Spatial and temporal variability of \( p\text{CO}_2 \) and \( \text{CO}_2 \) emissions from the Dongjiang River in South China

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Abstract. \( \text{CO}_2 \) efflux at the water–air interface is an essential component of the riverine carbon cycle. However, the lack of spatially resolved \( \text{CO}_2 \) emission measurement still hinges the accuracy of estimates on global riverine \( \text{CO}_2 \) emissions. By deploying floating chambers, seasonal changes in river water \( \text{CO}_2 \) partial pressure (\( p\text{CO}_2 \)) and \( \text{CO}_2 \) evasion from the Dongjiang River in South China were investigated.

Spatial and temporal patterns of \( p\text{CO}_2 \). Lateral soil \( \text{CO}_2 \) input and dilution effect caused by precipitation played critical roles in controlling riverine \( p\text{CO}_2 \) in small rivers, while the decomposition of allochthonous organic carbon is responsible for \( p\text{CO}_2 \)-variability in large rivers. Spatial and temporal patterns of \( p\text{CO}_2 \) were mainly affected by terrestrial carbon inputs and in-stream metabolism, both of which varied due to differential catchment settings, land cover, and hydrological conditions. Temperature-normalized gas transfer velocity (\( k_{600} \)) in small rivers were 8.29 ± 11.29 m d\(^{-1}\) and 4.90 ± 3.82 m d\(^{-1}\) for the wet season and dry season, respectively, which were nearly 70 % higher than that of large rivers (3.90 ± 5.55 m d\(^{-1}\) during the wet season and 2.25 ± 1.61 m d\(^{-1}\) during the dry season). A significant correlation was observed between \( k_{600} \) and flow velocity but not wind speed regardless of river size. Majority of the surveyed rivers were net \( \text{CO}_2 \) source, while exhibiting substantial seasonal variations. The mean \( \text{CO}_2 \) flux was 300.1 and 264.2 mmol m\(^{-2}\) d\(^{-1}\) during the wet season for large and small rivers, respectively, 2-fold larger than that during the dry season. However, no significant difference in \( \text{CO}_2 \) flux was observed between small and large rivers. The absence of commonly observed higher \( \text{CO}_2 \) fluxes in small rivers could be associated with the depletion effect caused by abundant and consistent precipitation in this subtropical monsoon catchment.
River networks act as a processor that transfers and emits the carbon entering the water, rather than just a passive pipe that transports carbon from the terrestrial ecosystem to the ocean (Cole et al., 2007; Battin et al., 2009; Drake et al., 2018). CO₂ emissions at the water–air interface are an essential component of the riverine carbon cycle. CO₂ emitted from inland waters to the atmosphere reaches up to 2.9 PgC yr⁻¹, surpassing that transported from land to ocean through rivers (Sawakuchi et al., 2017; Drake et al., 2018). Understanding the role that rivers play in the global carbon cycle is still hindered by uncertainty on the estimate of CO₂ flux outgassing from rivers (Cole et al., 2007; Raymond et al., 2013; Sawakuchi et al., 2017; Drake et al., 2018). Riverine carbon emissions have significant temporal and spatial variations, making it challenging to quantify carbon emissions accurately. In addition, watershed geomorphology, hydrological conditions, climate, and other environmental factors can affect the CO₂ efflux in rivers (Alin et al., 2011; Abril et al., 2014; Almeida et al., 2017; Ran et al., 2017a; Borges et al., 2018). Thus, there are substantial differences in CO₂ efflux among rivers in different climate regions, or the same river but between different seasons (Denfeld et al., 2013; Rasera et al., 2013). An enhanced understanding of the temporal and spatial characteristics of the water–air CO₂ flux will facilitate a more robust estimate. However, global riverine carbon emission estimates were largely based on data disproportionately focusing on temperate and boreal regions, including North America and Europe (Raymond et al., 2013; Lauerwald et al., 2015; Drake et al., 2018). In light of this data gap, more studies are required in other data-poor regions to achieve a more accurate estimate.

Rivers in tropical and subtropical regions of East Asia and Southeast Asia are among those underrepresented regions that need more attention since they are essential participants in riverine carbon transport (Ran et al., 2015; Ran et al., 2017b; Drake et al., 2018). The high temperature in this region facilitated a high net primary productivity in the terrestrial ecosystem and intense biochemical activities, and both contributed to the carbon input dynamic from soil to rivers (Li et al., 2018). Meanwhile, rivers in this region are under the heavy influence of monsoon, and riverine CO₂ emissions vary significantly among seasons due to the changes in temperature and precipitation. In addition, different rivers in this region may have contrasting trends in CO₂ dynamic due to different underlying controlling factors. Some rivers have the highest CO₂ efflux in the wet season (Li et al., 2013; Le et al., 2018; Ni et al., 2019), while others have the highest CO₂ efflux in the dry season (Luo et al., 2019) (Li et al., 2013; Le et al., 2018; Ni et al., 2019), suggesting that an increase in wet season runoff can have two distinct
consequences. One possibility is that it increases external carbon inputs and CO₂ emissions (Hope et al., 2004; Johnson et al., 2008), while the other is that it leads to a dilution of CO₂ in rivers and accordingly a reduction in CO₂ emissions (Ran et al., 2017b; Li et al., 2018). Since starkly different outcomes can occur, it is important to investigate the processes behind such diverse response of rivers to the monsoon.

The Dongjiang River (DJR), located in the subtropical region of South China, is one of the three tributaries of the Pearl River. Previous studies on riverine carbon transportation and emissions in the Pearl rivers mainly focused on the Xijiang River, which was characterized by widely distributed carbonate rocks, and the estuary area of the Pearl River Delta (Yao et al., 2007; Zhang et al., 2015; Zhang et al., 2019; Liang et al., 2020). Though some studies have been conducted in the Dongjiang River basin (DJRB) focusing on carbon transport and the carbon sink effect of chemical weathering (Tao et al., 2011; Fu et al., 2014), there is still a lack of understanding of the characteristics of catchment-wide CO₂ emissions in DJRB. Furthermore, a predominantly hilly landscape combined with abundant precipitation favors the formation of a great number of small rivers in DJRB (Ding et al., 2015). However, the current estimate of basin-wide CO₂ emission from the river network was mostly based on the data from large rivers, and small rivers are heavily underrepresented (Raymond et al., 2013; Drake et al., 2018). Because the controlling factors and the input of carbon could be significantly different between large and small rivers (Johnson et al., 2008; Dinsmore et al., 2013; Hotchkiss et al., 2015; Marx et al., 2017), which can lead to very distinctive pattern of carbon dioxide evasion, more comprehensive quantification of CO₂ evasion from small headwater streams is necessary. Therefore, studies on the characteristics of riverine CO₂ emission in DJRB should be conducted among river size spectrums, and the impact of monsoon ought to be considered.

