ mmol (m}^2 \text{ d)}^{-1}$ and $574.8 \pm 288.4 \text{ mmol (m}^2 \text{ d)}^{-1}$, respectively. The CO_2 fluxes in the karst rivers were within the intermediate published range. Additionally, the large coefficient of variation in physicochemical parameters like pH and water temperature in the same river indicates that pCO_2 and FCO_2 have obvious spatial heterogeneity, and tributaries have higher pCO_2 and FCO_2 than mainstreams.

The FCO_2 of karst lakes fell in the range of $-34.5 \pm 12.9 \sim 206.8 \pm 27.3 \text{ mmol (m}^2 \text{ d)}^{-1}$, and the highest value was shown in the San José (mesotrophic) and San Lorenzo (eutrophic) lakes during the wet season in Mexico, and the lowest value was recorded in Caohai, which is a typical macrophytic lake in China. Although the FCO_2 of karst reservoirs is higher than that of lakes, it is still lower than that of karst rivers in general, and it is lower than that of the Three Gorges Reservoir in China and the average value of global reservoirs. Meanwhile, the karst lakes, reservoirs, and deep-water rivers have the characteristic that pCO_2 increases with depth. In addition, Table 2 shows significant differences in the pCO_2 and FCO_2 data obtained from different studies for the same reservoir (e.g., Baihua, Hongfeng), which may be related to the difference in monitoring time, e.g., Wang et al. (2011) used monthly monitoring throughout the year, Wang et al. (2021) used quarterly monitoring throughout the year, and Li et al. (2022b) used only single-month monitoring data.

4.2 Seasonal and hydrological cycle variation

Due to seasonal rainfall, temperature, and aquatic plant growth, the pCO_2 and FCO_2 in surface water in karst areas have significant seasonal fluctuations. Zhang (2018) showed that the CO_2 exchange in a typical section of the Li River was larger in the rainy season than in the dry season, and some months showed the characteristic of absorbing atmospheric CO_2 in the dry season. The accelerated degradation of organic matter by microorganisms and rainfall brought soil CO_2 into the river in summer, resulting in a higher pCO_2 and FCO_2 in the river in summer. Yang et al. (2021) showed that the pCO_2 and its diffusive flux were, on average, $-34.49 \text{ mmol (m}^2 \text{ d)}^{-1}$ and $55.94 \text{ } \mu\text{atm}$, respectively, during the wet season. The pCO_2 and FCO_2 in the dry season were higher than those in the wet season, but they still showed the characteristics of absorbing atmospheric CO_2 . In addition, the pCO_2 of deep-water lakes (reservoirs) in karst areas in different seasons increased overall in the vertical direction with increasing water depth, resulting in higher pCO_2 in the outgoing water of reservoirs than in the inflowing river water (Liu 2021; Wang et al. 2021).

4.3 Diurnal variation characteristics

The metabolic activities of aquatic photosynthetic organisms and the solar cycle driving water temperature changes in surface water resulted in the pCO_2 and FCO_2 in the water exhibiting obvious diurnal characteristics. During the day-time, the water temperature is relatively higher, and the process of stream CO_2 degassing and the ability of aquatic plants to use HCO_3^- in the water for photosynthesis are enhanced, causing the pH of the water to rise, calcite supersaturation and calcium carbonate deposition, which in turn reduce the pCO_2 and FCO_2 in the karst water. However, the respiration of aquatic organisms at night releases CO_2 into the water, which leads to an increase in the concentration of DIC, resulting in higher pCO_2 and FCO_2 in the water. In addition, the vertical movement of phytoplankton can cause density changes, which is also one of the factors affecting the diurnal variation in CO_2 partial pressure and its diffusion flux in karst reservoirs (Li et al. 2015b, 2014; Mo et al. 2014).

