Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-505
Manuscript under review for journal Biogeosciences
Discussion started: 13 December 2017

CO_2 partial pressure and CO_2 emissions from the lower Red River (Vietnam)

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Abstract. The Red River (Vietnam) is a good example of a South-East Asian river system, strongly affected by climate and human activities. This study aims to quantify the spatial and seasonal variability of carbon dynamic and CO_2 outgassing at the water-air interface of the lower Red River system. The monitoring of water quality and CO_2 emission were carried out for 24h cyclings at the five stations during the dry and monsoon seasons. The riverine water pCO_2 was supersaturated with CO_2 in contrast to the atmospheric equilibrium (400 ppm), averaging about 1588.6 ± 884.6 ppm, thus resulting in a water–air CO_2 flux of 26.9 ± 18.4 mmol m^{-2} day^{-1}. The CO_2 outgassing rate was characterized by significant spatial variations, highest at Hoa Binh station (Da River) due to the dam impoundment and the highest river flow. Surprisingly, CO_2 outgassing was higher in the day time (30.4 ± 21.2 mmol m^{-2} day^{-1}) than in the night time (23.3 ± 15.4 mmol m^{-2} day^{-1}), probably as a result of the combined effect of higher wind speed and water temperature in the day time. Seasonal differences were also observed, higher in the wet season (30.7 ± 23.1 mmol m^{-2} day^{-1}) than in the dry season (23.0 ± 12.2 mmol m^{-2} day^{-1}), due to higher river discharges and higher external inputs of organic matters from watersheds. Conversely during dry season, temperature was among the main factors influencing C dynamic, with higher pCO_2 and fluxes, probably as a result of increased metabolic rates.

Keywords: carbon, CO_2 outgassing, Red River, Vietnam

1 Introduction

Natural hydrological processes and biogeochemistry of many rivers in the world have suffered from the influences of climate change and human activities in their drainage basins. Riverine carbon fluxes and outgassing are important parts of the carbon exchange among terrestrial, oceanic and atmospheric environment. Rivers and streams not only transfer various forms of carbon (dissolved and particulate) to oceans, but also evade a significant amount of carbon to the atmosphere (Battin et al., 2009; Richey

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et al., 2002). Due to CO_2 evasion, the flux of carbon that leaves the terrestrial biosphere through global fluvial network was suggested to be twice larger than the amount that ultimately reaches the coastal ocean (Bauer et al., 2013; Regnier et al., 2013). The existence of hotspot of CO_2 evasion represented 70 % of the emission for only 20 % of the land surface (Raymond et al., 2013). Previous estimates proposed that inland water bodies transport, mineralize and bury 2.7 Pg C yr^{-1}, which is similar to the terrestrial carbon sink for anthropogenic emissions of 2.8 Pg C yr^{-1} (Tranvik et al., 2009). However, more recent studies proposed a lower value of global evasion rate from inland waters, being about 2.1 Pg C yr^{-1} or even less (Raymond et al, 2013; Lauerward et al., 2015).

Carbon fluxes and emissions from rivers are impacted by both natural (plate margin tectonics, volcanic deposits, high elevations, steep slopes, and high intensive rainfall) and anthropogenic factors (high population density, deforestation, reservoir impoundment, intensive agricultures, and urbanization). However, there is a limited understanding of spatial and temporal dynamics of carbon exchange between terrestrial, oceanic and atmospheric environments for the large Asian rivers. In southeast Asia, the river water discharge and sediment loads have been altered dramatically over the past decades as a result of reservoir impoundment, land use, population, and climate changes (Walling and Fang, 2003, 2006; Lu, 2004). Solid sediment loads not only directly contribute to increase the organic carbon content, but also affect chemical weathering and hence carbon consumption and possible carbon emission. Therefore, studies of carbon emission from the large Asian rivers are crucial to quantify geochemical cycles accurately in the context of global change. Some studies noted that data concerning CO_2 evasion (or pCO_2) of Southeast Asian rivers is a high priority in order to precise the global evasion rate from inland water (Raymond et al., 2013; Lauerward et al., 2015).

The Red River with a basin area of 156,450 km^2 is a typical East Asia river that is strongly affected by climate and human activities (Fig. 1). Previous studies reported about the hydrology and suspended sediment load associated to some elements loads (N, P, C) of the Red River (Dang et al., 2010; Lu et al., 2015; Le et al., 2015). Recently, the transfer of organic carbon of the Red River to ocean has been studied (Dang et al., 2010; Le et al., 2017). However, the knowledge of carbon exchange at the air-water interface of the Red River is still limited.

This study aims: i) to investigate spatial and temporal (wet and dry, and day-night) variations of CO_2 partial pressure (pCO_2) and CO_2 flux at the water-air surface of the lower Red River, from the upstream to the downstream part; and ii) to identify some of the factors that may control pCO_2 and CO_2 outgassing rates of the lower Red River. To our knowledge, the present study introduced the first measurement and estimation of CO_2 evasion from the lower Red River.

2 Methods

2.1 Study sites

Five stations were studied in the lower Red River (Vietnam): Yen Bai, Hoa Binh, Vu Quang, Hanoi and Ba Lat (Fig. 1). Yen Bai station was located at the outlet of the Thao river; Hoa Binh station (after Son La and Hoa Binh reservoirs) at the outlet of the Da River; Vu Quang at the outlet of the Lo River;

Hanoi and Ba Lat in the main course of the Red River downstream. The Ba Lat station is located in the Red River mouth, about 50 km from the sea.

The climate in the Red River basin, of tropical East Asia monsoon type, is controlled by the North East monsoon in winter and South West monsoon in summer. It is, thus, characterized by two distinct seasons: rainy and dry season. The rainy season lasts from May to October and cumulates 85 – 90 % of the total annual rainfall in the Red River catchment, whereas the dry season covers the period from November to next April. The monsoon climate weather results in a hydrologic regime characterized by large runoffs during the wet season and low runoffs during the dry season (see below for the detail river discharge in 2014). A series of dams-reservoirs are impounded in both Chinese and Vietnamese territories of the Red River upstream part (Le et al., 2017). In the Da River, two large dams Hoa Binh and Son La were constructed in the river main course whereas in the Lo River, two large dams Thac Ba and Tuyen Quang were constructed in its tributaries.

The upstream part of the Red River in the Chinese part is dominated by mountain areas, which are tectonically active and unstable, and this, combined with intense rainfall, causes high erosion (Fullen et al., 1998) whereas in the Vietnamese part, soils are mostly (70 %) grey and alluvial soils (Le et al., 2017).

Land use was quite different in the three upstream river basins Thao, Da and Lo: Industrial crops dominate (58 %) in the Lo basin, forests and bare land (74 %) in the Da basin, and paddy rice fields (66 %) in the delta area. The Thao basin is characterized by a larger diversity of land use including forest, paddy rice fields, and industrial crops (85 %) (Le et al., 2015).

Population density varied from the upstream to the downstream part of the Red River basin. The delta area, where the Hanoi and Ba Lat stations are located, is characterized by high population density (> 1,000 inhabitant km^2). In the upstream part, where the Yen Bai station (in Thao River), Hoa Binh station (in Da River) and Vu Quang station (in Lo River) situate, population density was much lower, about 100 inhabitants km^{-2} (Le et al., 2015).

2.2 Sampling procedures and analysis

Sampling campaigns were conducted in September (rainy season) and November (dry season) 2014 at the five gauging stations.

Physico-chemical parameters were automatically recorded at the interval of 1 min during 24h for each sampling campaign: pH, turbidity, salinity, chlorophyll *a* by the sensor YSI6920 (YSI, USA); temperature and dissolved oxygen (DO) by a HOBO sensor (USA). These sensors have been calibrated with standard solutions before each measurement campaign. All solutions used for calibration should be at ambient temperature to ensure quality of calibration and all data must be entered on the documents.

In parallel of in-situ measurement, river water samples were hourly collected for analysis of other water quality variables (TSS, DOC, POC, and alkalinity) during 24h. A known volume of well-mixed sample was filtered immediately by vacuum filtration through pre-combusted (at 450 $^{\circ}$C for 6 h) glass fiber filters (Whatman GF/F, 47 mm diameter). The filters were then kept in a freezer (-20 $^{\circ}$C) until analysis of TSS and POC. For the measurement of TSS, each filter was dried for 1h at 105 °C and then weighed. Taking into account the filtered volume, the increase in weight of the filter represented the total TSS per unit volume (mg L^{-1}).

POC concentrations were estimated on the same filters. Filters were then weighed before and after calcination at 550 °C for 4 hours. The difference in weight before and after calcination was multiplied by 0.4 to provide an estimation of the POC content (Servais et al., 1995).