By using directly measured river water CO₂ partial pressure (pCO₂) and CO₂ efflux data from DJRB, and in conjunction with hydrological and physicochemical data, the objectives of this study were to 1) investigate the spatial and temporal pattern of pCO₂ and CO₂ emission along stream size spectrum, 2) examine the differences in hydrological and physicochemical controls of pCO₂ and the CO₂ evasion between small headwater streams and large rivers. The results of this study could shed light on the underlying controls of the spatial and temporal distribution of riverine pCO₂ and support a refined estimate of regional and global carbon budgets.
2 Material and methods

2.1 Site Description

The DJR in South China is one of the three major tributaries of the Pearl River system (Figure 1). It has a 562 km long mainstem channel and a drainage area of 35,340 km$^2$ (Chen et al., 2011). Due to its subtropical monsoon climate, precipitation in DJRB exhibits significant seasonal variability (Figure 2a). The multi-annual average precipitation is about 1800 mm, 80% of which is concentrated during the wet season from April to September. The Boluo Hydrological Gauge is the lowermost gauge of the Dongjiang River mainstem channel, controlling a drainage area of ~23,000 km$^2$. The multi-annual average water discharge at Boluo Hydrological Gauge is 23.7 km$^3$ (Zhang et al., 2008). About 80–90% of this discharge is transported during the wet season (Figure 2b). The landscape is characterized by plains and hills, accounting for 87.3% of the river basin area (Ding et al., 2015), and the dominant land use of the catchment is highly diverse evergreen forests of broad-leaved and needle-leaved species (Ran et al., 2012; Chen et al., 2013). The impacts of human activities on land use vary among three regions in the DJRB. Urban expansion and agricultural activities have substantially altered the land use in Lower and Middle Dongjiang River Basin (LDJRB and MDJRB), respectively, while the Upper Dongjiang River Basin (UDJRB) is less affected by human activities (Figure 1), and the landscape is characterized by plains and hills, accounting for 87.3% of the river basin area (Ding et al., 2015).
**Figure 1** Location map of the Dongjiang River Basin, sampling sites, and Boluo Gauge.

**Figure 1** Sample sites and land cover in the DJRB. Yearly average $p$CO$_2$ at each sample site was displayed. Based on land cover dataset: FROM-GLC10 (http://data.ess.tsinghua.edu.cn).

**Figure 2** Monthly variations in (a) precipitation of the DJRB and (b) water discharge at the Boluo hydrological gauge, based on data provided by the Hydrological Bureau of Guangdong Province.
2.2 Field Measurement and Analysis

In total, there were 43 sampling sites from spanning seven Strahler stream orders. Fourth to seven order streams were mainstem and major tributaries, while first to third order streams were small tributaries. River widths were measured by a laser rangefinder. Sampled rivers were categorized, according to their stream orders, into small rivers (first to third order streams, SR) and large rivers (fourth to seventh order streams, LR). The small rivers had an average width of $15.4 \pm 10.2$ m ($4.8 \pm 2.3$ m, $10.4 \pm 5.6$ m, $22.9 \pm 8.1$ m for first to third order streams, respectively), while large rivers have an average width of $180.8 \pm 156.0$ m ($75.2 \pm 51.0$ m, $168.0 \pm 48.6$ m, $235.7 \pm 29.6$ m, $433.4 \pm 78.0$ m for fourth to seventh order streams, respectively). Those sampling sites were widely distributed in the mainstem and nine major subcatchments among three regions with different topographic features and land cover (Figure 1).

In order to investigate CO$_2$ emissions during different hydrological conditions, we performed five fieldwork campaigns from December 2018 to October 2019, including three in the wet season (early wet season - late April, middle wet season - early July, and late wet season - late August) and two in the dry season (middle dry season - December 2018 to early January 2019 and early dry season - late October 2019. Sample sites were measured in the daytime over two weeks for each field trip. Three rounds of campaigns in the wet season allow each sample site to be measured under different hydrological conditions, and the two-week duration of each campaign allowed streams with different orders and sizes to be measured under various discharges. As for the dry season, the hydrological condition was relatively stable due to low precipitation. However, field measurements conducted during the daytime could lead to an underestimate in pCO$_2$ and CO$_2$ emission (Reiman and Xu, 2019a). In order to investigate CO$_2$ emissions during different hydrological conditions, we performed five fieldwork campaigns from December 2018 to October 2019, including late December 2018 to early January 2019 (middle dry season), April (early wet season), early July (middle wet season), late August (late wet season) and late October 2019 (early dry season). Nocturnal CO$_2$ emission rates in rivers could be 27% greater than the daytime rates (Gómez-Gener et al., 2021).

During the field trips, water temperature, pH, and dissolved oxygen (DO) were measured with a portable multiparameter probe (Multi 3430, WTW GmbH, Germany). The pH probe was calibrated before each field trip with standard pH buffers (4.01 and 7.00). Measurements were conducted 10 cm below the water
To evaluate the contribution of metabolism on DO changes, ΔCO₂ and ΔO₂ were calculated as described by Stets et al. (2017) using:

\[ \Delta CO_2 = CO_{2w} - CO_{2a} \tag{1} \]

and

\[ \Delta O_2 = O_{2w} - O_{2a} \tag{2} \]

Where CO₂w and O₂w are measured concentrations of CO₂ and O₂ in water sample, while CO₂a and O₂a are the equilibrium CO₂ and O₂ concentrations (μmol L⁻¹).

Flow velocity was determined by using a Global Water Flow Probe FP111 with a precision of 0.1 m s⁻¹. Flow velocity was determined using a flow meter, while wind speed at 1.5 m above the water surface was measured with a Kestrel 2500 handheld anemometer and normalized to a height of 10 m (U10) using the equation from Alin et al. (2011). As the flow velocity was measured near the riverbanks, an underestimation of the flow velocity is possible. Flow velocity measured near the riverbanks is only about 40% of the maximum flow velocity at the cross-section (Moramarco et al., 2004; Le Coz et al., 2008).

We also collected water for analyzing total alkalinity (TA) and dissolved organic carbon (DOC). Firstly, 100 ml of water samples were filtered through a pre-combusted glass fiber filter (pore size: 0.47 μm, Whatman GF/F, GE Healthcare Life Sciences, USA). Then, 50 ml of water used for TA analysis was titrated with 0.1 mol L⁻¹ HCl at on the same day of sampling. The remaining 50 ml of water for DOC analysis was poisoned with concentrated H₂SO₄ to pH < 2 and preserved in a cooler with ice bags before analysis. DOC was determined by the high-temperature combustion method using a TOC Analyzer (Elementar Analysensysteme GmbH, Langenselbold, Germany) that has a precision better than 3 %.

