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The impact of damming on geochemical behavior of dissolved inorganic carbon in a karst river

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Abstract To determine the impact of damming on the geochemical behavior of dissolved inorganic carbon (DIC) in the Wujiang River basin, field measurements and samples were collected semimonthly for a year. The surface waters of the reservoirs contained concentrations of chlorophyll a up to 5.6 times higher than the upstream river. Compared with the entering waters, the contributions of HCO_3 ⁻ and dissolved CO_2 to DIC decreased, and the contribution of CO_3^2 to DIC and the carbon isotopic composition of DIC ($\delta^{13}C_{\text{DIC}}$) increased in the surface waters of the reservoirs, while in the waters released, the DIC species showed reverse geochemical behaviors. The δ^{13} C_{DIC} ranged from -10.2 ‰ to 2.5 ‰, indicating that significant contributions were from carbonate weathering, photosynthesis, and respiration. After the damming of a river, the bioactivity of phytoplankton was enhanced, and this affected the geochemistry of DIC compared to an unimpacted river and $\delta^{13}C_{\text{DIC}}$ can be used to discern these changes. High-frequency monitoring of river-reservoir systems is necessary to evaluate the efflux of $CO₂$ and provide a better understanding of the carbon sinks and sources in the impounded river.

Keywords Dam - Dissolved inorganic carbon - Carbon isotope compositions · Phytoplankton · Wujiang River

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1 Introduction

The Earth's carbon cycle restricts the development of various resource and environment problems [\[1](#page-7-0)]. Rivers are the main conduit for the exchange of material and energy between the land and the ocean and play an important role in the global carbon cycle. Rivers carry the products of weathering from the land to the ocean in the form of dissolved substances and particulate matter, and the concentrations and fluxes of minerals are the function of environmental factors such as the regional climate, exposed rock, soils, agricultural activities, and anthropogenic emissions [[2\]](#page-7-0). In recent years, the natural properties of rivers have been increasingly affected by human activities [\[3](#page-7-0), [4](#page-7-0)]. Worldwide, 42000 dams had been constructed through 1996 [\[5](#page-7-0)]. A ''reservoir effect'', induced by damming, changes elemental cycles in rivers. This impact has become a popular issue for scientific study.

Carbon forms the basis for living systems on Earth. The impact of damming on the carbon cycle is observed as a variation in the concentration of dissolved inorganic carbon (DIC) and its isotopic composition ($\delta^{13}C_{\text{DIC}}$), by which the impact of a reservoir can be traced $[6, 7]$ $[6, 7]$ $[6, 7]$ $[6, 7]$. The DIC concentration includes CO_2^* (free CO_2 , which equals dissolved CO_2 plus H_2CO_3), HCO_3^- , and $CO_3^2^-$. As the impounded river develops limnological characteristics, phytoplankton in the reservoirs exhibits daily, monthly, seasonal, and yearly variations [\[8](#page-7-0)]. Therefore, in order to accurately assess the impact of damming on the riverine carbon cycle, the changes must be monitored on a frequent basis; however, studies typically involve seasonal and annual sampling [\[2](#page-7-0), [6](#page-7-0), [9](#page-7-0), [10](#page-7-0)]. In our study, four variously aged cascade reservoirs and the corresponding rivers in the Wujiang River basin were sampled twice per month between May,

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2011 and May, 2012. The main purpose of this study was to gain a better understanding of the impact of damming on the biogeochemical behavior of riverine DIC.

2 Study area

The Wujiang River is a tributary on the right bank of the Changjiang River, with a total length of 1,037 km and a drainage area of $88,267$ km². The Wujiang River has a fall of 2,124 m and is one of the main rivers in a west-to-east power transmission project. A total of 11 cascade reservoirs have been built within the Wujiang River basin. The study area is characteristic of the subtropical monsoon humid climate, and its average annual temperature is 12.3 °C, with extreme temperatures of 35.4 °C in the summer and -10.1 °C in the winter. The average temperatures in January (the coldest month) and July (the hottest month) are 3.5 and 26 \degree C, respectively. The annual precipitation ranges from 1,100 to 1,300 mm, and precipitation from May to October accounts for about 75 % of the total annual precipitation. The predominant lithological character of the Wujiang River basin is Pre-Jurassic strata, and carbonate rock is widespread in this area. Permian system, Triassic carbonate rock, coal-bearing petrofabric, and basalt predominate in the upper reaches of the Wujiang River. Permian system, Triassic limestone, dolomitic limestone, and dolostone are widespread in the middle reaches of the Wujiang River. Carbonatite petrofabric including mudstone, shale, and siltite comprise a vast expanse in the lower reaches of the Wujiang River, and Sinian basic ultra-base pyroclastic rock and magmatite emerge in some regions.

