



Carbon dioxide emission from surface water in cascade reservoirs—river system on the Maotiao River, southwest of China

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ABSTRACT

Recently, controversies about whether hydropower is still a clean energy have been arisen up with the studies about high CO₂ emission flux from hydroelectric reservoirs in boreal and tropical regions. In this study, four subtropical reservoirs and their related reaches, draining on karstic area in southwest of China, were investigated to understand their CO₂ emission, with monthly sampling strategy from July 2007 to June 2008. *p*CO₂ values in the surface water of these reservoirs ranged from 38 to 3300 μ atm, indicating that reservoir surface could be not only source but also sink to atmosphere CO₂ in different seasons. In Hongfeng reservoir, the flux of CO₂ from surface water varied from −9 to 70 mmol m^{−2} d^{−2} with an average of 15 mmol m^{−2} d^{−2}, and in Baihua reservoir, it had a range from −8 to 77 mmol m^{−2} d^{−2} with an average of 24 mmol m^{−2} d^{−2}. Hongyan reservoir had similar average flux of CO₂ to Baihua reservoir. Xiuwen had the highest average flux of CO₂ with a value of 47 mmol m^{−2} d^{−2} among the studied reservoirs. Downstream the dams discharged by hydropower generation from these reservoirs generally had quite high flux of CO₂, with an average of 489 ± 297 mmol m^{−2} d^{−2}, which is close to those from tropical rivers. This means that water releasing from these reservoirs would be an important way for CO₂ emission into atmosphere. The results showed that dam construction has significant impacts on the river water chemistry, with abrupt changes in *p*CO₂, DO, T, pH and SiC in surface water and their outlets. In addition, with the development of thermal gradient in warm seasons, water chemistry along the water column of reservoirs also showed seasonal variations, except in Xiuwen reservoir which only has daily storage capacity.

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1. Introduction

During the last century, human activities have seriously disturbed the terrestrial water cycle. The most noticeable example is hydrological alterations associated with dam and reservoir development. In 1996, there were approximately 42,000 large dams in the world (Rosenberg et al., 2000). For a long time, hydroelectricity power is thought to be the principal source of clean energy that has been technically well developed so far and generated in a large scale, and can be used to replace the fossil fuel energy to significantly reduce the release of anthropogenic

greenhouse gas (GHG). However, some recent researches are calling the green credentials of hydropower into question (Giles, 2006). For example, data on GHG from some hydroelectric reservoirs in boreal and tropical regions showed quite high CO₂ emission flux from surface water to atmosphere (St Louis et al., 2000; Tremblay et al., 2004; Abril et al., 2005; Guérin et al., 2006; Dos Santos et al., 2006). Especially, some hydroelectric reservoirs in tropical region were reported emitting more CO₂ per unit generating capacity than thermal power did. These conclusions, together with other negative reports about dams, lead people to hesitate the necessity of dam construction (Milliman, 1997; Fearnside, 2002, 2004; Hart et al., 2002; Stokstad, 2006).

Recently, the “damming effect” on dissolved silicon retention, fishery resource of downstream, fluvial flux of nutrients, ecological risks, as well as earthquake and social economy has been well documented (Li and Zhang, 1997; Campo and Sancholuz, 1998; Conley et al., 2000; Jackson and Sleigh, 2000; Saito et al., 2001; Avilés and Niell, 2007; Devi et al., 2008). In comparison, GHG

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emission from reservoirs was less reported, of which, most of the data on GHG were from research in boreal and tropical regions (e.g. Petit Saut reservoir in French Guiana and a few Brazilian reservoirs). GHG emission by reservoirs in subtropical region, was largely overlooked. For instance, over 40,000 reservoirs are presently in operation in Changjiang drainage basin in subtropical region but few reports concern their GHG emission.

Carbonate rock is widely distributed in this area, especially in southwest of China. As a result, the relief there had been incised into many deep canyons, which are also extremely advantaged for cascade hydropower exploitation, due to the strong chemical weathering and large river slope. Then, how is GHG emission in reservoirs in this area and what impact do cascade reservoirs have on $p\text{CO}_2$ in river water become a major concern.

Consequently, we focus our study on four cascade reservoirs in karstic area in southwest China, which belong to Changjiang drainage basin and have climate of subtropical zone. The main objective of this study is to investigate the potential impacts of cascade reservoirs, on dissolved CO_2 along river course. Firstly, the partial pressure of CO_2 in surface waters of river and in reservoirs was reported; secondly, the emission flux of CO_2 from surface water to atmosphere was calculated.

2. Study area and methods

2.1. Study area

The Maotiao River, located in the middle of Guizhou province, China, is a southern tributary of Wujiang River, which is an important tributary to Changjiang River (Fig. 1). This river is developed in karstic area, and the climate there is subtropical rainy monsoon with an average annual rainfall of 1200 mm and annual mean temperature of 13.8 °C. The terrain in this area is highly vegetated. Along the Maotiao River catchment are widely developed limestone, dolomitic limestone, and partly shale.

Hongfeng reservoir, Baihua reservoir, Xiuwen and Hongyan reservoirs are situated northwest of Guiyang, the capital of Guizhou Province (Fig. 1). These four reservoirs are closely connected, and

were constructed on the mainstream of Maotiao River in 1958, 1960, 1960 and 1971 respectively.

Currently, Hongfeng and Baihua reservoirs are in a state of eutrophication, due to the cage culture in these reservoirs. Under this case, deep water is easily to become anoxic, especially in warm seasons.