4.4 Long-term scale changes

Currently, the sampling periods of studies of pCO_2 and FCO_2 in karst surface water are mostly monthly, quarterly, hydrological period (wet/dry/flat seasons) or diurnal frequency sampling in a year, and there are relatively few studies on multiyear continuous high-frequency sampling. Long-term monitoring can help to obtain more accurate information on carbon sources/sinks and their control mechanisms. According to the results of a 23-month continuous monitoring study at Dalongdong Reservoir in Southwest China, although the reservoir is a carbon source most of the time, the CO_2 emission flux at the water–gas interface accounts for only a small portion of the DIC carbon pool in the reservoir, the pCO_2 increases significantly along the reservoir from upstream to downstream, and the reservoir have a low CO_2 release during water temperature stratification, with considerable CO_2 absorption into the reservoir carbon cycle during the reservoir thermal stratification season (Li et al. 2022a). Therefore, the sampling monitoring strategies need to be considered in detail to provide more reliable estimates of regional karst surface water CO_2 emissions (Zhang et al. 2020c).

5 Factors influencing the pCO_2 and FCO_2 in karst surface water

5.1 Physicochemical parameters

The pH, temperature, and precipitation are important factors affecting pCO_2 in karst surface water. pH can impact the dissolution of CO_2 by affecting the carbonate balance

in the water ($\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$). When the pH value decreases, the pCO_2 and FCO_2 increase, and conversely, the pCO_2 and FCO_2 decrease (Wang et al. 2022b). If the pH value is greater than > 9 , it can cause the reaction of atmospheric $\text{CO}_{2(g)}$ with OH^- in the water ($\text{CO}_{2(g)} + \text{OH}^- = \text{HCO}_3^-$) (Herczeg and Fairbanks 1987). The increase in water temperature not only facilitates the decomposition of organic matter and microbial metabolism in the aquatic ecosystem but also affects gas solubility and the balance of the carbonate system in the water, which in turn affects the concentration of CO_2 in the water (Wang et al. 2017); meanwhile, the increased water temperature may promote some primary production and decrease the pCO_2 (Peng et al. 2018), though the increase in air temperature could enhance soil respiration near the river and increase the input of CO_2 to the soil in the terrestrial domain (Zhang 2018). For deep-water karst lakes or reservoirs, changes in water temperature can cause thermal stratification, limiting the upward and downward exchange processes of water and elements, and changing the vertical pCO_2 distribution (Li et al. 2022a; Pu et al. 2020; Wang and Li 2021; Wang et al. 2021). In addition, reservoir water retention time (annual/monthly, weekly/daily) affects photosynthetic intensity, which in response leads to differences in CO_2 emissions from karst reservoirs (Wang et al. 2020a, b; Yi et al. 2022).

Due to the increased rainfall during the wet season, the seasonal variation in the CO_2 exchange in karst rivers is usually interrupted by rainfall, which leads to the input of high soil CO_2 concentrations into the rivers and thus increases the CO_2 exchange, making the pCO_2 and FCO_2 in the wet (rainy) season greater than those in the dry season (Qian et al. 2017). At the same time, the large amount of precipitation increases the river flow, and the CO_2 concentration in rivers can also be diluted by a high precipitation (Zhang et al. 2020b). Since rivers are lotic ecosystems, and rivers in karst areas mostly originate from mountainous areas, the aeration process generated by plunging water and ripples also increases the gas exchange at the water–gas interface, while tributaries tend to have larger specific drop and flow velocity, and main streams have larger flow rates; thus, the dilution effect and river structure are important factors for the lower CO_2 fluxes at the water–gas interface in the mainstreams of karst rivers compared with its tributaries. In contrast, lakes and reservoirs are lentic ecosystems with open water areas, and the water is not easily disturbed, while the direct recharge of rainfall to the water surface reduces the CO_2 concentration. In addition, lentic ecosystems are conducive to the growth of aquatic photosynthetic organisms, and their primary productivity is generally higher than that of rivers. These

factors make the pCO_2 and FCO_2 of karst lakes (reservoirs) lower than those of rivers.

