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Diel Variability of pCO_2 and CO_2 Outgassing from the Lower Mississippi River: Implications for Riverine CO_2 Outgassing Estimation

Jeremy H. Reiman [1] and Y. Jun Xu [1,2,*]

[1] School of Renewable Natural Resources, Louisiana State University Agricultural Center, Baton Rouge, LA 70803, USA; jreima1@lsu.edu
[2] Coastal Studies Institute, Louisiana State University, Baton Rouge, LA 70803, USA
* Correspondence: yjxu@lsu.edu; Tel.: +1-225-578-4168

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Abstract: Carbon dioxide (CO_2) outgassing from river surface waters is an important component of the global carbon cycle currently not well constrained. To test the hypothesis that riverine partial pressure of CO_2 (pCO_2) and CO_2 outgassing rates differ between daylight and darkness, we conducted in-situ pCO_2 and ambient water measurements over four 24-h periods in the spring and summer of 2018 in the Lower Mississippi River under varying flow regimes. We hypothesized that diel pCO_2 variation will correlate inversely with solar radiation due to light-induced photosynthesis. Despite differing ambient conditions between seasons, we found a consistent diel cycle of riverine pCO_2, with highest values before sunset and lowest values during peak daylight. Recorded pCO_2 measurements varied by 206–607 µatm in spring and 344–377 µatm in summer, with significantly lower records during daylight in summer. CO_2 outgassing was significantly lower during daylight in both seasons, with diel variation ranging between 1.5–4.4 mmol m^{-2} h^{-1} in spring and 1.9–2.1 mmol m^{-2} h^{-1} in summer. Daily outgassing rates calculated incorporating diel variation resulted in significantly greater rates (26.2 $\pm$ std. 12.7 mmol m^{-2} d^{-1}) than calculations using a single daily pCO_2 value. This study suggests a likely substantial underestimation of carbon outgassed from higher order rivers that make up a majority of the global river water surface. The findings highlight the need for high temporal resolution data and further research on diel CO_2 outgassing in different climate regions to constrain uncertainties in riverine flux estimation.

Keywords: aquatic carbon cycle; freshwater CO_2; diel river metabolism; river carbon accounting; Mississippi River

1. Introduction

Outgassing of carbon dioxide (CO_2) from rivers has been identified as a significant piece of the carbon cycle [1–3]. The process has been attributed to an oversaturation of dissolved CO_2 in the water column, resulting in diffusion of CO_2 into the atmosphere. The two primary inputs of CO_2 into the water column of large river systems are (1) in-situ respiration of organic material and (2) flushing of CO_2 produced in soil pores from terrestrial and wetland environments via decomposition of organic material and root respiration [4]. The principal removal mechanism of aqueous CO_2 is in-situ primary production, or photosynthesis [4]. Many of the world's largest rivers are supersaturated in CO_2 with respect to the atmosphere, resulting in a large flux of CO_2 from the water surface [1,5,6].

Current estimates of global CO_2 flux from rivers to the atmosphere vary largely from 230 to 1800 Tg yr^{-1} [2,3,7], calculated using partial pressure estimates of dissolved CO_2 (pCO_2), many of which are derived from low-time resolution (i.e., weekly or monthly) measurements of river alkalinity, pH, and water temperature. This method of pCO_2 calculation has been scrutinized for its great degree of uncertainty in temperate and tropical freshwaters due to the potential of significant contributions of organic acids to total alkalinity and low pH systems greatly over-estimating calculations [8]. The higher range of outgassing estimates is much greater than global estimates for the export of dissolved organic (200–360 Tg yr^{-1}) and inorganic carbon (381–410 Tg yr^{-1}), as well as particulate organic (180–240 Tg yr^{-1}), and inorganic carbon (170 Tg yr^{-1}) to the oceans [9–12]. Variation in estimates stem largely from differences in methods and data availability and resolution. One of the pioneering attempts in calculating total CO_2 outgassing from rivers by Cole and others [2] estimated 230 Tg yr^{-1} based on data from approximately 80 rivers. Several years later, Raymond and others [3] estimated an annual outgassing of 1800 Tg yr^{-1} from rivers, globally incorporating data collected from all stream orders with little requirements of data resolution. The most recent estimates by Lauerwald and others [7] excluded first order stream measurements and only included rivers with multiple samples collected across varying seasons, resulting in a global average riverine pCO_2 value 700 µatm less than Raymond et al. (i.e., 2400 vs. 3100 µatm) and an annual outgassing flux nearly one-third of the Raymond and others. Great strides have been made to improve freshwater CO_2 outgassing calculations and models through refining gas transfer velocities and pCO_2 calculations based on regional hydrologic, climate, and atmospheric conditions. Yet, it is clear based on the large discrepancies in outgassing estimates stemming from the difference in spatial and temporal data resolution, that the lack of high resolution pCO_2 data is a limiting factor on the accuracy of calculations.

Aquatic pCO_2 can fluctuate both spatially and seasonally due to differences in land-use, discharge, water temperatures, and rates of biological respiration and photosynthesis [13–17]. Furthermore, aquatic respiration and photosynthesis rates can vary greatly over the span of a day due to a change in temperature and sunlight availability [18], resulting in a significant variability of pCO_2 in water bodies between night and day [19–21]. A few recent studies have highlighted the importance of diel variation of pCO_2 and CO_2 evasion from lakes and reservoirs. In a study conducted in Lochaber Lake in eastern Nova Scotia, Canada, Spafford and Risk [22] found that 65–95% of the total CO_2 release in a 24-h period occurred during the nocturnal period. From another reservoir study in Central Mississippi, USA, Liu et al. [23] reported that CO_2 effluxes at night were about 70% higher than those during the day. To date, this phenomenon has not been documented in a large, biologically productive river system. If the former theory is true for large rivers, it could have serious implications on the accuracy of calculating carbon budgets in freshwater systems, which are mostly based on low time-resolution measurements gathered during daylight hours.

