



# High Riverine CO<sub>2</sub> Outgassing affected by Land Cover Types in the Yellow River Source Region

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Abstract: Rivers connect the land and the oceans, acting as both active pipes and containers transporting carbon and other substances from terrestrial ecosystems to aquatic ecosystems. Meanwhile, rivers can release huge amounts of  $CO_2$  to the atmosphere. However, estimates of global riverine  $CO_2$  emissions remain greatly uncertain owing to the absence of a comprehensive spatially and temporally  $CO_2$ 

- 20 emissions measurement, especially in river source regions. In this study, riverine partial pressure of CO<sub>2</sub> (*p*CO<sub>2</sub>) and CO<sub>2</sub> efflux (*F*CO<sub>2</sub>) in the Yellow River source region under different landcover types, including glaciers, permafrost, wetlands, and grasslands, were investigated in April, June, August, and October 2016. The relevant chemical parameters and environmental parameters, including pH, dissolved oxygen (DO), and dissolved organic carbon (DOC), were analyzed to explore the main control factors of
- 25 riverine pCO<sub>2</sub> and FCO<sub>2</sub>. The results showed that the rivers in the Yellow River source region were a net CO<sub>2</sub> source, with the pCO<sub>2</sub> ranging from 181 to 2441 µatm and the FCO<sub>2</sub> from -221 to 6892 g C m<sup>-2</sup> yr<sup>-1</sup>. Both the pCO<sub>2</sub> and FCO<sub>2</sub> showed strong spatial and temporal variations. The average FCO<sub>2</sub> in August was higher than that in other months, with the lowest in October. In alpine climates, low temperature conditions played a crucial role in limiting biological activity and reducing CO<sub>2</sub> emissions. The lowest
- 30 FCO<sub>2</sub> values (-221 g C m<sup>-2</sup> yr<sup>-1</sup>) were observed in the glacier and permafrost regions. By integrating seasonal changes of water surface area, the total CO<sub>2</sub> efflux was estimated at 0.37±0.49 Tg C yr<sup>-1</sup>, which is significantly higher than previous studies. Although it is still a small proportion of CO<sub>2</sub> emissions compared with the whole Yellow River Basin, but there is a huge carbon emissions potential. Since the permafrost in the source region of the Yellow River is rich in large amounts of ice and organic carbon,
- 35 the continuously increasing temperature due to global warming will accelerate not only the mobilization of organic carbon in permafrost, but also the degradation of organic carbon by soil microorganisms. As a consequence, huge amounts of CO<sub>2</sub> release from soils and rivers is anticipated.

Key words: pCO2, CO2 outgassing; glaciers; permafrost; wetland; grassland; Yellow River source region





## 1. Introduction

- 40 Rivers connect the land and the oceans, acting as both pipes and containers transporting carbon and other substances from terrestrial ecosystems to aquatic ecosystems. At the same time, they receive organic or inorganic carbon from the terrestrial carbon pool, degrade and ultimately release as CO<sub>2</sub> or buried in the riverine sediments. The existing studies on riverine CO<sub>2</sub> evasion mainly focuses on the spatial and temporal dynamics of partial pressure of CO<sub>2</sub> (*p*CO<sub>2</sub>) and CO<sub>2</sub> efflux (*F*CO<sub>2</sub>). (Cole et al.,2001;
- 45 Aufdenkampe et al., 2011; Raymond et al., 2013; Abril et al., 2014). Many researchers believe that river water CO<sub>2</sub> is mainly derived from the respiration of terrestrial ecosystems and the decomposition of organic matter in river waters, but the source and impact mechanism of CO<sub>2</sub> evolution from rivers is still not clear (Raymond et al., 2013; Hotchkiss et al., 2015; Schelker et al., 2016; Ran et al., 2017). Therefore, in order to accurately estimate the riverine CO<sub>2</sub> outgassing and in-deep understanding its control mechanism, more research within the river in particular climates (i.e., alpine climate) and special regions
- (i.e., headwater region or intermitted rivers) are needed. It will provide a better understanding of regional or global carbon balance processes and future climate change trends.
- With respect to global-scale CO<sub>2</sub> outgassing, available estimates are characterized by great uncertainty.
  For example, recent CO<sub>2</sub> outgassing fluxes from global rivers and streams combined range from 1.8 to 3.2 P g C yr<sup>-1</sup> (Raymond et al., 2013; Drake et al., 2017), which are significantly higher than earlier estimate by Cole et al. (2007) (i.e., 0.75 P g C yr<sup>-1</sup> based on the data of 80 major rivers in the world). A major reason for the huge range is because of the absence of a global CO<sub>2</sub> outgassing database which includes CO<sub>2</sub> emissions measurement over different rivers and under different climate and land cover
  types (Raymond et al., 2013; Cole et al., 2007; Aufdenkampe et al., 2011; Drake et al., 2017). Thus, more

field measurements based on global river systems are strongly needed to increase the accuracy of the





estimates.

