CO_2 AND CH_4 PARTIAL PRESS AND FLUX ACROSS WATER-AIR INTERFACE IN THE DOWNSTREAM OF JINSHA RIVER, CHINA

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Abstract. This paper takes some typical points at downstream of Jinsha River in China as examples for the overall evaluation of greenhouse gas emissions. In reference of previous literature, this study adopted the combination of headspace balance method and model estimation to obtain the partial pressures of carbon dioxide and methane in surface water and exchange fluxes of CO_2 and methane. Additionally, this paper also used field measuring instruments to measure the physical and chemical variables. The Spearman correlation index based on SPSS software are applied to analyse the relationship between between the partial pressures and fluxes of CO_2 and methane and environment variables. Experiments' results showed that mean value for partial pressure of CO_2 ($p(CO_2)$) was (1785.87 ± 451.18) µatm, ranked medium in worldwide rivers. In contrast, the average value for $p(CH_4)$ was (22.63 ± 11.48) µatm ranked relatively low in worldwide rivers. Among all sampling sites, the $p(CH_4)$ for Linjiaba, Shaonvping, Lizhuang located in reservoir area were higher than that for other sites. And the diffusion of CO_2 flux was in medium level compared with other major rivers in the world, at (1.71 ± 0.55) mmol/(m^2·h), while that of CH_4 flux kept in low level at (0.0009 ± 0.0005) mmol/(m^2·h), and all benthic flux of CO_2 and CH_4 were positive indicated the Jinsha River was the source of producing greenhouse gas., the trend of the partial pressure and flux almost remained the same. Moreover, $p(CO_2)$ in surface waters showed positive correlations with alkalinity (TA) and dissolved organic carbon(DOC), and $p(CH_4)$ showed significant positive correlations with Chl-a and temperature. CO_2 flux showed positively correlation with the $p(CO_2)$, DOC, alkalinity (TA), and CH_4 flux is positively related to $p(CH_4)$, wind speed. Other environmental factors showed vague effects on the fluxes.
Keywords: *carbon input, environmental indicators, greenhouse gas, greenhouse effect, river*

Introduction

Although the water area takes up for approximately 2% of global inland area, it largely influences the global carbon cycle (Guo et al., 2011). As the crucial connection between terrestrial ecosystem and marine ecosystem which are two main carbon carriers, river has become vital part of global carbon cycle (Ludwig et al., 1996). The carbon output from rivers is closely responsible for the change of coastal environment, marine carbon cycle and the global climate system. However, in recent years, human activities accelerate land erosion-deposition, which to a large extent stimulates the disturbance and redeposition of carbon pool in land ecosystem, and strengthens carbon transport from rivers to ocean. About 1 Gt carbon containing 60% inorganic carbon and 40% organic carbon is estimated to be transported from river to sea (Ludwig et al., 1996; Zhang et al., 2013; Cole et al., 2007). Meanwhile, river releases and absorbs carbon dioxide and methane though air-water interface, of which the amount of released CO_2 can reach at least 10^7 t/a (Li et al., 2013; Degens et al., 1991). These two typical gases emission significantly contributes 80–85% of greenhouse effect (Clarke et al., 2007). This percentage has not changed for the last 20–30 years, but the total radiative forcing which causes the increase in the planet's temperature has increased consistently

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over this time window (Getoff, 2006). The primary effect for greenhouse effect gives Planet Earth its hospitable average temperature of c. 17 °C, and the smaller secondary effect which has been in existence for only 250–300 years and is caused by an increase in concentration of greenhouse gases (Yao and Gao, 2005). As a result, measuring CO_2 and CH_4 benthic flux among water-air interface in river in a right way contribute to a better understanding the role that river play in regional or global carbon cycle and a more systematical grasp of carbon budget in river basin. Considerable researches about gas fluxes in the last decades on water-air interface almost adopted eddy covariance method, model estimation method, remote sensing inversion, etc (Zhao et al., 2011b). Among these methods, field monitoring usually employs model estimation method for its simplicity, flexibility and practicality. Precisely, Model evaluation method applies the Fick law to evaluate the flux in accordance with Gas concentration gradient between air and water interface where difference of gas concentration between two medias Mass Transfer Coefficient are critical (Urabe et al., 2010; Jonsson et al., 2007; Huang and Wang, 2009).

Jinsha River is the upper reaches of the Yangtze River flowing though east northern of The Yunnan-Guizhou Plateau and west southern part of Sichuan Highland to the Minjiang River in Yibin City. Its length is 2326 km and its basin acreage which takes up 26% of the Yangtze River is 47.3×10^4 KM^2. In addition, it means annual discharge is 4750 m^3/s. Due to the large area covered by Jinsha River, systematic and correct measure of greenhouse gas budget is critical for carbon cycle research. What should be noted is the processes of gas exchange between water-air interfaces are not only impacted by wind speed and temperature, but also related to depth and acreage of waters. Adopting the model estimation method to measure the CO_2 and CH_4 benthic flux, while there were few researches, should take the following factors into consideration, while there were few researches. In this paper, aiming at the downwards of Jinsha River from Panzhihua City to Yibin City, the research obtained the live data of CO_2 and CH_4 partial pressure in surface water and environmental parameters for field monitoring. Then the research used thin boundary layer method to estimate benthic flux of greenhouse gas and elementarily analyze the correlation between the environmental parameter and the partial pressure as well as the benthic flux. In downstream of Jinsha River, Wudongde hydropower station and Baihetan hydrogen station are being constructed, and Xiluodu hydrogen station and Xiangjiaba hydrogen station have been put into effect. The operation of newly-built hydropower stations will impact the carbon cycle in this area. A research on greenhouse flux on water–air interface is critical to illustrate variation change of carbon cycle after constructing plants and give information for reliability of hydropower energy system.