2.3 Calculation of pCO₂ and CO₂ emission flux

The surface water pCO₂ was determined using the headspace equilibrium method, which could avoid the possible overestimation of using TA and pH to calculate pCO₂ in rivers with a relatively low pH (Abril et al., 2015). We used a 625 mL reagent bottle to collect 400 mL of water from ~10 cm below the surface, leaving 225 mL of space filled with ambient air as headspace. The bottle was then immediately capped and shaken vigorously for at least 1 min to achieve an equilibrium between the water and the CO₂ in the
headspace (Hope et al., 1994). Then, the bottle was connected to the calibrated Li-850 CO₂/H₂O gas analyzer (Li-Cor, Inc, USA), and the equilibrated gas in this closed loop was measured. The measurements at each site were repeated twice, and the average was then calculated. The variation between the two measurements was less than 5%, and the accuracy of Li-850 is within 1.5% of the reading. The ambient air pCO₂ (pCO₂air) was measured before the headspace measurements and the chamber deployments. The pCO₂air value varied between 380 and 450 μatm. The ambient air pCO₂ (pCO₂air) was measured before the chamber deployments and varied between 380 and 450 μatm. The measurements at each site were repeated three times, and the average was then calculated. The original surface water pCO₂ (pCO₂water,i) was finally calculated by using solubility constants (K₀) for CO₂ from Weiss (1974), Carbonate constants (K₁, K₂) from (Millero et al., 2006), and the volume of the flask, headspace, and residual system (line and gas analyzer) (Dickson et al., 2007; Ran et al., 2017a; Tian et al., 2019) using:

\[
pCO₂^{water,i} = pCO₂^{headspace,f} + \left(\frac{V_r}{V_w}\right)(pCO₂^{h+r} - pCO₂^{headspace,i})/\left[RTK₀(1 + \frac{K₁}{[H^{+}]} + \frac{K₁K₂}{[H^{+}]})\right]
\]

(3)

Where Vₕ, Vᵣ, and Vₜ, are the headspace volume, residence system volume, and water volume, respectively. R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), T is the water temperature in Kelvin (K), and [H⁺] is the concentration of hydrogen ion. pCO₂^{headspace,i} and pCO₂^{headspace,f} are pCO₂ before and after the headspace equilibration, respectively. pCO₂^{h+r} is the pCO₂ of the mixed gas in the headspace and residual system during the measurement. The pCO₂^{headspace,i} was taken as the pCO₂ in ambient air before the measurement, while pCO₂^{headspace,f} was calculated using:

\[
pCO₂^{headspace,f} = pCO₂^{h+r} + \left(\frac{V_r}{V_h}\right)(pCO₂^{h+r} - pCO₂^{headspace,i})
\]

(4)

For measuring Vᵣ. We filled the headspace with gas, which had a known pCO₂, and measured the pCO₂ in the closed loop. Vᵣ was then estimated according to equation (23). A comparative analysis of the syringe and bottle headspace method has been conducted to evaluate the accuracy of the headspace extraction method used in this study (Table S2 and Figure S2). Overall, our method could cause a 1–5% underestimation in pCO₂.

To reduce the artificial turbulence induced by anchored chambers, we used a small unmanned boat in the measurement, which allowed us to deploy drifting chambers freely in rivers deeper than 0.2 m and with
a high flow velocity up to 2 m s\(^{-1}\). During the deployment, CO\(_2\) emission was determined using a circular, 8.5 L floating chamber with a water surface area of 0.113 m\(^2\). The chamber walls were lowered about 2 cm into the water and mounted with a pneumatic rubber tire. The chamber was connected to an infrared Li-850 CO\(_2\)/H\(_2\)O gas analyzer (Li-Cor, Inc, USA) in a floating storage box through Polyurethane tubes for CO\(_2\) analysis. An unmanned boat connected to both the chamber and box with ropes was used to deploy them near the central line of the river. Once the entire setup reached its designated location, the readings on the Li-850 were recorded at 0.5 s intervals. During the entire measurement process, the box drifted freely with the current. The Li-850 was calibrated by the manufacturer before field trips. The rate of CO\(_2\) efflux (FCO\(_2\) in mmol m\(^{-2}\) d\(^{-1}\)) was calculated from the observed change rate of the mole fraction S (ppm s\(^{-1}\)) using:

\[
FCO_2 = (S \cdot V / A) \cdot t_1 \cdot t_2
\]  

(5)

Where S is the slope of CO\(_2\) accumulation in the chamber (μatm s\(^{-1}\)), V is chamber gas volume (m\(^3\)), A is the chamber area (m\(^2\)), \(t_1 = 8.64 \cdot 10^4\) s d\(^{-1}\) is the conversion factor from seconds to days, and \(t_2\) is a conversion factor from mole fraction (ppm) to concentration (mmol m\(^{-3}\)) at in situ temperature (T in K) and atmospheric pressure (p in Pa), according to the ideal gas law:

\[
t_2 = p / (8.31 J K^{-1} \text{mole}^{-1} \cdot T) \cdot 1000
\]  

(6)

The gas transfer velocity (k) was calculated from FCO\(_2\) and pCO\(_2\) in both water and ambient air using:

\[
k = FCO_2 / (K_0 \cdot (pCO_{water,i} - pCO_{air})
\]  

(7)

To compare gas transfer velocity values among different sites, k was standardized to \(k_{600}\) as described by Alin et al. (2011) using:

\[
k_{600} = k (600 / Sc)^{-0.5}
\]  

(8)

Where, Sc is the Schmidt number, which is dependent on temperature (T) in degree Celsius (Wanninkhof, 1992):

\[
Sc = 1911.1 - 118.11T + 3.4527T^2 - 0.4132T^3
\]  

(9)
In total, 196 chamber measurements were made. In 19 out of 215 sample sites, the drifting chamber was unable to deploy due to shallow water or high flow velocity. Meanwhile, 8 out of 196 \( k_{600} \) data with the air–water \( pCO_2 \) gradient less than 200 \( \mu \text{atm} \) were also excluded, as the error in these calculations could be considerable (Borges et al., 2004).

3 Result

3.1 Physical and Biochemical Characteristics

The Dongjiang River was characterized by substantial seasonal variations in hydrologic regimes (Table 2). Stream width in the wet season was 17.0% and 45.6% larger than that in the dry season for small and large rivers, respectively (Table S1). The Q discharge ranged 5-4 orders of magnitude from 0.01 m\(^3\) s\(^{-1}\) in the small headwater streams during the dry season to 6690 m\(^3\) s\(^{-1}\) in the main stem during the wet season (Figure S1). Water temperature was higher in July and August (21.4–33 and 21–33.4°C, respectively) than that in January (8.1–22.2°C), April (16.5–26.9°C), and October (17.4–29.7°C). pH varied from 6.38 to 8.14, with a mean of 7.08. There was no significant (independent sample t test, \( p > 0.05 \)) change in pH between wet and dry seasons. U10 based on all stream sites was higher in large rivers (0.86 ± 0.91 and 1.43 ± 1.58 m s\(^{-1}\) in wet and dry season, respectively) than in small rivers (0.62 ± 0.61 and 0.76 ± 0.73 m s\(^{-1}\) in wet and dry season, respectively).

The streams presented low alkalinity ranging from 225 to 3025 μmol L\(^{-1}\). Overall, lower alkalinity was observed in wet season than in dry season (Table 1). In small rivers, the alkalinity in wet season (656 ± 265 μmol L\(^{-1}\)) was 21.1% lower than the dry season (831 ± 460 μmol L\(^{-1}\)), and the lowest alkalinity was observed in April (615 ± 262 μmol L\(^{-1}\)), which was 30.4% lower than in January (883 ± 548 μmol L\(^{-1}\)). Similarly, the alkalinity in large rivers was 790 ± 402 μmol L\(^{-1}\) in wet season, 14.5% lower than 924 ± 411 μmol L\(^{-1}\) in dry season. However, the lowest value of alkalinity in large rivers was observed in August (739 ± 312 μmol L\(^{-1}\)) instead of April in small rivers.