The main features of these reservoirs are described in Table 1.

2.2. Sampling and methods

2.2.1. Sampling

Water samplings for water chemistry determination were conducted monthly from July 2007 to June 2008. The sampling stations are indicated in Fig. 1. In each reservoir, samples downstream the dams were collected 0.5 m under water surface below the dams, while water sampling along the water column was carried out in the central part of the reservoir (0.4–0.5 km upstream the dam) using a Niskin bottle. For the tributaries, water was taken 0.5 m under water surface. In January, 2008, southern China encountered serious ice rain weather, affected by which, water storage in Xiuwen and Hongyan reservoirs was suspended from January to March. During this period, these two reservoirs were emptied. As a result, downstream the Baihua reservoir became an “original” river without impoundment, in these months. In Xiuwen reservoir, water samples were not collected in February and March, because this reservoir was empty at that time. In Hongyan reservoir, samples of January and March were not collected for the same reason, and in February only the surface water sample were collected.

2.2.2. Methods

The pH, dissolved oxygen (DO) and temperature were measured at the sampling sites with a portable pH and salt conductivity meter (YSI-6600v2). Measurements were performed every five meters along the water column. HCO_3^- was titrated with HCl *in situ*. Major cations (Mg^{2+} , Ca^{2+} , K^+ , and Na^+) were analyzed by ICP-OES, and the anions (SO_4^{2-} , Cl^- , and NO_3^-) by high performance liquid chromatography. The typical precisions of major ions are about $\pm 5\%$.

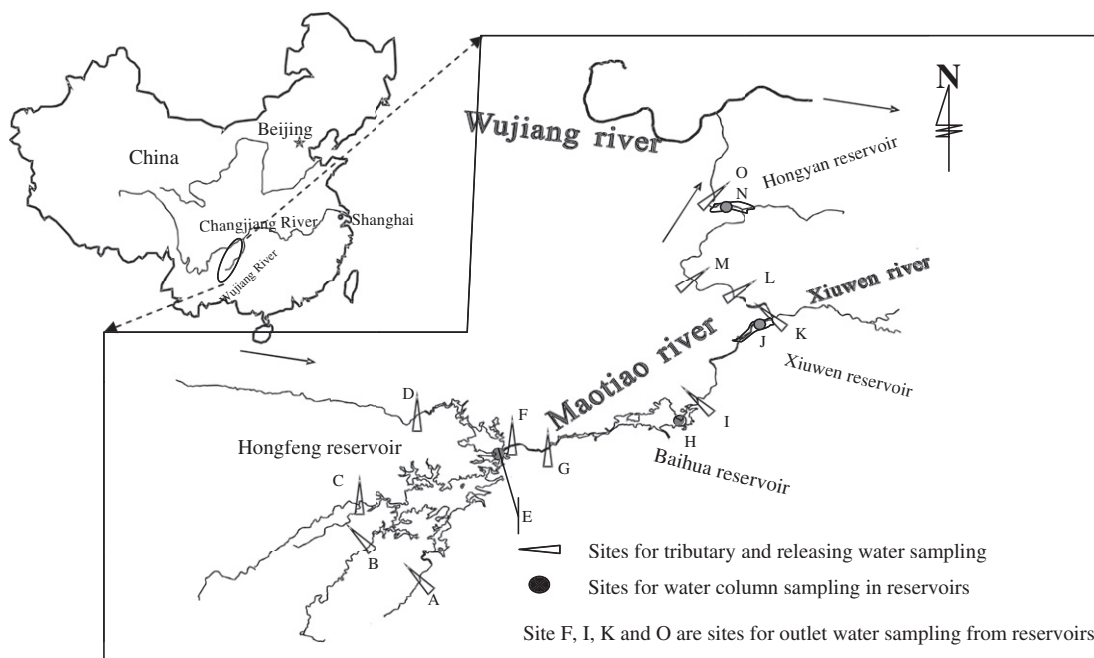


Figure 1. Map showing sampling locations.

Table 1
The main features of the studied reservoirs.

Reservoirs	Drainage area (km ²)	Height of dam m ⁻¹	Normal level/dead storage level (m)	Total volume (10 ⁸ m ³)	Water surface area (km ²)	Mean depth (m ⁻¹)	Time of construction	Storage capacity
Hongfeng	1596	54	1240/1227.5	7.5288	57.2	20	1958	Over year regulation
Baihua	1895	50	1195/1188	2.2082	14.5	12	1960	Yearly regulation
Xiuwen	2145	49	1131/1120	0.114	Not obtained	Not obtained	1960	Daily regulation
Hongyan	2792	60	884/876	0.304	Not obtained	Not obtained	1971	Daily regulation

For $p\text{CO}_2$ calculation, firstly, Henry's constant (K_H) and the first dissociation constants for CO_2 gas in water (K_1) were corrected for temperature. Then, $p\text{CO}_2$ was calculated from HCO_3^- and pH, with the corrections for temperature, and ionic strength (Stumm and Morgan, 1981).

The diffusion flux of CO_2 can be calculated with the Eq. (1):

$$F = k(p\text{CO}_{2w} - g\text{a}_{\text{sat}})K_H \quad (1)$$

Where, F is the diffusion flux of CO_2 between water and the atmosphere; $p\text{CO}_{2w}$ is the partial pressure of CO_2 in the surface water, and $g\text{a}_{\text{sat}}$ is the equilibrium concentration of atmospheric CO_2 (365 μatm) in water (Åberg et al., 2004). K_H is Henry's constant, corrected using temperature.

