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

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SUMMARY

Rivers have been under sampled to investigate carbon degassing, especially in the tropical and subtropical regions. An unprecedented high-temporal-resolution (daily) sampling during July 2008–August 2009 was conducted in the Longchuan 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 using Henry's constant and CO_2SYS. The pCO_2 levels ranged from 230 to 8300 μatm with an average of 1230 μatm and obvious daily and seasonal variations. More than 92% samples were supersaturated with CO_2 in contrast to the atmospheric equilibrium (380 μatm). pCO_2 values in the river water in the wet season were relatively low, except in the flooding event in November, due to a dilution effect by heavy rainfall. In contrast, the pCO_2 levels in the dry season were much higher, due to lower pH resulted from anthropogenic activities. Net CO_2 degassing and pCO_2 were strongly correlated with dissolved nitrogen, 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 Longchuan River was about 27 mol/m^2/yr, with the upper limit of 50 mol/m^2/yr. Our study also indicated that among the carbon remobilized from land to water, around 7% (2800 t C/yr) of the total carbon was emitted to the atmosphere, 42% (17,000 t C/yr) deposited in the river-reservoirs system and 51% (21,000 t C/yr) exported further downstream. High spatial and temporal resolution of estimates of CO_2 emission from the world large rivers is required due to extremely heterogeneous catchment characteristics and anthropogenic activities in space and time.

1. Introduction

Fluvial exports of organic and inorganic carbon to oceans (ca. 1 Pg/yr) 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 reservoirs is higher than its equilibrium concentration relative to CO_2 in the atmosphere (i.e., 380 μatm), indicating that fresh waters have a potential of large CO_2 degassing 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). For example, water-to-air CO_2 evasion (470 Tg C/yr) was six times higher than the total fluxes of riverine TOC (36 Tg C/yr) and DIC (35 Tg C/yr) for Amazonian River (Richey et al., 2002). Carbon emissions as CO_2 from global inland waters to the atmosphere were 1.4 Pg/yr (Tranvik et al., 2009), of which, 0.35 Pg C/yr 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 (pCO_2) of aqueous carbon dioxide 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; Zhang et al., 2009a). The aqueous CO_2 in rivers

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generally has two sources: (1) allochthonous, i.e., soil CO_2 from mineralization/decomposition of terrestrial organic 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 various 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 oversaturation of dissolved CO_2 in rivers could be misestimated if the estimation is conducted using a specific temporal and spatial scale. 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 because of suitable temperature and hydrological conditions for plankton, leading to a poor quantification of carbon emission from inland waters, especially in Asia and Africa where such data are very deficient. 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; Wang et al., 2007; Yao et al., 2007; Zhai et al., 2005, 2007; Chen et al., 2008; Zhai and Dai, 2009; Zhang et al., 2009b). Despite many research efforts devoted to the major element geochemistry and associated 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 et al., 2009a), little information on CO_2 emission is available, especially in its headwater. Although carbon diffusion flux from the entire Yangtze basin has been estimated (cf. Wang et al., 2007), mere use of the datasets obtained in the Datong station of the lower Yangtze could result in large uncertainties due to distinct spatio-temporal discrepancies in water chemistry, nutrient supply and human disturbance in the river basin.

In this paper, we selected the Longchuan River in the upper Yangtze River, to perform a preliminary investigation on aqueous pCO_2 through daily sampling across an entire hydrological year. The main objectives of this study are to reveal the daily and seasonal variations of pCO_2 and examine the controls of the variations, as well as to quantify water-to-air CO_2 flux. Past studies on the Longchuan River included major ion geochemistry and chemical weathering, transports and fluxes of nutrients and organic carbon (Li et al., 2011; Lu et al., 2011, 2012).

2. Materials and methods

2.1. Study area

The Longchuan River originates from 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 in the upper Yangtze River (Fig. 1). The main channel drains a length of 231 km and the total elevation fall is 2300 m (from 3000 to 700 m a.s.l). 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, 2008b). 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 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., 2012). 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., 2011). Very high riverine dissolved solutes were from Chuxiong City, adjacent to the sampling location (Li et al., 2011).

2.2. Sampling and analyses

Monthly precipitation (June 2008–August 2009), daily discharge and sediment flux (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 8:00 am were conducted from 15 June, 2008 to 31 August, 2009 at the Xiaohekou gauge station, and a total of 295 samples were collected due to low sampling frequency in the winter. 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 °C 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 hydrochloric acid on 100 ml of filtrated sample water on the sampling day (Telmer and Veizer, 1999; Yao et al., 2007; Wang et al., 2011), the concentrations of alkalinity presented were the averages. All the containers were rinsed with Millipore-Q water (18.2 MΩ) and dried for acid-washed vials. 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 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

