Biogeosciences Discuss., https://doi.org/10.5194/bg-2018-227
Manuscript under review for journal Biogeosciences
Discussion started: 4 June 2018

Gas transfer velocities of CO_2 in subtropical monsoonal climate streams and small rivers

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Biogeosciences Discuss., https://doi.org/10.5194/bg-2018-227
Manuscript under review for journal Biogeosciences
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Abstract

CO_2 outgassing from rivers is a critical component for evaluating riverine carbon cycle, but it is poorly quantified largely due to limited measurements and modeling of gas transfer velocity (k) in subtropical streams and rivers. We measured CO_2 flux rates, k and partial pressure (pCO_2) in river networks of the Three Gorges Reservoir (TGR) region, a typical area in the upper Yangtze River with monsoonal climate and mountainous terrain. The observed k values (k_{600}=48.4±53.2 cm/h) were showed large variability due to spatial variations in physical controls on surface water turbulence. Our k measurements using chambers were comparable with model derived velocities. Unlike in open waters, k is more pertinent to flow velocity and water depth in the studied small rivers. Our results show that TGR river networks emitted approx. 1.4 Tg CO_2/y using varying approaches such as chambers, measured k and developed k model. This study suggests that incorporating scale-appropriate k measurements into extensive pCO_2 investigation is required to refine basin-wide carbon budgets in the subtropical streams and small rivers. We concluded that simple parameterization of k as a function of morphological characteristics was site specific and hence highly variable. k models should be developed for stream studies to evaluate the contribution of these regions to atmospheric CO_2.

Key words: CO_2 outgassing, riverine C flux, flow velocity, physical controls, Three Gorge Reservoir, Yangtze River

1. Introduction

Rivers serve as a significant contributor of CO_2 to the atmosphere (Cole *et al.*, 2007; Tranvik *et al.*, 2009; Li *et al.*, 2012; Raymond *et al.*, 2013). As a consequence, accurate quantification of riverine CO_2 emissions is a key component to estimate net continental carbon (C) flux (Bastviken *et al.*, 2011). More detailed observational data and new accurate measurement techniques are critical to refine the riverine C budgets (Raymond and Cole, 2001; Li and Bush, 2015). Generally two methods are used to estimate CO_2 areal fluxes from the river system, such as direct measurements floating chambers (FCs), and indirect calculation of thin boundary layer (TBL) model that depends on gas concentration at air-water gradient and gas transfer velocity, k (Guerin *et al.*, 2007; Xiao *et al.*, 2014). Direct measurements are normally laborious, while the latter method shows ease and simplicity and thus is preferred (Butman and Raymond, 2011; Li *et al.*, 2012; Li *et al.*, 2013; Lauerwald *et al.*, 2015; Ran *et al.*, 2015).

The areal flux of CO_2 (F, unit in mmol/m^2/d) *via* the water–air interface by TBL is described as follows:

$$F = k \times K_h \times \triangle pCO_2 \qquad (1)$$

$$K_h = 10^{-(1.11 + 0.016 * T - 0.00007 * T^2)} \qquad (2)$$

where k (unit in m/d) is the gas transfer velocity of CO_2 (also referred to as piston velocity) at the *in situ* temperature (Li *et al.*, 2016). $\triangle pCO_2$ (unit in μatm) is the air-water gradient of pCO_2 (Borges *et al.*, 2004a). K_h (mmol/m^3/μatm) is the aqueous-phase solubility coefficient of CO_2 corrected using temperature (T in ℃) (Li *et al.*, 2016).