Materials and methods

Research objective

We researched at the downwards of Jinsha River (N24°29'—28°53' to E100°57'—104°38') from Panzhihua City (the junction of Yalong River and Jinsha River) to Yibin City (the junction of Min River and Jinsha River) in China, of which the length was 768 km and and fall of water level was 719 m. From the upstream to downstream, a series of sampling positions were Geliping (GLP), Longjiedu (LJD), Jiaopingdu (JPD), Geledu (GLD), Yanziyan (YZY), Linjiaba (LJB), Shaonvping (SNP), Lizhuang (LZ), of which the locations were shown in *Table 1* and *Figure 1*. Among 8 sampling sites,

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Shaonvping and Yanziyan are located in the reservoir area in front of Xiangjiaba hydropower station and Xiluodu hydropower station respectively, and Linjiaba site is located at the reservoir area between these two hydropower stations. We collected samples by taking local boat along the waterway in January 2016. Due to the rapid flow in Jinsha River, we gathered the water samples as well as relative environmental indicators in central of waterway. The scenes for sampling at Shaonvping, Gelefu, Yanziyan, Lizhuang are shown in *Figure 2*.

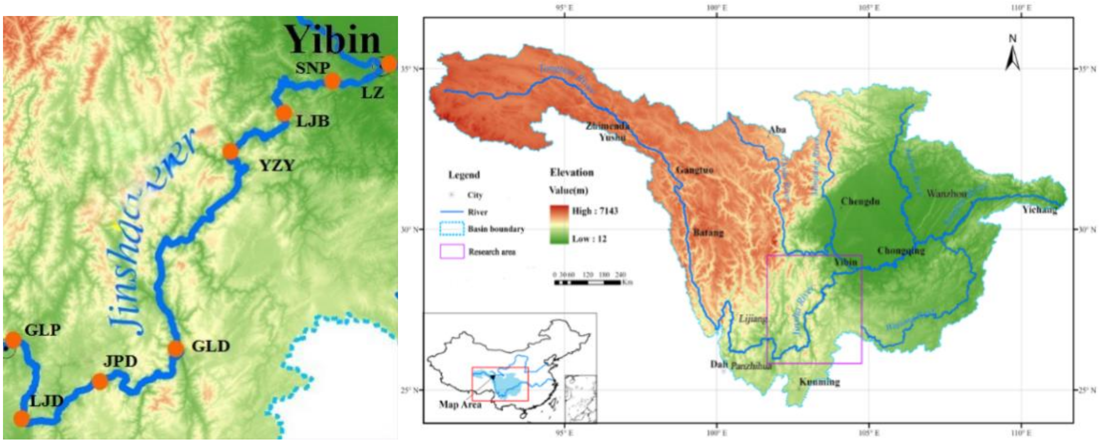

Figure 1. *Sketch map of research area and sampling spots in the downstream of Jinsha River*

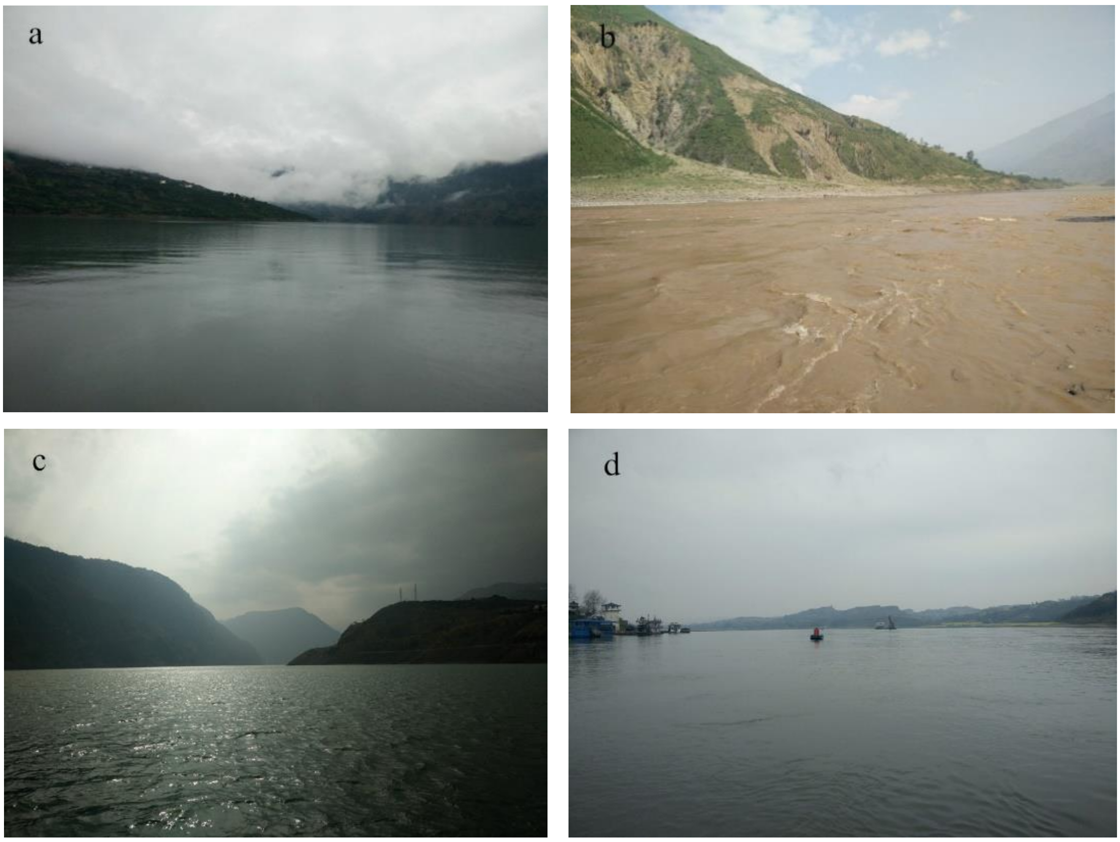

Figure 2. *Photoes of the sampling spots of Shaonvping (a), Geledu (b), Yanziyan (c) and Lizhuang (d) of the downstream of Jinsha River*

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Table 1. *The locations of the sampling spots in downstream of Jinsha River*