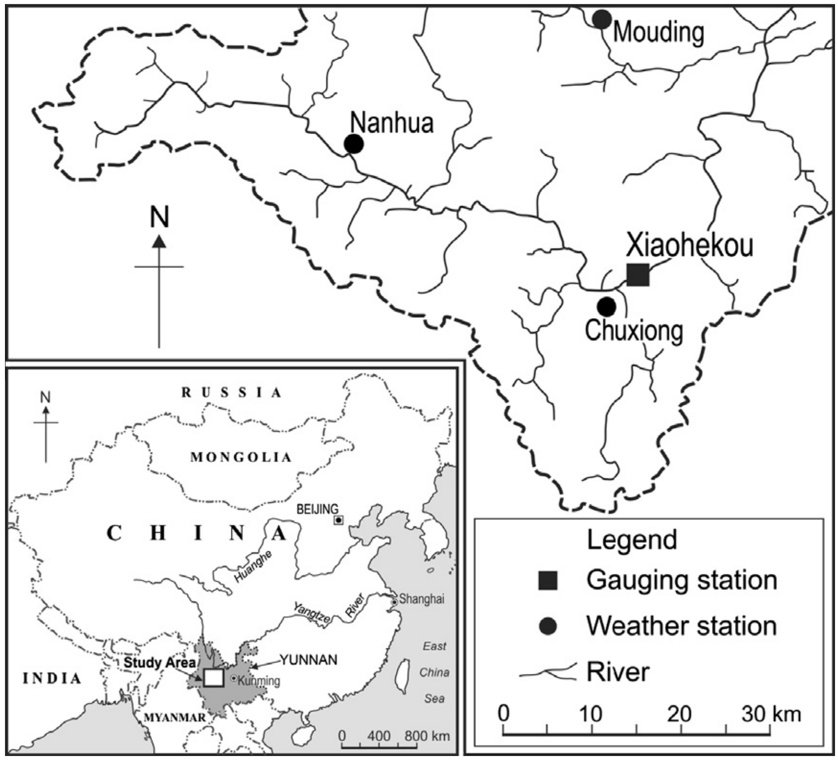

Fig. 1. Location map of the Longchuan River with sampling site and gauge station, China.

riverine DIC species and calculated using the following equations (Telmer and Veizer, 1999; Yao et al., 2007):

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

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

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

where $pK = -\lg K$

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

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

Zhang et al. (2009a) reported the contribution of 2.1% of carbonate to total alkalinity even in the waters with high pH 8.42 in China's carbonate-controlled rivers. 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 7.4–8.5 for those samples representing natural processes in the Longchuan River (Yao et al., 2007). This method has been widely used and demonstrated high riverine pCO_2 in the China's river systems (e.g., Yao et al., 2007; Wang et al., 2011). To compare its effect for aqueous pCO_2, pCO_2 and DIC species were also derived from CO2SYS (Lewis and Wallace, 1998), which is proved to be close to PHREEQC (Hunt et al., 2011).

2.4. Correlating with other variables

Temporal changes of environmental variables can influence river water chemistry. Net CO_2 degassing and pCO_2 were linked to other variables to identify key control factors. 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 selected to quantify their relations with net CO_2 flux and pCO_2. Major ions and dissolved Si were from Li et al. (2011), where twice per month sampling over a 2-year period for measurements of *T*, pH, DIC and major ions. Monthly averages (July 2008–August 2009) of DOC and POC were from Lu et al. (2012), while averages of nutrients (July 2008–March 2009) from Lu et al. (2011). 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. All the statistical procedures were performed using statistical product and service solution (SPSS) 15.0 for Windows.

2.5. Data quality

Alkalinity can be titrated using HCl with various concentrations ranging from 0.01 M (Zhang et al., 2009a) to 0.1 M (Hunt et al., 2011). For our study, alkalinity was titrated using a 0.0226 M HCl with the indicator of tropeolin D. Two replicates for individual sample indicated the uncertainty of 0–10% with a total average of 2.4% (indicated by standard deviation/mean × 100%).

It has been reported the overestimation of aqueous pCO_2 due to the presence of significant non-carbonate alkalinity (NC-Alk) in several USA and Canadian rivers, and this NC-Alk was dominated by nitrogen, phosphorus, silicate, and organic species in particular (Hunt et al., 2011). In the Longchuan River, dissolved inorganic nitrogen (DIN) was contributed by NO_3^- and NH_4^+ (Lu et al., 2011), and dissolved phosphorus (0.5–1.8 with the average of 1.1 μM) (Lu et al., 2011) and dissolved silicates (228 μM) (Li et al., 2011) represented a very small proportion of NC-Alk (Oczkowski, 2002). Thus, the potential uncertainty of our titration could be caused by organic species. Dissolved organic carbon (DOC) ranged from 430–1290 μM with an average of 710 μM in the Longchuan River (Lu et al., 2012), and around 250 μM NC-Alk contributed 8% to the total alkalinity (~3100 μM) in the River (assuming NC-Alk representing ~36% of DOC concentration;

Hunt et al., 2011). Further, the linear regression between NC-Alk and pH demonstrated that NC-Alk could be neglected when pH > 7.4 even in the enriched humic acids rivers (i.e., Hunt et al., 2011). In the Longchuan River, more than 90% of the samples had pH values >7.4. Thus, an overestimation of CO_2 release to atmosphere would be minimum in the Longchuan River, where DOC was low compared to alkalinity over the measured pH averaging 8.