△pCO_2 can be measured precisely in various aquatic systems, however, the accuracy of the estimation of flux is depended on the k value. Broad ranges of k for CO_2 (Raymond and Cole, 2001; Borges *et al.*, 2004a; Raymond *et al.*, 2012) were reported due to variations in techniques, tracers used and governing processes. k is controlled by turbulence at the surface aqueous boundary layer, hence, k_{600} is parameterized as a function of wind speed in open water systems of reservoirs, lakes, and oceans (Borges *et al.*, 2004b; Guerin *et al.*, 2007; Wanninkhof *et al.*, 2009). While in streams and small rivers, turbulence at the water-air interface is generated by shear stresses at streambed, thus k is modeled using channel slope, water depth, and water velocity in particular (Alin *et al.*, 2011; Raymond *et al.*, 2012). Variable formulations of k have been established by numerous theoretical, laboratory and field studies, nonetheless, better constraint on k levels is still required as its levels are very significant and specific due to large heterogeneity in hydrodynamics and physical characteristics of river networks. This highlights the importance of k measurements in a wide range of environments for the accurate upscaling of CO_2 evasion, and for parameterizing the physical controls on k_{600}. However, only few studies provide information of k for riverine CO_2 flux in Asia (Alin *et al.*, 2011; Ran *et al.*, 2015), and those studies do not address the variability of k in China's small rivers and streams.

Limited studies demonstrated that higher levels of k in the Chinese large rivers (Alin *et al.*, 2011; Ran *et al.*, 2015; Liu *et al.*, 2017; Ran *et al.*, 2017), which contributed to much higher CO_2 areal flux particularly in China's monsoonal rivers that are impacted by concentrated seasonal precipitation. The monsoonal flow pattern and thus flow velocity is expected to be different than other rivers in the world, as a consequence, k levels should be different than others, and potentially is higher in subtropical monsoonal rivers.

Considerable efforts, such as purposeful (Jean-Baptiste and Poisson, 2000; Crusius and Wanninkhof, 2003) and natural tracers (Wanninkhof, 1992) and FCs (Borges *et al.*, 2004b; Guerin *et al.*, 2007; Alin *et al.*, 2011; Prytherch *et al.*, 2017), have been carried out to estimate accurate k values. The direct determination of k by FCs is more popular due to simplicity of the technique for short-term CO_2 flux measurements (Raymond and Cole, 2001; Xiao *et al.*, 2014; Prytherch *et al.*, 2017). Prior reports, however, have demonstrated that k values and the parameterization of k as a function of wind and/or flow velocity (probably water depth) vary widely across rivers and streams (Raymond and Cole, 2001; Raymond *et al.*, 2012). To contribute to this debate, extensive investigation was accomplished for determination of k in rivers and streams of the upper Yangtze using FC method. Our new contributions to the literature are (1) providing first determination of k levels for small rivers and streams in China, and (2) comparisons of two methods for CO_2 areal fluxes by FCs and models developed. The outcome of this study is expected to help in accurate estimation of CO_2 evasion from subtropical rivers and streams, and thus refine riverine C budget over a regional/basin scale.

2. Materials and methods

2.1. Study areas

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All field measurements were carried out in the rivers and streams of the Three Gorges Reservoir (TGR) region (28°44′–31°40′N, 106°10′–111°10′E) that is locating in the upper Yangtze River, China (Fig. S1). This region is subject to humid subtropical monsoon climate with an average annual temperature ranging between15 and 19 ℃. Average annual precipitation is approx. 1250 mm with large intra- and inter-annual variability. About 75% of the annual total rainfall is concentrated in April through September.

The river sub-catchments include large scale river networks covering the majority of the tributaries of the Yangtze in the TGR region, i.e., 32 first-order tributaries and 16 second-order tributaries. These tributaries have drainage areas that vary widely from 100 to 4400 km^2 with width ranging from 1 m to less than 100 m. The annual discharges from these tributaries have a broad spectrum of 1.8 – 112 m^3/s. Detailed samplings were conducted in the two largest rivers of Daning (35 sampling sites) and Qijiang (32 sites) in the TGR region. These two river basins drain catchment areas of 4200 and 4400 km^2 with maximal third-order tributaries. The location of sampling sites is deciphered in Fig. S1. The detailed information on sampling sites and primary data are presented in the Supplement Materials (Appendix Table A1). The sampling sites are outside the Reservoirs and are not affected by dam operation.