A volume of 30 ml sub-sample of filtrate was acidified with 35 µl 85 % H_3PO_4 acid and then stored at 4 °C in amber glass bottles until measurement of the DOC concentrations using a TOC-V_E (Shimadzu, Japan). The samples, standards and blank measurements were measured in triplicate.

Total alkalinity was hourly determined on non-filtered water samples in situ by titration method (APHA, 1995).

Wind speed and air temperature were measured hourly during 24 h of all sampling campaigns by a handle digital thermometer/anemometer (GM 8901, Total meter, Taiwan).

2.3 Hydrological data collection

Daily and hourly data of river water discharges in 2014 at the 5 hydrological stations studied were collected from the Vietnam Ministry of Natural Resources and Environment (MONRE, 2016). The daily data were collected for all days in 2014, whereas hourly data were obtained for the exact dates of field measurements at the 5 sites (Table 1). The mean annual river flows in 2014 of the Thao, Da, Lo Rivers and in the main axe of the Red River at the Hanoi and Ba Lat stations were: 527 ± 515; 1369 ± 833; 1302 ± 517; 1867 ± 1089; 615 ± 293 m^3 s^{-1}, respectively. Higher values of river discharges were observed in wet season (May to October) than in dry season (January-April; November-December) at all sites (Table 1).

2.4 CO_2 fluxes determination

CO_2 fluxes were determined using direct methods: i) from pCO_2 in the water column measured using an equilibrator connected to an IRGA ii) from pCO_2 determined by the calculation using T_{alk} and pH measured in-situ.

2.4.1 From measured pCO_2

Equilibrator was used to determine the pCO_2 in water balanced with the air. The equilibrator was designed, as described in Frankignoulle et al. (2001), as follow: a vertical plastic tube (height: 73 cm, diameter: 9 cm) which is filled up with about 250 glass marbles (diameter = 1.5 cm) in order to increase the surface exchange between water and air. The river water (water inlet) through a submerged pump at 20 cm below the river surface water comes into the equilibrator from the top of the tube. The water inlet can be regulated by a flow controller installed under the tygon tubing, which joins the water inlet with the pump. A closed air circuit ensures circulation through the equilibrator (from the bottom to the top), a water trap, a particle filter, a regulator and an IRGA (Licor 820, Licor®, USA), which was calibrated before each sampling campaign using a series of standards concentrations of 0, 551 and 2756 ppm CO_2 (Air Liquide®). The IRGA was connected to a computer interface, which allows recording the pCO_2 every second. Values were recorded during 24 h continuously.

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Manuscript under review for journal Biogeosciences
Discussion started: 13 December 2017

The water-air CO_2 fluxes from the equilibrator measurement at each site were calculated by the formula proposed by Raymond and Cole (2011) as followings:

$F_{Equi} = k_{600} * \alpha * (pCO_2\ water – pCO_2\ air)$ Eq. (1)

Where F was the CO_2 flux from water (µmol m^{-2} s^{-1}) and converted in mmol m^{-2} d^{-1};

$k_{600,}$ was gas transfer velocity of CO_2 or piston velocity (cm h^{-1}), and was calculated according to a wind speed function (k vs. U_{10}). K_{600} was calculated using the equation from Raymond and Cole (2001)*,* which developed from a data set of different estuaries and rivers as follow:

$k_{600} = 1.91 \times exp(0.35 \times U_{10}) \times (Sc / 600)^{-0.5}$ Eq. (2)

Where U_{10} was the wind speed (m s^{-1}) at 10 m height above the surface water (was calculate from the wind speed (m s^{-1}) at 2 m height, (“Appendix 8.6-Wind Speed Calculations” 2010); and Sc was the Schmidt number, normalized to Schmidt number of 600 (Cole and Caraco, 1998).

α was the solubility coefficient of CO_2 for given temperature and salinity (Weiss, 1974) (mol L^{-1} atm^{-1}). In this case, $\alpha = 0.034$ mol L^{-1} atm^{-1}

pCO_2 water was CO_2 concentration in surface river water from Equilibrator measurement or from CO2_SYS calculation.

pCO_2 air was considered as a constant of 400 ppm

Since we measured wind speed on field at a height of 2 meters (Uz = 2) with a handle anemometer, the formula of Amorocho and DeVries (1980) was used to estimate the wind speed at 10 m height (U10).

The determination of the emissions depends on the gas exchange velocities (k_{600}), and the latter may represent a considerable source of uncertainty when calculating water-air CO_2 outgassing flux (Raymond et al., 2012; Raymond et al., 2013). There were some studies focused on the estimation of k_{600}, based on empirical equations with different techniques (Jähne et al., 1984; Liss and Merlivat, 1986), for different type of ecosystems and specific weather conditions (Devol et al., 1987; Marino and Howarth, 1993; Clark et al., 1995; Carini et al., 1996; Guérin et al., 2007; Vachon et al., 2010). As a result, different empirical equations have been proposed, which lead to different quantitative estimations of k_{600} coefficient. In our study, we decided to use the empirical equation of k_{600}-wind from Raymond and Cole (2001) developed from a data set of different estuaries and rivers.

Some studies indicate that k_{600} values are closely related to flow velocity and channel gradient for rivers (Alin et al., 2011), less related to wind velocity as in lakes and oceans (Abril et al., 2000; Abril and Borges, 2004; Abril et al., 2009) and that water current can strongly affect the magnitude of k_{600}, especially in location where the wind speed is low but water current is high (Borges et al., 2003). In our study, k_{600} is determined by the Eq. (2) on which a wind speed function (k vs. U_{10}) strongly affected that may lead to underestimate $k_{600.}$ The underestimation of k_{600} may lead to lower CO_2 flux out-gassing. Thus, we consider that the CO_2 outgassing fluxes in our study reflected likely a low estimate.

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2.4 From calculated pCO_2

DIC content may be calculated from the sum of total dissolved inorganic carbon in water including HCO_3^-, CO_3^{2-}, H_2CO_3 and CO_2, or can be calculated from a combination of any two of the following measured parameters total alkalinity, pH, or partial pressure of CO_2 (pCO_2) (Cai et al., 2008; Sun et al., 2010). In this study, DIC contents were calculated from the sum of including HCO_3^-, CO_3^{2-}, H_2CO_3 and CO_2 contents, which were given by the calculation from the CO_2-SYS Software (version 2.0) basing on the total alkalinity contents and pH values measured in-situ as described above (Sect. 2.3).

In order to compare with pCO_2 in water, which was measured by the equilibrator, pCO_2 in water at the 5 sites was also simultaneously calculated on the CO2-SYS EXCEL Macro Software basing on total alkalinity contents and pH values measured in-situ at the 5 sites as described above (Sect. 2.3).

We feel confident about our measurements of pCO_2, because both methods yielded similar results.

2.5. Statistical analysis

To detect the correlation between environmental variables and pCO_2 or CO_2 outgassing flux, statistical software R version 3.3.2 (R Core Team, 2016) was applied to calculate the Pearson correlation coefficients. Some environmental variables were evaluated by "cor" to compare the correlation and selected representative variables. PCA analysis was then used for identifying representative variables that could relate to the dynamic of pCO_2 or CO_2 flux.

3. Results

3.1. Physical and chemical variables of the lower Red River

Water temperature varied from 23.3 to 29.4 °C, and the mean value in rainy period (27.4 °C) was higher than the one in dry period (24.5 °C) at almost all stations, except at the Hoa Binh site where the water temperatures did not show seasonal variations, remaining around 26.3 - 26.5 °C. Among the five hydrological stations, the higher water temperatures were recorded at the Hanoi and Ba Lat stations, ranging from 28 to 29 °C in the wet period, whereas they were close to 23 °C during the dry period. Temperatures at the Yen Bai and Vu Quang stations were approximately 26°C in the wet period and 24 °C in the dry period (Table 2, Fig. 2).

pH values were not hugely different among the two periods. pH was slightly basic, ranging from 7.7 to 8.2 with an average 8.1 for all the sites. The lowest pH values were observed at the Hoa Binh in both periods (< 8), whereas they ranged between 8.0 and 8.4 at the other sites. pH was slightly higher in dry season than in the wet season at all the sites (Table 2, Fig. 2).The percentage of dissolved oxygen (% DO) varied from 50.5 to 70.7 % with an average value of 64.3 %. There were not significant differences in % DO with season, 63.6 % during the rainy seasons and 64.9 during the dry

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Manuscript under review for journal Biogeosciences
Discussion started: 13 December 2017

season (Table 2). The mean values were the highest for the Yen Bai station (70.1 %) in the wet period, and 69.5 % for the Ba Lat station in the dry period. The lowest values were observed at the Hoa Binh station in both periods (55.0 % in the wet period, 51.4% in the dry period) (Table 2, Fig. 2).