Past studies reported that pCO_2 in the Yangtze River basin can be as much as 29 times the atmosphere (Chen et al., 2002). In our study, the extremely high pCO_2 values due to sewages were carefully scrutinized.

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), the minimum value was in April 2008 (0.12 m^3/s) (Fig. 2b). Total water flow (3.5×10^8 m^3/yr) was close to the average water discharge of 3.2×10^8 m^3/yr (cf. Lu, 2005). Water discharge from May to November accounted for 91% of the total water discharge. Sediment flux exhibited a strong synchrony with water flows and varied from 0 kg/s in the dry season to 643 kg in the beginning of November due to the large storm (Fig. 2b). The sediment load (2.7×10^5 t/yr) was lower than the annual average of 4×10^5 t/yr for the period 1970–2001 (cf. Lu, 2005), indicating a large amount of sediment trapped behind dams and soil erosion control through vegetation recovery.

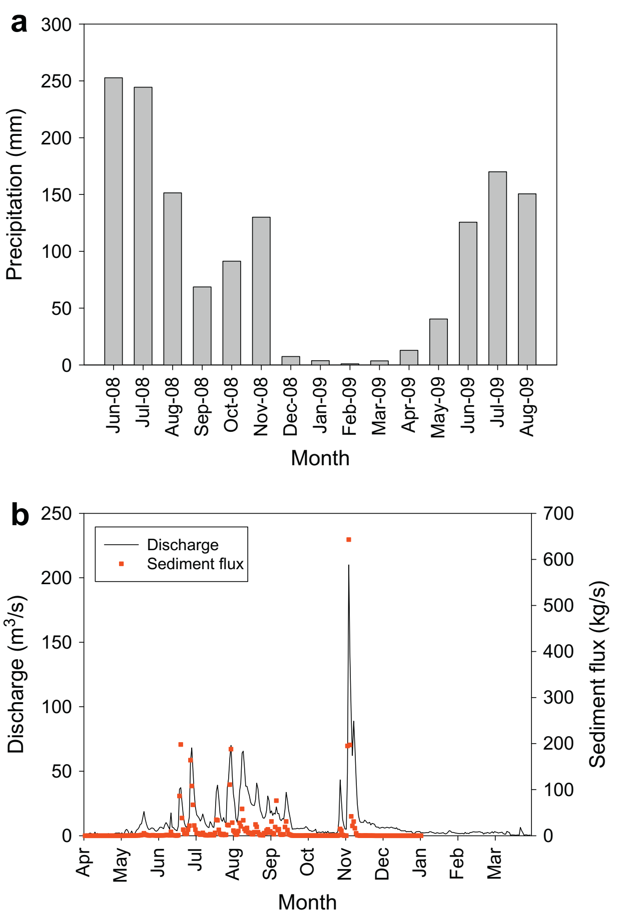

Fig. 2. Hydrological characteristics in the upper Longchuan River (observed at the Xiaohekou gauge station in the outlet of the river basin): (a) monthly precipitation (mm) from June 2008–August 2009, and (b) daily water discharge (m^3/s) and sediment flux (kg/s) from April 2008 to March 2009.

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 (July 2008) and 4577 μmol/l (April 2009) (Fig. 3), with a negative correlation with water discharge ($HCO_3^- = 3.69Q^{-0.116}$; $R^2 = 0.6$, $p < 0.01$; HCO_3^- in mmol/l and Q in m^3/s). The slight decrease with a drastic increase in water discharge in the flood period was due to the enhanced dissolution of carbonates and detrital calcite as a result of intensified soil erosion during flooding season (Chen et al., 2002; Li et al., 2011).

The partial pressure of 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 above 3300 μatm, nine times the atmosphere level.

The abnormal high pCO_2 (62,712 μatm) occurred in the beginning of November 2008, slightly lagging behind the large flooding