The Hongjiadu Reservoir, Dongfengdu Reservoir, and Wujiangdu Reservoir are located on the middle and upper reaches of the Wujiangdu River (Fig. 1) and were constructed in 2001, 1989, and 1971, respectively. The Hongfeng Lake is located on the Maotiao River, a chief tributary of the Wujiang River, and was constructed in 1959. The annual runoff for the site at Liuchong River accounts for 87.2 % of the total water of Hongjiadu Reservoir and represents the unimpacted river. The annual runoff at the sampling site in Liuguang River accounts for 88.8 % of the total water of Wujiangdu Reservoir and can represent the impacted river affected by damming.

3 Sampling and analysis

The Liuchong River (LCH), Hongjiadu Reservoir (HJD), the water released from the Hongjiadu Reservoir (HJD-R), Dongfengdu Reservoir (DFD), the water released from Dongfengdu Reservoir (DFD-R), the Liuguang River (LGH), the Wujiangdu Reservoir (WJD), the water released from the Wujiangdu Reservoir (WJD-R), and Hongfeng Lake (HFH) were sampled semimonthly in the Wujiang River basin (Fig. 1) between May, 2011 and May, 2012. Samples were collected from the surface (upper 0.5 m).

Fig. 1 A map of the region showing the sampling sites

The pH, water temperature (T) , and dissolved oxygen (DO) were measured in situ with an automated multiparameter profiler (model YSI 6600), and alkalinity (ALK) was determined by titration with HCl in the field. Concentrations of chlorophyll a (Chl-a) were measured with a Phyto-PAM (WALZ, Germany). Water samples were filtered through glass fiber filters $(0.70 \text{ }\mu\text{m}, \text{ Whatman GF/F})$ within 24 h. The filtered water was divided for the analyses of anions, cations, and $\delta^{13}C_{\text{DIC}}$. Samples for cation analysis were acidified to pH $\langle 2 \rangle$ with ultra-purified HNO₃. Major cations $(Ca^{2+}, Mg^{2+}, K^+, and Na^+)$ were determined using inductively coupled plasma-optical emission spectrometry (ICP-OES), with a minimum detection limit of 0.01 mg L^{-1} . The anions $(SO_4^{2-}, Cl^-, and NO_3^-)$ were determined using high performance liquid chromatography ICS-90 (Dionex, USA), with a minimum detection limit of 0.01 mg L^{-1} . Saturated HgCl₂ was added into the samples for preservation for the $\delta^{13}C_{\text{DIC}}$ measurement; the vessels were then immediately capped without a headspace, sealed with Parafilm, and placed in cold storage. Samples for $\delta^{13}C_{\text{DIC}}$ measurements were injected into evacuated glass bottles containing pure phosphoric acid and a small magnetic stirrer bar and then heated at 50 °C for the $CO₂$ extraction. The extracted $CO₂$ was frozen in the evacuated vial using liquid nitrogen, and the resulting gas was ana-lyzed on a MAT252 mass spectrometer [\[11](#page-7-0)]. The $\delta^{13}C_{\text{DIC}}$ measurements were normalized to a Pee Dee Belemnite standard (PDB) (Formula 1) with an analytical precision of ± 0.1 ‰.

$$
\delta^{13}C_{\text{DIC}}\left(\substack{\circ}{\right)_{\text{oo}}}\right) = \left[\left(R_{\text{sample}} - R_{\text{PDB}}\right) / R_{\text{PDB}}\right] \times 1000. \tag{1}
$$

