CO2 emissions from karst cascade hydropower reservoirs: mechanisms and reservoir effect

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CO₂ emissions from karst cascade hydropower reservoirs: mechanisms and reservoir effect

Wanfa Wang 1, Si-Liang Li 1,2, Jun Zhong 1, Lichun Wang 1, Hong Yang 1, Huayun Xiao 1 and Cong-Qiang Liu 1

1 Institute of Surface-Earth System Science, School of Earth System Science, Tianjin University, Tianjin 300072, People’s Republic of China
2 State Key laboratory of Hydraulic Engineering Simulation and Safety, Tianjin University, Tianjin 300072, People’s Republic of China
3 Department of Geography and Environmental Science, University of Reading, Whiteknights, Reading RG6 6AB, United Kingdom

* Author to whom any correspondence should be addressed.
E-mail: siliang.li@tju.edu.cn

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Supplementary material for this article is available online

Abstract
Carbon dioxide (CO₂) emissions from aquatic surface to the atmosphere has been recognized as a significant factor contributing to the global carbon budget and environmental change. The influence of river damming on the CO₂ emissions from reservoirs remains poorly constrained. This is hypothetically due to the change of hydraulic retention time (HRT) and thermal stratification intensity of reservoirs (related to the normal water level, NWL). To test this hypothesis, we quantified CO₂ fluxes and related parameters in eight karst reservoirs on the Wujiang River, Southwest China. Our results showed that there was a significant difference in the values of pCO₂ (mean = 3205.7 µatm, SD = 2183.4 µatm) and δ¹³C_CO₂ (mean = −18.9‰, SD = 1.6‰) in the cascade reservoirs, suggesting that multiple processes regulate CO₂ production. Moreover, the calculated CO₂ fluxes showed obvious spatiotemporal variations, ranging from 9.0 to 2269.3 mmol m⁻² d⁻¹, with an average of 260.1 mmol m⁻² d⁻¹. Interestingly, the CO₂ flux and δ¹³C_CO₂ from reservoirs of this study and other reservoirs around the world had an exponential function with the reservoir effect index (R*, HRT/NWL), suggesting the viability of our hypothesis on reservoir CO₂ emission. This empirical function will help to estimate CO₂ emissions from global reservoirs and provide theoretical support for reservoir regulation to mitigate carbon emission.

1. Introduction
Carbon dioxide (CO₂) is one of the dominant greenhouse gases (GHGs), contributing 65% to global warming effects that has led to many environmental problems (Smith et al 2013), such as glacier melting, sea-level rise (Deemer et al 2016). Therefore, it is critical to fully understand the global carbon cycle, especially regarding CO₂ emissions from inland waters that was regarded as an important game player (Tranvik et al 2009, Raymond et al 2013, Räsänen et al 2018, Li et al 2018a, Maavara et al 2020). For example, Cole et al (2007) have estimated that 0.75 Pg C y⁻¹ in terms of CO₂ flux outgassed from inland waters, while Raymond et al (2013) proposed that CO₂ outgassing rate can be up to 2.1 Pg C y⁻¹. Aside from natural processes, anthropogenic activities further exacerbate global environmental change by establishing numerous dams on rivers at the global scale where GHGs significantly emerge from the dam-regulated reservoir surface and degas from the released water (St. Louis et al 2000, Abril et al 2005, Guérin et al 2006, Barros et al 2011, Deemer et al 2016, Li 2018c, Liang et al 2019, Chen et al 2021). The dams are favorable since hydropower station has been regarded as a ‘green’ energy source for providing an inexhaustible supply of electrical power (ICOLD). Till now, more than 67% of the world’s rivers have been dammed, especially in densely populated and energy-deficient areas (Grill et al 2019).

It is well known that cascade reservoirs have aggravated the fragmentation of rives, leading to the
appreciable changes in the carbon biogeochemical behavior (Grill et al 2015, Gibson et al 2017, Li et al 2018b, Wang et al 2020a, Yi et al 2021). Many researchers have studied the CO\(_2\) emissions from individual reservoirs (Huttunen et al 2003, Guérin et al 2006, Pu et al 2020), but only a few scholars researched CO\(_2\) production and emission mechanism of cascade reservoirs with different hydrodynamic conditions, altitudes, and artificial regulation (Li et al 2015, 2018a, Shi et al 2017). This is particularly important for cascade reservoirs located in the karst region, since carbonate weathering of karst rivers has been recognized as an important carbon sink, which markedly influences the global carbon cycling (Ford and Williams 2007). Carbonate weathering would cause the proportion of bicarbonate (HCO\(_3^-\)) to be more than 80% of the total anions in waters (Gaillardet et al 1999, Meybeck 2003), resulting in higher dissolved inorganic carbon (DIC) concentration in karst rivers (Beaulieu et al 2012, Goudie and Viles 2012). Moreover, the mineralization of organic matter (OM) is the dominant source of CO\(_2\) in the reservoirs (Barros et al 2011, Shi et al 2017) and would lead to lower pH in the hypolimnion and released water, accelerating the dissolution of carbonate rocks and causing higher pCO\(_2\) (Guérin et al 2006, Pu et al 2019, Wang et al 2020a). Thus, karst reservoirs may enhance carbon cycle and result in more CO\(_2\) emission to atmosphere (Huttunen et al 2003, Butman and Raymond 2011).

