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CO_2 partial pressure and CO_2 emission along the lower Red River (Vietnam)

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Abstract. The Red River (Vietnam) is representative 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 CO_2 partial pressure and CO_2 emissions of the lower Red River system. Water quality monitoring and riverine $p\mathrm{CO_2}$ measurements were carried out for 24 h at five stations distributed along the lower Red River system during the dry and the wet seasons. The riverine $p\mathrm{CO_2}$ was supersaturated relative to the atmospheric equilibrium (400 ppm), averaging about 1589 ± 43 ppm and resulting in a water–air CO_2 flux of $530.3 \pm 16.9\,\mathrm{mmol\,m^{-2}\,d^{-1}}$ for the lower Red River. $p\mathrm{CO_2}$ and CO_2 outgassing rates were characterized by significant spatial variation along this system, with the highest values measured at Hoa Binh station, located downstream of the Hoa Binh Dam, on the Da River. Seasonal $p\mathrm{CO_2}$ and CO_2 outgassing rate variations were also observed, with higher values measured during the wet season at almost all sites. The higher river discharges, enhanced external inputs of organic matter from watersheds and direct inputs of CO_2 from soils or wetland were responsible for higher $p\mathrm{CO_2}$ and CO_2 outgassing rates. The difference in $p\mathrm{CO_2}$ between the daytime and the night-time was not significant, suggesting weak photosynthesis processes in the water column of the Red River due to its high sediment load.

1 Introduction

Natural hydrological processes and biogeochemistry of many rivers in the world have suffered from the influences of climate change and human activity in their drainage basins. Riverine carbon fluxes and outgassing are important parts of the carbon exchange among terrestrial, oceanic and atmospheric environments. Rivers and streams not only transfer various forms of carbon (dissolved and particulate) to the oceans but also emit a significant amount of carbon to the atmosphere (Richey et al., 2002; Battin et al., 2009). Due to CO_2 emissions, the flux of carbon that leaves the terrestrial biosphere through the global fluvial network was suggested to be twice as large as the amount that ultimately reaches the coastal ocean (Bauer et al., 2013; Regnier et al., 2013). Raymond et al. (2013) estimated a global evasion rate of $2.1\,\mathrm{Pg\,C\,yr^{-1}}$ from inland waters and that global hotspots in stream and rivers which occupy only 20 % of the global land surface represented 70 % of the emission. They emphasised that further studies are needed for identifying the mechanisms controlling CO_2 evasion on a global scale.

Riverine carbon concentrations and CO_2 outgassing from rivers are impacted by both natural and human factors (Liu et al., 2016, 2017). Recently, spatial and temporal dynamics of $p\mathrm{CO_2}$ and CO_2 outgassing of Asian rivers are attract-

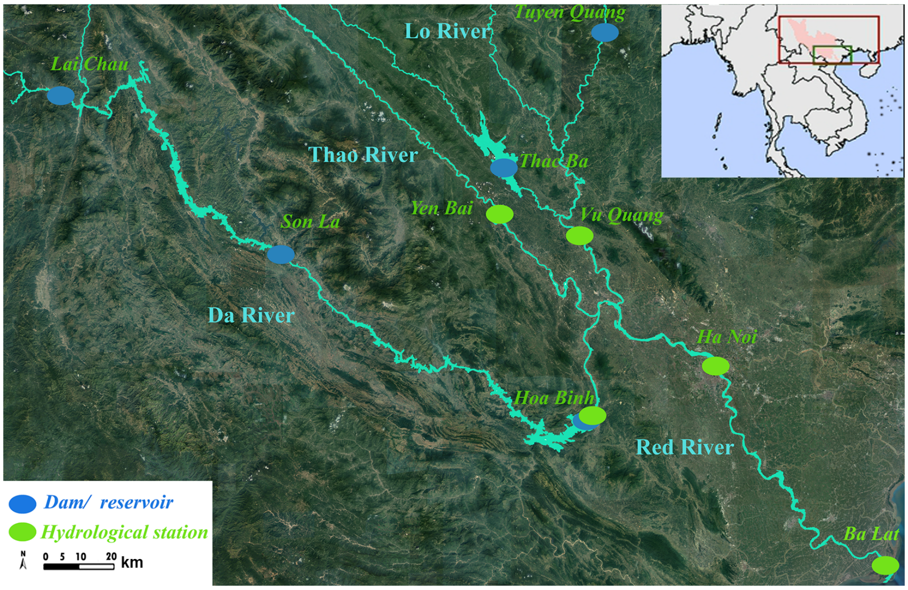

Figure 1. The Red River system and sampling sites (hydrological station).

ing the attention of scientists. Studies of pCO_2 and CO_2 outgassing from the large south-east Asian rivers are crucial to quantify geochemical cycles accurately in the context of global changes because the river water discharge, suspended solids and biogeochemical cycles of these rivers 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 increasing the organic carbon content but also affect chemical weathering and hence carbon consumption and possible pCO_2 (Ran et al., 2015b). Some studies emphasized that data concerning CO_2 outgassing of south-east Asian rivers are highly useful for improving the global evasion rate from inland waters (Raymond et al., 2013; Lauerward et al., 2015).

The Red River, with a basin area of 156 450 km^2, is a typical east Asian river that is strongly affected by climate and human activities. Previous studies reported the hydrology and suspended sediment load associated with some element loads (N, P, C) of the Red River (Dang et al., 2010; Le et al., 2015; Lu et al., 2015). Recently, the transfer of organic carbon of the Red River to the ocean has been studied (Dang et al., 2010; Le et al., 2017). However, there is a lack of data concerning CO_2 outgassing and the carbon budget of the lower Red River (Trinh et al., 2012; Nguyen et al., 2018).

Consequently, the objectives of this study were (i) to investigate spatial and temporal (seasonal and diurnal) variations of CO_2 partial pressure (pCO_2) and CO_2 fluxes at the water–air surface of the lower Red River; and (ii) to identify some of the factors that may control pCO_2 and CO_2 outgassing rates in this system. To our knowledge, our study introduced the first measurement and estimation of CO_2 evasion from the lower Red River.

2 Methods

2.1 Study sites

The five stations were studied along the lower Red River (Vietnam): Yen Bai station (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) and Hanoi and Ba Lat stations (in the main stem of the downstream part of the Red River). The three stations, Yen Bai, Vu Quang and Hoa Binh, are representative of the water quality of the three main tributaries (Thao, Da and Lo) of the upstream Red River, whereas the Hanoi station is representative of the main stem of the Red River after the confluence of the three main tributaries. Only the Ba Lat station, which is located at the Red River mouth (about 13 km from the sea), is influenced by seawater intrusion (Fig. 1). A more detailed description of the river characteristics of the Thao, Da, Lo and the main stem of the Red River can be found in Le et al. (2007).