Sample site	***p*(CO_2)/μatm**
Geliping (GLP)	N26°35.511', E101°31.857'
Longjiedu (LJD)	N25°57.729', E101°52.894'
Jiaopingdu (JPD)	N26°17.590', E102°22.912'
Geledu (GLD)	N26°31.251', E103°03.132'
Yanziyan (YZY)	N28°14.594', E103°36.370'
Linjiaba (LJB)	N28°39.347', E103°50.405'
Shaonvping (SNP)	N28°37.614', E104°19.174'
Lizhuang (LZ)	N28°48.933', E104°48.072'

Measure method for CH_4 and CO_2 in water-air interface

To measure water-air interface gas partial press, recent research mainly adopted following two methods: static closed chamber- Gas chromatography method and the headspace equilibrium method and thin boundary layer method. However, on the condition of wind blows and flowing water, the disturbance caused by friction between the chamber and surface water may cause extra emission of greenhouse gas which will influence the accuracy of experimental result from the former method (Pumpanen et al., 2004). And this method is labor-intensive and it is unfit for large-scale and long-term observation (Tremblay et al., 2005; Kolb and Ettre, 2006). As a result, the static closed chamber technique only suits static water. Considering that the rapid flow of Jinsha River, long distance between sampling spots and poor weather condition during experiments, we use the latter method to observe the water-air interface greenhouse gas emission in the downstream of Jinsha River.

The principle of headspace equilibrium method

The principle of headspace equilibrium method is to obtain partial press of testing gas in water before equilibrium by measuring the concentration of the gas in upper space when gas concentration in water and air stay balance after rapid shake in the glass bottle filled with water sample and inert gas. The calculation is show as follows (Goldenfum, 2010):

$$p_{(Gas)} = \frac{(p_{final} \times K_{equilibrium}) + \left(\left(\frac{HS}{S}\right) \times \frac{(p_{final} - p_{initial})}{V_m}\right)}{K_{sample}} \quad \text{(Eq.1)}$$

where the $p_{(Gas)}$ illustrates partial press of testing gas (μatm), and $p_{initial}$ and p_{final} denote testing gas partial press in upper part of bottle before and after equilibrium (μatm), and *HS/S* represents The volumetric properties for the gas mixture (mol/L), V_m demonstrate the molar volume of gas, K_{sample} and $K_{equilibrium}$ show solubility of testing gas at weather in bottle when sampling and experimenting respectively (mol/(L·atm)). And Henry coefficient of different gases can be calculated by following equations (Weiss, 1974; Weast and Astle, 1987):

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$$\ln K_0(CO_2) = -58.0931 + 90.5069 \times (\frac{100}{T_K}) + 22.294 \times \ln(\frac{T_K}{100}) + s \times (0.027766 - 0.02588 \times (\frac{T_K}{100}) + 0.0050578 \times (\frac{T_K}{100})^2) \quad \text{(Eq.2)}$$

$$\ln K_0(CH_4) = -115.6477 + \frac{155.5756}{(T_K/100)} + 65.2553 \times \ln(\frac{T_K}{100}) - 6.1698 \times (\frac{T_K}{100}) \quad \text{(Eq.3)}$$

$$V_m = 1 \times 0.082057 \times (273.15 + T) \times \left(\frac{101.325}{p}\right) \quad \text{(Eq.4)}$$

where T is temperature when sampling (°C) and p is atmospheric pressure when sampling (kpa). 2.2.2 Water-air interface gas benthic flux

The water-air interface gas benthic flux mainly impacted by partial press of gas in surface waters and gas transfer coefficient which is influenced by flowing speed, blowing speed and weather, etc. According to Fick Law, for freshwater bodies, the water-air interface gas benthic flux is obtained as follows (Weast and Astle, 1987):

$$Flux = k_x \left(C_{water} - C_{equilibrium}\right) \quad \text{(Eq.5)}$$

with *Flux* as greenhouse diffusion flux (mmol/(m^2·h)), k_x as gas exchange coefficient (cm/h), C_{water} as the gas concentration in water (mmol/L), $C_{equilibrium}$ as greenhouse gas saturation concentration in site weather and atmospheric pressure (mmol/L).

And k_x is estimated worldwide mainly by following empirical equation adopted by Jähne et al. (1989):

$$k_x = k_{600}\left(\frac{600}{Sc}\right)^{0.67} \quad \text{(Eq.6)}$$

with k_{600} as exchange coefficient of sulfur hexafluoride (SF_6) gas (cm/h). Considering sampling spots are being constructing or have been constructed hydraulic power plant, we choose the exchange coefficient for CO_2 and CH_4 for lakes and reservoir eco-system from empirical formula (shown as *Equations 7* and *8*, respectively (Cole and Caraco, 1998; Macintyre et al., 2006)

$$k_{600} = 2.07 + 0.215 \times U_{10}^{1.7} \quad \text{(Eq.7)}$$

$$k_{600} = 2.07 + 0.215 \times U_{10}^{1.7} \quad \text{(Eq.8)}$$

U_{10} illustrates wind speed on 10 m above the water (m/s). It is usually acquired by following formula using wind speed U1 above water body measured at site (Crusius and Wanninkhof, 2003).

$$U_{10} = 1.22 \times U_1 \quad \text{(Eq.9)}$$

where U_1 denotes instantaneous wind speed above water level from meteorological station (accuracy is 0.1 m/s).

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And *Sc* denotes Schmidt constant at t °C. For freshwater, it can be calculated as follows (Roehm et al., 2009; Wanninkhof et al., 1992):

$$Sc(CO_2) = 1911.1 - 118.11t + 3.4527t^2 - 0.04132t^3 \quad \text{(Eq.10)}$$

$$Sc(CH_4) = 1897.8 - 114.28t + 3.2902t^2 - 0.03906t^3 \quad \text{(Eq.11)}$$

Then, greenhouse gas saturation concentration in water sample will be achieved by that partial press of greenhouse gas multiply by Henry coefficient shown as follows (Morel, 1982; Anderson, 2002; Zhang et al., 2009):

$$C_{equilibrium} = K_0 \times p(Gas) \quad \text{(Eq.12)}$$

In *Equation 12*, K_0 denotes Henry coefficient which is defined as gas solubility (mol/(L·atm)) and *p(Gas)* show atmospheric pressure when experimenting (μatm).