5.2 Biological factors

The metabolic process of aquatic organisms is not only an important source of CO_2 in karst aquatic ecosystems (Fig. 3) but also an important influencing factor in controlling CO_2 emissions. As producers in the water body, aquatic photosynthetic organisms can directly use dissolved CO_2 or use HCO_3^- for photosynthesis based on the carbon concentration mechanism (CCM), and this process can increase dissolved oxygen (DO) concentration and reduce pCO_2 and FCO_2 in water, giving rise to a significant negative correlation between pCO_2 and DO in karst surface water (de Montety et al. 2011; He et al. 2022; Liu 2021; Mo et al. 2014). Moreover, enhanced respiration of aquatic photosynthetic organisms and other heterotrophic organisms causes more CO_2 to enter the water, which decreases DO concentration and increases pCO_2 and FCO_2 in the water. Therefore, the pCO_2 of karst aquatic ecosystems has obvious daily and seasonal variation characteristics.

Previous studies have shown that the formation of organic carbon by aquatic algae and submerged plants with large amounts of DIC is an important component of the karst carbon sink (Ni and Li 2022), which will make the inorganic carbon produced by karst geological processes finally form buried endogenous organic carbon (OC) and enhance the stability of the karst geological carbon sink (Zhang et al. 2022). The dissolved organic carbon (DOC) formed therein is an important component of endogenous OC, and the formed endogenous DOC will be converted to recalcitrant dissolved organic carbon (RDOC) under the metabolism of microorganisms, the proportion of RDOC accounts for an average of 78% of the total DOC in karst surface water (Xiao et al. 2020b), showing the high stability of autochthonous dissolved organic matter in karst water environments (Xia et al. 2022).

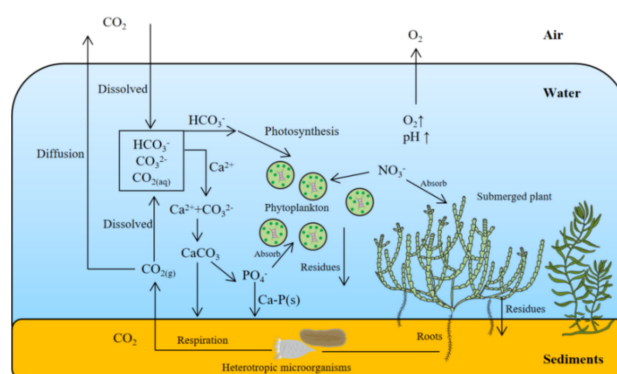


Fig. 3 Schematic diagram of the effect of the carbon cycling process effect on the inorganic elements within karst aquatic ecosystems

5.3 Nutrients

Nitrogen (N) and phosphorus (P) are biogenic elements that mainly control the trophic state of aquatic ecosystems, and they are the main substrates for the metabolism of microorganisms and aquatic vegetation, which can change the balance between primary productivity and respiration in aquatic ecosystems (Gu et al. 2022). Moderate nutrient inputs will increase aquatic primary productivity promoted by high nutrient loading and reduce CO₂ emissions (Fig. 3), while excessive nutrient input will enhance water respiration and promote CO₂ production (Liu 2022). As shown in Table 2, the eutrophic San Lorenzo in the tropical karst region increased CO₂ evasion rates to the atmosphere, and this was due to the persistence of anoxia in most of the lake's water column, which maintained high rates of anaerobic respiration coupled with the anaerobic oxidation of methane (Vargas-Sánchez et al. 2023).

Meanwhile, studies on the effects of N and P on carbon emissions from karst aquatic ecosystems have varied widely; there was a significant positive relation between the pCO₂ and TP, indicating that the river is in a P-limited nutrient state (Liu et al. 2021a), and Chen (2019) pointed out that there was no significant correlation between TP and TN and CO₂ release fluxes at the water–air interface in Aha Lake and its inflowing rivers in Southwest China. However, Li et al. (2022b) found a significant positive correlation between pCO₂ and ammonia nitrogen in Aha Lake. In addition, prior studies found that when the N and P concentrations in the water are controlled, the CO₂ fertilization effect may significantly affect the growth of cyanobacteria, diatoms, and submerged plants (Zhang et al. 2023), suggesting that the primary productivity of karst lake water is limited not only by P or N but also by DIC. Therefore, the effects of increasing nutrient loading into karst aquatic ecosystems on CO₂ emission still need to be better understood.

