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Daily CO_2 partial pressure and CO_2 outgassing in the upper Yangtze River basin: a case study of Longchuanjiang, China

S. Y. Li[1], X. X. Lu[2,3], M. He[2], Y. Zhou[2], L. Li[2], and A. D. Ziegler[3]

[1]Institute of Water Policy, Lee Kuan Yew School of Public Policy, National University of Singapore, 259772, Singapore
[2]Global Change and Watershed Management Center, Yunnan University of Finance and Economics, Kunming 650221, China
[3]Department of Geography, National University of Singapore, 117570, Singapore

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Correspondence to: X. X. Lu (geoluxx@nus.edu.sg)

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Abstract

Rivers have been under sampled to establish them as sinks or sources of the atmospheric carbon oxide (CO_2). Such poor coverage is well known for tropical and sub-tropical, particularly monsoon driven rivers. An unprecedented high-temporal-resolution (daily) sampling during July 2008–August 2009 were conducted from the Longchuanjiang River of the upper Yangtze basin, a subtropical monsoon river in China to reveal the daily-to-seasonal dynamics of the partial pressure of CO_2 (pCO_2) and CO_2 degassing flux from the river. The pCO_2 levels were supersaturated in CO_2 with respect to atmospheric equilibrium (380 µatm) during the entire survey period with obvious daily and seasonal variations, ranging from 450 to 63 000 µatm with an average of 3900 µatm. pCO_2 values in the surface water in the wet season were relatively low, except flooding period in November, due to a dilution effect by heavy rainfall. However, both daily and monthly minimal and maximal pCO_2 also occurred in this period. In contrast, the pCO_2 levels in the dry season were much higher, mainly resulted from lower pH by anthropogenic activities. Net CO_2 flux and pCO_2 were strongly correlated with pH, but weakly with water temperature, dissolved inorganic carbon and water discharge, and uncorrelated with particulate nutrients and biogenic elements. The estimated water-to-air CO_2 degassing flux in the Longchuanjiang River was about 110 $mol\,m^{-2}\,yr^{-1}$, with the upper limit of 460 $mol\,m^{-2}\,yr^{-1}$. Our study also indicated that among the total organic carbon remobilized through soil erosion, around 17 % (11 400 $t\,C\,yr^{-1}$) of was emitted to the atmosphere, 52 % (35 000 $t\,C\,yr^{-1}$) deposited in the river-reservoirs system and 31 % (21 000 $t\,C\,yr^{-1}$) exported further downstream. High spatial and temporal resolution of estimates of CO_2 emission from the world large rivers is required due to that catchment characteristics and anthropogenic activities are extremely heterogeneous in space and time.

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1 Introduction

Fluvial exports of organic and inorganic carbon to oceans (ca. 1 Pg yr^{-1}) represent the major biogeochemical role of river systems in the global carbon cycling (Degens et al., 1991; Ludwig et al., 1996). Recent results have demonstrated that concentration of dissolved CO_2 in rivers, lakes and coastal areas is higher than its equilibrium concentration relative to CO_2 in the atmosphere (i.e. 380 µatm), indicating that surface waters are capable of large CO_2 degassing fluxes to the atmosphere (Cole et al. 1994, 2007; St. Louis et al., 2000; Richey et al., 2002; Wang et al., 2007; Bastviken et al., 2011). Amazonian River, for example, 6 times more carbon (470 Tg C yr^{-1}) by CO_2 evasion than by the sums of riverine TOC (36 Tg C yr^{-1}) and DIC (35 Tg C yr^{-1}) were exported (Richey et al., 2002). Carbon emissions as CO_2 from global inland waters to the atmosphere were 1.4 Pg yr^{-1} (Tranvik et al., 2009), of which, 0.35 Pg C yr^{-1} from river systems including estuaries (Cole et al., 2007), nearly equivalent to riverine total organic carbon (Ludwig et al., 1996) or dissolved inorganic carbon (DIC) (Gaillardet et al., 1999). CO_2 evasion from rivers to the atmosphere is therefore a significant component of global and regional net carbon budget. Thus, direct measurements of land-atmosphere CO_2 gas exchange without consideration of water-borne fluxes lead to significantly overestimating terrestrial carbon accumulation (Hope et al., 2001). Such a large CO_2 source further compels us to reassess the global carbon budget because freshwater bodies such as lakes, impoundments and rivers are parts of terrestrial landscape, but they have not been included in the terrestrial carbon balance (Battin et al., 2009).

The partial pressure of aqueous carbon dioxide (pCO_2) in rivers, reflecting both internal carbon dynamics and upstream terrestrial biogeochemical processes, represents the intensity of gas exchange at the water-to-air interface and demonstrates the source or sink of atmospheric CO_2 for rivers (Richey et al., 2002; Richey, 2003; Yao et al., 2007; S. R. Zhang et al., 2009). The aqueous CO_2 in rivers generally has two sources: (1) allochthonous, i.e. soil CO_2 from mineralization/decomposition of terrestrial organic

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matter and root respiration of plants; (2) autochthonous, i.e. CO_2 emission from in situ respiration of aqueous organic carbon and photodegradation of dissolved organic matter, as well as CO_2 from precipitation of carbonates. Thus, rivers with varying physical characteristics and anthropogenic activities showed large seasonal and spatial heterogeneities in pCO_2 and thereby water-to-air CO_2 flux (Finlay et al., 2009; Guo et al., 2011). As a result, pCO_2 and over-saturation of dissolved CO_2 in rivers could be misestimated if the estimation is conducted using a specific temporal and spatial scale. Environmental changes relative to the terrestrial ecosystem and data paucity especially for most large rivers further result in a large uncertainty (Borges et al., 2005). Hence, high-temporal-resolution sampling needs to be conducted for a better understanding of carbon biogeochemistry in the river systems.