The calculation procedure for greenhouse gas partial press and flux

The $p(CO_2)$ and $p(CH_4)$ in water were calculated within headspace equilibrium method though Agilent 7820A gas chromatograph according to Henry coefficient, water temperature, atmospheric pressure, volumetric property of gas and liquid in headspace bottle (5/7). And k_x is in connection with Schmidt constant from water weather and U_{10} obtained from *Equation 11* (m/s). The downstream of Jinsha River was rarely impacted by farmland, wetlands and human, we determined the mean concentration of CO_2 and CH_4 in atmosphere as 390.5 ppm and 1.803 ppm respectively with reference to Gui's and Zhang's research on the Yellow River an d the Yangtze river (Zhang et al., 2009; Gui, 2007). The whole process of calculation for greenhouse gas measurement by Headspace equilibrium method and Thin Boundary Layer Equation (TBL) method were shown in *Figure 3*. All field measuring apparatus had been calibrated standardly.

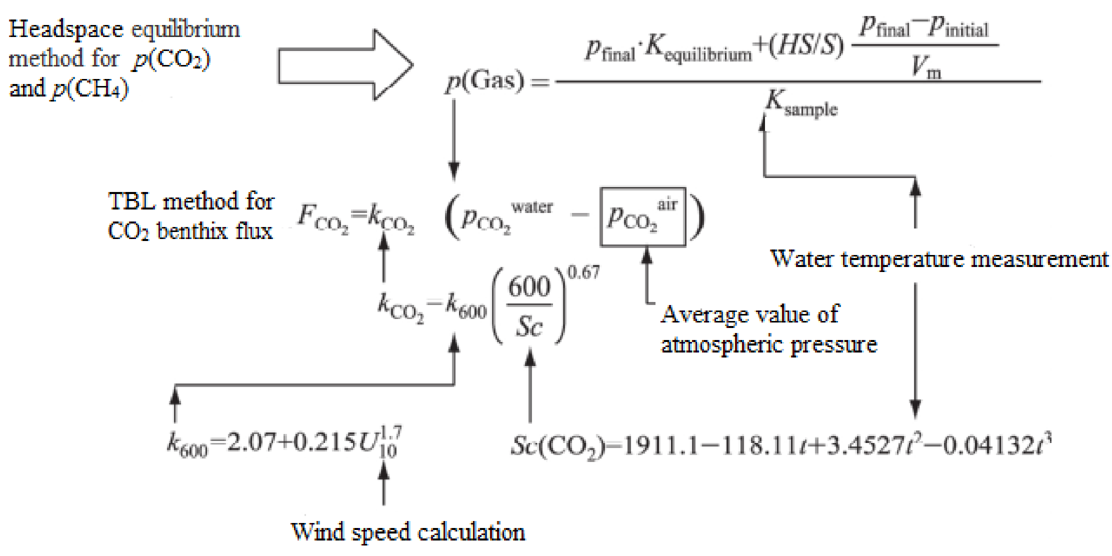

Figure 3. *The process of calculation for greenhouse gas*

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Researching material and methods for sampling

Water sample was collected at 0.5 m depth by water sampler where headspace bottle was place inside to seal when submerging at each spot, and the water samples and headspace bottles were preserved at low temperature.

For environmental parameters measurements, pH, electrical conductivity and salinity were measured by YSI Multi-parameter instrument, temperature and atmospheric pressure were measured by handheld digital atmospheric pressure gauge, alkalinity (TA) was accessed from titration with standard sulfuric acid solution by microtiter from HACH Company (accuracy is 1.25 μl), the effective intensity of photosynthesis was measured by LI-COR19OSA Light quantum instrument, the solar radiation intensity came from the illuminometer, water temperature and Dissolved Oxygen (DO) were obtained by site measurements with YSI ProODO Dissolved oxygen meter (accuracy is 0.1 °C, 0.01 mg/L respectively), Chlorophyll-a(Chl-a) adopted acetylacetone spectrophotometric method, concentration for Dissolved Total Nitrogen (DTN) and dissolved inorganic carbon (DIC) were measured by Shimadzu® TOC-V total carbon analyser from filtrates though What-man GF/F fibrous glass filter paper heated for 4 hours at 450 °C (Bates et al., 2011). Concentration for dissolved total phosphorus (DTP) measurements adopted Potassium persulphate- spectrophotometric method.

Researching method for analysis

The statistical analysis and calculation of this study data are proceeded by SPSS ® or Origin ®. And the spearman correlation analysis are adopted to understand the linear correlation between data changes and chlorophyll - a regression analysis relating to p (CO_2), p (CH_4), CO_2 and CH_4 fluxes and various physical and chemical indicators (pH, TA, DO, DOC, etc.), water temperature. The significant correlation are judged by the value for coefficient p shown as follow, when value for p which are below 0.05 means significant correlation and when value for p which are below 0.01 means extreme significant correlation.

$$\rho = \frac{\sum_i (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_i (x_i - \bar{x})^2 \sum_i (y_i - \bar{y})^2}}. \quad \text{(Eq.13)}$$

Result and analysis

Partial press of CO_2 and CH_4 in surface water and water-air interface benthic flux

The partial press of carbon dioxide $p(CO_2)$ and methane $p(CH_4)$ in surface water in the downstream of Jinsha River in January 2016 are shown in *Figure 4*. Along the flowing orientation, $p(CH_4)$ approximately grew. The highest $p(CH_4)$ appeared at lZ sampling site (45.62 μatm), while the lowest point showed at GLD sampling site(12.01 μatm). The average value of $p(CH_4)$ was 22.63 ± 11.48 μatm. $p(CO_2)$ showed no definite change. The highest and lowest points are GLD (2491.23 μatm) and LJB (1030.11 μatm) respectively, and the mean value of $p(CO_2)$ was 1785.87 ± 451.18 μatm. The value of $p(CH_4)$ at YZY, LJB, SNP three sampling sites were relatively low.

