Partial pressure of CO_2 and CO_2 emission in a monsoon-driven hydroelectric reservoir (Danjiangkou Reservoir), China.

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Abstract

Hydroelectric reservoirs have been under sampled to establish them as sources or sinks of the atmospheric carbon dioxide (CO_2). Such poor coverage is well known for subtropic, particularly monsoon driven reservoirs in China. Our study presented the spatiotemporal changes of the carbonate system and CO_2 flux in a hydroelectric reservoir (Dangjiankou Reservoir) locating in a subtropical monsoon climate region. Our 21 filed surveys conducted during 2004-2011 revealed significantly spatial and monthly variations of surface water partial pressure of CO_2 (pCO_2) in the Reservoir. pCO_2, showing higher concentrations in the wet and warm seasons, averaged 595±545 μatm (ranging from 53-3751 μatm) in the reservoir surface, while substantially higher pCO_2 (1132±1220 μatm) was observed in the river below~~downstream~~ the dam. A clear pCO_2 drawdown in the reservoir as water flows demonstrated a significantly descending order of Dan Reservoir>site close to dam>Han Reservoir. This spatial contrast can also be seen in the distributions of dissolved inorganic carbon and total alkalinity. Pronounced seasonality in pCO_2 was controlled by seasonal monsoon rainfall, while photosynthetic CO_2 uptake dominated spatial patterns and dry-month variability of pCO_2. We further related pCO_2 to water chemical properties and indicated that pCO_2 had strong positive correlations with Si, P speciations, TOC~~TP~~ and DOC, negative correlations with DO saturation, TN and Chl-a, while weak correlations with other variables~~ including biogenic elements~~. CO_2 flux from the Reservoir surface showed a bottom average of 9 mmol/m^2/d in comparison with other hydroelectric reservoir in China. River downstream the dam had quite high flux of

CO_2 (119 mmol/m^2/d), which was intermediate between temperate rivers and compared to global rivers' average. This means that water releasing from reservoir would be an important channel for atmospheric CO_2 sources. The annual CO_2 emission from the Danjiangkou Reservoir was estimated at~~to be~~ 3.4×10^9 mol C. Remarkably spatial and temporal heterogeneities in CO_2 flux from China's hydroelectric reservoirs are urgently included for advancing global models of reservoirs' carbon emissions.

Key words: partial pressure of CO_2 (pCO_2), CO_2 flux, carbon emission, hydroelectric reservoir, dissolved inorganic carbon, seasonal and spatial variations.

1. Introduction

Inland waters including rivers, lakes and reservoirs have been identified as potentially important sources of green house gas (GHG) including methane (CH_4) and carbon dioxide (CO_2) (St. Louis et al., 2000; Cole et al., 2007; Lima et al., 2008; Battin et al., 2009; Tranvik et al., 2009; Aufdenkamp et al., 2011; Barros et al., 2011; Bastviken et al., 2011; Butman and Raymond, 2011; Fearnside and Pueyo, 2012; Li et al., 2012; Chen et al., 2013). Previous studies reported 1.4 Pg C emission estimate per year as CO_2 from freshwaters, higher than the river-borne carbon transport (1 Pg C/yr) to the ocean (Tranvik et al., 2009; Amiotte Suchet et al., 2003), this estimated CO_2 emission together with CH_4 emission of 103 Tg CH_4/yr (0.7 Pg C (CO_2eq)/yr expressed as CO_2 equivalents (eq)) have balance the terrestrial carbon sink (Bastviken et al., 2011) and thus represent a critical component of global carbon cycling.

Artificial reservoirs especially the traditional clean hydroelectric reservoirs have been increasingly concerned due to their huge contributions to GHG emissions (St. Louis et al., 2000;~~Giles, 2006;~~ Lima et al., 2008; Barros et al., 2011; Fearnside and Pueyo, 2012). Recent researches particularly on the tropic reservoirs demonstrated quite high C emission fluxes *via* water-air interface (cf. Fearnside et al., 1995; 2005; ~~Richey et al., 2002;~~ Rosa et al., 2004; Abril et al., 2005; Dos Santos et al., 2006; Guerin et al., 2006; Roland et al., 2010; Kemenes et al., 2007; 2011), and the “green” credentials of hydroelectricity have been quashed (Giles, 2006). For instance hydropower reservoirs such as Samuel, Tres Marias, and Barra Bonita, in the tropic zone posted higher C emission than their equivalent thermo-power counterparts (Dos

Santos et al., 2006; Delmas et al., 2001). These observations cause the doubts on the effects of hydroelectricity on global GHG reduction.

The more recent work by Barros et al (2011 *in Nature Geoscience*) estimated 48 Tg C as CO_2 and 3 Tg C as CH_4 annually from hydroelectricity, respectively, a downgrade from earlier estimates of 321 Tg C per year (St. Louis et al., 2001). The estimate was based on 85 globally distributed hydroelectric reservoirs from the Americas and Northern Europe. No reservoirs from Asia especially from China were included, which could be a key component that limits the C emission quantification due to more than 80, 000 reservoirs in operation and many projected in China, as reflected by Barros et al. (2011) that carbon fluxes from reservoirs correlate well to reservoir age, size, latitude, and environmental factors. This was corroborated by distinct sample size and incomplete coverage of spatial cases in particular, which contributed to large variability of CO_2 releases from global reservoirs. For example, the areal flux of CO_2 in the temperate reservoirs averaged 387-1400 mg $CO_2/m^2/d$ (St. Louis et al., 2000; Barros et al., 2011). A broad ranges were also found for CH_4 release from global hydroelectric reservoirs, i.e., from 4 Tg CH_4/yr (Barros et al., 2011) to 100 Tg CH_4/yr (Lima et al., 2008). Thus, more data particularly in China is urgently fueled for precise assessment on the liberation of GHG from hydroelectric reservoirs.

China, one of the largest hydroelectricity producer has a hydropower capacity of 654×10^9 kWh per year, contributing 14% to the total national electricity. More than 40, 000 reservoirs are located in the Yangtze basin with subtropical monsoon climate, while very few reports concern their GHG emissions. Until now, methane efflux has only been studied for the Three Gorges Reservoir (TGR) (Chen et al., 2009; 2011; Yang et al, 2012; Zhao et al., 2013), Miyun (Yang et al., 2011) and Ertan (Zheng et al., 2011), however, more limited studies were conducted on CO_2 emissions from hydropower reservoirs, i.e., two papers from ISI-listed journals (e.g., ~~cascade reservoirs (Hongfeng, Baihua, Xiuwen and Hongyan) in the Wujiang of the Yangtze basin by~~ Wang et al., 2011;~~, as well as TGR by~~ Zhao et al., 2013), and five Chinese journal papers (~~Hongjiadu by~~ Yu et al., 2008; ~~Xin'anjiang by~~ Yao et al., 2010; ~~Nihe by~~ Lu et al., 2010; ~~Wan'an by~~ Mei et al., 2011; ~~Shuibuya by~~ Zhao et al., 2012, which are not readable by international scholars). ~~Therefore, carbon emission from reservoirs in China largely lags behind.~~ Combining very limited studies with clearly spatial (cf. 10-90 mg $CO_2/m^2/h$ for) and temporal (cf. -22-330 mg $CO_2/m^2/h$) heterogeneities in CO_2 flux relating to China's hydroelectricity, we can urge that current data paucity of carbon release from China's reservoirs is constraining the accurate quantification of global carbon emission from hydroelectric reservoirs.

Similar to its adjacent reservoir (ca. 1.7±2.7 mg $CH_4/m^2/h$ for Nam Leuk in Laos; Chanudet et al., 2011) and reservoirs in the tropical zone (cf. Abril et al., 2005), Chinese hydroelectric reservoirs also receive world-wide concerns mainly because of very high methane flux (6.7±13.3 mg $CH_4/m^2/h$) and CO_2 flux (88-175 mmol/m^2/d) from the Three Gorges Reservoir (TGR) (Chen et al., 2009; Zhao et al., 2013) and have been described as "GHG menace" reported in Nature News (Qiu, 2009). However, a recent estimate gave a~~this perspective is challenging by the~~ drastically downward revision of the previous emission rate. For example, estimated ~~the subsequent measurements of~~ 0.29 mg $CH_4/m^2/h$ and 0.18 mg $CH_4/m^2/h$ (Yang et al., 2012), 3%-4% of the previous CH_4 flux in the drawdown area of the TGR (Chen et al., 2011), implied carbon emission from hydroelectricity could be largely over-estimated. Previous reports suggested that s~~S~~patiotemporal sampling ~~and varied calculated methods~~ could cause~~d~~ large differences in CO_2 flux ~~from monsoonal rivers such as Yangtze and Pearl River systems~~ (Yao et al., 2007; Wang et al., 2011; Li et al., 2012). These could complicate the quantification of reservoirs' carbon emission~~potentially cause an over-estimate of CO_2 flux from TGR, where extremely high level occurs when compared to other China's hydropower reservoirs and is comparable to the tropical reservoirs (e.g., Petit Saut and Balbina) (cf. Zhao et al., 2013; Guerin et al., 2006)~~. Therefore, more cases should be developed to better constrain the GHG emission from China's hydroelectricity

Consequently, our study here focuses on the Danjiangkou Reservoir in the Han River, which belongs to Yangtze drainage basin and has a subtropical monsoon climate. The main objectivities are to (1) examine the spatial and temporal changes of partial pressure CO_2 (pCO_2), (2) unravel the mechanisms controlling the variability of pCO_2 and (3) quantify the water-air interface CO_2 flux in the surface water of the reservoir.

2. Material and methods

2.1. Study area

The Danjiangkou Reservoir (32°36′-33°48′N, 110°59′-111°49′E) built in 1970s is situated at the confluence of Han River and Dan River~~in the juncture of Hubei and Henan provinces~~, Central China. The reservoir is accordingly divided into two distinct arms (Han Reservoir and Dan Reservoir; Fig. 1). It has a drainage area of approx. 95, 000 km^2 which includes the upper Han River and Dan River basins (Fig. 1; Li et al., 2008b; 2009a). The Reservoir drains a region of northern subtropical monsoon climate with distinct transitional climatic characteristics. The annual mean temperature is 15-17~~6~~℃ (Fig. 2). The average annual precipitation is 800-14~~0~~00 mm with large inter and intra-annual variability, and 80%-90% of which concentrates in the time period of May through October (Fig. 2; Li et al., 2009a; Li and Zhang, 2010). Similar to the rainfall patterns, the 41.1×10^9 m^3/yr runoff from its upper basin to the Reservoir also shows large annual and interannual variability. For example, in the historical records, the flood peak was 34, 300 m^3/s, the mean maximum monthly flow was 7500 m^3/s in the wet season and the minimum flow in the dry season was 64 m^3/s (cf. Li et al., 2009a).

Currently, the maximal water level of the Reservoir is 157 m, and its corresponding water surface area and storage capacity are 745 km^2 and 17.5×10^9 m^3, respectively. The historical minimal water level is 134 m. Due to the China's South to North Water Transfer Project, the water level will be 170 m with the dam height increasing from the current 162 m to 176.6 m, the water surface area will reach 1050 km^2 when the project is finished in 2014. In our study, five sampling sites during 2004-2006 while eight sites for 2007-2011 were geolocated in the Reservoir using a portable Global Position System (Table 1 and Fig. 1). Distance from dam for DJK 1 is around 30 km, 22 km for DJK2, 19 km for DJK3 and 18 km for D1 in the Dan Reservoir, while 22 km for DJK4 and 10 km for D2 in the Han Reservoir, and D3 and DJK 5 are respectively distributed 1 km from the upper and below the dam. In our considered period, wet season includes June through November, while dry season includes December through May.

2.2. Water sampling and analyses

21 field surveys were conducted for water samplings in the Danjiangkou Reservoir during 2004-2011 (Table 2). A total of 432 grab water samples (3 liters), consisting of three replicates within a 200-m diameter circle, were taken from 50-100 cm depth below water surface using previously acid-washed high-density polyethylene (HDPE) containers. Thus, a total of 144 samples were pretreated for laboratory analysis after mixing with replicates. The acid-washed containers were rinsed thrice with sampled water on site, and the rinsing process was carried out downwind. A 500 ml subsample was filtered *in situ* through a previously acid-washed 0.45 μm pore Millipore nitrocellulose membrane filter. The initial portion of the filtration was discarded to clean the membrane. A small portion of the filtrate was used for measuring major anions Cl^-, F^- and SO_4^{2-}, while another portion for major cation analyses was acidified to pH<2 using ultra-pure concentrated nitric acid. Filtrates for measurements of dissolved organic carbon (DOC), dissolved nitrogen (DN) and solute reactive phosphate (SRP) were also prepared. Raw water samples for determination of total

phosphorus (TP), total nitrogen (TN), total organic carbon (TOC), biogeochemical oxygen demand (BOD) and chemical oxygen demand (COD_{Mn}) were acidified with 10% (v/v) sulphuric acid to pH<2. Filtrates and raw samples were all stored in pre-cleaned HDPE bottles, and transported to the laboratory in a refrigerator at 4 ℃.

Water temperature (T), pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), electrical conductivity (EC), turbidity, nitrate-nitrogen (NO_3^--N) and ammonium-nitrogen (NH_4^--N) were determined on site using a YSI 6920 (YSI Inc., Yellow Springs, Ohio, USA). The instrument was calibrated at 0 and 100% oxygen saturation before and after usage for DO measurement. The pH electrode was calibrated at 7 and 10, and turbidity electrode at 123 and 0 before sampling. The nitrogen sondes were both calibrated at 100 and 1 mg/l before sampling. The membranes used for filtration were dried at 63 ℃ to constant weight, and total suspended solid (TSS) was calculated from the difference in the filter paper weights before and after filtering. Alkalinity, a measurement of bicarbonate buffering components in solution, was determined by titration of hydrochloric acid (0.020 M) *in situ* to pH 4.5 using Methyl orange (Li and Zhang, 2008; 2009; 2010). Total phosphorus (TP) was analysed with acidified molybdate to form reduced phosphor-molybdenum blue and measured spectrophotometrically at 700 nm, with the method detection limit (MDL) of 0.01 mg/L (CSEPB, 2002). SRP was determined by the same analytical method as TP, but measured spectrophotometrically at 882 nm (CSEPB, 2002). TN and DN were determined by alkaline potassium persulfate digestion-UV spectrophotometric method, and TOC and DOC were determined using

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TOC analyzer (MultiN/C2100 TOC/TN, Jena). Chlorophyll-a (Chl-a) was analysed using spectrophotometer (PE-Lambda45, USA). Determinations of BOD and COD_{Mn} were following Li et al. (2008a). The methods given by the Chinese State Environment Protection Bureau were followed in all the procedures (CSEPB, 2002).

pH is critical for $p$$CO_2$ calculations, we very carefully vetted the values as follows: (1) the records of pH probe were~~was~~ carefully calibrated to be respectively 7.00 and 10.00 using standard pH 7 buffer and pH 10 buffer solution (1 pint/475 ml from YSI)~~, the records could be respectively 7.00 and 10.00 for standard pH 7 and pH 10 buffer solution,~~ (2) we record the *in situ* pH levels when the pH levels stabilize in a unit of 0.01 for 2 minutes (30 records for 2 minutes). For alkalinity determination, two or three replicates for individual sample indicated that the differences between duplicates were within 5%.

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Anions (Cl^-, F^- and SO_4^{2-}) were measured using a Dionex Ion Chromatograph (Dionex Corporation, Sunnyvale, California, USA). An inductively-coupled plasma optical emission spectrometer (ICP-OES) (IRIS Intrepid II XSP DUO, USA) was used to determine the concentrations of major cations (K^+, Ca^{2+}, Na^+ and Mg^{2+}), Si and dissolved phosphorus. Reagent and procedural blanks were determined in parallel to the sample treatment using identical procedures. Each calibration curve was evaluated by analyses of these quality control standards before, during and after the analyses of a set of samples. Our analytical precision for major cations was better than ±10%, and ±5% for major anions.