Although the effect of single reservoirs on the carbon cycle has been studied, little is known about the river cascade damming with the distinct characteristics of different hydraulic retention time (HRT) by anthropogenic regulation (Wang et al 2015, Liang et al 2019). Moreover, different altitudes with the varying atmospheric temperature can affect the thermal stratification in the reservoirs and thus affect carbon transport and transformation (Barros et al 2011, Wang et al 2020a). To address the unresolved question on the effect of cascade reservoirs on carbon cycle regarding CO\(_2\) emission, we hypothesized that CO\(_2\) emission from cascade reservoirs is controlled by both of normal water level (NWL, a metric to represent the atmospheric temperature’s effect) and HRT. To test this hypothesis, we calculated pCO\(_2\), CO\(_2\) fluxes and other relevant properties in eight reservoirs with different HRT and NWL. In this study, we studied seven reservoirs along the mainstream including the reservoirs of Hongjiadu (HJD), Dongfeng (DF), Suofengying (SFY), Wujian (WJD), Silin (SL), Pengshui (PS), and Yinpan (YP). Besides, Hongfeng (HF) reservoir in the main tributary (Maotiao River) was also investigated for a better comparison (figure 1). All the eight reservoirs have different serving roles and characteristics due to their physical geography, meteorology, and hydrologic feature. Specifically, HJD and HF reservoirs are responsible for regulating, shipping, storing industrial water, supply drinking water and irrigation in the upstream; DF, WJD and SL reservoirs are responsible for regulating and generating electricity, while SFY, PS, and YP reservoirs are mainly used for providing electricity. Thus, the Wujiang cascade reservoir system is an ideal place to study the cascade damming effect on CO\(_2\) emissions in karst rivers, because of the various natural factors and anthropogenic regulations. The detailed information of the eight reservoirs are listed in table 1.

2. Materials and methods

2.1. Study area

The Wujiang River is located in Southwest China, one of the largest karst region in the world (Ford and Williams 2007). It is also the largest tributary in the upper reaches and south bank of the Yangtze River with a subtropical monsoon humid climate (figure 1). The river has a total length of 1037 km, an area of \(8.79 \times 10^4\) km\(^2\), and an elevation difference of 2124 m, with the consequence of obvious spatiotemporal heterogeneity of air temperature (Wang et al 2020a). The climate is typical, rain and heat synchronization with rich rainfall (the average annual rainfall up to 1100 mm) and high air temperature (average annual temperature of 13 \(^\circ\)C–18 \(^\circ\)C), and more than 80% of the precipitation occurs in the warm season (April to September) (Wang et al 2020a). Due to the abundant hydropower resources (up to 1042.59 \(\times\) 10\(^4\) kw), more than 1000 dams have been built on Wujiang River, and it has been one of the ten hydropower bases in China (EBHHHC 2007, Gzpwd 2017).

In this study, we studied seven reservoirs along the mainstream including the reservoirs of Hongjiadu (HJD), Dongfeng (DF), Suofengying (SFY), Wujian (WJD), Silin (SL), Pengshui (PS), and Yinpan (YP). Besides, Hongfeng (HF) reservoir in the main tributary (Maotiao River) was also investigated for a better comparison (figure 1). All the eight reservoirs have different serving roles and characteristics due to their physical geography, meteorology, and hydrologic feature. Specifically, HJD and HF reservoirs are responsible for regulating, shipping, storing industrial water, supply drinking water and irrigation in the upstream; DF, WJD and SL reservoirs are responsible for regulating and generating electricity, while SFY, PS, and YP reservoirs are mainly used for providing electricity. Thus, the Wujiang cascade reservoir system is an ideal place to study the cascade damming effect on CO\(_2\) emissions in karst rivers, because of the various natural factors and anthropogenic regulations. The detailed information of the eight reservoirs are listed in table 1.

2.2. Field sampling and analysis

Four field surveys were conducted at 40 sites (figure 1) in January (Winter), April (Spring), July (Summer), and October (Autumn) 2017 for collecting the inflowing (mainstream and tributaries), lentic profiles, and environmental parameters were measured and quantified. By compiling exhaustive previous studies focusing on CO\(_2\) emissions from the cascade reservoirs, our study demonstrate our hypothesis is viable. Importantly, the established predictive function between CO\(_2\) fluxes and influencing factors (HRT and NWL) in this study allows to estimate the contribution of CO\(_2\) emissions from reservoirs to global carbon budget.
at the depths of 0.5, 10, 20, 30, and 60 m in SL (W19-W20) and PS (W23-W24), at the depth of 0.5, 5, 10, 20, 30, and 40 m in YP (W27) and at the depth of 0.5, 5, 10, 15, and 25 m in HF (M2-M4), respectively. We measured the physical and chemical properties of collected samples \textit{in situ} using a multiparameter profiler (model: YSI EXO1), including water temperature ($T_w$), pH, dissolved oxygen (DO), oxygen saturation (DO (%)), and chlorophyll (Chl). The detail information about sampling and analysis for DIC, calcium ion ($Ca^{2+}$), partial pressure of CO$_2$ ($pCO_2$), and carbon isotope composition of DIC ($\delta^{13}C_{DIC}$) were shown in text S1 (supplementary materials) (available online at stacks.iop.org/ERL/16/044013/mmedia).

2.3. Estimation of CO$_2$ fluxes

The CO$_2$ fluxes ($F_{CO2}$) across the water-atmosphere interface in the cascade reservoirs were estimated based on a theoretical diffusion model proposed by Cole and Caraco (1998), Teodoru et al (2009), and Butman and Raymond (2011).

$$F_{CO2} = K_T \times K_H \times [pCO_2\text{ (water)} - pCO_2\text{ (air)}]$$

(1)

$$K_H = 10^{-\left(1.11 + 0.016 - 0.00007 \times T^3\right)}$$

(2)

where $F_{CO2}$ is the CO$_2$ flux from water to air unit in (mmol m$^{-2}$ d$^{-1}$), $K_T$ is the exchange velocity of gas CO$_2$ (m d$^{-1}$), $K_H$ is Henry’s constant corrected for temperature $T$ ($\degree$C) expressed in (mmol m$^{-3}$ µatm$^{-1}$) (Harned and Davis 1943); $pCO_2\text{ (water)}$ (µatm) is partial pressure CO$_2$ in the water (Clark and Fritz 1997). $pCO_2\text{ (air)}$ is the partial pressure of CO$_2$ in the air (∼400 µatm, based on www.esrl.noaa.gov/gmd/ccgg/trends/full.html).