4 Calculation of inorganic carbon speciation

The first and second dissociation constants (pK_1 and pK_2) of carbonic acid and the dissociation constant for water and $CO₂$ (pK_w , pK_{CO}) were calculated from the water temperature (K) $[8, 12]$ $[8, 12]$ $[8, 12]$ $[8, 12]$ $[8, 12]$:

$$
CO2 + H2O \Leftrightarrow H2CO3* \Leftrightarrow H+ + HCO3-
$$

$$
\Leftrightarrow 2H+ + CO32, \qquad (2)
$$

$$
pK_1 = (3404.71/T) + 0.03279T - 14.84,
$$
\n(3)

$$
pK_2 = (2902.39/T) + 0.02379T - 6.50,
$$
\n(4)

$$
pK_w = (4470.99/T) + 0.01706T - 6.09,
$$
\n(5)

$$
pK_{\text{CO}_2} = -7 \times 10^{-5}T^2 + 0.016T + 1.11. \tag{6}
$$

The temperature-dependent dissociation constants were corrected for ionic strength with the Güntelberg approximation [\[13](#page-7-0)]:

$$
pK' = pK + \frac{0.5(Z_{\text{HB}}^2 - Z_{\text{B}}^2)\sqrt{I}}{1 + \sqrt{I}}.
$$
\n(7)

 Z_{HB} is the acid charge, Z_{B} is the base charge, and pK' is the dissociation constant corrected for temperature and ionic strength (I) . 0.5 is the Debye-Hückel constant and did not vary with temperature. Equilibrium concentrations (mmol L^{-1}) of HCO_3^- , $CO_3^2^-$, CO_2^* , and the partial pressure of carbon dioxide $(pCO₂)$ were calculated using ALK, pH, and the appropriate temperature-dependent values of pK' :

$$
[HCO_3^-] = 1/(1 + 2(10^{(pH - pK_2')})(ALK - [OH^-]),
$$
 (8)

$$
[CO_3^{2-}] = (10^{(pH - pK_2')})/(1 + 2(10^{(pH - pK_2')}))
$$

$$
[CO_3^{2-}] = (10^{(pH-pK_2')})/(1+2(10^{(pH-pK_2')}))
$$

(ALK – [OH⁻]), (9)

$$
[CO_2^*] = (10^{(pK_1'-pH)})/(1+2(10^{(pH-pK_2')}))
$$

(ALK – [OH^-]), (10)

$$
pCO_2 = [H_2CO_3^*]/K_{CO_2} = [H^+][HCO_3^-]/(K_{CO_2} \times K_1).
$$
\n(11)

5 Results

5.1 Basic physical, chemical, and biological parameters

Temperature (T) ranged from 8.1 to 24.4 \degree C in the rivers with an average of 17.0 °C, from 6.6 to 29.7 °C in the reservoirs with an average of 18.7 °C, and from 9.2 to 24.6 °C in the waters released with an average of 15.8 \degree C (Fig. [2a](#page-4-0)). The pH ranged from 7.8 to 8.6 in the rivers with an average of 8.1, with little seasonal variation; the pH ranged from 7.5 to 8.9 in the reservoirs with an average of 8.2, and the pH of the warm season was greater than that of the cold season; the pH ranged from 7.4 to 8.1 in the waters released with an average of 7.8, and the pH of the cold season was greater than that of the warm season (Fig. [2b](#page-4-0)). The concentration of DO ranged from 7.4 to 11.1 mg L^{-1} in the rivers with an average of 9.2 mg L^{-1} , from 3.9 to 12.5 mg L^{-1} in the reservoirs with an average of 8.3 mg L^{-1} , and from 4.5 to 11.8 mg L^{-1} in the waters released with an average of 7.8 mg L^{-1} . The concentration of DO in the rivers and the waters released was greater in the cold season than in the warm season while that in the reservoirs was greater in the warm season than in the cold season (Fig. [2](#page-4-0)c).

The concentration of Chl-a ranged from 0.9 to 3.5 μ g L⁻¹ in the rivers with an average of 1.9 μ g L⁻¹, from 1.5 to 49.3 µg L^{-1} in the reservoirs with an average of 10.6 µg L^{-1} , and from 1.1 to 4.9 μ g L⁻¹ in the waters released with an average of 2.1 μ g L⁻¹. Generally, the concentration of Chl-a was higher in the warm season than in the cold season (Figure [2](#page-4-0)d). The order of Chl-a concentrations within the reservoirs was: $HFH > WJD > DFD > HJD$ (Table [1](#page-4-0)).