The climate in the Red River basin is a tropical east Asian monsoon type and 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. 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

Table 1. Average values (and standard deviation) of river water discharge at five studied sites of the Red River in 2014 (MONRE, 2014; Le, 2008).

Studied sites	Altitude (m a.s.l.)	Latitude	Mean water velocity, $m\,s^{-1}$ Wet	Mean water velocity, $m\,s^{-1}$ Dry	Mean water depth, m Wet	Mean water depth, m Dry	Mean slope	Average daily water discharge 2014, $m^3\,s^{-1}$	Water discharge, $m^3\,s^{-1}$ – Wet season: Mean value wet season in 2014 (May–Oct)	Wet season: On the date of measurement Sep 2014	Dry season: Mean value wet season in 2014 (May–Oct)	Dry season: On the date of measurement in Nov 2014
Yen Bai	56	21°42′00.0″ N 104°52′00.0″ E	1.0	0.9	4.8	3.7	0.0012	527 ± 515	788 ± 459	840 ± 68	262 ± 530	260 ± 18
Hoa Binh	23	20°54′00.0″ N 105°21′00.0″ E	0.5	0.4	11.5	9.9	0.0015	1369 ± 833	1907 ± 451	2189 ± 39	825 ± 515	868 ± 319
Vu Quang	25	21°33′00″ N 105°16′00″ E	0.5	0.3	12.3	9.2	0.0018	1302 ± 517	1618 ± 378	2240 ± 88	982 ± 284	725 ± 11
Hanoi	5	21°02′00″ N 105°52′00″ E	1.0	0.9	4.7	3.9	0.0012	1867 ± 1089	2598 ± 780	3296 ± 86	1127 ± 490	1915 ± 149
Ba Lat	0	20°18′07.6″ N 106°32′25.4″ E	0.4	0.3	2.1	1.4	0.0003	615 ± 293	824 ± 200	1269 ± 93	403 ± 96	453 ± 31

regime characterized by large run-off during the wet season and low run-off during the dry season (Table 1).

A series of dams and reservoirs was impounded in both Chinese and Vietnamese territories of the upstream part of Red River (Le et al., 2017). In the Da River, two large dams, Hoa Binh and Son La, were constructed in the river main stem, whereas in the Lo River, two large dams, Thác Bà and Tuyên Quang, were constructed in its tributaries.

The upstream part of the Red River in the Chinese part is dominated by mountainous areas, which are tectonically active and unstable, and this, combined with intense rainfall, causes high erosion rates (Fullen et al., 1998), whereas in the Vietnamese part, soils are mostly (70 %) grey and alluvial (Le et al., 2017). The delta 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). Previous studies showed the difference in lithology in the three upstream tributaries: Paleozoic sedimentary rocks (55.5 %), Mesozoic silicic rocks (18.0 %) and Mesozoic carbonated rocks (16.7 %) dominate in the Thao basin, whereas Paleozoic sedimentary rocks (85.3 %) and Mesozoic carbonated rocks (14.7 %) cover the Da River basin, and the Lo is composed of Mesozoic silicic rocks (21.5 %) and Paleozoic sedimentary rocks (72.7 %) (Le et al., 2007; Moon et al., 2007). The delta area is mostly covered by alluvial deposits (80 %).

Land use was quite different in the three upstream river basins Thao, Da and Lo: industrial crops dominate (58 %) in the Lo basin, forests (70 %) 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 (> 1000 inhabitants 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) are situated, the 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 (the rainy season) and November (the dry season) 2014 at the five gauging stations: Yen Bai, Hoa Binh, Vu Quang, Hanoi and Ba Lat.

Physico-chemical parameters were automatically recorded every minute over 24 h for each sampling campaign: pH, turbidity, salinity, chlorophyll *a* by a YSI6920 multi-parameter probe (YSI, USA); temperature and dissolved oxygen (DO) by a HOBO sensor (USA). These sensors have been calibrated with suitable standard solutions before each measurement campaign: pH electrode (YSI6920) was calibrated using standard solutions (pH = 4.01 and pH = 6.88, Merck) and the pH precision and accuracy was ±0.01; the DO electrode was calibrated using the saturated $Na_2S_2O_3$ solution (Japan) and the DO accuracy was 0.1.

Parallel to the in situ measurements, river water samples were collected hourly for analysis of other water quality variables (TSS, DOC, POC and total alkalinity) over 24 h. A known volume of well-mixed sample was filtered immediately by vacuum filtration through precombusted (at 450 °C for 6 h) glass fibre filters (Whatman GF / F, 47 mm diameter). The filters were then kept in a freezer (−20 °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 h. 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 the DOC concentrations were measured using a TOC-V_E (Shimadzu, Japan). The samples, standards and blank measurements were measured in triplicate and the analytical error was below 3 %.

Total alkalinity of the hourly samples was immediately determined on non-filtered water samples (30 mL water sample) in situ by titration method with 0.01M HCl (APHA, 1995). For each sample, triplicates were titrated and the analytical error was below 3 %.

2.3 Hydrological data collection

Daily and hourly data of river water discharges in 2014 at the five hydrological stations studied were collected from the Vietnam Ministry of Natural Resources and Environment (MONRE, 2014). The daily data were collected for all days in 2014 (Fig. S1 in the Supplement), whereas hourly data were obtained for the exact dates of field measurements at the five sites (Table 1). The mean annual river flows in 2014 of the Thao, Da, Lo Rivers and in the main stem of the Red River at the Hanoi and Ba Lat stations were 527 ± 515, 1369 ± 833, 1302 ± 517, 1867 ± 1089, $615 \pm 293\,m^3\,s^{-1}$ respectively. Higher values of river discharges were observed in the wet season (May to October) than in the dry season (January–April; November–December) at all sites (Table 1).

Water velocity at the five sites varied from $0.3\,m\,s^{-1}$ at the Vu Quang site in the dry season to $1.0\,m\,s^{-1}$ at the Hoa Binh and Yen Bai sites in the wet season. The mean water depth varied with the highest values recorded at the Vu Quang site in the rainy season and the lowest at Ba Lat estuary in both the rainy and the dry seasons (Table 1).

2.4 $p\mathrm{CO_2}$ determination

$p\mathrm{CO_2}$ in the water column was measured using an equilibrator connected to a portable infrared gas analyser (IRGA) and also calculated using T_{alk} and pH measured in situ.

2.4.1 $p\mathrm{CO_2}$

An equilibrator was used to determine the $p\mathrm{CO_2}$ in water equilibrated with the air. The equilibrator was designed, as described in Frankignoulle et al. (2001), as follows: a vertical plastic tube (height: 73 cm, diameter: 9 cm) 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) comes into the equilibrator from the top of the tube through a submerged pump at 20 cm below the river surface water. 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 flow regulator and a portable infrared gas analyser (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 the $p\mathrm{CO_2}$ to record every second. Values were recorded continuously over 24 h. The accuracy is < 3 % of the reading.