The exchange velocity of CO$_2$ was determined by wind speed, current velocity, water temperature, and other factors (Wanninkhof 1992). $K_T$ is the gas-exchange coefficient expressed in (cm h$^{-1}$) and it was calculated from the following equation from Jähne et al (1987).

$$K_T = K_{600} \times \left(S_c/600\right)^{-n}$$

(3)

$$K_{600} = 2.07 + 0.215U_{10}^{1.7}$$

(4)

where $K_{600}$ was calculated according to the equation from Cole and Caraco (1998). $U_{10}$ (m s$^{-1}$) is the
Table 1. The basic characteristics of the studied reservoirs on the Wujiang River, Southwest China.

| Reservoirs | Altitude (m) | Average air temperature (°C) | Catchment area (km²) | Surface area (km²) | Normal/dead water level (m) | Discharge (10⁸ m³ y⁻¹) | Installed capacity (10 kw) | Storage coefficient (%) | Year of construction | Type of regulation | Drainage basin |
|------------|--------------|-----------------------------|---------------------|-------------------|----------------------------|------------------------|---------------------------|------------------------|---------------------|-------------------|---------------|
| HJD        | 1093         | 15.2                        | 9900                | 80.5              | 1140/1076                  | 48.9                   | 600                       | 68.8                   | 2001                | Multi-year       | Mainstream     |
| DF         | 965          | 17.4                        | 18161               | 19.1              | 970/936                    | 108.8                  | 695                       | 4.5                    | 1994                | Seasonal         | Mainstream     |
| SFY        | 850          | 17.4                        | 21862               | 5.7               | 835/813                    | 134.7                  | 600                       | 0.6                    | 2002                | Daily             | Mainstream     |
| WJD        | 760          | 17.2                        | 27790               | 47.8              | 760/720                    | 158.3                  | 1250                      | 8.5                    | 1979                | Seasonal         | Mainstream     |
| SL         | 457          | 20.3                        | 48558               | 38.4              | 440/431                    | 266.2                  | 1050                      | 1.2                    | 2006                | Monthly           | Mainstream     |
| PS         | 336          | 20.6                        | 69000               | 15.3              | 293/278                    | 410.0                  | 1750                      | 1.3                    | 2003                | Monthly           | Mainstream     |
| YP         | 285          | 20.2                        | 74910               | 11.4              | 215/211.5                  | 438.4                  | 600                       | 0.1                    | 2007                | Daily             | Mainstream     |
| HF         | 1230         | 14.9                        | 1596                | 57.2              | 1240/1227.5                | 9.2                    | 20                        | 48.2                   | 1958                | Multi-year       | Tributary      |

The storage coefficient (%) (β, the ratio of the mean reservoir regulation storage to the discharge) can represent the daily (β < 1%), monthly (1% < β < 3%), seasonal (3% < β < 10%), yearly (10% < β < 30%) and multi-year (30% < β) regulated reservoirs (Wang et al. 2020a).

HRT is hydraulic retention time.
frictionless wind speed at a height of 10 m above the water surface, and \( n = 1/2 \) or 2/3 for wind speeds exceeding 3.7 m s\(^{-1}\) or below 3.7 m s\(^{-1}\), respectively (Guérin et al 2006). \( S_n \) is the Schmidt number for CO\(_2\) in freshwater and it varies with temperature (Wanninkhof 1992). Considering the difficulty to carry out long-term monitoring on all sampling points and also data quality and representative, we collected the monthly average wind speed from meteorological stations (www.cma.gov.cn/) around the sampling points for the value of \( U_{10} \).

Notably, in the warm season, when the low flow speed was <0.5 m s\(^{-1}\) in the reservoirs (HF; HJD, DF, WJD, and SL) with long HRT, the \( K_{600} \) was calculated using the equation (4). However, \( K_{600} \) can be affected by various factors such as wind speed, current, and turbidity (Guérin et al 2006, Raymond et al 2012). Due to the high flow speeds in the tributary, inflowing, released water, and short HRT in the run-of-river type reservoirs, the equation (4) may not be appropriate for estimating \( K_{600} \). Alternatively, we estimated \( K_{600} \) following Butman and Raymond (2011) and Raymond et al (2012): \[
K_{600} = 2.03 + S \times V \times 2841.6
\] (6)
where \( S \) is the slope (%/o) and \( V \) is river flow velocity (m s\(^{-1}\)). The detail information about the calculation of \( K_{600} \) at the sampling point with high flow speed has shown in the text S2.

Upon the estimated CO\(_2\) flux as mentioned above, the CO\(_2\) emissions (ton CO\(_2\)-C y\(^{-1}\)) from the reservoirs was calculated as the product of the average emission flux and the typical reservoir surface area, which was calculated based on the NWL of the reservoirs (Liang et al 2019).

2.4. Comprehensive analysis of chemical components

The water temperature dependence of the fractionation for \( ^{13}\)C between the DIC and CO\(_2\) (aq) was calculated according to the following equation by Mook et al (1974) and Rau et al (1996): \[
\delta^{13}\text{C}\text{CO}_2(\%) = \delta^{13}\text{C}\text{DIC} + 23.644
- 9701.5 / (T + 273.15)
\] (7)
where \( T \) is the water temperature expressed in (°C) and the \( \delta^{13}\text{C} \) value of DIC is approximately equal to that of HCO\(_3^-\) (Goudie and Viles 2012, Wang et al 2020a).

To reveal the major influencing factors and processes related to CO\(_2\) emissions in cascade reservoirs, we calculated the changing degree of \( \delta^{13}\text{C}\text{CO}_2(\%) \) and pCO\(_2\) considering water going through reservoirs as follows (Wang et al 2020a):

\[
\Delta \left[ \delta^{13}\text{C}\text{CO}_2(\%) \right] = 100 \times \left( \left[ \delta^{13}\text{C}\text{CO}_2(\%) \right]_S \right. \\
- \left[ \delta^{13}\text{C}\text{CO}_2(\%) \right]_I / \left[ \delta^{13}\text{C}\text{CO}_2(\%) \right]_I \times (\%)
\] (8)
\[
\Delta [\text{pCO}_2] = 100 \times \left( [\text{pCO}_2]_S / [\text{pCO}_2]_I \right) \times (\%)
\] (9)
where \( \Delta \left[ \delta^{13}\text{C}\text{CO}_2(\%) \right] \) and \( \Delta [\text{pCO}_2] \) represent the % change of \( \delta^{13}\text{C}\text{CO}_2(\%) \) and pCO\(_2\) in depth-profiles and outflow waters compared with inflow waters, respectively.