2.2. Water sampling and analyses

Three fieldwork campaigns from the main river networks in the TGR region were undertaken during May through August in 2016 (i.e., 18-22 May for Daning, 21 June-2 July for the entire tributaries of TGR, and 15-18 August for Qijiang). A total of 115 discrete grab samples were collected (each sample consists of three replicates). Running waters were taken using pre acid-washed 5-L high density polyethylene (HDPE) plastic containers from depths of 10 cm below surface. The samples were filtered through pre-baked Whatman GF/F (0.7-μm pore size) filters on the sampling day and immediately stored in acid-washed HDPE bottles. The bottles were transported in ice box to the laboratory and stored at 4 ℃ for analysis. Concentrations of dissolved organic carbon (DOC), dissolved total nitrogen (DTN), and dissolved total phosphorus (DTP) were determined within 7 days of water collection (Mao *et al.*, 2017).

Water temperature (T), *p*H, DO saturation (DO%) and electrical conductivity (EC) were measured *in situ* by the calibrated multi-parameter sondes (HQ40d HACH, USA, and YSI 6600, YSI incorporated, USA). pH, the key parameter for pCO_2 calculation, was measured to a precision of ±0.002, and pH sonde is calibrated by the certified reference materials (CRMs) before measurements with an accuracy is better than 0.2%. Atmospheric CO_2 concentrations were determined *in situ* using PP Systems EGM-4 (USA). Total alkalinity was measured using a fixed endpoint titration method with 0.0200 mol/L hydrochloric acid (HCl) on the sampling day. DOC concentration was measured using a total organic carbon analyzer (TOC-5000, Shimadzu, Japan) with a precision better than 3% (Mao *et al.*, 2017). DTN and DTP

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concentrations were determined using a continuous-flow autoanalyzer (AA3, Seal Analytical, Germany) and/or spectrophotometer following peroxodisulfate oxidation (Ebina *et al.*, 1983). Analytical reagent grade chemical were used for all experiments.

Wind speed at 1 m over the water surface (U_1) and air temperature (Ta) were measured with a Testo 410-1 handheld anemometer (Germany). Wind speed at 10 m height (U_{10}, unit in m/s) was calculated using the following formula (Crusius and Wanninkhof, 2003):

$$U_{10} = U_Z\left[1+\frac{(C_{d10})^{1/2}}{K}\times\ln\left(\frac{10}{z}\right)\right] \qquad (3)$$

where C_{d10} is the drag coefficient at 10 m height (0.0013 m/s), and K is the von Karman constant (0.41), and z is the height (m) of wind speed measurement. The relationship was yielded when z=1 (U_{10}=1.208×U_1).

Aqueous pCO_2 was computed from the measurements of pH, total alkalinity, and water temperature using CO_2 system (k_1 and k_2 are from Millero, 1979), which have been identified as high quality data (Borges *et al.*, 2004a; Li *et al.*, 2012; Li *et al.*, 2013).

2.3. Water-to-air CO_2 fluxes using FC method

FCs (30 cm in diameter, 30 cm in height) were deployed to measure air-water CO_2 fluxes and transfer velocities. They were made of cylindrical polyvinyl chloride (PVC) pipe with a volume of 21.20 L and a surface area of 0.071 m^2. These non-transparent, thermally insulated vertical tubes, covered by aluminum foil, were connected *via* CO_2 impermeable tubing (with outer and inner diameters of 0.5 cm and 0.35 cm, respectively) to a portable non-dispersive infrared CO_2 analyzer EGM-4 (PPSystems). Air was circulated through the EGM-4 instrument *via* an air filter using an integral DC pump at a flow rate of 350 ml/min. The chamber method was widely used and more details of advantages and limits on chambers were reviewed elsewhere (Borges *et al.*, 2004b; Alin *et al.*, 2011; Xiao *et al.*, 2014).