However, there are limited studied on  $CO_2$  effluxes of rivers in extreme geographical and climatic conditions, such as alpine rivers (Wu et al., 2008;Zhang et al., 2013). Crawford et al. (2013) investigated the riverine  $CO_2$  outgassing in the Alaska region and explored its temporal and spatial changes by connecting it to land use types. Crawford et al. (2015) further studied carbon emissions from the rivers and lakes in alpine areas around Estes Park in the United States and found the average  $pCO_2$  was only 417 µatm. They concluded that the high altitude and low vegetation coverage are the primary factors

- 70 limiting CO<sub>2</sub> outgassing. Weyhenmeyer et al. (2015) collected data from 5,118 alpine lakes and concluded that the production of CO<sub>2</sub> in the lake was usually half of the CO<sub>2</sub> emissions and most of the emitted CO<sub>2</sub> derived from dissolved inorganic carbon (DIC). Humborg et al. (2010) surveyed rivers in central and northern Sweden and concluded that the average *p*CO<sub>2</sub> was 1445 µatm and the average *F*CO<sub>2</sub> value was 3033 g C m<sup>-2</sup> yr<sup>-1</sup>. A comprehensive analysis indicated that groundwater and respiration of
- 75 soil maintained the riverine CO<sub>2</sub> excess with the consumption of terrestrial organic matter as the major source of riverine CO<sub>2</sub>.Overall, compared with the temperate and tropical rivers, riverine CO<sub>2</sub> outgassing under the alpine climate is at a relatively low level. It is mainly due to the cold climate with low temperature and high altitude that limit riverine CO<sub>2</sub> emissions, and the underlying control mechanisms are not the same as these in temperate and tropical climates (Peter et al., 2014).

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The riverine  $CO_2$  emissions in the Yellow River Basin has been studied and some preliminary results have been reported. Su et al. (2005) reported that the  $pCO_2$  value of the mainstream was between 1100 and 1700 µatm, which were in the intermediate-low level of the world rivers. The main controlling factor was its carbonate system. Zhang et al. (2008) measured  $pCO_2$  of 1570 µatm at Lijin Hydrological Station





on the lower Yellow River during sediment regulation period (June–July), which was significantly higher than in the other periods. Zhang et al. (2009) measured the FCO<sub>2</sub> of the Yellow River and concluded that the Yellow River water was a source of atmospheric CO<sub>2</sub> during the autumn. The amount was about 0.0174 Tg C, and the flux was similar to that of the Ottawa River but far less than that of the Amazon. Ran et al. (2015b) estimated that the annual CO<sub>2</sub> emissions of the whole Yellow River at 7.9 Tg C, which is close to the basin-wide carbon deposition of 8.7 Tg C while larger than the amount of marine import (i.e., 6 Tg C).

These studies on  $CO_2$  emissions from the Yellow River were mainly confined to its middle and lower reaches and the estuary. In contrast, there are few studies on the upper reaches, especially the source

- 95 region on the Tibetan Plateau. The Yellow River source region is located in the alpine zone with the Yellow River mainstream and its tributaries flowing through a variety of land cover types, including grassland, wetland, glacier, and permafrost. Affected by increasing temperature as a result of global warming, the alpine rivers in this region have become hot spots of riverine carbon cycle studies and warrant a thorough understanding of their implications in the context of global climate change (Ulseth et
- 100 al., 2018; Peter et al., 2014; Hoodet al., 2015). In particular, although Ran et al., (2015a,b) used compiled water chemistry data to estimate  $pCO_2$  and  $FCO_2$ , there are no field-based direct measurements of  $CO_2$ emissions from these alpine rivers.

In order to accurately determine the intensity of riverine CO<sub>2</sub> outgassing and fully understand the 105 underlying control mechanisms in the alpine climate region, we conducted in situ measurements of CO<sub>2</sub> emissions from the alpine rivers under different land cover types, including grassland, peatland, glacier, and permafrost, in the Yellow River source region. Here we aim to address three questions regarding CO<sub>2</sub>





emissions in the Yellow River source region: (1) the spatiotemporal patterns of CO<sub>2</sub> emissions under different land cover types; (2) the magnitudes of stream CO<sub>2</sub> emissions; and (3) the source of riverine CO<sub>2</sub> in this alpine river system. Answers to these questions will lead to a better understanding of riverine carbon export and CO<sub>2</sub> emissions, especially for alpine rivers, which will help refine the global estimation of riverine *F*CO<sub>2</sub>.

#### 2. Materials and methods

#### 115 2.1 Site description

The Yellow River originates from the north part of the Bayanhar Mountains in the Tibetan Plateau, then flows through the Loess Plateau and the North China Plain, and eventually empties into the Bohai Sea. Generally, the drainage basin above the Toudaoguai hydrological station is called the upper reach and the region above the Tangnaihai hydrological station is known as the Yellow River source region (Figure 1).

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The study area is situated from  $32^{\circ}3'N 95^{\circ}5'E$  to  $36^{\circ}1'N 103^{\circ}3'E$  (Figure 1). In the Yellow River source region, most of the rivers flow through the Tibetan Plateau at an altitude of 3000-4000 m with meandering river channels. The study area is about  $1.32 \times 10^5$  km<sup>2</sup>, accounting for about 17.6 % of the Yellow River basin. The Yellow River source region is located in an alpine zone, which is a typical

125 plateau continental climate, mainly affected by plateau monsoon. The northern part belongs to the semiarid climate zone, while the middle and southern part is in the humid and sub-humid climate zone (Yang et al.,1991).

The annual mean precipitation is 486 mm, which is the dominant factor of runoff (Sun et al., 2009), accounting for approximately 95.9% of the total runoff in the source area (Liu et al., 2005). The annual





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evaporation varies from 800 to 1200 mm. Although the area of source region accounts for only 17.6% of the whole basin, it supplies over 33% water of the Yellow River, providing an important water resource for both middle and lower reaches of the Yellow River (Sun et al., 2009). In recent decades, although the precipitation has slightly increased (Chang et al., 2007), the water discharge in the middle and lower reaches has decreased significantly, which has aggravated the water shortage of the downstream region, especially in the non-flood season (Zhang et al., 2012).