2.5. Reservoir effect index

Upon the knowledge of CO\(_2\) emission, we hypothesize and proposed that CO\(_2\) emission is primarily related to the reservoir effect index (\( R_s \), d m\(^{-1}\)), which serves as a metric to assess the effects of residence time and thermal characteristics on CO\(_2\) emission. \( R_s \) is defined as:

\[
R_s = \frac{\text{HRT}}{\text{NWL}},
\] (10)
where HRT (days) is the hydraulic retention time of the reservoirs and NWL (m) refers to the normal water level of the reservoir.

2.6. Metadata compiling and established function between \( R_s \) and CO\(_2\) emission

In addition to our studied sites, we searched published studies on CO\(_2\) emission in reservoirs, and found more than 100 reservoirs (St. Louis et al 2000, Rosa et al 2004, Tremblay et al 2005, Dos Santos et al 2006, Guérin et al 2006, Barros et al 2011, Li et al 2015, Wen et al 2017). However, to investigate the relationship between CO\(_2\) flux and \( R_s \) only the sites which were documented simultaneously with reservoir morphometrics (geographical locations, area) and CO\(_2\) flux during the study year (more than two samples in non-frozen reservoirs and one sample in frozen reservoirs) were included. Consequently, 43 reservoirs from tropical to boreal areas were included and analyzed in this study. Specifically, there were 14 sites from Asia, 3 sites from Europe, 15 sites from North America, and 11 sites from South America (table S1).

The correlation of pCO\(_2\), \( \delta^{13}\text{C}\text{CO}_2\), average \( T_A \), and CO\(_2\) flux with the concerned environmental parameters in the studied reservoirs were analyzed using Pearson’s correlation coefficient, and a one-way analysis of variance was conducted to analyze the differences. Besides, a \( t \)-test approach was used to compare the linear regression slopes. All the analyses were performed using the SPSS 19.0 statistical software package (SPSS Inc.) and the level of significance used was \( P < 0.05 \) was accepted as the level of significance.
3. Results

3.1. Characteristics of meteorological and water chemical components

The average $T_A$ were 16.6 °C and 19.6 °C in the upstream and downstream of the Wujiang River while the average precipitation was close in the two reaches (1068.3 mm and 1062.8 mm) (Gzpwd 2017). Generally speaking, $T_A$, and precipitation during the warm season (April to September) were much higher than in the cold season (October to next March) (figure 2). The water temperature ($T_W$) varied seasonally ranging from 8.2 °C to 29.8 °C (mean = 18.0 °C, SD = 3.9), and $T_W$ variations in the warm season was much larger than those in the cold season (table 2 and figure 2). In addition, $T_W$ decreased markedly with depth in reservoirs (HF, HJD, DF, WJD, and SL) with an obvious thermal stratification and kept almost constant in the hypolimnion (figure 3). Similar to $T_W$, DO (mean = 7.6 mg l$^{-1}$, SD = 2.4), Chl (mean = 2.5 µg l$^{-1}$, SD = 4.4), and pH (mean = 7.9, SD = 0.3) declined with the increase of water depths. Unlike $T_W$, DIC (mean = 148.3 mg l$^{-1}$, SD = 21.1) and Ca$^{2+}$ (mean = 60.4 mg l$^{-1}$, SD = 9.4) increased along the depth profile and the lowest and highest values appeared in the epilimnion of the warm season and hypolimnion in the cold season, respectively. The water chemical components had less variations with depth in the SFY, PS, and YP reservoirs (figure 3), where the seasonal thermal stratifications were weak due to shorter HRT.

3.2. Spatiotemporal patterns of $p$CO$_2$ and $\delta^{13}$C$_{CO_2}$

Overall, $p$CO$_2$ in the Wujiang River had obvious spatiotemporal heterogeneity, ranging from 55.6 to 21 057.3 µatm (mean = 3205.7 µatm, SD = 2183.4) (figure 4(a)). The variations in $p$CO$_2$ in the warm season were obviously larger than those in the cold season, and the variations gradually lessened from upstream to downstream (table 2 and figure 4(a)). $p$CO$_2$ decreased in the order (released water > inflowing water > water in the reservoir) in all reservoirs except for the SL reservoir (table 2). Moreover, $p$CO$_2$ increased obviously along the vertical profiles (i.e. depth) at HF, HJD, DF, WJD, and SL with longer HRT, while stabled at SFY, PS, and YP reservoirs with shorter HRT. In this study, the highest $p$CO$_2$ (21 057.3 µatm) in the hypolimnion and the lowest values (55.6 µatm) in the epilimnion were all recorded in the warm season of the SL reservoir.

