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Diurnal variations of *p*CO_2 in relation to environmental factors in the cascade reservoirs along the Wujiang River, China

PENG Xi[1,2], WANG Baoli[1*], LIU Congqiang[1], LIU Xiaolong[1,2], and WANG Fushun[3]
[1] *State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China*
[2] *Graduate University of Chinese Academy of Sciences, Beijing 100049, China*
[3] *Applied Radiation Institute, School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200433, China*
* *Corresponding author, E-mail: baoliwang@163.com*

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Abstract We have investigated the diurnal variations of the *p*CO_2 and related environmental factors in the cascade reservoirs with different trophic levels along Wujiang River. In surface water the *p*CO_2 was 357±11 μatm in Hongjiadu Reservoir, 338±48 μatm in Dongfeng Reservoir, 682±303 μatm in Wujiangdu Reservoir, and 1677±429 μatm in Liuguang, respectively. The results indicated that these cascade reservoirs had much lower *p*CO_2 values in surface water than river did, and hypereutrophic reservoir showed larger diurnal variations of *p*CO_2 than meso-eutrophic reservoir. In water column, *p*CO_2 tended to increase with the depth. Phytoplankton and the environmental factors such as temperature and pH had different influences on *p*CO_2 diurnal variations due to different trophic levels, and the effect of phytoplankton on *p*CO_2 variation increased with the increase of trophic level in these reservoirs.

Key words diurnal variations; *p*CO_2; environmental factor; cascade reservoirs

1 Introduction

In recent years, the frequency of extreme climatic event presents a growing tendency in the world (An Zhisheng and Fu Longbin, 2001), and thus the related scientific research highlights concern about emission of greenhouse gases (GHGs). Global atmospheric concentrations of GHGs have increased markedly as a result of human activities since 1750, and the atmospheric concentrations of CO_2 (379 μatm) and CH_4 (1774 μatm) in 2005 exceeded by far the natural range over the last 650000 years (IPCC, 2007). Thus the greenhouse effect enhances and thereby becomes a serious environmental problem (Stephen, 1988; Cook et al., 2007; Korhomen et al., 1993; Nusbaumer and Matsumoto, 2008). In the past people thought fossil fuel as one of the major contributors of CO_2 and hydroelectricity as clean energy and they were not related to the global warming (Fearnside, 2002). However, at present the phenomenon that reservoirs release GHGs is paid more and more attention, which causing fierce arguments in the scientific community (Rosa et al., 2004; Milliman, 1997; Fearnside, 2005).

There is consequently growing worldwide concern to determine the contribution of freshwater reservoirs to increasing GHGs concentrations in the atmosphere (St. Louis et al., 2000). Moreover, evaluation of net GHG emissions from reservoirs is becoming more and more crucial to ensure accurate comparisons of energy production methods, evaluations of CO_2 credits, and determination of national GHGs inventories (Demarty, 2009). In this study, we have investigated diurnal variations of the *p*CO_2 in the cascade reservoirs with different trophic levels along the impounded Wujiang River. Our aim is to understand the diurnal variations of the *p*CO_2 in relation to the environmental factors in these cascade reservoirs and this work may have an important significance in choosing the applicable sampling time for the *p*CO_2 research in the impounded river in a large scale.

2 Study sites and methods

2.1 Study sites

The 1037 km-long Wujiang River is a southern tributary of the Yangtse River, and it has a runoff of 53.4 billion cubic meters with a fall of 2124 m. The river is a major power source for China's massive West-to-East Power Transmission Project. The study area belongs to subtropical monsoon humid climate zone with the average annual temperature of 12.3℃.

The average temperatures in January (the coldest month) and July (the hottest month) are 3.5 and 26.0℃, respectively. The annual precipitation ranges from 1100 to 1300 mm, and the precipitation from May to October accounts for about 75% of the total annual precipitation.