Compared to river systems, estuaries have been well documented, illustrating higher pCO_2 levels in the European estuaries (Zhai et al., 2007). In China, the previous studies on the Yangtze, the Yellow and the Pearl rivers and their estuaries in particular indicated higher pCO_2 and thus high carbon emissions (Su et al., 2005; Want et al., 2007; Yao et al., 2007; Zhai et al., 2005, 2007; Zhai and Dai, 2009; L. J. Zhang et al., 2009). Despite many research efforts devoted to the major element geochemistry and associating CO_2 consumption in the Yangtze River basin (i.e. Chen et al. 2002; Chetelat et al., 2008; Wu et al., 2008a, b; Li and Zhang, 2008, 2009; Li, S. et al., 2009), little information on CO_2 emission is available in its headwater. Though carbon diffusion flux from the entire Yangtze basin has been elucidated recently (i.e. Wang et al., 2007), this estimate using data sets in the Datong station (the lower Yangtze) understandably resulted in large uncertainties due to distinct spatio-temporal discrepancies in water chemistry, nutrient supply and human disturbance in the river basin. Meanwhile, the significance of riverine CO_2 outgassing on a global scale needs to be investigated based on regional cases with better seasonal controls. Tropical and sub-tropical river systems are likely to have high respiration and gas transfer velocity of CO_2, leading to a poor quantification of carbon emission from inland waters, especially in Asia and Africa where such data are very deficient.

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In this paper, we thus chose the Longchuanjiang in the upper Yangtze River, to perform a preliminary investigation on aqueous pCO_2 through daily sampling within a whole hydrological year. The main objectives of this study are to reveal the daily and seasonal variations of pCO_2 and examine the mechanism controlling this variability, as well as to estimate water-to-air CO_2 flux. Past studies on the Longchuanjiang included major ion geochemistry and chemical weathering, transports and fluxes of nutrients and organic carbon, indicating the great impacts of anthropogenic activities on water quality (Li et al., 2011; Lu et al., 2011a, b).

2 Materials and methods

2.1 Study area

The Longchuanjiang originates near Nanhua County and drains an area of 5560 km^2 (24°45′ N–26°15′ N and 100°56′ E–102°02′ E) before joining into the Jinshajiang, a tributary of the upper Yangtze River (Fig. 1). The main channel drains a length of 231 km and the total elevation fall is 2300 m (from 700 to 3000 m a.s.l), respectively. The 1788 km^2 upper catchment (upper the Xiaohekou station) has a sub-tropical monsoon climate, characterized by annual mean temperature of 15.6 °C. The average annual precipitation is 825 mm with 86–94 % of the total precipitation occurring in the wet season from May to October. The mean annual runoff and mean annual sediment load at the Xiaohekou Station were 3.2×10^8 m^3 and 4×10^8 t with pronounced intra-annual and inter-annual variations (Lu, 2005; Li et al., 2011).

The geology of the catchment is composed of low-grade metamorphic rocks, and in particular, clastic rocks (Wu et al, 2008a,b). The area is dominated by purple soil under the Chinese soil classification (Zhu et al., 2007, 2008), which is very susceptible to water erosion and weathering. Erosion was accelerated by growing populations and economic growth, which have contributed to deforestation (in earlier times), intensified agriculture activity, reservoir building, stone excavation and road construction. There

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are some small sized reservoirs situated in the drainage basin, resulting in reduction of sediment and organic carbon exports at Xiaohekou hydrological station (Lu et al., 2011b). Also, several counties (Nanhua and Chuxiong) along the riverine network, where industrial and domestic wastes discharge directly, leads to the river polluted by nitrogen (Lu et al., 2011a). Chuxiong County, adjacent to the sampling location, greatly contributes to riverine dissolved solutes (Li et al., 2011).

2.2 Sampling and analyses

Daily precipitation (June 2008–August 2009) and daily discharge (April 2008–March 2009) were recorded by station staff at the Xiaohekou discharge gauging station location in the Chuxiong County (Fig. 1). Daily sampling and field measurements at 08:00 a.m. were conducted from 15 June, 2008 to 31 August, 2009 at the Xiaohekou gauge station. All water samples were collected ~ 0.5 m below the surface water from the central part of the river in acid-washed 5-l high density polyethylene (HDPE) containers. Determination of pH and water temperature (T) was performed in situ using an Orion 230A pH/Temp meter, which was calibrated before each sampling occasion using pH-7 and pH-10 buffer solutions. Replicate measurements were conducted with a precision of ± 0.04 unit for pH and ± 0.1° for T, respectively. However, T and pH from 15 June to 20 July in 2008 were absent. Alkalinity was titrated with two parallel samples using 0.0226 mol l^{-1} hydrochloric acid on 100 ml of filtrated sample water on the sampling day, the concentrations of alkalinity presented were the averages.

In addition, DIC systems in the September 2007–August 2008 sourced from Li et al. (2011) were adopted for monthly pCO_2 calculations.

2.3 DIC species calculations

Total dissolved inorganic carbon (DIC) in river systems is the sum of biocarbonate (HCO_3^-), carbonate acid (H_2CO_3), carbonate (CO_3^{2-}) and aqueous CO_2 (CO_2aq), and these species are in temperature- and pH-dependant equilibrium with another, such

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as the equilibriums between atmosphere CO_2 and aqueous CO_2, and the dissolved ions caused by CO_2. DIC species can be calculated by the Henry's Law (Stumm and Morgan, 1981):

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

$$K_0 = [H_2CO_3^*]/[pCO_2] \quad (2)$$

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

$$K_2 = [H^+][CO_3^{2-}]/[HCO_3^-] \quad (4)$$

Where, $H_2CO_3^*$ is the sum of CO_2aq and the true H_2CO_3. K, the Henrys Constant, is temperature dependant dissociation constant in the riverine DIC species and calculated using the following equations:

$$pK_0 = -7 \times 10^{-5}T^2 + 0.016T + 1.11 \quad (5)$$

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

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

where $pK = -\lg K$.

Thus, the partial pressure of aqueous carbon oxide (pCO_2) can be simply expresses as the following equation:

$$pCO_2 = [H_2CO_3^*]/K_0 = [H^+][HCO_3^-]/K_0K_1 \quad (8)$$

In the present work, HCO_3^- is considered equaling to alkalinity (i.e. accounting for more than 99 % of the total alkalinity) because of the pH values ranging from 6.31–8.51 in the Longchuajiang (Yao et al., 2007).

2.4 Correlating temporal variability

Temporal changes of environmental variables thought to influence river water chemistry, production and CO_2 flux were compared to those of net CO_2 flux and pCO_2 to

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identify potential mechanisms mediating the carbon dynamics, also to evaluate the relative modes of key factors dominating the calculations of net CO_2 flux. In the present study, water conditions (pH, DIC, temperature), nutrient status (DOC, POC, TN, DN, NO_3^--N, NH_4^+-N, PN, DP, PAP, TP, dissolved Si), and major elements (K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}) were chosen to quantify their relations with net CO_2 flux and pCO_2. Major ions and Si were from Li et al. (2011), where twice per month sampling over a two-year period for measurements of T, pH, DIC and major ions. Monthly averages (July 2008–August 2009) of DOC and POC were obtained from Lu et al. (2011b), while averages of nutrients (July 2008–March 2009) from Lu et al. (2011a), and their associations with monthly values of net CO_2 flux and pCO_2 (July 2008–August 2009; Table 1) were determined. Correlation analyses were conducted using Spearman coefficient with the significance at $p < 0.05$. In addition, stepwise multiple regression was used to identify possible predictor variables for net CO_2 outgassing flux. All the statistical procedures were performed using statistical product and service solution (SPSS) 15.0 for Windows.