#### 2.2 Fieldwork and laboratory analysis

- In this study, four rounds of field work in April, June, August, and October 2016 were conducted. The 140 riverine *p*CO<sub>2</sub> and related environmental factors, including water temperature, pH, dissolved oxygen (DO), were monitored in the field under different land cover types in the Yellow River source region. In total, there are 36 sampling points (Figure 1) within the study area and they can be categorized on the basis of the complexity of river network structure and the land cover types (i.e., glacier, permafrost, wetland, and grassland) (Table 1). In addition, three groundwater samples in grassland covered area were
- taken to determine its pCO<sub>2</sub>. The temperature, pH, and DO were measured by using a Multi 3420 analyzer (WTW, Germany) with the accuracies of ±0.2 °C, ±0.004, and ±1.5%, respectively. Before the measurement, the pH probe was calibrated by three pH buffers (e.g., pH 4.01, pH 7.00, and pH 10.01, respectively).
- 150 The prior study suggested that, when the pH ranges from 7 to 10, HCO<sub>3</sub><sup>-</sup> represents 96% of alkalinity, alkalinity can be used to calculate DIC (Hunt et al., 2011). Alkalinity was determined by on-site titration. The collected water sample was subjected to low-pressure suction filtration through a glass fiber filter (Whatman GF/F) with a pore diameter of 0.7 μm. The fiber filter was pre-fired in a muffle furnace at





450 °C. For each water sample, the alkalinity was titrated with 0.1 mol L<sup>-1</sup> HCl within 12 hours after sampling. Each titration was repeated three times to assure the analytical error below 3%. The Methyl orange indicator was used to determine the endpoint of the reaction at pH=4.5. Another 100 mL of the filtered water sample was transferred into the specific bottle, added with nitric acid, and preserved in refrigerator at 4 °C condition for dissolved organic carbon (DOC) measurement in laboratory. DOC was analyzed with the Vario total nitrogen/organic carbon analyzer (Elementar, German), which has a precision less than 3%.

### 2.3 Calculation of $CO_2$ emission

In this study, FCO<sub>2</sub> was measured by the floating chamber method (Ran et al.,2017) connected with a Li-7000 CO<sub>2</sub>/H<sub>2</sub>O analyzer (Li-Cor, Inc, USA). The Li-7000 instrument was calibrated with standard CO<sub>2</sub> gases of 500 ppm and 2000 ppm before each measurement.

The volume of rectangular floating chamber is 17.8 L and the covered water area is 0.09 m<sup>2</sup>. The chamber walls were lowered 3 cm into the water and mounted with plastic foams that had streamlined ends to limit artificial disruptions to near-surface turbulence. The chamber is covered with tin foil to reduce the

170 influence of sun light's heating. The temperature inside the chamber was measured with a waterproof thermometer. At the beginning of each experiment, the chamber was placed in the air near the monitoring point and the air inside the chamber was continuously circulated in a closed loop that was connected to an infrared Li-7000 gas analyzer through rubber-polymer tubes for CO<sub>2</sub> analysis. The instrument automatically records the air CO<sub>2</sub> concentration and ambient atmospheric pressure. When the chamber 175 was placed on the water surface, the analyzer recorded the CO<sub>2</sub> concentration every 2 seconds, and each

measurement lasted for 6–10 mins. In large rivers with relatively favorable flow conditions, we fixed the 8





chamber on a small rubber boat and drifted along the water to measure the  $FCO_2$ . In contrast, we used the static chamber method to measurement the  $FCO_2$  in the small rivers or streams which could lead an overestimate of  $CO_2$  evasion to some extent. (Lorke et al., 2015).

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The CO<sub>2</sub> flux from water is calculated using the following equation (Frankignoulle et al., 1988):

$$FCO_2 = 1000 \times (dpCO_2/dt) (V/RTS)$$
(1)

where,  $dp CO_2/dt$  is the slope of CO<sub>2</sub> change within the chamber (Pa d<sup>-1</sup>; converted from µatm min<sup>-1</sup>), *V* is the chamber volume (17.8 L), *R* is the gas constant, *T* is chamber temperature (K), and *S* is the area of the chamber covering the water surface (0.09 m<sup>2</sup>).

Conventionally, FCO<sub>2</sub> can also be estimated from the following equation.

$$FCO_2 = k \cdot K_H \cdot \Delta p CO_2 \tag{2}$$

Where, *k* is gas transfer velocity (cm h<sup>-1</sup>), K<sub>H</sub> is the Henry's constant for CO<sub>2</sub> at a given temperature, the *F*CO<sub>2</sub> is the in situ measured riverine CO<sub>2</sub> efflux, and the  $\Delta p$ CO<sub>2</sub> is the difference between the surface