Salinity at the four upstream sites was under the detection limit both in the rainy and dry seasons, but in the estuary downstream river at the Ba Lat station, values up to 8.75 were measured during the dry season (Table 2).

Alkalinity concentrations ranged from 84.3±1.9 to 152.9±6.6 mg L^{-1}, with higher values in the dry season than in the rainy season, except at Vu Quang station. Conductivity ranged from 0.2±0.0 to 6.6±3.4 mS cm^{-1}, but did not show a clear variation between the dry and rainy season (Table 2, Fig. 2).

Chlorophyll *a* was quite low during the two sampling campaigns, ranging from 0.23 to 2.77 µg L^{-1}, with an average of 1.61 µg L^{-1}. Higher values in the rainy season than in the dry season were observed at almost sites. From Yen Bai to Ba Lat, Chl-a concentrations in the main axe (at Yen Bai and Hanoi stations) were higher than in the two tributaries Da and Lo (Table 2, Fig. 2), even under the higher values of turbidity.

The wind speed ranged from 0.2±0.3 to 3.1±1.5 m s^{-1}, and the highest value occurred in the dry season at Ba Lat. The results showed a clear variation in wind speed between day and night, with the higher values during the day time for all stations (Table 3).

3.2. Carbon concentrations of the lower Red River

During the two sampling campaigns, DOC concentration ranged from 0.5 to 4.6 mgC L^{-1}, averaging 1.5 mgC L^{-1}. Higher values were observed during the rainy season (2.0 mgC L^{-1} vs.1.5 mgC L^{-1} during the dry season), and the highest value was recorded at Hanoi site (Table 2). POC concentrations varied from 0.4 to 4.6 mgC L^{-1}. The mean value in the rainy season was 1.6 mgC L^{-1}, slightly higher than in dry season (1.4 mgC L^{-1}). Among the 5 sites, POC concentrations in the main reach of the Red River (Yen Bai, Hanoi and Ba Lat sites) were higher than in the two tributaries Da and Lo, where dams were constructed (Table 2, Fig. 2).

DIC concentrations at the five sites fluctuated from 16.7 to 32.9 mgC L^{-1}, averaging 23.8 mgC L^{-1}. Lower values were observed in the rainy season (22.3 mgC L^{-1}), lower than the values in the dry season (25.3 mgC L^{-1}) (Table 2, Fig. 2).

3.3. Comparisons of the pCO$_2$ results for the two methods

pCO_2 along the lower Red River (Vietnam) in the dry and monsoon seasons were determined by two methods: i) direct measurements using an equilibrator connected to an IRGA, ii) calculated from pH and alkalinity using the CO_2-SYS® software. The direct measurements gave higher values than the calculated (Table 2), but the values of two methods were well correlated (R^2 = 0.76, Fig. 3). This result is opposite to what was observed in organic-rich freshwater (Abril et al., 2015) or in estuarine mangrove waters (Leopold et al., 2017), where large overestimation of the calculated pCO_2 was observed. The higher calculated values compared to direct measurements were related to a more significant contribution of organic acids anions to total alkalinity in waters with low carbonate alkalinity and high DOC concentrations, and to a lower buffering capacity of the carbonate system at low pH (Abril et al., 2015). However along the Red River, pH values remained around 8 and DOC concentrations were lower than 2 mg L^{-1} (Table 2), which may explain for the lower calculated pCO_2 values (Table 2). Thus, in this study, we used the results of the measured pCO_2 for the discussion and to determine the CO_2 emissions from the lower Red River to the atmosphere (Fig. 4).

3.4. Daily variations of pCO_2 and CO_2 emissions

The riverine water pCO_2 was supersaturated with CO_2 in contrast to the atmospheric equilibrium (400 ppm), averaging 1,588.6 ± 884.6 ppm. In general, the results did not show a clear variation in pCO_2 between the day and night at all stations, except higher values at the night time in the dry season at the Ba Lat site (Table 2, Fig. 2).

CO_2 flux values in the day time were higher than in the night time for all the stations during all sampling campaigns (Table 3, Fig. 4). Previous studies revealed that photosynthesis of phytoplankton may have a strong influence on circadian variation of CO_2 outgassing, since this process consumes CO_2 during the day (Linn and Doran, 1984; Cole et al., 2000). However, in the present study, very low Chl-a concentrations were measured, from 0.5 to 3.1 µg L^{-1}, probably as a result of the high turbidity limiting light penetration in the water column. Thus, phytoplankton activity had a low influence on C dynamic in the lower Red River system.

In the present study, water temperature was slightly higher in the day time than in the night time (around 0.1 – 0.5 ºC) (Table 2), and positive correlations between temperature and CO_2 flux was observed at Hoa Binh and Yen Bai station (R^2= 0.72 and 0.84, respectively). Water temperature could alter the riverine pCO_2 value. Previous studies indicated that CO_2 water solubility decreases with the temperature increase during the day (Parkin and Kaspar, 2003; Roulet et al., 1997), leading to higher CO_2 outgassing from river water interface. This effect was observed for some rivers in the world (Roulet et al., 1997; Guasch et al., 1998; Dornblaser and Striegl, 2013). However for the Ba Lat site, CO_2 fluxes were higher during the day but it was not always the case for pCO_2, suggesting that another factors may be responsible for these results. The other parameter that differed during the night and day was the wind speed which was higher during the day (Table 3). Previous studies suggested that the large changes of CO_2 fluxes observed between the day and night can be caused not only by biological cycle but also mainly by daily wind patterns (Hamilton et al., 1994). Small changes in wind pattern may modify the direction and magnitude of the CO_2 flux during the day-night cycle (Sellers et al., 1995). Our results were in agreement with some reports for rivers in tropical region (e.g. the Shark River in USA (Ho et al., 2016)), which emphasised the influence of strong diurnal signal in wind speed leading to higher k values in the day time than in night time (Rey et al., 2012; Ho et al., 2016).

Different explanations were given for the day-night variation of pCO_2 and CO_2 flux for aquatic ecosystems in the world. Ho et al. (2016) found higher CO_2 flux in the Shark River (USA) during the day than at night was due to the strong diurnal signal in u10. Similar results have also been reported for the Yangtze River Delta (China) (Xu et al., 2017). Roulet et al. (1997) reported that CO_2 flux in some ponds in Canada were always higher during the day because of higher water temperature. Higher CO_2 concentrations in day time were also observed for the two second-order Mediterranean streams: Riera Major, a siliceous shaded stream and La Solana, a calcareous open stream where changes in CO_2 concentration was greatly influenced by stream metabolism (Guasch et al., 1998). However, average CO_2 outgassing during the night higher than during day by up to 1.8 times was also observed for the Alpine streams, where temperature and hydrology were major drivers of pCO_2 dynamics (Peter et al., 2014). CO_2 increased in the night time with the values of 6-46% higher than the day time values during each 24-h period have been described by Sellers et al. (1995) for the lake Northwest Ontario, Canada. Thus, it is possible that the contrast between day and night time concentrations being a consequence of specific features of the measuring sites (Wang et al., 2010).

3.5. Seasonal variations of pCO_2 and CO_2 emission

pCO_2 values fluctuated from 694 ppm (at Yen Bai) in the dry season to 3,887 ppm (at Hoa Binh) in the wet season. The mean values were highest for the Hoa Binh site in both seasons whereas the lowest one was observed at the Yen Bai site. Higher values of pCO_2 in the wet season than in the dry season were observed at almost sites, except at Yen Bai (Table 2).

CO_2 flux values varied with seasons, and ranged from 4.4±2.0 mmol m^{-2} d^{-1} (at Vu Quang) in the dry season to 48.4±23.4 mmol m^{-2} d^{-1} (at Hoa Binh) in the wet season. CO_2 flux values were higher in the wet season for all stations (Table 3, Fig. 4). During the monsoon season, the river discharges were about 2 to 3 times higher at all the sites (Table 1). As known in tropical regions, the wet season usually experienced higher pCO_2 than the dry season because of the intense rainfall that induces higher OM inputs into the river. This process was observed in some subtropical rivers: the Longchuan River (Li et al., 2012) and the Xijiang River (Yao et al., 2007), with pCO_2 values increasing significantly when baseflow and interflow increased, and flushed significant amount of carbon into the streams. In addition, it was suggested a link between the seasonal variation in soil CO_2 content and riverine CO_2 outgassing due to porewater export (Hope et al., 2004; Melack et al., 2009; Rudorff et al., 2011). Thus the higher pCO_2 values observed along the lower Red River during the rainy season may reflect the influence of soil organic matter inputs to the riverine water column, evidenced by the higher values of DOC and POC in the rainy seasons at all the sites.