$\delta^{13}$C$_{CO_2}$ changed from −22.5‰ to −10.7‰ (mean = −18.9‰, SD = 1.6) (figure 4(a)). Similar to
Table 2. Water chemical parameters of the studied reservoirs on the Wujiang River, Southwest China*.

| Parameters | Inflowing* | HF (n = 50) | HJD (n = 64) | DF (n = 40) | SFY (n = 20) | WJD (n = 72) | SL (n = 48) | PS (n = 48) | YP (n = 20) | Released water (n = 28) |
|------------|------------|------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------------------|
| $T_W$ (°C) | 18.40 ± 4.34 | 17.73 ± 5.40 | 16.73 ± 3.77 | 16.95 ± 3.52 | 17.20 ± 2.67 | 18.40 ± 3.63 | 19.10 ± 3.64 | 18.84 ± 2.77 | 18.95 ± 2.89 | 17.59 ± 2.73 |
| pH         | 7.90 ± 0.28  | 8.17 ± 0.38  | 7.83 ± 0.27  | 7.93 ± 0.29  | 7.76 ± 0.78  | 7.85 ± 0.25  | 8.15 ± 0.47  | 7.81 ± 0.15  | 7.82 ± 0.16  | 7.75 ± 0.22  |
| DO (mg l$^{-1}$) | 8.25 ± 1.73 | 6.23 ± 3.45 | 6.63 ± 1.91 | 8.35 ± 1.93 | 7.90 ± 1.27 | 7.63 ± 2.64 | 6.78 ± 3.46 | 8.29 ± 0.72 | 8.39 ± 0.63 | 8.38 ± 1.55 |
| DIC (mg l$^{-1}$) | 67.29 ± 5.51 | 53.5 ± 3.60 | 128 ± 1.95 | 134.48 ± 17.33 | 135.08 ± 12.21 | 144.54 ± 15.1 | 143.41 ± 10.7 | 161.37 ± 16.96 | 153.68 ± 11.5 | 145.81 ± 6.48 |
| Chl (µg l$^{-1}$) | 2.84 ± 3.33 | 2.23 ± 1.73 | 3.08 ± 1.58 | 2.78 ± 1.51 | 3.21 ± 1.89 | 3.09 ± 1.49 | 4.88 ± 2.87 | 4.86 ± 1.01 | 2.68 ± 1.03 | 3.57 ± 2.1 |
| $p$CO$_2$ (10$^3$ µatm) | 3.51 ± 14.33 | 48.82 ± 6.23 | 60.50 ± 6.87 | 61.53 ± 7.71 | 63.87 ± 4.48 | 63.86 ± 3.41 | 63.24 ± 6.86 | 55.36 ± 2.38 | 52.86 ± 3.69 | 61.93 ± 7.35 |
| $\delta^{13}$DIC (%o) | −9.2 ± 1.3 | −7.5 ± 2.0 | −8.5 ± 1.8 | −8.9 ± 1.8 | −9.3 ± 0.7 | −9.2 ± 0.9 | −9.9 ± 1.1 | −10.3 ± 0.7 | −10.4 ± 0.6 | −9.9 ± 0.7 |
| $\delta^{13}$CO$_2$ (%o) | −18.9 ± 1.3 | −17.2 ± 2.0 | −18.4 ± 2.1 | −18.7 ± 1.8 | −19.1 ± 0.6 | −18.8 ± 1.2 | −19.4 ± 1.4 | −19.9 ± 0.7 | −20.0 ± 0.7 | −19.6 ± 0.6 |

*a The data are presented as the mean ± standard error; n is the number of measurements. The sampling sites were divided into three categories: inflowing water, released water, and reservoir water of the eight reservoirs.
*b Inflowing: the water that was from the stations in the reservoir sections that directly received river inflows and the sites in the tributaries.
*c HRT is hydraulic retention time.
*d Average pH is calculated geometrically.
\[ \text{Figure 3.} \text{ Depth profiles of pH, T, DO, DIC, Ca}^{2+}, \text{Chl, DO (\%), and } \delta^{13}\text{C}_{\text{DIC}} \text{ in the eight reservoirs. The data of pH, T, DO, and DIC are symbolized by the solid lines. The values of Ca}^{2+}, \text{Chl, DO (\%), and } \delta^{13}\text{C}_{\text{DIC}} \text{ are presented as mean } \pm \text{ standard error.} \]

\[ \text{Figure 4.} \text{ (a) Variations in } p\text{CO}_2 \text{ in the surface water of the reservoirs on the Wujiang River. The data are presented as mean } \pm \text{ standard error. (b) Variations in the } CO_2 \text{ fluxes and emissions in the reservoirs on the Wujiang River. For the } CO_2 \text{ flux data, the boxes and whiskers indicate the 25th to 75th and 10th and 90th percentiles, respectively. The central lines indicate the median and the outliers are not included. The data for the } CO_2 \text{ emissions are presented as mean } \pm \text{ standard error. (c) Depth profiles of } p\text{CO}_2 \text{ and } \delta^{13}\text{C}_{\text{CO2}} \text{ in the reservoirs on the Wujiang River. The name abbreviations of each reservoir refer to figure 1.)} \]

\[ p\text{CO}_2, \text{ the variations of } \delta^{13}\text{C}_{\text{CO2}} \text{ in the warm season were larger than those in the cold season. However, different from } p\text{CO}_2, \text{ } \delta^{13}\text{C}_{\text{CO2}} \text{ decreased from the upstream to the downstream (table 2 and figure 4(a)). } \delta^{13}\text{C}_{\text{CO2}} \text{ values varied between reservoirs, ranged from } -20.5\% \text{ to } -10.7\% \text{ (mean } = -18.4\%, \text{ SD } = 2.1) \text{ in the HJD reservoir with the longest HRT. Whereas } \delta^{13}\text{C}_{\text{CO2}} \text{ ranged from } -21.0\% \text{ to } -19.0\% \text{ (mean } = -20.0\%, \text{ SD } = 0.7) \text{ in the YP reservoir with the shortest HRT. The highest } (-10.7\%) \text{ and lowest} \]

values (−22.4‰) of δ13C CO2 were recorded in multi-year regulated reservoirs of HJD and HF, respectively.

3.3. Amounts of CO2 flux and CO2 emission

CO2 fluxes from all the studied sites ranged from −9.0 mmol m⁻² d⁻¹ to 2269.3 mmol m⁻² d⁻¹ (mean = 260.1 mmol m⁻² d⁻¹, SD = 314.1). In the SFY, PS, and YP reservoirs with short HRT, there was no discernable difference in CO2 flux between the reservoir water and released water (figure 4(b) and table 2). However, in the HF, HJD, DF, WJD, and SL reservoirs with longer HRT, CO2 fluxes in released water were larger than those in reservoir water. In particular, the HJD reservoir showed a large difference in CO2 flux between released water (469.8 mmol m⁻² d⁻¹) and reservoir water (46.8 mmol m⁻² d⁻¹), more than 10 times (figure 4(b)). In addition, the highest (240.6 mmol m⁻² d⁻¹) and the lowest (42.5 mmol m⁻² d⁻¹) mean CO2 flux were observed in the SL and HF reservoirs, respectively.