5.4 Anthropogenic activities

5.4.1 Urban construction

Rapid urbanization has been reported to affect the carbon biogeochemical cycle in rivers (Tang et al. 2021), and urban construction can significantly increase CO₂ production and emission from karst surface water (Chen 2019; Li et al. 2022b; Liu et al. 2021a; Lv 2018; Ni et al. 2019). This effect is mainly due to the multifold increase in nutrient loads and organic matter concentration in river water caused by urban surface pollution and direct discharge of wastewater, which in turn leads to the development of enhanced heterotrophic systems in karst surface water ecosystems (Li et al. 2020), resulting in intensifying the

CO₂ emission rate. In addition, although urban wastewater treatment plant discharges meet the discharge standards, the treated discharge effluent has lower pH and higher concentrations of DOC, DIC, and nutrients compared to the surrounding natural water (Yoon et al. 2017), which could be another reason for increasing the carbon emission intensity of the receiving karst water (Yang et al. 2018). With economic and social development, the urbanization rate of karst areas is increasing year by year, e.g., the urban area in karst areas of China has grown from 0.88% in 1980 to 2.03% in 2020, especially in the last decade when the urban area almost doubled (Liu et al. 2022). Therefore, the acceleration of urban construction in karst areas will further affect the accuracy of CO₂ emission flux estimation in karst surface waters.

5.4.2 Agricultural development

Generally, the carbonate weathering by H₂CO₃ (natural weathering pathway), in addition to nitric acid (HNO₃) has been demonstrated to be a strong weathering acid, which is mainly oxidation of reducing nitrogen from fertilizer (ONF), resulting in enhanced carbonate weathering rates ($\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3 + \text{HNO}_3 \rightarrow (1-x)\text{Ca}^{2+} + x\text{Mg}^{2+} + \text{NO}_3^- + \text{HCO}_3^-$) (Perrin et al. 2008). Additionally, the protons released by ONF may be neutralized by HCO₃[−] to produce H₂CO₃ in receiving water, which dehydrates to CO_{2(g)} (Xu et al. 2021), and according to the carbonate balance system in karst water, which give rise to increase pCO₂ and FCO₂. At the same time, these nitrate ions are, in turn, essential for the growth of aquatic organisms; thus, previous studies have also pointed out that the increasing nutrient loadings from agricultural effluents may have led to increasing OC but decreasing pCO₂ in karst waters (Liu et al. 2021b). However, we also noted that there are high levels of pesticide residues in the aquatic environment in China since the extensive pesticide use to increase agricultural yields began (Grung et al. 2015), which could have detrimental effects on aquatic microorganisms. Meanwhile, herbicides are generally more toxic to phototrophic microorganisms, exhibiting toxicity by disrupting photosynthesis (DeLorenzo et al. 2001). Thus, the impact of agricultural development on CO₂ release from the karst surface water environment needs to be further explored.

5.4.3 Mining activities

Mineral resource development is the material basis for national economic and social development, and mineral resources such as coal and metal sulfides are abundant in Southwest China, and the mining activities have deteriorated the quality of karst surface water (Jiang et al. 2020; Liang et al. 2019). The mining process often causes sulfide

minerals (mainly pyrite) to be exposed, and under the combined action of air, water, and bacteria, acidic solutions with low pH (< 4.5), high iron, high sulfate, and rich in heavy metal acid mine drainage (AMD) are formed, and AMD produces an obvious carbon source excitation effect in karst areas.