The water-air interface benthic flux of carbon dioxide and methane in surface water at all sampling sites in the downstream of Jinsha River in January 2016 are shown in *Figure 5*. The flux of CO_2 and CH_4 were all positive which means the downstream of

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Jinsha river was the source of greenhouse gas emission. The mean value of CH_4 and CO_2 were 0.0022 ± 0.0002 mmol/(m^2·h) and 2.27 ± 0.48 mmol/(m^2·h) respectively. The streamwise flux variation for each gas was similar to partial pressure variation of that gas. Because the TBL model method only concerned about the benthic partial press of gas and did not concern about the bubble diffusion which was the main diffuse means for CH_4, the measurement results of CH_4 flux might be smaller than actual level.

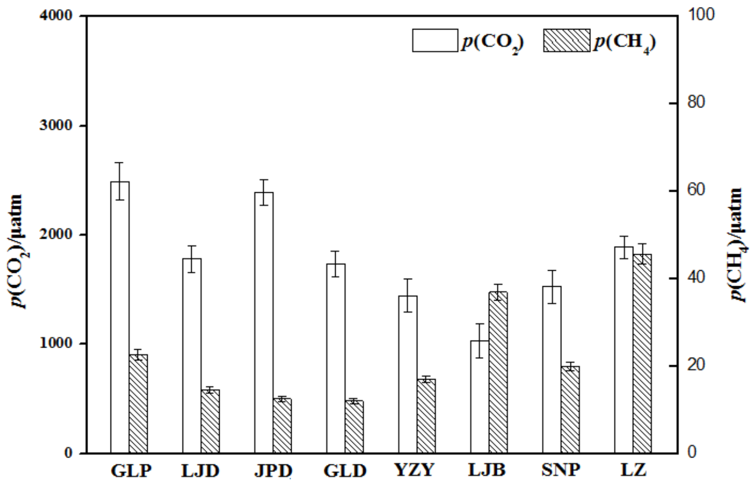

Figure 4. *Variation of streamwise of surface water of p(CO_2) with p(CH_4)*

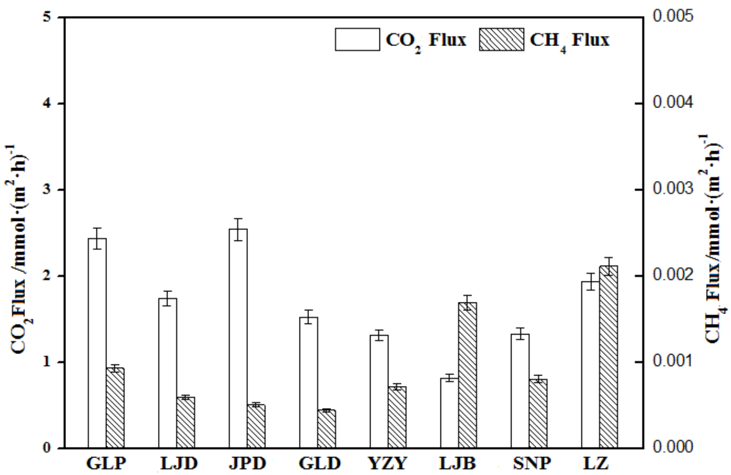

Figure 5. *Variation of streamwise of exchange flux of CO_2 and CH_4 between water and air*

Variation of environmental indicators

Water temperature and pH

The water temperature and pH variation along the river flowing route is shown in *Figure 6*. In January 2016, water weather changed a little in all sampling sites. The mean temperature was 14.7 ± 1.5 °C. The highest water weather was measured at GLP site, at 17.4 °C, in contrast, the water weather at GLD site was lowest, at 12.8 °C. The pH of surface water was almost same. The mean pH value was 7.14 ± 0.22 which

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demonstrate the surface water of downstream of Jinsha River in winter was neutral. The pH value at LJD site was highest at 7.43 while the lowest pH value was at YZY site, at 6.78. And there was no obvious change tendency in all sampling sites on the flowing direction.

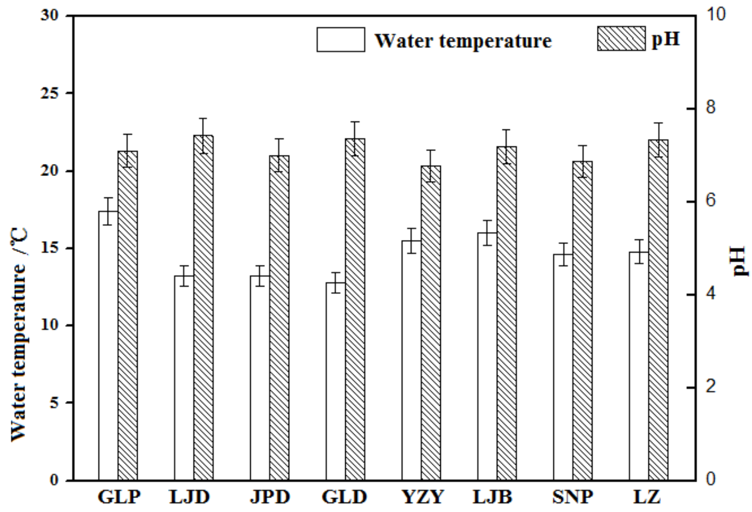

Figure 6. *Variation of streamwise of water temperature and pH in the water*

TA and Chl-a

The changes of TA and Chl-a along the river flowing route is shown in *Figure 7*. The highest Chl-a appeared at LJB site (30.456 mg·L^{-1}), and Chl-a values in YZY, LJB, SNP sampling sites were relatively high. Because SNP, YZY, LJB site are located at the reservoir area of Xiangjiaba and Xiluodu hydropower stations. In reservoir area, the flowing speed is lower than the other area, and water capacity is larger. As a result, the reservoir area is suitable for growth of phytoplankton, and Chl-a was relatively bigger than that in other area. On the other hand, TA showed no obvious change mode, and the value of TA changed a little in all sampling sites.