2.4.2 Calculated $p\mathrm{CO_2}$

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 from a combination of any two of the following measured parameters: total alkalinity, pH or partial pressure of CO_2 ($p\mathrm{CO_2}$) (Park, 1969). In this study, DIC contents were calculated from the sum of HCO_{3^-}, CO_3^{2-}, H_2CO_3 and CO_2 contents, which were given by the calculation from the CO_2-SYS Excel Macro software (version 2.0) based on the total alkalinity contents and pH values measured in situ as described above (Sect. 2.3).

2.5 CO_2 fluxes determination

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 follows:

$$F_{\mathrm{Equi}} = k_{600} \times \alpha \times (p\mathrm{CO_2}\,\mathrm{water} - p\mathrm{CO_2}\,\mathrm{air}), \quad (1)$$

where F is the CO_2 flux from water ($\mu mol\,m^{-2}\,s^{-1}$) and converted in $mmol\,m^{-2}\,d^{-1}$; k_{600} was gas transfer velocity of CO_2 or piston velocity ($cm\,h^{-1}$). Some studies indicate that k_{600} values are closely related to flow velocity and channel gradient for rivers (Alin et al., 2011). In this study, k_{600} was calculated using the equation from Raymond et al. (2012)

based on stream velocity (V, in $m\,s^{-1}$), slope (S, unitless), depth (D, in metres) and discharge (Q, in $m\,s^{-1}$) as follows:

$$k_{600} = 4725 \pm 445 \times (V \times S)^{0.86 \pm 0.016} \times Q^{-0.14 \pm 0.012} \times D^{0.66 \pm 0.029}. \quad (2)$$

α is the solubility coefficient of CO_2 for given temperature and salinity (Weiss, 1974) ($mol\,L^{-1}\,atm^{-1}$). In this case, $\alpha = 0.034\,mol\,L^{-1}\,atm^{-1}$. In this study, salinity variation was low, except for the Ba Lat station. Temperature did not change a lot. We checked the influence of different α values in the dry ($\alpha = 3.941 \times 10^{-2}\,mol\,L^{-1}\,atm^{-1}$ at 24 °C) and the wet season ($\alpha = 3.138 \times 10^{-2}\,mol\,L^{-1}\,atm^{-1}$ at 27 °C) at the five sites and compared them with the constant α value of $0.034\,mol\,L^{-1}\,atm^{-1}$.

Both pCO_2 in the water determined from the equilibrator measurement (in ppm) and from the CO_2-SYS calculation (in atm) were converted into µmol when calculating the flux of CO_2 outgassing.

2.6 Statistical analysis

To detect the correlation between environmental variables and pCO_2, 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 to identify representative variables that could relate to the dynamic of pCO_2.

Student's t test was used to test the difference in variables values between the two different times (the wet and the dry) and (the day and the night), whereas ANOVA was used to test the difference in variables within stations on the measured mean variables. Probabilities (p) were determined and a p value of < 0.05 was considered to be significant.

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 the rainy period (27.4 °C) was higher than the one in the dry period (24.5 °C) at almost all stations, except at the Hoa Binh site, where the water temperatures did not show seasonal variation, 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). No clear difference for water temperature during the daytime and night-time was observed at the five sites in both the rainy and the dry season ($p < 0.05$).

pH values were slightly different between the two periods, being higher in the dry season than in the wet season at all the sites (Table 2) ($p < 0.05$). pH ranged from 7.7 to 8.2 with an average of 8.1 for all the sites. The lowest pH values were measured at Hoa Binh in both periods (< 8), whereas they ranged between 8.0 and 8.4 at the other sites.

The percentage of dissolved oxygen (% DO) varied from 50.5 % to 70.7 % with an average value of 64.3 % (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). DO showed the seasonal and spatial variations but no clear day–night difference was observed ($p < 0.05$).

Salinity values at the four upstream sites were under the detection limit both in the rainy and dry seasons, but downstream of the river estuary at the Ba Lat station, values up to 8.75 were measured during the dry season (Table 2). Conductivity followed the same trend as salinity, was close to $0.2 \pm 0.0\,mS\,cm^{-1}$ for the four upstream sites and reached $6.6 \pm 3.4\,mS\,cm^{-1}$ at Ba Lat (Table 2).

Total alkalinity ranged from 84.3 ± 1.9 to $152.9 \pm 6.6\,mg\,L^{-1}$, with higher values measured in the dry season than in the rainy season ($p < 0.05$), except at Vu Quang station. The difference in total alkalinity was spatially recorded but no clear variation appeared between values in daytime and night-time at five sites ($p < 0.05$).

Chlorophyll a was quite low during the two sampling campaigns, ranging from 0.23 to 2.77 $\mu g\,L^{-1}$, with an average of 1.61 $\mu g\,L^{-1}$. Higher values in the rainy season than in the dry season were observed but no clear day–night difference was observed at almost sites ($p < 0.05$). From Yen Bai to Ba Lat, Chl a concentrations in the main stem (at Yen Bai and Hanoi stations) were higher than in the two tributaries Da and Lo (Table 2), even under the higher values of turbidity.

3.2 Carbon concentrations of the lower Red River

During the two sampling campaigns, DOC concentrations 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 vs. 1.5 $mgC\,L^{-1}$ during the dry season), and the highest value was recorded at Hanoi station (Table 2). POC concentrations varied from 0.4 to 4.6 $mgC\,L^{-1}$. Among the five 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. Spatial and seasonal variations of DOC and POC were observed but no clear difference between day and night-time was found ($p < 0.05$) (Table 2, Table S1 in the Supplement).

DIC concentrations at the five sites fluctuated between 16.7 and 32.9 $mgC\,L^{-1}$, averaging 23.8 $mgC\,L^{-1}$. Lower values were measured in the rainy season (22.3 $mgC\,L^{-1}$) than

Table 2. Average values at daytime and night-time of the different physico-chemical variables (average value and standard deviation) at the five sites in wet and dry seasons in 2014.