In addition, seasonal variation of temperature may also explain the seasonal variability of pCO_2 values of the Red River, being higher during the hot rainy season. Some authors suggested that higher water temperatures in wet season in tropical regions were responsible for increased pCO_2 and higher CO_2 emissions towards the atmosphere (Chanda et al., 2013; Takahashi et al., 2002). Dessert et al., (2003) suggested that higher temperature should induce higher weathering rates, leading to higher

DIC export. This effect was not only observed in tropical rivers but also in mixed mangrove forest in India (Chanda et al., 2013), or in the Southern Ocean (Nomura et al., 2014). Increase in temperature decreases CO_2 solubility but increase OM decomposition processes, which produce CO_2. This may partly explain the higher pCO_2 of the Red River during the hot rainy season. However, direct relationship between temperature and pCO_2 during the rainy season was not evident, probably because riverine inputs were the dominant factor driving pCO_2, while during the dry season pCO_2 clearly increased with temperature, suggesting that metabolic rate controlled pCO_2 when adjacent soils inputs are limited (Fig. 5).

4. Discussion

PCA and Pearson correlation coefficient were performed to analyze the relationships between nine environmental variables and pCO_2 or CO_2 evasion flux at five sampling stations of the lower Red River in the wet season (September 2014) and dry season (November 2014). The PCA of the seasonal data for five sampling stations presented a clear separation between two periods: rainy and dry season (Fig. 6). The rainy period was characterized by high levels of temperature, pCO_2, CO_2 flux, POC, DOC and Chl *a*. The Pearson correlation coefficient showed a low positive correlation between pCO_2 and DIC and oxygen saturation (%) ($r = 0.19$) and between CO_2 flux and DOC (0.17). Both pCO_2 and CO_2 flux were found to be negatively correlated with pH ($r = -0.3$) (Table 4).

Consequently, we suggest that the pCO_2 and CO_2 outgassing are the results of a combination of multiple parameters, rather than a single one: season (including precipitation and temperature), dam construction, population density, geomorphological characteristics of the catchment, etc.

4.1. Influence of dams on pCO_2 and CO_2 emission

Along the lower Red River, pCO_2 values were characterized by significant spatial variations (Table 2, Fig. 2). In the upstream part, pCO_2 ranged from 964 to 3,830 ppm. Within the three tributaries, in addition to the two large dams (Hoa Binh and Son La) in the Vietnamese part, a series of dams in the Chinese territory were constructed in the 2000s for the Da River, whereas only some small dams/reservoirs were built up in the Thao River in the Chinese territory. In the present study, the highest pCO_2 values and the lower pH values were measured at the Hoa Binh site, which is situated downstream a series of reservoirs. Previously, reservoirs were suggested to decrease river pCO_2 due to increased residence times and autotrophic production (Wang et al., 2007). However, Lauerward et al., (2015) found a low negative correlation between them. Abril et al., (2005) noted that intense mineralization of organic matter (OM) originating from the reservoir was possibly a significant source for pCO_2 value in downstream river. Thus, the high pCO_2 measured at this site may reflect the increased decomposition of OM and/or the water perturbation due to dam construction in this study.

4.2 Influence of water discharge and geomorphological characteristics on pCO_2 and CO_2 emission

pCO_2 differences between the three upstream tributaries and the main downstream axe of the Red River are suggested to be partially related to different hydrological characteristics and management of the

Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-505
Manuscript under review for journal Biogeosciences
Discussion started: 13 December 2017

three sub-basins and delta area, as observed in other systems (Yao et al., 2007; Li et al., 2012). Our results showed that within the 3 upstream sites studied, the highest pCO_2 values were always measured in the Da River at Hoa Binh site, where river discharges were the highest (2,189 ± 39 m^3 s^{-1} in wet season and 868 ± 319 m^3 s^{-1} in dry season), whereas the lowest pCO_2 were measured at the Yen Bai station of the Thao River, where river discharges were the lowest (840 ± 68 m^3 s^{-1} in wet season and 260 ± 18 m^3 s^{-1} in dry season) (Table 1 and Table 2). Figure 7 showed the increased trend of both pCO_2 and fCO_2 when river discharge increased in both rainy and dry seasons for the lower Red River.

Differences in geomorphological characteristics between the upstream and downstream parts of the lower Red River may be another reason responsible for the variability of pCO_2 observed among the five stations. As presented above, the upstream part of the Red River is located in mountainous areas, where chemical and mechanical erosion are among the world highest (500 mm per 1,000 years) (Meybeck et al., 1989), whereas the downstream part is located in a very flat and low land, with an elevation ranging from 0.4 to 12 m above sea level (Nguyen Ngoc Sinh et al., 1995). Regarding the Ba Lat site, which is situated in the Red River estuary and thus in a very low and flat land, pCO_2 values were lower than in Hanoi. It is interesting to observe that the river water discharge at Hanoi site (3,296 ± 86 and 1,915 ± 149 m^3 s^{-1}) was about 3 times higher than the one at Ba Lat (1,269 ± 93 and 453 ± 31 m^3 s^{-1}) in both wet and dry seasons respectively (Table 1), whereas higher pCO_2 values were measured during the dry season in Hanoi than in Ba Lat (1,150 and 800 ppm, respectively), but during the rainy season the values were close, i.e. around 1,450 ppm. We think that dilution by seawater may lead to a reduction of riverine surface water pCO_2, especially in the dry season when the river flow was lower. The higher salinity values measured at Ba Lat site in the dry season (3.6) than in the wet season (0.2) may confirm our suggestion that tidal action influenced at Ba Lat site in the Red River estuary. This result is consistent with previous observations in the Changjiang River estuary (Chen et al., 2008; Bai et al., 2015) or in the Pearl River Estuary (Semiletov et al., 2004; Delille, 2006; Zemmelink et al., 2006).

4.3 Influence of population density on pCO_2 and CO_2 emission

From the upstream to the downstream part of the main axe of the lower Red River, pCO_2 increased from Yen Bai (mean value of 995 ppm) to Hanoi (mean value of 1,256 ppm) and then decreased to the estuary at Ba Lat (mean value of 1,154 ppm). Higher values at Hanoi than at Yen Bai may be explained by carbon inputs from the Hanoi wastewater system (Trinh et al., 2007). Indeed, high CO_2 efflux in the peri-urban rivers of the Red River Delta that run through megacity Hanoi, e.g. the Day River (Trinh et al., 2009) and the Nhue River (Trinh et al., 2012) was reported, whereas the upstream zone (Yen Bai) is less subject to anthropogenic pressure. The higher values of both DOC and POC concentrations in Hanoi site than in Yen Bai site may further indicate the influence of organic matter inputs at Hanoi site.

4.4. Comparison with World Rivers

CO_2 emissions from the Red River, as determined in the present study, were higher than the ones of some Asian rivers such as the Lupar River (13±3.0 mmol m^{-2} d^{-1}) and the Saribas River (14.6 ± 3.3 mmol m^{-2} d^{-1}) in Malaysia (Wit et al., 2015), and much higher than the results from some rivers in

Indonesia (Musi, Batanghari, Indragiri, Siak Rivers: 5±1.1, 1.8±0.4, 9.7±2.2, 8.3±1.9 mmol m^{-2} d^{-1}, respectively) (Wit et al., 2015) or in upper Yukon River (6 mmol m^{-2} d^{-1}) (Striegl et al., 2007). However, CO_2 outgassing from the lower Red River system was found much lower than the ones of many rivers in America and Africa such as the Capibaribe river with 225 mmol m^{-2} d^{-1} (Moacyr et al., 2013), the Amazon river 190 ± 55 mmol m^{-2} d^{-1} (Richey et al., 2002), the Mississipi River (270 mmol m^{-2} d^{-1}) (Dubois et al., 2010), some rivers in South America reported by Rasera et al. (2013) such as the Negro, the Solimoes, the Caxiuana rivers (855±294, 518±17, 778±17 mmol m^{-2} d^{-1}, respectively), or even much lower than the ones of some large Asian rivers as the Yellow river (856±409 mmol m^{-2} d^{-1}) (Ran et al., 2015) and the Xijiang river (357 mmol m^{-2} d^{-1}) (Yao et al., 2007) (Table 5). Our lower values for the Red River were surprising when considering that large Asian rivers (in Himalayas and Tibet Plateau regions) played important role in terms of chemical weathering (via carbon consumption due to tectonic forcing) (Raymo and Ruddiman, 1992) and carbon burial (France-Lanord and Derry, 1997). The present low value of the Red River CO_2 outgassing may be related to the large decrease of suspended solids, associated with strong decrease of particulate organic carbon due to a series of dam construction in the upstream part of the Red River (Le et al., 2017) or due to low water flow in the measured year.