3 Results

3.1 Hydrological characteristics

The whole hydrological year was relatively wet compared to the mean level in the study area. The annual precipitation (ca. June 2008–May 2009) in the Xiaohekou gauge station was 1000 mm (Fig. 2a), higher than the mean level of annual precipitation during the period from the 1950s to 2000 (825 mm) (cf. Lu, 2005). About 97 % of precipitation occurred in the wet season from May to November. The daily mean water discharge was the highest in the beginning of November 2008 ($210\,m^3\,s^{-1}$), the minimum value was in April 2008 ($0.12\,m^3\,s^{-1}$) (Fig. 2b). Total water flow ($3.5 \times 10^8\,m^3\,yr^{-1}$) was close to the average water discharge of $3.2 \times 10^8\,m^3\,yr^{-1}$ (cf. Lu, 2005). Water discharge through May to November accounted for 91 % of the total water discharge. Sediment

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flux exhibited strong synchrony with water flows and varied from 0 kg s^{-1} to 643 kg s^{-1} (November 2008). It peaked at the beginning of November due to the large storm (Fig. 2b). The sediment transports (2.7×10^5 t yr^{-1}) was lower than the annual average of 4×10^5 t yr^{-1} for the period 1970–2001 (cf. Lu, 2005), demonstrating large amounts of sediment trapped behind dams and soil erosion control through vegetation recovery.

3.2 Daily and monthly variations in DIC species

pH ranged from 6.31 to 8.51 with lower values occurred from November to April (Fig. 3). HCO_3^- (alkalinity) varied between 1808 µmol l^{-1} (July 2008) and 4577 µmol l^{-1} (April 2009) (Fig. 3), with a close correlation with water discharge ($HCO_3^- = 3.69Q^{-0.116}$; $R^2 = 0.6$, $p < 0.01$; HCO_3^- in mmol l^{-1} and Q in m^3 s^{-1}). This slight decrease with a drastic increase in water discharge in the flood period was due to the enhanced dissolution of carbonates and detrial calcite as a result of intensified soil erosion during flooding season (Chen et al., 2002; Li et al., 2011).

The partial pressure of surface water CO_2 (pCO_2) showed obvious daily and monthly variations ranging from 451 µatm (August) to 62 712 µatm (November) with an average of 3954 ± 8720 µatm (Fig. 4a). High pCO_2 indicated the river was characterized by CO_2 oversaturation during the entire survey period, being 1.2–165 times the atmospheric pCO_2 (380 µatm), and more than 80 % of samples had pCO_2 of 3300 µatm, 9 times the atmosphere level (Fig. 5).

The abnormal high pCO_2 (62 712 µatm) occurred in the beginning of November 2008, slightly lagging behind the large flooding on the second and third day of November (Figs. 2, 4). This large pCO_2 values lasted till the initial May (the beginning of the wet season), but pCO_2 in the February was low (Fig. 4a; Table 1). Despite that one or two values of pCO_2 in June and July were close or higher than 10 000 µatm, more than 90 % of its values was smaller than 2600 µatm (Fig. 4a). In the remaining wet season, the pCO_2 were lower, especially from July to September 2008 (Table 1).

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Random sampling (i.e. twice per month) indicated pCO_2 ranging from 670 to 12 700 µatm with an average of 2600 µatm (Fig. 4b), much lower than the averaged data from daily measurements. This was primarily contributed by samplings in the dry season (Table 1; Fig. 4b). Monthly pCO_2 in July–September 2008, however, was higher than averages from the daily measurements (Table 1; Fig. 4b), demonstrating the necessity of more extensive sampling for CO_2 degassing flux.

Daily and monthly variations in pCO_2 and CO_2 degassing flux were correlated strongly and inversely with changes in pH ($r = -0.96$ and -0.99, $p < 0.001$), and positively with dissolved nitrogen, but only weakly with T ($r = 0.15$, $p < 0.05$), DIC ($r = 0.56$, $p < 0.001$) and Ca^{2+} ($r = 0.29$, $p < 0.05$), but uncorrelated with other chemical parameters such as phosphorus species, silicate, K^+, Na^+ and Mg^{2+} (Table 2).

4 Discussion

4.1 Controls on aqueous pCO_2

The pCO_2 in the river water is controlled by four major physical and biogenic processes (Richey et al., 2003; Wang et al., 2007; Yao et al., 2007): (1) transport of soil CO_2 (i.e. root respiration and decomposition of organic matter) through baseflow and interflow, (2) in situ respiration and decomposition of organic carbon, (3) photosynthesis of aquatic plants, and (4) CO_2 evasion from water to air. The first two processes contribute to CO_2 and rise in pCO_2, while the last two processes can be responsible for the decline of pCO_2.

The surface water pCO_2 is closely related to soil CO_2 content in the drainage basin, and is positively correlated with seasonal variability of temperature and precipitation (Hope et al., 2004). During the wet season, wetted soils by precipitation, proper temperature and high retention times of waters in soils, together with active bacterial activities, produce significant CO_2. Aqueous pCO_2 values are also impacted by the intensity of rainfall, hydrological flow path and river discharge, i.e. heavy rain directly flowing into

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the stream will dilute the pCO_2 in rivers (Finlay, 2003; Hope et al., 2004). On the other hand, biogenic pCO_2 uptake and release in the river mediate aqueous pCO_2, which is mainly controlled by spatial and seasonal variations in temperature, turbulence and water flow velocity (Barth and Veizer, 1999). All of these above-mentioned physical and biogenic processes contributed to high seasonal variability of pCO_2 in the Longchuanjiang (Fig. 4a).