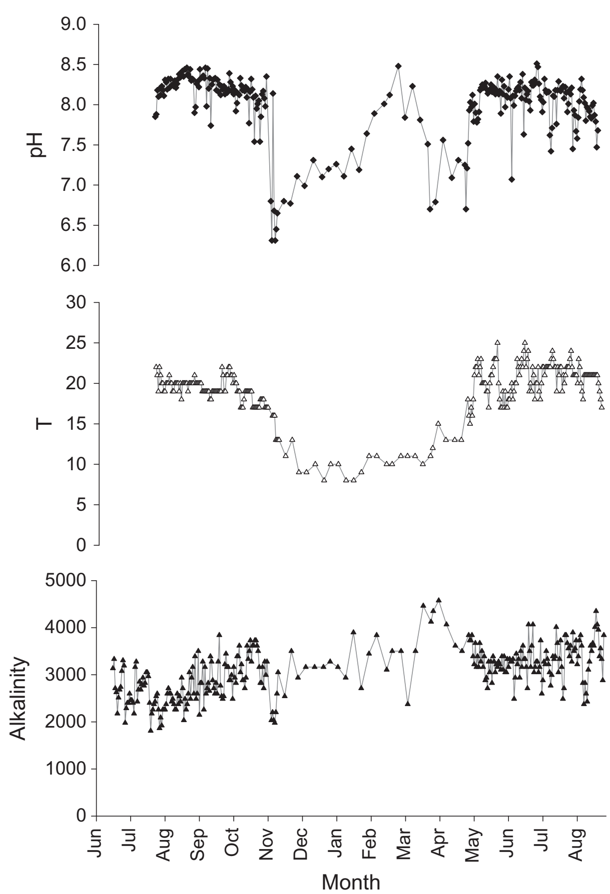

Fig. 3. Daily pH, T (°C) and alkalinity (μmol/l) in the Longchuan River during June 2008–August 2009, China.

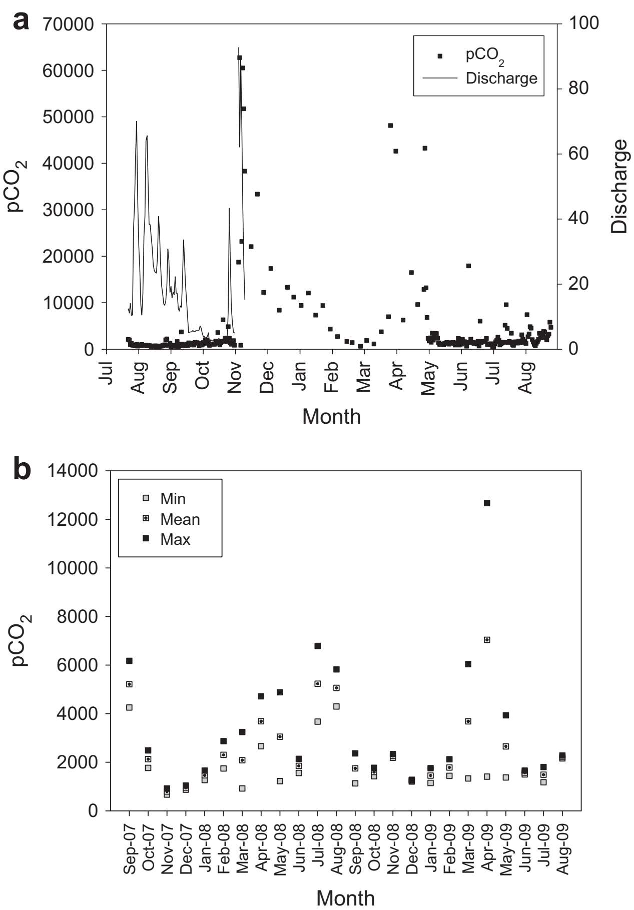

Fig. 4. Daily variability of pCO_2 (μatm) during July 2008–August 2009 (a) and monthly pCO_2 (μatm) during September 2007–August 2009 using data from Li et al. (2011) (b) in the upper Longchuan River, China.

on the second and third day of November (Fig. 2 and 4). This large pCO_2 values lasted till the initial May (the beginning of the wet season) and further till February (Fig. 4a). 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 the values were smaller than 2600 μatm (Fig. 4a). The pCO_2 were lower in the remaining wet season, especially from July to September 2008.

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 (Fig. 4b). Monthly pCO_2 in July–September 2008, however, was higher than averages from the daily measurements (Fig. 4b), demonstrating the necessity of more extensive sampling for pCO_2 gradient and thus CO_2 degassing flux.

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, 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 organisms, and (4) CO_2 evasion from water to air. The first two processes contribute pCO_2 increase, while the last two processes can be responsible for pCO_2 decrease.

The 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. This could result in as high as 50,000 μatm of pCO_2 for soil atmosphere (Telmer and Veizer, 1999). 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 the stream will dilute the pCO_2 in rivers (Finlay, 2003; Hope et al., 2004). On the other hand, biogenic CO_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 Longchuan River (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 in the high and low flows, respectively) in the Longchuan River (Lu et al., 2012). This seems 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; Zhang et al., 2009a), and other rivers in the world (i.e., Barth et al., 2003). Simultaneously, aqueous photosynthesis was at a low level given the highly turbid environment, reflected by a high suspended solid concentration of 150–450 mg/l in the high flow condition (Lu et al., 2012). On the other hand, inactive microbial activities in soils and *in situ* promoting photosynthesis due to high water clarity can decrease pCO_2 in the dry season (Yao et al., 2007). The pCO_2 of our study showed an obvious increase in the dry season and possibly can be due to input of pollutants. During the dry season, industrial and domestic wastes from the adjacent city (Chuxiong) caused lower pH values (Fig. 3 and 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. During the wet season, concentrated rainfall diluted aqueous pCO_2 and the waste waters from the adjacent city (i.e., Chuxiong) and subsequent pH rise in the Longchuan River, resulting in lower pCO_2 levels.