2.2 Sampling

Sample collection was carried out in the Hongjiadu Reservoir (HJD), Dongfeng Reservoir (DF), Wujiangdu Reservoir (WJD), and Liuguang Reservoir (LG) during August 18th–24th, 2008 (Fig.1). Surface water sample was gotten every two hours and for water profile sample every six hours in each study sites. Data of pH, water temperature, chlorophyll, and dissolved oxygen were measured in situ by using an automated multi-parameter profiler (model YSI 6600), and alkalinity was titrated with HCl on the spot. Samples for major cations and anions were filtered through 0.45 μm filters. Samples for cation analysis were acidified to pH 2 with ultrapurified HNO_3. Major cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) were analyzed with atomic absorption spectrometry (AAS, PE51002, America) and the anions (SO_4^{2-}, Cl^-, and NO_3^-) by using high performance liquid chromatography (HP1100, SHIMADZU, Japan). Water samples for dissolved organic carbon (DOC) were filtered through glass fiber filter, and were added into concentrated H_2SO_4, and then were kept frozen until analysis. DOC was determined using OI Analytical Aurora 1030 TOC analyzer with limit of detection of 0.01 mg m^{-3}.

2.3 Calculation of the partial pressure of carbon dioxide

The partial pressure of carbon dioxide (pCO_2) in the water body can be calculated from water temperature, pH, the concentrations of cations and anions based on the balance principle of CO_2 in the water body [formula (1)–formula (4)] (e.g. Yao Guanrong et al., 2007; Yu Yuanxiu et al., 2008).

$$CO_2\ H_2O \Leftrightarrow H_2CO_3^* \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow 2H^+ + CO_3^{2-} \quad (1)$$

$$Kco_2 = [H_2CO_3^*]/[pCO_2] \quad (2)$$

$$K_1 = [H^+]\,[HCO_3^-]/[H_2CO_3^*] \quad (3)$$

$$K_2 = [H^+]\,[CO_3^-]/[HCO_3^-] \quad (4)$$

In above formulas K_i are equilibrium constants and can be calculated through below formulas.

$$pKco_2 = -7 \times 10^{-5}T^2 + 0.016T + 1.11 \quad (5)$$

$$pK_1 = 1.1 \times 10^{-4}T^2 - 0.012T + 6.58 \quad (6)$$

$$pK_2 = 9 \times 10^{-5}T^2 - 0.0137T + 10.62 \quad (7)$$

According to Henry's law, we can calculate pCO_2 through following formulas.

$$pCO_2 = [H_2CO_3^*]/Kco_2 = \alpha(H^+) \cdot \alpha(HCO_3^-)/(Kco_2 \times K_1) \quad (8)$$

In above formula, α (H^+) and α (HCO_3^-) are activities of H^+ and HCO_3^-, respectively.

$$\alpha(H^+) = 10^{-[\,pH\,]} \quad (9)$$

$$\alpha(HCO_3^-) = [HCO_3^-] \times 10^{-0.5 \times \sqrt{I}} \quad (10)$$

$$I = 0.5 \times ([K^+] + [Ca^{2+}] \times 4 + [Na^+] + [Mg^{2+}] \times 4 + [Cl^-] + [SO_4^{2-}] \times 4 + [NO_3^-] + [HCO_3^-])/1000000 \quad (11)$$

In the last formula I is ionic strength.

2.4 Statistical analysis

Statistical analysis of data was mainly conducted with the software SPSS (version 16.0; SPSS Inc.). Pearson's correlation coefficient analysis was carried out.

3. Results

3.1 Hydrographic geochemical conditions

The Wujiang River drainage basin is located in the karst area of Guizhou Province. The river water chemistry is controlled by carbonate dissolution by both carbonic and sulfuric acid, and dominated by Ca^{2+}, HCO_3^-, Mg^{2+}, and SO_4^{2-} (Table 1). The ions K^+, Ca^{2+}, Na^+, Mg^{2+}, Cl^-, SO_4^{2-} and NO_3^- did not show significant diurnal variations in concentration in this study, however, HCO_3^- did.