There are enhanced dissolved soil CO_2 via baseflow and interflow, in situ increased oxidation of organic matter as a result of both higher temperature and increased organic carbon load during the wet season (9800 vs. 290 t TOC yr^{-1} in the high and low flows, respectively) in the Longchuanjiang (Lu et al., 2011b). Simultaneously, aqueous photosynthesis was at a low level given the highly turbid environment, reflecting by a high suspended solid concentration of 150–450 mg l^{-1} in the high flow condition (Lu et al., 2011b). On the other hand, inactive microbial activities in soils and in situ promoting photosynthesis because of high water clarity in the dry season (Yao et al., 2007). These seem to result in high values of pCO_2 in the wet season, such as Luodingjiang and Xijiang in the Pearl River systems (Yao et al., 2007; S. R. Zhang et al., 2009), and other rivers in the world (i.e. Barth et al., 2003). However, the surface pCO_2 of our study showed an obvious increase in the dry season and possibly can be due to input of pollutants in the dry season. During the dry season, industrial and domestic wastes from the adjacent county (Chuxiong) caused lower pH values (Figs. 3, 6), resulting in "extra" pCO_2 (cf. Duarte et al., 2008; Finlay et al., 2009), while the biogenic processes (i.e. photosynthesis) contributed little to pCO_2. However, during the wet season, concentrated rainfall diluted aqueous pCO_2, and also the waste waters from the adjacent counties (i.e. Chuxiong) and subsequent pH rise in the Longchuanjiang River, resulting in lower pCO_2 levels.

Rains occurred in the beginning of May after a long dry period (Fig. 2). The rainwater penetrated into the soil, coupling with increasing temperature, which promoted bacterial activities in soils and thus resulted in higher water pCO_2 level in May 2009 relative to other months during the wet season (cf. Yao et al., 2007). With the constant storms,

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rain waters directly entered rivers and thus diluted the aqueous pCO_2, resulting in the pCO_2 levels in a sequence of May > June > July, and then increased in August 2009 (Table 1). In the later October, little rain occurred and thus abruptly large storm in the beginning (91.3 mm in the first day) of November greatly elevated pCO_2 (62 700 µatm) in the Longchuanjiang River (Figs. 2, 4). The consequent largest sediment concentration (Fig. 2) and negligible photosynthesis corroborated pCO_2 was dominantly controlled by soil CO_2. Then the pCO_2 dramatically decreased due to the dilution effect particularly during the second huge flood. The monthly minimum pCO_2 of 856 µatm occurred immediately after the heavy storms was a good evidence (Fig. 4a). During this period, biogenic CO_2 release and uptake must be small because of the high turbidity and turbulence, fast-velocity flow, and the short residence time of waters.

4.2 CO_2 outgassing to the atmosphere

CO_2 outgassing from river water to the atmosphere is a function of pCO_2 difference between the water and the atmosphere, surface area of water, and the gas exchange coefficient (D/z). The diffusion flux of CO_2 can be calculated with the following theoretical diffusion model:

$$F = D/z \times (C_{air} - C_{water})$$

Where F is the degassing flux of CO_2 between river water and the atmosphere, D is the diffusion coefficient of CO_2 in the river, z is the thickness of boundary layer, C_{air} in µatm represents the CO_2 concentration in equilibrium with atmosphere, and C_{water} in µatm represents the measured dissolved CO_2 concentration in the river waters.

The exchanging rate D/z at the water-to-air interface varies greatly (i.e. 4–115 cm h^{-1}) due to several contributing factors, such as river runoff, turbidity, flow velocity, water depth and wind speed (Aucour et al., 1999; Richey et al., 2002; Wang et al., 2007). Considering the annual mean wind speed of 1.7 m s^{-1} and hydrological features in the Longchuanjiang Rver basin, D/z is estimated to be 8 cm h^{-1} for the calculation of CO_2 degassing flux. The similar D/z was also adopted by Wang et al. (2007) for

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calculations of CO_2 outgassing from the Yangtze basin. We also designated the upper limit value of 15 cm h^{-1} for D/z (Wang et al., 2007; Yao et al., 2007).

Estimate results showed that the Longchuajiang had a CO_2 diffusing flux around 111 mol m^{-2} yr^{-1}, and the corresponding upper limit was 210 mol m^{-2} yr^{-1}. They were obviously higher than that of most world large rivers, but comparable to that of the Xijiang River, and the karst-terrain Maotiao River in the Wujiang (Table 3). When considering average monthly values of pCO_2 during November–April, and daily pCO_2 in the rest months of a hydrological year (September 2008–August 2009), CO_2 diffusing flux in the Longchuanjiang River was estimated to be 244 mol m^{-2} yr^{-1}. The maximal CO_2 diffusing flux from the river was calculated up to 460 mol m^{-2} yr^{-1} with an upper limit of D/z (ca. 15 cm h^{-1}).

Considering that the water surface area is about 8.6 km^2 in the upper Longchuanjiang River (waters accounted for 0.48 % of the total land area; Li, W. et al., 2009b), the upper river will release 9.5×10^8 mol C yr^{-1} to the atmosphere. Thus, the CO_2 degassed from the catchment was close to its fluvial TOC flux (7.1×10^8 mol C yr^{-1}) or DIC flux (7.9×10^8 mol C yr^{-1}) (Lu et al., 2011a). Previous study reported the CO_2 degassing flux of 14 mol m^{-2} yr^{-1} in the 1990s from the entire Yangtze basin (Wang et al., 2007), which is only 1/8 of the Longchuanjiang River. Therefore, headwater streams tended to have higher net CO_2 flux than the lower basin (Finlay et al., 2009), and previous CO_2 emission from the Yangtze basin using the data in the Datong station could be underestimated due to spatio-temporal heterogeneity of catchment characteristics. Similar to the Yangtze, limited spatio-temporal data of dissolved inorganic carbon system in most large rivers is challenging the recent view that carbon emissions from freshwater are much lower than estimated previously (Barros et al., 2011). Our result concluded the upper Yangtze basin undoubtedly is an important net source of atmosphere CO_2.