Rains occurred in the beginning of May after a long dry period (Fig. 2). The rainwater infiltrated into the soil, coupling with increasing temperature, 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, 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. Little rain occurred in October, followed by large storms in the beginning (91.3 mm in the first day) of November, partially resulting in an elevated pCO_2 (62,700 μatm) in the Longchuan River (Figs. 2 and 4). However, it is yet unclear that whether these extremely values were representative of riverine processes or were from sewages. The consequent largest sediment concentration (Fig. 2) and negligible photosynthesis corroborated pCO_2 dominantly controlled by soil CO_2. The pCO_2 dramatically decreased due to the dilution effect particularly during the second huge flood, e.g. the monthly minimum pCO_2 of 856 μatm occurred immediately after the heavy storms (Fig. 4a). During this period, biogenic CO_2 release and uptake must be small because of the high turbidity and turbulence, fast flow, and the short residence time of waters.

Low pH values occurred during higher water discharge, though there were no significant linear correlation between daily water discharge and pH (i.e., $Q > 25\ m^3/s$; Fig. 2b; Fig. 3). Monthly pH values in the wet season (May–October) showed significant relations

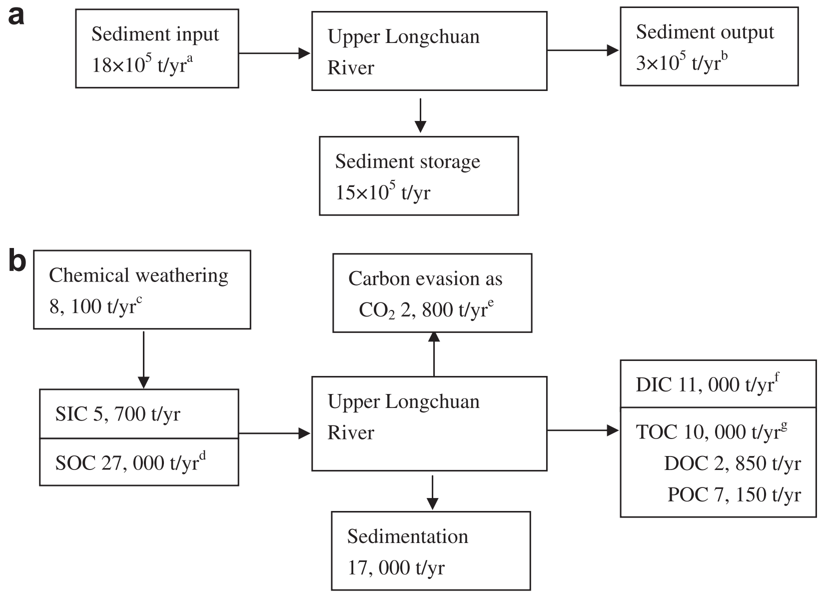

Fig. 6. Sediment (a) and carbon (b) budgets for the upper Longchuan River using the "active pipe" concept by Cole et al. (2007) and Tranvik et al. (2009). Inputs of carbon include carbon by chemical weathering and soil organic carbon (SOC) and soil inorganic carbon (SIC) via upstream flow, groundwater, 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. (2012); this study; c – Li et al. (2011); d – 1.5% of SOC; Zhang et al. (2008); e –This study; f – Lu et al. (2012); g – Lu et al. (2012).

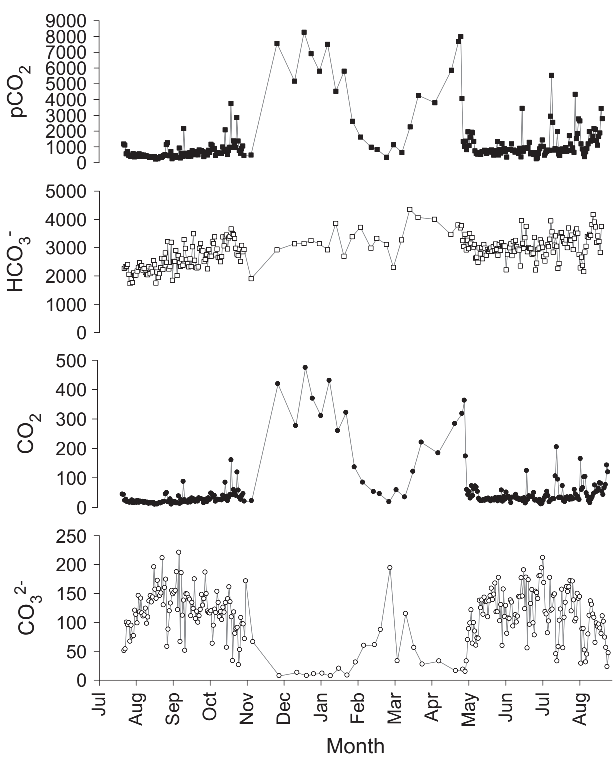

Fig. 5. pCO_2 (μatm) and DIC species (HCO_3^-, CO_2 and CO_3^{2-} in μmol/l) during July 2008–August 2009 from CO_2SYS.