Spatial and seasonal changes in DOC concentration were also observed in the surveyed rivers (Table 1). DOC concentration in large rivers (1.94 ± 1.52 mg L\(^{-1}\)) was 41.6% higher than that in small rivers (1.37 ± 0.72 mg L\(^{-1}\)). Meanwhile, DOC concentrations in the wet season were 2.22 ± 1.82 mg L\(^{-1}\) and 1.54 ± 0.72 mg L\(^{-1}\) for large and small rivers, respectively, which were 45.1% and 54% higher than that in the dry season (1.53 ± 0.72 and 1.11 ± 0.63 mg L\(^{-1}\) for large and small rivers, respectively).
Table 1 Seasonal Variations of Physical and Biochemical Characteristics, expressed as Mean ± SD.

| Stream size | Season | Month | Water Temperature (°C) | pH       | Alkalinity (μmol L⁻¹) | DOC (mg L⁻¹) |
|-------------|--------|-------|------------------------|----------|-----------------------|--------------|
| small       | Dry    | January | 14.3 ± 4.1            | 7.05 ± 0.31 | 883 ± 548              | 1.07 ± 0.37  |
|             | Wet    | April  | 19.9 ± 1.9            | 7.19 ± 0.26 | 615 ± 262              | 1.51 ± 0.58  |
|             | Wet    | July   | 25.7 ± 2.3            | 7.17 ± 0.27 | 676 ± 227              | 1.59 ± 0.97  |
|             | Wet    | August | 27.1 ± 3.0            | 7.13 ± 0.38 | 678 ± 308              | 1.51 ± 0.56  |
|             | Dry    | October| 21.5 ± 2.6            | 7.08 ± 0.23 | 778 ± 358              | 1.16 ± 0.82  |
| large       | Dry    | January | 16.9 ± 5.5            | 7.00 ± 0.27 | 961 ± 409              | 1.70 ± 1.52  |
|             | Wet    | April  | 22.1 ± 3.7            | 7.20 ± 0.27 | 890 ± 386              | 2.22 ± 1.65  |
|             | Wet    | July   | 27.8 ± 2.9            | 6.92 ± 0.25 | 740 ± 305              | 1.97 ± 1.77  |
|             | Wet    | August | 28.9 ± 3.3            | 6.92 ± 0.26 | 739 ± 312              | 2.47 ± 2.04  |
|             | Dry    | October| 25.2 ± 3.1            | 7.13 ± 0.29 | 887 ± 331              | 1.37 ± 0.67  |

3.2 Spatial and Seasonal variation in pCO₂

The pCO₂ ranged from 15 to 6323 μatm with a catchment-wide average of 1748 μatm and showed considerable temporal and spatial variation throughout the sampling period. There was an increasing trend of observed pCO₂ from small to large rivers (Figure 3a). On average, the pCO₂ values were 856 ± 444, 1481 ± 979, 1354 ± 753, 2332 ± 1330, 2142 ± 1016, 2271 ± 1121, and 2168 ± 1046 μatm for streams from first to seventh order, respectively (Figure 3a). The stronger increase in pCO₂ occurred between third and fourth order streams (from 1354 ± 753 to 2332 ± 1330 μatm, Figure 3a). Overall, pCO₂ in large rivers (2250 ± 1178 μatm) was 76.3 % higher than that in small rivers (1276 ± 796 μatm). Meanwhile, there was also an increasing trend of pCO₂ from rivers in UDJRB to those in LDJRB. The pCO₂ values were 2105 ± 959 and 2487 ± 1276 μatm for small and large rivers respectively in LDJRB, which were 146.7% and 70% higher than that in UDJRB, respectively (Figure 3b).
Figure 3 Spatial variations in pCO₂. (a) Yearly average pCO₂ in the seven stream orders, standard errors (SE) are displayed by error bars. (b) Measured pCO₂ in small and large rivers among three regions in the DJRB. The box mid-lines represent medians; the interquartile range (IQR) is represented by top and bottom of the box, respectively; whiskers indicate the range of 1.5 IQR; the white square symbols represent means, and the other symbols represent pCO₂ values for each sampled site.

Seasonal variations of pCO₂ differ across the stream size spectrum (Figure 3b4). In small rivers, the highest pCO₂ was observed in April (1506 ± 880 μatm), which was 50.3 % higher compared to January (1002 ± 660 μatm). pCO₂ then decreased in July (1131 ± 589 μatm) and increased in August (1325 ± 863 μatm) and October (1414 ± 900 μatm). Compared to small rivers, the peak of pCO₂ in large rivers occurred later but persisted for a longer period of time. In large rivers, an increase in pCO₂ was not observed until July. pCO₂ in April was 1831 ± 793 μatm, which was similar to 1805 ± 1010 μatm in January, and it increased 39.3 % to 2550 ± 1210 μatm in July. pCO₂ peaked in August (2885 ± 1351 μatm) and then decreased to 2176 ± 1166 in October. Overall, pCO₂ was 9.3 % and 21.7 % higher in wet season than in dry season for small and large rivers, respectively.
Figure 3.4 Spatial and Seasonal variations in $pCO_2$. (a) Yearly average $pCO_2$ in the seven stream orders, standard errors (SE) are displayed by error bars. (b) Seasonal $pCO_2$ in small and large rivers. The box mid-lines represent medians; the interquartile range (IQR) is represented by top and bottom of the box, respectively; whiskers indicate the range of 1.5 IQR; the white square symbols represent means, and the other symbols represent $pCO_2$ values for each sampled site.

3.3 CO$_2$ effluxes and $k_{600}$

CO$_2$ effluxes ranged from $-129.8$ to $3874.8$ mmol m$^{-2}$ d$^{-1}$ with a mean of $225.2$ mmol m$^{-2}$ d$^{-1}$. More than 95% of the 196 samples had positive FCO$_2$ values, indicating that the majority of the surveyed rivers is a carbon source. Overall, we observed higher FCO$_2$ during wet season than during dry season in both small and large rivers (Figure 4a and 4b). FCO$_2$ in small rivers and large rivers were $264.2 \pm 410.0$ and $300.1$
± 511.7 mmol m^{-2} d^{-1} respectively during the wet season, which was 87.2 % and 123.1 % higher compared to than that in the dry season (141.1 ± 188.7 and 134.5 ± 129.5 mmol m^{-2} d^{-1} for small and large rivers respectively). No significant (independent sample t test, p > 0.05) difference in FCO2 was observed between small and large rivers.

$k_{600}$ differs greatly between river size classes and among hydrological periods (Figure 5b). $k_{600}$ values in small rivers were significantly (independent sample t test, p < 0.001) higher on average than in large rivers. The mean values of $k_{600}$ in small rivers were 8.29 ± 11.29 m d^{-1} and 4.90 ± 3.82 m d^{-1} for the wet season and dry season, respectively, which were 112.6 % and 70 % higher than that of large rivers (3.90 ± 5.55 m d^{-1} in the wet season and 2.25 ± 1.61 m d^{-1} in the dry season). $k_{600}$ during the wet season were also significantly (independent sample t test, p < 0.05) higher than the dry season. $k_{600}$ increased 112.7 % and 118.2 % from dry season to wet season in small and large rivers, respectively. However, comparisons between different phases in the same hydrological period (e.g. early, middle, and late wet season) did not differ significantly (paired sample t test, p > 0.05) for both river size classes.