The piston velocity, k (cm h^{-1}), of CO_2 at the water–air interface, can be affected by different factors such as river runoff, turbidity, velocity of flow, wind speed and water depth (Abril et al., 2000).

The k varies from 115 cm h^{-1} in a turbulent flow, to 8 cm h^{-1} in the rivers without agitation (Aucour et al., 1999). For instance, in River Rhône and Saône, the k was estimated as 8–15 cm h^{-1} (Aucour et al., 1999), and in Amazon mainstream and tributary, it was 10 and 5 cm h^{-1} respectively (Richey et al., 2002). In St Lawrence, k was reported as 15 cm h^{-1} (Yang et al., 1996). River Ottawa and Hudson have a k of 4 cm h^{-1} (Bakker et al., 1999; Telmer and Veizer, 1999).

Considering that the mean wind speed in Maotiao River basin is about 2.5 m s^{-1} , as well as by the comparison of hydrographic features between this river and world rivers, we estimated a k of 10 cm h^{-1} at the tributaries flowing into reservoirs and downstream the dams, and we also gave the upper and lower limit of k with values of 15 and 8 cm h^{-1} (Yang et al., 1996; Aucour et al., 1999; Wang et al., 2007; Yao et al., 2007). As for the water surface in reservoirs, the k reported at other lakes and reservoirs was taken into consideration (Abril et al., 2005; Cole and Caraco, 1998; Guérin et al., 2006). Then, in our studied reservoirs, we used the k of 3 cm h^{-1} , with 2 and 4 cm h^{-1} as its lower and upper limit.

Calcite saturation index (SIc) was calculated from the following Eq. (2):

$$\text{SIc} = \log\left(\frac{(\text{Ca}^{2+})(\text{CO}_3^{2-})}{K_c}\right) \quad (2)$$

Where activities are denoted by brackets, and K_c is the temperature dependent equilibrium constant for calcite dissociation. If $\text{SIc} > 0$, water is super saturated with respect to calcite, and calcium carbonate could deposit; if $\text{SIc} < 0$, water is aggressive to calcite, and calcium carbonate dissolution could happen; and if $\text{SIc} = 0$, the system reaches equilibrium (Liu et al., 2008).

3. Results

3.1. Variation of water temperature, pH and dissolved oxygen (DO) along the Maotiao River

In Fig. 2, data of monthly monitoring was divided into groups of warm seasons (i.e. from March to August) and cold seasons (i.e. from

September to February), according to variations in atmospheric temperature. Data of warm and cold seasons were averaged and then plotted against the distance from head water. In Fig. 2, both temperature and pH in the surface water in our sampling seasons kept a similar trend along the mainstream of the Maotiao River. In cold seasons, water temperature had less variation longitudinally.

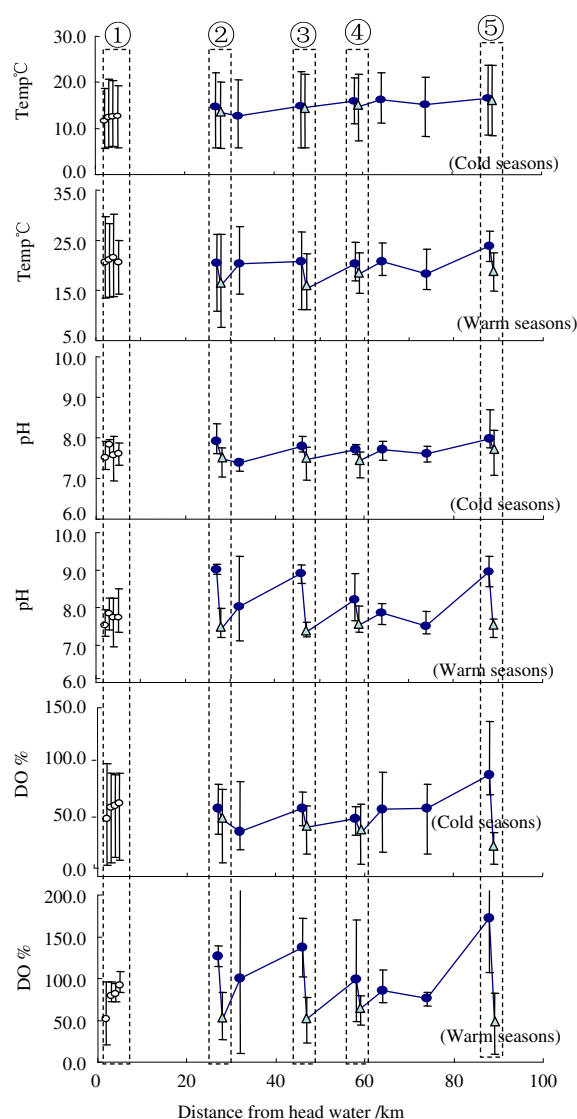


Figure 2. Variations of water temperature, DO, and pH in surface water along the mainstream of Maotiao River, in cold (from September to February) and warm seasons (from March to August). 1 stands for the major tributaries (Site A, B, C and D in Fig. 1); 2, 3, 4 and 5 stand for the locations of the dams of Hongfeng, Baihua, Xiuwen, and Hongyan reservoirs, respectively. At each location, two sampling sites were included, i.e. surface water and the outlet from reservoir. Error bar shows the variation scope of the specific parameters. Open circle refers to the major tributaries; black spot refers to the surface water, and triangle is the downstream the dams.