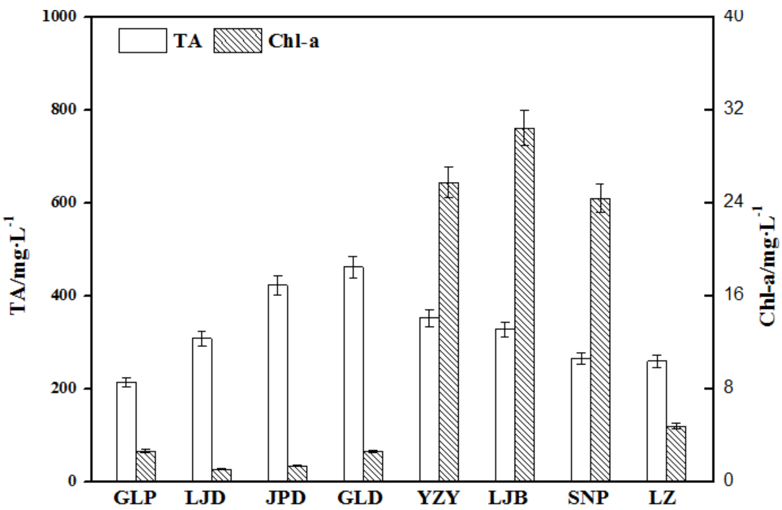

Figure 7. *Variation of streamwise of TA and Chl-a in the water*

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DTN and DTP

The changes of DTN and DTP in 8 sampling sites along the river flowing route are shown in *Figure 8*. The fluctuation of DTP was similar to that of DTN among all sampling sites. The value of DTP and DTN in LJD were both highest, at 0.39 mg·L^{-1} and 5.3709 mg·L^{-1}, respectively, in contrast, Chl-a in LJD site was lowest. And DTP and DTN in YZY, LJB and SNP were relatively low while Chl-a in these three sites were comparatively high. This proved phosphorus and nitrogen were absorbed adequately by phytoplankton.

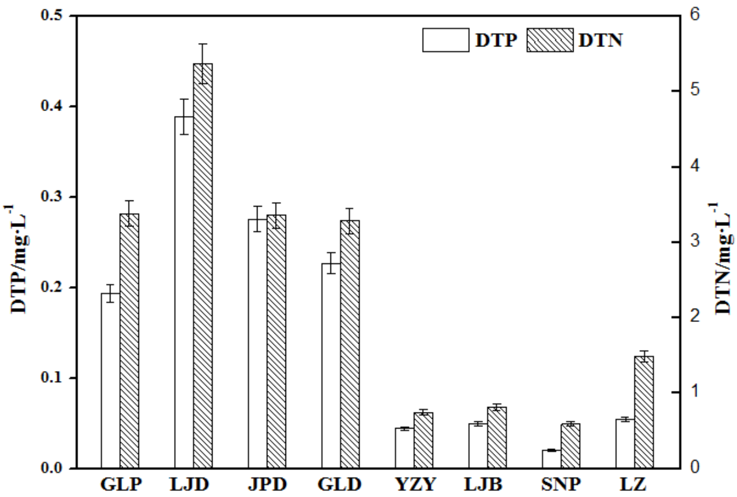

Figure 8. *Variation of streamwise of DTN and DTP in the water*

DO and DOC

The distribution of DO and DOC at all sampling sites in downstream of Jinsha River along the river flowing route are shown in *Figure 9*. DO in surface water generally climbed streamwise, companying with some decrease in last three sites. The average value for DO in water was (9.53 ± 1.00) mg·L^{-1}, the highest and lowest DO were measured at SNP site (11.22 mg·L^{-1}) and LJD site (7.94 mg·L^{-1}) respectively. DOC in water varied a little along the flowing route which showed no obvious law. The mean value for DOC in January 2016 was (3.37 ± 0.14) mg·L^{-1}, DOC in LJB and LZ sampling sites were highest 7 (3.60 mg·L^{-1}) and lowest (3.19 mg·L^{-1}) respectively among all sites in downstream of Jinsha River.

Discussion

The fluctuation of measured parameters on the streamwise

In the research, we focus on the partial pressure and flux of carbon dioxide and methane as well as the physical and physicochemical indicators at several sampling sites. From the experimental result, some changes appear along the river flowing direction, especially at last three sites near the reservoir. *p*(CH_4) and flux of methane showed generally the same tendency of change, which have both increased at these three sites. This phenomenon indicates that these three sites have large water capacity contributing to low flowing speed, the stable water environment give rise to forming

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strong microbial community construction. As a result, water provides suitable and better environment for microbial community construction. In addition, neighbour reservoir contains amount of organic matter after submerging the surrounding ecosystem, and these substances are the best nutrients for microorganism in surrounding area. After decaying and decomposing process, methane is generated and emitted (Wang, 2017; Jin and Wei, 2008). Similarly, Roehm and Tremblay (2006) found that there was a significant correlation between the concentration of methane between the environment in the deep water of the reservoir and environment in the downstream rivers (R^2 = 0.80 and 0.70). It is also estimated that about 70% of methane and 40% of carbon dioxide emissions have occurred in the river downstream of the Petit Saute reservoir in Guiala, France for more than a decade (Friedl and Wuest, 2002). In conclusion, existence of reservoir is proved to impact the greenhouse gas emission and ecosystem in surrounding water environment.