In this study, we monitored hourly fluctuations of pCO_2 in the surface water of the Lower Mississippi River and calculated hourly CO_2 outgassing over four 24-h periods in May and August 2018. The primary goal of this study was to identify whether a diel shift in pCO_2 driven by solar radiation during the day results in significantly different pCO_2 and CO_2 outgassing rates between daylight and darkness hours. The specific objectives of the study included (1) analyzing diel variability of pCO_2 in the Lower Mississippi River; (2) estimating diel CO_2 outgassing with field measurements of pCO_2; and (3) identifying environmental factors most influencing any notable diel variation. By achieving these objectives, we tested the hypothesis that riverine pCO_2 will decrease over the span of daylight, likely due to a diel increase in photosynthesis driven by daytime surges in solar radiation and temperature. Likewise, riverine pCO_2 should increase from sunset to dawn due to a net CO_2 input from river water respiration. This diel fluctuation of riverine pCO_2 should cause a distinct daily cycle of riverine CO_2 outgassing, resulting in significantly higher outgassing rates during darkness hours.

2. Materials and Methods

This study was conducted in the Lower Mississippi River at Baton Rouge, Louisiana, USA (30°26′16.6″ N, 91°11′31.6″ W, Figure 1), approximately 369 river km upstream of the river's outlet to the Gulf of Mexico. The Mississippi is the largest river in North America, draining 3.2 million km^2 of land and discharging approximately 680 km^3 of freshwater into the Gulf annually, in combination with the Atchafalaya River [24]. Due to the vast drainage size and diverse land use, the Mississippi River carries dissolved inorganic and organic carbon (DIC and DOC) from various sources, with an average DIC and DOC flux rate of 12.6 Tg yr^{-1} and 4.1 Tg yr^{-1}, respectively, at Baton Rouge during the past three years [25]. DIC fluxes over recent years are very similar to those reported in the Mississippi River at this location approximately one decade ago [26], however, recent DOC fluxes are nearly double some past estimates [27–29]. The large fluxes of diverse organic materials [30] and nutrients [31] provide the resources necessary for in-situ respiration, or production of CO_2. The river reach in our study area is approximately 750 m wide by 15 m deep, depending on the river stage, with a minimal slope [32], providing a slow-moving environment conducive of in-situ biological processing. The climate in southcentral Louisiana is considered subtropical, characterized by short, mild winters paired with humid, hot summer months. Based on these meteorological, physical, and biogeochemical characteristics of the river at our study site, we believe this portion of the river is biologically productive, especially as Dodds and others [33] found high rates of both in-situ photosynthesis and respiration in the river approximately 40 km downstream of our study site. We are only aware of one previous study [29] analyzing calculated pCO_2 and CO_2 outgassing values in the Lower Mississippi River, which suggested that the river was regularly super-saturated in pCO_2 with respect to the atmosphere due to a combination of in-situ and terrestrial respiration of organic material. Two other studies [34,35] have reported a significant amount of carbon processing in the Lower Mississippi River's coastal plume near the river's mouth to the Gulf of Mexico.

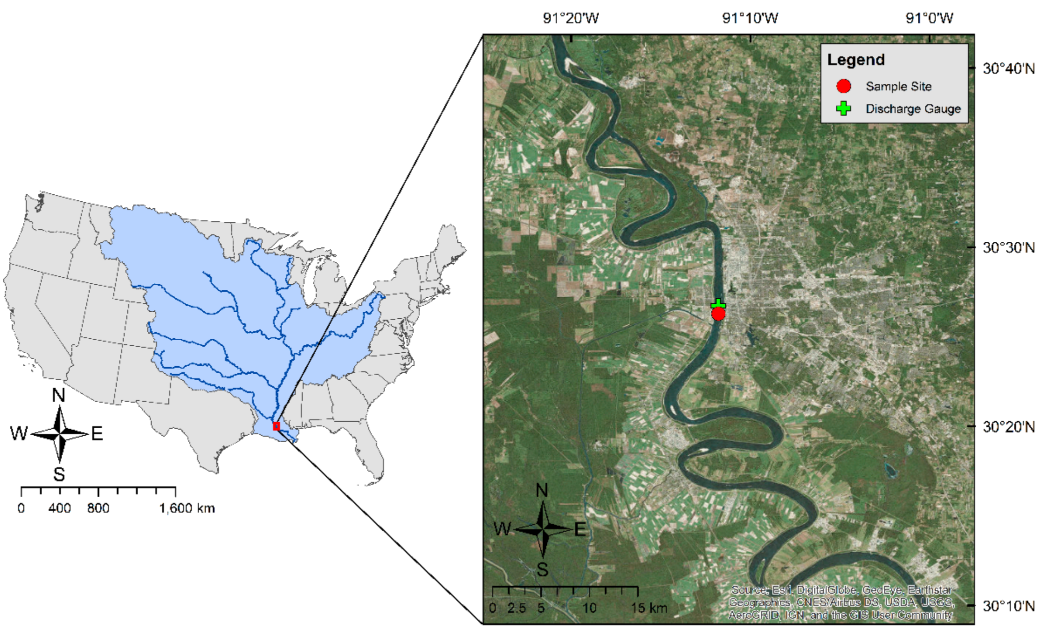

Figure 1. Mississippi River Basin with a vast drainage area of 3.2 million km^2 and the locations of the sampling site and U.S. Geological Survey gauge station (USGS #07374000).