Stations	Temperature °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	963.9 ± 9.4	699.1 ± 86.1
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	981.3 ± 7.7	609.1 ± 26.5
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	1169.2 ± 131.2
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	1058.5 ± 33.0
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	2125.9 ± 294.5
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	1747.0 ± 56.8
4 Hanoi												
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	1412.6 ± 4.0	888.7 ± 108.3
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	1411.0 ± 7.0	768.6 ± 47.3
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 ± 0.2	66.1 ± 1.4	1499.2 ± 103.2	1312.2 ± 267.3
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	1471.3 ± 118.1	1156.7 ± 77.6
Dry season												
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	896.8 ± 320.3
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	655.0 ± 19.5
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	756.2 ± 81.7
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	604.2 ± 35.0
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	0.5 ± 0.1	51.5 ± 0.4	2399.3 ± 33.6	2091.7 ± 227.2
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	0.5 ± 0.1	51.3 ± 0.2	2458.9 ± 14.0	2003.9 ± 200.7
4 Hanoi												
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	797.7 ± 95.4
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	726.1 ± 5.9
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	753.6 ± 56.5
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	795.1 ± 46.3

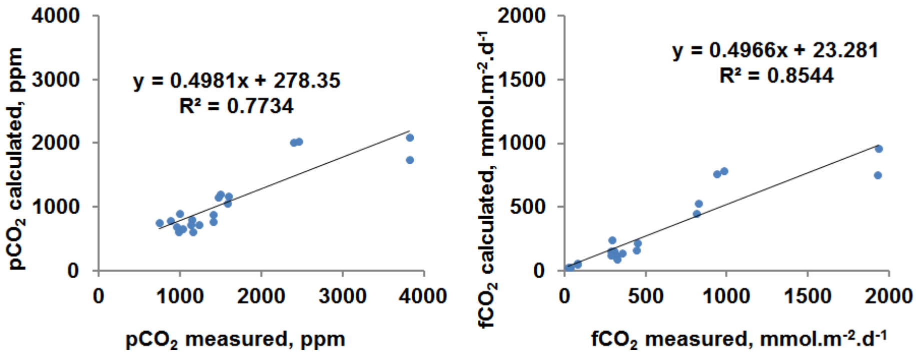

Figure 2. Comparison of the results of riverine pCO_2 and fCO_2 at five sites studied at the lower Red River by the measured (equilibrator) and calculated (CO_2-SYS) methods

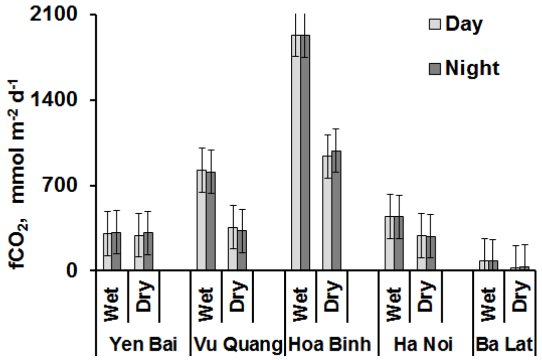

Figure 3. Spatial and seasonal variation of CO_2 flux outgassing in the Red River system in 2014.

in the dry season (25.3 mgC L^{-1}) and the difference in DIC was noted for the five sites ($p < 0.05$) (Table 2).

3.3 Comparisons of the pCO_2 results obtained by the two methods

pCO_2 along the lower Red River (Vietnam) in the dry and the wet seasons were determined by two methods: (i) direct measurements using an equilibrator connected to an IRGA, (ii) calculations from pH and alkalinity using the CO_2-SYS® software. The direct pCO_2 measurements gave slightly higher values than the calculated ones (Table 2), but the values of the two methods were similar and presented the same trend of spatial and seasonal variations ($R^2 = 0.77$, Fig. 2; Table 2). Lower values of the calculated pCO_2 in this study may be caused by the analytical errors in pH or underestimation of total alkalinity. Similarly, the CO_2 outgassing rates which were calculated from measured pCO_2 from the equilibrator were higher than the ones derived from the calculated pCO_2 from CO_2-SYS; however they are in the same order and have similar variation trends (Table 3, Fig 2).

Below, we use the results of pCO_2 (and fCO_2) from direct measurements to discuss the spatial and seasonal variations of pCO_2 (and fCO_2) of the lower Red River.

3.4 Relations between pCO_2 and water chemistry variables

The riverine water pCO_2 was supersaturated with CO_2 in contrast to the atmospheric equilibrium (400 ppm), averaging 1589 ± 43 ppm for all sites observed. In general, the results did not show a clear variation in pCO_2 between day and night, except for higher values at night-time at the Ba Lat site and higher values in the daytime at Vu Quang in the dry season ($p < 0.05$) (Table 2). This leads to the same trends in CO_2 outgassing rates: no clear difference between daytime (548.9 ± 17.9 mmol m^{-2} day^{-1}) and night-time (551.8 ± 15.9 mmol m^{-2} day^{-1}) ($p < 0.05$) (Table 3, Fig. 3).

pCO_2 values fluctuated from 694 ppm (at Yen Bai) in the dry season to 3887 ppm (at Hoa Binh) in the wet season in 2014. The mean values were the highest for the Hoa Binh station in both seasons, whereas the lowest one was observed at the Yen Bai site. Spatial variation of both pCO_2 and fCO_2 fluxes for all five sites was observed ($p < 0.05$). Higher values of pCO_2 in the wet season than in the dry season were observed at almost all the sites ($p < 0.05$) (Table 2).

CO_2 outgassing rates of the five stations of the lower Red River showed seasonal and spatial variations ($p < 0.05$). The highest value was recorded at the Hoa Binh site in both the rainy and dry seasons, averaging 1447.5 ± 27.4 mmol m^{-2} d^{-1}, and the lowest value was observed at the Ba Lat site, averaging 54.6 ± 6.5 mmol m^{-2} d^{-1}. CO_2 outgassing rates were higher in the wet season than in the dry season at all sites (Table 3, Fig. 3).

PCA and Pearson correlation coefficients were performed to analyse the relationships between nine environmental variables and pCO_2 at the five sampling stations of the lower Red River in the wet season (September 2014) and the dry season (November 2014). The PCA of the seasonal data for five sampling stations presented a clear separation between two periods (Fig. 4a). The rainy period was characterized by the factors of flow, temperature, pCO_2, POC, DOC, turbidity and Chl a. The dry season is mainly governed by the factors of DIC, salinity and conductivity. The spatial differences