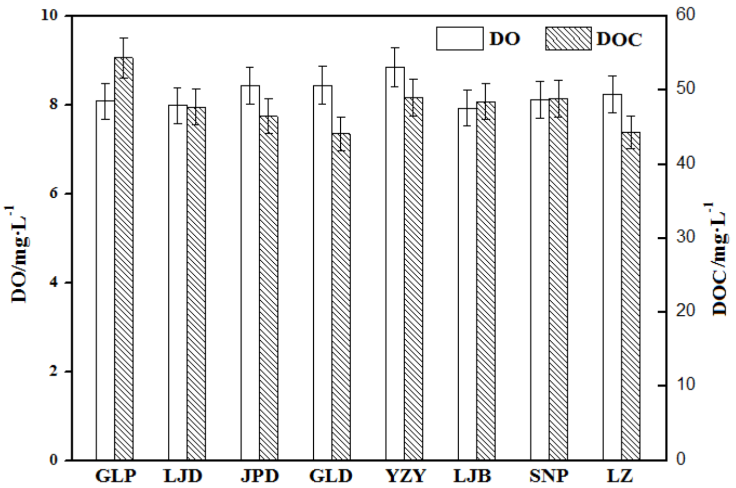

Figure 9. *Variation of streamwise of DO and DOC in the water*

Partial physical and chemical indexes also changed in these three sites. The concentration of Chl-a increased while DTN and DTP showed the reverse trend. The large capacity of water shapes better environment for photosynthesis contributing to the rise of concentration of Chl-a. Studies have shown that nitrogen content and nitrogen use efficiency of most plant leaves are positively correlated with photosynthetic capacity, which is one of the inherent physiological and ecological characteristics of plants (Evans, 2002; Cheng et al., 2012). Therefore, in the three sampling sites where photosynthesis effects increase, plants' utilization of ammonia nitrogen became stronger, so that DTN in water decreased (Wang and Xu, 2005). In terms of other estimators, the flux and partial pressure of carbon dioxide, water temperature, pH, TA and DOC showed no significant fluctuation law along streamwise orientation.

The correlation analysis between the partial press and flux of CO_2 and CH_4 and environmental indicators

We raised Spearman connection analysis method to illustrate the relationship between $p(CO_2)$, $p(CH_4)$, CO_2 flux, CH_4 flux and environmental indicators. The result given in *Table 2* showed that $p(CO_2)$ in surface water has significant positive correlation

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with DTN, DTP and negative correlation with DO, Chl-a, DOC. This proved the photosynthesis of phytoplankton in water was stronger than its respiration. The stronger photosynthesis worked, the more Chl-a was measured, the more CO_2 were fixed which decrease $p(CO_2)$ in water, the more nitrogen and phosphorus DTP and DTN in water was absorbed, the more DO and DOC were produced. The CO_2 flux demonstrated positive correlation with $p(CO_2)$, wind speed and negative correlation with DO, Chl-a, DOC which resemble $p(CO_2)$. And the wind blow would enhance the diffusion of CO_2.The $p(CH_4)$ showed negative correlation with Chl-a, TA and positive correlation with wind speed and water temperature. It is determined that the higher water temperature decreased the solubility of CH_4 in water, and naturally, $p(CH_4)$ increased when CH_4 diffused into surface water. In addition, relatively higher temperature and vigorous growth of phytoplankton provide a suitable metabolism environment for methanogen that contribute to producing CH_4 (Hong et al., 2004). Meanwhile, wind blowing will give rise to diffusion of CH_4 in surface water. The CH_4 flux showed positive correlation with $p(CH_4)$, wind speed, water temperature and negative correlation with Chl-a, TA which was similar to correlation of $p(CH_4)$. What can be proved is the larger value of $p(CH_4)$ indicated the larger CH_4 flux.

Table 2. *Correlations between $p(CO_2)$, $p(CH_4)$, flux of CO_2, flux of CH_4 flux and environment factors*

Indicators	$p(CO_2)$	$p(CH_4)$	CO_2 flux	CH_4 flux
Wind speed	-	0.819*	0.976**	0.819*
Water temperature	-	0.778*	-	0.778*
DO	-0.714*	-	-0.738*	-
Chl-a	-0.738*	-0.730*	-0.738*	-0.730*
TA	-	-0.762*	-	-0.762*
DTN	0.714*	-	-	-
DTP	0.712*	-	-	-
DOC	-0.833*	-	-0.857**	-
$p(CO_2)$	1	-	0.976**	-
$p(CH_4)$	-	1	-	1*

"–" indicates no obvious correlation, "*" showed obvious correlation (Sig. ≤ 0.05), "**" illustrated extreme correlation (Sig. ≤ 0. 01)

Comparison of Jinsha River with other worldwide rivers for greenhouse gas concentration and flux

Comparison for CH_4 concentration and flux in Jinsha River and other rivers

Methane in general river mainly stem from direct produce, release from sediment and input of water enriching CH_4 in surrounding. Considering particulate organic carbons take minority of total suspended particulates, a small amount of CH_4 produced directly at site comparing to other two producing methods. Relative research indicated that concentration of CH_4 in surface water of downstream of Jinsha River was relatively low no matter in summer and in winter, because not only methane produced a little at site, but also a few human lived on the riverside of Jinsha River, and input of CH_4 from branch of Jinsha River is relatively low. In reference of previous researches, considering the wide river basin and large covering area of Jinsha River, we chose several typical

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large rivers to make comparison. *Table 3* showed *p*(CH_4) and CH_4 flux in the surface water of the world rivers. Average concentration of CH_4 in surface water was (39.35 ± 20.32) nmol·L^{-1}, lower than other river worldwide. And average value for CH_4 diffusion flux in Jinsha River was (23.36 ± 0.67) μmol/(m^2·d), and it was lower than other river. It might be caused by measure method and calculation equation that need further research.