The total CO2 emission from the reservoirs was 1.25 × 105 ton CO2-C y⁻¹. Notably, CO2 emissions from HJD, WJD, SL, and PS reservoirs (1.49 × 104 ton CO2-C y⁻¹ to 4.04 × 104 ton CO2-C y⁻¹) were significant higher than these from HF, DF, SFY, and YP reservoirs (4.18 × 103 ton CO2-C y⁻¹ to 1.06 × 104 ton CO2-C y⁻¹) (figure 4(b)). Moreover, the largest CO2 emissions (4.04 × 105 ton CO2-C y⁻¹) appeared in SL reservoir, which was nearly 10 times and 4 times higher than the daily-regulated reservoirs of SFY (upstream) and YP (downstream).

4. Discussion

4.1. CO2 production impacted by biogeochemical processes in the reservoirs

Previous studies have reported that the river damming can capture suspended particles and lead to large accumulation of organic carbon (OC), suggesting that the high concentration of CO2 in reservoirs is more likely to be controlled by OC mineralization (St. Louis et al 2000, Abril et al 2005, Li et al 2018b, Wang et al 2019b). However, CO2 production is more complicated because pCO2 showed seasonal variation in karst cascade reservoir system (Pu et al 2020, Wang et al 2020b). Our study based on the multiple regression analysis suggested that pH and DO were the dominant indicator parameters for tracing CO2 characteristics in the inflowing and released water (table 3). However, the results also suggested that CO2 production in karst cascade reservoirs may be influenced by multiple influence factors (table 3). It is hence important to understand the damming effect on carbon cycle by comparing the differences between reservoir water and inflowing water (Goudie and Viles 2012, Wang et al 2020a). Moreover, variations in CO2 concentration and δ13C CO2 signature in the waters can indicate complicated processes (Maberly et al 2012). To parse out the relative importance of various biogeochemical processes on CO2 production, we resorted to Δ[pCO2] and Δ[δ13C CO2], which theoretically follows a strong quadratic relationship (figure 5(a)). All plausible biogeochemical processes were then applied to decipher the quadratic relationship between Δ[pCO2] and Δ[δ13C CO2] as further explained as below.

4.2. CO2 dynamics in the reservoirs with relatively long hydraulic residence time

The reservoirs with long HRT were prone to develop strong thermal stratification in the warm season; this provide a favorable environment for phytoplankton growth and was thus responsible for the higher Chl concentration in reservoirs (figure 3) (Li et al 2018a, Yang et al 2020, Wang et al 2020a). We proposed that phytoplankton photosynthesis and assimilation the light C isotopes (13C) of CO2 (aq) as C source led to depletion of CO2 and 13C enrichment of residual inorganic C in the epilimnion (Van Breugel et al 2005, Doctor et al 2008). This is supported by the significant correlation between Chl concentration with pCO2 and δ13C CO2, where CO2 was mainly consumed by phytoplankton photosynthesis (table 3). Thus, the above-mentioned two processes would lead to a decrease of both Δ[pCO2] and Δ[δ13C CO2] in the epilimnion (figure 5(a)). Moreover, due to the biological production, pH increase obviously in the epilimnion, which increase water supersaturation coefficient and accelerate the secondary carbonate precipitation (Van Breugel et al 2005, Pu et al 2020). The Ca²⁺ concentration and pCO2 decreased markedly in the epilimnion and the positive correlation between Ca²⁺ and pCO2 confirms carbonate precipitation (figure 3 and table 3).

In the thermocline and hypolimnion, DO, pH and δ13C CO2 decreased, while pCO2 and Ca²⁺ increased markedly, indicating that OM degradation is the dominant process that accelerates the carbonate dissolution (Wang et al 2019b, Binet et al 2020). In July, from epilimnion to hypolimnion, Ca²⁺ in HF and HJD reservoirs increased by 69.75% (33.6 mg l⁻¹ to 40.1 mg l⁻¹) and 35.30% (46.3 mg l⁻¹ to 62.7 mg l⁻¹), respectively. This further proved that the dissolution rate of carbonate was accelerated in the hypolimnion (Pu et al 2020, Wang et al 2020b). In addition, thermal stratification would seriously hinder water exchange in the column (Encinas Fernandez et al 2014), which caused high pCO2 in the hypolimnion and be responsible for the high values of Δ[pCO2] and Δ[δ13C CO2] in released water (figures 4 and 5) (Goudie and Viles 2012, Binet et al 2020). Moreover, pCO2 was maintained at a high level due to the released water with lower pH and the process of oxygen input, which further accelerated OM degradation and carbonate dissolution (figure 4(c)) (Tranvik et al 2009). Regarding the epilimnion, in the cold
Table 3. The correlation of \( pCO_2 \) and \( \delta^{13}C_{CO_2}(‰) \) with the concerned environmental parameters in the studied reservoirs on Wujiang River*.