Table 1 Concentrations of main ions in this study (mmol·L^{-1})

K^+	Na^+	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-	NO_3^-	SO_4^{2-}
0.042±0.008[a]	0.204±0.040	1.558±0.116	0.426±0.066	2.032±0.246	0.105±0.022	0.281±0.042	1.044±0.099

[a] Average value ± standard deviation.

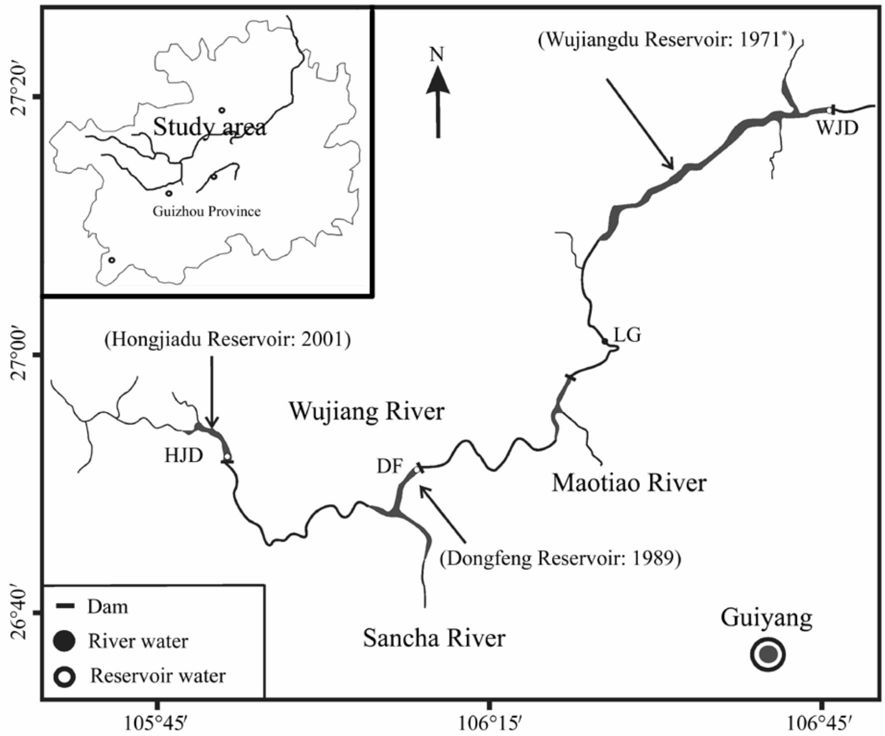

Fig. 1. The location of sampling sites. * Impounded time.

Temperature (T), pH, chlorophyll, and dissolved oxygen (DO) were determined in this work (Table 2). T, pH, and DO tended to decrease with depth and the diurnal variations of water temperature at the same depth were small (Fig. 3). Chlorophyll concentrations of each study site were different from each other. For example, Wujiangdu Reservoir showed chlorophyll at value of 3.00±3.47 $\mu g \cdot L^{-1}$ and Liuguang at value of 0.74±0.42 $\mu g \cdot L^{-1}$. In the water column of these reservoirs, chlorophyll was mainly distributed in the up water and reduced with the depth, and the diurnal variations of chlorophyll concentration were obvious at the same depth (Fig. 3). In the surface water of Hongjiadu Reservoir and Dongfeng Reservoir the concentrations of chlorophyll were lower during the daytime than during the night, and that of Wujiangdu Reservoir was higher during the daytime than during the night (Fig. 2).

3.2 Variations of HCO_3^-, DOC, and pCO_2

Values of pH in the study sites were generally larger than 7.5, indicating a predominance of bicarbonate in dissolved inorganic carbon. The profile variations of HCO_3^- in Hongjiadu Reservoir and Dongfeng Reservoir were obvious; however, this phenomenon was not found in Wujiangdu Reservoir (Fig. 4). As for surface water, concentration of HCO_3^- didn't show obvious diurnal fluctuations in all the study sites (Fig. 2). The concentration of DOC in these reservoirs was higher in the surface and bottom water than that in the middle water and the diurnal variations were also large (Figs. 2 and 4). The DOC concentrations of the three reservoirs were higher than that of Liuguang (Table 2).