Table 3. *The p(CH_4) and exchange flux of CH_4 in the surface water of the world rivers*

Country	River	*c*(CH_4)/nmol·L^{-1}	CH_4 exchange flux/(μmol/(m^2·d))	Reference
Germany	Weser River	830~8490	-	Grunwald et al. (2009)
USA	Yaquina River	276~1730	193.8~4437.5	Angelis and Lilley (2003)
USA	Mckenzie	5~79	75~225	Angelis and Lilley (2003)
USA	Willamette	155~298	343.8~2250	Angelis and Lilley (2003)
China	Yangze River	51~604	37.3~1125.3	Zhao et al. (2011a)
China	Downsrtream of Jinsha River	39.35 ± 20.32	23.36 ± 0.67	Author

Comparison for CO_2 concentration and flux in Jinsha River and other rivers

CO_2 in worldwide majority river were oversaturated where *p*(CO_2) were measured at 2000 to 8000 μatm and *p*(CO_2) in some tributary even surpassed 10000 μatm (Cole and Caraco, 2001; Richey et al., 2002). In recent years, there were some researches about *p*(CO_2) in river. Gui's research demonstrates *p*(CO_2) was 790-1600 μatm in mainstream of Yellow River in fall and Zhang's research showed *p*(CO_2) was 860-1600 μatm in mainstream of Yangze River in a whole year (Gui, 2007; Zhang et al., 2009). Because these rivers are the typical worldwide rivers, through comparing the carbon dioxide emission in these rivers can understand the CO_2 emission level in Jinsha River. *Table 4* illustrated *p*(CO_2) and CO_2 flux in the surface water of the these rivers. From *Table 4*, the average value of *p*(CO_2) in surface water in downstream of Jinsha River was 1785.87 ± 451.18 μatm that ranked medium comparing to worldwide other river such as Amazonian rivers, Hudson River. And average value of CO_2 diffusion flux on water-air interface was (1.71 ± 0.55 mmol/(m^2·h) ranked medium when comparing with other worldwide rivers.

Table 4. *The p(CO_2) and exchange flux of CO_2 in the surface water of the world rivers*

Country	River	*p*(CO_2)/μatm	CO_2 exchange flux/(mmol/(m^2·h))	Reference
Brazil	Amazonian rivers	4350 ± 1900	5.61~10.18	Grunwald et al. (2009)
USA	Hudson River	1014	0.67~1.5	Zhao et al. (2011b)
China	The Yellow River	790~1600	0.82	Bates et al., (2011)
China	Yangze River	860~1600	0.74	Zhang et al. (2009)
World	Worldwide river	679~9475	-	Cole and Caraco (2001)
China	Downstream of Jinsha River in winter	1785.87 ± 451.18	1.71 ± 0.55	Author

There are four hydropower stations being constructed and constructing in downstream of Jinsha River: XIangjiaba hydropower station and XIluodu hydropower station have been put into production since 2014, Baihexi hydropower station will begin working in 2020, and Wudongde hydropower station is going to be in operation by 2021. The operation of hydropower stations and reservoir storage might impact carbon

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cycle in Jinsha River. It is vital to discover the impact of operation of hydropower station study upon greenhouse gas emission in downstream of Jinsha River, and it also plays crucial role of researching in carbon cycle development in this area. From our study, at Yanziyan site, Shaonvping site and Linjiaba site that located in reservoir district, $p(CH_4)$ and CH_4 exchange flux were relatively higher than other sites, while $p(CO_2)$ in these sites were lower than other sites and CO_2 flux showed no obvious change in these 3 sites. It can be proved from current data that the construction and operation of hydropower station did not cause severe greenhouse effect, and this need further research.

Conclusion

A systematic and correct acknowledge the greenhouse gas concentration and benthic flux in river can get a better understanding of the role river played in carbon cycle. And the construction of hydroelectric station may influence the carbon flow in eco system in surrounding area. There are 4 newly-built hydroelectric stations on the downstream of Jinsha River, the major river in China where measurement of CO_2 and CH_4 partial press and flux will illustrate the effect of hydroelectric plant upon carbon cycle and demonstrate whether hydroelectric plant will enhance the greenhouse effect. Considering the rapid current in Jinsha River, we adopted the headspace equilibrium method with combination of TBL model methods to obtain the partial press and concentration of carbon dioxide and methane.

At first, the brief introduction of research objective, Jinsha River and the specific sampling sites were illustrated. Then we reported the principle of headspace equilibrium method to obtain partial press and TBL model estimation method for benthic flux based on the Fick Law with gas transfer coefficient considering the impact of flow speed, wind speed and temperature. And we conclude the calculation procedure for partial press and flux from *Equations 1* to *12*. Moreover, environmental indicators measure method, apparatus and experimenting material were listed to show the measurement procedure.

In result and analysis part, firstly, we demonstrated the partial press and flux of CH_4 and CO_2. The $p(CH_4)$ generally climbed with the mean value of (22.63 ± 11.48) μatm showed the methane increasing in reservoir sites. The $p(CO_2)$ showed no obvious changing trend along the flowing route with the mean value of (1785.87 ± 451.18) μatm. And the flux of CH_4 and CO_2 variation trend was similar to $p(CH_4)$ and $p(CO_2)$ respectively, and them were both positive proved Jinsha River was the source of greenhouse gas emission. Then the variations of environmental indicators including water temperature, pH, Chl-a, TA, DTP, DTN, DO and DOC were displayed to show the differences between the natural sampling site (GLP, LJD, JPD, GLD, YZY) and sampling sites in reservoir area (LJB, SNP, LZ). From the fluctuation, Chl-a and flux and partial pressure of CO_2 increased in reservoir area while DTN and DTP dropped in reservoir area, and TA, DO and DOC showed no obvious variation which indicated phytoplankton grew prosperously would absorb N and P in suitable water temperature. And in winter, pH was neutral in downstream of Jinsha River. It is acknowledged the existence of reservoir will influence the surrounding water environment. Furthermore, the discussion part showed the correlation between partial press and flux of greenhouse gas and environmental indicators by Spearman correlation analysis method. The result came out that $p(CO_2)$ in surface waters showed positive correlations with alkalinity

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(TA) and DOC, and $p(CH_4)$ showed significant positive correlations with Chl-a and temperature. CO_2 flux showed positively correlation with the $p(CO_2)$, DOC, alkalinity (TA), and CH_4 flux is positively related to $p(CH_4)$, wind speed. And $p(CO_2)$ and flux for CO_2 was ranked as medium while $p(CH_4)$ was ranked as low comparing to other worldwide rivers.

All in all, $p(CH_4)$ and CH_4 diffusion flux were relatively higher in reservoir area, $p(CO_2)$ was lower in reservoir area than that in natural area, and CO_2 diffusion was not obvious in reservoir area. So it can be demonstrated that the construction and operation of hydroelectric stations impact not much at greenhouse effect and this need more research to complement.

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