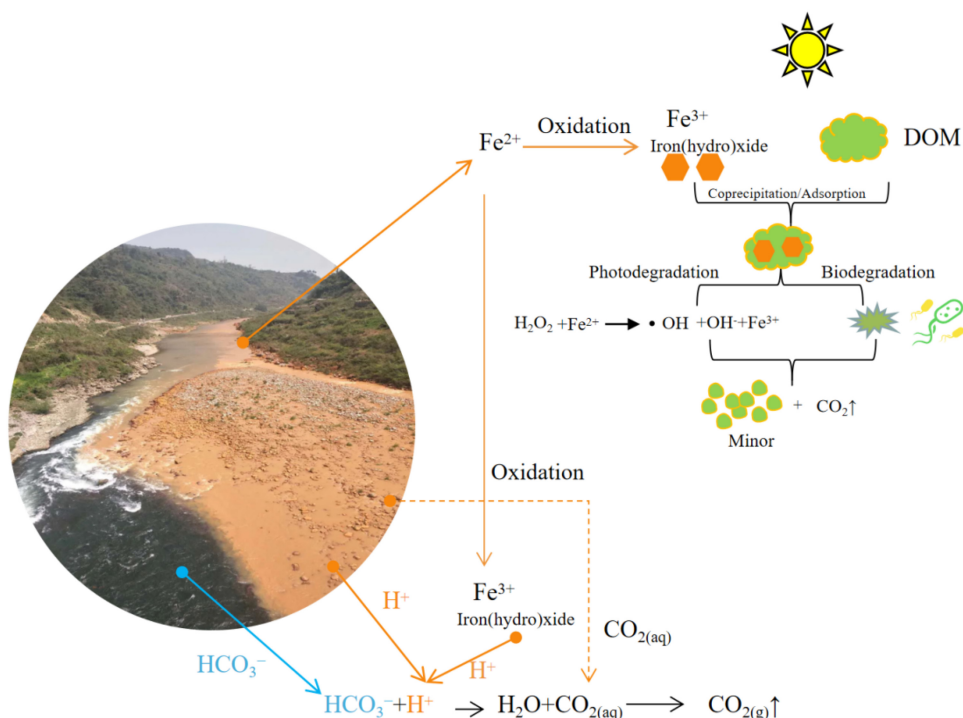
Firstly, AMD can accelerate the dissolution of carbonate rocks $[2(\text{Ca}_{1-x}\text{Mg}_x)\text{CO}_3 + \text{H}_2\text{SO}_4 \rightarrow 2(1-x)\text{Ca}^{2+} + 2x\text{Mg}^{2+} + 2\text{HCO}_3^- + \text{SO}_4^{2-}]$ (Torres et al. 2014), and since this kind of “water–rock” reaction process not only consumes CO_2 in the atmosphere/soil but also increases the HCO_3^- concentration in the water (Li et al. 2013a), it causes an increase in the flux of DIC from karst rivers to the ocean, which in turn results in a relative reduction in karst geological carbon sinks (Liu et al. 2008a), according to the carbonate equilibrium system, which would also make karst rivers affected by AMD exhibit higher pCO_2 and FCO_2 (Lv 2018). Secondly, after AMD is discharged directly into karst surface water without treatment (Fig. 4), the large amount of H^+ it contains cause a degassing reaction with DIC in the receiving water ($\text{HCO}_3^- + \text{H}^+ \rightarrow \text{CO}_2\uparrow + \text{H}_2\text{O}$) (Huang et al. 2022), which makes the confluence area of AMD and karst rivers show higher pCO_2 (Zhou 2022), and the initial mixing between AMD and karst water can rapidly cause a DIC loss of approximately $41.0 \pm 11.8\%$ (Cao et al. 2022). Moreover, the dissolved organic carbon in the receiving water will be adsorbed by Fe/Al hydroxide in AMD (Fig. 4) and catalyzed by Fe ions, which accelerates the photooxidation

of DOC to inorganic carbon (Li et al. 2024), making the DOC concentration in the receiving water decrease and further increasing the CO_2 release. Finally, heavy metal ions in AMD can reduce the biological carbon sink process by affecting the growth of algae and affecting the carbon morphology and stability in water, thus indirectly affecting the karst geological carbon sink effect (Hua 2013). These results have shown that mining has a significant impact on carbon emissions from karst rivers, but there are still not enough studies on this aspect. In particular, the CO_2 release from karst lakes and reservoirs affected by mining is rarely reported, and there is a lack of high-precision observation data, so it is necessary to systematically assess the impact of mining on the carbon cycle in karst river basins from the perspective of hydrogeological changes in mines.