In May and August 2018, we conducted in-situ measurements at 3-h intervals over a span of 24 h starting at 6:00 Central Standard Time (CST) in the U.S. and ending on 6:00 CST the following day for two days in spring (11–12 May and 17–18 May) and two days in summer (13–14 August and 15–16 August). The field schedule was designed to capture high and low flow conditions as well as two different water temperature regimes, which typically occur in the Mississippi River during spring and summer months. During each field trip, in-situ measurements of partial pressure of carbon dioxide (pCO_2) (C-Sense^{TM} pCO_2 sensor, Turner Designs, San Jose, CA, USA), water temperature, dissolved oxygen (YSI 556 multi-probe meter, YSI Inc., Yellow, Springs, OH, USA), pH (Orion Star A221, Thermo Scientific, Beverly, MA, USA), and turbidity (T100, Oakton Instruments, Vernon Hills, IL, USA) were collected. The C-SenseTM measures pCO_2 in-stream by gas diffusion across a hydrophobic membrane into an isolated headspace chamber, where the wavelength of pCO_2 is absorbed using infrared sensors. The sensor was calibrated at 20 °C at average sea-level atmospheric pressure less than six months prior to the field campaign using a manufacturer developed equation to convert sensor voltage output (V) to gaseous CO_2 concentration (ppm). All pCO_2 data are temperature corrected in real time, with a measurement range of 0–10,000 µatm and 3% full scale accuracy. Both the C-Sense and YSI sensors equilibrated for 15 min and recorded for approximately 20 min during each sample, with the C-Sense collecting data every 30 s and the YSI every 5 s. Relevant atmospheric parameters, including hourly solar radiation, atmospheric temperature, and wind speed, were collected from the Louisiana State University Agricultural Center Ben Hur Research Station in Baton Rouge, LA (30°21′52″ N, 91°10′02″ W), located approximately 7 km southeast from the river sampling site. Solar radiation at Ben Hur Station is measured at the 400–1100 nm waveband interval using a LI200R-L pyranometer (Campbell Scientific, Logan, UT, USA). Hourly river discharge records of the Mississippi River at Baton Rouge were downloaded from the U.S. Geological Survey's gauging station, #07374000. These data built a foundation of ambient conditions for our pCO_2 and CO_2 outgassing analyses.

The flux of CO_2, or outgassing, between surface water and atmosphere (FCO_2 in mmol CO_2 m^{-2} h^{-1}) was calculated utilizing the following equation developed by Cai and Wang [36]:

$$FCO_2 = K_T K_H (pCO_{2water} - pCO_{2air}), \quad (1)$$

where K_T is the gas transfer velocity (m d^{-1}), K_H is a solubility constant (mol L^{-1} atm^{-1}), pCO_{2water} is the partial pressure of dissolved CO_2 in the water column (µatm), and pCO_{2air} is the partial pressure of atmospheric CO_2 (µatm), which was fixed as 400 µatm [37] for the study period. It is well understood that atmospheric CO_2 can demonstrate diel variation on terrestrial land, yet the pattern of this variation can vary between and even within land-uses [38,39]. The nearest FLUXNET eddy covariance tower with atmospheric CO_2 data is located several hundred kilometers from the study site and does not have data available for the study period. While using a fixed value does not account for any potential diel variation in atmospheric CO_2, applying diel variation found in an environment very different and far from the study area to our study area would introduce great uncertainty to the outgassing analysis. Additionally, a fixed atmospheric value is a widely-used method that reduces these assumptions and increases the ability to reproduce similar studies in the future, though the limitations of a fixed value should not be overlooked when considering the conclusions of this study. We selected a K_T value of 4.3 m d^{-1}, which is a rate lower than the global average of 5.7 m d^{-1} [3]; however, this has been reported as being more representative of large low-land rivers [3,40]. The solubility constant (K_H) was calculated using the following equation by Weiss [41]:

$$\ln K_H = A_1 + A_2\left(\frac{100}{T}\right) + A_3 \ln\left(\frac{100}{T}\right) + S\left[B_1 + B_2\left(\frac{T}{100}\right) + B_3\left(\frac{T}{100}\right)^2\right] \quad (2)$$

where $A_1 = -58.0931$, $A_2 = 90.5069$, $A_3 = 22.2940$, $B_1 = 0.027766$, $B_2 = -0.025888$, B3 = 0.0050578, T is the absolute temperature of water in Kelvin, and S is the salinity. The study area is classified as a freshwater system; therefore, an S of 0 was used for calculating K_H. Daily CO_2 outgassing (mmol m^{-2} d^{-1}) was calculated for each 24-h period using two difference methods. The first extrapolated the hourly flux rate at the 15:00 CST sample over the entire 24-h period. The second used linear interpolation to estimate hourly flux rates between 3-h sample intervals and then summed all hourly fluxes over the 24-h period.

Statistical analysis was conducted using SAS 9.2 software. Student's unpaired t-test was used to compare differences of means between seasons, samples within seasons, and samples experiencing solar radiation to those not. Only solar radiation readings during daylight hours were used to compare solar radiation between seasons and samples dates. Pearson correlation coefficients were calculated as a simple analysis of the relationships between pCO_2, ambient water parameters, and atmospheric parameters. An α of 0.05 was used for all statistical analysis.

3. Results

3.1. Hourly River Discharge, Water Conditions, and Atmospheric Measurements

During the study period, discharge in the Mississippi River at Baton Rouge (USGS #0774000) was three times greater in May (24,530 std. ± 1996 $m^3 s^{-1}$) than in August (8912 ± 57 $m^3 s^{-1}$), which is representative of the typical long-term hydrograph of the river. Gathering samples over such a wide range of flow conditions allowed us to compare diel pCO_2 dynamics under high and low flow regimes. In spring, river discharge marginally decreased over the diel period (Figure 2a). In summer river discharge remained constant over the 24-h samples.