The spatial and temporal variation of CO2 efflux generally coincided with the changes in $pCO_2$ and $k_{600}$ since high FCO2 occurred when $k_{600}$ or $pCO_2$ were elevated. In small rivers, the highest CO2 effluxes were 346.8 ± 625.2 mmol m^{-2} d^{-1} during April, consistent with the high $k_{600}$ and $pCO_2$ in this period. In large rivers, high CO2 effluxes were observed in both April (339.9 ± 828.6 mmol m^{-2} d^{-1}) and August (329.9 ± 270.0 mmol m^{-2} d^{-1}), which were attributed to high $k_{600}$ in April and high $pCO_2$ in August.
4. Discussions

4.1 Underlying Processes of $p$CO$_2$ dynamics

Previous studies show that riverine CO$_2$ originated from both lateral soil CO$_2$ input and in-stream metabolism (Yao et al., 2007; Li et al., 2013; Abril et al., 2014). The river water $p$CO$_2$ was positively related to DOC and negatively related to DO (Figure 5), indicating that decomposition of terrestrial organic carbon is an important source for $p$CO$_2$ (Stets et al., 2017; Liang et al., 2020). To compare the contribution of internal metabolism on $p$CO$_2$ in small and large rivers, $\Delta$CO$_2$: $\Delta$O$_2$ stoichiometry was used to evaluate the impact of respiration and photosynthesis processes on the concentration of O$_2$ and CO$_2$ in water bodies (Stets et al., 2017). The inverse relation between $\Delta$CO$_2$ and $\Delta$O$_2$ (Figure 6) demonstrated that metabolic processes are important for CO$_2$ variation (Amaral et al., 2020). However, the imbalanced $\Delta$CO$_2$: $\Delta$O$_2$ stoichiometry (Figure 6) indicates that, in addition to in-stream metabolic processes, other factors also affect the CO$_2$ and O$_2$ in the water (Stets et al., 2017). For example, 183 out of 215 observations are above the 1:1 $\Delta$CO$_2$: $\Delta$O$_2$ line, suggesting additional sources of carbon input. The difference in the $\Delta$CO$_2$: $\Delta$O$_2$ stoichiometry between small and large rivers reflects their differences in the controlling processes (Rasera et al., 2013). In large rivers, the $\Delta$CO$_2$: $\Delta$O$_2$ stoichiometry is closer to the 1:1 line than in small rivers, suggesting large rivers are more affected by the metabolic processes (Jeffrey et al., 2018; Amaral et al., 2020). In comparison, the deviation from the 1:1 line in small rivers indicates a stronger impact of additional carbon sources (Abril et al., 2014; Amaral et al., 2020).

The spatial pattern of $p$CO$_2$ in the DJRB is likely resulting from changes in the intensity of in-stream metabolism. Our data showed that river water $p$CO$_2$ was negatively related to DO and positively related to DOC (Figure 6), suggesting that metabolic processes are important for CO$_2$ variation (Amaral et al., 2020). High $p$CO$_2$ and low DO in large rivers could result from more favorable conditions for OC composition. Terrestrial organic carbons are difficult to convert into CO$_2$ in small rivers due to the high flow velocity and short water residence time (Hotchkiss et al., 2015). Conversely, a greater fraction of OC could be transported and fuel the heterotrophic respiration in large rivers, where low flow velocity
and long water residence time facilitated the decomposition of organic carbon within the water column (Denfeld et al., 2013).

**Figure 5.6** Relationship between seasonal average $p$CO$_2$ and (a) DO and (b) DOC. Error bars for the $p$CO$_2$ represent 1 standard deviation from the seasonal mean. The DO–$p$CO$_2$ and DOC–$p$CO$_2$ relationship are shown as solid lines.

**Figure 6** The relationship between ΔCO$_2$ and ΔO$_2$. Points greater than zero are oversaturated, and less than zero are undersaturated. Points above the 1:1 line would have extra carbon sources in addition to in-stream metabolic processes.

Differences in seasonal changes of $p$CO$_2$ between small and large rivers also suggest various primary controlling processes. $p$CO$_2$ in small rivers are mainly controlled by changes in lateral soil CO$_2$ input. The highest value of $p$CO$_2$ observed in April could be attributed to a rapid surge of additional soil CO$_2$ input caused by increasing precipitation (Figure 7). In spring, warming temperatures increase the net primary productivity of the terrestrial ecosystem, with a corresponding increase in soil carbon content. Meanwhile, increased precipitation in April
facilitates the transportation of the soil carbon from land to the river system (Rasera et al., 2013). Thus, the temperature and precipitation in April dominantly control the soil CO$_2$ concentration, and hence mediate aqueous pCO$_2$ (Hope et al., 2004; Yao et al., 2007; Johnson et al., 2008). In contrast, a decrease of pCO$_2$ in July was observed, and it was likely the result of the CO$_2$ depletion effect in the soil combined with the dilution effect of precipitation. The soil carbon has experienced a depletion effect due to the continuous precipitation and soil erosion since April, limiting the supply of terrestrial carbon input for rivers in July (Hope et al., 2004; Johnson et al., 2007; Dinsmore et al., 2013). Meanwhile, the increase in precipitation and runoff can also cause a dilution effect, which leads to a decrease of pCO$_2$ (Ran et al., 2017b; Li et al., 2018). Seasonal variations in alkalinity substantiate the dilution effect and the depletion effect in July. Although the lowest alkalinity in small rivers was recorded in April, the highest pCO$_2$ values in small rivers were recorded in that month. It suggests that the effect of increased soil CO$_2$ input outweighs the dilution effects, both of which are caused by precipitation increase. In contrast, the synchronous upward trend of the alkalinity and pCO$_2$ in the later months of the year implies that the rise in pCO$_2$ results from weakened dilution effect (Ni et al., 2019). Moreover, low pCO$_2$ during dry season demonstrates inorganic carbon input via groundwater plays a minor role. Therefore, the variation of soil CO$_2$ input and dilution effect caused by precipitation are the main controlling factors of seasonal changes in riverine CO$_2$ among small rivers.