- 190 water and the atmosphere. Using the field-measured  $pCO_2$  in surface water and air, k can be computed by rearranging Equation (2). In order to facility compare our k with the results of other studies, we standardized it to a Schmidt number of 600 ( $k_{600}$ ) by assigning the Schmidt number exponent value of 0.5 (Jähne et al., 1987).
- 195 Surface water pCO<sub>2</sub> was calculated using a headspace equilibrium method (Ran et al., 2017). By using an 1100 mL conical flask, 800 mL of water were collected in the depth of 10 cm below the water surface and the remaining volume of 300 mL was filled with ambient air. The flask was immediately closed with a lid and vigorously shaken for 1 min to equilibrate the gas in water and air. The equilibrated gas was





automatically injected into the calibrated Li-7000 gas analyzer. The measurements at each site were 200 repeated 3 times and the average was calculated (analytical error below 3%). Surface water  $pCO_2$  was calculated based on the equations from Dickson et al. (2007):

$$pCO_2^{water,i} \approx pCO_2^{headspace,f} + \frac{vh}{vw} (pCO_2^{headspace,f} - pCO_2^{headspace,i}) / (K_0 RT)$$

Where, the superscripts *i* and *f* represent initial and final  $pCO_2$  (µatm), *Vh* and *Vw* are the headspace volume and water volume, respectively,  $K_0$  is the solubility of CO<sub>2</sub> in water calculated on the basis of

205 solubility constants for CO<sub>2</sub> from *Weiss* (1974), *R* is the universal gas constant (8.314 J mol<sup>-1</sup>K<sup>-1</sup>), and *T* is the water temperature on Kelvin scale (K). Temperature in the flask after equilibration was measured to correct for changes in temperature compared to in-situ water. The initial pCO<sub>2</sub> was taken as the CO<sub>2</sub> concentration in ambient air before the headspace equilibration measurement.

#### 210 3.Results

#### 3.1 Characteristics of hydro-chemical variables

Water temperature (Tw) varied from 0.1 to 27.7 °C with an average of  $11.9\pm5.7$  °C. Average Tw in June (15.1±3.5 °C) and August (17.0±5.4 °C) is significantly higher than that in April (8.4±3.8 °C) and October (7.3±2.4 °C). Seasonal Tw difference was more significant at the wetland (14.4±6.4 °C) and

215 grassland (12.5±5.4 °C) sites than that in the glacier (7.5±4.1 °C) and permafrost (10.0±4.0 °C) sites. These results were expected as the water temperature depends mainly on the air temperature. Spatial variability of the air temperature was consistent with that of the water temperature at almost all the sites, although in some case it was as high as 33 °C. The annual average air temperature in the study area was16.7±6.3 °C.

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Water pH ranged from 7.0 to 9.0 with an average of 7.9  $\pm 0.6$  (Table 1). Mean pH based on all the stream 10 \$10





samples was  $8.3\pm0.4$ ,  $8.6\pm0.4$ ,  $7.2\pm0.2$ , and  $7.5\pm0.4$  in April, June, August, and October, respectively. A slight decreasing trend is observed with the different land cover types in the order of permafrost > glaciers>grassland>wetland, with the average pH value at  $8.1\pm0.9$ ,  $7.93\pm0.55$ ,  $7.85\pm0.59$ , and  $7.7\pm0.5$ ,

respectively (Table 1). Alkalinity ranged from 600 to 7600  $\mu$ mol L<sup>-1</sup> with an average 2871±1381  $\mu$ mol L<sup>-1</sup> (Table 1). Alkalinity was higher in the cold months (3378  $\mu$ mol L<sup>-1</sup> in April and 2941  $\mu$ mol L<sup>-1</sup> in October) than in the warm months (2644  $\mu$ mol L<sup>-1</sup> in June and 2326  $\mu$ mol L<sup>-1</sup> in August). Alkalinity of the river water in glaciers covered area showed consistently the lowest level throughout the year (Table 1), due to the low coverage of carbonate rocks.

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DO values ranged from 2.7 mg L<sup>-1</sup> to 12.1 mg L<sup>-1</sup> and the basin-wide mean DO was 7.8±0.6 mg L<sup>-1</sup> in April, 7.1±1.4 mg L<sup>-1</sup> in June, 6.7±0.7 mg L<sup>-1</sup> in August and 7.7±0.7 mg L<sup>-1</sup> in October, respectively (Table 1). For the land cover types, the highest level of DO were in the glacier, with the annual average of 7.6±0.8 mg L<sup>-1</sup>, followed by the permafrost with 7.4±1.4 mg L<sup>-1</sup>, the grassland with 7.3±0.9 mg L<sup>-1</sup>, and peatland with 7.2±1.1 mg L<sup>-1</sup>, respectively (Table 1).

DOC ranged from 0.2 to 12.2 mg L<sup>-1</sup> with an average of  $4.7\pm2.7$  mg L<sup>-1</sup> (Table 1). DOC exhibited strong seasonality across the rivers. The highest DOC concentration occurred in April ( $5.0\pm1.6$  mg L<sup>-1</sup>), followed by in August ( $4.9\pm3.6$  mg L<sup>-1</sup>) and June ( $4.7\pm2.9$  mg L<sup>-1</sup>), and the lowest was found in October

240 (4.0 $\pm$ 2.2 mg L<sup>-1</sup>). For the land cover types, the highest level of DOC was in the peatland covered area, with the annual average of 5.1 $\pm$ 3.7 mg L<sup>-1</sup>, followed by the permafrost with 4.9 $\pm$ 2.4mg L<sup>-1</sup>, the grassland with 4.6 $\pm$ 2.3mg L<sup>-1</sup>, and the glaciers with 3.4 $\pm$ 1.1mg L<sup>-1</sup>, respectively (Table 1).