| Parameter | Inflowing | Reservoir | Released water |
|-----------|-----------|-----------|----------------|
| \( T_w (°C) \) | 0.039/0.143 | 0.749/0.244 | 68 | -0.89/0.38 \(^b\) | 0.091/0.001 | 362 | 0.261/−0.097 | 0.180/0.623 | 28 |
| pH | -0.82 \(^b\)/0.444 \(^b\) | < 0.001/< 0.001 | 68 | -0.84 \(^b\)/0.72 \(^b\) | < 0.001/< 0.001 | 362 | -0.913\(^b\)/0.091 | < 0.001/0.645 | 28 |
| DO (mg l\(^{-1}\)) | -0.45 \(^b\)/0.361 \(^b\) | < 0.001/0.003 | 68 | -0.63 \(^b\)/0.43 \(^b\) | < 0.001/< 0.001 | 362 | -0.646\(^b\)/0.290 | < 0.001/0.135 | 28 |
| Chl (µg l\(^{-1}\)) | -0.086/0.417 \(^b\) | 0.493/< 0.001 | 68 | -0.33 \(^b\)/0.55 \(^b\) | < 0.001/< 0.001 | 362 | 0.402/−0.142 | 0.034/0.472 | 28 |
| DIC (mg l\(^{-1}\)) | 0.304\(^b\)/−0.159 | 0.012/0.196 | 68 | 0.309\(^b\)/−0.46 \(^b\) | < 0.001/< 0.001 | 362 | 0.237/−0.124 | 0.226/0.531 | 28 |
| Ca\(^{2+}\) (mg l\(^{-1}\)) | −0.017/0.222 | 0.890/0.068 | 68 | 0.352\(^b\)/−0.49 \(^b\) | < 0.001/< 0.001 | 362 | 0.261/0.325 | 0.180/0.092 | 28 |

* \( n \) is the number of samples, while \( P \) is the significance level.
\(^b\) The correlation was significant at the 0.01 level.
\(^c\) The correlation was significant at the 0.05 level.
season, $pCO_2$ was significantly higher but $\delta^{13}C_{CO_2}$ was lower than that in the warm season, indicating that the decrease in atmospheric temperature led to weak thermal stratification (Boehrer and Schultze 2008, López Bellido et al 2009), which enhanced the hydrodynamics condition. Consequently, the biological effect was inhibited and $CO_2$ was released from the hypolimnion (figure 3) (Borges et al 2012). Thus, the source of $CO_2$ is mainly controlled by the degradation of OM and carbonate dissolution in the cold season.

4.3. $CO_2$ dynamics in the reservoirs with relatively shorter hydraulic residence time

In the SFY, PS, and YP reservoirs with relative shorter HRT, there was no obvious thermal stratification all year due to the strong hydrodynamics (figure 3). However, the $\delta^{13}C_{CO_2}$ in the downstream is larger than the upstream, indicating that the higher air temperature may accelerate OM degradation in the downstream (Maberly et al 2012). In this study, SL reservoir is the only reservoir with seasonal thermal stratification in the downstream (figure 3). Although the HRT of SL reservoir (22 d) was shorter than those of HJD (368 d), HF (302 d), DF (29 d) and WJD (49 d) reservoirs in the upstream, the lower mean value of $\delta^{13}C_{CO_2}$ ($-19.4\%$) and higher $pCO_2$ (4878.0 $\mu$atm) appeared in SL reservoir, which may indicate that the thermal stratification of water became weaker in the cold season and this accelerated OM degradation and was responsible for the higher $pCO_2$ and lower $\delta^{13}C_{CO_2}$ at higher air temperatures (mean = 20.3 °C) in the downstream (figure 4(a)). However, in the downstream of SL reservoir, $pCO_2$ remained stable in PS and YP reservoirs, indicating that the cumulative damming effect on carbon is not significant in cascade reservoirs. In the reservoirs with shorter HRT, the thermal stratification was weak and water chemical characteristics were similar to river system. Thus, our results suggest that $CO_2$ production in the riverine area was mainly influenced by the carbonate weathering and degradation of OM (Chen et al 2020, Zhong et al 2020, Yi et al 2021), while was also gradually affected by the multiple processes including, carbonate dissolution and precipitation, biological production, OM degradation, $CO_2$ outgassing and oxygen input in the karst river-reservoir system (figures 5(a) and 6). In conclusion, the damming effect on carbon cycle is significantly smaller in the reservoirs with short HRT of daily and weekly regulation than in the reservoirs with long HRT of monthly and annual regulation. This is mainly because that even if the air temperature is high, the reservoir water is difficult to form stable thermal stratification due to strong hydrodynamic force in the reservoirs with short HRT. Therefore, reservoir manager could reduce negative damming effects by adjusting the HRT.

4.4. Environmental factors control of the $CO_2$ flux in the cascade reservoirs

The $CO_2$ flux is influenced by multiple environmental factors such as reservoir age (St. Louis et al 2000,
Sobek et al 2005, Barros et al 2011, Binet et al 2020), air temperature (Sobek et al 2005, Binet et al 2020), HRT (Wang et al 2015, Catalán et al 2016, Li et al 2018a, Kumar et al 2019), water depth (Yang et al 2020), windspeed (Richey et al 2002, Borges et al 2012), latitude (Barros et al 2011, Li 2018c) and so on. In cascade reservoirs, the formation of thermal stratification, which is mainly controlled by the TA and HRT, can influence the water depth, reservoir area, physiology of organisms and carbon cycle (Boehrer and Schultze 2008, Barros et al 2011, Wang et al 2015, 2020a, Catalán et al 2016, Xiao et al 2021). In this study, with the decrease of altitude from upstream to downstream, air temperature increased obviously (table 1 and figure 5(b)). Moreover, three were significant relationships between NWL with the CO$_2$ flux (significant negative relationship) and $\delta^{13}$CO$_2$ (significant positive correlation) (figures 5(c) and (d)). It is suggested that with the decrease of NWL in the downstream, higher air and water temperatures accelerated OM degradation and were responsible for the high CO$_2$ fluxes (Tranvik et al 2009). The CO$_2$ fluxes in HJD and HF reservoirs (longer HRT and higher NWL) were markedly lower than those in PS and YP reservoirs (shorter HRT and lower NWL), indicating the accelerated OM degradation in the downstream (table 2 and figure 4(b)). Since the reservoir water is discharged at the bottom of the dam, the released water from the hypolimnion is responsible for the higher CO$_2$ fluxes (Goudie and Viles 2012, Li et al 2018a). Although HJD reservoir had the longest HRT, CO$_2$ fluxes in HJD reservoir (mean $= 81.3$ mmol m$^{-2}$ d$^{-1}$) was obviously lower than those in SL reservoir (mean $= 216.2$ mmol m$^{-2}$ d$^{-1}$). This indicates that under the condition of lower NWL, higher air temperature and obvious thermal stratification can enhance the accumulation of CO$_2$ in the hypolimnion and enhance the CO$_2$ emission in the released water. Thus, our study suggests that NWL and HRT are two important parameters for jointly controlling CO$_2$ fluxes in the reservoir area and released water.