Compared to surface water of the three reservoirs, pCO_2 of surface water in Liuguang showed much higher value (Table 2), suggesting reservoir created by the dam on river could reduce the release of CO_2 from river. Wujiangdu Reservoir and Liuguang behaved as carbon source, while Hongjiadu Reservoir and Dongfeng Reservoir behaved as carbon sink (Fig. 2). Among the three reservoirs, surface water in Wujiangdu Reservoir exhibited more obvious diurnal pCO_2 variation than that in other two reservoirs (Fig. 2). In water column, pCO_2 tended to increase with depth in all the reservoirs and it showed different diurnal variations due to different reservoirs (Fig. 4).

4 Discussion

4.1 Biogeochemical processes affecting the pCO_2 variations

Photosynthesis and respiration are two major biogeochemical processes influencing pCO_2 variation. Photosynthesis is a process that converting CO_2 into organic compounds by using the energy from sunlight and respiration is a reverse process that translating organism into CO_2 and releasing energy. Thus, both photosynthesis and respiration are very important processes affecting carbon biogeochemical cycle. The influences of photosynthesis and respiration on pCO_2 variation depend on the extent of phytoplankton involved. The chlorophyll concentrations in Hongjiadu Reservoir, Dongfeng Reservoir, Wujiangdu Reservoir, and Liuguang were 1.39±1.43 $\mu g \cdot L^{-1}$, 0.77±0.78 $\mu g \cdot L^{-1}$, 3.00±3.47 $\mu g \cdot L^{-1}$, and 0.74±0.42 $\mu g \cdot L^{-1}$, respectively. In Wujiangdu Reservoir with high chlorophyll concentration, the average value of pCO_2 in surface water was 502 µatm during the daytime (from 10:00 am to 20:00 pm) with strong photosynthesis, and 862 µatm during the whole night (from 22:00 pm to 8:00) while only respiration occurred. However, this phenomenon was not found in Dongfeng Reservoir with low chlorophyll concentration, which suggested that higher primary productivity may affect the absorption and release of CO_2 in an aquatic system, but the exact reasons still need to be found. In water profile, pCO_2 values increased with water depth as the strength of photosynthesis declined and that of respiration increased.

Table 2 The investigated factors in each study site

	T (℃)	pH	Chlorophyll ($\mu g \cdot L^{-1}$)	DO ($mg \cdot L^{-1}$)	HCO_3^- ($mg \cdot L^{-1}$)	DOC ($mg \cdot L^{-1}$)	pCO_2[b] (µatm)	pCO_2[c] ($mg \cdot L^{-1}$)
HJD	23.31±3.22[a]	8.09±0.48	1.39±1.43	—	101.94±11.15	6.10±3.02	1543±1687	357±11
DF	22.43±4.25	8.15±0.43	0.77±0.78	7.86±1.72	110.97±20.02	5.24±3.85	1390±1700	338±48
WJD	24.26±3.34	7.94±0.41	3.00±3.47	6.00±1.86	134.00±5.69	5.00±1.72	2125±1444	682±303
LG	21.12±0.21	7.85±0.09	0.74±0.42	9.38±0.46	123.15±1.21	2.74±0.79	1677±429	1677±429

Note: [a] Average value ± standard deviation; [b] pCO_2 for all the water sample in each site; [c] pCO_2 for surface water sample in each site; — stands for not detected.