But in warm seasons, it had an obvious decline when river water passing through the dams. Such as, at site N and O (zone 5), the difference of mean temperature can reach more than 5 °C. This is because that thermal gradient of water column in the studied reservoirs was gradually developed from May to September, and deep water was introduced for power generation. Among these reservoirs, Baihua reservoir can form an obvious thermal stratification, with a difference in water temperature between surface water and deep water more than 15 °C in July. Hongfeng and Hongyan reservoirs had a relatively small thermal gradient along the water column, in summer. But in Xiuwen reservoir, due to its small storage capacity, thermal stratification is not easy to form. In colder seasons water column became well mixed, in these reservoirs.

Water downstream the dams also had lower pH than surface water in the same reservoirs, in warm seasons. In cold seasons, pH in surface water varied less along the river course. After entering into the downstream course, both pH and temperature in the water gradually increased during their transport downstream reservoirs (Fig. 2).

DO is an important index of the balance between photosynthesis and respiration. DO in surface water in the Maotiao River, varied from 23% to 90%, with an average value of 55%, in cold seasons. In warm seasons, it ranged from 49% to 170%, with a mean DO concentration of 88%. Generally, surface water of these reservoirs had higher DO concentrations than tributaries and downstream the dams did, and in particular in warm seasons, it could have DO over 100%, suggesting the strong photosynthesis. In all seasons, downstream dam waters had lower DO concentration than the surface water of reservoirs, and in warm seasons, the maximal difference between them could reach to more than 100% (such as in Hongyan reservoir) (Fig. 2).

3.2. Longitudinal patterns of HCO_3^- , $p\text{CO}_2$, saturation index of calcite (Sic) of calcite (Sic)

HCO_3^- concentrations in the major tributaries (zone 1), were generally higher than that in the mainstream of Maotiao River, with an averaged value of 3.02 mM in cold seasons and 2.6 mM in warm seasons (Fig. 3). HCO_3^- concentrations downstream the dams had an obvious increase, compared with that of the surface water of the same reservoir, in warm seasons. For instance, the difference of HCO_3^- concentrations between the surface water and outlet was about 0.5 mM, except in Xiuwen reservoir (zone 4 of Fig. 2, site J and K, Fig. 1) which is a daily regulation reservoir.

In cold seasons, $p\text{CO}_2$ in the surface water along the Maotiao River varied between 1610 and 5636 μatm , with an average value of 3585 μatm , and the major tributaries had an averaged $p\text{CO}_2$ of 3740 μatm (Fig. 3). $p\text{CO}_2$ in surface water showed a clear discontinuity upstream and downstream the dams, with an increase of more than 2500 μatm in outlet water of each reservoir.

In warm seasons, great variation from 85 μatm to 6269 μatm of $p\text{CO}_2$ in surface water of Maotiao River could be observed. Generally, river downstream the studied reservoirs had an averaged $p\text{CO}_2$ around 5000 μatm , which was similar to that in cold seasons. At the opposite, surface water of reservoirs (except Xiuwen) $p\text{CO}_2$ was quite low, and even lower than the atmosphere level, showing the sink effect to atmospheric CO_2 . In Xiuwen reservoir, only in August, the $p\text{CO}_2$ in surface water was lower than the atmosphere level, with a value of 137 μatm .

Calcite saturation index (Sic) is to judge the precipitation or dissolution of calcite in water. In cold seasons, Sic of surface water in the major tributaries and the mainstream of Maotiao River generally had less variation, with an average value of 0 (Fig. 3), indicating the steady state of calcite. Only in the downstream of reservoirs Sic was below 0, which may cause the possible

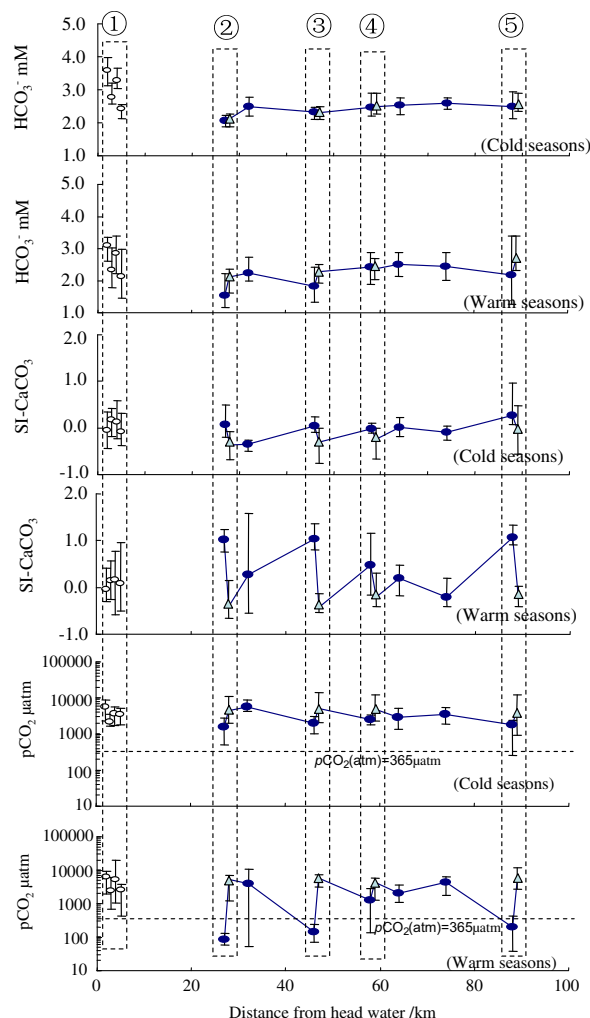


Figure 3. Variations of HCO_3^- , Sic and $p\text{CO}_2$ in surface water along the mainstream of Maotiao River, in cold (i.e. from September to February) and warm seasons (i.e. from March to August). Figure legends are same as in Fig. 2.

dissolution of bedrock. However, in warm seasons, Sic varied significantly along the mainstream. Especially in the surface water of reservoirs, Sic can reach to over 1.0. As a result, calcite precipitation in the surface water of these reservoirs should be favored.