Table 3. k_{600} parameterization and calculated water–air CO_2 fluxes for daytime and night-time at five hydrological stations at 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)
Wet season			
Yen Bai			
Day	1.1 ± 0.6	66.1 ± 0.55	304.5 ± 3.9
Night	0.5 ± 0.6	66.5 ± 0.09	315.2 ± 4.0
Vu Quang			
Day	0.9 ± 0.7	84.2 ± 0.12	824.0 ± 36.7
Night	0.4 ± 0.6	84.1 ± 0.02	811.8 ± 25.1
Hoa Binh			
Day	1.3 ± 1.1	69.1 ± 0.27	1935.2 ± 38.3
Night	0.2 ± 0.5	69.0 ± 0.03	1931.3 ± 10.0
Hanoi			
Day	1.8 ± 0.7	54.0 ± 0.96	446.6 ± 8.7
Night	1.2 ± 0.6	53.5 ± 0.17	441.6 ± 3.6
Ba Lat			
Day	0.5 ± 0.5	9.1 ± 0.05	81.1 ± 7.8
Night	0.2 ± 0.3	9.1 ± 0.02	79.4 ± 8.6
Dry season			
Yen Bai			
Day	1.4 ± 0.9	59.6 ± 0.72	290.5 ± 8.2
Night	0.5 ± 0.8	60.1 ± 0.54	309.3 ± 13.3
Vu Quang			
Day	1.3 ± 0.6	52.4 ± 0.11	356.6 ± 33.0
Night	0.7 ± 1.3	52.4 ± 0.15	326.3 ± 37.0
Hoa Binh			
Day	1.2 ± 0.8	58.4 ± 2.85	938.4 ± 22.7
Night	0.5 ± 0.5	58.5 ± 1.97	985.0 ± 38.6
Hanoi			
Day	2.4 ± 0.5	47.4 ± 0.60	287.0 ± 16.2
Night	1.4 ± 0.5	47.3 ± 0.57	284.2 ± 12.7
Ba Lat			
Day	3.1 ± 1.5	8.6 ± 0.07	24.7 ± 3.5
Night	1.3 ± 0.8	8.5 ± 0.03	33.5 ± 6.1

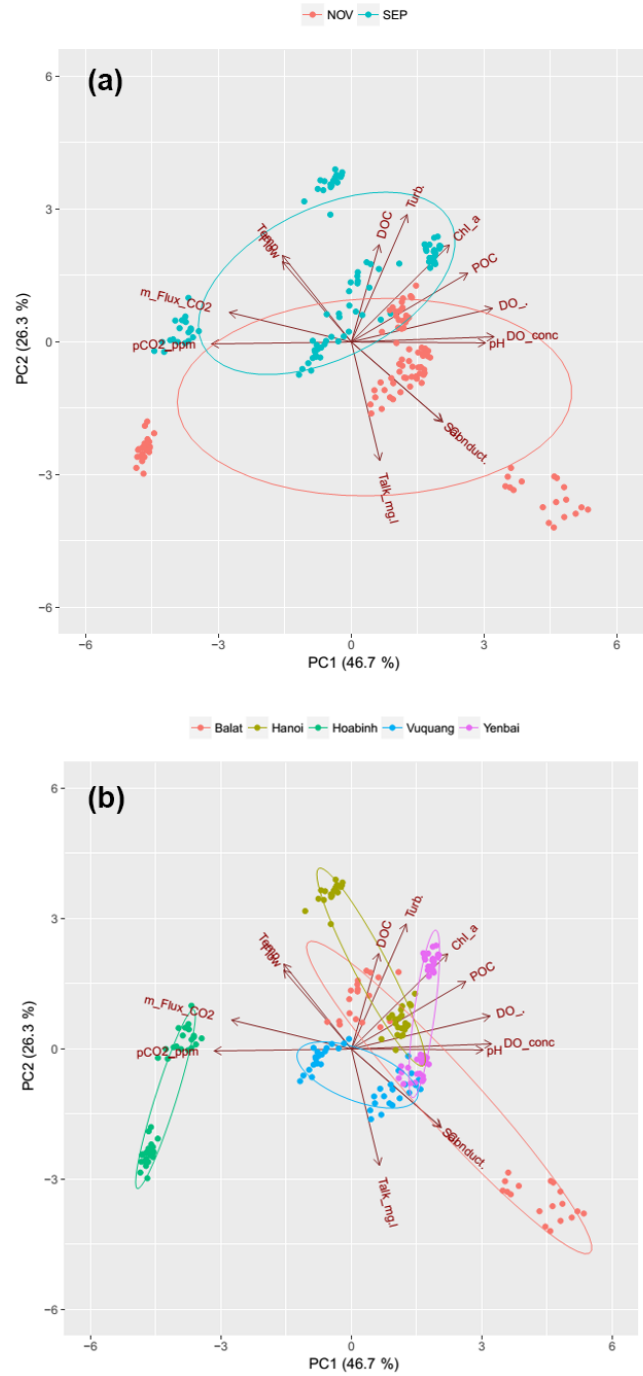

Figure 4. (a) Seasonal variation of different variables at five sites at the lower Red River in dry (Nov) and wet (Sep) seasons in 2014 **(b)** Spatial variation of different variables at five sites at the lower Red River in dry and wet seasons in 2014.

appeared for almost variables in both wet and dry seasons (Fig. 4b). Among the five stations, the Hoa Binh station is characterized by the pCO_2 and CO_2 fluxes, whereas the Ba Lat station had strong influences from salinity and conductivity. The other stations showed a combination of different factors. The Hoa Binh station has the highest flows, which correlate with the pCO_2 and CO_2 fluxes.

The Pearson correlation coefficient showed a strong negative correlation between pCO_2 and pH and oxygen saturation

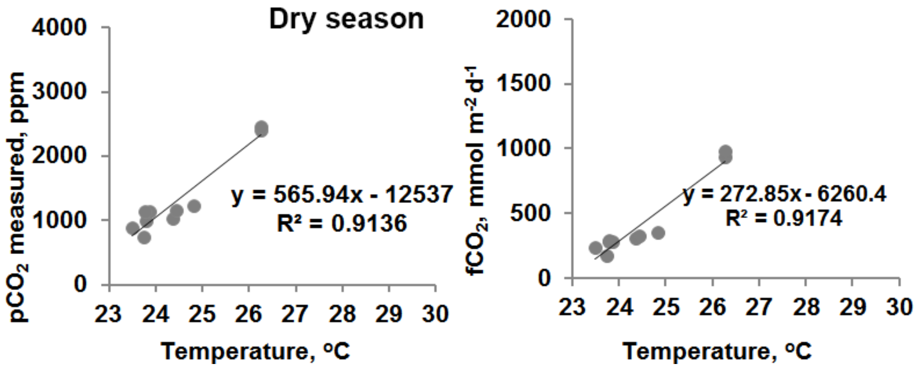

Figure 5. Relationship between pCO_2– water temperature and fCO_2– water temperature at five sites observed at the lower Red River in the dry season in 2014.

(%) ($r \sim -0.8$ for both). A low positive correlation between pCO_2 and DIC and DOC was found ($r \sim 0.15$) (Table 4). However, the pCO_2 is positively correlated with the flow of the river ($r = 0.3$). Consequently, we mentioned that the pCO_2 are the results of a combination of multiple parameters, rather than a single one, such as the flow of river, season (including precipitation and temperature), dam construction, population density and geomorphological characteristics of the catchment.