2.3. *p*CO_2 calculations

There are direct and indirect methods using acidimetric titrations for *p*CO_2 determinations. The direct method, named the headspace technique, has been described in detail by Hope et al (1995). The indirect method, much simplified procedure of alkalinity determination by titration to pH 4.5, has been widely used, i.e., *p*CO_2 is calculated via pH/DIC and pH/alkalinity in particular (Neal et al., 1998a, 1998b; Telmer and Veizer, 1999; Yao et al., 2007; Butman and Raymond., 2011; Wang et al., 2011; Li et al., 2012). This titration based method for measurements of dissolved CO_2 are well acknowledged especially for natural rivers with pH > 6 and low organic carbon content.

Popular methods for measurements of *p*CO_2 include temperature-dependent constants in the chemistry equilibrium *via* pH/alkalinity (commonly used) (i.e., Neal et al., 1998a; 1998b; Telmer and Veizer, 1999; Yao et al., 2007; Wang et al., 2011; Li et al., 2012) and CO_2SYS (Lewis and Wallace, 1998). The former detailed algorithm has been presented elsewhere (i.e., Yao et al., 2007; Wang et al., 2011; Li et al., 2012). The program CO_2SYS dependent on measured pH using YSI pH probe, alkalinity and water temperature, employed in our work, was considered to be reliable (cf. Hunt et al., 2011; Butman and Raymond, 2011; Sarma et al., 2011). Our *p*CO_2 values with an assumption of pH shifts in a ±0.01 unit demonstrated a precision of <±5%.

2.4. Water-air interface CO_2 flux calculations

The diffusion flux of CO_2 (F) across the water-air interface can be estimated based on a theoretical diffusion model: $F=k\times K_h\times(pCO_{2water}-pCO_{2air})$ Where k is the gas transfer velocity of CO_2 (also referred to as piston velocity), pCO_{2water} in μatm is the partial pressure of CO_2 in the surface water, and pCO_{2air} in μatm is the CO_2 concentration in equilibrium with atmosphere. K_h is the solubility of CO_2 corrected using temperature. This model has been widely used (i.e., Telmer and Veizer, 1999; Richey et al., 2002; Yao et al., 2007; Teodoru et al., 2009; Alin et al., 2011; Wang et al., 2011; Li el., 2012; 2014).

~~The piston velocity (k in cm/h) of CO_2 at the water-air interface is affected by different basin physical factors but largely by wind speed and water turbulence (Telmer and Veizer, 1999; Alin et al., 2011).~~ Extensive efforts have been made to constrain ~~improve the reliability of~~ the k term ~~term~~ for highly precise and accurate quantification~~methods~~ of water-air CO_2 evasion, such as k values from a suit of empirical functions of wind speed (i.e., Wanninkhof, 1992; Guerin et al., 2007; Raymond and Cole, 2001; Frost and Upstill-Goddard, 2002; Vachon et al., 2010; Alin et al., 2011). ~~However, k values from their models showed large differences (Zhai et al., 2007).~~ Heterogeneous basin physical characteristics particularly wind speed and water turbulence, however, result in wide ranges of k levels (Telmer and Veizer, 1999; Alin et al., 2011), for example, 3 cm/h to 115 cm/h (Aucour et al., 1999; Raymond and Cole, 2001).

~~The riverine k values showed wide ranges of 3 cm/h to 115 cm/h (Aucour et al., 1999; Raymond and Cole, 2001), however,~~ 8-15 cm/h for k values has been widely

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adopted for large rivers, for instance k values (8-15) in the River Rhone and Saone (Aucour et al., 1999), 10 cm/h for Amazon mainstream (Raymond and Cole, 2001) and 15 cm/h for St Lawrence (Yang et al., 1996).~~. Albeit 8-15 cm/h of k value was~~ 8-15 cm/h of k values was also designated in some Asian rivers such as Xijiang River and Wujiang River (Yao et al., 2007; Wang et al., 2011),~~;~~ however, Alin et al. (2011) got a~~the~~ k_{600} level of 22 cm/h ~~at a temperature of 20 °C~~ for the Asian monsoon river of Mekong~~(e.g., Mekong)~~ through field measurements.~~,~~ This level was comparable to~~and~~ 20 cm/h for temperate rivers (Aufdenkampe et al., 2011). Thus, we estimated an averaged k of 15 cm/h in the river downstream the dam considering the normal k level of 10 cm/h due to the similar hydrographic features with other Yangtze River system and world rivers (Aucour et al., 1999; Yao et al., 2007; Wang et al., 2011), and 20 cm/h for reservoir discharge with high turbulence.

Considering the mean wind speed in the Dnajiangkou Reservoir is around 2.5 m/s, thus, the k level of water surface in the Danjiangkou Reservoir can be calculated using a function of wind speed and temperature (Cole and Caraco, 1998):

$$k_{600}=2.07+0.215U_{10}^{1.7} \quad (1)$$

$$k_{600}=k_T\left(\frac{600}{S_{CT}}\right)^{-0.5} \quad (2)$$

$$S_{CT}=1911.1-118.11T+3.4527T^2-0.04132T^3 \quad (3)$$ (Wanninkhof, 1992)

Where k_T is the measured values *in situ* temperature (T), S_{CT} is the Schmidt number of temperature T (unit in ℃), and U_{10} is the wind speed at 10 m above waters (m/s). Here, T=20 ℃, S_{CT}=600 and k_{600}=3.1 cm/h~~, which is comparable to other reservoirs in China, i.e., 2-4 for k value (cf. Yao et al., 2010; Mei et al., 2011; Wang et~~

~~al., 2011)~~. Then we can get the *in site* temperature-dependent k levels using the equations (2) and (3). For both the river below the dam and the reservoir, the use of two extreme values of k_{600} allowed us to give a ranges for the emissions (2 cm/h and 4 cm/h as lower and upper limit for reservoir, while 10 cm/h and 20 cm/h for river) (cf. Yao et al., 2010; Mei et al., 2011; Wang et al., 2011).

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2.5. Statistical analyses

Multivariate statistics such as correlation analyses and analysis of variance (ANOVA) were used in our study. Correlation analyses was employed for relations between pCO_2 and environmental parameters, while ANOVA was performed for differences of spatial and monthly DIC system with significance at $p<0.05$. The statistical processes were conducted using SPSS 16.0 (Li and Zhang, 2009; Li et al., 2013b).

3. Results

3.1. Hydro-climatology

The annual mean air temperature was 16.1℃ with maximal and minimal daily values of 34.2 ℃and -2℃ during the period of 2004-2011. Mean monthly air temperature had significant differences with highest and lowest in July (24.2±1.2℃) and January (3.5 ±1.1℃) (Fig. 2). Annual rainfall ranged from 768 mm (2006) to 1422 mm (2010) with an average of 1077 mm. Monthly mean precipitation was 88 mm, minimum and maximum values were respectively 1.6±1.7 (January) and 256±152 mm (July). The precipitation from May to October accounted for 86% of the total annual.

3.2~~1~~. Variability of water temperature, pH and alkalinity

The original data of water temperature (T), pH and alkalinity were presented in Fig. S1. Their descriptive statistics were listed in Tables S2 and S3. T averaged 9 ±0.4 ℃ to 29 ±1.4 ℃ with minimum and maximum in the dry season~~winter~~ (Jan. 2010) and wet season~~summer~~ (Jul. 2008), respectively. pH showed lower values in the monsoon rainy season, for example, June through November, ranging from 7.81 ±0.18 (Nov. 2009) to 8.65 ±0.09 (Jan. 2010). Alkalinity ranged from 1795 ±456 (Aug. 2010) to 3241±332 μmol/l (Nov. 2008) (Table S2). In total, water temperature, pH and alkalinity averaged 18.75 ℃, 8.22 and 2385 μmol/l, respectively and all of them exhibited significant monthly differences ($p<0.01$ by ANOVA; Table 2~~4~~a).

Contrary to the monthly variations, T and pH in the Danjiangkou Reservoir showed insignificant variability among sampling sites (Table 2~~4~~b). T and pH levels in the Reservoir surface were higher than the site downstream the dam (DJK5) with lowest averages of 16.4 ±8 ℃ for T and 8.01 ±0.38 for pH (Table S3). However, alkalinity showed significant variations among sites with highest and lowest levels of 2736±437 μmol/l (DJK1 in the Dan Reservoir) and 2117±390 μmol/l (DJK4 in the Han Reservoir), respectively. Generally, alkalinity significantly decreased in the Dan Reservoir as water flows (R^2=0.68, $p<0.01$) till the site (DJK 4) in the Han Reservoir, and then increased significantly onward till the downstream of the dam (R^2=0.93, $p<0.01$). In total, alkalinity in the different zones of the Reservoir was following in an

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order of Dan Reservoir >river downstream the Reservoir>site close to dam>Han Reservoir.

3.3~~2~~. Dissolved inorganic carbon (DIC) species

The DIC species calculated using CO_2SYS were presented in Figs. 3, 4, and 5.~~2, 3 and 4.~~ HCO_3^-, showing similar trends with DIC in space and month, was the dominant component of DIC for all samples, accounting for ~93.5% of DIC on average, followed by dissolved CO_3^{2-} and CO_2, accounting for 5.3% and 1.2%, respectively. Also, HCO_3^- accounted for almost all of the alkalinity, up to an average of 97.4%.

There were pronounced monthly and spatial variations in pCO_2 illustrated by box-whiskers plots (Figs. 3, 4, and 5~~Figs 2, 3, and 4~~). Monthly statistics of pCO$_2$ in the Reservoir area generally showed same medians and means with the ratio of 0.83-1.17 (median/mean), while extremely spatial variations resulted in that the mean concentration (491 μatm) was three-fold the median (154 μatm) in July 2006 (Fig. 2). Both of them displayed the minimal and maximal concentrations in the flooding season (ca. June-November), i.e., pCO$_2$ median values ranged 90 μatm in Aug. 2009 to 1530 μatm in Nov. 2008, while 110 (Aug. 2009)-1580 μatm (Nov. 2008) for pCO$_2$ mean values (Fig. 3~~2~~).

As for pCO$_2$ downstream the Reservoir, highest level (4764 μatm) occurred in July, and lowest level (155 μatm) in January 2010 (Fig. 3). pCO$_2$ concentrations in the site downstream the dam were consistently higher in relation to those in the reservoir surface when November 2008 was excluded (Figs. 3 and 4~~2 and 3~~).

Spatial patterns indicated great variations from 53-3751 µatm and 155-4764 µatm of pCO_2 upstream and downstream the dam, respectively (Fig. 5~~4~~). The box-whiskers plots illustrated that pCO_2 median levels significantly decreased as water flows in the Dan Reservoir (R^2=0.41, p<0.05). There was a significant decrease (R^2=0.61, p<0.05) in terms of pCO_2 medians from Dan Reservoir-Han Reservoir-Dam with lowest level (320 µatm) in the site close to Dam. The maximal median (702 µatm) was observed downstream the dam (Fig. 5~~4~~).

pCO_2 mean values significantly decreased from the Dan Reservoir to Han Reservoir (R^2=0.42, p<0.05), then increased quickly till the downstream of dam (R^2=0.88, p<0.05) with lowest (477 µatm) and highest levels (1132 µatm) in sites D2 (Han Reservoir) and DJK5 (downstream of the dam), respectively. The pCO_2 mean values were consistently higher relative to pCO_2 medians, reflected by the ratio of mean to median from 1.14 (D1 in the Dan Reservoir)-1.87 (D3 close to the dam). Regarding to respective sampling site, large variation factors of pCO_2 (max./min.) varied from 9 at DJK2 in the Dan Reservoir to 31 at the river downstream the Reservoir (Fig. 5~~4~~). pCO_2 totally averaged 595±545 µatm (mean±S.D) in the reservoir surface area, which was around 1/2 of the average downstream the Reservoir (1132±1220 µatm).

3.4~~3~~. CO_2 diffusion fluxes of the Danjiangkou Reservoir

The average CO_2 diffusion fluxes (FCO_2) were calculated, as illustrated in Fig.

6~~5~~. FCO_2 was generally higher in the wet season, with averages of -8.2-31.4 mmol/m^2/d, and in the dry season, it ranged from -5.8-10.6 mmol/m^2/d in the reservoir surface waters. Similar to the distribution of pCO_2, FCO_2 demonstrated remarkable variations upstream and downstream the dam in each sampling month. Generally, FCO_2 downstream the dam was quite high, with ranges of -20-703 mmol/m^2/d in the wet season, and -38-125 mmol/m^2/d in the dry season (Fig. 6~~5~~a).

Spatial FCO_2 in the reservoir surface demonstrated the following descending order: Dan Reservoir (3.2-13.7 mmol/m^2/d) > the site close to dam (6 mmol/m^2/d)> Han Reservoir (3-3.4 mmol/m^2/d) (Fig. 6~~5~~b). FCO_2 downstream the dam was much higher than the reservoir surface, i.e., averages of 119 vs 9 mmol/m^2/d for downstream and upstream the dam, respectively (Fig. 6~~5~~). In total, the Danjiangkou Reservoir emitted 2.4×10^9 mol CO_2/yr in the current situation while 3.4×10^9 mol CO_2/yr from 2014 onward, respectively representing 8.3% and 11.7% the CO_2 emission from Three Gorges Reservoir (ca. 29.5×10^9 mol CO_2/yr; Zhao et al., 2013).

3.5. Ancillary data

Seasonal and spatial characteristics of water quality variables are illustrated in Fig. 7. Major ions such as Cl, SO_4, Na, K, Ca and Mg showed higher concentrations in the dry season than the wet season. Concentrations of major ions decreased as water flows in the Dan Reservoir, and tended to reach the minimal in the Han Reservoir. Concentrations in site close to Dam were comparable to the Han Reservoir due to much higher contribution of runoff from Han River (40 km^3/yr vs 1 km^3/yr for Han

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River and Dan River). TSS, COD_{Mn}, TOC showed higher concentrations in the wet season, while DOC tended to have higher concentration in the dry season. Chl-a was higher in the wet season with high temperature and nutrient loads. Nutrient variables such as nitrate and DP showed higher concentrations in the wet season, while other variables had mixed seasonality (Fig. 7). Nutrients were consistently the highest in the river below the Dam when their spatial patterns considered (Fig. 7).

Trophic level index (TLI) and trophic state index (TSI) are used to evaluate lake's eutrophication (cf. Liu et al., 2012). Our results indicated that TLI of COD_{Mn} was in the range of oligotrophic status, TLIs of TP and Chl-a were included in the mesotrophic ranges, while TLI of TN was very high (64-92). TSI levels of TP ranged between 74 and 85, which were comparable to the acknowledged eutrophic lakes in the Yunan Plateau (Liu et al., 2012). Danjiangkou Reservoir thus can be regarded as mesotrophic and eutrophic (Fig. S2).

4. Discussion

4.1. Controls on aqueous pCO$_2$ (CO_2 flux)

Potential processes such as soil CO_2 by runoff and *in situ* aquatic respiration of organic carbon would elevate aquatic pCO$_2$ ~~in water~~, and resulted in oversaturated CO_2 in the rivers worldwide with respect to atmosphere (cf. Cole and Caraco, 2001; Richey et al., 2002; Yao et al., 2007; Sarma et al., 2011; Wang et al., 2007; 2011; Li et al., 2012), albeit photosynthesis and water-air interface CO_2 evasion decrease the aqueous pCO$_2$ (Cole and Caraco, 2001; Zeng and Masiello, 2010). Temperature and

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monsoonal precipitation in the upper catchment~~upstream~~ of the Danjiangkou Reservoir (Fig. 2~~6~~) thus have large effects on aquatic pCO$_2$ levels due to that rainfall alters the biogeochemical processes in the terrestrial ecosystem and organic carbon composition in the Reservoir (Yao et al., 2007; Zeng and Masiello, 2010). This hypothesis was corroborated by pronounced seasonality in pCO$_2$ concentrations (Figs. 3~~2~~ and 4~~3~~). Previous researches reported that negative or positive contributions of rainfall events to pCO$_2$ depend on rainfall intensity and basin impermeability (Ho et al., 1997; Yao et al., 2007; Zeng and Masiello, 2010; Li et al., 2012), for example, initial rainfall enhances the export of soil CO$_2$ and soil organic carbon load to river system, while the following~~continued rain~~ especially the concentrated precipitation lowers soil permeability and consequently shows dominant dilution effects. Moreover, pH was lower in the initial rainfall than the latter (Fig. S3), and each storm event increased the rainfall pH, i.e., increase in pH from 6.02 (12 May) to 7.85 (13 June) and from 6.6 (3 August) to 7.1 (7 August). This suggests that the following storm facilitates the transformation of CO$_2$ to alkalinity. These mechanisms are relevant to~~could explain~~ large variability in pCO$_2$ occurring in the wet months (ca. August 2005 vs August 2009) (Fig. 3~~2~~). In the year of 2009, persistent precipitation (22 July to 5 August) and particularly the extreme storm (i.e., 62 mm/d) from the onset of August (Fig. 2~~6~~) had flushed out the soil CO$_2$ and hence storm dilution effects dominated, which resulted in the trough of pCO$_2$ on 11 August (Fig. 3~~2~~).