3.3. Monthly variations of $p\text{CO}_2$ and DO inner the reservoirs

On the whole, DO in the deep water of these reservoirs was under saturated (Fig. 4). In Hongfeng and Baihua reservoirs, from April to September, the surface water could have DO concentration super saturated (more than 100%), but their deep water become quite anoxic (Fig. 4a,b). The differences of DO concentrations along the water columns of Xiuwen and Hongyan reservoirs were not as large as that in Hongfeng and Baihua reservoirs (Fig. 4c,d), corresponding to their thermal structure along water column.

As shown in Fig. 5, $p\text{CO}_2$ varied significantly along the water column. Generally, water in deep water of these reservoirs had quite high $p\text{CO}_2$ in warm seasons, especially in summer. In cold seasons, due to the elimination of thermal gradient, $p\text{CO}_2$ varied less vertically. It is interesting that, from March to August, surface water in Hongfeng and Baihua reservoirs had $p\text{CO}_2$ lower than atmospheric level (in Fig. 5a,b, dash line showing the equilibrium $p\text{CO}_2$ between water and atmosphere), indicating the strong

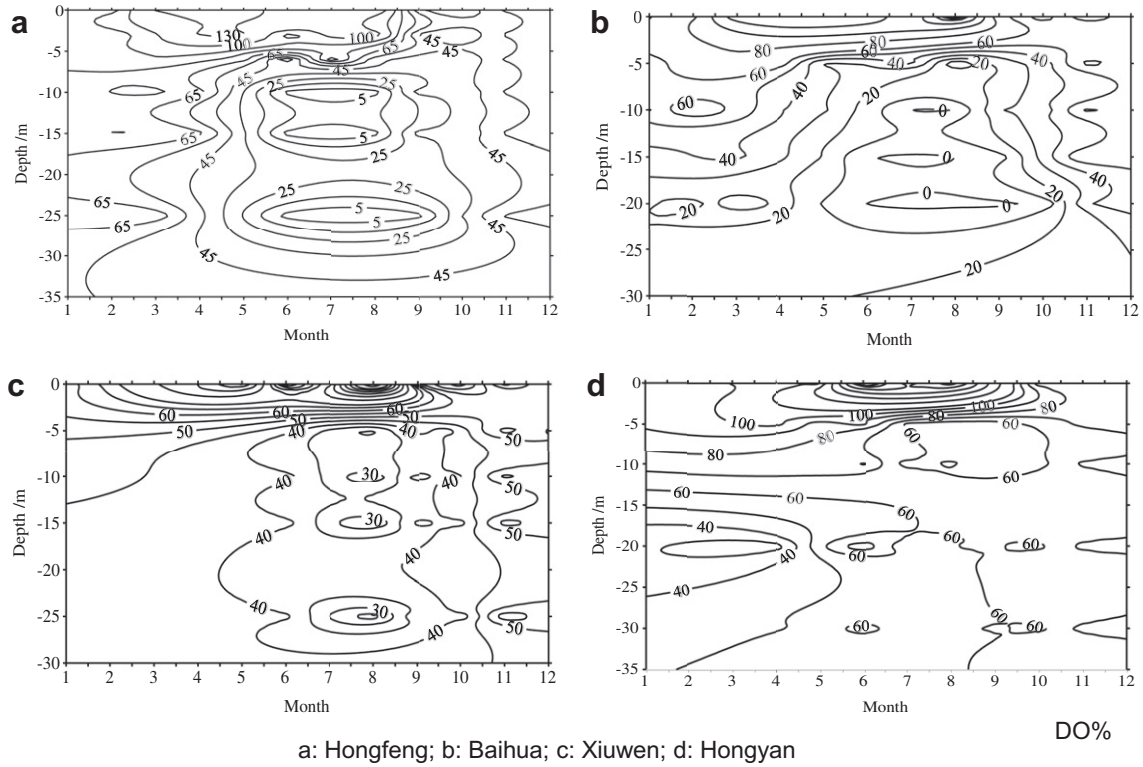


Figure 4. Contours of monthly variations of DO saturation degree in water columns of Hongfeng (HF, site E), Baihua (BH, site H), Xiuwen (XW, site J) and Hongyan (HY, site N) reservoirs.