We used the measured flow velocity and channel slope to predict the  $k_{600}$  based on the Model 5 presented





- by Raymond et al. (2012). The computed  $k_{600}$  showed strong statistically significant but weak agreement with the model results (Figure 2a). Given the chamber's dampening effect of wind (Matthews et al., 2003), there was not any statistically significant relationship between wind and  $k_{600}$  for streams. Instead, flow velocity is a relatively good predictor variable of  $k_{600}$  and can approximately explain 15% of its variability (Figure 2b). Although we deployed the floating chamber very carefully, but the whole
- 250 statistical analysis could not reflect the multi interaction of variety environment factors beyond different land cover types through our 36 sampling sites. Additionally, in some sampling points, the Model 5 overestimated some  $k_{600}$  values especially in some mountainous rivers, mainly due to the water temperature played a crucial role in limiting CO<sub>2</sub> transfer between the air-water interface in the plateau region although the higher channel slope supported enough condition for water turbulence (Battin et al., 2008).

#### 3.2 Spatial and temporal variations of pCO<sub>2</sub>

The pCO<sub>2</sub> ranged from 181 to 2441 μatm with an average of 774±377 μatm, nearly twofold the ambient air pCO<sub>2</sub>. To better illustrate the spatial variability pCO<sub>2</sub>, Figure 3a, 4a, and 3c showed its changes with
land cover types. The highest average pCO<sub>2</sub> value appeared in the peatland covered area (937±466 µatm), followed by grassland (818±394µatm), glacier (645±253 µatm), and the permafrost (600±212 µatm).

The  $pCO_2$  value showed different temporal variation characteristics for the four land cover types (Figure 3a, 4a, and 4c). In grassland covered area, the average river  $pCO_2$  value in April, June, August, and

265 October was  $836\pm258$  µatm,  $609\pm297$  µatm,  $1086\pm551$  µatm, and  $734\pm253$  µatm, respectively. In peatland covered area, the average river  $pCO_2$  value of April, June, August and October was  $875\pm436$  µatm,  $792\pm436$ µatm,  $1156\pm630$  µatm and  $926\pm285$  µatm, respectively. The water  $pCO_2$  in these two land





cover types showed the same temporal variation pattern, with the highest pCO<sub>2</sub> occurred in August and the lowest in June for all the land cover types.

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Unlike in the peatland and grassland regions, the riverine  $pCO_2$  in the glacier and permafrost regions showed relatively small variations, but still had the similar seasonal variation trends. In the glacier covered area, the average river  $pCO_2$  value of April, June, August and October was  $635\pm122 \mu$ atm,  $506\pm31 \mu$ atm,  $738\pm449 \mu$ atm, and  $632\pm132 \mu$ atm respectively. In the permafrost covered area, the average river  $pCO_2$  value of April, June, August, and October was  $465\pm216 \mu$ atm,  $586\pm227 \mu$ atm,  $591\pm74 \mu$ atm, and  $756\pm231 \mu$ atm, respectively.

#### 3.3 Spatial and temporal variations of FCO2

CO<sub>2</sub> emissions exhibited significant spatial and seasonal variations among the 36 stream sites (Table 1,

Figure 3b, 4b, and 4d). The CO<sub>2</sub> effluxes ranged from -221 to 1469 g C m<sup>-2</sup> yr<sup>-1</sup> in April, -144 to 6892 g C m<sup>-2</sup> yr<sup>-1</sup> in August, and -34 to 2321 g C m<sup>-2</sup> yr<sup>-1</sup> in October. While the highest FCO<sub>2</sub> was measured at the wetland covered sites (Site Pt 3 in August, 6892 g C m<sup>-2</sup> yr<sup>-1</sup>), the lowest FCO<sub>2</sub> was observed at permafrost covered sites (Site Pm 3 in April, -221 g C m<sup>-2</sup> yr<sup>-1</sup>) (Table 1). The averaged FCO<sub>2</sub> of all sites was 479±436, 261±205, 873±1220, and 714±633 g C m<sup>-2</sup> yr<sup>-1</sup> in April, June, August, and October, respectively. Clearly, rivers in the Yellow River source region were net carbon sources for the atmosphere, despite the great FCO<sub>2</sub> variations over space and time. Grouped by land cover types, the mean CO<sub>2</sub> efflux shows a significant decreasing trend from wetland (767±1644 g C m<sup>-2</sup> yr<sup>-1</sup>). Because the intensity of FCO<sub>2</sub> depends on pCO<sub>2</sub> in stream water, the FCO<sub>2</sub> showed a similar spatial and temporal pattern to the

 $pCO_2$ , although the highest and lowest  $pCO_2$  and  $FCO_2$  value were not found at the same sampling sites.





# 4. Discussion

#### 4.1 Impact of land cover types on riverine pCO<sub>2</sub> and CO<sub>2</sub> outgassing

Among all land cover types, the lowest FCO<sub>2</sub> appeared in the permafrost covered region, with the annual