Fig. 8. depicts the ~~Samplings in 2005 allowed us analyze~~ seasonal controls on pCO$_2$ in a hydrological year~~ (Fig. 7)~~. Little rainfall occurred between the date of

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sampling in January and April in 2005, while rise in temperature and algae blooming increased photosynthesis in pre-monsoonal month (April) ~~the Spring season~~ would reduce aquatic pCO_2 (from 372 to 294 μatm). Albeit there was no sampling in May 2005, enhanced pCO_2 in this month could be assumed due to export of soil CO_2 *via* monsoonal rainfall events f~~F~~rom May afterward~~, more rainfall events~~ ~~occurred due to monsoonal effects, and enhanced pCO_2 in May could be assumed albeit no sampling in May 2005~~. This, ~~However, this~~ could be supported by the pCO_2 concentrations observed in May 2007 (582 μatm) and May 2011 (650 μatm)~~, which was likely caused by export of soil CO_2 by rain runoff~~. Weak~~er~~ biological CO_2 uptake through photosynthesis due to lower sun angle and high-turbid water might be additional reasons for the rapid pCO_2 increase. The continued rain especially the storm water with lower permeability or without infiltration into soil contributed to the trough of pCO_2 (150 μatm) in June. However, from the late of July to the mid-August, proper temperature and wetted soils by lower precipitation favored soil bacterial respiration and thus higher soil CO_2 content, consequently making elevated aqueous pCO_2 via baseflow and interflow albeit more rainfall events in 13-19 August partially contributed to dilution effects. As expected, precipitation showed a quick decrease from the mid-October onward, evenly distributed precipitation and appropriate rainfall, however, provided optimum environment for soil respiration (cf. Zeng and Masiello, 2010; Li et al., 2012). This allowed the rain water to infiltrate and flush out soil CO_2 to the river with limited dilut~~ion~~ed effects, and therefore contributed to the crest level of pCO_2 in November (Fig. 8~~7~~), similar to~~as indicated by~~ other two major

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pCO_2 peaks in November in 2008 and 2009 (Fig. 3~~2~~). Henceforth, little rainfall and lowest temperature in December through January limited the export of soil CO_2 to rivers, leading to~~which resulted in~~ very low pCO_2 in January (the most cold and dry month) (Figs. 2 and 8~~7~~).

Consistent with previous studies (Richey et al., 2002; Yao et al., 2007; Zeng and Masiello, 2010; Li et al., 2012), pCO_2 in the reservoir surface was generally higher in the warm and wet season (May-November) than in cold and dry season (December-April) (Figs. 3~~2~~ and 8~~7~~). We also concluded that enhanced photosynthesis ~~due to~~with abundant phytoplankton and high water temperature could not explain clearly pCO_2 fluctuations by a factor of more than 10 in the monsoonal season (Fig. 3~~2~~) (Cole et al., 1992). This was corroborated by previous studies (cf. Lu et al., 2010; Zeng and Masiello, 2010) that diurnal pCO_2 showed little changes in the sunny or cloudy day ~~with little rain~~ while large differences in the rainier day~~, as well as little differences of diurnal pCO_2 in the Nihe Reservoir, China (Lu et al., 2010)~~.

Different monthly patterns of pCO_2 occurred in the river downstream the Danjiangkou Dam when compared to reservoir surface waters (Fig. 4~~3~~). This could be responsible for artificial water regulation, for example, water discharges *via* deep turbines before monsoonal flooding arrival for flood control strategy made the extreme pCO_2 in July. However, the second pCO_2 peak level in November 2009 was due to autumn flooding.

As water flows in the reservoir, aquatic ecosystem gradually transformed from "heterotrophy" to "autotrophy" with more photosynthetic uptake of CO_2 close to dam

(Saito et al., 2001). This could explain the significant decrease as water flows in the Dan Reservoir (R^2=0.41, p<0.05 for pCO_2 medians). However, both pCO_2 medians and means were higher in the Dan Reservoir than in the Han Reservoir, which could be contributable to higher pollution load (i.e., COD_{Mn}, BOD and N; Fig. 7) and thus relatively lower pH in the Dan Reservoir zone (Li et al., 2009a). Shifts of hydrological dynamics, nutrient structure and complicated biogeochemical process in the Reservoir generally reduced the pCO_2 close to the dam, as indicated by significant decreases in pCO_2 medians from Dan Reservoir-Han Reservoir-Dam (R^2=0.61, p<0.05; Fig. 5~~4~~), as well as other cases in China such as Wan'an (Mei et al., 2011) and Xin'anjiang Reservoirs (Yao et al., 2010). Turbines with intake of deep water in the Danjiangkou Reservoir produce a hydroelectricity of 45×10^8 kW~~w.~~h/yr, this water releases had hypoxic environment with lower pH and higher CO_2 concentration (cf. Wang et al., 2011), as well as considerably enhanced pCO_2 in the river below~~downstream the~~ dam. Similar results were obtained in China's other hydroelectric reservoirs such as Hongjiadu (Yu et al., 2008) and Xin'anjiang (Yao et al., 2010).

4.2. Correlations between water quality and pCO_2

Apart from precipitation prevailing on monthly pCO_2 variations, as well as hydrological and biogeochemical processes on spatial pCO_2 variations in the reservoir area, water chemical variables including nutrients (ammonium-N, nitrate-N, total-N, dissolved N, soluble reactive phosphorus, dissolved phosphorus, total phosphorus (TP), DO%), organic carbon (TOC, DOC), biogenic elements (Cl^-, SO_4^{2-}, Na^+, K^+,

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Ca^{2+}, Mg^{2+} and Si), water pollution parameters (chemical oxygen demand (COD$_{Mn}$), biochemical oxygen demand (BOD), total suspended solid (TSS), turbidity) and Chl-a were correlated to pCO$_2$ to gain insights of the possible controls (Table 3; Fig. S3~~8; Table S2~~). Our data demonstrated varied relationships between pCO$_2$ and water quality parameters. Generally, ~~indicated that~~ pCO$_2$ was significantly and positively related to Si, P species, TOC~~TP~~ and DOC, and negatively to DO saturation, TN and Chl-a, while slightly to other chemical~~water~~ variables including biogenic elements.

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The increased nitrogen could enhance aquatic photosynthesis and thus O$_2$ production, while reduce dissolved CO$_2$ level (e.g., Cole and Caraco, 2011; Wang et al., 2007), which was relevant to the negative relationships between pCO$_2$ and nitrogen, Chl-a and DO concentration (Table 3~~S2~~). Higher organic carbon appeared to facilitate high bacteria respiration (cf. Sarma et al., 2009; 2011; Zeng and Masiello, 2010), and thus led to increase in pCO$_2$, while O$_2$ was consumed simultaneously. This process was consistent with the algal photosynthesis process that caused opposite changes between pCO$_2$ and O$_2$~~-~~. The results were in excellent agreement with the observations in other China's hydropower reservoirs, e.g., Shuibuya (Zhao et al., 2012), Wan'an (Mei et al., 2011) and Three Gorges Reservoir (Zhao et al., 2011; 2013).

Moreover, aquatic ecosystems tend to have an optimum nutrient stoichiometry of phytoplankton (e.g., Redfield Ratio; Redfield, 1958). Phytoplankton *via* photosynthesis therefore assimilates dissolved CO$_2$ and nutrients such as nitrogen, phosphorus, and silica in a stable element stoichiometric ratio. Thus, dramatic increase in nitrogen load due to anthropogenic inputs in the upper basin of the Reservoir (Li et al., 2009b; 2013) could stimulate the assimilation of dissolved CO_2 and P and Si by aquatic photosynthesis. Slightly increase in P and exclusive source from silicate weathering for Si in the upper Han River (Li et al., 2009c) understandably resulted in positive correlations between pCO_2 and Si and P. These trends were, in general, in concurrence with the results elsewhere (cf. Wang et al., 2007). Yet these processes could not explain the associations between pCO_2 and nitrogen species and biogenic elements, this could be attributed to large anthropogenic-driven effects on nitrogen or multi-collinear effects of water quality properties, for example, varied effects of nitrate on pCO_2 were observed (cf. Wang et al., 2007; Li et al., 2012).

4.3. Comparison with other water areas

CO_2 efflux (9 mmol/m^2/d) from the Danjiangkou Reservoir surface area was at the bottom in contrast to other China's hydroelectric reservoirs (e.g., 6-96 mmol/m^2/d), which resulted in that total CO_2 emission from the Danjiangkou was an order of magnitude lower than the TGR albeit they have same water surface area (Zhao et al., 2013). Our estimated CO_2 emission rate was much higher than some temperate reservoirs (e.g., Wallula, New Melones and Dworkshak): these three reservoirs acted as the atmospheric CO_2 sink, however, much lower than those from boreal and tropic reservoirs. For example, the estimate of CO_2 flux was around 40% of that from Arrow-Upper (boreal) and only 1% that from Samuel (tropic) (see Table 4~~5~~).

On the basis of the available literature, Barros et al. (2011) recently estimated an average of CO_2 flux ~8.8 mmol/m^2/d from temperate hydroelectric reservoirs (25-50 º latitudinal belt). Our calculated CO_2 flux from the Danjiangkou Reservoir equaled to the currently estimated global average for the mid-latitude reservoirs, however, there exited significantly geographical heterogeneities in CO_2 flux from China’s hydroelectric reservoirs (see Table 4~~5~~). For the global estimates, data on CO_2 emission from China's reservoirs have been excluded (cf. St Louis et al., 2000; McCully, 2006; Aufdenkampe et al., 2011; Barros et al., 2011). This indicated that the current global estimation of CO_2 emission from reservoirs could be under-estimated or overestimated, as reflected by the wide ranges (see Table 4~~5~~). It is clear therefore that more data particularly in China, where a large number of hydropower dams exist with many planned for the future, are mandatory to better constrain the global CO_2 emission from hydroelectric reservoirs.

Worldwide riverine pCO_2 was primarily 2-20 times supersaturated in CO_2 relative to the atmosphere (Cole and Caraco, 2001), our calculations of 1132±1220 μatm (ranges of 155-4764 μatm) in the river downstream ~~of~~ the Reservoir was three times lower than global river’s average (3230 μatm calculated from world 47 large rivers; Cole and Caraco, 2001). However, our results were comparable to the Chinese Rivers such as Yangtze (1297±901 μatm; Wang et al., 2007), Pearl (450-2360 μatm; Zhang et al., 2007), Yellow (1137±189 μatm; Cole and Caraco, 2001), and other Asian river such as Mekong (703-1475 μatm, Alin et al., 2011; 1090±290 μatm;~~–~~ Li et al., 2014~~unpublished~~), and other world Rivers, i.e., Hudson (1125±403 μatm, Raymond et al., 1997), St. Lawrence (1300 µatm, Helli et al., 2002), Ottawa rivers (1200 µatm, Telmer and Veizer, 1999) and Mississippi (1335±130 µatm, Dubois et al., 2010).

Our areal flux of CO_2 in the river downstream the dam was intermediate relative to rivers in China (Table 4~~5~~). For example, the riverine CO_2 emission rate ~~in the river~~ downstream the Danjiangkou Reservoir was 8 times higher than that in the main channel of the Yangtze (ca.14 mmol/m^2/d), while it was much lower with respect to the river reach downstream the dams in the Maotiao River (ca. 489 mmol/m^2/d) and the Xijiang (ca. 274 mmol/m^2/d). When compared to the world rivers, the estimated CO_2 emission flux per unit area was much lower than those in tropic rivers (e.g., Amazon) or river stretches below tropical dams, while was intermediate between those of temperate rivers and comparable to the global average (e.g., 147 mmol/m^2/d).

Similar to other reservoirs in China, downstream waters had quite high flux of CO_2 (cf. Yu et al., 2008; Wang et al., 2011). This could be explained as follows: turbines for hydroelectricity generation are located in the deep water areas, and this deep water with prevailing respiration property shows very high dissolved CO_2 concentration due to low permeability light and thermocline in particular. For example, CO_2 flux in the reservoir downstream was 13 fold that from reservoir surface in the Danjiangkou, and this could reach as high as 15 for Hongjiadu (Yu et al., 2008) and 33 for Hongfeng (Wang et al., 2011) (see Table 4~~5~~). This suggested deep water releases *via* turbines is an important sources of atmospheric CO_2 (cf. Kemenes et al., 2011).

5. Conclusion

CO_2 outgassing flux across water-air interface in the Danjiangkou Reservoir was 1/13 lower than the flux from the river downstream the dam. Average CO_2 flux and annual CO_2 emission from the Reservoir were respectively 9 mmol/m^2/d and 3.4×10^9 mol C/yr~~, respectively~~. CO_2 flux from the Danjiangkou Reservoir was near the lower end of the ranges from hydroelectric reservoirs in China, clearly lower than other global estimates for reservoirs (e.g., St Louis et al., 2000; McCully, 2006; Aufdenkampe et al., 2011) and natural lakes (Barros et al., 2011), while similar to global average for temperate hydroelectric reservoirs estimated by Barros et al. (2011).

Substantially monthly and spatial variations in $p$$CO_2$ and CO_2 flux demonstrated the dominant control of rainfall events particularly in the monsoon seasons, while biologic CO_2 uptake through aquatic photosynthesis dominated the spatial distributions in the reservoir area. The much higher CO_2 flux in the river downstream the Reservoir was due to deep water releasing for power generation. Similar to other hydroelectric reservoirs in China, reservoir surface waters were generally supersaturated with CO_2 relative to atmosphere, while lower values of $p$$CO_2$ than the atmospheric level of CO_2 often occurred in the concentrated rainfall months and dry season. We concluded remarkably spatiotemporal variability in $p$$CO_2$ and CO_2 fluxes from China's reservoirs are urgently included for a substantial revision of global estimate of carbon emission, and water discharge from reservoirs should deserve extra attention for assessment of reservoirs' source and sink effects on atmospheric CO_2.

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Figure legends

Fig. 1. Locations of eight sampling sites in the Danjiangkou Reservoir, China (DJK1, DJK2, D1 and DJK3 are located in the Dan Reservoir zone, DJK4 and D2 in the Han Reservoir zone, and D3 and DJK5 in the upstream and downstream of the dam, respectively. D1, D2 and D3 were added from 2007 afterward).

Fig. 2. Daily air temperature (℃) and rainfall (mm) in the upstream of the Danjiangkou Reservoir, China (Ankang station as an example, Ankang station is a most important station closest to the Reservoir; Data from NOAA).

Fig. 3~~2~~. Monthly DIC species illustrated by box-whiskers plots in the Danjiangkou Reservoir, China (The lower and upper boundary of a box represent the first (Q1) and the third quartile (Q3), respectively. The black and the red lines within the box represent the median and mean of the data set, respectively).

Fig. 4~~3~~. Monthly DIC species in the river downstream the Danjiangkou Dam, China.

Fig. 5~~4~~. Spatial variability in DIC species in the Danjiangkou Reservoir, China. (box-whiskers plots, the black and red lines, lower and upper edges, bars and dots in or outside the boxes represent median and mean values, 25th and 75th, 5th and 95th, and <5th and >95th percentiles of all data, respectively).