4 Discussion

4.1 Temporal variation of pCO_2 and CO_2 fluxes of the lower Red River

Different explanations were given for the day–night variation of pCO_2 and CO_2 fluxes for aquatic ecosystems across the world. Previous studies indicated that water temperature could alter the riverine pCO_2 value because CO_2 solubility decreases with temperature increase during the day (Parkin and Kaspar, 2003). This effect was observed for some rivers in the world (Guasch et al., 1998; Dornblaser and Striegl, 2013; Peter et al., 2014). Other studies revealed that photosynthesis of phytoplankton may have a strong influence on circadian variation of pCO_2 or CO_2 outgassing, since this process consumes CO_2 during the day (Linn and Doran, 1984).

Concerning the lower Red River, water temperature did not show clear variation between day and night. In addition, 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 the C dynamic in the lower Red River system. Consequently, there is no clear variation in pCO_2 and CO_2 fluxes between daytime and night-time at the different stations along the lower Red River.

Regarding seasonal variation, some authors suggested that higher water temperatures in the wet season in tropical regions were responsible for increased pCO_2 and higher CO_2 emissions to the atmosphere (Hope et al., 2004; Li et al., 2012). Dessert et al. (2003) suggested that higher temperatures should also induce higher weathering rates, leading to higher DIC exports. An increase in temperature decreases CO_2 solubility but increase OM decomposition processes, which produce CO_2. These processes may partly explain the higher pCO_2 of the lower Red River during the hot and rainy season. However, a direct relationship between temperature and pCO_2 was not evidenced during the rainy season, probably because riverine inputs were the dominant factor driving pCO_2. Conversely, during the dry season, pCO_2 clearly increased with temperature, suggesting that the metabolic rate controlled pCO_2 when adjacent soils inputs are limited (Fig. 5).

Another important factor that impacted pCO_2 seasonal variation in the lower Red River was the river discharge. Indeed, during the monsoon season, the Red River discharges were about 2 to 3 times higher at all the sites ($p < 0.05$) (Table 1). Higher pCO_2 and CO_2 fluxes values were observed in the wet season at almost all sites ($p < 0.05$). CO_2 flux varied from 54.6 ± 6.5 mmol m^{-2} d^{-1} (at Ba Lat) in the dry season to 1447.5 ± 27.4 mmol m^{-2} d^{-1} (at Hoa Binh) in the wet season. The higher pCO_2 and CO_2 flux values observed during the wet 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 measured in our study ($p < 0.05$). In tropical regions, the wet season usually experienced higher pCO_2 than the dry season because the intense rainfall induced higher OM inputs into the river (Richey et al., 2002) or, in addition, inputs of CO_2 from wetlands. 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 a significant amount of carbon into the streams. Another example which could be mentioned is the case of the Godavari River in Indonesia, where extremely high values of pCO_2 were measured, up to ∼ 30 000 ppm, probably due to significant organic carbon decomposition during the peak discharge period. This was in contrast with the very low values measured (< 500 ppm) during the dry season for this river (Sharma et al., 2011).

To conclude, no clear day–night-time variation of both pCO_2 and fCO_2 at five sites at the lower Red River in 2014 was found but our results showed clear seasonal variation of both pCO_2 and fCO_2. The spatial variation of pCO_2 and fCO_2 at five sites of the lower Red River under natural and anthropogenic factors will be discussed below.

4.2 Spatial variation in pCO_2 and fCO_2 outgassing

4.2.1 Influence of geomorphological characteristics

The upstream part of the Red River is located in mountainous areas, where chemical and mechanical erosion are among the world's highest (500 mm per 1000 years) (Meybeck et al., 1989), which may be included in the elevated pCO_2 values measured. The geologic substratum of the upstream Red River is dominated by consolidated paleozoic sedimentary rocks, with variable contributions of mesozoic silicic or carbonate rocks. During rainfall events, the erosion of these rocks may increase pCO_2 in the tributary river waters of the Thao, Da and Lo, which were supersaturated with CO_2 in air about 2 to 14 times. Our results showed that the pCO_2 mean value of the lower Red River (1589 ± 43 ppm) was close to the ones of some Asian rivers such as the downstream Mekong River, 703–1597 ppm (Alin et al., 2011); the Longchuan River, 2101–2601 ppm (Li et al., 2012); the Changjiang River, 1297 ± 901 ppm (Wang et al., 2007), and the Yellow River, 2811 ± 1986 ppm (Ran et al., 2015a) (Table 5). However, very high pCO_2 values, up to 11 000 ppm, were also observed for other Asian rivers, like the Xijiang River (Yao et al., 2007).

CO_2 emissions from the lower Red River varied with a large range, from 54.6 ± 6.5 to 1447.5 ± 27.4 mmol m^{-2} d^{-1}, averaging 550.3 ± 16.9 mmol m^{-2} d^{-1}. They were close to the values of some large Asian rivers such as the Yellow River (856 ± 409 mmol m^{-2} d^{-1}) (Ran et al., 2015b) and the Xijiang River (357 mmol m^{-2} d^{-1}) (Yao et al., 2007) or 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) (Table 5). Thus, the high alkalinity, pCO_2 and fCO_2 in the Red River in this study can be partly explained by wide distribution of carbonate–silicate rocks in the upper Red River drainage area, especially during high water discharge as observed for other Asian rivers.

4.2.2 Influence of hydrological characteristics

Spatially, pCO_2 differences between the three upstream tributaries and the main downstream stem of the Red River are suggested to be partially related to different hydrological characteristics and management of the three sub-basins and

Table 4. Relationship of pCO_2 and fCO_2 with other water quality variables.

	Temp, °C	DOC, mg L^{-1}	POC, mg L^{-1}	Talk, mg L^{-1}	pCO_2, ppm	pH	DO, mg L^{-1}	Sal, %	Chl *a*, g L^{-1}	DO, %	Turb., NTU	Conduct., mS cm^{-1}	River Flow, m^3 s^{-1}	fCO_2, mmol m^{-2} d^{-1}
Temp, °C	1													
DOC, mg L^{-1}	0.29	1.00												
POC, mg L^{-1}	0.00	0.36	1.00											
Talk, mg L^{-1}	−0.47	−0.52	−0.08	1.00										
pCO_2, ppm	0.31	−0.14	−0.64	−0.15	1.00									
pH	−0.50	0.01	0.60	0.28	−0.85	1.00								
DO_conc, mg L^{-1}	−0.58	0.02	0.62	0.18	−0.83	0.91	1.00							
Sal, %	−0.37	−0.08	0.30	0.50	−0.26	0.31	0.33	1.00						
Chl *a*, μg L^{-1}	0.30	0.32	0.66	−0.46	−0.48	0.41	0.43	0.02	1.00					
DO, %	−0.33	0.12	0.71	0.05	−0.86	0.89	0.96	0.25	0.60	1.00				
Turb., NTU	0.34	0.33	0.57	−0.56	−0.33	0.25	0.27	−0.23	0.87	0.44	1.00			
Conduct., mS cm^{-1}	−0.38	−0.08	0.32	0.51	−0.27	0.32	0.34	0.99	0.02	0.25	−0.23	1.00		
River flow, m^3 s^{-1}	0.53	0.57	0.10	−0.33	0.36	−0.34	−0.44	−0.30	0.07	−0.33	0.18	−0.31	1.00	
fCO_2, mmol m^{-2} d^{-1}	0.21	−0.16	−0.56	−0.12	0.95	−0.75	−0.75	−0.28	−0.48	−0.79	−0.27	−0.29	0.38	1

Table 5. pCO$_2$ (average value and standard deviation) of some world rivers.