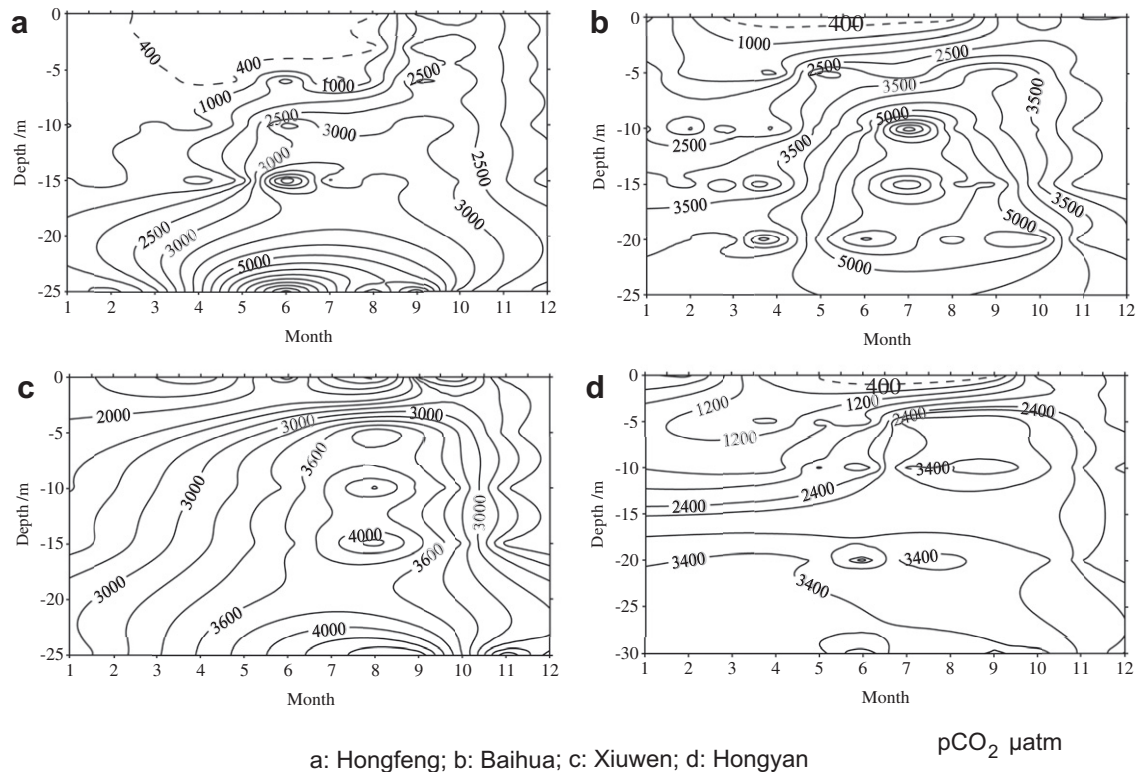


Figure 5. Contours of monthly variations of pCO₂ in water columns of Hongfeng (HF, site E), Baihua (BH, site H), Xiuwen (XW, site J) and Hongyan (HY, site N) reservoirs. Dash line stands the equilibrium pCO₂ between water and atmosphere.

photosynthesis during this period. In Hongyan reservoir, only from May to the end of August, surface water has $p\text{CO}_2$ lower than atmospheric level (Fig. 5d). Xiuwen reservoir generally had high values of $p\text{CO}_2$ in its surface water year-round, an indication of CO_2 source to atmosphere.

3.4. CO_2 diffusion fluxes of Maotiao River

3.4.1. The variations of CO_2 diffusion fluxes along the river course

Based on the average $p\text{CO}_2$ in the surface water of Maotiao River, the average CO_2 diffusion fluxes ($F\text{CO}_2$) in cold and warm seasons along the river course were calculated, as shown in Fig. 6. Totally, $F\text{CO}_2$ was higher in cold seasons, with an average of $337 \text{ mmol m}^{-2} \text{ d}^{-1}$, and in warm seasons, it was $285 \text{ mmol m}^{-2} \text{ d}^{-1}$. Similar to the distribution of $p\text{CO}_2$, $F\text{CO}_2$ demonstrated significant variations upstream and downstream the dams, in all seasons (Fig. 6). Generally, compared with that at major tributaries and downstream the dams, $F\text{CO}_2$ at the reservoir surface were quite low, with $53 \text{ mmol m}^{-2} \text{ d}^{-1}$ in cold seasons and only $1.7 \text{ mmol m}^{-2} \text{ d}^{-1}$ in warm seasons. However, downstream of the studied reservoirs had relatively constant $F\text{CO}_2$, around $490 \text{ mmol m}^{-2} \text{ d}^{-1}$, and had less variation seasonally.

3.4.2. Monthly variation of CO_2 diffusion fluxes from reservoirs

Different to the major tributaries and outlets, surface water of these reservoirs showed great seasonal variations of CO_2 diffusion fluxes (Fig. 7). For instance, from Fig. 7, it is clear that in cold seasons, reservoirs had higher $F\text{CO}_2$. But in Hongfeng, Baihua and Hongyan reservoir, surface water even became a sink to atmosphere CO_2 in warm seasons. Due to its rapid discharge capacity of Xiuwen, this reservoir was revealed to be a CO_2 source to atmosphere year round, except in August. In yearly average, Hongfeng had the lowest $F\text{CO}_2$, with a value of $15 \text{ mmol m}^{-2} \text{ d}^{-1}$, and Xiuwen had the highest $F\text{CO}_2$ of $47.2 \text{ mmol m}^{-2} \text{ d}^{-1}$. In Baihua and Hongyan reservoirs, it was 23 and $24 \text{ mmol m}^{-2} \text{ d}^{-1}$, respectively.