- 295 average  $FCO_2$  of  $302\pm349$  g C m<sup>-2</sup> yr<sup>-1</sup>. It is well known that the riverine CO<sub>2</sub> is derived from land (Dinsmore and Billett., 2013; Hope et al., 2004), and the area covered by permafrost has a high density of organic carbon in soil (Zeng et al., 2004), these soil organic carbons can support large quantities of DOC to the rivers and cause enormous riverine CO<sub>2</sub> outgassing. The correlation analysis between various hydro-chemical parameters and  $pCO_2$  in the permafrost region showed that alkalinity, DO were not highly
- 300 correlated with  $pCO_2$  and pH, DOC indeed had a close relation with  $pCO_2$  (Figure 5). The negative relationship between  $pCO_2$  and pH is explained as dissolved  $CO_2$  acts as an acid in water (Stumm and Morgan., 1996), and in poorly buffered systems,  $CO_2$  can be a strong control on the stream pH (Neal et al., 1998; Waldron et al., 2007). This positive correlation between DOC and  $pCO_2$  suggests the terrestrial related DOC might support partial riverine  $CO_2$  concentration (Liu et al., 2016). This indicates that DOC
- 305 is one of the important sources of permafrost river CO<sub>2</sub>. The DOC concentration in the rivers in the permafrost covered area is relatively high, averaging at  $5.0\pm2.4$  mg L<sup>-1</sup>, which exceeded  $3.6\pm1.1$  mg L<sup>-1</sup> in glacier areas and  $4.6\pm2.3$  mg L<sup>-1</sup> in grasslands, but was close to  $5.1\pm3.7$  mg L<sup>-1</sup> in peatlands, and sometimes even exceeded the DOC concentration of rivers in the peatland covered region. Additionally, the average alkalinity concentration in that region is the highest among four types. However, the *p*CO<sub>2</sub>
- and FCO<sub>2</sub> value in this region were always the lowest during the four campaigns. This was due to the area covered by permafrost usually with the highest elevation and the lowest average temperature among the four types of land cover with the average water temperature around 9.99 °C. These conditions limited the soil respiration and riverine organic matter degradation (Battin et al., 2008). Additionally, in terms of





gas diffusion, although there is sufficient dissolved CO<sub>2</sub> in the river water, it is not easy for CO<sub>2</sub> emission
 from rivers to the atmosphere in the condition of low temperature and low flow velocity (average: 0.8±0.5 m s<sup>-1</sup>) (Alin et al., 2014). In summary, the lower temperature is the main cause of high riverine DOC concentrations and low CO<sub>2</sub> outgassing rate in the permafrost covered region.

The glaciers covered region has the similar temperatures and elevations to the permafrost, thus its  $pCO_2$ 

- and  $FCO_2$  values were also lower in the permafrost covered region, with the average value only at  $657\pm240 \text{ gC} \text{ m}^{-2} \text{ yr}^{-1}$ . This is probably because all the sampling sites are located on the 1–2 order streams characterized by strong hydrologic connection with the terrestrial landscape (Sorribas et al., 2017; Smits et al., 2017), and the surrounded environment lack of exogenous terrestrial carbon support. For the glacier area, only DOC was related to  $pCO_2$  (Figure 6d, r<sup>2</sup>=0.56, p < 0.001). The sampling points under the
- 325 glaciers are mainly located around the Aemye Ma-chhen Range. Some glacial sampling sites all have some ice and snow melting water supply. The glacial-covered river water has the lowest DOC concentration with a lowest value of four land cover types (3.6±1.1 mg L<sup>-1</sup>). The area around the Aemye Ma-chhen Range without enough vegetation coverage because of the harsh environment of high elevation and low annual average water temperature, limiting the DOC source. Poor soil, short water retention, and
- 330 low precipitation are the main reason of the low vegetation coverage in this region (Lu et al., 2001). The river near the sampling sites of the snow mountain has been cut deep into the B horizon of soils as a result of glacial erosion and retreat. Almost all glacial sampling sites are covered with gravel, limiting the supply of terrestrial organic carbon to river carbon pools. As a result, the measured DOC concentrations in most glacial areas were very low. In glacial rivers, if there is no external supply of DOC, the whole water DOC contribution only amounted to 0.34 µmol L<sup>-1</sup> CO<sub>2</sub> gain. This highlight that the CO<sub>2</sub>
- produced by DOC degradation in the glacial river cannot maintain such a high CO<sub>2</sub> outgassing rate.





Although there is low content of carbon in ice and snow of that region (Wu et al., 2008), the meltwater of ice and snow continues to erode the surrounding bedrock during long-distance transport, resulting in more limestone in the rivers. Previous studies have shown that glaciers contain large amounts of CO<sub>2</sub>

(Meese et al., 1997) and DOC (Hood et al., 2009; Singer et al., 2012), which are important sources of  $CO_2$  in glacier rivers. Our observations found that with the increasing distance from the Aemye Machhen Range, the riverine  $pCO_2$  exhibited a decrease trend, which could be explained by the dilution effect of water snow-melting water  $pCO_2$ . Therefore, the  $CO_2$  in the region is highly likely to be explained by the  $CO_2$  storage from glacier. As the glaciers melt,  $CO_2$  in the glaciers was brought into the river.

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The river FCO<sub>2</sub> is the highest in the peatland coverage area among the 4 studied types. The relation showed that only pH has a negative linear relationship and alkalinity have a weak linear relationship with the pCO<sub>2</sub> (Figure 7). In the peatland rivers, the terrestrial-related organic carbon is an important source of riverine CO<sub>2</sub> (Abril et al., 2014; Müller et al., 2015; Billett et al., 2015, Huet al., 2015). There are many sources of DOC in the peatland. First, the soil in the wetland ecosystem is rich in peat soil. The amount of peat stock in Zoige Peatland is estimated to be 1.9 billion tons, which accounts for about 40% of China's marsh wetland carbon storage (Wang et al., 2012). These carbon supplies to river carbon pools are an important driver for the high FCO<sub>2</sub> in the wetlands rivers. On the other hand, soil pore water enriched with high concentrations of dissolved CO<sub>2</sub> continues to enter river waters, and it also provides

355 sufficient carbon sources for rivers (Butman et al., 2011). In addition, the vegetation in the peatland region can also import large amounts of CO<sub>2</sub> into the river water through two other mechanisms. First, vegetation litter and root exudates release unstable organic carbon into the water. These organic carbons are being further decomposed and served as a carbon source for heterotrophic microorganisms. During this process, heterotrophic organisms release CO<sub>2</sub> into water (Abril et al., 2014). On the other hand, the





360 respiration of plant roots and soil microorganisms that are submerged in wetland soils releases CO<sub>2</sub> directly into the water (Abril et al., 2014). The combined effects of these factors have resulted in rivers with high DOC and high FCO<sub>2</sub>value in wetlands.