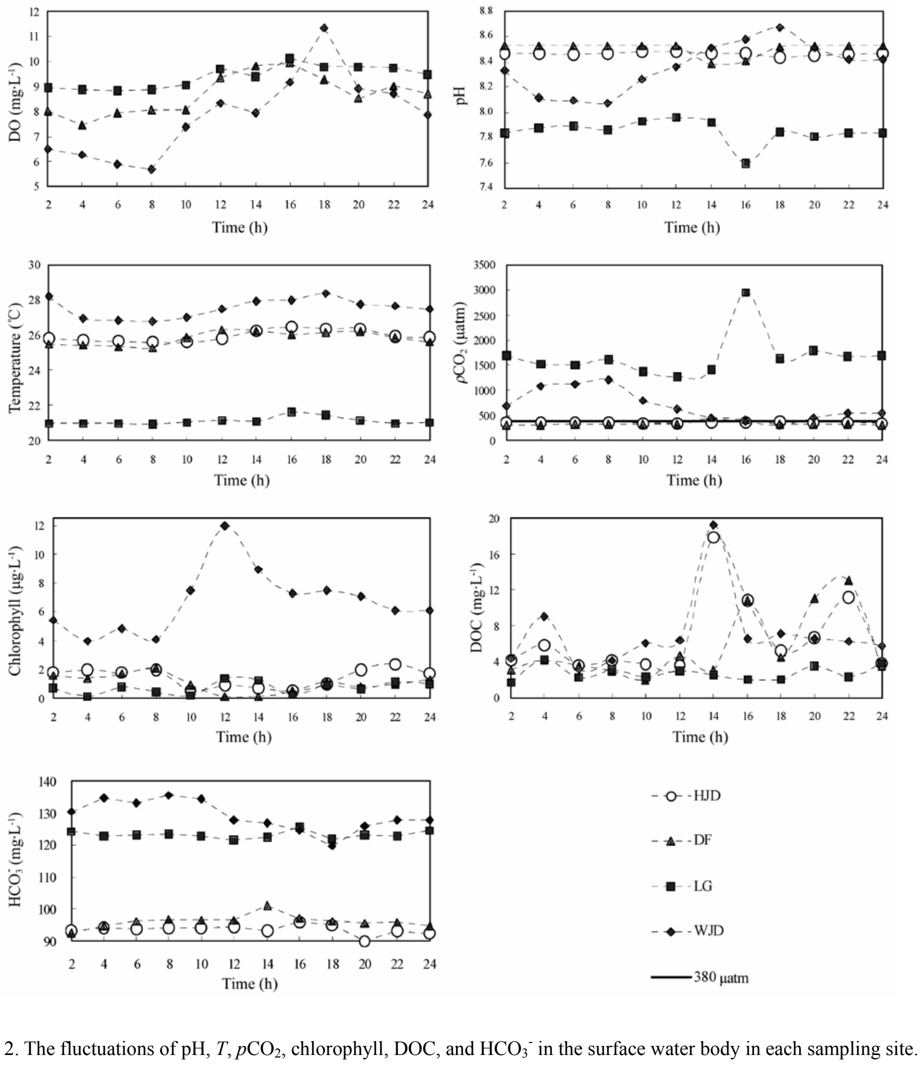

Fig. 2. The fluctuations of pH, T, pCO_2, chlorophyll, DOC, and HCO_3^- in the surface water body in each sampling site.