River or tributary	Location	Country	Mean pCO$_2$ ppm	F_{CO_2} mmol m^{-2} day^{-1}	$k_{600} \pm$ SD cm h^{-1}	References
Red		Vietnam	1589 ± 43	550.3 ± 16.9	50.9 ± 27	This study
Mekong	Downstream	Laos and Cambodia	703–1597	88.1–378.4	12.4–44.5	Alin et al. (2011)
Tonle Sap	Stung Siem Reap	Cambodia	3067	139.1	5.6 ± 0.9	Alin et al. (2011)
Tonle Sap	Pousat River	Cambodia	1404	98.5	10.8 ± 2.8	Alin et al. (2011)
Musi		Indonesia	4317 ± 928	5 ± 1.1	21.8 ± 4.7	Wit et al. (2015)
Batanghari		Indonesia	2401 ± 18	1.8 ± 0.4	21.8 ± 4.7	Wit et al. (2015)
Indragiri		Indonesia	5779 ± 527	9.7 ± 2.2	21.8 ± 4.7	Wit et al. (2015
Siak		Indonesia	8557 ± 528	8.3 ± 1.9	22.0 ± 4.7	Wit et al. (2015
Lupar		Malaysia	1274 ± 148	13 ± 3.0	26.5 ± 9.3	Wit et al. (2015
Saribas		Malaysia	1159 ± 29	14.6 ± 3.3	17.0 ± 13.6	Wit et al. (2015
Changjiang		China	1297 ± 901	143	8–15	Wang et al. (2007
Maotiao		China	3741	108	10	Wang et al. (2011)
Longchuan		China	2101	156	8	Li et al. (2012)
Yellow		China	2811 ± 1986	856 ± 409	42.1 ± 16.9	Ran et al. (2015)
Xijiang		China	600–7200	160–357	15	Yao et al. (2007)
Krishna		India	$17\,210 \pm 3501$		nd[a]	Sarma et al. (2012)
Godavari			$49\,832 \pm 1042$			
Mahanadi			$95\,884 \pm 2235$			
Ganges			5030 ± 100			
Gaderu Creek		India	2216 ± 864[b]	56.0 ± 100.9	4 ± 5	Borges et al. (2003)
Rhone		France	2016 ± 944	nd	15	Cole et al. (2001
Hudson		USA	1125 ± 403	nd	4.1	Raymond et al. (1997)
Ottawa		Canada	1200	80.8	4	Telmer and Veizer (1999)
Amazon			4351 ± 1900	190 ± 55	9.6 ± 3.8	Richey et al. (2002)
Mississippi			100–600	270	3.9	Dubois et al. (2010); Lohrenz and Cai (2006)
Nagada Creek	The northern Papua New Guinea coast		799 ± 357	43.6 ± 33.2	8 ± 6	Borges et al. (2003)
Negro	South America		3011 ± 304	534 ± 148	20.3 ± 7.6	Rasera et al. (2013)
Solimoes			5685 ± 464	488 ± 83	7.3 ± 2.4	
Arguaia			1012 ± 309	153 ± 44	8.4 ± 2.4	
Javaes			1673 ± 273	108 ± 34	7.2 ± 2.7	
Caxiuana			3216 ± 496	335 ± 61	11.3 ± 3.5	
Teles Pires			1419 ± 224	100 ± 27	10.1 ± 1.5	
Cristalino			1938 ± 201	202 ± 31	15.7 ± 2.2	
Yukon	Upper	North America	1220 ± 9	6	1.25	Striegl et al. (2007, 2012)
	Middle		1890 ± 10	62	7.92	
	Lower		3091 ± 17	193	15	
Congo			2019–6855	298.6	9.3–10.3	Wang et al. (2013)

[a] nd. is no data. [b] calculated the values for the pCO$_2$ water–air gradient (ΔpCO$_2$ in ppm).

delta area, as observed in other systems (Yao et al., 2007; Li et al., 2012). Our results showed that within the three upstream sites studied, the highest pCO$_2$ values were always measured in the Da River at the Hoa Binh site, where river discharges were the highest (2189 ± 39 m s^{-1} in the wet season and 868 ± 319 m s^{-1} in the dry season) ($p < 0.05$), whereas the lowest pCO$_2$ values were measured at the Yen Bai station of the Thao River, where river discharges were lowest (840 ± 68 m s^{-1} in the wet season and 260 ± 18 m s^{-1} in the dry season) (Tables 1 and 2). Figure 4 showed the clear difference in pCO$_2$, CO_2 flux and river discharges in the rainy and the dry seasons for the lower Red River.

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 the Hanoi site (3296 ± 86 and 1915 ± 149 m s^{-1}) was about 3 times higher than the one at Ba Lat (1269 ± 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 (1150 and 800 ppm respectively), but during the rainy season the values were close, i.e. around 1450 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 ($p < 0.05$). The higher salinity values measured at the Ba Lat site in the dry season (3.6) than in the wet season (0.2) may confirm our suggestion that tidal action influenced the 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).

4.2.3 Influence of land-use on $p\mathrm{CO_2}$ and CO_2 emissions

Land cover in the river basin may play a considerable role in controlling riverine $p\mathrm{CO_2}$. As is known, severe erosion due to sparse vegetation cover may enhance chemical weathering by increasing the exposure surface of fresh minerals to the atmosphere (Millot et al., 2002). Li and Bush (2015) demonstrated that deforestation and agricultural expansion in the Mekong River basin accelerated chemical and physical weathering rates, leading to changes in riverine carbon fluxes. In fact, very high $p\mathrm{CO_2}$ values (up to 30 008 ppm) were observed in the Godavari estuary due to large-scale erosion and deforestation in the catchment area, which accelerated the export of organic carbon into the river, especially in the wet season (Sharma et al., 2011). In contrast, recently in another study, $p\mathrm{CO_2}$ in one sub-basin (HR), lower than the average of the Yellow River basin, was observed because of the development of an alpine meadow ecosystem reducing soil erosion (Ran et al., 2015a). For the Red River, the highest riverine $p\mathrm{CO_2}$ and CO_2 flux values were observed in the Da at the Hoa Binh site even though this sub-basin is dominated by forest. This may suggest that other factors (reservoir impoundment and geological characteristics) may strongly control $p\mathrm{CO_2}$ and CO_2 fluxes of the Da River.