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4.3 Relationships between environmental variables and pCO_2/CO_2 flux

Water flows partly contributed to pCO_2, as observed by Yao et al. (2007), this could be reflected by our monthly variability of pCO_2 and huge fluctuations of pCO_2 in the flooding period (i.e. November), however, they showed weak associations ($r = -0.47$, $p < 0.001$; $n = 131$; Figs. 4, 5; Table 3). Yao et al. (2007) ascribed the weak relations between hydrology and pCO_2 to insufficient samplings. Our high-temporal-resolution sampling indicated that water discharge was not a good predictor for aqueous pCO_2. Nonetheless, the absence of water discharge from April onward in 2009 was a limitation for precisely determining the impacts of hydrology on pCO_2.

pCO_2 and CO_2 degassing flux were more affected by pH than by other physical and chemical parameters on the basis of their correlations, partially because of the high variation in daily pH (6.3–8.5). For example, variation in pH resulted in nearly 10-fold variation in pCO_2 than did any other dissolved compounds (DIC, ammonium, nitrate, DIC) or temperature. Our result also demonstrated that temperature variation partially regulated pCO_2 levels by altering the alkalinity or DIC concentration, reflecting by the daily and monthly variations of alkalinity content (Fig. 3), as well as observed correlations between pCO_2 and DIC ($r = 0.56$, $p < 0.01$). Further investigations into riverine net productivity (Chl-*a*, plankton, gross primarily production and respiration) should be conducted to quantify their potential roles on net CO_2 flux.

Strong predictive relationships between pH and pCO_2 and CO_2 degassing flux allowed us to identify critical thresholds of the Longchuanjiang River switch from CO_2 uptake to gas emitter (Fig. 6). When the pH exceeded 8.7, the river acted as carbon sponges, and when pH dropped below 8.7, the Longchuanjiang River carbon source. Similar findings were also reported in many lake systems (Duarte et al., 2008; Finlay et al., 2009), indicating pH dependence of CO_2 flux. This could weaken the relationships between other variables including water discharge and pCO_2.

It should be noted worldwide water acidification (Reuss et al., 1987; Sullivan et al., 2005; Ginn et al., 2007; Dual et al., 2011). In the Yangtze River basin specifically the

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tributary river of the upper Yangtze River in Southwestern China, sulfate concentrations in river waters increased rapidly and pH declined due to acid deposition and other anthropogenic activities (Chen et al., 2002; Dual et al., 2011). This will exponentially increase carbon emission from river waters. For example, pCO_2 in the Longchuanjiang River will increase by three times assuming pH reduction from 8 to 7.5 and ten folds from 8 to 7.

4.4 Riverine carbon input and output

There are several fates like burial in sediments, transport to the sea (or downstream), or evasion to the atmosphere for soil carbon reaching freshwaters (Battin et al., 2009; Bastviken et al., 2011), depicting individual inland water such as river system as a combined conduit and reactor for inorganic and organic carbon. However, related observation is rare particularly in the Asian rivers (Tranvik et al., 2009). A carbon budget using the "active pipe" concept by Cole et al. (2007) can be developed to understand the regional and global carbon cycling in the riverine system.

The trap efficiency of sediment around 90 % in the upper Yangtze (Lu and Higgitt, 2001) was adopted in our work (Fig. 7a), which was mainly attributed to many reservoirs in the upper catchment. Assuming soil erosion rate was about 1700 t km^{-2} yr^{-1} in the upper Longchuanjiang River, and sediment input from catchment to the river was about 30×10^5 t yr^{-1}, comparable to the observation by Zhou et al. (2004).

Our budget indicated that 67 400 t C yr^{-1} input from the catchment to river, of which inorganic carbon accounted for 33 % (22 400 t yr^{-1}). Overall, 17 % (11 400 t yr^{-1}) of the total carbon from catchment released to atmosphere, while 52 % (35 000 t yr^{-1}) of the carbon was trapped primarily by dams (Fig. 7b). Our estimate was in the range of 1 % to 69 % of carbon emission as CO_2 from land (Tranvik et al., 2009).

Higher concentrations and areal exports of organic carbon in the upper Longchuanjiang catchment (Lu et al., 2011b) could contribute to CO_2 evasion. Our results, however, did not show significant relations between CO_2 degassing flux and DOC or POC (Table 2). Elevating soil erosion rate by the intensified anthropogenic activities (Zhou

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et al., 2004; Lu, 2005) could increase sediment transport to river system. However, more than 50 % of soil carbon was trapped behind dams in the river basin. The deposited carbon would increase the potential of high carbon evasion due to global warming and local climate change.

5 Conclusions

The surface water pCO_2 was supersaturated with respect to atmospheric CO_2 during the whole survey period, averaging about 3 954 µatm, thus resulting in a water-to-air interface CO_2 outgassing flux of around 100 mol m^{-2} yr^{-1} in the Longchuanjiang River. The aqueous pCO_2 levels displayed obvious daily and monthly variations due to temporal changes of external biogeochemical processes, in situ biogenic activities and water environment particularly pH by anthropogenic processes. pH was by far the strongest control to pCO_2 and net CO_2 flux that included daily and monthly data, resulting in higher pCO_2 levels in the dry season. In contrast, the pCO_2 in the wet season except November showed lower monthly averages, both minima and maxima pCO_2 occurring in this period. The higher pCO_2 in the early wet season (May) were mainly contributable to increasing baseflow and interflow flushing soil CO_2 into streams. Whereas, the lower pCO_2 onward (June–October) in the wet season primarily resulted from the diluted effect by precipitation. The Longchuanjiang River in the upper Yangtze basin was a huge carbon source of atmospheric CO_2. Water acidification and carbon primarily trapped behind dams also contributed to higher carbon emission. Further study should include potential metabolic controls on CO_2 outgassing flux.

The global land carbon sink is estimated to be 2.6 Pg of C per year without consideration of inland waters as a part of terrestrial landscape (Bastviken et al., 2011). Carbon emission from freshwaters thus will greatly counterbalance terrestrial carbon sink. Anthropogenic activities coupled with changing to cascade rivers in the Yangtze River are altering riverine carbon biogeochemical processes, similar to other world large rivers. Moreover, water acidification in most rivers undoubtedly increases CO_2 degassing flux.

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CO_2 emission from the entire basin estimated using one or two specific sampling stations particularly in the downstream will be under-estimated. Therefore, re-evaluation of CO_2 diffusion flux at the water-to-air interface becomes an increasingly important issue in re-assessing global terrestrial carbon balance.

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Table 1. Monthly pCO_2 (µatm) in the upper Longchuanjiang River, China.