- Fig. 2 Temporal and spatial variations of the investigated parame-b ters. Warm season was from April to September and cold season from October to the following March in this study. Data are shown as average \pm standard deviation. *LCH* Liuchong River, *HJD* Hongjiadu Reservoir, HJD-R releases from Hongjiadu Reservoir, DFD Dongfengdu Reservoir, DFD-R releases from Dongfengdu Reservoir, LGH Liuguang River, WJD Wujiangdu Reservoir, WJD-R releases from Wujiangdu Reservoir, HFH Hongfeng Lake
	- 5.2 Temporal and spatial variation of DIC, HCO_3^- , CO_3^2 , pCO₂, and $\delta^{13}C_{\text{DIC}}$

The basic water chemistry was mainly controlled by carbonate weathering, with the main cations being Ca^{2+} and Mg^{2+} and the main anions SO_4^{2-} and HCO_3^- [[14\]](#page-7-0). The concentration of DIC ranged from 1.68 to 2.82 mmol L^{-1} in the rivers with an average of 2.07 mmol L^{-1} , from 0.83 to 2.48 mmol L^{-1} in the reservoirs with an average of 1.84 mmol L^{-1} , and from 1.66 to 2.74 mmol L^{-1} in the waters released with an average of 2.04 mmol L^{-1} . The concentration of DIC in the rivers and the reservoirs was slightly greater in the cold season than in the warm season (Fig. 2e). The concentration of DIC in the reservoirs was the lowest among these three different water sources, and the concentration of DIC in HFH was the lowest among the four reservoirs (Table 1). DIC was dominated by HCO_3^- , which accounted for 89.7 % of the total DIC. The concentration of HCO_3 ⁻ in the rivers ranged from 1.39 to 2.64 mmol L^{-1} with an average of 1.84 mmol L^{-1} , and that was slightly higher in the cold season than in the warm season (Fig. 2f). The concentration of HCO_3^- ranged from 0.52 to 2.33 mmol L^{-1} in the reservoirs with an average of 1.58 mmol L^{-1} , and that was higher in the cold season than in the warm season. The concentration of $HCO_3^$ ranged from 1.61 to 2.65 mmol L^{-1} in the waters released

Table 1 The annual means of the hydrogeochemical parameters

with an average of 1.92 mmol L^{-1} , and that showed little seasonal variation. HCO₃ had similar temporal and spatial variations compared to DIC. CO_3^2 ⁻ accounted for 5.2 % of the total DIC. The concentration of CO_3^2 ranged from 0.05 to 0.27 mmol L^{-1} in the rivers with an average of 0.12 mmol L^{-1} , from 0.03 to 0.28 mmol L^{-1} in the reservoirs with an average of 0.13 mmol L^{-1} , and from 0.02 to 0.10 mmol L^{-1} in the waters released with an average of 0.06 mmol L^{-1} . The CO_3^2 concentration in the rivers and the waters released showed little seasonal variation (Fig. 2g). The concentration of CO_3^2 showed similar values between the rivers and the reservoirs, but low values in the waters released (Fig. 2g).

The $pCO₂$ ranged from 300 to 2,555 µatm in the rivers with an average of $1,102$ μ atm and did not show clear seasonal changes (Fig. 2h). The $pCO₂$ ranged from 66 to 3,770 μ atm in the reservoirs with an average of 1,523 latm, and that was lower in the warm season than in the cold season. The $pCO₂$ ranged from 840 to 5,312 µatm in the waters released with an average of $2,169$ μ atm, and that was higher in the warm season than in the cold season. Compared to the upstream waters and the reservoirs, the waters released showed high $pCO₂$. WJD had the highest $pCO₂$, while HFH had the lowest $pCO₂$.

The $\delta^{13}C_{\text{DIC}}$ ranged from -9.4 % to -6.4 % in the rivers with an average of -8.1 ‰, from -10.0 ‰ to 2.5 $\%$ in the reservoirs with an average of -6.1% , and from -10.2 ‰ to -7.1 ‰ in the waters released with an average of -8.3 ‰. The $\delta^{13}C_{\text{DIC}}$ in the rivers and the waters released did not show clear seasonal changes (Fig. 2i). The $\delta^{13}C_{\text{DIC}}$ in the rivers and the waters released was more negative than that in the reservoirs, and the $\delta^{13}C_{\text{DIC}}$ of HJD was more positive than that of DFD and WJD (Table 1).