Fig. 6~~5~~. Monthly (a) and spatial (b) variations of CO_2 diffusion fluxes in the Danjiangkou Reservoir, China.

~~**Fig. 6.** Daily (a) and monthly (b) air temperature (℃) and rainfall (mm) in the upstream of the Danjiangkou Reservoir, China (Ankang station as an example, Ankang station is a most important station closest to the Reservoir; Data from~~

~~NOAA).~~

Fig. 7. Ancillary water quality parameters in the Danjiangkou Reservoir, China (unit in mg/l except ORP in mV, Chl-a in μg/l). The error bars represent standard deviations.~~Daily air temperature (℃), rainfall (mm) and pCO_2 (μatm) in the year 2005 of Ankang station.~~

Fig. 8. Scatter plots between pCO_2 and some key water chemicals in the Danjiangkou Reservoir, China (Spearman's rho coefficients for pCO_2 and all the hydrogeochemical variables were tabulated in Table S2).

~~**Table 1**. The main features of the Danjiangkou Reservoir, China.~~

	~~Drainage area km^2~~	~~Height of dam m~~	~~Normal water level m~~	~~Total volume billion m^3~~	~~Water surface area km^2~~	~~Time of construction~~	~~Installed capacity MW~~	~~Power density W/m^2~~	~~Hydropower capacity 10^8 kw.h/yr~~
~~1968-2013~~	~~95200~~	~~162~~	~~157~~	~~17.45~~	~~745~~	~~1968~~	~~900~~	~~1.21~~	~~45~~
~~2014 afterward~~	~~95200~~	~~176.6~~	~~172~~	~~29.05~~	~~1050~~	~~2014~~			

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Table 2. Descriptive statistics of monthly variability in T (°C), pH and alkalinity (μmol/l) of the Danjiangkou Reservoir, China.

	T					pH					Alkalinity				
—	N	Mean	S. D.	Min.	Max.	N	Mean	S. D.	Min.	Max.	N	Mean	S. D.	Min.	Max.
Nov.2004	5	16.84	0.58	15.84	17.24	5	8.22	0.08	8.14	8.34	5	2440	219	2200	2600
Jan. 2005	5	9.19	0.64	8.08	9.65	5	8.28	0.07	8.20	8.37	5	2360	207	2200	2700
Apr.2005	5	12.44	3.64	7.96	16.72	5	8.42	0.07	8.29	8.47	5	2600	524	2200	3500
Jun.2005	5	27.75	4.33	20.16	30.52	5	8.52	0.35	7.92	8.85	5	2409	291	1900	2643
Aug.2005	5	24.49	0.95	23.00	25.34	5	7.98	0.13	7.81	8.13	5	2180	192	1900	2400
Nov.2005	5	18.26	0.43	17.73	18.65	5	7.91	0.06	7.81	7.96	5	2280	286	1900	2600
Apr.2006	5	15.30	2.54	11.06	17.46	5	8.26	0.10	8.09	8.38	5	2432	489	2080	3280
Jul.2006	5	27.89	3.86	21.00	29.99	5	8.28	0.50	7.64	8.70	5	2192	485	1520	2880
May 2007	8	24.82	0.85	23.54	26.53	8	8.19	0.10	7.98	8.35	8	2520	363	2080	3280
Nov.2007	8	14.94	1.78	12.00	17.00										
Jul.2008	8	29.10	1.35	25.86	29.99	8	8.01	0.38	7.21	8.37	8	1937	345	1616	2644
Nov.2008	8	12.03	0.66	11.27	12.87	8	8.01	0.41	7.45	8.63	8	3241	332	2920	3968
Apr.2009	8	15.32	1.51	11.68	16.26	8	8.08	0.15	7.82	8.26	8	2489	384	2206	3422
Aug.2009	8	27.36	1.46	23.97	28.47	8	8.64	0.28	7.99	8.91	8	2037	222	1814	2359
Nov.2009	8	16.87	0.20	16.56	17.10	8	7.81	0.18	7.39	7.95	8	2354	151	2160	2576
Jan.2010	7	9.00	0.35	8.48	9.49	7	8.65	0.09	8.53	8.75	7	2354	166	2120	2560
Apr.2010	8	14.67	1.38	11.98	16.46	8	8.44	0.21	7.97	8.62	8	2409	226	2000	2680
Aug.2010											8	1795	456	1200	2360
Nov.2010											8	2475	92	2280	2600
Mar.2011											8	2407	257	2104	2736
May 2011	8	20.84	0.79	19.19	21.53	8	8.14	0.14	7.99	8.34	8	2717	226	2440	3000
Total	119	18.75	6.65	7.96	30.52	111	8.22	0.33	7.21	8.91	135	2385	425	1200	3968

S.D.-Standard deviation; Min.- Minimum; Max.- Maximum.

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~~**Table 3.** Descriptive statistics of spatial variability in T, pH and alkalinity of the Danjiangkou Reservoir, China (T in °C, Alkalinity in μmol/l).~~

		T					pH					Alkalinity				
	—	N	Mean	S. D.	Min.	Max.	N	Mean	S. D.	Min.	Max.	N	Mean	S. D.	Min.	Max.
Dan Reservoir	DJK1	17	20.45	6.49	9.26	30.52	16	8.15	0.27	7.76	8.62	19	2736	437	2000	3500
	DJK2	18	19.11	6.95	8.67	29.61	17	8.29	0.27	7.86	8.74	20	2473	292	2020	3360
	D3	10	18.97	6.96	8.85	29.53	9	8.26	0.36	7.68	8.79	12	2475	338	1960	3080
	DJK3	18	18.77	7.25	8.08	29.53	17	8.26	0.34	7.45	8.75	20	2444	284	1946	3120
Han Reservoir	DJK4	18	19.14	6.90	9.08	30.38	17	8.28	0.32	7.81	8.85	20	2117	390	1200	2960
	D2	10	18.68	6.88	9.23	29.66	9	8.31	0.34	7.80	8.91	12	2134	424	1280	2920
Dam	D3	10	18.61	6.85	9.18	29.91	9	8.28	0.35	7.78	8.82	12	2222	509	1320	3320
River downstream Dam	DJK5	18	16.39	5.82	7.96	25.86	17	8.01	0.38	7.21	8.64	20	2367	428	1951	3968
	Total	119	18.75	6.65	7.96	30.52	111	8.22	0.33	7.21	8.91	135	2385	425	1200	3968

~~S.D.-Standard deviation; Min.- Minimum; Max.- Maximum.~~

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~~**Table 4.** ANOVA for T, pH and alkalinity in month (a) and space (b) of the Danjiangkou Reservoir, China.~~

~~(a)~~

		~~(a) Month~~					~~(b) Space~~				
		~~Sum of Squares~~	~~df~~	~~Mean Square~~	~~F~~	~~p~~	~~Sum of Squares~~	~~df~~	~~Mean Square~~	~~F~~	~~p~~
~~T~~	~~Between Groups~~	~~4902~~	~~17~~	~~288~~	~~92.99~~	~~0.00~~	~~155~~	~~7~~	~~22~~	~~0.49~~	~~0.84~~
~~pH~~	~~Between Groups~~	~~7~~	~~16~~	~~0~~	~~7.52~~	~~0.00~~	~~1~~	~~7~~	~~0~~	~~1.49~~	~~0.18~~
~~Alkalinity~~	~~Between Groups~~	~~13139931~~	~~19~~	~~691575~~	~~7.17~~	~~0.00~~	~~5184811~~	~~7~~	~~740687~~	~~4.94~~	~~0.00~~
~~DIC~~	~~Between Groups~~	~~12346199~~	~~16~~	~~771637~~	~~7.88~~	~~0.00~~	~~4311564~~	~~7~~	~~615938~~	~~3.68~~	~~0.00~~
~~pCO_2~~	~~Between Groups~~	~~17957436~~	~~16~~	~~1122340~~	~~2.80~~	~~0.00~~	~~5381767~~	~~7~~	~~768824~~	~~1.58~~	~~0.15~~
~~HCO_3^-~~	~~Between Groups~~	~~13884313~~	~~16~~	~~867770~~	~~8.95~~	~~0.00~~	~~4193418~~	~~7~~	~~599060~~	~~3.28~~	~~0.00~~
~~CO_3^{2-}~~	~~Between Groups~~	~~479575~~	~~16~~	~~29973~~	~~8.98~~	~~0.00~~	~~46508~~	~~7~~	~~6644~~	~~0.92~~	~~0.50~~
~~CO_2~~	~~Between Groups~~	~~35614~~	~~16~~	~~2226~~	~~3.45~~	~~0.00~~	~~7679~~	~~7~~	~~1097~~	~~1.28~~	~~0.27~~

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Table 5. Flux of CO_2 from the surface of rivers and reservoirs.

Name	Sites	Climate	FCO_2 mmol/m^2/d	References
Reservoirs				
Danjiangkou	**China**	**Subtropical**	**9**	**This study**
Three Gorges Reservoir	China	Subtropical	96	Zhao et al., 2013
Three Gorges Reservoir (Xiangxi River)	China	Subtropical	42	Zhao et al., 2011
Hongfeng	China	Subtropical	15	Wang et al., 2011
Baihua	China	Subtropical	24	Wang et al., 2011
Xiuwen	China	Subtropical	47	Wang et al., 2011
Hongyan	China	Subtropical	22.4	Wang et al., 2011
Hongjiadu	China	Subtropical	6.2	Yu et al., 2008
Nihe	China	Subtropical	14.5	Lu et al., 2010
Wan'an	China	Subtropical	12.8	Mei at al., 2011
Xin'anjiang	China	Subtropical	7	Yao et al., 2010
Shuibuya	China	Subtropical	18	Zhao et al., 2012
Shasta		Temperate	28.3	Soumis et al., 2004
Day Lake		Temperate	15.9	St. Louis et al., 2000
Wallula		Temperate	-7.9	Soumis et al., 2004
New Melones		Temperate	-27	Soumis et al., 2004
Dworkshak		Temperate	-27.3	Soumis et al., 2004
Arrow Upper		Boreal	23.6	Tremblay et al., 2005
La Grande 3		Boreal	38.8	Tremblay et al., 2005
Lokka		Boreal	34.6	Huttunen et al., 2002
Petit Saut		Tropic	133	Guerin et al., 2006
Balbina		Tropic	76	Guerin et al., 2006
Balbina		Tropic	314.7	Kemenes et al., 2007, 2011
Samuel		Tropic	976	Guerin et al., 2006
Tucurui		Tropic	308.3	St. Louis et al., 2000
Tucurui		Tropic	181.8	Rosa et al., 2004
Global Reservoirs		Temperate	31.8	St Louis et al., 2000
Global Reservoirs		Temperate	12	McCully, 2006
Global Reservoirs		Temperate	8.8	Barros et al., 2011
Global Reservoirs		Temperate	18.3	Aufdenkampe et al., 2011
Global hydropower reservoirs			32.2	Barros et al., 2011
Global artificial reservoirs			41.5	Barros et al., 2011
Natural lakes			28.8	Barros et al., 2011
Rivers				
River downstream the Dangjiangkou Reservoir		**Subtropical**	**119**	**This study**
Downstream the dams in the Maotiao		Subtropical	489	Wang et al., 2011
Upstream the Wan'an Reservoir		Subtropical	210	Mei et al., 2011
Downstream the Hongjiadu Reservoir		Subtropical	92.5	Yu et al., 2008

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带格式的：两端对齐，无孤行控制
带格式的：两端对齐，无孤行控制

~~Xijiang~~		~~Subtropical~~	~~274~~	~~Yao et al., 2007~~
~~Changjiang~~		~~Subtropical~~	~~14.2~~	~~Wang et al., 2007~~
~~Maotiao River in the Changjiang~~		~~Subtropical~~	~~362~~	~~Wang et al., 2011~~
~~Longchuanjiang in the Changjiang~~		~~Subtropical~~	~~74~~	~~Li et al., 2012~~
~~Amazon~~	~~Brazil~~	~~Tropic~~	~~189~~	~~Richey et al., 2002~~
~~Amazon~~	~~Brazil~~	~~Tropic~~	~~345.2~~	~~Alin et al., 2011~~
~~St.Lawrence~~	~~Canada~~	~~Temperate~~	~~78.1-294.5~~	~~Helli et al., 2001~~
~~Ottawa~~	~~Canada~~	~~Temperate~~	~~80.8~~	~~Telmer and Veizer, 1999~~
~~Hudson~~	~~USA~~	~~Temperate~~	~~15.9-37~~	~~Raymond et al., 1997~~
~~Mississippi~~		~~Temperate~~	~~269.9~~	~~Dubois et al., 2010~~
~~USA rivers~~			~~202.7-915.1~~	~~Butman and Raymond, 2011~~
~~York River~~		~~Warm~~	~~22.7~~	~~Raymond and Bauer, 2000~~
~~Yukon~~		~~Boreal~~	~~171.2~~	~~Striegl et al., 2012~~
~~Global rivers~~			~~146.8~~	~~Cole et al., 2007~~

~~[a]Carbon emission as CO_2 of 0.23 Pg/yr from Cole et al. (2007), river water surface water of 357627 km^2 from Bastviken et al. (2011).~~

带格式的：两端对齐，无孤行控制

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带格式的：两端对齐，无孤行控制

带格式的：两端对齐，无孤行控制

带格式的：两端对齐，定义网格后自动调整右缩进，行距：单倍行距，无孤行控制，调整中文与西文文字的间距，调整中文与数字的间距

带格式的：两端对齐

Table 1. The main features of the Danjiangkou Reservoir, China.

	Drainage area km^2	Height of dam m	Normal water level m	Total volume billion m^3	Water surface area km^2	Time of construction	Installed capacity M W	Power density W/m^2	Hydropower capacity 10^8 kw.h/yr
1968-2013	95200	162	157	17.45	745	1968	900	1.21	45
2014 afterward	95200	176.6	172	29.05	1050	2014			

Table 2. Descriptive statistics of monthly variability in T (°C), pH and alkalinity (μmol/l) of the Danjiangkou Reservoir, China.

	T					pH					Alkalinity				
—	N	Mean	S. D.	Min.	Max.	N	Mean	S. D.	Min.	Max.	N	Mean	S. D.	Min.	Max.
Nov.2004	5	16.84	0.58	15.84	17.24	5	8.22	0.08	8.14	8.34	5	2440	219	2200	2600
Jan. 2005	5	9.19	0.64	8.08	9.65	5	8.28	0.07	8.20	8.37	5	2360	207	2200	2700
Apr.2005	5	12.44	3.64	7.96	16.72	5	8.42	0.07	8.29	8.47	5	2600	524	2200	3500
Jun.2005	5	27.75	4.33	20.16	30.52	5	8.52	0.35	7.92	8.85	5	2409	291	1900	2643
Aug.2005	5	24.49	0.95	23.00	25.34	5	7.98	0.13	7.81	8.13	5	2180	192	1900	2400
Nov.2005	5	18.26	0.43	17.73	18.65	5	7.91	0.06	7.81	7.96	5	2280	286	1900	2600
Apr.2006	5	15.30	2.54	11.06	17.46	5	8.26	0.10	8.09	8.38	5	2432	489	2080	3280
Jul.2006	5	27.89	3.86	21.00	29.99	5	8.28	0.50	7.64	8.70	5	2192	485	1520	2880
May 2007	8	24.82	0.85	23.54	26.53	8	8.19	0.10	7.98	8.35	8	2520	363	2080	3280
Nov.2007	8	14.94	1.78	12.00	17.00										
Jul.2008	8	29.10	1.35	25.86	29.99	8	8.01	0.38	7.21	8.37	8	1937	345	1616	2644
Nov.2008	8	12.03	0.66	11.27	12.87	8	8.01	0.41	7.45	8.63	8	3241	332	2920	3968
Apr.2009	8	15.32	1.51	11.68	16.26	8	8.08	0.15	7.82	8.26	8	2489	384	2206	3422
Aug.2009	8	27.36	1.46	23.97	28.47	8	8.64	0.28	7.99	8.91	8	2037	222	1814	2359
Nov.2009	8	16.87	0.20	16.56	17.10	8	7.81	0.18	7.39	7.95	8	2354	151	2160	2576
Jan.2010	7	9.00	0.35	8.48	9.49	7	8.65	0.09	8.53	8.75	7	2354	166	2120	2560
Apr.2010	8	14.67	1.38	11.98	16.46	8	8.44	0.21	7.97	8.62	8	2409	226	2000	2680
Aug.2010											8	1795	456	1200	2360
Nov.2010											8	2475	92	2280	2600
Mar.2011											8	2407	257	2104	2736
May 2011	8	20.84	0.79	19.19	21.53	8	8.14	0.14	7.99	8.34	8	2717	226	2440	3000
Total	119	18.75	6.65	7.96	30.52	111	8.22	0.33	7.21	8.91	135	2385	425	1200	3968

S.D.-Standard deviation; Min.- Minimum; Max.- Maximum.