	N	Mean	Std. Deviation	Minimum	Maximum
Jul 2008	11	1101	499	676	2102
Aug 2008	31	846	379	451	2219
Sep 2008	30	1100	571	580	3721
Oct 2008	31	1820	1165	839	6326
Nov 2008	10	32 366	20 812	856	62 712
Dec 2008	4	12 573	3775	8399	17 357
Jan 2009	5	8514	2887	4327	12 095
Feb 2009	3	1933	683	1440	2713
Mar 2009	6	10 416	18 614	636	48 117
Apr 2009	4	18 749	16 465	6283	42 612
May 2009	31	3942	7892	891	43 235
Jun 2009	30	2191	3111	661	17 922
Jul 2009	31	1895	1752	478	9565
Aug 2009	31	2769	1514	720	7445
Total	258	3954	8720	451	62 712

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Table 2. Relations between pCO_2/CO_2 outgassing flux and environmental variables in the Longchuanjiang River, China (tested by non-parametric correlations using Spearman's rho).

	T	PH	DIC	*Q*	DOC	POC	TN	DN	NO_3-N	NH_4-N	PN	DP	PAP	TP
pCO_2	–0.15	–0.96	0.56	–0.47	–0.37	–0.17	0.37	0.68	0.82	0.73	–0.52	0.25	–0.24	–0.25
JCO_2	–0.15	–0.96	0.56	–0.47	–0.37	–0.17	0.37	0.68	0.82	0.73	–0.52	0.25	–0.24	–0.25
p	0.013	0.000	0.000	0.000	0.191	0.572	0.332	0.042	0.007	0.025	0.154	0.516	0.529	0.516
n	258	258	258	131	14	14	9	9	9	9	9	9	9	9

(a) Links between pCO_2/CO_2 outgassing flux (JCO_2) and *T*, pH, DIC and water discharge using daily data, while and nutrients using monthly averages.

	pH	K^+	Na^+	Ca^{2+}	Mg^{2+}	Si	Cl^-	SO_4^{2-}	TDS
pCO_2	–0.99	–0.02	–0.16	–0.29	0.13	–0.18	–0.12	0.17	–0.23
JCO_2	–0.99	–0.02	–0.16	–0.29	0.13	–0.18	–0.12	0.17	–0.23
p	0.000	0.904	0.274	0.048	0.370	0.211	0.431	0.252	0.119
n	48	48	48	48	48	48	48	48	48

(b) Links between pCO_2/CO_2 outgassing flux (JCO_2) and major elements using instantaneous sampling twice per month in a two-year period (September 2007 to August 2008).

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Table 3. The mean pCO_2 and CO_2 outgassing in world rivers, lakes and reservoirs.

River	Sites	Climate	D/z	Mean pCO_2 (µatm)	CO_2 degassing flux (mol m^{-2} yr^{-1})	References
Longchuanjiang	China	Subtropic	8	3954	111	This study
Upper stream of Maotiao River	China	Subtropic	10	3740	107.5	Wang et al. (2011)
Luodingjiang	China	Humid subtropic		600–7200		S. R. Zhang et al. (2009)
Xijiang	China	Humid subtropic	8–15	2600	69–130	Yao et al. (2007)
Yangtze	China	Subtropic		600–9600		Chen et al. (2002)
Yangtze (Datong)	China	Subtropic	8	1297	54 in 1960s and 14 in 1990s	Wang et al. (2007)
Amazon	Brazil	Tropic	10	4350	69	Richey et al. (2002)
St. Lawrence	Canada	Temperate	15	576 (Spring)	9–30	Yang et al. (1996)
				1300	28.5–107.5	Helli et al. (2002)
Ottawa	Canada	Temperate	4	1200	14	Telmer and Veizer (1999)
Hudson	USA	Temperate	4	1125	5.8–13.5	Raymond et al. (1997)
Rivers*					53.6	Cole et al. (2003)
Nature lakes					10.5	Tranvik et al. (2009)
Artificial reservoirs waters					15	Barros et al. (2011)
Hydroelectric reservoirs					11.8	Barros et al. (2011)

* Carbon emission as CO_2 of 0.23 Pg yr^{-1} from Cole et al. (2003), river water surface water of 357 627 km^2 from Bastviken et al. (2011).

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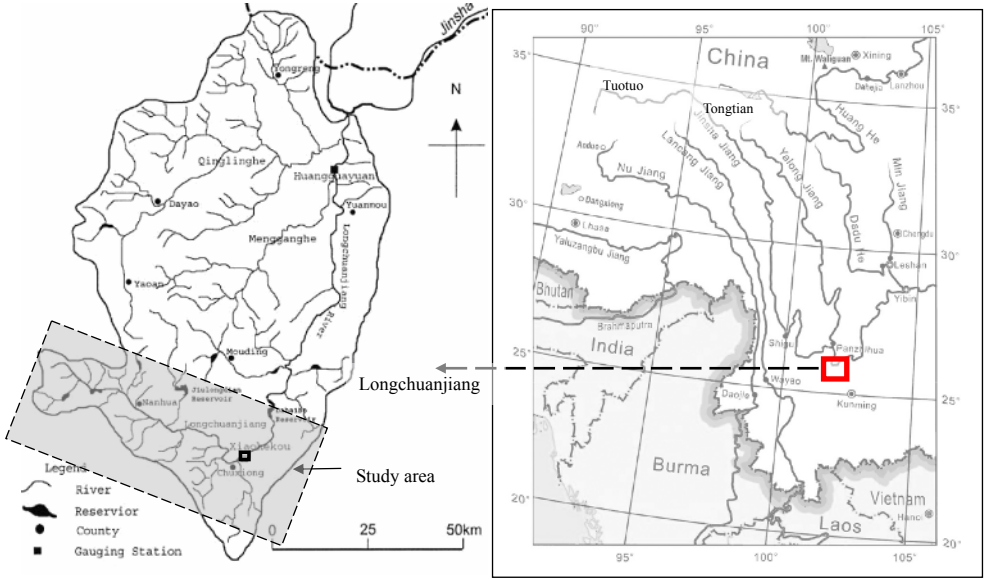

Fig. 1. Location map of the Longchuanjiang River with sampling sites and gauge stations, and other Changjiang's tributaries, China.