5.4.4 Dam construction

The karst region in Southwest China is rich in water resources and has many canyon landscapes resulting in large river drops, which make it easy to build dams to stop water for power generation, making the region an important area for hydroelectric power generation from now to the future (Liu et al. 2009). Previous studies have shown that CO_2 emissions from karst reservoirs are subject to various dynamic processes and changes in reservoir age, hydraulic retention time (HRT), thermal stratification, and aquatic biological activities (Fig. 5). The DIC concentration in rivers draining karst areas is significantly higher

Fig. 4 The AMD effect on the dissolved inorganic/organic carbon cycle



than that in non-karst areas due to the dissolution of carbonate rocks, which gives rise to the higher potential CO_2 diffusion fluxes of karst reservoirs. The mean concentrations of $\text{CO}_{2(\text{aq})}$ decreased in the order of released water > inflowing water > reservoir water (Han et al. 2018), and this is mainly because the pCO_2 in the reservoir bottom increases significantly after the continuous degradation of organic matter in the reservoir sediment, which also leads to the higher pCO_2 in the release water (Wang et al. 2022a). However, during the thermal stratification of karst reservoirs, a large amount of CO_2 is absorbed into the reservoir carbon cycle, indicating that the karst reservoir has a significant carbon sink role under long-term thermal stratification conditions (Li et al. 2022a; Pu et al. 2020). In general, karst reservoirs are likely to be more responsive to increased anthropogenic activities than non-karst reservoirs, which implies that the role of karst reservoirs in the global warming trend needs to be more accurately assessed.

6 Conclusions and perspectives

In the present paper, a literature review is carried out on CO_2 emissions from karst surface ecosystems. Based on available data, surface aquatic ecosystems play a vital role in the karst carbon cycle, and it is important to carry out research on CO_2 emissions from karst aquatic ecosystems to accurately evaluate the effect of karst carbon sinks. The process of CO_2 transformation in karst surface water environments is complex and involves multiple internal and external factors (Fig. 6). However, although much research work has been carried out and certain results have been achieved, the understanding of CO_2 emissions from aquatic ecosystems is still insufficient due to the complexity of their sources and transformation processes.

Therefore, future research should also be conducted in the following five areas.

1. Expanding the research area and deepening the understanding of the influencing factors of CO_2 emissions from karst surface water. Presently, there are relatively more studies on CO_2 emissions at the water–gas interface of karst rivers and lakes (reservoirs) in temperate zones, while there are fewer research objects in boreal and tropical karst areas, which cannot reveal the CO_2 emission characteristics of the karst surface water environment in detail and comprehensively. In addition, the influence of factors such as river width, water depth, substrate type, and other hydrogeomorphic structures of rivers and changes in lake (reservoir) water level still need to be further explored to improve the framework of influencing factors.
2. Conduct high-frequency monitoring of CO_2 emissions from karst surface water. Previous studies tend to monitor in short time scales, such as monthly, quarterly, and hydrological periods, and most of the sampling time is conducted during the daytime. Due to the influence of biological, climatic, hydrological, and anthropogenic activities, it is difficult to accurately grasp the short-term and long-term scale variation patterns of CO_2 at the karst water–gas interface with low-frequency sampling activities. Therefore, automated monitoring instruments or high-frequency sampling should be used in the future to systematically reveal the spatial and temporal dynamic characteristics of CO_2 emissions at the karst water–gas interface and their response to environmental changes.
3. Understanding the intensity of CO_2 emissions at the water–air interface from a watershed scale. Many studies have estimated only the CO_2 diffusion fluxes

Fig. 5 The migration and transformation of DIC in karst reservoirs, modified from Pu et al. (2020) and Wang et al. (2020a)