~~**Table 3.** Descriptive statistics of spatial variability in T, pH and alkalinity of the Danjiangkou Reservoir, China (T in °C, Alkalinity in μmol/l).~~

		T					pH					Alkalinity				
	—	N	Mean	S. D.	Min.	Max.	N	Mean	S. D.	Min.	Max.	N	Mean	S. D.	Min.	Max.
Dan Reservoir	DJK1	17	20.45	6.49	9.26	30.52	16	8.15	0.27	7.76	8.62	19	2736	437	2000	3500
	DJK2	18	19.11	6.95	8.67	29.61	17	8.29	0.27	7.86	8.74	20	2473	292	2020	3360
	D3	10	18.97	6.96	8.85	29.53	9	8.26	0.36	7.68	8.79	12	2475	338	1960	3080
	DJK3	18	18.77	7.25	8.08	29.53	17	8.26	0.34	7.45	8.75	20	2444	284	1946	3120
Han Reservoir	DJK4	18	19.14	6.90	9.08	30.38	17	8.28	0.32	7.81	8.85	20	2117	390	1200	2960
	D2	10	18.68	6.88	9.23	29.66	9	8.31	0.34	7.80	8.91	12	2134	424	1280	2920
Dam	D3	10	18.61	6.85	9.18	29.91	9	8.28	0.35	7.78	8.82	12	2222	509	1320	3320
River downstream Dam	DJK5	18	16.39	5.82	7.96	25.86	17	8.01	0.38	7.21	8.64	20	2367	428	1951	3968
	Total	119	18.75	6.65	7.96	30.52	111	8.22	0.33	7.21	8.91	135	2385	425	1200	3968

~~S.D.-Standard deviation; Min.- Minimum; Max.- Maximum.~~

Table 24. ANOVA for T, pH and alkalinity in month (a) and space (b) of the Danjiangkou Reservoir, China.
(a)

	(a) Month						(b) Space				
		Sum of Squares	df	Mean Square	F	p	Sum of Squares	df	Mean Square	F	p
T	Between Groups	4902	17	288	92.99	0.00	155	7	22	0.49	0.84
pH	Between Groups	7	16	0	7.52	0.00	1	7	0	1.49	0.18
Alkalinity	Between Groups	13139931	19	691575	7.17	0.00	5184811	7	740687	4.94	0.00
DIC	Between Groups	12346199	16	771637	7.88	0.00	4311564	7	615938	3.68	0.00
pCO_2	Between Groups	17957436	16	1122340	2.80	0.00	5381767	7	768824	1.58	0.15
HCO_3^-	Between Groups	13884313	16	867770	8.95	0.00	4193418	7	599060	3.28	0.00
CO_3^{2-}	Between Groups	479575	16	29973	8.98	0.00	46508	7	6644	0.92	0.50
CO_2	Between Groups	35614	16	2226	3.45	0.00	7679	7	1097	1.28	0.27

Table 3. Pearson R coefficients between pCO_2 and water chemical parameters for each season and each station in the Danjiangkou Reservoir, China.

	Han Res.						Dan Res.						Dam			River below Dam					
	Dry			Wet			Dry			Wet						Dry			Wet		
	R	p	N	R	p	N	R	p	N	R	p	N	R	p	N	R	p	N	R	p	N
F^-	-0.76	0.03	8	0.56	0.15	8	0.10	0.73	15	0.09	0.75	16	0.65	0.08	8	0.67	0.33	4	0.63	0.38	4
Cl^-	0.12	0.72	12	-0.32	0.30	12	0.28	0.16	27	-0.04	0.85	28	-0.48	0.23	8	0.17	0.69	8	0.91	0.00	8
SO_4^{2-}	-0.50	0.10	12	-0.47	0.12	12	0.06	0.78	27	-0.04	0.82	28	-0.29	0.49	8	-0.30	0.46	8	-0.03	0.95	8
Na	0.30	0.30	14	-0.29	0.35	12	0.19	0.31	31	-0.19	0.34	28	-0.27	0.49	9	0.35	0.36	9	0.77	0.02	8
K	0.20	0.51	14	0.43	0.17	12	-0.13	0.49	31	0.09	0.64	28	0.03	0.94	9	0.07	0.85	9	0.61	0.11	8
Ca	0.32	0.26	14	0.36	0.26	12	0.46	0.01	31	0.14	0.47	28	-0.14	0.73	9	0.26	0.49	9	0.50	0.21	8
Mg	0.34	0.23	14	0.19	0.56	12	0.58	0.00	31	0.17	0.39	28	-0.29	0.46	9	0.05	0.89	9	0.63	0.10	8
Si	-0.55	0.12	9	0.86	0.00	11	0.33	0.18	18	0.46	0.02	25	0.65	0.08	8	-0.27	0.66	5	0.52	0.23	7
TSS	0.29	0.36	12	0.14	0.69	10	0.20	0.31	27	0.35	0.10	24	-0.47	0.29	7	0.59	0.12	8	0.22	0.64	7
Turbidity	0.27	0.35	14	0.15	0.63	12	0.16	0.40	31	0.30	0.12	28	-0.16	0.69	9	-0.29	0.45	9	0.01	0.98	8
COD_{Mn}	-0.12	0.71	12	-0.36	0.25	12	0.21	0.29	27	-0.04	0.83	28	-0.55	0.16	8	0.34	0.40	8	-0.36	0.38	8
BOD5	-0.04	0.98	3	0.94	0.23	3	0.64	0.07	9	0.24	0.54	9				0.82	0.39	3	0.05	0.97	3
DO	0.02	0.96	8	-0.24	0.45	12	-0.25	0.24	23	0.15	0.45	28	0.67	0.15	6	-0.22	0.64	7	-0.64	0.09	8
DO%	0.41	0.36	7	-0.74	0.01	12	0.33	0.15	20	-0.40	0.03	28	0.10	0.85	6	0.32	0.53	6	-0.73	0.04	8
ORP	-0.33	0.25	14	0.05	0.92	8	-0.24	0.20	31	-0.22	0.36	20	-0.53	0.22	7	-0.53	0.14	9	-0.27	0.61	6
AmmoniumN	0.62	0.10	8	-0.26	0.47	10	0.75	0.00	20	-0.37	0.07	24	0.01	0.99	5	0.44	0.39	6	-0.40	0.43	6
NitrateN	0.25	0.55	8	-0.42	0.18	12	-0.10	0.66	20	-0.18	0.35	28	-0.47	0.35	6	-0.21	0.66	7	0.96	0.00	6
DIN	0.97	0.03	4	-0.07	0.93	4	0.52	0.09	12	0.02	0.96	12				0.66	0.34	4	-0.34	0.66	4
DN	-0.72	0.05	8	0.14	0.75	8	0.23	0.41	15	-0.30	0.26	16	-0.25	0.55	8	-0.93	0.07	4	-0.63	0.37	4

TN	-0.77	0.03	8	0.31	0.45	8	-0.25	0.37	15	-0.27	0.35	14	-0.39	0.34	8	-0.92	0.08	4	-0.63	0.37	4
SRP	-0.34	0.41	8	0.44	0.28	8	0.82	0.00	15	-0.20	0.46	16	0.03	0.94	8	0.75	0.25	4	0.67	0.33	4
DP	-0.38	0.41	7	-0.48	0.16	10	0.79	0.00	12	-0.51	0.02	20	-0.34	0.41	8	0.80	0.06	6	0.64	0.12	7
TP	0.28	0.43	10	0.23	0.58	8	0.32	0.19	19	0.14	0.61	16	-0.01	0.98	9	0.85	0.07	5	0.55	0.45	4
TOC	0.25	0.55	8	-0.13	0.76	8	0.67	0.01	15	-0.03	0.93	16	0.21	0.63	8	0.97	0.03	4	-0.60	0.40	4
DOC	0.73	0.04	8	-0.10	0.82	8	0.45	0.09	15	0.29	0.28	16	0.38	0.36	8	0.32	0.68	4	-0.26	0.74	4
Chl-a	0.13	0.76	8	-0.89	0.00	8	0.34	0.22	15	-0.26	0.35	15	-0.66	0.07	8	0.81	0.19	4	0.71	0.50	3

Correlation is significant at the 0.05 level (2-tailed).

We split sampling months to wet and dry periods, and sampling sites to four categories (Han Res., Dan Res., Dam, and river below the Dam).

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Table ~~4~~5. Flux of CO_2 from the surface of rivers and reservoirs.

Name	Sites	Climate	FCO_2 mmol/m^2/d	References
Reservoirs				
Danjiangkou	**China**	**Subtropical**	**9** (5.8-11.6)	**This study**
Three Gorges Reservoir	China	Subtropical	96	Zhao et al., 2013
Three Gorges Reservoir (Xiangxi River)	China	Subtropical	42	Zhao et al., 2011
Hongfeng	China	Subtropical	15	Wang et al., 2011
Baihua	China	Subtropical	24	Wang et al., 2011
Xiuwen	China	Subtropical	47	Wang et al., 2011
Hongyan	China	Subtropical	22.4	Wang et al., 2011
Hongjiadu	China	Subtropical	6.2	Yu et al., 2008
Nihe	China	Subtropical	14.5	Lu et al., 2010
Wan'an	China	Subtropical	12.8	Mei at al., 2011
Xin'anjiang	China	Subtropical	7	Yao et al., 2010
Shuibuya	China	Subtropical	18	Zhao et al., 2012
Nam Ngum	Laos	Tropic	-16	Chanudet et al., 2011
Nam Leuk	Laos	Tropic	3.1	Chanudet et al., 2011
Shasta		Temperate	28.3	Soumis et al., 2004
Day Lake		Temperate	15.9	St. Louis et al., 2000
Wallula		Temperate	-7.9	Soumis et al., 2004
New Melones		Temperate	-27	Soumis et al., 2004
Dworkshak		Temperate	-27.3	Soumis et al., 2004
Arrow-Upper		Boreal	23.6	Tremblay et al., 2005
La Grande 3		Boreal	38.8	Tremblay et al., 2005
Lokka		Boreal	34.6	Huttunen et al., 2002
Petit Saut (May 2003)		Tropic	133	Abril et al., 2005; Guerin et al., 2006
Petit Saut (Dec. 2003)		Tropic	131	Abril et al., 2005; Guerin et al., 2006
Petit Saut (Mar. 2005)		Tropic	103	Guerin et al., 2006
Petit Saut (May 2005)		Tropic	102	Guerin et al., 2006
Balbina		Tropic	76	Guerin et al., 2006
Balbina		Tropic	314.7	Kemenes et al., 2007, 2011
Samuel		Tropic	976	Guerin et al., 2006
Tucurui		Tropic	308.3	St. Louis et al., 2000
Tucurui		Tropic	181.8	Rosa et al., 2004
Global Reservoirs		Temperate	31.8	St Louis et al., 2000
Global Reservoirs		Temperate	12	McCully, 2006
Global Reservoirs		Temperate	8.8	Barros et al., 2011
Global Reservoirs		Temperate	18.3	Aufdenkampe et al., 2011
Global hydropower reservoirs			32.2	Barros et al., 2011
Global artificial reservoirs			41.5	Barros et al., 2011
Natural lakes			28.8	Barros et al., 2011
Rivers				

带格式的：字体：(中文) +中文正文

River downstream the Dangjiangkou Reservoir		**Subtropical**	**119** (79.3-158.7)	**This study**
Downstream the dams in the Maotiao		Subtropical	489	Wang et al., 2011
Upstream the Wan'an Reservoir		Subtropical	210	Mei et al., 2011
Downstream the Hongjiadu Reservoir		Subtropical	92.5	Yu et al., 2008
Downstream Petit Saut (May 2003)		Tropic	1003	Abril et al., 2005
Downstream Petit Saut (Dec. 2003)		Tropic	928	Abril et al., 2005
Petit Saut (Mar. 2005)		Tropic	802	Guerin et al., 2006
Petit Saut (May 2005)		Tropic	670	Guerin et al., 2006
Xijiang		Subtropical	274	Yao et al., 2007
Changjiang		Subtropical	14.2	Wang et al., 2007
Maotiao River in the Changjiang		Subtropical	362	Wang et al., 2011
Longchuanjiang in the Changjiang		Subtropical	74	Li et al., 2012
Lower Mekong River		Tropic	195	Li et al., 2013a4
Amazon	Brazil	Tropic	189	Richey et al., 2002
Amazon	Brazil	Tropic	345.2	Alin et al., 2011
St.Lawrence	Canada	Temperate	78.1-294.5	Helli et al., 2001
Ottawa	Canada	Temperate	80.8	Telmer and Veizer, 1999
Hudson	USA	Temperate	15.9-37	Raymond et al., 1997
Mississippi		Temperate	269.9	Dubois et al., 2010
USA rivers			202.7-915.1	Butman and Raymond, 2011
York River		Warm	22.7	Raymond and Bauer, 2000
Yukon		Boreal	171.2	Striegl et al., 2012
Global rivers			146.8	Cole et al., 2007

[a]Carbon emission as CO_2 of 0.23 Pg/yr from Cole et al. (2007), river water surface water of 357627 km^2 from Bastviken et al. (2011).