with water discharge using power function ($pH = 8.3Q^{-0.023}$, $R^2 = 0.26$, $p < 0.05$). In the wet season, POC and TOC concentrations (mg/l) linearly increased with water discharge (m^3/s) ($TOC = 0.36Q + 12.73$, $R^2 = 0.46$, $p < 0.01$; $POC = 0.40Q + 3.29$; $R^2 = 0.67$, $p < 0.01$), indicating a mixture of soil erosion and urban sewage via rain runoff. The high ratio (>30) of carbon to nitrogen in particulate organic matter (POM) in the flood season also reflected the contributions of urban wastewaters (Lu et al., 2012). Anthropogenic markers of elements such as K^+, Na^+, Mg^{2+}, Cl^- and SO_4^{2-} with slight fluctuations compared to water discharge (Table 1), also indicated additional inputs from the urban sewage compensating the diluted effects of precipitation. Therefore, large and rapid pH fluctuations during the flooding in November pointed out that lower pH and consequent extremely high pCO_2 values were from urban sewage and these extremely values (November 2008 and the initial of May 2009) together with pCO_2 values in the end of the March by instantaneous pollution should be removed for calculations of water–air CO_2 exchange.

Therefore, pCO_2 values below 13,000 μatm representing the riverine processes were remained (total 244 out of 258 removed). Their values were comparable to the monthly values (670–12,700 μatm) and the pCO_2 values (600–9600 μatm) in the Yangtze River reported by Chen et al. (2002). Their revised monthly average values were exhibited in the Table 2. The pCO_2 averaged 2100 ± 2300 μatm, comparable to monthly average of 2600 μatm (Fig. 4b) and also consistent with the more than 90% of pCO_2 values <2600 μatm (Fig. 4a). Their correlations with environmental variables were shown in Table 3.

pCO_2 from CO_2SYS and Henry's law showed similar trends ($pCO_{2CO2SYS} = 0.6pCO_{2Henry}$; $R^2 = 0.997$, $p < 0.001$), ranging from 230–8270 μatm with an average of 1230 ± 1440 μatm (those values representing anthropogenic disturbances excluded) (Fig. 5). There were total 20 values below 380 μatm (only five samples with $pCO_2 < 300$ μatm; accounting 2% of the total samples), and these unsaturated pCO_2 values were primarily found in August 2010 due to high water discharge (Fig. 4a). Contribution of carbonate to total alkalinity (CO_3-Alk) accounted for 0.5–15% with a mean value of 7.3% in the Longchuan River, thus, the riverine pCO_2 could be over-estimated without considering CO_3-Alk in the Chinese rivers like Luodingjiang and Xijiang (i.e., Yao et al., 2007; Zhang et al., 2009a). Moreover, there were significant and positive relations between the CO_3-Alk contributions and pH values ($CO_3\text{-Alk}\% = 7 \times 10^{-17}\ pH^{18.71}$; $R^2 = 0.98$, $p < 0.01$), thus carbonate contribution

Table 1
Relations (Spearman's rho) between water discharge and environmental variables and pH during the wet season (September–October 2007, May–November 2008 and May–August 2009; two samples per month).

	pH	K^+	Na^+	Ca^{2+}	Mg^{2+}	Si	Cl^-	SO_4^{2-}	HCO_3^-	TDS
Q	−0.47	−0.12	−0.14	−0.68	0.03	−0.68	−0.20	−0.19	−0.65	−0.61
p	0.021	0.567	0.527	0.000	0.907	0.000	0.349	0.377	0.001	0.002
n	24	24	24	24	24	24	24	24	24	24

Table 2
Monthly pCO_2 (μatm) in the upper Longchuan River, China (those values representing anthropogenic pollution were excluded).

	N	Mean	Std. deviation	Minimum	Maximum
July-2008	11	1101	499	676	2102
August-2008	31	846	379	451	2219
September-2008	30	1100	571	580	3721
October-2008	31	1820	1165	839	6326
November-2008	2	6541	8040	856	12,226
December-2008	3	10,869	2319	8399	13,000
January-2009	5	8514	2887	4327	12,095
February-2009	3	1933	683	1440	2713
March-2009	5	2876	2584	636	6986
April-2009	2	7952	2360	6283	9621
May-2009	30	2626	3046	891	13,000
June-2009	29	1649	938	661	6061
July-2009	31	1895	1752	478	9565
August-2009	31	2769	1514	720	7445
Total	244	2145	2332	451	13,000

(<2%) could be neglected when pH < 7.5. However, pH vales ranged from 7.5–8 in most natural river waters. Although it is possible to over-estimate water–air CO_2 degassing without consideration of CO_3-Alk, Eqs. (1)–(8) has been widely used (i.e., Yao et al., 2007). Aqueous CO_2 concentrations ranged from 9–474 μmol/l with an average 53 μmol/l, and were negatively related with pH ($CO_2aq = 2 \times 10^{11}e^{-2.75pH}$; $R^2 = 0.96$, $p < 0.01$).