The average FCO<sub>2</sub> in the grassland-covered rivers of 818±394 g C m<sup>-2</sup> yr<sup>-1</sup> is at a moderate level, below

- 365 the wetland  $FCO_2$  but significantly higher than the riverine  $FCO_2$  in the glaciers and permafrost covered regions. Correlation analysis between water chemistry parameters and riverine  $pCO_2$  in this area showed that both pH and DOC had weak correlation with  $pCO_2$  (Figure 8). This also shows that the pH of river water in the area is partial affected by the CO<sub>2</sub> concentration in water. Due to the temperate environment, grassland is the most human-affected area in the study area, mainly in the form of grazing. As a result,
- 370 beside the DOC derived from the physical erosion, the pollutants produced by grazing are also important sources of riverine DOC. The average  $pCO_2$  in peatland is 15% higher, but the average DOC concentration in wetlands is 11% higher than that in grassland, and the alkalinity in grassland is 46% higher than that in wetlands. Therefore, DIC is an important source of riverine CO<sub>2</sub> in grasslands. While stream DIC source are highly variable across space and time (Smits et al., 2017), the DIC mainly
- originated from groundwater (Marx et al., 2017). Although groundwater is participated in the carbon cycle of the river in the entire study area, it is higher in the grassland than in other regions, indicating that the supplemental effect of groundwater on the river CO<sub>2</sub> in the grassland is the biggest. We also take three groundwater samples in grassland covered area. The average *p*CO<sub>2</sub> of groundwater samples in grassland-covered areas is 1976 µatm, which is 2.5 times the average value of the water in the Yellow
  River source region. Therefore, in the grass-covered areas, the CO<sub>2</sub> excess in the rivers is maintained by
  - both the terrestrial vegetation organic carbon and the inorganic carbon in the groundwater.





#### 4.2 Significance and implications for riverine carbon budgets

The annual average pCO2 is 771±380 µatm and FCO2 is 590±766 gC m<sup>-2</sup> yr<sup>-1</sup> in the Yellow River source 385 region. In the whole Yellow basin, Ran et al. (2015a, b) estimated the a significantly lower pCO<sub>2</sub> value of 241±79 µatm and the areal CO<sub>2</sub> efflux of this region is -221±112 g C m<sup>2</sup> yr<sup>-1</sup>, indicative of a strong carbon uptake from the atmosphere. Combining the water surface area of wet season (122 days and the area of 770 km<sup>2</sup>) and dry season (243 days and the area of 560 km<sup>2</sup>), we estimated total CO<sub>2</sub> efflux from the Yellow River source region at about 0.37±0.49 Tg C yr<sup>-1</sup>, suggesting a net carbon source for the 390 atmosphere. This efflux contrasts with the earlier estimate by Ran et al. (2015b) which reported a carbon

sink of -0.168±0.084 Tg C yr<sup>-1</sup>.

Unlike our systematic sampling within the Yellow River source region, Ran et al. (2015b) estimated the riverine CO2 outgassing of the Yellow River source region by only using sampling results at five sampling

- 395 sites. There are a number of reasons for the huge CO<sub>2</sub> efflux difference. Firstly, the sampling by Ran et al. (2015b) was confined to the mainstream channel of the Yellow River and its major tributaries, which may have underestimated riverine CO<sub>2</sub> emissions in lower-order streams. For example, our study on the rivers of the Zoige peatland indicated that the higher FCO2 was observed at the lower-order headstream tributaries (i.e.,  $767\pm1144$  g C m<sup>-2</sup> yr<sup>-1</sup>) instead of the mainstream (i.e.,  $351\pm306$  g C m<sup>-2</sup> yr<sup>-1</sup>). This is
- 400 because the soil carbon-rich peatland around the rivers can be rapidly transported into the river network by strong physical erosion. However, with increasing flow discharge and enhanced erosion, the river channels are heavily cut into the bedrock, mobilization the subsurface soils with less soil carbon content has likely caused the dilution effect of  $pCO_2$  in the mainstream (Crawford et al., 2013). Another reason is that the number of sampling points limited the accuracy of CO2 emissions of relatively large watershed, especially in the alpine area and intermitted rivers. This is due to the fact that in the rivers of the source





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sampling points.

area, the high-concentration dissolved CO<sub>2</sub> groundwater is an important source of river CO<sub>2</sub>, two groundwater samples collected in the grassland covered area showed an average pCO<sub>2</sub> of 1976 µatm, 2.5 times larger than that in the river (771±380 µatm). The CO<sub>2</sub> which originates from groundwater can be quickly released to the atmosphere within a short distance (Hotchkiss et al., 2015). In the case of point deployment, this process is difficult to monitor without the high-density sampling points arrange. Therefore, it is easy to neglect this part of CO<sub>2</sub> by representing the entire basin with relatively few

The area of the Yellow River source region account for about 17.6% of the whole Yellow River basin and
support around 4% of the total CO<sub>2</sub> efflux. Although it is still a small proportion of CO<sub>2</sub> emissions compared with the whole Yellow River Basin, but there is a huge carbon emissions potential. Since the permafrost in the source region of the Yellow River is rich in large amounts of ice and organic carbon, the continuously increasing temperature due to global warming will accelerate not only the mobilization of organic carbon in permafrost, but also the degradation of organic carbon by soil microorganisms. As
a consequence, huge amounts of CO<sub>2</sub> release from soils is anticipated and relevant studies will be needed to comprehensively understand the implications of changes in riverine carbon fluxes.