5. Conclusions

This work presented the estimates of CO_2 emissions at the water-air interface at the 5 sites along the lower Red River system in the dry and rainy seasons. The riverine water pCO_2 was supersaturated with CO_2 in contrast to the atmospheric equilibrium (400 ppm), averaging about 1,588.6 ± 884.6 ppm, thus resulting in a mean water–air CO_2 flux of 26.9 ± 18.4 mmol m^{-2} day^{-1} from the lower Red River system. The CO_2 outgassing rate from the water surface Red River network was characterized by significant spatial variations, being the highest at the Hoa Binh dam downstream and in the main axe at Hanoi station. The highest value obtained at Hoa Binh site may reflect the important impact of a series of large dams (Son La, Hoa Binh) in the Da river, but also the high water discharge, whereas the high pCO_2 value in Hanoi may reflect the influence of population density, notably through the release of elevated amount of organic carbon into the river. The monsoon season resulted in an increased amount of OM inputs from adjacent soil, and combined to an increase of temperature, led to higher pCO_2 values. During the dry season, temperature appeared to be the main factor controlling pCO_2. Regarding CO_2 evasion, differences appearred between the day and night in both dry and rainy seasons at almost all sites with higher values found in the day time (30.4 ± 21.2 mmol m^{-2} day^{-1}) than in the night time (23.3 ± 15.4 mmol m^{-2} day^{-1}). This result was related to the combined higher wind speed and higher temperatures during the day. Consequently, this study evidenced that CO_2 dynamic along the lower Red River was controlled by both anthropogenic activities (dam, urban effluents), and natural meteorological-hydrological characteristics (rainfall- river discharge and temperature).

Author contribution

Le TPQ, Marchand C and Ho TC designed the experiments. Le TPQ, Ho TC and Vu DA carried the in-situ experiments. Phuong KD and Le ND contribute to data treatment and calculations. Le TPQ and Marchand C prepared the manuscript with the contributions from all co-authors.

Acknowledgements

This work was performed in the framework of the *ARCP2014-03CMY-Quynh/ARCP2013-06CMY-Quynh/ARCP2012-11MY-Quynh* and the *Vietnam-NAFOSTED 105.09-2012.10* projects. The authors would like to thank and the Asia-Pacific Network for Global Change Research (APN) and the Vietnam's National Foundation for Science and Technology Development (NAFOSTED-Vietnam) for their financial supports. We thank Ms Nguyen Bich Ngoc and Mr Nguyen Trung Kien for helping field work.

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Discussion started: 13 December 2017

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Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-505
Manuscript under review for journal Biogeosciences
Discussion started: 13 December 2017

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Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-505
Manuscript under review for journal Biogeosciences
Discussion started: 13 December 2017

List of tables

Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-505
Manuscript under review for journal Biogeosciences
Discussion started: 13 December 2017

Table 1. Average values of river water discharge at five hydrological stations of the Red River in 2014.

Hydrological stations	**Altitude (m a.s.l.)**	**Latitude**	**Average daily water discharge in 2014, $m^3 s^{-1}$**	**Water discharge, $m^3 s^{-1}$**			
				Wet season		***Dry season***	
				Mean value in wet season in 2014 (May – Oct)	On the date of measurement Sept 2014	Mean value in wet season in 2014 (May – Oct)	On the date of measurement in Nov 2014
Yen Bai	56	104⁰51'- 21⁰42'	527 ± 515	788 ± 459	840 ± 68	262 ± 530	260 ± 18
Hoa Binh	23	105⁰19'- 20⁰49'	1,369 ± 833	1,907 ± 451	2,189 ± 39	825 ± 515	868 ± 319
Vu Quang	25	105⁰15'- 21⁰34'	1,302 ± 517	1,618 ± 378	2,240 ± 88	982 ± 284	725 ± 11
Hanoi	5	105⁰51'- 21⁰01	1,867 ± 1089	2,598 ± 780	3,296 ± 86	1,127 ± 490	1,915 ± 149
Ba Lat	0	106⁰00' - 19⁰30'	615 ± 293	824 ± 200	1,269 ± 93	403 ± 96	453 ± 31

Table 2. Average values in day and night times of the different physico-chemical variables at 5 sites in wet and dry seasons in 2014.

Stations	Temperature ^{0}C	pH	TAlk mg L^{-1}	Salinity	Chl-a µg L^{-1}	Turbidity NTU	Conductivity mS cm^{-1}	DOC mg L^{-1}	POC mg L^{-1}	DO %	Measured pCO_2 ppm	Calculated pCO_2 ppm
Wet season												
1-Yen Bai												
Day	26.4± 0.1	8.2±0.1	105.1±5.2	0.1±0.0	3.1±0.1	141.6±8.6	0.2±0.0	1.5±0.2	2.1±0.4	69.9±0.2	964.3±9.9	269.6±36.4
Night	26.6±0.0	8.3±0.0	103.8±3.3	0.1±0.0	3.1±0.1	135.4±4.0	0.2±0.0	1.4±0.2	1.9±0.2	70.4±0.1	979.5±9.6	225.7±10.4
2-Vu Quang												
Day	26.8±0.1	8.1±0.0	148.9±6.7	0.1±0.0	1.2±0.2	51.4±7.5	0.2±0.0	1.1±0.3	1.4±0.2	63.6±1.2	1598.7±53.3	453.8±55.2
Night	27.0±0.1	8.2±0.0	144.9±3.3	0.1±0.0	1.2±0.2	49.9±5.3	0.2±0.0	1.0±0.2	1.4±0.2	63.2±0.7	1583.0±36.6	404.0±12.5
3-Hoa Binh												
Day	26.5±0.1	7.8±0.0	110.4±3.3	0.1±0.0	0.8±0.3	42.5±4.7	0.2±0.0	1.5±0.4	1.1±0.2	54.9±0.2	3827.1±60.6	881.1±123.0
Night	26.4±0.0	7.8±0.0	107.8±5.4	0.1±0.0	1.2±0.0	41.0±0.1	0.2±0.0	1.3±0.2	1.1±0.1	55.1±0.6	3830.2±19.1	722.0±23.4
4-Ha Noi												
Day	28.6±0.2	8.0±0.0	84.3±1.9	0.1±0.0	2.0±0.6	88.9±1.3	0.2±0.0	4.7±0.6	2.0±0.3	64.0±0.4	1412.3±4.2	336.6±38.6
Night	28.6±0.2	8.1±0.0	84.5±1.5	0.1±0.0	2.7±0.1	88.5±2.7	0.2±0.0	4.2±0.9	2.2±0.4	63.5±0.3	1411.4±6.7	279.4±18.7
5-Ba Lat												
Day	28.9±0.4	8.0±0.1	116.4±4.6	0.3±0.3	1.8±0.3	47.7±8.8	0.6±0.6	1.5±0.4	1.1±0.4	66.1±1.4	1489.1±104.2	495.4±108.6
Night	28.8±0.3	8.1±0.0	114.9±3.5	0.1±0.1	2.5±0.1	81.3±10.0	0.3±0.2	1.7±0.5	1.5±0.2	65.1±1.6	1483.1±117.5	430.2±31.8
Dry season												

Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-505
Manuscript under review for journal Biogeosciences
Discussion started: 13 December 2017