**Figure 7 Seasonal variations of pCO$_2$, alkalinity, and precipitation.**

The spatial pattern of pCO$_2$ was also related to the variation in carbon input due to different land cover (Borges et al., 2018). The higher pCO$_2$ in large rivers than small rivers was associated with a higher percentage of urban and cropland cover and lower forest cover (Figure S3). Compared with the forest, cropland could provide a more favorable condition for soil erosion and the transfer of organic matter from land to rivers, contributing to a higher pCO$_2$. Intensification of agricultural practices could promote the decomposition of soil organic matter (Borges et al., 2018) and increase the concentration of liable DOC, which is more sensitive to in-stream metabolism after entering the rivers (Lambert et al., 2017; Li et al., 2019). Meanwhile, the input of wastewater with high organic matter concentration from the urban area could also contribute to an increase in riverine pCO$_2$ (Xuan et al., 2020; Zhang et al., 2021).
Moreover, our result showed increasing $pCO_2$ from forest-dominated streams in UDJRB to those in agricultural and urban impacted catchments in MDJRB and LDJRB (Figure 3b). Over 70% of forest cover in UDJRB (Figure 1) can reduce the soil erosion associated with precipitation (Ran et al., 2018). Meanwhile, the organic matter from forest tend to be more aromatic, thus more capable of surviving biodegradation (Kalbitz and Kaiser, 2008), leading to a relatively low riverine $pCO_2$ value. In contrast, cropland, occupying about 49% of the land cover (Figure 1), was the primary land use type in the MDJRB substituting forest, and urban areas accounting for about 17% of the land cover in the LDJRB. The higher $pCO_2$ in the MDJRB and LDJRB is likely under the influence of agricultural practices and wastewater input. Overall, land use mainly affects the spatial distribution of $pCO_2$ by altering the amount and lability of carbon inputs to the rivers.

However, DOC concentration is not likely the primary control of different in-stream metabolism intensities in small and large rivers. Our result showed that large rivers had similar DOC concentration but higher $pCO_2$ compared with small rivers with similar land cover (Figure 7) when the percentage of forest area was over 65% or the percentage of combined cropland and urban area was less than 30%. This suggested that large rivers have more intense OC decomposition than small rivers with similar DOC concentrations. Therefore, favorable conditions for OC decomposition were more likely to be responsible for the spatial pattern. Another possible carbon source of river water CO$_2$ is direct soil CO$_2$ input. However, it is unlikely the major contributor of CO$_2$ for large rivers in the DJRB, since the contribution of soil CO$_2$ tends to decrease with the increased stream order and leads to higher $pCO_2$ in small rivers (Marx et al., 2017), which contradicted with the spatial pattern in this study.
Figure 7 (a) the relationship between yearly average $pCO_2$ at each site and the percentage of cropland and urban area combined (b) the relationship between yearly average $pCO_2$ at each site and the percentage of forest area (c) the relationship between yearly average DOC at each site and the percentage of cropland and urban area combined (d) the relationship between yearly average DOC at each site and the percentage of forest area. On the other hand, high $pCO_2$ in large rivers is mainly a consequence of decomposition of organic carbon. Relatively low $pCO_2$ in April indicates a carbon source other than soil CO$_2$ input. When soil carbon dioxide enters river systems, it is readily emitted from the rivers into the air, with little reaching the larger rivers downstream (Denfeld et al., 2013; Drake et al., 2018). The contribution of soil CO$_2$ input to $pCO_2$ could only be secondary. In large rivers, $pCO_2$ increased by 39.3 % from $1831 \pm 793 \mu$atm in April to $2550 \pm 1210 \mu$atm in July. The rise in temperature from April to July promoted a substantial increase in the net primary productivity of the terrestrial ecosystem and the content of terrestrial organic carbon entering the river (Borges et al., 2018). (vonk et al., 2013; Dean et al., 2019) Yet, those terrestrial organic carbons are difficult to convert into CO$_2$ in small rivers due to the high flow velocity and short water residence time (Hotchkiss et al., 2015). Thus, a possible explanation of increasing $pCO_2$ in large rivers is that a greater fraction of OC could be transported and fuel the heterotrophic respiration in large rivers, where long water residence time combined with the high temperature in July facilitate OC decomposition (Denfeld et al., 2013). For large rivers, recent studies have shown that the biological decomposition of allochthonous organic carbon caused by energetic microbial metabolism is the primary source of riverine CO$_2$ (Amaral et al., 2018; Jeffrey et al., 2018; Borges et al., 2018; Ran et al., 2018; Borges et al., 2018; Lambert et al., 2017; Li et al., 2019; Xuan et al., 2020; Zhang et al., 2021).
On the other hand, the temporal pattern is likely the consequence of changes in terrestrial carbon input and in-stream metabolism intensity. Our result showed that higher \( p\text{CO}_2 \) occurred in the wet season than the dry season for both small and large rivers (Figure 4). The elevated temperature in the wet season could promote a substantial increase in the net primary productivity of the terrestrial ecosystem, while increased precipitation facilitated the transfer of terrestrial carbon (Rasera et al., 2013), including both soil \( \text{CO}_2 \) and \( \text{OC} \), from land to rivers. This could either enhance riverine \( p\text{CO}_2 \) directly or by fuelling \( \text{OC} \) decomposition (Borges et al., 2018). However, differences in seasonal changes of \( p\text{CO}_2 \) between small and large rivers (Figure 4) also suggested that their primary controlling process could be different. For small rivers, the highest value of \( p\text{CO}_2 \) was observed in April (Figure 4), which is consistent with the rapid surge of terrestrial C input, usually occurring at the beginning of the wet season (Hope et al., 2004; Yao et al., 2007; Johnson et al., 2008). However, such an increase in \( p\text{CO}_2 \) was not observed in large rivers (Figure 4), even though DOC in large rivers, increased during the same period, similar to small rivers (Table 1). A possible explanation is that observed \( p\text{CO}_2 \) rise was mainly originated from soil \( \text{CO}_2 \), which was readily emitted from the small rivers into the air, with little reaching the larger rivers downstream (Denfeld et al., 2013; Drake et al., 2018). Differences in \( p\text{CO}_2 \) dynamic in July and August also reflected differential controlling processes in small and large rivers. A decline in \( p\text{CO}_2 \) in July in small rivers suggested that it might have experienced the depletion effect occurring at middle and late wet season (Hope et al., 2004), during which soil \( \text{CO}_2 \) decreased due to the continual precipitation. In contrast, the increase in \( p\text{CO}_2 \) occurring in large rivers in July indicated that the decrease in soil \( \text{CO}_2 \) input could hardly affect the \( p\text{CO}_2 \) in large rivers during this period. Instead, stronger in-stream metabolism caused by \( \text{OC} \) input and favorable conditions for \( \text{OC} \) decomposition is more likely to be responsible for the rising \( p\text{CO}_2 \).