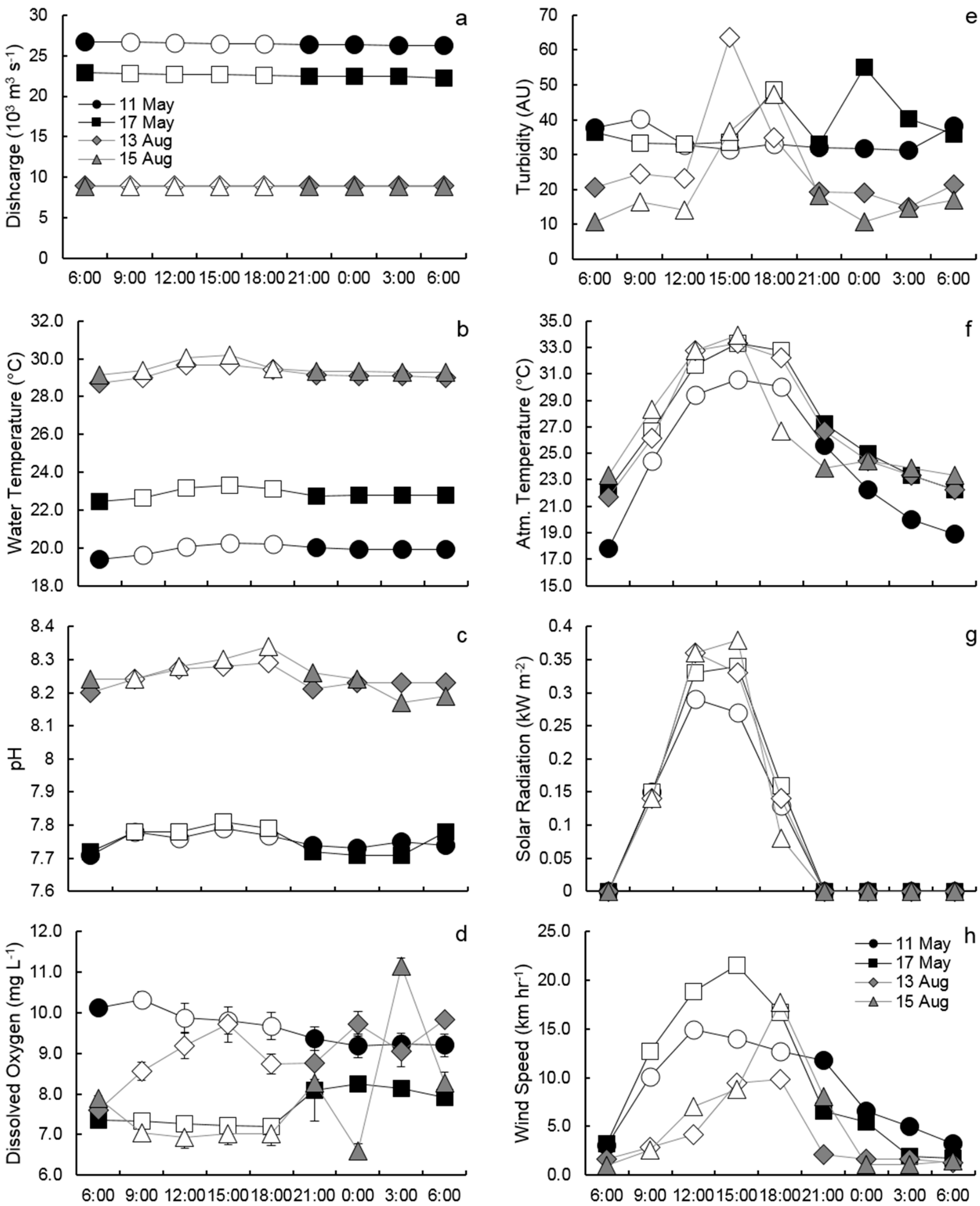

Figure 2. Diel variation of river discharge (**a**), water temperature (**b**), pH (**c**), dissolved oxygen (**d**), turbidity (**e**), atmospheric temperature (**f**), solar radiation (**g**), and wind speed (**h**) during the study period. Hollow data points represent samples collected during daylight hours (i.e., solar radiation >0.00 kW m^{-2}). The daily hours are Central Standard Time of the United States.

The magnitude of some ambient water parameters varied greatly between the seasons, however, diel variability was consistent between spring and summer. Water temperature was nearly 8 °C warmer in summer than spring, averaging 29.3 (±0.4) and 21.4 °C (±1.5), respectively. The pattern and degree of variability in water temperature was similar between all samples, with temperatures rising during daylight hours until 15:00 CST, gradually decreasing over the remainder of daylight, then remaining constant over evening hours (Figure 2b). Water temperatures on average varied by 0.9 °C (±0.1) over the 24-h periods, but demonstrated no significant difference between daylight and darkness hours. pH was also higher in summer than spring, averaging 7.75 (±0.03) in spring and 8.25 (±0.04) in summer. Diel variation in pH was similar to water temperature, with maximum measurements at 15:00 CST and lowest measurements during darkness hours (Figure 2c). pH varied on average by 0.09 (±0.01), resulting in measurements during daylight being significantly higher than during darkness ($p < 0.0001$). DO averaged 8.64 (±1.11) in spring and 8.41 mg L^{-1} (±1.25) in summer.). The diel variability of DO was greater in summer, however, no clear diel pattern could be discerned (Figure 2d). Water turbidity was slightly higher in spring than summer, averaging 37 (±6) and 24 NTUs (±14), respectively. During the majority of sample periods, turbidity was highest during daylight hours (Figure 2e), likely due to daytime boat traffic in the river.