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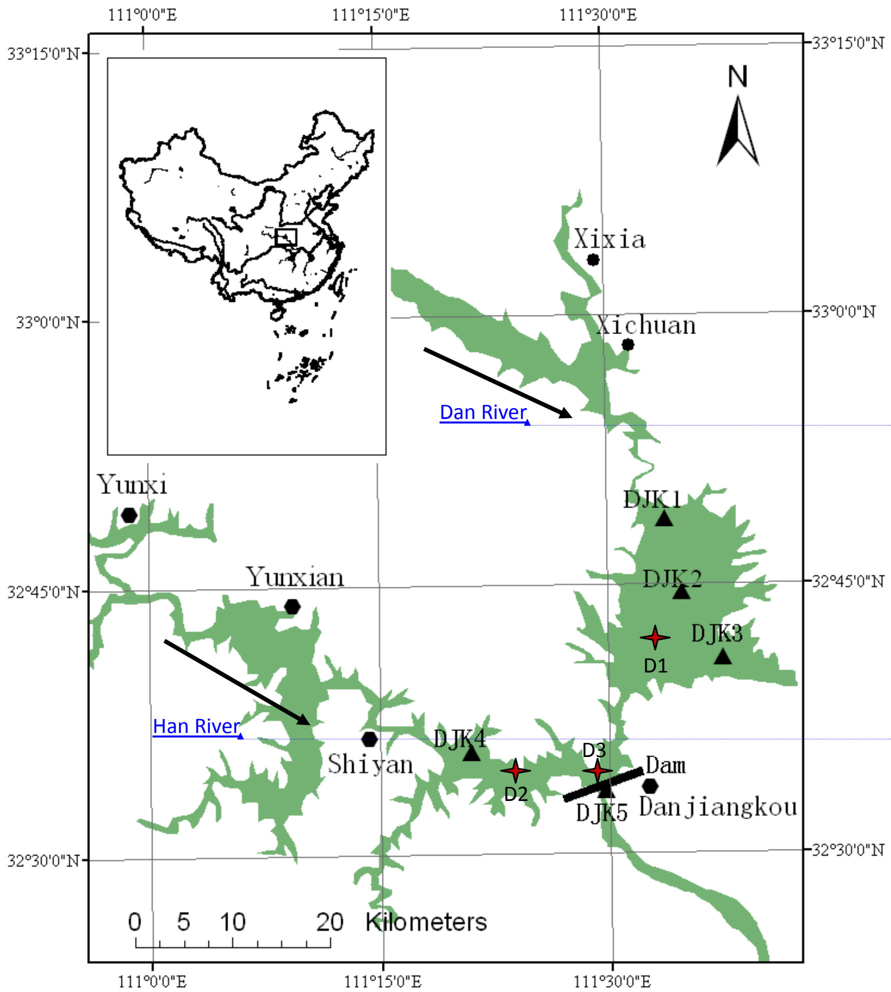

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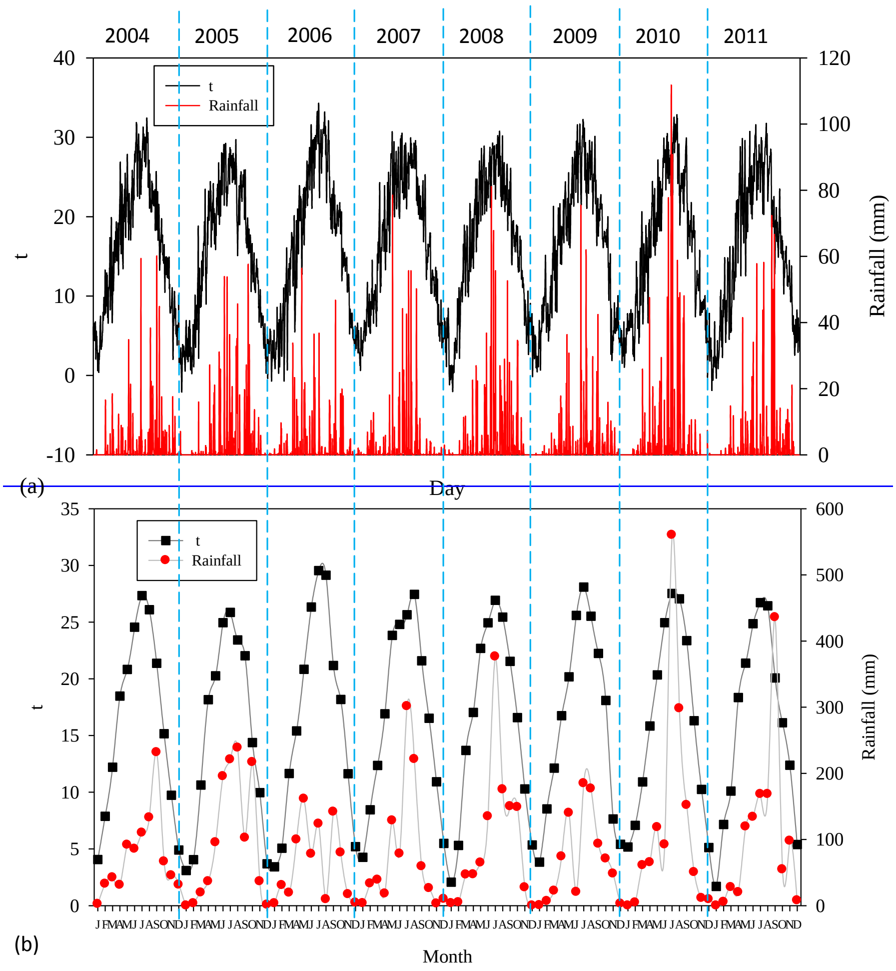
Fig. 1.



2004
2005
2006
2007
2008
2009
2010
2011
t
Rainfall
Rainfall (mm)
Day
(a)
(b)
Month

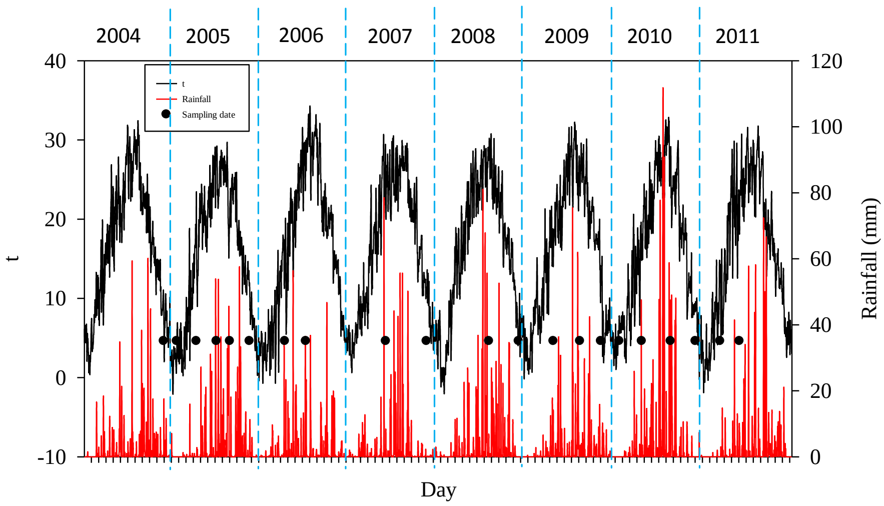


Fig. 2~~6~~.

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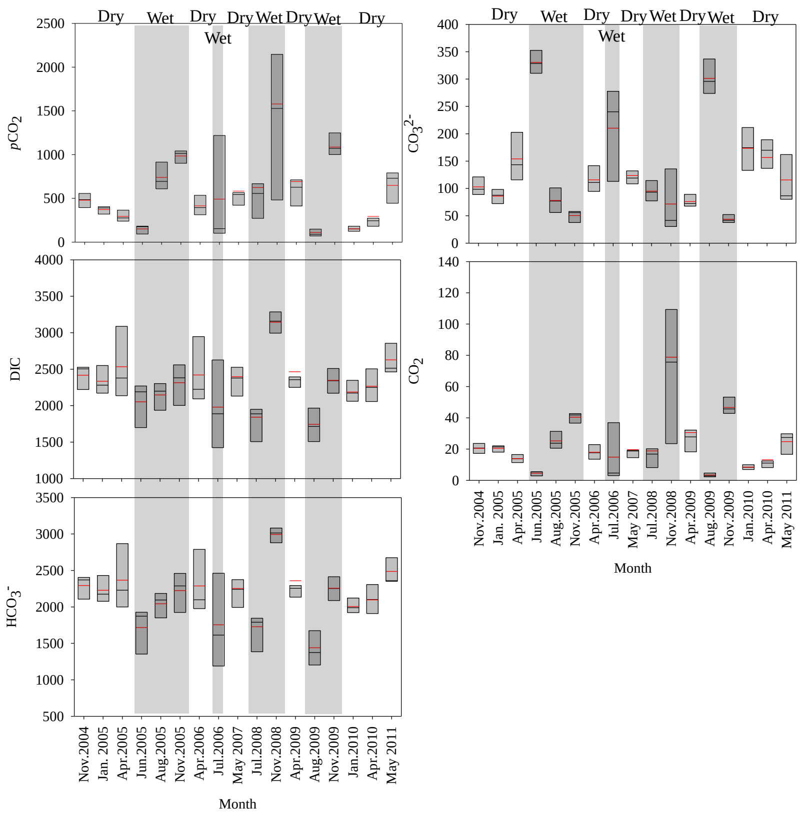
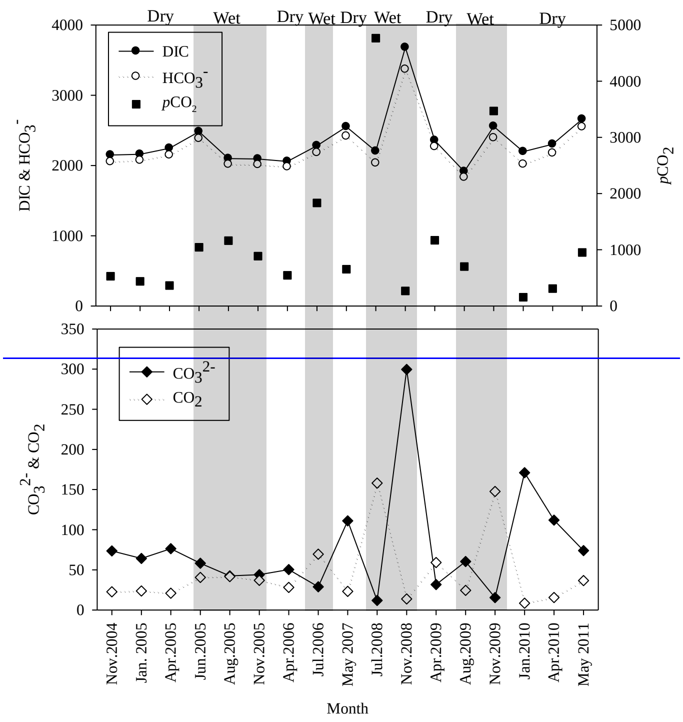


Dry
Wet
Dry
Wet
Dry
Wet
Dry
Wet
Dry
pCO2
DIC
HCO3-
CO3 2-
CO2
Nov.2004
Jan. 2005
Apr.2005
Jun.2005
Aug.2005
Nov.2005
Apr.2006
Jul.2006
May 2007
Jul.2008
Nov.2008
Apr.2009
Aug.2009
Nov.2009
Jan.2010
Apr.2010
May 2011
Month

Fig. ~~2~~3.



Dry
Wet
Dry
Wet
Dry
Wet
Dry
Wet
Dry
DIC
HCO3-
pCO2
DIC & HCO3-
pCO2
4000
3000
2000
1000
0
5000
4000
3000
2000
1000
0
CO32-
CO2
CO32- & CO2
350
300
250
200
150
100
50
0
Nov.2004
Jan. 2005
Apr.2005
Jun.2005
Aug.2005
Nov.2005
Apr.2006
Jul.2006
May 2007
Jul.2008
Nov.2008
Apr.2009
Aug.2009
Nov.2009
Jan.2010
Apr.2010
May 2011
Month

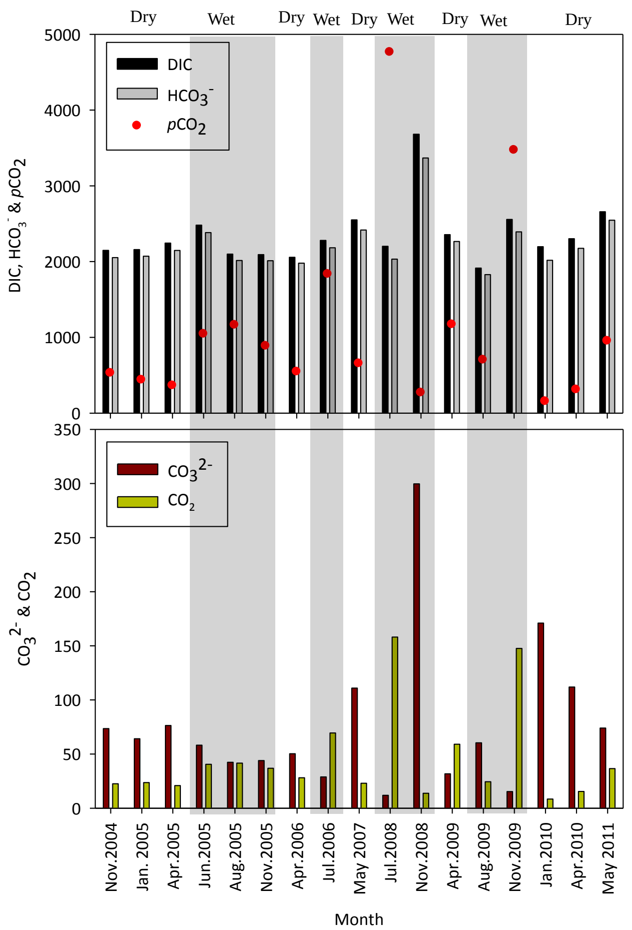


Fig. 43.

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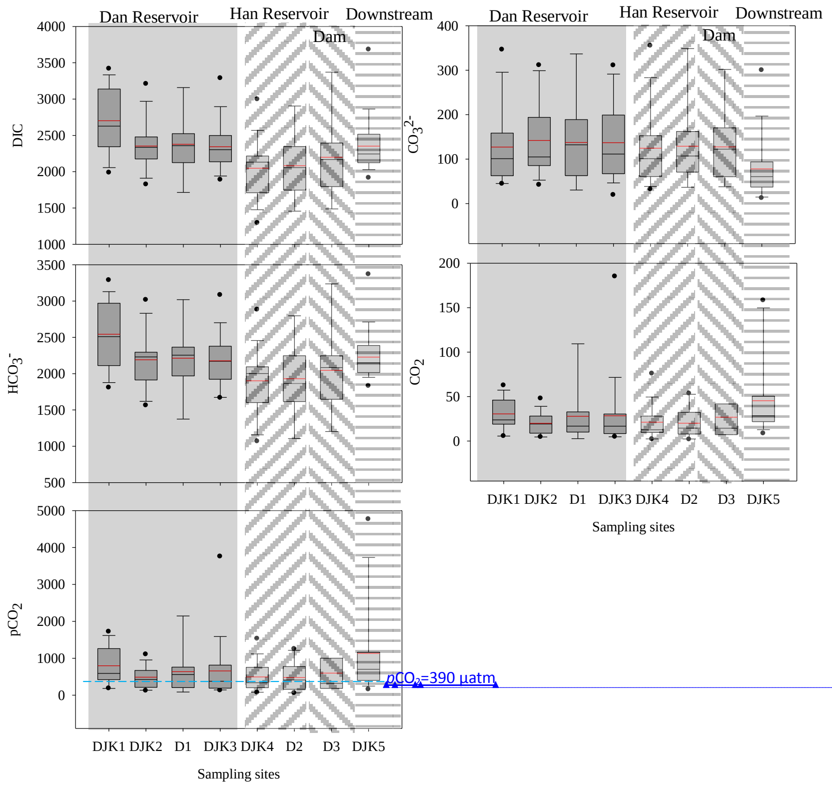