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 (cf. Richey et al., 2002):

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

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) 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 and hydrological features in the Longchuan Rver basin, D/z is estimated to be 8 cm/h for the calculation of CO_2 degassing flux. The similar D/z was also adopted by Wang et al. (2007) for calculations of CO_2 outgassing from the Yangtze basin. We also designated the upper limit value of 15 cm/h for D/z (Wang et al., 2007; Yao et al., 2007).

Estimate results showed that the Longchuan River had a CO_2 diffusing flux around 57 mol/m^2/yr, and the corresponding upper limit was 100 mol/m^2/yr. Our results were obviously higher than that of most world large rivers, but comparable to that of the Xijiang River, and lower than the karst-terrain Maotiao River in the Wujiang (Table 4). However, 27 and upper limit of 50 mol/m^2/yr for water–air CO_2 efflux in the Longchuan River using CO_2SYS, were much lower (cf. half of the values from Henry's law). This was due to equilibrium constants in the DIC system, and roughly estimates of HCO_3 equaling to alkalinity using Eq. (8). Our results demonstrated that CO_2 degassing from China's rivers, such as Xijiang and Maotiao rivers, could be significantly over-estimated, resulting in CO_2 diffusion fluxes higher than in the Amazon River (Table 4).

Considering that the water surface area is about 8.6 km^2 in the upper Longchuan River (waters accounted for 0.48% of the total land area; Li et al., 2009b), the river will release CO_2 2.3×10^8 mol C/yr to the atmosphere. Thus, the CO_2 degassed from the catchment accounted for approximately 30% of its fluvial TOC flux (7.1×10^8 mol C/yr) or DIC flux (7.9×10^8 mol C/yr) (Lu et al., 2012). Previous study reported the CO_2 degassing flux of 14 mol/m^2/yr in the 1990s from the entire Yangtze basin (Wang et al., 2007). 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

Table 3
Relations between pCO_2/CO_2 outgassing flux and environmental variables in the Longchuan 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
(a) Links between pCO$_2$/CO$_2$ outgassing flux (fCO$_2$) and T, pH, DIC and water discharge using daily data, while and nutrients using monthly averages														
pCO_2	−0.15	−0.96	0.56	−0.47	−0.51	−0.29	0.43	0.77	0.67	0.70	−0.55	0.40	−0.41	−0.43
fCO_2	−0.15	−0.96	0.56	−0.47	−0.51	−0.29	0.43	0.77	0.67	0.70	−0.55	0.40	−0.41	−0.43
p	0.013	0.000	0.000	0.000	0.064	0.313	0.244	0.016	0.050	0.036	0.125	0.286	0.273	0.244
n	258	258	258	131	14	14	9	9	9	9	9	9	9	9

	pH	K^+	Na^+	Ca^{2+}	Mg^{2+}	Si	Cl^-	SO_4^{2-}	TDS
(b) Links between pCO$_2$/CO$_2$ outgassing flux (fCO$_2$) and major elements using instantaneous sampling twice per month in a 2-year period (September 2007–August 2008)									
pCO_2	−0.99	−0.02	−0.16	−0.29	0.13	−0.18	−0.12	0.17	−0.23
fCO_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

Table 4
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)	References
Longchuan River	China	Subtropic	8	2100	57[a]	This study
				1230	27[b]	
Upper stream of Maotiao River	China	Subtropic	10	3740	107.5	Wang et al. (2011)
Luodingjiang	China	Humid subtropic		600–7200		Zhang et al. (2009a)
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	Hélie et al. (2001)
Ottawa	Canada	Temperate	4	1200	29.5	Telmer and Veizer (1999)
Hudson	USA	Temperate	4	1125	5.8–13.5	Raymond et al. (1997)
Rivers[c]					53.6	Cole et al. (2007)
Nature lakes					10.5	Tranvik et al. (2009)
Artificial reservoirs waters					15	Barros et al. (2011)
Hydroelectric reservoirs					11.8	Barros et al. (2011)

[a] Using Henry's law without consideration of carbonate-alkalinity.
[b] Calculated using CO2SYS.
[c] Carbon emission as CO_2 of 0.23 Pg/yr from Cole et al. (2007), river water surface water of 357,627 km^2 from Bastviken et al. (2011).

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.

4.3. Relations with environmental variables

Water flows partly contributed to pCO_2 as observed by Yao et al. (2007). Although this could be reflected by our monthly variability of pCO_2 and huge fluctuations of pCO_2 in the flooding period (i.e., November), their relation was weak ($r = -0.47$, $p < 0.001$; $n = 131$; Fig. 4; Table 3). Yao et al. (2007) ascribed the weak relation between hydrology and pCO_2 to insufficient samplings. Our high-temporal-resolution sampling indicated that water discharge was not a good indicator of aqueous pCO_2.

pCO_2 and CO_2 degassing flux vs. environmental variables demonstrated that temperature variation partially regulated pCO_2 levels by altering the alkalinity or DIC concentration (Table 3). This could be reflected by the daily and monthly variations of alkalinity content (Fig. 3), as well as observed correlations between pCO_2 and DIC ($r = 0.56$, $p < 0.01$). pCO_2 was positively related to dissolved nitrogen, and slightly to phosphorus and biogenic variables. Although increasing nitrogen could elevate aquatic photosynthesis and reduce dissolved CO_2 level, organic matter decomposition and respiration would result in CO_2 production. Thus, there exited different relations between pCO_2 and nutrient levels (e.g., Wang et al., 2007), and 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.