4. Discussion

Terrestrial organic carbon (OC) is an important carbon source for aquatic biological processes. This organic carbon, including POC and

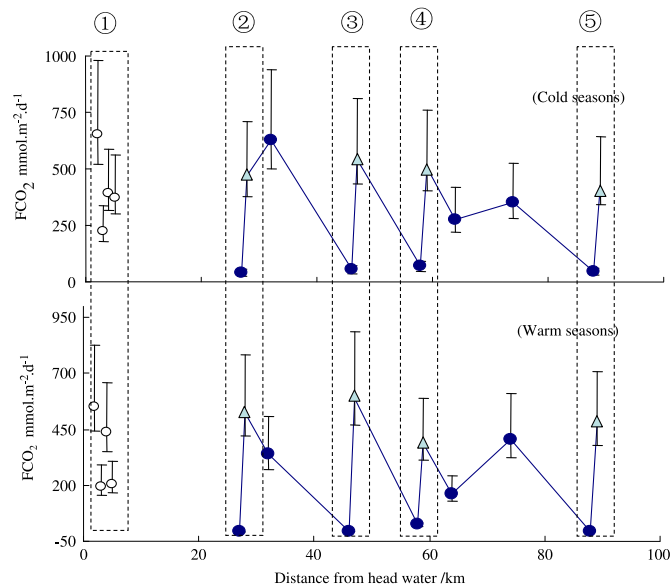


Figure 6. Variations of CO_2 diffusion fluxes at the surface water along the mainstream of Maotiao River, in cold (i.e. from September to February) and warm seasons (i.e. from March to August). Legends are same as in Fig. 2.

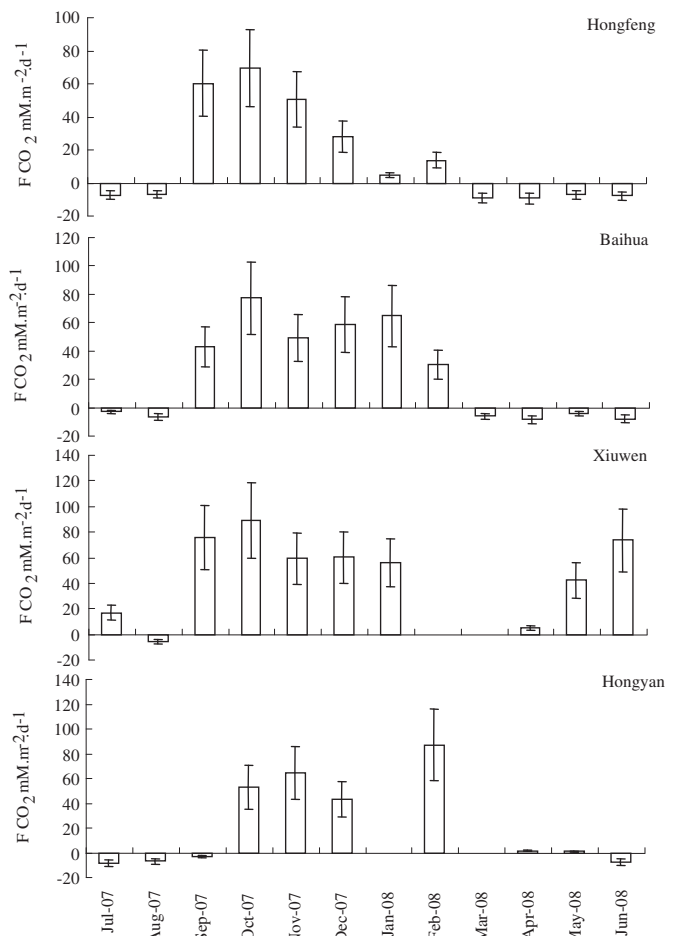


Figure 7. Monthly variation of CO_2 diffusion fluxes at the surface water of Hongfeng, Baihua, Xiuwen and Hongyan reservoirs.

DOC, usually is of higher proportion in riverine total organic carbon (TOC) (Cole and Caraco, 2001; Raymond and Bauer, 2001). The decomposition of organic carbon in river would raise the $p\text{CO}_2$ in water, which process generally made the CO_2 over saturated in rivers world wide (Barth et al., 2003; Cole and Caraco, 2001; Hélie et al., 2002; Jarvic et al., 1997; Raymond et al., 1997; Richey et al., 2002; Salinger et al., 1983). Such as, central Amazon has a mean $p\text{CO}_2$ of $4350 \mu\text{atm}$ (Richey et al., 2002), and the major tributaries of Maotiao River has an averaged $p\text{CO}_2$ of $3930 \mu\text{atm}$ (Fig. 3, zone 1).

However, river damming converts river into “artificial lake”, and generally leads to a decrease in suspended solids and turbidity, an increase in water residence times, thermal stratification and light conditions in water column. The river’s pristine status in hydrological condition, nutrients structure and aquatic ecosystem gradually shifted to “lacustrine/reservoir” autotrophic type prevailing with planktons (Saito et al., 2001). Consequently, the shift of the balance between photosynthesis and respiration along the water column in reservoir, become an important factor responsible for the variation of the $p\text{CO}_2$ in water.

As limited by the light condition, aquatic photosynthesis is prevailing in the surface water of reservoirs. Because freshwater algae generally utilize dissolved CO_2 (Meyers, 1997), the enhancement of photosynthesis will draw down the $p\text{CO}_2$ in water. Under the condition of algae bloom, dissolved CO_2 could become limited, with $p\text{CO}_2$ lower than atmospheric level. For instance, as shown in Fig. 3 and Fig. 5, surface water of reservoirs has lower $p\text{CO}_2$ in warm seasons, and hence become the sink to atmosphere CO_2 (Figs. 6 and 7). At the same

Table 2
Fluxes of CO₂ from the surface of river, natural lakes and reservoirs.