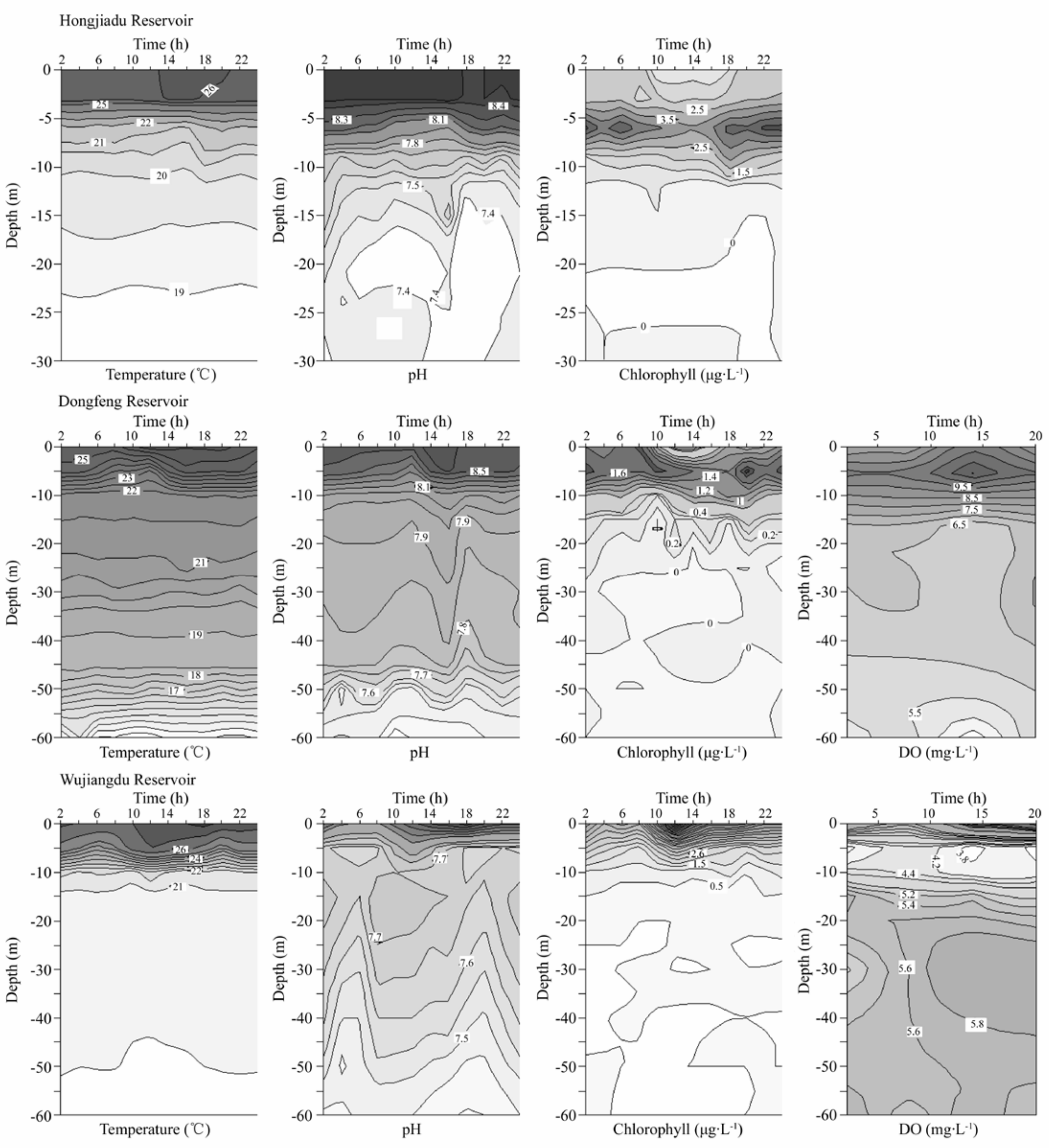

Fig. 3. Profile of temperature, pH, chlorophyll, and DO in the investigated reservoirs.

4.2 The relation between pCO_2 and environmental factors

Factors influencing pCO_2 are complex. Dissolved CO_2 could be originated from HCO_3^-, decomposition of organic matter, and atmospheric CO_2. pCO_2 showed significant positive correlation with HCO_3^- (Table 3), suggesting that HCO_3^- was an important source of dissolved CO_2 here. pH is one factor controlling pCO_2 variation. According to formula (1), improving pH can lead to the decrease of CO_2 concentration and pCO_2 thus exhibited a significant negative correlation to pH (Table 3). Temperature is another factor influencing pCO_2. In these reservoirs, enhancing temperature may stimulate phytoplankton growth (e.g. Wang Baoli et al. 2009). Phytoplankton consumes CO_2 and releases O_2 in the process of photosynthesis and, as a result, we could find that pCO_2 in these reservoirs showed the significant negative correlation with temperature, chlorophyll, and DO, respectively. However, these phenomena were not found in Liuguang. According to Pearson's correlation coefficient analysis in Liuguang, the influence of phytoplankton on pCO_2 could be ignored and pH dominantly controlled pCO_2 variation in this karst river.