1-Yen Bai												
Day	24.1±0.5	8.1±0.1	113.9±7.9	0.1±0.0	1.2±0.3	49.3±7.9	0.2±0.0	1.3±0.3	1.4±0.1	69.3±0.7	995.8±17.5	376.6±140.1
Night	24.2±0.3	8.2±0.0	109.3±2.8	0.1±0.0	1.6±0.2	42.5±4.7	0.2±0.0	1.2±0.2	1.2±0.3	69.1±0.5	1030.6±21.5	266.6±7.8
2-Vu Quang												
Day	24.7±0.2	8.3±0.0	134.9±5.1	0.1±0.0	1.0±0.2	28.1±1.7	0.2±0.0	1.1±0.2	1.1±0.2	67.0±0.9	1235.3±76.2	301.8±36.4
Night	24.8±0.4	8.4±0.0	129.3±2.7	0.1±0.0	1.4±0.2	32.4±3.7	0.2±0.0	1.1±0.2	1.2±0.1	69.0±0.9	1163.3±86.3	235.2±13.0
3-Hoa Binh												
Day	26.3±0.0	7.8±0.0	122.5±6.1	0.1±0.0	0.5±0.1	16.9±0.3	0.2±0.0	0.9±0.2	1.0±0.2	51.5±0.4	2399.3±33.6	869.7±96.9
Night	26.3±0.0	7.8±0.0	120.6±6.1	0.1±0.0	0.5±0.1	17.1±0.5	0.2±0.0	0.9±0.2	1.1±0.2	51.3±0.2	2458.9±14.0	833.1±85.3
4-Ha Noi												
Day	23.8±0.1	8.2±0.0	123.5±2.4	0.1±0.0	1.7±0.2	65.2±1.8	0.2±0.0	2.7±0.7	1.5±0.3	66.8±0.4	1141.3±33.5	333.5±43.2
Night	23.8±0.1	8.3±0.0	123.8±1.5	0.1±0.0	1.6±0.1	62.6±0.7	0.2±0.0	2.0±0.7	1.3±0.1	67.1±0.3	1136.0±24.2	300.6 ± 12.6
5-Ba Lat												
Day	23.7±0.1	8.3±0.0	152.9±6.6	3.9±2.4	1.8±0.2	34.1±8.3	6.6±3.4	1.4±0.2	2.0±0.4	70.0±0.5	751.4±49.3	311.8± 20.5
Night	23.4±0.1	8.3±0.0	150.3±5.6	3.3±1.6	1.3±0.2	28.8±4.2	5.7±2.6	1.2±0.2	1.9±0.4	68.8±0.6	881.0±88.4	331.6± 20.4

Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-505
Manuscript under review for journal Biogeosciences
Discussion started: 13 December 2017

Table 3. Wind speed, k_{600} parameterization, and calculated water-air CO_2 fluxes for daytime and nighttime at five hydrological stations of the Red River in dry and wet seasons in 2014.

	Wind speed m s^{-1}	k_{600} cm h^{-1}	Water-air CO_2 flux mmol m^{-2} d^{-1}	
			With pCO_2 measured from equilibrator	With pCO_2 calculated from CO_2-SYS
Wet season				
Yen Bai				
Day	1.1±0.6	2.9±0.6	13.0±2.7	7.2±2.3
Night	0.5±0.6	2.3±0.5	10.9±2.5	4.0±1.0
Vu Quang				
Day	0.9±0.7	2.7±0.7	27.7±7.3	16.8±5.6
Night	0.4±0.6	2.3±0.5	20.4±3.9	12.2±2.9
Hoa Binh				
Day	1.3±1.1	3.3±1.2	82.7±36.3	48.4±23.4
Night	0.2±0.5	2.1±0.5	61.3±15.3	23.1±4.3
Hanoi				
Day	1.8±0.7	3.6±0.8	29.4±7.1	15.0±4.6
Night	1.2±0.6	2.9±0.6	24.8±4.6	8.7±2.8
Ba Lat				
Day	0.5±0.5	2.3±0.5	19.0±2.3	17.9±7.8
Night	0.2±0.3	2.0±0.3	18.1±4.0	12.7±2.5
Dry season				
1-Yen Bai				
Day	1.4±0.9	3.2±1.0	14.4±3.7	12.0±7.1
Night	0.5±0.8	2.4±0.8	12.5±4.7	4.9±1.7
2-Vu Quang				
Day	1.3±0.6	3.1±0.6	20.3±5.1	8.9±3.1
Night	0.7±1.3	2.8±1.5	15.8±8.0	4.4±2.0
3- Hoa Binh				
Day	1.2±0.8	3.0±0.8	50.2±13.6	40.3±8.9
Night	0.5±0.5	2.3±0.5	37.2±6.9	29.8±4.8
4-Hanoi				
Day	2.4±0.5	4.6±0.9	28.5±5.8	15.2±6.6
Night	1.4±0.5	3.2±0.5	19.3±3.0	8.5±1.3
5-Ba Lat				
Day	3.1±1.5	6.5±3.8	18.9±14.6	18.4±10.7
Night	1.3±0.8	3.1±0.8	13.1±2.8	9.9±1.9

Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-505
Manuscript under review for journal Biogeosciences
Discussion started: 13 December 2017

Table 4. Relationship between CO_2 outgassing flux with other water quality variables at Hanoi station

Variables	**Temp.**	**DOC**	**POC**	**DIC**	***p*CO₂**	**pH**	**Chl-a**	**%DO**	**CO₂ Flux**
Temp.	1								
DOC	**0.72**	1							
POC	**0.74**	0.53	1						
DIC	**-0.99**	-0.73	-0.73	1					
***p*CO₂**	-0.11	-0.05	0.00	0.19	1				
pH	**-0.90**	-0.69	-0.70	**0.87**	-0.31	1			
Chl_a	**0.65**	0.29	0.47	-0.65	-0.51	-0.37	1		
%DO	**-0.96**	-0.70	-0.72	**0.97**	0.19	**0.84**	-0.65	1	
CO₂ Flux	0.06	0.17	0.04	-0.02	**0.60**	-0.31	-0.11	-0.05	1

Table 5. CO_2 flux out-gassing in some World Rivers.

River or Tributary	Location	Country	Mean pCO_2 µatm	F_{CO2} mmol m^{-2} day^{-1}	k_{600} ± SD cm h^{-1}	U_{10} m s^{-1}	References
Red		Vietnam	1,589	28.6 ± 19.3	3.25 ± 0.92	1.2 ± 0.7	This study
Mekong	Downstream	Laos and Cambodia	703 – 1597	88.1 -378.4	12.4 - 44.5	1.3 – 4.9	*Alin et al.*, 2011
Tonle Sap	Stung Siem Reap	Cambodia	3,066	139.1	5.6 ± 0.9	0.8	*Alin et al.*, 2011
Tonle Sap	Pousat River	Cambodia	1,404	98.5	10.8 ± 2.8	nd	*Alin et al.*, 2011
Musi		Indonesia	4,316±928	5±1.1	21.8±4.7	nd	*Wit et al.*, 2015
Batanghari		Indonesia	2,400±18	1.8±0.4	21.8±4.7	nd	*Wit et al.*, 2015
Indragiri		Indonesia	5,777±527	9.7±2.2	21.8±4.7	nd	*Wit et al.*, 2015
Siak		Indonesia	8,555±528	8.3±1.9	22.0±4.7	nd	*Wit et al.*, 2015
Lupar		Malaysia	1,274±148	13±3.0	26.5±9.3	nd	*Wit et al.*, 2015
Saribas		Malaysia	1,159±29	14.6±3.3	17.0±13.6	nd	*Wit et al.*, 2015
Changjiang		China	1,297±901	143	8 - 15	5	*Wang et al.*, 2007
Maotiao		China	3740	108	10	nd	*Wang et al.* 2011
Longchuan		China	2,100	156	8	nd	*Li et al.*, 2012
Yellow		China	2,810 ± 1,985	856±409	42.1 ± 16.9	nd	*Ran et al.*, 2015
Xijiang		China	2,600	357	15	2.7	*Yao et al.*, 2007
Negro	South America		4,260±1387	855±294	38.3±19.1	nd	*Rasera et al.*, 2013
Solimoes			6,691±55	518±17	8.0±2.2		
Arguaia			2,674±802	207±104	9.0±1.8		
Javaes			3,065±1208	156±69	5.0±0.9		
Caxiuana			4,849±208	778±17	20.5±2.5		
Teles Pires			1,624±425	78±43	9.2±2.3		
Cristalino			3,507±482	nd	8.1±1.9		
Krishna		India	**17,205±3500**		nd	nd	*Sarma et al.*, 2012
Godavari			**49,819±1042**				
Mahanadi			**95,859±2234**				
Ganges			5,029±100				

Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-505
Manuscript under review for journal Biogeosciences
Discussion started: 13 December 2017