While pCO_2 and CO_2 degassing flux vs. the thermodynamic variable (pH) was undoubted, their strong predictive relations allowed us to identify critical thresholds shifting from CO_2 uptake to gas emitter ($pCO_2 = 10^{12}e^{-2.59\text{pH}}$; $R^2 = 0.95$, $p < 0.01$). When the pH exceeded 8.3, the river acted as carbon sink, but when pH dropped below 8.3, it acted as 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 mask the importance of other variables including water discharge. There is no doubt that parameters including soil characteristics, *in situ* respiration and photosynthesis control pH in undisturbed river systems, and thus regulated chemistry equilibrium of DIC system (Cole and Caraco, 2001). Riverine respiration of allochthonous organic matter produces CO_2, decreases pH and increases pCO_2.

It should be noted water acidification is a world-wide problem (Reuss et al., 1987; Sullivan et al., 2005; Ginn et al., 2007; Duan et al., 2011). In the Yangtze River basin specifically the tributaries 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; Duan et al., 2011). This could increase carbon emission from river waters. For example, pCO_2 in the Longchuan 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 83% in the upper Yangtze (Lu and Higgitt, 2001) was adopted in our work (Fig. 6a), which was mainly attributed to many reservoirs in the upper catchment. Assuming soil erosion rate was about 1000 t/km^2/yr in the upper Longchuan River, and sediment input from catchment to the river was about 18×10^5 t/yr, comparable to the observation by Zhou et al. (2004).

Our budget indicated that 40,800 t C/yr input from the catchment to river, of which inorganic carbon accounted for 34% (13,800 t/yr). Overall, 7% (2800 t/yr) of the total carbon or 20% of inorganic carbon from catchment released to atmosphere, while 42% (17,000 t/yr) of the carbon was trapped primarily by reservoirs and river channels (Fig. 6b). Past studies reported large variations of release rate of atmospheric carbon from rivers to the atmosphere (2–30%; Liu et al., 2010).

Higher concentrations and areal exports of organic carbon in the upper Longchuan catchment (Lu et al., 2012) could contribute to CO_2 evasion. Our results, however, did not show significant relations between CO_2 degassing flux and DOC or POC (Table 3). Elevating soil erosion rate by the intensified anthropogenic activities (Zhou et al., 2004; Lu, 2005) could increase sediment transport to river system. However, more than 40% 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. For example, more organic species in the river-reservoir system could increase the potential rate of the decomposition of organic carbon particularly under global warming (Cole et al., 2007; Tranvik et al., 2009), thus decreasing pH, and this also could change the net heterotrophy and the amount of terrestrial organic matter respired in the river (Cole and Caraco, 2001), increasing pCO_2 and CO_2 efflux. Future efforts are to quantify the potential roles of riverine respiration and aquatic photosynthetic CO_2 uptake on the CO_2 flux (Liu et al., 2010, 2011).

5. Conclusion

The riverine water pCO_2 was supersaturated with respect to atmospheric CO_2, averaging about 1230 μatm, thus resulting in a water-to-air interface CO_2 outgassing flux of around 27 mol/m^2/yr in the Longchuan River. Carbon efflux from CO2SYS was one half of the value calculated using Henry's law without considering carbonate-alkalinity, demonstrating significant over-estimation of CO_2 degassing from China's rivers. The aqueous pCO_2 levels displayed obvious daily and monthly variations due to temporal changes of external biogeochemical processes, *in situ* biogenic activities, nutrients and the thermodynamic variable pH in particular by anthropogenic processes. pH was by far the strongest control on pCO_2 and net CO_2 flux. Higher pCO_2 levels occurred in the dry season, but the pCO_2 was lower in the wet season, except in November when both minima and maxima pCO_2 were observed during storm events. The higher pCO_2 in the early wet season (May) was mainly due to increasing baseflow and interflow flushing soil CO_2 into streams, whereas the lower pCO_2 in the wet season (June–October) primarily resulted from the diluted effect by precipitation. The river was a carbon source of atmospheric CO_2. Water acidification can contribute to higher carbon emission. Further study should include potential metabolic controls such as riverine respiration and aquatic photosynthesis by phytoplankton 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 like reservoirs construction in the Yangtze River are altering riverine carbon biogeochemical processes. Water acidification in most rivers undoubtedly increases CO_2 degassing flux. Estimate for an entire basin using one or two specific sampling stations particularly in the downstream will under-estimate CO_2 emission. Therefore, re-evaluation of CO_2 diffusion flux at the water-to-air interface using high-resolution methods, i.e., intensified sampling and more accurate geochemical modeling becomes an increasingly important issue in re-assessing global terrestrial carbon balance.

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