In addition, agricultural soil in the river basin may have a significant impact on riverine $p\mathrm{CO_2}$. A study concerning the long-term variation of $p\mathrm{CO_2}$ of the Yellow River showed that high pH in irrigation water caused the increase in riverine pH, leading to a further reduction in $p\mathrm{CO_2}$ (Ran et al., 2015a). This agrees with our results for $p\mathrm{CO_2}$ in the Red River when considering the decrease in the $p\mathrm{CO_2}$ values, especially in the dry season from the upstream delta area at Hanoi (1139 ± 29 ppm) to the estuary at Ba Lat (mean value of 816 ± 69 ppm), where rice field and irrigation channels are very dense.

4.2.4 Influence of dams on $p\mathrm{CO_2}$ and CO_2 emission

Previously, it was suggested that reservoirs decrease riverine $p\mathrm{CO_2}$ 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 of $p\mathrm{CO_2}$ in the downstream part of the river. In addition, the influence of the dam on the gas transfer velocity and then CO_2 outgassing flux in the river, downstream of the dam, was also demonstrated in the study of the Sinnamary River (Guérin et al., 2007). In the present study, in the upstream part, $p\mathrm{CO_2}$ ranged from 964 ppm (at Yen Bai) to 3830 ppm (at Hoa Binh), being highest at the Hoa Binh site where the lowest pH values were measured. Higher k_{600} values (from 63 to 68 $\mathrm{cm\,h^{-1}}$) were also observed at the Hoa Binh and Vu Quang sites. Note that the Hoa Binh site is situated downstream of a series of reservoirs, which have been constructed in both the Chinese and Vietnamese parts including two large dams Hoa Binh (in 1989) and Son La (in 2010). The Vu Quang site is located in the downstream part of a series of reservoirs, including two important reservoirs, Thác Bà (in 1970) and Tuyên Quang (in 2010). Previous studies emphasized that these dams have impacted water and sediment discharge downstream (Ha and Vu, 2012; Ngo et al., 2014; Lu et al., 2015) with significant sediment deposition being observed in the reservoirs (Dang et al., 2010; Vinh et al., 2014; Lu et al., 2015). Thus, the higher $p\mathrm{CO_2}$ measured at these sites (average value of 3129 ± 32 ppm) may reflect the increased decomposition of OM and/or the water perturbation due to dam construction, especially for the Da River. The impact of dams on downstream $p\mathrm{CO_2}$ may be less for the Lo and the Thao Rivers (average values of 1395 ± 63 ppm and 993 ± 14 ppm respectively), where lower numbers and sizes (only small and medium) of dams/reservoirs were built up in their upstream parts. Thus, the high $p\mathrm{CO_2}$ measured at these stations may reflect the increased decomposition of OM and/or the water perturbation due to the large dam construction.

4.2.5 Influence of population density on $p\mathrm{CO_2}$ and $p\mathrm{CO_2}$ emission

Previous studies demonstrated very high values of $p\mathrm{CO_2}$ in river estuaries as a result of different human activities. For instance, $p\mathrm{CO_2}$ up to $\sim 25\,000$ ppm was measured in the Rhine estuary (Kempe, 1982) and up to $\sim 15\,200$ ppm in the Scheldt estuaries due to high discharge of pollutants (Borges and Frankignoulle, 2002).

Concerning the Red River, from the upstream to the downstream part of the main stem, $p\mathrm{CO_2}$ together with an CO_2 outgassing flux, slightly increased from Yen Bai (993 ± 14 ppm and 364.9 ± 10.3 $\mathrm{mmol\,m^{-2}\,d^{-1}}$ respectively) to Hanoi (1275 ± 17 ppm and 304 ± 7.3 $\mathrm{mmol\,m^{-2}\,d^{-1}}$), regardless of the season. However, it is worth noting that since the Hanoi station was located within the city itself and at this station, the river had not yet received the wastewater discharge of the whole city. Consequently, the Hanoi station in this study may not reflect the influence of the whole city, and probably had lower O_2 and higher $p\mathrm{CO_2}$ levels as observed for other urban rivers in the Red River delta (Trinh et al., 2007, 2009, 2012).

Consequently, our results revealed that $p\mathrm{CO_2}$ and CO_2 fluxes along the lower Red River were spatially different, which reflect the influence of both anthropogenic activities (dam, urban effluents) and natural characteristics (rainfall–river discharge, temperature and geology) in the watershed.

5 Conclusions

This work presented the spatial and seasonal variability of $p\mathrm{CO_2}$ along the lower Red River system. The riverine water was supersaturated with CO_2 in contrast to the atmospheric equilibrium (400 ppm), with $p\mathrm{CO_2}$ values averaging about 1589 ± 43 ppm, resulting in a water–air CO_2 flux of $550.3 \pm 16\,\mathrm{mmol\,m^{-2}\,d^{-1}}$ from the lower Red River system. The $p\mathrm{CO_2}$ from the water surface of the lower Red River network was characterized by significant spatial variation, being highest at the Hoa Binh Dam downstream and in the main stem at Hanoi station. The highest value obtained at the Hoa Binh site may reflect the important impact of a series of large dams (Son La, Hoa Binh) and geomorphological characteristics in the Da River but also the high water discharge, whereas the high $p\mathrm{CO_2}$ value in Hanoi may partly reflect the influence of population density through the release of organic carbon into the river. The monsoon season resulted in an increased amount of OM inputs from adjacent soil leading to higher $p\mathrm{CO_2}$ and CO_2 flux values. Consequently, this study evidenced that $p\mathrm{CO_2}$ and CO_2 fluxes along the lower Red River were controlled by both anthropogenic activities (dam, urban effluents) and natural characteristics (rainfall–river discharge, temperature and geology) in the watershed. Long-term variation in $p\mathrm{CO_2}$ and CO_2 outgassing fluxes of the Red River may be studied in a future research effort to contribute to studies of regional and global carbon emission under natural and anthropogenic impacts.

Data availability. The data used are available in the Supplement and can also be requested from the corresponding author.

The Supplement related to this article is available online at https://doi.org/10.5194/bg-15-4799-2018-supplement.

Author contributions. TPQL, CM and TCH designed the experiments. TPQL, TCH and DAV carried out the in situ experiments. TPQL, NDL and KDP contributed to data treatment and calculations. TPQL and CM prepared the manuscript with contributions from all co-authors.

Competing interests. The authors declare that they have no conflict of interest.

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