Gaderu Creek		India	2,215 ± 864a	56.0 ± 100.9	4 ± 5	1.4 ± 1.9	*Borges et al.,* 2003
Rhone		France	2,015±944	nd	15	nd	*Cole et al.,* 2001
Negro	South America		4,260±1387	855±294	38.3±19.1	nd	*Rasera et al.,* 2013
Solimoes			6,691±55	518±17	8.0±2.2		
Arguaia			2,674±802	207±104	9.0±1.8		
Javaes			3,065±1208	156±69	5.0±0.9		
Caxiuana			4,849±208	778±17	20.5±2.5		
Teles Pires			1,624±425	78±43	9.2±2.3		
Cristalino			3,507±482	nd	8.1±1.9		
Capibaribe	Coastal region of the State of Pernambuco	Brazil	8,340	225	nd	2.2	*Moacyr et al.,* 2013
Hudson		USA	1,125±403	nd	4.1	3.5± 2.0	*Raymond et al.,* 1997
Yukon	Upper	North America	1,220 ± 9.1	6	1.25	nd	*Striegl et al.,* 2007; 2012
	Middle		1,890 ± 9.9	62	7.92	nd	
	Lower		3,090 ± 16.5	193	15	nd	
Ottawa		Canada	1,200	80.8	4	nd	*Telmer and Veizer,* 1999
Amazon			4,350 ± 1900	190 ± 55	9.6 ± 3.8	1 - 3	*Richey et al.,* 2002
Mississippi			100 - 600	270	3.9	5.3	*Dubois et al.,* 2010; *Lohrenz and Cai,* 2006
Nagada Creek	The northern Papua New Guinea coast		799 ± 357a	43.6 ± 33.2	8 ± 6	3.0 ± 2.1	*Borges et al.,* 2003
Norman's Pond	Bahamas archipelago		165 ± 86a	13.8 ± 8.3	13 ± 3	5.5 ± 1.3	*Borges et al.,* 2003

[a] calculated the values for the $p\mathrm{CO_2}$ Water-Air Gradient ($\Delta p\mathrm{CO_2}$ in µatm)

nd. No data

Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-505
Manuscript under review for journal Biogeosciences
Discussion started: 13 December 2017

List of figures

Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-505
Manuscript under review for journal Biogeosciences
Discussion started: 13 December 2017

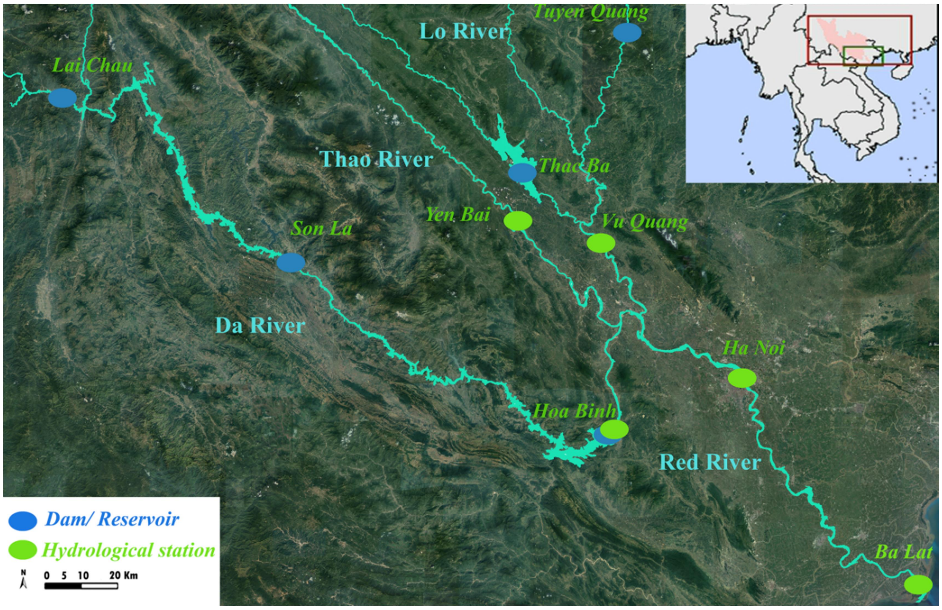

Figure 1. **The Red River system and sampling sites**

Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-505
Manuscript under review for journal Biogeosciences
Discussion started: 13 December 2017

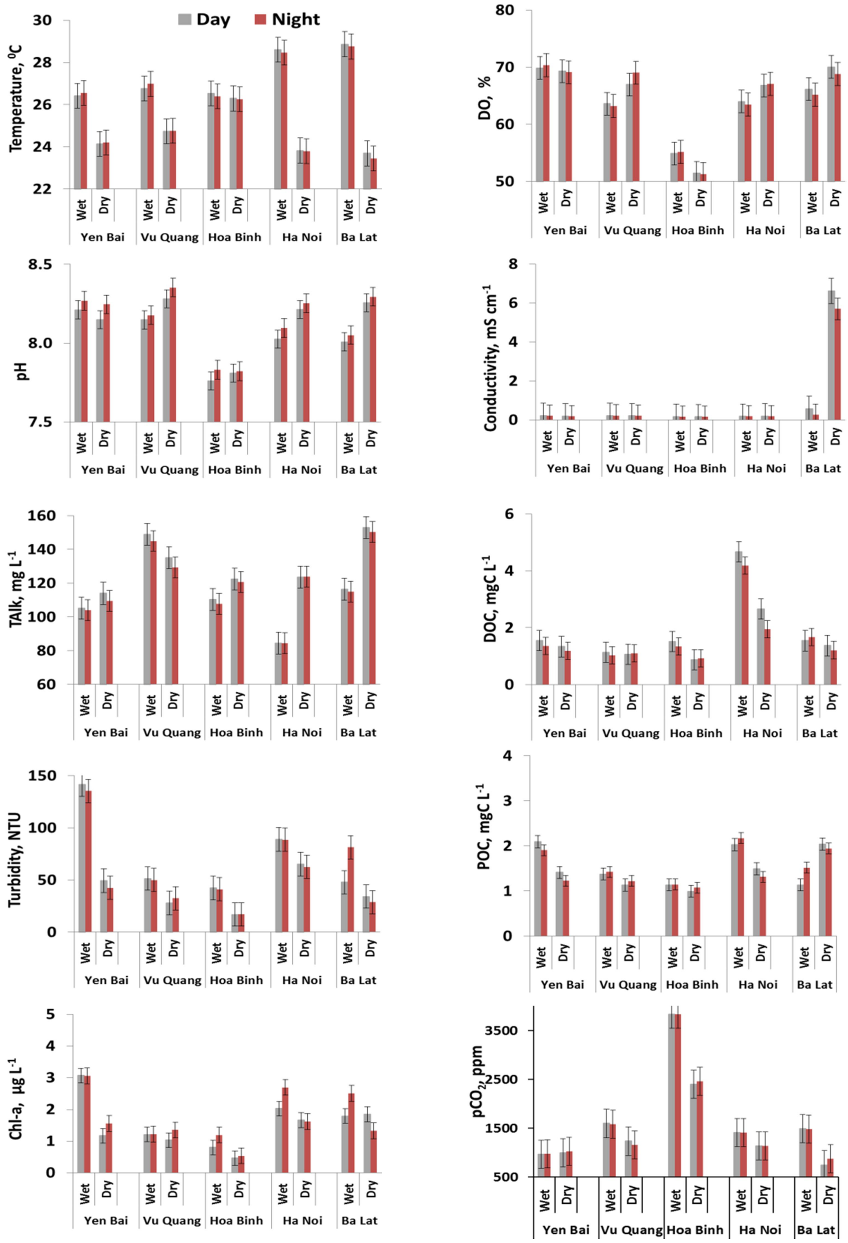

Figure 2. Spatial and seasonal variation of different environmental variables in the Red River system in 2014

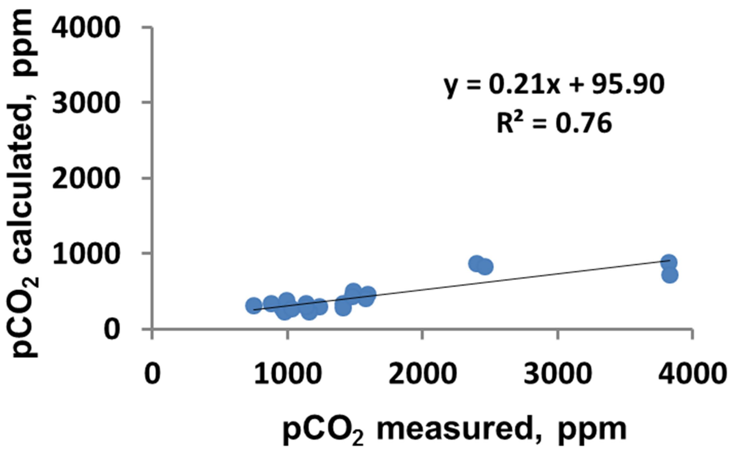

Figure 3. Comparison the result of riverine *p*CO_2 of the lower Red River by measured (equilibrator) and calculated (CO2_SYS) methods