To compare the contribution of internal metabolism on \( p\text{CO}_2 \) in small and large rivers, \( \Delta\text{CO}_2: \Delta\text{O}_2 \) stoichiometry was used to evaluate the impact of respiration and photosynthesis processes on the concentration of \( \text{O}_2 \) and \( \text{CO}_2 \) in water bodies (Stets et al., 2017). The inverse relation between \( \Delta\text{CO}_2 \) and \( \Delta\text{O}_2 \) (Figure 8) demonstrated that metabolic processes are important for \( \text{CO}_2 \) variation (Amaral et al., 2020). It is also supported by the positive relation between river water \( p\text{CO}_2 \) and DOC and the negative relation between \( p\text{CO}_2 \) and DO (Figure 6). However, the imbalanced \( \Delta\text{CO}_2: \Delta\text{O}_2 \) stoichiometry (Figure 7) indicates that, in addition to in-stream metabolic processes, other factors also affect the \( \text{CO}_2 \) and \( \text{O}_2 \) in the water (Stets et al., 2017). For example, 183 out of 215 observations were above the 1:1 \( \Delta\text{CO}_2: \Delta\text{O}_2 \)
line, suggesting additional sources of carbon input. The difference in the ΔCO₂:ΔO₂ stoichiometry between small and large rivers reflects their differences in the controlling processes (Rasera et al., 2013). In large rivers, the ΔCO₂:ΔO₂ stoichiometry is closer to the 1:1 line than in small rivers, suggesting large rivers are more affected by the metabolic processes (Jeffrey et al., 2018; Amaral et al., 2020). In comparison, the deviation from the 1:1 line in small rivers indicates a stronger impact of external carbon sources (Abril et al., 2014; Amaral et al., 2020), which substantiates our finding that pCO₂ of small rivers are more likely affected by soil CO₂ input. Furthermore, there were other processes that could affect the riverine pCO₂. For example, stronger solar radiation during summer could increase photo-oxidation in rivers. However, commonly observed lower daytime CO₂ emission rates than nocturnal rates (Gómez-Gener et al., 2021) suggests that photosynthesis overrides photo-oxidation in CO₂ dynamics. Nonetheless, the low DO concentration observed in the surveyed rivers (Figure 8) suggested that photosynthesis is not the primary control of the seasonal variation of pCO₂.

**Figure 8** The relationship between ΔCO₂ and ΔO₂. Points greater than zero are oversaturated, and less than zero are undersaturated. Points above the 1:1 line indicate the existence of additional carbon sources, apart from in-stream metabolic processes.

### 4.2 Environmental Control of k₆₀₀ variation

Environmental factors, including wind speed and hydrological variables, could affect the gas exchange at the water–air interface and were typically used to explain the variance in k₆₀₀ (Alin et al., 2011; Raymond et al., 2012). Flow velocity generally determine the k₆₀₀ in rivers, while wind speed becomes a
more important factor in controlling the \( k_{600} \) in large rivers, reservoirs and estuary (Guérin et al., 2007; Rasera et al., 2013; Amaral et al., 2020). In our surveyed rivers, \( k_{600} \) displayed a significant linear correlation (Pearson correlation, \( p < 0.001 \)) with the flow velocity. Our \( k_{600} \) model (Figure 8) base on 188 field measurement data is similar to that developed by Alin et al. (2011) \( (k_{600} = 13.82 + 0.35v) \). However, in our studied rivers, no significant correlation (Pearson correlation, \( p > 0.05 \)) was found between wind speed and \( k_{600} \) regardless of stream size. This could be explained by the lower wind speed (Table 2, 0.68 ± 0.66 m s\(^{-1}\) and 1.09 ± 1.06 m s\(^{-1}\) for small and large rivers, respectively) (Guérin et al., 2007). As the wind speed decreases, the impact of flow velocity on \( k_{600} \) will increase considerably (Borges et al., 2004). Therefore, the accuracy of \( k_{600} \) estimation based on wind speed in nearby regions should be examined using measurement data (Yao et al., 2007; Li et al., 2018). The temporal heterogeneities of \( k_{600} \) between small and large rivers reveal the differences in flow regime. \( k_{600} \) in small rivers are significantly (independent sample t test, \( p < 0.001 \)) higher than in large rivers, which could be explained by higher flow velocity in small rivers due to a higher gradient. Meanwhile, significantly higher \( k_{600} \) (independent sample t test, \( p < 0.05 \)) was also observed in the wet season compared to the dry season, which is the result of increasing flow velocity and turbulence due to plentiful monsoon-induced precipitation during wet season (Guérin et al., 2007; Alin et al., 2011; Ho et al., 2018).
Figure 8.9 Relationship between $k_{600}$ and flow velocity. The dashed line represents the parameterization of Alin et al (2011).

Table 2. Seasonal variation of $k_{600}$ and environmental factors in small and large rivers.

| Stream size | Season | Current velocity $(\text{m s}^{-1})$ | $U_{10}$ $(\text{m s}^{-1})$ | $k_{600}$ $(\text{m d}^{-1})$ |
|-------------|--------|-------------------------------------|----------------------------|-------------------------------|
| small       | Wet    | $0.66 \pm 0.47$                     | $0.62 \pm 0.61$           | $8.29 \pm 11.29$             |
|             | Dry    | $0.43 \pm 0.27$                     | $0.76 \pm 0.73$           | $4.90 \pm 3.82$              |
| large       | Wet    | $0.32 \pm 0.32$                     | $0.86 \pm 0.91$           | $3.90 \pm 5.55$              |
|             | Dry    | $0.17 \pm 0.19$                     | $1.43 \pm 1.58$           | $2.25 \pm 1.61$              |

$y = 11.03 (\pm 1.16) x + 0.57 (\pm 0.64)$

$r^2 = 0.33$  $p < 0.001$
Exceptionally high \( k_{600} \) values were observed in the surveyed rivers (Figure 8). The highest \( k_{600} \) in large and small rivers were 41.83 and 79.97 \( \text{m} \text{d}^{-1} \), which were 5-fold and 3-fold larger than calculated \( k_{600} \), respectively. This is the result of the exponential increase in \( k_{600} \) due to extreme flood events. Generally, flood events associated with heavy rainfall during the wet season can increase flow velocity and turbulence at the water–air interface (Almeida et al., 2017; Geeraert et al., 2017), leading to substantially higher \( k_{600} \). Yet, neither our model nor the one from Alin et al. (2011) was suitable for the estimation of \( k_{600} \) during extreme flood events because the calculated \( k_{600} \) could deviate far from the measured \( k_{600} \) when they occurred. Therefore, the extent to which flood events affect \( k_{600} \) and riverine \( \text{CO}_2 \) emission is still uncertain and warrant continued research (Drake et al., 2018).

### 4.3 A Comparison of \( \text{CO}_2 \) Emissions to Other Rivers

The mean \( \text{CO}_2 \) fluxes of 225.2 mmol m\(^{-2}\)d\(^{-1}\) in DJRB is comparable to those observed in tropical and subtropical rivers in the Americas, Africa, and Southeast Asia (Table 3). Although the magnitude of the \( \text{CO}_2 \) evasion of these river basins is similar, the seasonal variations and drivers behind them could differ. The higher \( \text{CO}_2 \) emission in the Dongjiang Basin was observed in the wet season compared to the dry season, and this seasonal pattern is similar to that observed in the Xijiang and Daning rivers (Yao et al., 2007; Ni et al., 2019) but different from the one from Jinshui River in the upper reaches of the Yangtze River, where \( p\text{CO}_2 \) is high in winter and low in summer (Luo et al., 2019), even though all four rivers are in the East Asia Monsoon climate region. The difference in seasonal pattern can be explained by the drivers of \( p\text{CO}_2 \) variability as the seasonal variation of riverine \( p\text{CO}_2 \) is the likely resulting from result of the increase changes of external \( \text{CO}_2 \) input, carbon input, internal production of \( \text{CO}_2 \) (Yao et al., 2007), and the dilution effect caused by precipitation (Johnson et al., 2007). For rivers where \( p\text{CO}_2 \) is lower in summer than in winter, the dilution effect overrides the effect of increased carbon input and internal \( \text{CO}_2 \) production (Luo et al., 2019). In contrast, for rivers like the Dongjiang river, although the dilution effect remains, increased \( \text{CO}_2 \) input and metabolism are more significant factors in controlling \( p\text{CO}_2 \), thus leading to higher summer \( p\text{CO}_2 \). In addition, the controlling processes of the Dongjiang River may be different even when compared to rivers with similar seasonal variations in the same climatic zone. For instance, DO in the Xijiang river was supersaturated, indicating that photosynthetic activities in the water body mainly reduce the \( \text{CO}_2 \) concentration in the rivers (Yao et al., 2007). Therefore, other carbon sources like soil respiration and carbonate weathering should be responsible for high \( p\text{CO}_2 \) in summer (Zhang et al., 2019). In contrast, low DO value and a negative correlation between DO and \( p\text{CO}_2 \)
have been observed in the Dongjiang River, indicating that photosynthesis is relatively weak compared with the respiration in the water body, and the latter one is an essential source of riverine CO₂ (Stets et al., 2017) and results resulting in higher $p$CO₂ in summer.