Although we have made some improvements to evaluate the riverine CO<sub>2</sub> emission in the Yellow River source region, we have more accurately estimated the FCO<sub>2</sub> by in situ measurement and discussed the
riverine CO<sub>2</sub> outgassing within four land cover types, but there are still many uncertainties in our research. Firstly, despite the slight increase in sampling sites compare with the previous studies, there was less extensive research on single watersheds that are spatially representative. And in terms of time, there was a lack of continuous sampling of long sequences. Existing research suggests that the rainstorms will have





a huge shift on CO<sub>2</sub> emission (Smits et al., 2017) and we lacked the monitoring of CO<sub>2</sub> outgassing during
heavy rain period. These factors caused some uncertainties of the riverine CO<sub>2</sub> evasion research and
high frequency and long-time sequence studies under specific land cover types need to be performed in
the future.

#### 5. Conclusions

Based on four rounds of field direct measurements of CO<sub>2</sub> outgassing within the Yellow River source region, the average pCO<sub>2</sub> in the study area was estimated at 771±380 µatm, and the average FCO<sub>2</sub> was  $590\pm766 \text{ g C m}^{-2} \text{ yr}^{-1}$ . It is lower than other rivers in the world, and at a relatively low level compared to the middle and lower reaches of the Yellow River. The results showed that the rivers in the Yellow River source region were the source of CO<sub>2</sub>. Both the pCO<sub>2</sub> and FCO<sub>2</sub> showed strong spatial and temporal

440 the lowest was observed in June. When grouped into different land cover types. *F*CO<sub>2</sub> in the permafrost regions was the lowest among the four types of land cover. The highest *F*CO<sub>2</sub> Was found in peatland river, followed by grassland and glacier region.

variations. The largest CO2 release from rivers was found in August, followed by October and April, and

In alpine climates, low temperature conditions played a crucial role in limiting biological activity and reducing CO<sub>2</sub> emissions in the region. As a consequence, control both riverine CO<sub>2</sub> source and gas transfer velocity. The DOC has huge influence on all land cover types. In the permafrost region, the large amount soil related DOC could support riverine CO<sub>2</sub> concentration. In the glacier region, the glacial DOC and CO<sub>2</sub> may play an essential role in CO<sub>2</sub> outgassing. In the peatland and grassland region, the plants related DOC is an important source of riverine CO<sub>2</sub>.

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By integrating seasonal changes of water surface area, the  $\rm CO_2$  efflux was estimated at 0.37 $\pm$ 0.49 Tg C





 $yr^{-1}$ , which is significantly different from the earlier estimate by Ran et al. (2015). Very few studies have focused on the dynamics of riverine carbon cycling on the Tibetan Plateau river systems. This study provides insight into the riverine CO<sub>2</sub> outgassing in the Yellow River source region, which will help

455 better understanding of carbon emissions from alpine rivers in the world, in particular these located on the Tibetan Plateau.

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Discussions













Figure 1. Sampling sites of the Yellow River Source Region







Figure 2. (a) The relationship between actual and predicted  $k_{600}$  for streams; (b) Correlation between standardized gas transfer velocity ( $k_{600}$ ) and flow velocity over the 4 campaigns. High  $k_{600}$  values (>70 m d<sup>-1</sup>) were removed from analysis.









Figure 3. Spatial and temporal variations of average  $pCO_2(3a)$  and  $FCO_2(3b)$  within the Yellow River source region.







Figure 4. The box plots of pCO<sub>2</sub> and FCO<sub>2</sub> under four different land cover types within the Yellow River source region, expressed in the order of April, June, August, and October in Figure 4a, 4b. The pCO<sub>2</sub> data expressed in the order of grassland, peatland, glacier, permafrost, and groundwater in figure 4c, The FCO<sub>2</sub> expressed in the order of grassland, peatland, glacier, and groundwater in figure 4d.







Figure 5. The linear relationship of chemical parameters and pCO2 in permafrost covered region. (a) pH, (b) alkalinity,

(c) dissolved oxygen, and (d) dissolved organic carbon.







Figure 6. The linear relationship of chemical parameters and  $pCO_2$  in glacier covered region. (a) pH, (b) alkalinity, (c)

dissolved oxygen, and (d) dissolved organic carbon.







Figure 7. The linear relationship of chemical parameters and pCO<sub>2</sub> in peatland covered region. (a) pH, (b) alkalinity, (c)

dissolved oxygen, and (d) dissolved organic carbon.







Figure 8. The linear relationship of chemical parameters and pCO<sub>2</sub> in grassland covered region. (a) pH, (b) alkalinity, (c)

dissolved oxygen, and (d) dissolved organic carbon.