Names	Sites	Climate	FCO ₂ mmol m ⁻² d ⁻¹	References
Reservoirs				
Lokka	Finland	Temperate	24–45	(Huttunen et al., 2003)
Porttipahta	Finland	Temperate	35	(Huttunen et al., 2003)
Hydro-Quebec	Canada	Temperate	25	(Chamberland and Levesque, 1996)
Whatshan	Canada	Temperate	15	(St Louis et al., 2000)
Arrow	Canada	Temperate	30	(St Louis et al., 2000)
Skinmuddselet	Sweden	Temperate	20	(Åberg et al., 2004)
Balbina	Brazil	Tropical	76 ± 46	(Guérin et al., 2006)
Petit Saut	French Guiana	Tropical	133	(Abril et al., 2005)
Samuel	Brazil	Tropical	976 ± 1213	(Guérin et al., 2006)
Tucuruí	Brazil	Tropical	190	(Dos Santos et al., 2006)
Hongfeng	China	Subtropical	15 (–9 to 70)	This study
Baihua	China	Subtropical	24 (–8 to 77)	This study
Xiuwen	China	Subtropical	47 (–6 to 89)	This study
Hongyan	China	Subtropical	22.4 (–8 to 87)	This study
Natural lakes				
Lake Donghu	China	Subtropical	7.8 ± 3	(Xing et al., 2005)
Postilampi	Finland	Temperate	6.6 – 29	(Huttunen et al., 2003)
Kevätön	Finland	Temperate	14	(Huttunen et al., 2003)
Örträsket	Sweden	Temperate	25	(Åberg et al., 2004)
Average for natural lakes			16	(St Louis et al., 2000)
Rivers				
Sinnamary	French Guiana	Tropical	30 – 461	(Abril et al., 2005)
Amazon	Brazil	Tropical	560	(Richey et al., 2002)
Xijiang	China	Subtropical	274	(Yao et al., 2007)
Changjiang	China	Subtropical	14.2	(Wang et al., 2007)
St. Lawrence	Canada	Temperate	118	(Hélie et al., 2002)
Ottawa	Canada	Temperate	105	(Telmer and Veizer, 1999)
Upstream of Maotiao River	China	Subtropical	362 ± 395	This study
Downstream the dams in this study	China	Subtropical	489 ± 297	This study

time, photosynthesis will raise the DO concentration in water and generally make it over saturated (Figs. 2 and 4). pH was also obviously elevated due to the absence of dissolved CO₂ (Fig. 2). Correspondingly, SIc became above zero, and made the water over saturated to calcite (Fig. 3).

The newly formed organic matters, as well as the exogenous organic matter, may be decomposed during their sinking process in the water column and on the surface sediments. During this process, DO is consumed and the product will raise the *p*CO₂ in water. As a result, the decrease in pH and calcite saturation index would be favored, as well as the fall of DO. Deep waters hence have higher *p*CO₂, but generally with a lower pH and DO, specifically during the period of thermal stratification. After the elimination of thermal gradient in cold seasons, deep water with higher *p*CO₂ could invade up to surface, and lead to the high diffusion flux of CO₂ from reservoir surface, which process can be distinctly seen in the contours figures (Figs. 4 and 5), as well as the monthly variation of FCO₂ (Fig. 7).

Another important characteristic of the studied reservoirs is their deep water introduction for hydropower generation. By this way, water with respiration property was discharged downstream. Released water therefore had lower pH, DO, SIc and T, but higher *p*CO₂, as can be confirmed by the notable discontinuity in water chemistry along the river course (Fig. 2). Undoubtedly, deep water releasing would be an important way for CO₂ emission into the atmosphere, and also this releasing water would become erosive to the bedrock downstream for the reason of low SIc.

4.1. Comparison with other water area

Compared with other water area (including reservoirs, lakes and rivers in different climate regions), our studied area showed

similar diffusion fluxes of CO₂ from reservoir surface, to that from reservoirs in temperate regions, and had higher FCO₂ than the average level of natural lakes, but significantly lower than that from tropical reservoirs (Table 2). However, in this study, downstream waters had quite high flux of CO₂, close to that in tropical rivers (Table 2), because of deep water releasing from these reservoirs. The major tributaries (upstream) of Maotiao River also had high FCO₂, with an average value of 362 ± 395 mmol m⁻² d⁻¹.

5. Conclusion

In this study, the cascade reservoirs–river system showed great seasonal variations in the diffusion flux of CO₂. Firstly, the physical obstacle of dams has made the obvious discontinuity of water chemistry across the dams, i.e. the decline in pH, DO, T, SIc and the increase in HCO₃⁻ and *p*CO₂. Secondly, due to the enhancement in aquatic photosynthesis and the development of thermal gradient, *p*CO₂ in the surface water generally had lower values in warm seasons, and even lower than the atmospheric level of CO₂. As a result, FCO₂ from the surface of reservoirs showed negative values during this time, suggesting a potential sink of CO₂. Averagely, the studied reservoirs had similar fluxes of CO₂ from their surface, to that at temperate reservoirs, and somewhat higher than the average level of natural lakes.

However, downstream of these reservoirs kept quite high *p*CO₂ and FCO₂, in all the seasons. This is because that, deep water of the studied reservoirs is used for power generation, by which process respiration carbon was discharged to downstream. So, the outlet from reservoirs should be an important channel for the emission of CO₂ into the atmosphere, and should be paid more attention in the evolution of source and sink effect on CO₂ of reservoirs.

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Appendix. Supplementary material

Supplementary material related to this article can be found online at doi:10.1016/j.atmosenv.2011.04.014.

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