Meteorological parameters showed a minimal difference between spring and summer, but similar diel patterns between seasons. Air temperature averaged 25.7 °C (±4.8) in spring and 26.9 ± 4.3 °C in summer. Diel variation in air temperature was consistent between samples, rising from sunrise until 15:00, where it then gradually decreased through to 6:00 the following day (Figure 2f). This distinct diel pattern resulted in an average diel temperature range of 11.3 °C (±0.8) and air temperatures significantly ($p < 0.0001$) greater by 7.2 °C (±2.7) during daylight hours. Solar radiation did not vary between seasons, averaging 0.23 kW m^{-2} (±0.09) in spring and 0.24 kW m^{-2} (±0.13) in summer. During all sample days, solar radiation rose until 12:00 or 15:00 then decreased to 0 kW m^{-2} by 21:00 (Figure 2g). Maximum solar radiation readings ranged between 0.27–0.38 kW m^{-2}. Average wind speed was the only atmospheric parameter to reflect a large difference between seasons, with wind speeds on average two times higher in spring than summer (9.5 ± 6.2 vs. 4.6 ± 4.6 km hr^{-1}. Wind speed in spring demonstrated a noticeable diel trend similar to solar radiation's diel curve, however, wind speed in summer slowly increased until 18:00 followed by a sharp decrease in the evening (Figure 2h). As a result, wind speed during daylight hours was significantly ($p < 0.0001$) higher than during hours of darkness.

3.2. Diel pCO_2 Measurements

Mean pCO_2 during the study period was 1514 µatm (±652), with all samples measuring greater than atmospheric CO_2 pressure (400 µatm). Spring pCO_2 measurements were significantly ($p < 0.0001$) higher than summer measurements, averaging 2140 (±179) and 888 µatm (±124), respectively. There was no difference of means between summer measurements; however, mean pCO_2 was significantly ($p = 0.0105$) higher on 17 May than on 11 May (2246 ± 75 and 2033 ± 192 µatm, respectively). During all sample events, pCO_2 measurements were highest at 6:00 and lowest at 15:00 or 18:00 (Figure 3a,b). A diel trend was clear during all sample trips, with pCO_2 decreasing from 6:00 to 15:00 and gradually increasing from 15:00 to 6:00 the following day (Table 1).

In spring, pCO_2 levels dropped 9–18% from 6:00 to 15:00 and proceeded to rise 9–35% from 15:00 to 6:00 the following morning, demonstrating a diel range of 206–607 µatm. The 17 May sample did not demonstrate as linear of a rise in pCO_2 in the evening hours as 11 May. The diel pattern was much more drastic in summer, dropping 33% from early morning to late afternoon and rising 35–55% until the following morning, resulting in a diel range between 344–377 µatm. On the morning of 13 August, pCO_2 dropped until 12:00, rather than 15:00, and remained at a fairly consistent level until the 21:00 sample, resulting in not as strong of fit in our model (Table 1). This diel pattern resulted in summer pCO_2 measurements 25% (std. ± 10%) greater during darkness hours than daylight hours (Figure 4a). Spring darkness pCO_2 measurements were on average 7% (±8%) greater than daylight measurements.

These results partially affirm our hypothesis that pCO_2 is noticeably lower during daylight hours due to a diel pattern.

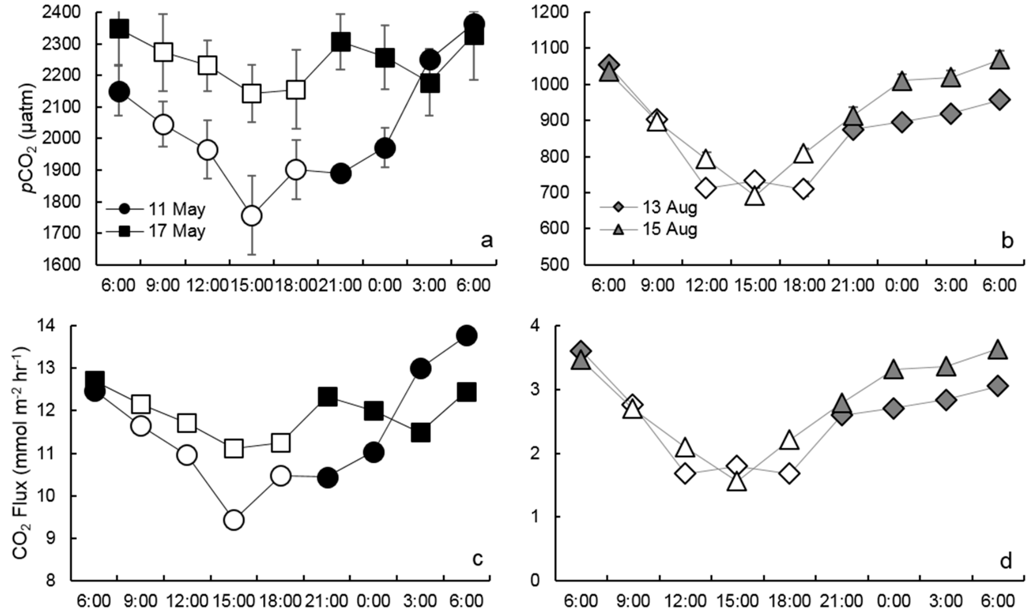

Figure 3. Daily variation in pCO_2 (**a**,**b**) and CO_2 flux (**c**,**d**) in the Lower Mississippi River during spring (**a**,**c**) and fall (**b**,**d**). Data points in (**a**) and (**b**) represent the mean pCO_2 value and error bars represent the standard deviation of the respective samples. The hollow data points represent samples collected during daylight hours (i.e., solar radiation > 0.00 kW m^{-2}). The daily hours are Central Standard Time of the United States.

Table 1. Linear regressions of pCO_2 and CO_2 flux (mmol m^{-2} h^{-1}) with hourly time steps (H) for 6:00 to 15:00 (Morning) and for 15:00 to 6:00 the following day (Evening). For example, "6:00" corresponds to "6" in the model. For 0:00, 3:00, and 6:00 the following day, the values 24, 27, and 30 were used. Statistical significance level $\alpha = 0.05$.