Besides the factors mentioned above, water velocity and wind speed can also affect pCO_2 diurnal variation. After impoundment the water velocity slows down and the transparence in water increases due to the decrease of particles, which providing a better condition for algae growth and promoting CO_2 to be absorbed. The wind speed will influence the flux of CO_2 in the water-air interface (Duchemin et al., 1995; Wanninkhof, 1992). In this work, the investigated sites have similar geography and the influence of wind speed may be same at each study site. However, it was not determined in this study.

4.3 Trophic level versus pCO_2

Damming river alters its hydrological condition, material cycle and then transforms aquatic ecosystem from riverine type to limnological type (Wetzel, 2001). Reservoirs created by dams show different trophic states due to different running time and geographical locations along the impounded river. In this work, Wujiangdu Reservoir was hypereutrophic, and Hongjiadu Reservoir and Dongfeng Reservoir were meso-eutrophic (Wang Baoli et al., 2008). At surface water, pCO_2 of Wujiangdu Reservoir was higher than atmospheric CO_2 partial pressure (380 μatm) and thus released CO_2, probably because of its high phytoplankton biomass with strong biological activity such as respiration. Compared with Wujiangdu Reservoir, Hongjiadu Reservoir and Dongfeng Reservoir possessed lower phytoplankton biomass with strong photosynthesis and absorbed CO_2 from atmosphere due to their pCO_2 in the surface water lower than that in the atmosphere. Without damming over Liuguang, it released CO_2 into the atmosphere. It is thus clear that difference in trophic level may have a significant effect on pCO_2 variation in these cascade reservoirs.