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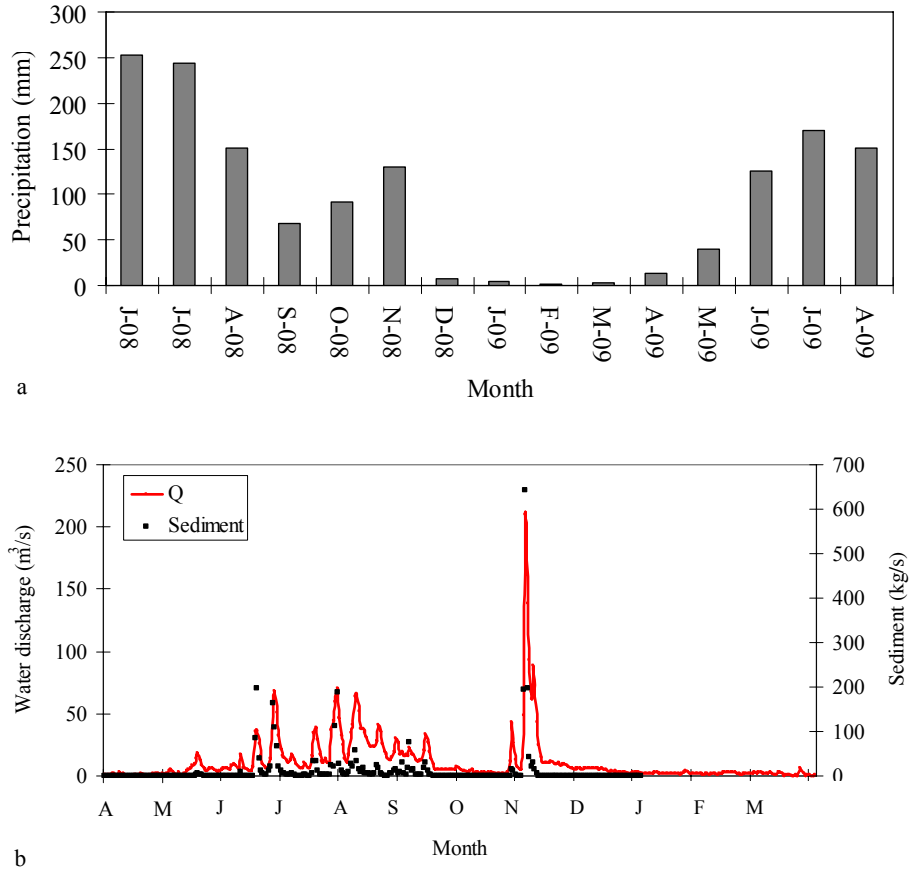

Fig. 2. Hydrological characteristics in the upper Longchuanjiang River from April 2008 to March 2009 (observed at the Xiaohekou gauge station in the outlet of the river basin): **(a)** monthly precipitation (mm) and **(b)** daily water discharge ($m^3\,s^{-1}$) and sediment flux ($kg\,s^{-1}$).

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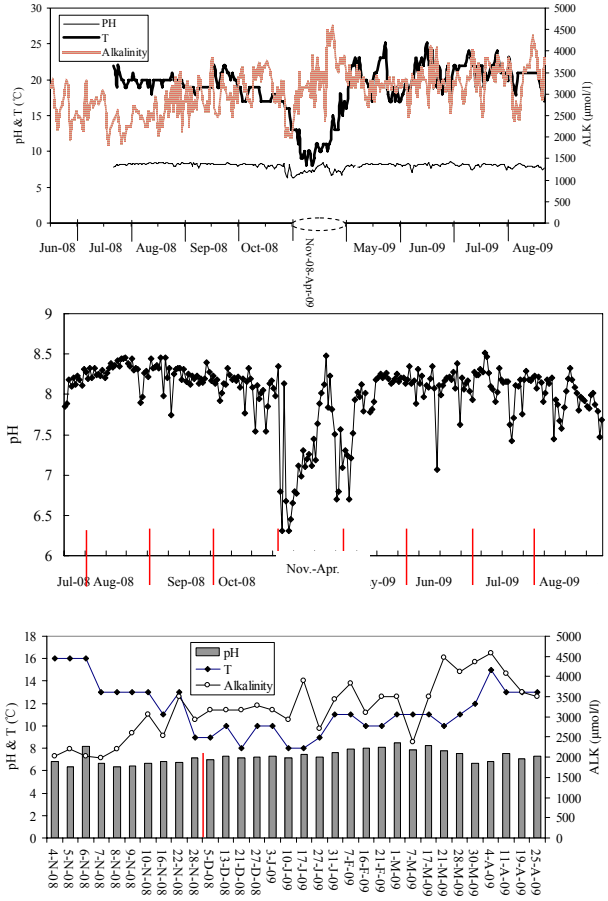

Fig. 3. Daily pH, *T* (°) and alkalinity (μmol l^{-1}) in the Longchuanjiang River, China.

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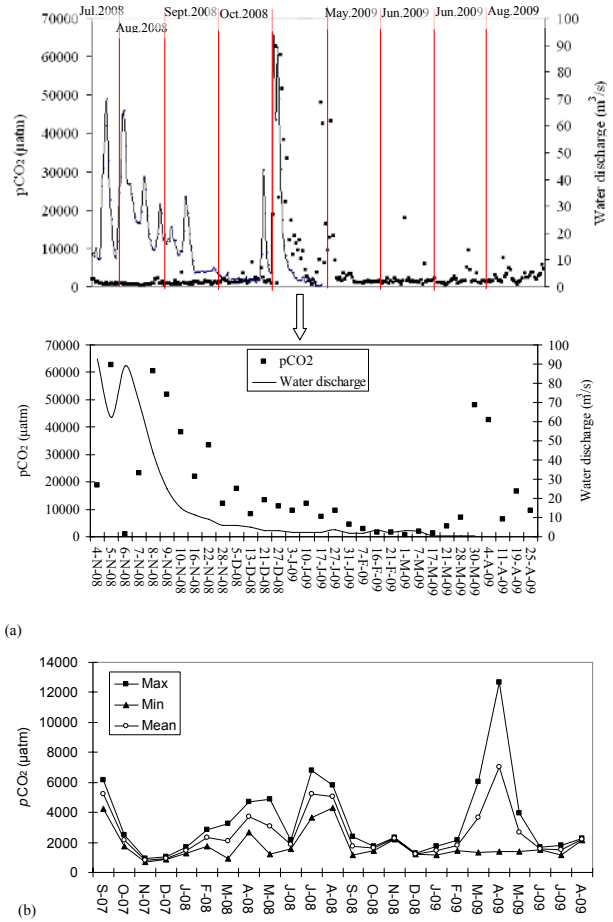

Fig. 4. Daily variability of pCO_2 (μatm) **(a)** and monthly pCO_2 in the September 2007–August 2008 using data from Li et al. (2011) **(b)** in the upper Longchuanjiang River, China.