^a LCH Liuchong River, HJD Hongjiadu Reservoir, HJD-R releases from Hongjiadu Reservoir, DFD Dongfengdu Reservoir, DFD-R releases from Dongfengdu Reservoir, LGH Liuguang River, WJD Wujiangdu Reservoir, WJD-R releases from Wujiangdu Reservoir, HFH Hongfeng Lake

 b Average \pm standard deviation

6 Discussion

6.1 The impact of damming on river hydrogeochemistry

After a river is intercepted by a dam, water velocity decreases and T and nutrient loads increase, and, therefore, the impounded waters are more suitable for phytoplankton growth [\[15](#page-7-0)]. Deep reservoirs are often found within a karst geology, and subsequently, physical and chemical stratifications occur. Reservoirs release waters from the bottom, and thus, the waters released reflect the geochemistry of the bottom waters. The average T in the reservoir surface waters was 25.6 \degree C and that of the waters released was 20.8 \degree C from July to September, suggesting that there was thermal stratification in these reservoirs during the warm seasons. Thermal stratification interrupted the riverine continuum, and the order of water T was: reservoir \gt river \gt waters released.

Phytoplankton synthesizes organic matter by photosynthesis, assimilating $CO₂$ and releasing $O₂$, associated with an increase of pH $[16]$ $[16]$:

$$
106CO2 + 16NO3- + HPO42- + 122H2O + 18H+\n\rightarrow C106H263O116N16P + 135O2
$$
\n(12)

For example, from May to August in WJD, the concentrations of Chl-a increased from 5.3 to 40.6 μ g L⁻¹ and, as a response, pH increased from 7.8 to 8.5. Due to thermal stratification in the warm seasons, $CO₂$ from the decomposition of organic matter in the bottom waters could not diffuse upward, which caused a decrease in pH of the bottom waters [\[17](#page-7-0)]. Thermal stratification disappeared in the cold seasons, and $CO₂$ could then diffuse upward. As a result, $pCO₂$ in the waters released was higher in the warm seasons than in the cold seasons.

6.2 The impact of damming on DIC geochemistry

The DIC in rivers mainly comes from: (1) the dissolution of carbonate; (2) soil $CO₂$; (3) respiration of riverine organic matters; (4) atmospheric precipitation. Source (4) contributes a minor amount to the riverine DIC $[18]$ $[18]$ and was neglected in this study. Soil $CO₂$ from the respiration of C3 plants has a δ^{13} C of -23 ‰, while marine carbonate has a δ^{13} C of 0 ‰ [\[19](#page-7-0)]. The δ^{13} C of atmospheric CO₂ is about -7 ‰ and will be -17 ‰ after being dissolved in water due to carbon isotopic fractionation. Therefore, the δ^{13} C of DIC derived from carbonate dissolution is about -8.5 ‰. The exchange between atmospheric $CO₂$ and the DIC in surface waters can be ignored, because the riverine $pCO₂$ is greater than atmospheric $pCO₂$. In addition, the precipitation of calcite causes $\delta^{13}C_{\text{DIC}}$ to be more positive by 0 ‰–3 ‰ [\[20](#page-7-0)].

The $\delta^{13}C_{\text{DIC}}$ in LCH showed a small amplitude and averaged -8.0 ‰, indicating that the $\delta^{13}C_{\text{DIC}}$ of a pristine karst river was mainly controlled by carbonate weathering. After impoundment, phytoplankton thrived and, as a result, δ^{13} C_{DIC} was then controlled by photosynthesis and respiration (Fig. [3\)](#page-6-0). Photosynthesis was dominant in reservoir surface waters. In the process of photosynthesis, $CO₂$ is absorbed and ${}^{12}C$ is preferentially taken up; thus, the residual DIC is enriched with ¹³C and the $\delta^{13}C_{\text{DIC}}$ is more positive. Therefore, $\delta^{13}C_{\text{DIC}}$ was significantly positively correlated to the Chl-a concentration ($R = 0.727$; $P < 0.01$). Respiration was dominant in the bottom waters. In the process of respiration, CO_2 with the same $\delta^{13}C$ value as the organic matter is released, causing a decrease in the $\delta^{13}C_{\text{DIC}}$ in the waters released (Fig. [3](#page-6-0)). Therefore, $\delta^{13}C_{\text{DIC}}$ was affected by the trophic status of these reservoirs. HJD is mesotrophic, DFD is eutrophic, and WJD and HFH are hypereutrophic [\[21](#page-7-0)]. As a response, the $\delta^{13}C_{\text{DIC}}$ of HFH was the most positive and that of HJD was the most negative.