Although CO$_2$ fluxes in the released water were higher, the reservoir surface area increased dramatically after the damming, leading to that overall amount of CO$_2$ emission in reservoir was larger than that in the released water (Abril et al 2005, Abril et al 2005) and Wang et al (2019a) suggested that the total CO$_2$ emissions from the reservoir area is nearly 10 times larger than the emission from released water. Therefore, previous studies mainly focused on CO$_2$ emissions from the reservoir area (Deemer et al 2016, Kumar et al 2019, Wang et al 2019b). Given the control of the hydrological and geographical factors for CO$_2$ emissions observed in this study, the CO$_2$ fluxes and reservoir effect index ($R_i$) from the other reservoirs around the world were collected from the references (table S1). In our studied eight karst reservoirs, $R_i$ and CO$_2$ fluxes were ranged from 0.005 to 0.3 d m$^{-1}$ (mean $= 0.1$, SD $= 0.1$) and 42.5 to 240.6 mmol m$^{-2}$ d$^{-1}$ (mean $= 137.9$ mmol m$^{-2}$ d$^{-1}$, SD $= 82.2$) in this study and were ranged from 0.005 to 10.2 d m$^{-1}$ (mean $= 1.6$, SD $= 2.1$) and 3.4 to 223.6 mmol m$^{-2}$ d$^{-1}$ (mean $= 52.1$ mmol m$^{-2}$ d$^{-1}$, SD $= 47.1$) in all reservoirs. Both $R_i$ and CO$_2$ fluxes showed significant spatial variation. Mean CO$_2$ fluxes in the eight karst reservoirs are similar to the results in other karst reservoirs, but they are much larger than those in non-karst reservoirs (table S1) (Wen et al 2017, Pu et al 2019). The significant relationship between HRT and CO$_2$ flux further proved that HRT is an important factor affecting the CO$_2$ flux (figure 6(b)) (Wang et al 2015, Li et al 2018a). In addition, $R_i$ which is constrained by both of the HRT and
NWLAS also showed a significant correlation with CO$_2$ flux. Since the x-coordinate data defined by $R_i$ are mainly concentrated in the range of 0–1, $R_i$ can better indicate the CO$_2$ fluxes in the surface of reservoirs (figure 6(c)). Besides, the significant positive relationship between $R_i$ and δ$^{13}$C$_{CO2}$ further indicates that the damming effect has significantly affected the characteristics and flux of CO$_2$ (figure 6(d)). Compared with HRT, $R_i$ would be a better index to predict the CO$_2$ flux in reservoirs. Thus, the empirical relationship between the CO$_2$ flux and $R_i$ will help to evaluate the reservoir CO$_2$ flux and carbon budget in a large spatial scale since the $R_i$ is more easily accessed than CO$_2$ flux.

As discussed above, in the reservoirs with longer HRT and lower NWL, CO$_2$ emissions was much larger (figure 4(b)). Moreover, although the HRT in WJD and SL reservoirs in the middle and lower reaches were much shorter than those in HF, HJD, and DF reservoirs in the upstream, the CO$_2$ emissions in WJD and SL reservoirs were much higher (figure 4(b)). In addition, although the air temperatures in PS and YP reservoirs were higher, there was no obvious thermal stratification in these two reservoirs due to short HRT. CO$_2$ emissions in PS and YP reservoirs were much lower than those in HF and HJD reservoir with higher NWL and longer HRT. The results indicate that the reduction of HRT by artificial regulation can reduce CO$_2$ emissions effectively, particularly playing an important role in reservoirs with lower altitude. Thus, our study suggested that government and scientists could consider coupling the hydrodynamics of reservoir and biogeochemical cycling to improve reservoir management. This is because that once these reservoirs form stable thermal stratification in lentic zone, damming effect on the carbon cycle may be stronger than reservoirs with lower temperatures and longer HRT. Artificial regulation could effectively weaken the side effect on carbon transport and transformation, especially in the cascade reservoirs.

5. Conclusion

To conclude, this study reveals the control mechanism and environmental impact of CO$_2$ production in cascade reservoirs by fitting the $\Delta[\rhoCO_2]$ and $\Delta[δ^{13}C_{CO2}(‰)]$. The reservoir CO$_2$ fluxes (240.6 mmol m$^{-2}$ d$^{-1}$) and emissions (40.4 ton CO$_2$ C y$^{-1}$) in SL reservoir (with higher HRT and lower NWL) are markedly higher than the average value of the eight cascade reservoirs (137.9 mmol m$^{-2}$ d$^{-1}$, 15.6 ton CO$_2$-C y$^{-1}$). Moreover, δ$^{13}$C$_{CO2}(‰)$ varied largely from $-20.6‰$ to $-13.6‰$ in SL reservoir, indicating that HRT and NWL are important environmental factors for controlling CO$_2$ flux. Thus, the relationships between the $R_i$ (HRT/NWL) and CO$_2$ production/emissions are crucial to estimate the carbon dynamics and budget accurately at riverine system in regional and global scale. The estimation of CO$_2$ dynamics in reservoirs would provide hints to optimize reservoirs management for environmental and ecological needs. Overall, our study not only enriches the understanding of the regulation of the hydrologic regime for CO$_2$ production and emissions in cascade reservoirs but also further provides theoretical support for the reservoir regulation to reduce CO$_2$ emissions.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

All data that support the findings of this study are included within the article (and any supplementary files).

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ORCID iD

Wanfa Wang  https://orcid.org/0000-0001-8835-9808

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