Fig. 5.4

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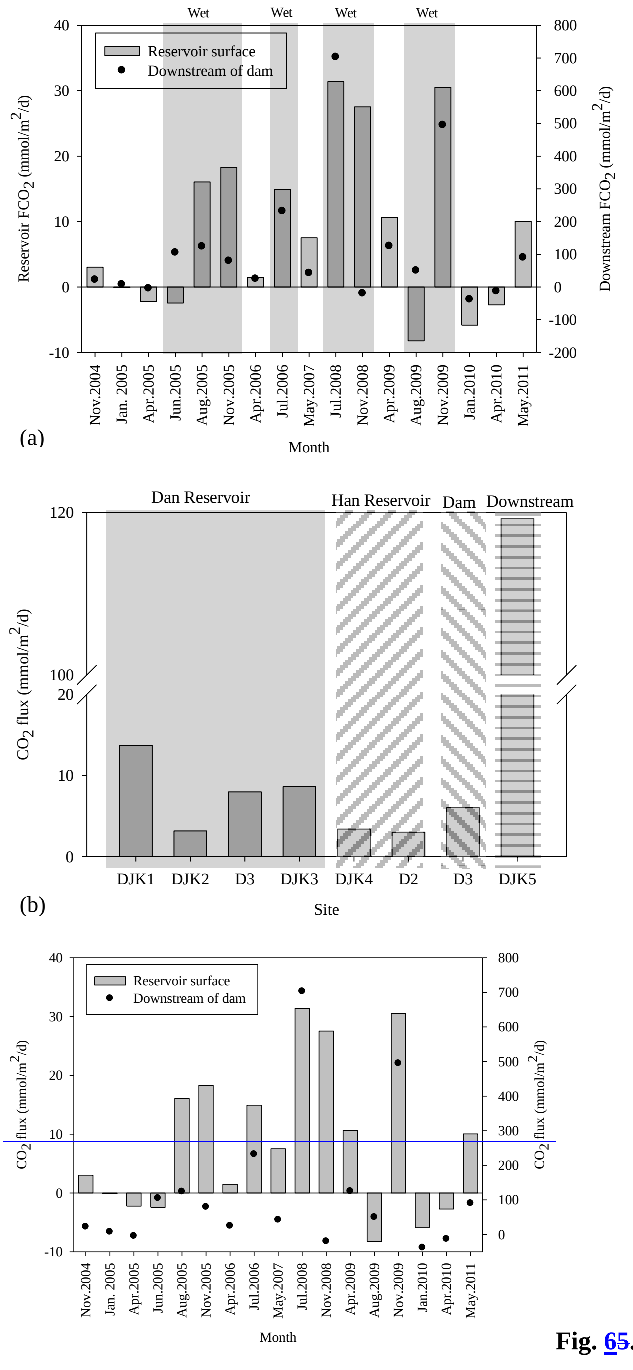
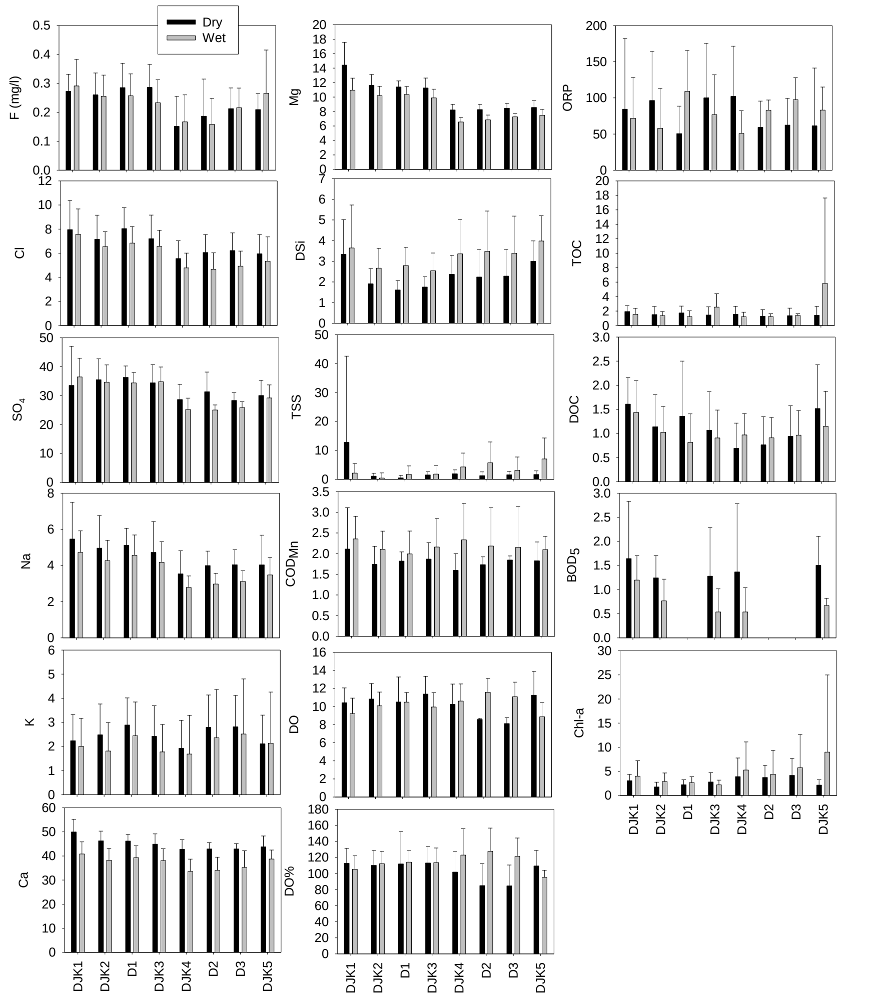


Wet
Wet
Wet
Wet
Reservoir surface
Downstream of dam
Reservoir FCO2 (mmol/m2/d)
Downstream FCO2 (mmol/m2/d)
Nov.2004
Jan. 2005
Apr.2005
Jun.2005
Aug.2005
Nov.2005
Apr.2006
Jul.2006
May.2007
Jul.2008
Nov.2008
Apr.2009
Aug.2009
Nov.2009
Jan.2010
Apr.2010
May.2011
Month
(a)
Dan Reservoir
Han Reservoir
Dam
Downstream
CO2 flux (mmol/m2/d)
DJK1
DJK2
D3
DJK3
DJK4
D2
D3
DJK5
Site
(b)
Reservoir surface
Downstream of dam
CO2 flux (mmol/m2/d)
Month

Fig. 6~~5~~.



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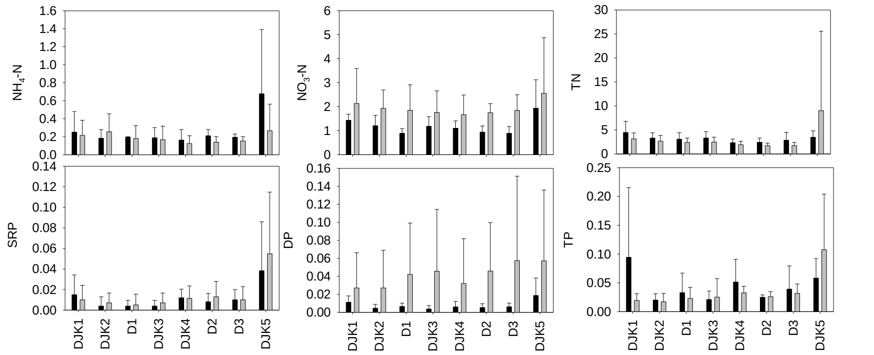

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Fig. 7. ~~Ancillary water quality parameters in the Danjiangkou Reservoir, China (unit in mg/l except~~

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~~ORP in mV, Chl-a in μg/l). The error bars represent standard deviations.~~

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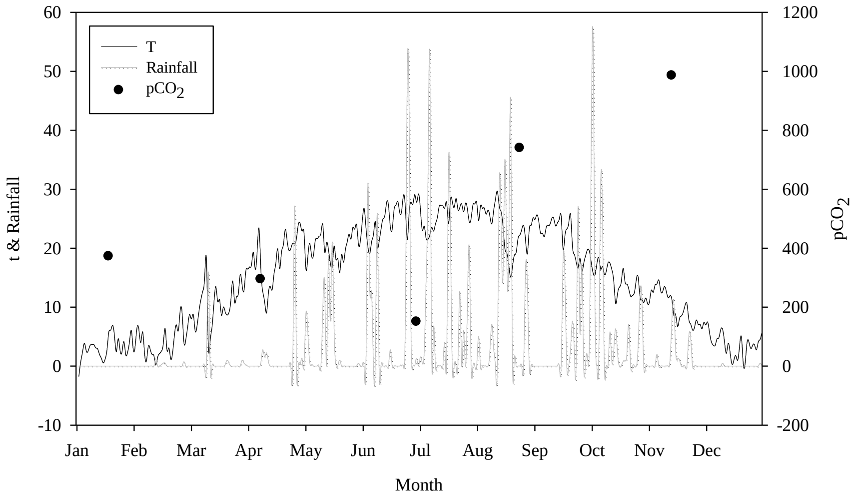

Fig. 8~~7~~.

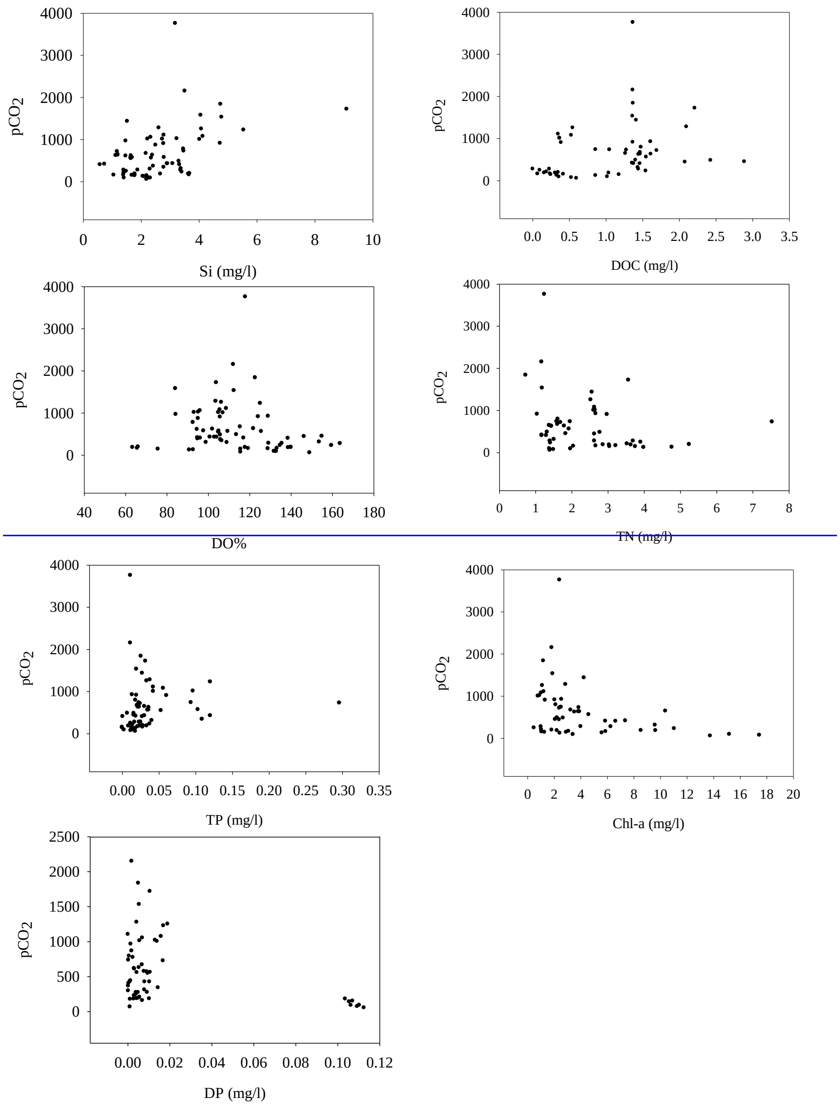

Fig. 8.

Supplements

Table S1. Detailed introduction for sampling in the Danjiangkou Reservoir, China.

Year	Month	Variables	Sites			
			Dan Reservoir	Han Reservoir	Site close dam	River downstream dam
2004	24 Nov.	A+B	DJK1-3	DJK4		DJK5
2005	17 Jan., 8 Apr., 30 Jun., 24 Aug., 13 Nov.	A+B	DJK1-3	DJK4		DJK5
2006	8 Apr., 3 Jul	A+B	DJK1-3	DJK4		DJK5
2007	31 May, 16 Nov.	A+C	DJK1, DJK2, D1, DJK3	DJK4, D2	D3	DJK5
2008	31 Jul., 30 Nov.	A+C	DJK1, DJK2, D1, DJK3	DJK4, D2	D3	DJK5
2009	23 Apr., 11 Aug., 5 Nov.	A+C	DJK1, DJK2, D1, DJK3	DJK4, D2	D3	DJK5
2010	20 Jan., 23 Apr., 20 Aug., 30 Nov.	A+C	DJK1, DJK2, D1, DJK3	DJK4, D2	D3	DJK5
2011	12 Mar., 31 May	A+C	DJK1, DJK2, D1, DJK3	DJK4, D2	D3	DJK5

5 samples for individual survey were collected during 2004-2006, while 8 samples for individual survey during 2007-2011. There were three replicates for each sampling, thus a total of 432 samples were collected while 144 water samples were determined.

Water chemical properties:

A-T, pH, Alkalinity, F-, Cl, SO_4, Na, K, Ca, Mg, DSi, TSS, Turbidity, DO%, ORP (oxidation reduction potential), COD_{Mn}, NH_4-N, NO_3-N, DP

B- BOD

C- SRP, TP, TOC, DOC, TDN, DIN, Chl-a

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Table S2. Descriptive statistics of monthly variability in T (°C), pH and alkalinity (μmol/l) of the Danjiangkou Reservoir, China.

	T					pH					Alkalinity				
	N	Mean	S. D.	Min.	Max.	N	Mean	S. D.	Min.	Max.	N	Mean	S. D.	Min.	Max.
Nov.2004	5	16.84	0.58	15.84	17.24	5	8.22	0.08	8.14	8.34	5	2440	219	2200	2600
Jan. 2005	5	9.19	0.64	8.08	9.65	5	8.28	0.07	8.20	8.37	5	2360	207	2200	2700
Apr.2005	5	12.44	3.64	7.96	16.72	5	8.42	0.07	8.29	8.47	5	2600	524	2200	3500
Jun.2005	5	27.75	4.33	20.16	30.52	5	8.52	0.35	7.92	8.85	5	2409	291	1900	2643
Aug.2005	5	24.49	0.95	23.00	25.34	5	7.98	0.13	7.81	8.13	5	2180	192	1900	2400
Nov.2005	5	18.26	0.43	17.73	18.65	5	7.91	0.06	7.81	7.96	5	2280	286	1900	2600
Apr.2006	5	15.30	2.54	11.06	17.46	5	8.26	0.10	8.09	8.38	5	2432	489	2080	3280
Jul.2006	5	27.89	3.86	21.00	29.99	5	8.28	0.50	7.64	8.70	5	2192	485	1520	2880
May 2007	8	24.82	0.85	23.54	26.53	8	8.19	0.10	7.98	8.35	8	2520	363	2080	3280
Nov.2007	8	14.94	1.78	12.00	17.00										
Jul.2008	8	29.10	1.35	25.86	29.99	8	8.01	0.38	7.21	8.37	8	1937	345	1616	2644
Nov.2008	8	12.03	0.66	11.27	12.87	8	8.01	0.41	7.45	8.63	8	3241	332	2920	3968
Apr.2009	8	15.32	1.51	11.68	16.26	8	8.08	0.15	7.82	8.26	8	2489	384	2206	3422
Aug.2009	8	27.36	1.46	23.97	28.47	8	8.64	0.28	7.99	8.91	8	2037	222	1814	2359
Nov.2009	8	16.87	0.20	16.56	17.10	8	7.81	0.18	7.39	7.95	8	2354	151	2160	2576
Jan.2010	7	9.00	0.35	8.48	9.49	7	8.65	0.09	8.53	8.75	7	2354	166	2120	2560
Apr.2010	8	14.67	1.38	11.98	16.46	8	8.44	0.21	7.97	8.62	8	2409	226	2000	2680
Aug.2010											8	1795	456	1200	2360
Nov.2010											8	2475	92	2280	2600
Mar.2011											8	2407	257	2104	2736
May 2011	8	20.84	0.79	19.19	21.53	8	8.14	0.14	7.99	8.34	8	2717	226	2440	3000
Total	119	18.75	6.65	7.96	30.52	111	8.22	0.33	7.21	8.91	135	2385	425	1200	3968

S.D.-Standard deviation; Min.- Minimum; Max.- Maximum.

Table S3. Descriptive statistics of spatial variability in T, pH and alkalinity of the Danjiangkou Reservoir, China (T in ℃, Alkalinity in μmol/l).

		T					pH					Alkalinity				
		N	Mean	S. D.	Min.	Max.	N	Mean	S. D.	Min.	Max.	N	Mean	S. D.	Min.	Max.
Dan Reservoir	DJK1	17	20.45	6.49	9.26	30.52	16	8.15	0.27	7.76	8.62	19	2736	437	2000	3500
	DJK2	18	19.11	6.95	8.67	29.61	17	8.29	0.27	7.86	8.74	20	2473	292	2020	3360
	D3	10	18.97	6.96	8.85	29.53	9	8.26	0.36	7.68	8.79	12	2475	338	1960	3080
	DJK3	18	18.77	7.25	8.08	29.53	17	8.26	0.34	7.45	8.75	20	2444	284	1946	3120
Han Reservoir	DJK4	18	19.14	6.90	9.08	30.38	17	8.28	0.32	7.81	8.85	20	2117	390	1200	2960
	D2	10	18.68	6.88	9.23	29.66	9	8.31	0.34	7.80	8.91	12	2134	424	1280	2920
Dam	D3	10	18.61	6.85	9.18	29.91	9	8.28	0.35	7.78	8.82	12	2222	509	1320	3320
River downstream Dam	DJK5	18	16.39	5.82	7.96	25.86	17	8.01	0.38	7.21	8.64	20	2367	428	1951	3968
	Total	119	18.75	6.65	7.96	30.52	111	8.22	0.33	7.21	8.91	135	2385	425	1200	3968

S.D.-Standard deviation; Min.- Minimum; Max.- Maximum.