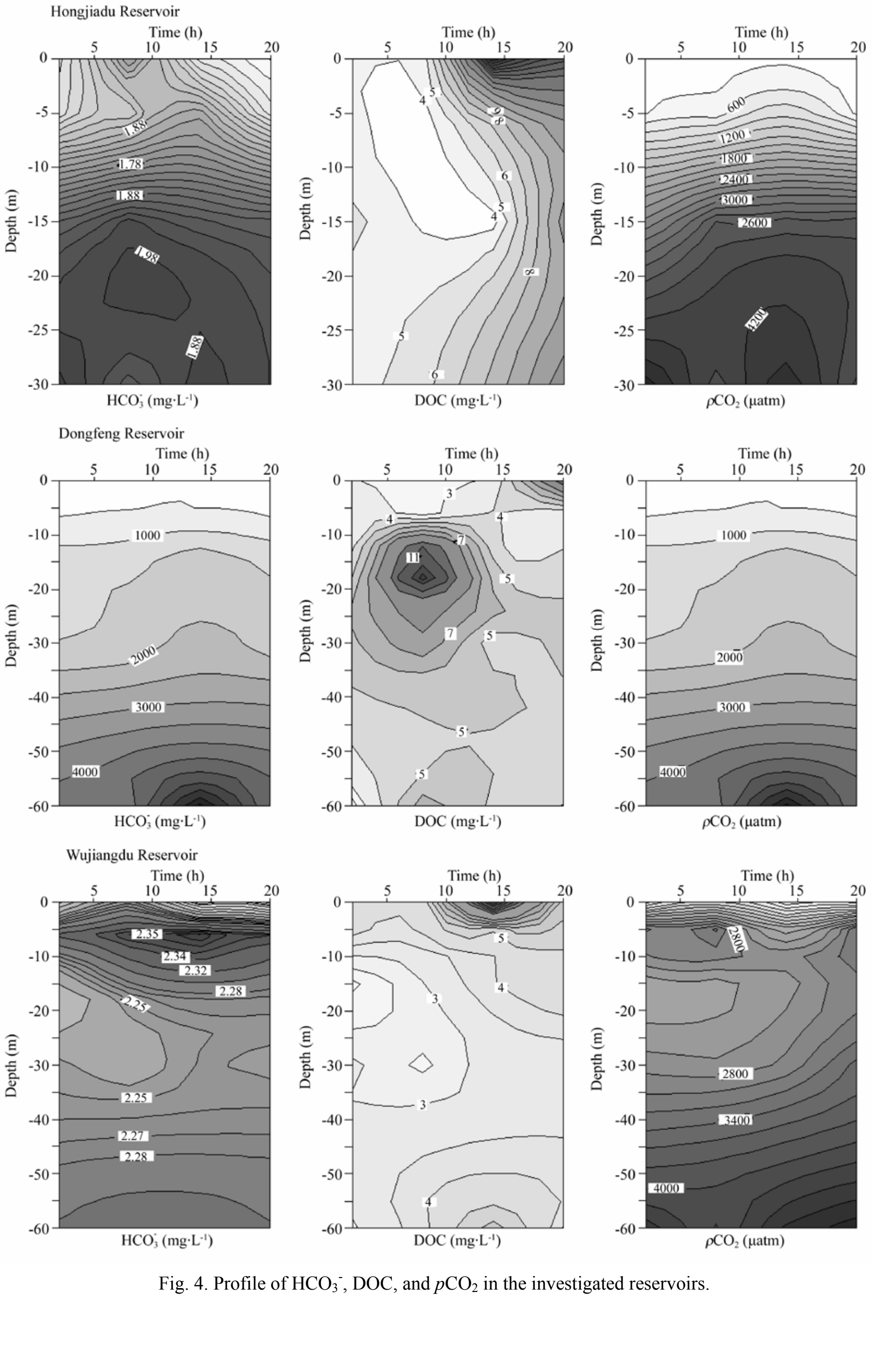

Fig. 4. Profile of HCO_3^-, DOC, and pCO_2 in the investigated reservoirs.

Table 3 Pearson's correlation coefficient between pCO_2 and environmental factors

		T	pH	Chlorophyll	HCO_3^-	DOC	DO
HJD	pCO_2	-0.948**a, 24b	-0.985**, 24	-0.621**, 24	-0.188, 24	0.091, 21	—
DF	pCO_2	-0.938**, 28	-0.908**, 28	-0.586**, 28	0.953**, 28	-0.060, 27	-0.802**, 28
LG	pCO_2	0.714**, 12	-0.990**, 12	-0.406, 12	0.785**, 12	-0.210, 12	0.527, 12
WJD	pCO_2	-0.848**, 28	-0.955**, 28	-0.846**, 28	0.768**, 28	-0.453*, 8	-0.678**, 28
0 m	pCO_2	-0.910**, 36	-0.978**, 36	-0.419*, 36	0.936**, 36	-0.426*, 34	0.561**, 24
5 m	pCO_2	0.296, 12	-0.973**, 12	-0.263, 12	0.963**, 12	0.023, 12	-0.944**, 8
15 m	pCO_2	-0.889**, 12	-0.989**, 12	-0.224, 12	0.080, 12	0.530, 11	-0.983**, 8
30 m	pCO_2	-0.728**, 12	-0.993**, 12	—	-0.115, 12	0.030, 11	-0.620, 8
60 m	pCO_2	-0.293, 8	-0.996**, 8	—	0.395, 8	0.143, 8	-0.822*, 8

[a] Correlation coefficient; [b] the number of samples; ** Correlation is significant at the 0.01 level (2-tailed); * Correlation is significant at the 0.05 level (2-tailed); — stands for not detected.

5 Conclusions

The cascade reservoirs showed different diurnal variations of pCO_2 from each other due to different trophic levels and had much lower pCO_2 values in surface water than river did. In water column and pCO_2 tended to increase with the depth. Phytoplankton and environmental factors such as temperature and pH have different influences on pCO_2 diurnal variations, and the effect of phytoplankton on pCO_2 variation increases with the increase of trophic level in these reservoirs. Our study may have an important significance for choosing the applicable sampling time on pCO_2 research in the impounded river in a large scale.

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