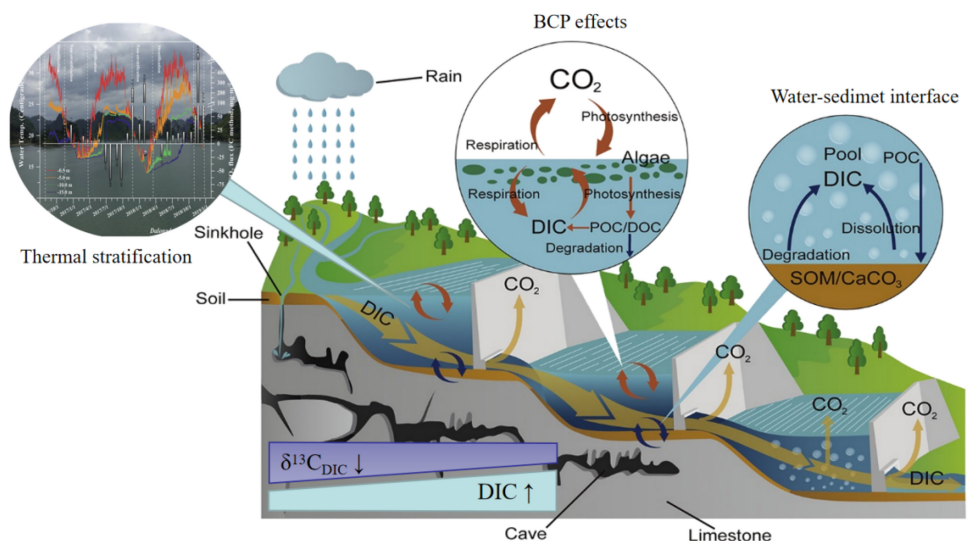


Fig. 6 Conceptual diagram illustrating the environmental impacts of reservoir, agriculture, mining, and urban development pressures on the CO₂ cycle in the karst aquatic ecosystem. Modified after Jane Hawkey (Integration and Application Network, University of Maryland Center for Environmental Science, <https://ian.umces.edu/media-library/>)



from one karst river or lake (reservoirs) and compared it with the emission scale of similar research subjects domestically and abroad. Based on the reversibility of the carbonate dissolution process, it is necessary to clarify the proportion of this emission to the karst geological carbon flux in the basin and to accurately grasp the effect of reducing the sink. In addition, more than 70% of global rivers are affected by dam construction; thus, to clarify the intensity of CO₂ emissions from typical karst reservoirs and their influencing factors, it is necessary to construct a relevant model and analyze the scale of CO₂ revenue and expenditure from reservoirs in karst areas using spatial autocorrelation.

4. Focus on the interference of human activities on CO₂ emissions from karst surface water. Due to the special geological background, the karst surface water environments are especially vulnerable to anthropogenic contamination. Therefore, it is necessary to conduct in-depth research on the response of CO₂ emission fluxes at the water–air interface of karst aquatic ecosystems to different types of human activities, and then we need to understand the spatial and temporal variation patterns and the main controlling factors to clarify the contribution of human activities to the DIC and DOC of karst surface water environments and provide a basis for optimizing carbon cycle research in karst areas.

5. Development of key technologies for water pollution control coupled with carbon sequestration and sink enhancement. Those nutrients generated by human activities are an important factor in enhancing CO₂ emissions from karst rivers and lakes (reservoirs). Because of the large biomass of submerged plants and their significant carbon sequestration capacity, as well as their role in improving the water quality, artificial intervention projects should be considered in the future to combine the cultivation of submerged plants with pollution management of the karst water environment. This method could not only reduce the input and output of pollutants, increase the diversity of the watershed landscape, and improve the water quality, but also increase the carbon sequestration and sink of karst aquatic photosynthetic organisms.

Acknowledgements We sincerely thank the anonymous reviewers and editors for their critical comments and suggestions on our manuscript. This study was financially supported by the National Natural Science Foundation of China (42163003), and the Project of Talent Base in Guizhou Province (No. RCJD2018-21).

Author contributions XC: Methodology, Software, Formal analysis, Investigation, Writing—original draft, Writing—review & editing, Project administration, Funding acquisition. QW: Conceptualization, Writing—original draft, Investigation. WW: Conceptualization, Writing—original draft, Investigation. PW: Conceptualization, Methodology, Validation, Investigation, Writing—review & editing, Supervision, Funding acquisition.

Declarations

Conflict of interest We declare no conflict of interest in this study.

Ethical approval All authors have approved the manuscript and agree with its submission.

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