The bioactivity of phytoplankton influences the percentages of the different species of DIC in the impounded river. During the process of phytoplankton photosynthesis, the concentrations of CO_2^* and HCO_3^- decreased, and the pH and CO_3^2 concentration increased. Therefore, the Chl-a concentration was significantly negatively correlated to $pCO₂(R = -0.356; P < 0.01)$ and positively correlated to CO_3^{2-} ($R = 0.414$; $P < 0.01$). Respiration in the bottom waters had a reverse influence on the DIC species; this resulted in the dissolved $CO₂$ increasing in the waters released, and the percentage of $CO₂$ increased from 1.0 % in reservoir surface waters to 2.0 % in the waters released, while the amount of CO_3^2 ⁻ decreased in the waters released and the percentage of CO_3^2 decreased from 7.5 % in reservoir surface waters to 2.9 % in the waters released. The amount of $HCO₃⁻$ was lowest in reservoir surface waters, and the percentage of HCO_3^- increased from 91.5 % in surface waters to 93.3 % in the waters released.

6.3 Frequency of monitoring

This study demonstrated that, compared to the unimpacted river, the impounded river showed a clearly different geochemistry. Sampling at a greater frequency helped provide a better understanding of these changes. We used $pCO₂$ as an example in this study. It can be seen from Fig. [4](#page-6-0) that $pCO₂$ fluctuated widely within short periods at all sites. This meant that, if the $CO₂$ average fluxes were calculated by a seasonal or monthly sampling frequency, the error within these calculated values, compared to the actual values, would be much greater. For example, the $pCO₂$ in the surface waters of LCH on July 4 was 916 µatm and that of August 4 was 932 µatm; the difference between

Fig. 3 Plots of Chl-a versus HCO₃⁻, CO₃²⁻, pCO₂, and δ ¹³C_{DIC}. Calculations of R and P are based on all the data

Fig. 4 Temporal variations of pCO₂. Lines 1-9 stand for average values of pCO₂ in LCH, HJD, HJD-R, DFD, DFD-R, LGH, WJD, WJD-R, and HFH, respectively. LCH Liuchong River, HJD Hongjiadu Reservoir, HJD-R releases from Hongjiadu Reservoir, DFD Dongfengdu Reservoir, DFD-R releases from Dongfengdu Reservoir, LGH Liuguang River, WJD Wujiangdu Reservoir, WJD-R releases from Wujiangdu Reservoir, HFH Hongfeng Lake

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these two results was small; however, the $pCO₂$ on July 19 was 622 µatm, 32.1 % less than that of July 4. Therefore, the calculation of $CO₂$ flux would bring in greater error without the sample taken on July 19th. This situation was found at the other sampling sites (Fig. [4](#page-6-0)). Thus, it is necessary to increase the frequency of sampling to capture this variation.

7 Conclusions

Damming changes the geochemical behaviors of DIC in an unimpacted river, and the $\delta^{13}C_{\text{DIC}}$ can be used to discern the changes in biogeochemical behaviors of DIC. The $\delta^{13}C_{\text{DIC}}$ in the unimpacted Wujiang River was primarily controlled by chemical weathering of carbonate rocks, and after impoundment, the $\delta^{13}C_{\text{DIC}}$ was mainly controlled by photosynthesis and respiration. Furthermore, impoundment changed the ratios of HCO_3^- , $CO_3^2^-$, and dissolved CO_2 to the total DIC, respectively. High-frequency monitoring was necessary to reveal the biogeochemical cycle of DIC, evaluate the efflux of $CO₂$ more accurately, and provide a better understanding of the carbon sinks and sources in the impounded river.

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