Date	Morning	R^2 (*p*-Value)	Evening	R^2 (*p*-Value)
11 May	$pCO_2 = -42.14H + 2421$	0.95 (0.0009)	$pCO_2 = 39.67H + 1130$	0.90 (0.0036)
17 May	$pCO_2 = -21.99H + 2479$	0.98 (0.0081)	$pCO_2 = 9.016H + 2025$	0.40 (0.1782)
13 Aug	$pCO_2 = -38.54H + 1254$	0.86 (0.0709)	$pCO_2 = 16.93H + 467.0$	0.86 (0.0081)
15 Aug	$pCO_2 = -37.78H + 1250$	0.99 (0.0033)	$pCO_2 = 24.96H + 357.1$	0.93 (0.0018)
11 May	$FCO_2 = -0.3285H + 14.58$	0.97 (0.0010)	$FCO_2 = 0.2859H + 4.923$	0.91 (0.0028)
17 May	$FCO_2 = -0.1767H + 13.78$	0.99 (0.0016)	$FCO_2 = 0.06883H + 10.22$	0.45 (0.1434)
13 Aug	$FCO_2 = -0.2178H + 4.743$	0.86 (0.0700)	$FCO_2 = 0.09467H + 0.3138$	0.86 (0.0077)
15 Aug	$FCO_2 = -0.2113H + 4.668$	0.99 (0.0037)	$FCO_2 = 0.1379H - 0.2888$	0.93 (0.0018)

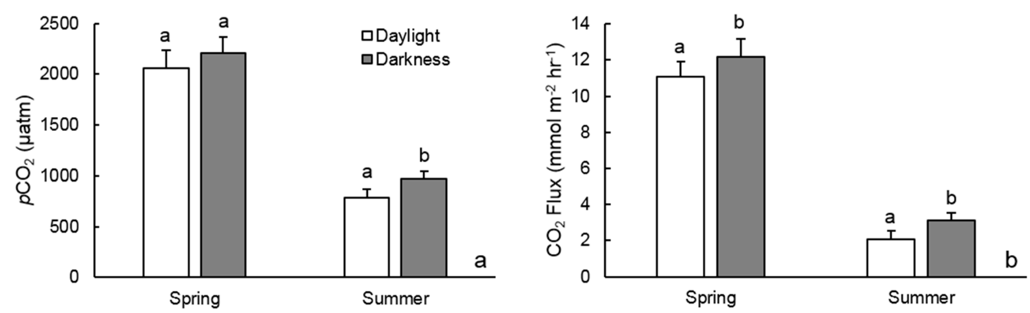

Figure 4. Mean pCO_2 (**a**) and CO_2 (**b**) outgassing rates during darkness and daylight hours by season. Bar pairs with different letters above them represent a significant difference between populations at $\alpha = 0.05$. Error bars represent standard deviations.

3.3. CO_2 Outgassing Estimates

Estimated rates of CO_2 outgassing averaged 7.2 mmol m^{-2} h^{-1} (±4.7) during the study period. Outgassing rates were significantly ($p < 0.0001$) higher in the spring than summer, averaging 11.7 (±1.1) and 2.7 (±0.7) mmol m^{-2} h^{-1}, respectively. There was no significant difference in CO_2 outgassing between samples in the same season. Similar to pCO_2, diel variability in CO_2 outgassing reflected a clear trend in both seasons (Figure 3c,d), decreasing from 6:00 to 15:00 and gradually increasing from 15:00 to 6:00 the following day (Table 1). In spring, outgassing rates gradually decreased by 13–24% from 6:00 to 15:00, followed by an increase of 12–46% until 6:00 the following day. Spring rates ranged by 1.5–4.4 mmol m^{-2} h^{-1} over a 24-h period. Much sharper diel increases and decreases occurred in the summer samples. CO_2 outgassing rates decreased by 54% from 6:00 to 12:00 on 13 August and by 55% from 6:00 to 15:00 on 15 August. Summer afternoon outgassing rates increased by 65–82% (1.4–2.1 mmol m^{-2} h^{-1}) from their respective minimums until 6:00 the following morning. This trend resulted in a summer diel range of 1.9–2.2 mmol m^{-2} h^{-1}. Consequently, CO_2 outgassing rates during hours of darkness were significantly ($p < 0.0001$) greater than daylight in both seasons (Figure 4b). Spring outgassing rates during darkness were on average 10% (std. ±8%) higher than during daylight hours, while darkness rates in summer were on average 25% (±10%) greater. Calculating daily outgassing (mmol m^{-2} d^{-1}) for sample days using linear interpolation between the 3-h intervals, rather than extrapolating the 15:00 measurement across the entire 24-h period, resulted in significantly higher daily outgassing rates in a paired t-test ($p = 0.0261$), ranging between 15.3 and 43.6 (mean 26.2, std. ±12.7 mmol m^{-2} d^{-1}) higher than the single measurement calculation (Figure 5). These results strongly support our initial hypothesis.