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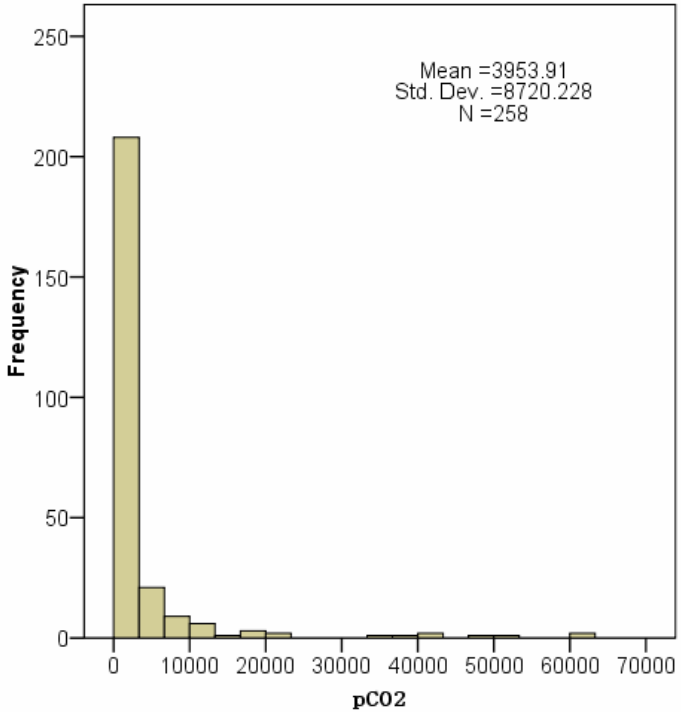

Fig. 5. pCO_2 (µatm) distribution in the upper Longchuanjiang River, China.

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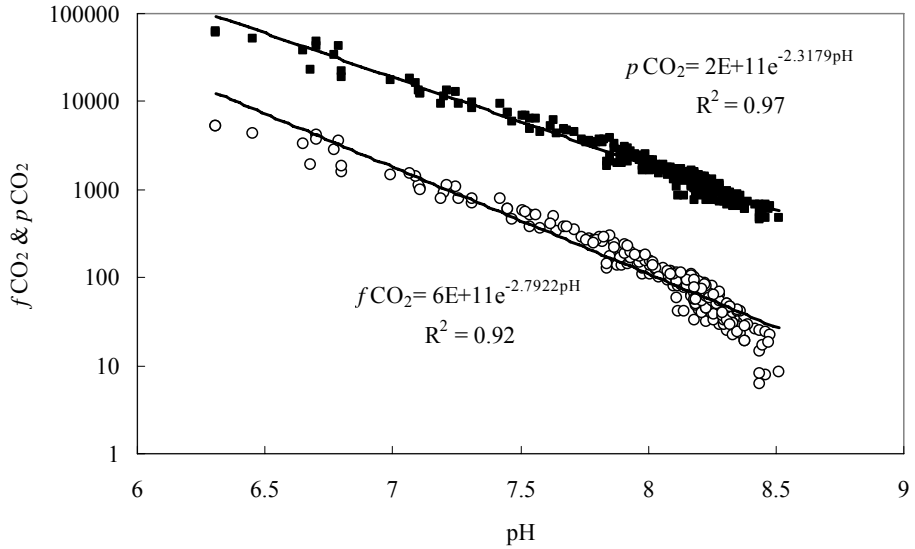

Fig. 6. Scatter plots between CO_2 diffusion flux (fCO_2) (mmol m^{-2} d^{-1}) and pCO_2 (μatm) and pH in the upper Longchuanjiang River, China ($p < 0.001$) (other variables which are not good predictor for fCO_2 are not listed).

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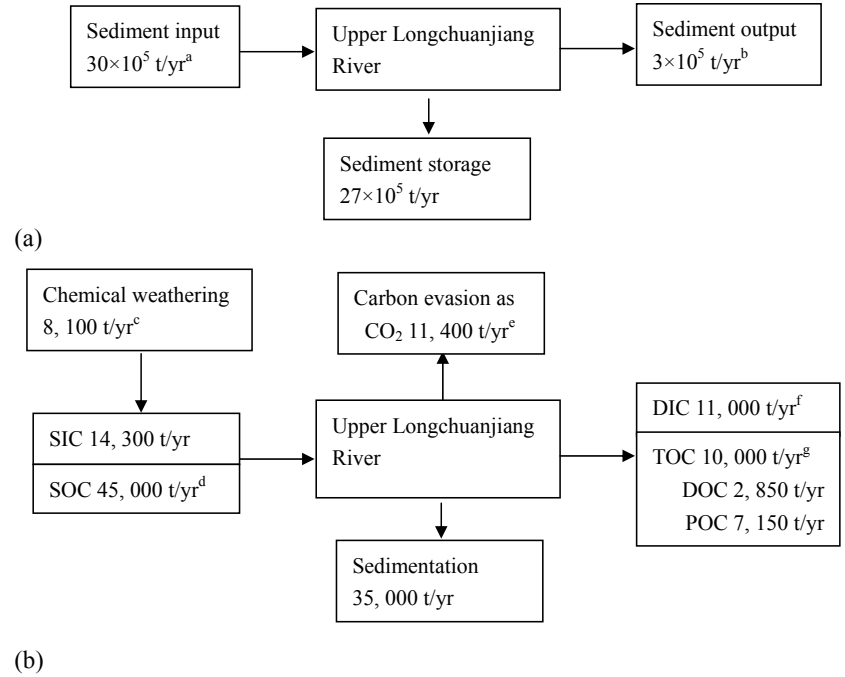

Fig. 7. Sediment **(a)** and carbon **(b)** budgets for the upper Longchuanjiang River using the "active pipe" concept by Cole et al. (2007) and Tranvik et al. (2009). Inputs of carbon include carbon by chemical weathering and soil organic carbon (SOC) and soil inorganic carbon (SIC) via upstream flow, groundwater, atmospheric deposition, and atmospheric CO_2 fixation. Loss of carbon includes inorganic and organic carbon sedimentation, CO_2 degassing to atmosphere, and transport to downstream and related transformations. In our study, SOC content of 1.5 % in soils is designated (Zhang et al., 2008), and transformations of carbon species and labile organic carbon are neglected. a: Lu and Higgitt (2001); Zhou et al. (2004); Ding et al. (2009) b: Lu et al. (2011b); this study c: Li et al. (2011) d: 1.5 % of SOC; Zhang et al. (2008) e: This study f: Lu et al. (2011b) g: Lu et al. (2011b).

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