Table S4~~2~~. Spearman's rho coefficients for pCO_2 and water chemical parameters in the sites of the Danjiangkou Reservoir, China.

	pCO_2 R ~~coefficient~~	p	N~~n~~
F^-	0.353**	0.01	55
Cl^-	-0.03	0.77	87
SO_4^{2-}	-0.09	0.39	87
Na	-0.05	0.66	94
K	0.02	0.83	94
Ca	0.06	0.57	94
Mg	0.15	0.14	94
Si	0.396**	0.00	71
COD	-0.07	0.51	87
BOD_5	0.25	0.24	24
DO	-0.17	0.15	77
DO%	-0.281*	0.02	73
ORP	-0.248*	0.03	80
Ammonium-N	0.03	0.81	67
Nitrate-N	-0.14	0.23	74
TSS	0.02	0.84	80
Turbidity	0.16	0.14	94
SRP	0.03	0.86	55
TP	0.395**	0.00	62
DP	-0.17	0.20	57
TOC	0.25	0.07	55
DOC	0.416**	0.00	55

TN	-0.314*	0.02	53
DN	-0.09	0.50	55
DIN	0.13	0.49	32
Chl-a	-0.408**	0.00	54

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).

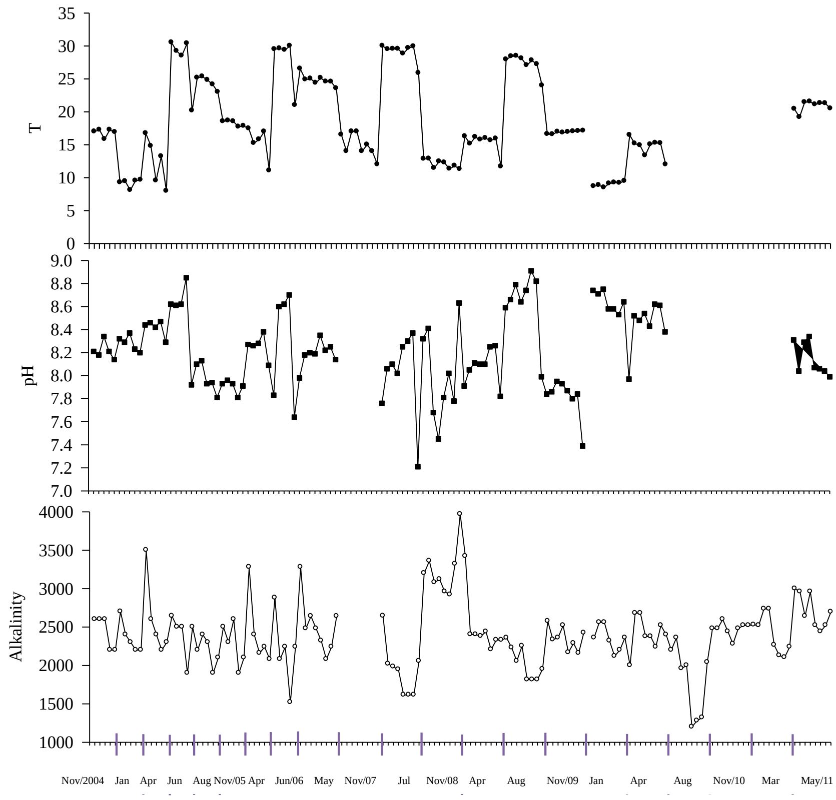

Fig. S1. T (℃), pH and alkalinity (μmol/l) in the Danjiangkou Reservoir during 2004-2011 (five sampling sites DJK1-DJK5 from left to right during 2004-2006; while eight sites DJK1, DJK2, D1, DJK3, DJK4, D2, D3 and DJK5 from 2007 afterwards).

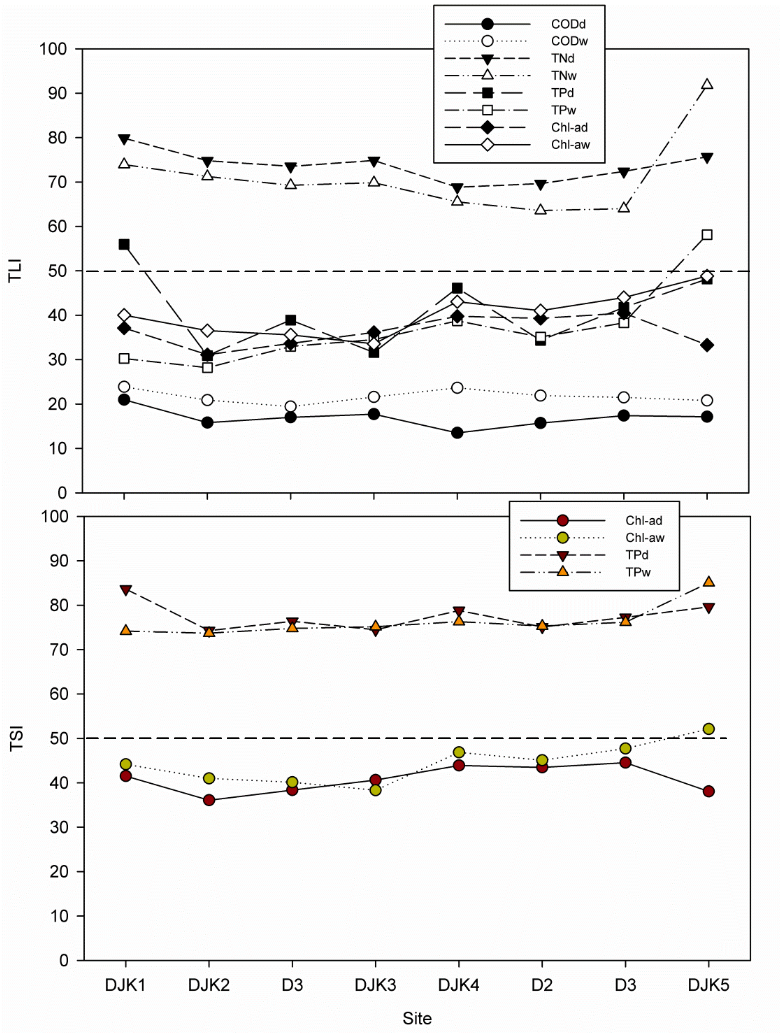

Fig. S2. Trophic state index (TSI) and trophic level index (TLI) of the sites in the Danjiangkou Reservoir, China (the letters d and w behind the variables mean dry and wet season).

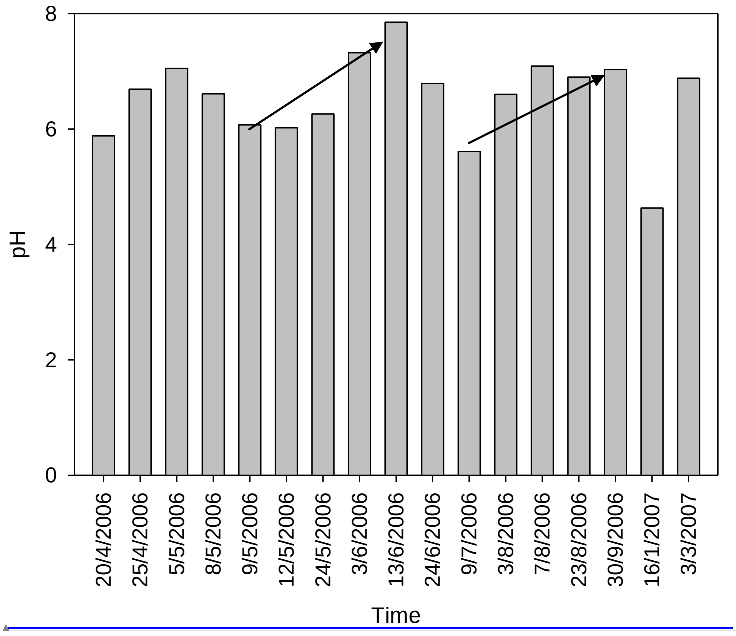

Fig. S3. Rain water pH in Wuhan City of the Han River estuary, Central China.

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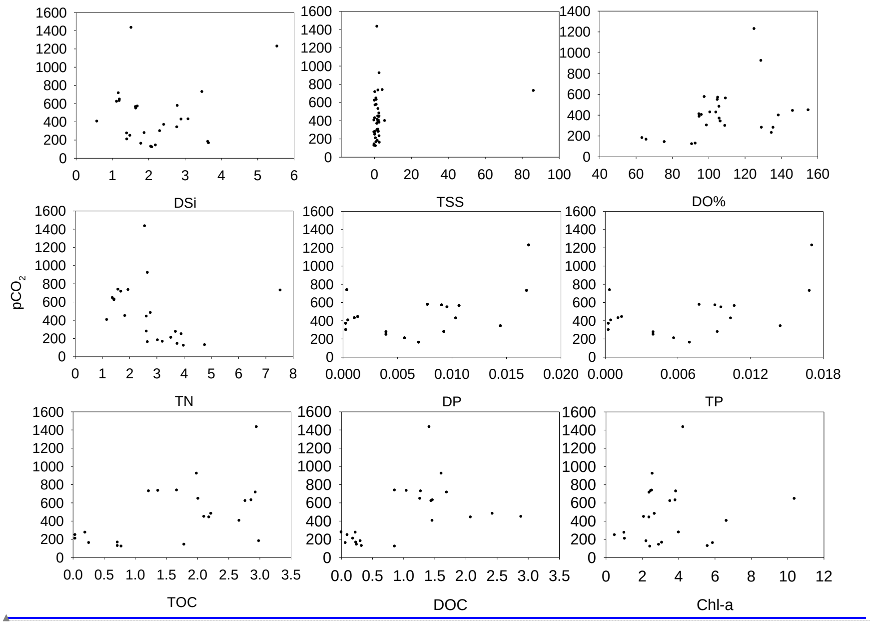
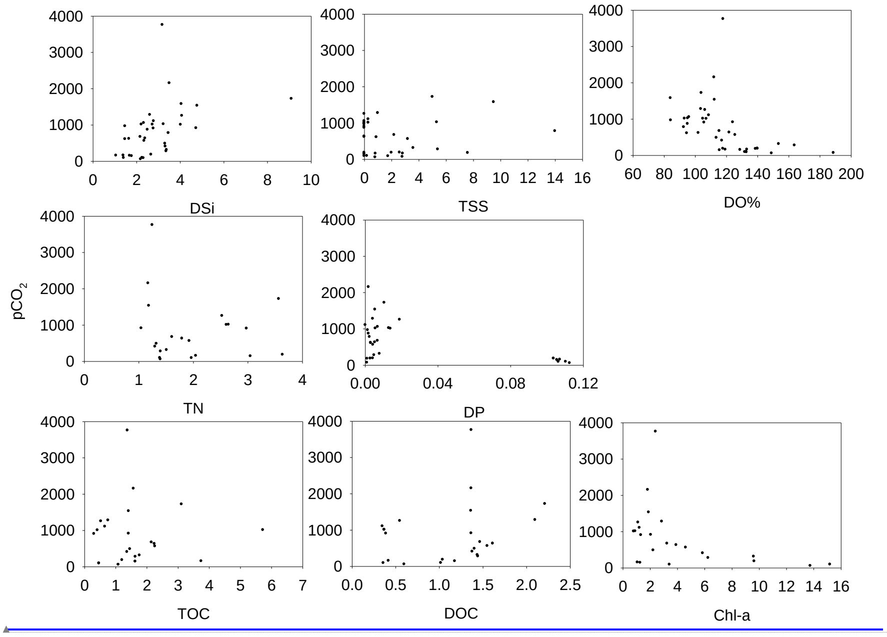


(a) Dry season in the Res (sites in the Dan and Han Res. are included).



(b) Wet season in the Res. (sites in the Dan and Han Res. are included).

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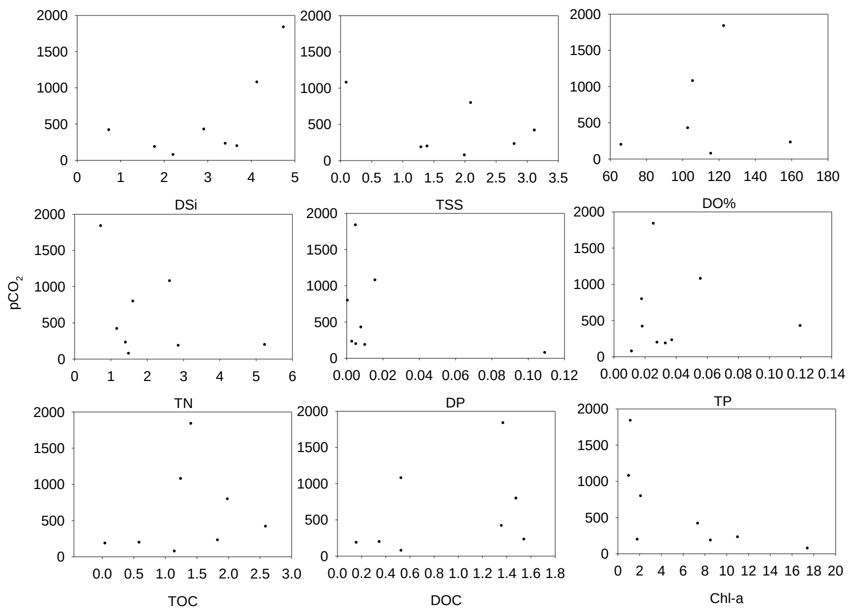

(c) Sites close to the Dam (limited samples ahead the Dam with negative effect by upper stream water discharge).

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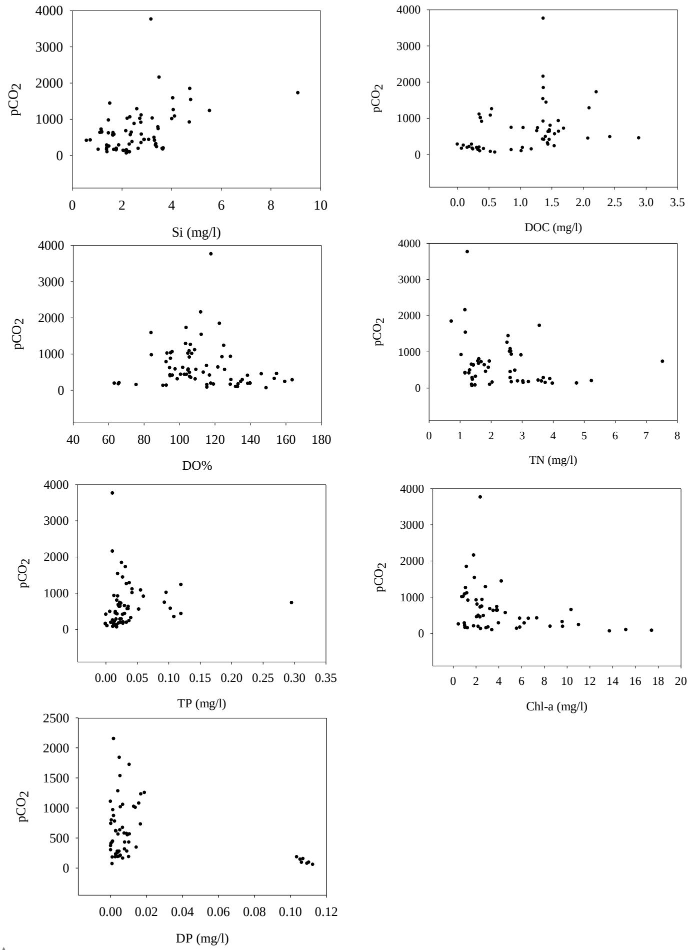

(d) Sites in the Res. without consideration of wet and dry periods.

Fig. S4. Scatter plots between pCO_2 and several key water chemicals in the Danjiangkou Reservoir, China (Pearson R coefficients for pCO_2 and all the water quality variables were tabulated in Table 3).

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