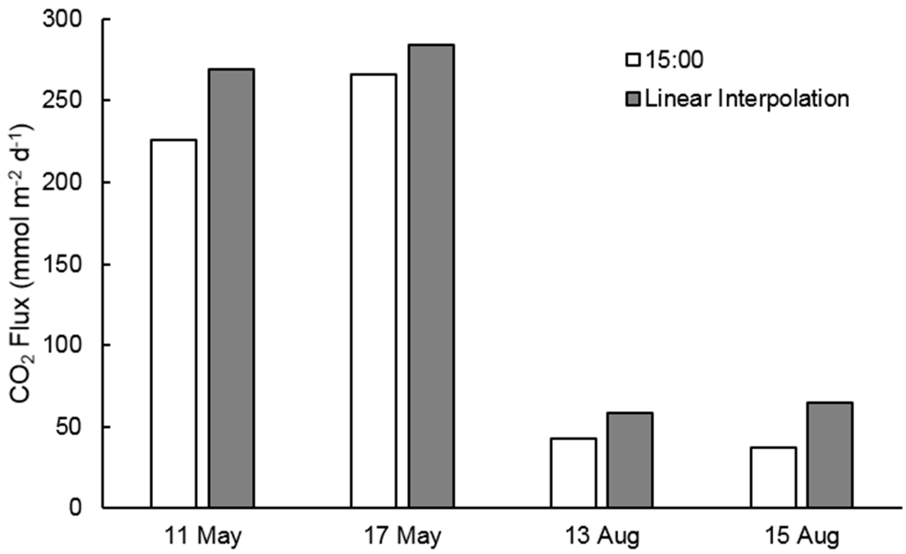

Figure 5. Comparison of daily outgassing calculations. "15:00" data represents extrapolating CO_2 flux rates at 15:00 CST over the 24-h period. "Linear Interpolation" data represents daily flux calculated by linear interpolation between 3-h intervals.

4. Discussion

4.1. Seasonal pCO_2 Differences

The difference in riverine pCO_2 between seasons can likely be explained by comparing the difference in ambient water and atmospheric parameters between seasons and analyzing their relationships with pCO_2. pCO_2 demonstrated positive correlations with river discharge and turbidity and inverse relationships with water temperature and pH (Table 2).

Table 2. Pearson correlation coefficients among pCO_2, water temperature (T_w), dissolved oxygen (DO), pH, turbidity (N), atmospheric temperature (T_a), wind speed (u), solar radiation (SR), and river discharge (Q). Only significant correlations at $\alpha = 0.05$ are shown.

	pCO_2	T_w	DO	pH	N	T_a	u	SR	Q
pCO_2	1.00	−0.92	-	−0.98	0.46	-	-	-	0.93
T_w		1.00	-	0.96	−0.46	-	-	-	−0.99
DO			1.00	-	-	-	-	-	-
pH				1.00	−0.47	-	-	0.76	−0.97
N					1.00	-	0.48	-	0.49
T_a						1.00	0.63	0.86	-
u							1.00	0.60	0.40
SR								1.00	-
Q									1.00

We postulate the difference in pCO_2 between seasons is primarily driven by two processes regulated by river discharge. First, the dissolution of soil pore-water CO_2 during the spring high-flow period caused higher pCO_2 levels in spring than summer. As soils become wetted and their temperatures begin to rise in spring months, conditions become more favorable for CO_2 producing microbial processes as found by Hope et al [42], resulting in soil pCO_2 concentrations generally much greater than atmospheric pCO_2 [43]. The flushing of soil pCO_2 into rivers via baseflow and interflow has been documented by Richey et al. [4] as a significant piece of the riverine CO_2 cycle. Second, the respiration of organic material delivered to the river during the spring high-flow period likely resulted in higher pCO_2 values. Organic carbon concentrations and community respiration are strongly correlated with discharge in the Mississippi River, which in-turn correlate with the greater production of pCO_2 and greater net heterotrophy in spring [26,33]. Despite a slower river flow velocity, greater water temperatures, and lower turbidity in summer providing an environment more conducive of biological processing [44], the lack of organic inputs associated with lower discharge likely limited pCO_2 production, resulting in a greater net removal of pCO_2. This phenomenon is reflected in significantly higher pH in the river during the summer and the inverse relationship between pCO_2 and river pH (Table 2).

4.2. Biological Processes Influencing Diel pCO_2 Variation

This is the first study to document significant diel variation of riverine pCO_2 and CO_2 outgassing utilizing actual in-stream measurements in the Lower Mississippi River. These findings are in coincidence with studies that have found a similar pattern of a reduction of atmospheric CO_2 over large water bodies during daylight hours [45,46] This variation is apparently driven by autotrophic processes, resulting in an increase in net ecosystem production (NEP = gross primary production (GPP)—community respiration (CR)) [47] over daylight hours. During all samples across both seasons, pCO_2 values were highest during the dark, early morning hours and lowest between 15–18:00 CST, following the peak of daylight (Figure 3a,b). The large variation suggests a diel change in the balance of processes producing and removing pCO_2 in the water column. Reduction in pCO_2 over daylight corresponded with a diel increase in water temperature and solar radiation (Figure 2b,g), both of which have shown to increase aquatic metabolism [48,49]. The decrease in pCO_2 also paired with an increase in pH over daylight hours (Figure 2c). This relationship suggests a diel increase in photosynthesis may be driving the decrease in pCO_2 as in-situ photosynthesis would drive up pH values. Our in-stream measurements confirm results of a past study of diel pCO_2 dynamics and stream metabolism in two acidic lower-order peatland streams by Dawson et al. [50], which found lowest pCO_2 levels during early afternoon hours, highest values in the early morning, and a diel increase in NEP, especially during warmer months. In a separate study of aquatic metabolism, Mulholland and others [47] also documented a diel increase in NEP in many of the streams studied due to a daily increase in GPP, but fairly consistent CR rates. The authors concluded the shift in NEP was driven primarily by solar radiation rather than water temperature. We hypothesize that the diel variation in pCO_2 in the Mississippi River can be explained by a similar shift in NEP, likely controlled by solar radiation driving up photosynthesis rates, as recent studies in the Mississippi and Chattahoochee Rivers have found that water temperature is not a strong predictor of GPP in either river [33]. Even though pCO_2 values were significantly lower during daylight hours in this study, water temperature showed minimal difference between daylight and darkness, suggesting that a minor shift in water temperature is not the main driver of diel variability.