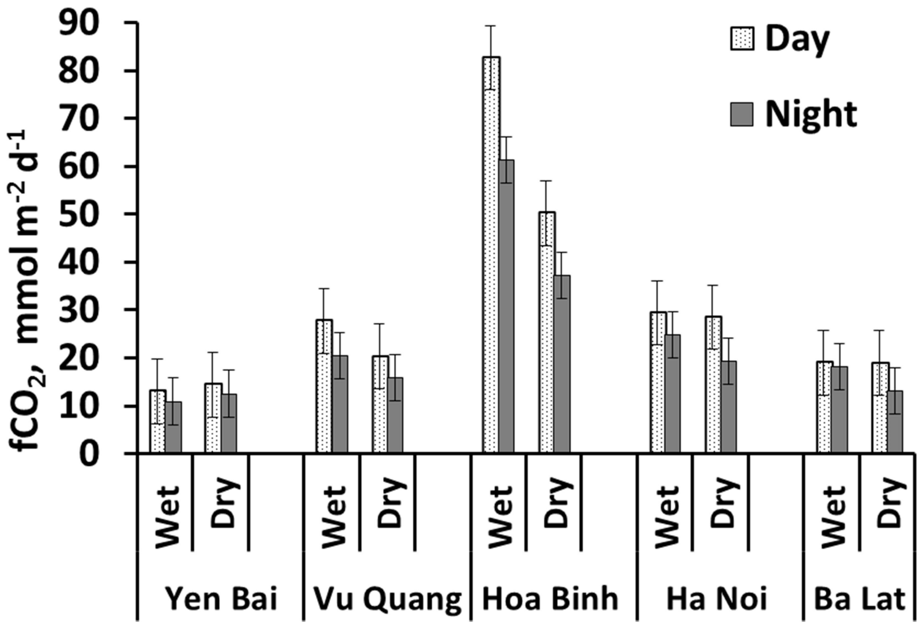

Figure 4. Spatial and seasonal variation of CO_2 flux out-gassing in the Red River system in 2014.

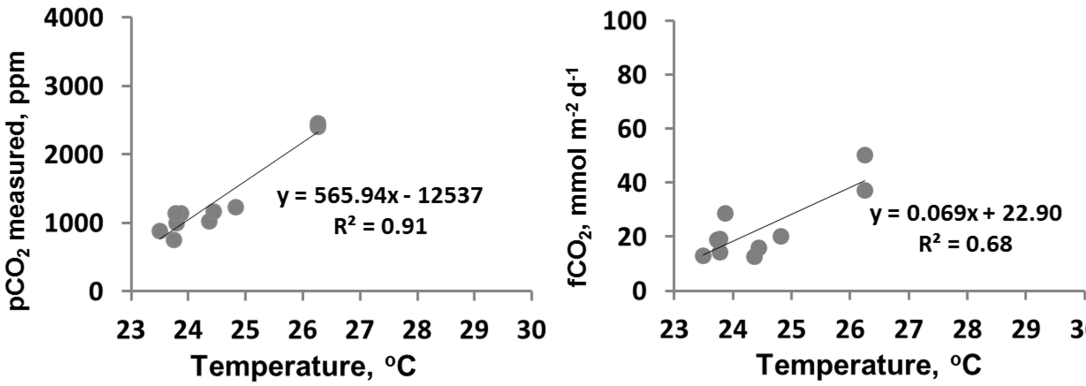

Figure 5. **Relationship between pCO_2, fCO_2 and water temperature at 5 sites observed of the lower Red River in dry season in 2014.**

Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-505
Manuscript under review for journal Biogeosciences
Discussion started: 13 December 2017

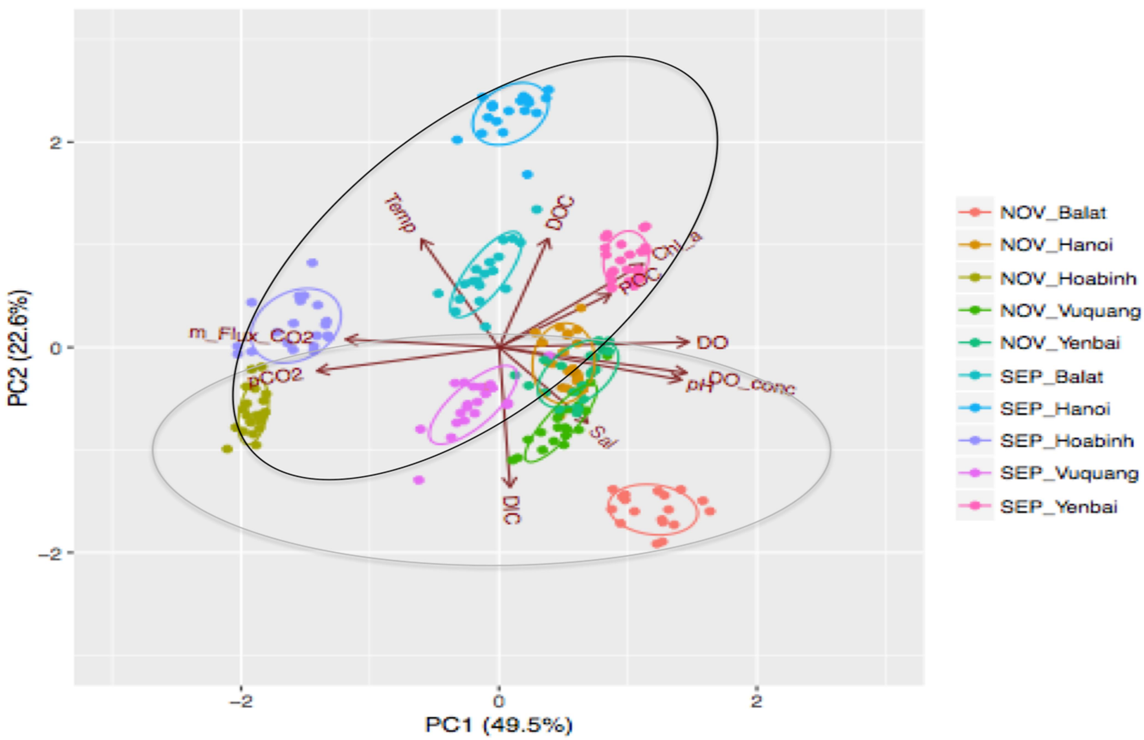

Figure 6. Relationship between environmental variables and *p*CO_2 or CO_2 flux at five sites of the Red River

Biogeosciences Discuss., https://doi.org/10.5194/bg-2017-505
Manuscript under review for journal Biogeosciences
Discussion started: 13 December 2017

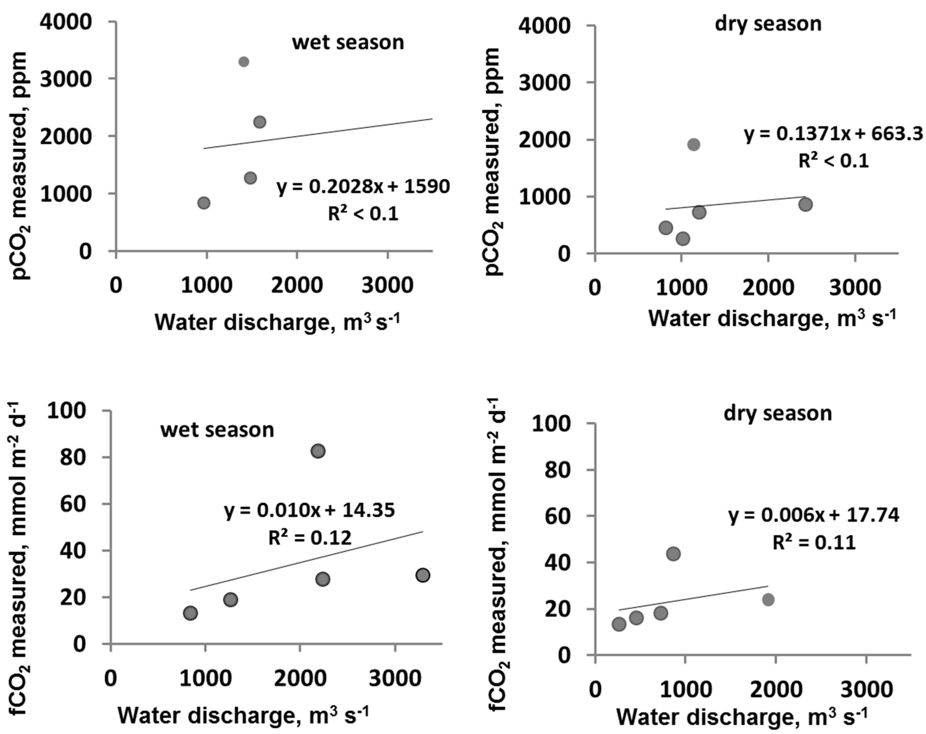

Figure 7. Relationship between pCO_2, fCO_2 and river discharge at 5 sites observed of the lower Red River in wet and dry season in 2014.