### Table 3. Comparison of CO₂ emission in subtropical and tropical rivers.

| Rivers                        | Climate       | Season | $p$CO₂ $\mu$atm | $k_{co2}$ m d⁻¹ | FCO₂ mmol m⁻² d⁻¹ | References                        |
|-------------------------------|---------------|--------|------------------|------------------|--------------------|-----------------------------------|
| The Dongjiang                 | Subtropical   | Wet    | 2422 ± 1209      | 3.90 ± 5.55      | 300.1 ± 511.8      | This study                        |
| River (Large rivers)          |                | Dry    | 1990 ± 1094      | 2.25 ± 1.61      | 134.5 ± 129.5      |                                   |
| The Dongjiang                 |                | Wet    | 1321 ± 792       | 8.29 ± 11.29     | 264.2 ± 410.0      |                                   |
| River (small rivers)          |                | Dry    | 1191 ± 825       | 4.90 ± 3.82      | 129.5 ± 197.2      |                                   |
| The Xijiang River (Mainstream)| Subtropical   | Wet    | 2600             |                  | 190.3–358.6        | (Yao et al., 2007)                |
| The Lower Meikong River       | Tropical      |        |                  |                  |                    |                                   |
| The Yangtze River             | Subtropical   | Dry    | 1147 ± 874       | 11.1 ± 4.5*      | 343 ± 413          | (Luo et al., 2019)                |
| (Jinshui River) (headwater stream) |            | Wet    | 1562 ± 975       | 8.29 ± 11.29     | 264.2 ± 410.0      |                                   |
| The upper Yangtze River       | Subtropical   | Rainy  | 1198.2 ± 1122.9  |                  | 329.8 ± 470.2      | (Ni et al., 2019)                |
| (Daning river)                |                | Dry    | 1243.7 ± 1111.5  | 8.1–14.1*        | 357.4 ± 483.7      |                                   |
| The Zambezi River             | Tropical      | Wet    | 3102.5 **        | 0.05–1.51        | 350.75             | (Teodoru et al., 2014)           |
| (headwater stream)            |                | Dry    | 1150 **          |                  | 51.92              |                                   |
| The Congo River               | Tropical      | High water | 6001 ± 5008      |                  | 1149 or 1520       | (Borges et al., 2015a; Borges et al., 2015b) |
|                               |               | Low water | 4867 ± 2578      |                  |                    |                                   |
|                               |               | Falling water | 5321 ± 3383     |                  |                    |                                   |
| The Lower Red River           | Tropical      | Wet    | 1589 ± 43        | 12.22 ± 6.48     | 530.3 ± 16.9       | (Le et al., 2018)                |
| Caboolture River              | Subtropical   |        |                  |                  |                    |                                   |
| Rajang River                  | Tropical      | wet    | 2531 ± 188       | 0.55–2.93        | 141.67             | (Müller-Dum et al., 2019)        |
|                               |                | dry    | 2337 ± 304       |                  | 125                | (Müller-Dum et al., 2019)        |
| Lower Mississippi             | Subtropical   |        |                  |                  |                    | (Reiman and Xu, 2016)            |
The $CO_2$ fluxes in small rivers are similar to that in large rivers, which is contradictory to the finding in previous studies that $CO_2$ effluxes should be higher in small rivers than in large rivers due to the input of $CO_2$-rich groundwater (Duvert et al., 2018). The depletion and diffusion effect may be responsible for the discrepancy (Johnson et al., 2007; Dinsmore et al., 2013). In the Dongjiang River Basin, groundwater could be easily diluted due to ample monsoon-induced precipitation, preventing it from supplying the small rivers with high concentrations of carbon dioxide. However, we recognize that the impact of groundwater on $pCO_2$ in small rivers may be overlooked in our sampling process since the $CO_2$ carried by groundwater can emit into the atmosphere within a very short distance (Duvert et al., 2018). In view of the above, it is recommended that further studies targeting the release of groundwater $CO_2$ to the atmosphere be carried out in the future.

### 5 Conclusion

Studying $CO_2$ emissions from subtropical rivers is an essential step toward more accurate estimates of global $CO_2$ evasion from river systems. By deploying floating chambers, seasonal changes in riverine $pCO_2$ and $CO_2$ evasion in the Dongjiang river catchment were investigated. Spatial and temporal patterns of $pCO_2$ were mainly affected by terrestrial carbon inputs and in-stream metabolism, both of which varied due to differential catchment settings, land cover, and hydrological conditions. Lateral soil $CO_2$ input and dilution effect caused by precipitation played critical roles in controlling riverine $pCO_2$ in small rivers, while the decomposition of allochthonous organic carbon is responsible for $pCO_2$ changes in large rivers as suggested by the $\Delta CO_2$- $\Delta O_2$ stoichiometry line. $k_{600}$ was higher in small rivers than large rivers and higher during the wet season than the dry season, both of which can be explained by the observed significant correlation between $k_{600}$ and the flow velocity. In contrast to previous studies, similar $CO_2$ fluxes were observed among small and large rivers in the DJRB. It is suggested that the absence of commonly observed higher $CO_2$ fluxes in small rivers could be associated with the depletion effect caused by abundant and persistent precipitation in this subtropical monsoon catchment. There is no doubt...
that the spatial and temporal variation of CO₂ evasion in the DJRB reflected the complexity and diversity of controlling factors. As a step towards a more accurate estimate of the carbon budget in the catchment, comprehensive and systematic measurements of CO₂ evasion covering a broad range of stream sizes and seasons are of paramount importance.

560 **Data availability.** CO₂ emission data used in this study are available online at: [https://doi.org/10.25442/hku.13416281.v1](https://doi.org/10.25442/hku.13416281.v1) (Liu, 2020). Other data are available from the corresponding author Lishan Ran upon request at lsran@hku.hk.

**Author contributions.** BL and LR conceived the study. BL, MT, CC, XY, and LR carried out the fieldwork. BL, MT, and KS designed and performed the laboratory analysis. BL composed the manuscript with contributions from all authors.

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

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