The diel decrease in pCO_2 was in coincidence with a diel increase in average wind speed during all sample events (Figure 2h). Some studies [15,40] found that an increase in wind speed can speed up the rate of pCO_2 lost to the atmosphere, especially in large bodies of water, by directly increasing the gas transfer velocity of CO_2. Wind can increase gas transfer velocity due mainly to creating surface water turbulence in stagnant water [51], which may, however, not be relevant for a large flowing river like the Mississippi River, that consistently experiences water turbulence. Also, if wind were the main factor driving variation, we would have anticipated a larger diel decrease in pCO_2 on days when wind speeds were greatest. Yet, we found the lowest variation in pCO_2 on 17 May when the average wind speed was highest (see the low β_1 values in Table 1). Based on the findings by Schubert and Forster [52] and Helbling et al. [53], an increase in wind speed could also increase the velocity of water column mixing, indirectly inhibiting photosynthesis in primary producers near the surface of the water column. Based on these findings, it is unclear whether wind speed has a significant influence on diel pCO_2 variability.

Diel fixation of CO_2 by aquatic plants is another potential removal mechanism in the water column, especially in CO_2 saturated waters [54]. Rich and others [55] studied photosynthesis of submerged aquatic vegetation at the diel scale in a pond and found that water column oxygen production and pH increased with solar radiation, while water column pCO_2 decreased. Additional past studies have found light availability as one of the most important factors limiting daily aquatic plant photosynthesis [56,57], suggesting potential for a diel CO_2 cycling due to photosynthesis. However, the levees of the Lower Mississippi through the study area are heavily industrialized and the river channel is regularly dredged for large freight ships, highly limiting the growth of natural vegetation. As a result, diel photosynthesis of aquatic plants is likely not a primary contributor to the diel CO_2 cycling in the water-column found in this study, however, this process could have a significant impact in vegetation rich streams.

4.3. Implications for Carbon Outgassing Estimates and Future Research Needs

This study found CO_2 outgassing rates significantly lower during daylight hours in spring and summer, resulting in a large underestimation of daily outgassing rates under varying flow and temperature regimes. As GPP is generally highest in the Mississippi River in autumn and winter months [33], we would anticipate a similar diel trend throughout these seasons. Though diel variation may not be as drastic in autumn and winter due to lower temperatures, shorter day-light lengths, and potential nutrient limitations [58]. These findings raise questions about the current global estimation of CO_2 outgassed from rivers. Assuming a 34% under-estimation of a total flux of 650 Tg C yr^{-1}, as recently calculated by Lauerwald and others [7], would result in an under-estimation of 221 Tg C outgassed from streams and rivers to the atmosphere, annually. However, it should be noted that many large tropical rivers that contribute significantly to fresh-water CO_2 emissions [59,60] may not experience this large of a diel cycle due to limited light attenuation and low nutrient levels limiting GPP [61,62], limiting the applications of this analysis. Nonetheless, several major world rivers have biogeochemical trends similar to the Mississippi River and diel variability may be even higher in other rivers depending on climate, nutrient, and organic matter availability, and varying day-night length ratios across geographic regions. Therefore, we argue that future high-resolution sampling studies analyzing diel pCO_2 and CO_2 outgassing dynamics in rivers at differing orders and varying latitudes would be beneficial for constraining the relationship between diel variability and the former environmental factors. Ideally, these relationships could be used to develop a collective day-night pCO_2 curve that could be used to incorporate diel variability in global CO_2 outgassing estimations.

The large range of values in global outgassing estimates highlights the need of high-resolution in-stream samples. High resolution sampling would not only constrain the diel variation found in this study, but also incorporate seasonal and spatial variation found in several past studies [12–16,45]. It is clear that the estimation of CO_2 outgassing has continued to increase as more data has been collected across rivers at varying orders and geographic locations, shifting the paradigm of the river's role in the carbon cycle. Estimates by Raymond and others [3] was the only study to include first-order streams, but was responsible for noting the very high pCO_2 values with low data resolution, which likely skewed their estimates of 1800 Tg yr^{-1} Therefore, conducting high-resolution sampling similar to that conducted in this study in varying geographic regions, as well as in lower order streams and along spatial gradients in large river systems, could help constrain concerns regarding the uncertainties in pCO_2 measurements driving variability in outgassing calculations from aquatic systems.

5. Conclusions

This study monitored in-stream pCO_2 and ambient water and weather conditions in spring and summer of 2018 in the Lower Mississippi River under varying river discharge and temperature regimes. Based on the field measurements at 3-h intervals, hourly CO_2 outgassing rates for this 10th-order, large river system were estimated. The ultimate goal of the study was to assess the diel riverine pCO_2 cycle and its influence on CO_2 outgassing calculations. To our best knowledge, this is the first field assessment on diel pCO_2 and CO_2 emissions from a large river, and the findings may have important implications for constraining the uncertainty of river CO_2 outgassing estimates. Seasonally, we found significantly higher pCO_2 values and CO_2 outgassing rates in spring than in summer, likely due to the higher input of carbon sources from river discharge. On a daily basis in the two seasons, both riverine pCO_2 and CO_2 outgassing showed a distinct diel cycle, with levels decreasing from sunrise to peak daylight hours, followed by a gradual increase during hours of darkness. pCO_2 measurements varied by 206–607 μatm over 24-h periods with significantly lower pCO_2 values during daylight hours in summer. CO_2 flux rates ranged by 1.5–4.4 mmol m^{-2} h^{-1} over the 24-h periods, with outgassing rates significantly lower during daylight hours in both seasons. Incorporating diel variation in daily CO_2 outgassing calculations resulted in outgassing rates 26.2 mmol m^{-2} d^{-1} (± std. 12.7) greater than calculations using a single daily pCO_2 measurement. Diel decreases in pCO_2 corresponded closely with increasing solar radiation and pH, suggesting strong autotrophic processes regulating CO_2 levels in this large river system as we initially hypothesized. As many outgassing calculations are based on low-resolution samples collected during daylight hours, we postulate that many river CO_2 emission estimates are likely underestimated. In order to constrain this uncertainty, future research utilizing high resolution pCO_2 measurements in streams spanning differing orders, geographic regions, and biological communities is needed.

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