Chamber measurements were conducted by deploying two replicate chambers or one chamber for two times at each site. Data were logged automatically and continuously at 1-min interval over a given span of time (normally 5-10 minutes) after enclosure. The CO_2 area flux ($mg/m^2/h$) was calculated using the following formula.

$$F = 60 \times \frac{dpco2 \times M \times P \times T_0}{dt \times V_0 \times P_0 \times T} H \qquad (4)$$

Where $dpco_2/dt$ is the rate of concentration change in FCs (µl/l/min); M is the molar mass of CO_2 (g/mol); P is the atmosphere pressure of the sampling site (Pa); T is the chamber absolute temperature of the sampling time (K); V_0, P_0, T_0 is the molar volume (22.4 l/mol), P_0 is atmosphere pressure (101325 Pa), and T_0 is absolute temperature (273.15 K) under the standard condition; H is the chamber height above the water surface (m) (Alin *et al.*, 2011). We accepted the flux data that had a good linear regression of flux against time ($R^2 \geq 0.95$, $p<0.01$).

2.4. Calculations of the gas transfer velocity

The k was computed with eq (1). To make comparisons, k is normalized to a Schmidt (Sc) number of 600 (k_{600}) at a temperature of 20 ℃.

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$$k_{600} = k_T\left(\frac{600}{S_{CT}}\right)^{-0.5} \quad (5)$$

$$S_{CT} = 1911.1 - 118.11T + 3.4527T^2 - 0.04132T^3 \quad (5)$$

Where k_T is the measured values at the *in situ* temperature (T, unit in ^{o}C), S_{CT} is the Schmidt number of temperature T. Dependency of k proportional to $Sc^{-0.5}$ was employed here as measurement were made in highly turbulent rivers and streams in this study (Wanninkhof, 1992; Borges *et al.*, 2004b; Alin *et al.*, 2011).

2.5. Data processing

Prior to statistical analysis, we excluded k_{600} data for samples with the air-water pCO_2 gradient <110 µatm, since the error in the k_{600} calculations drastically enhances when $\triangle pCO_2$ approaches zero (Borges *et al.*, 2004b). Spatial differences (Daning, Qijiang and entire tributaries of TGR region) were tested using the nonparametric Mann Whitney U-test. Multivariate statistics, such as correlation and stepwise multiple linear regression, were performed for the models of k_{600} using potential physical parameters, such as wind speed, water depth, and current velocity (Alin *et al.*, 2011). All statistical relationships were significant at $p < 0.05$. The statistical processes were conducted using SigmaPlot 11.0 and SPSS 16.0 for Windows (Li *et al.*, 2009; Li *et al.*, 2016).

3. Results

3.1. CO_2 partial pressure and key water quality variables

The significant spatial variations in water temperature, pH, pCO_2, DOC and

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nutrients (DTN and DTP) were observed among Daning, TGR and Qijiang rivers whereas alkalinity did not display such variability (Fig. S2). *p*H varied from 7.47 to 9.38 (mean of 8.39 ±0.29) and lower *p*H was observed in TGR rivers (8.21 ±0.33) (Table 1; Fig. S2). pCO_2 varied between 50 and 4830 µatm with mean of 846 ±819 µatm (Table 1), suggesting that all three rivers are supersaturated with reference to atmospheric CO_2 and act as a source for the atmospheric CO_2. The pCO_2 levels were 2.1 to 2.6-fold higher in TGR rivers than Daning (483 ±294 µatm) and Qijiang Rivers(614 ±316 µatm) (Fig. S2). The calculated pCO_2 levels were within the published range, but towards the lower-end of published concentrations compiled elsewhere (Cole and Caraco, 2001; Li *et al.*, 2013). The total mean pCO_2 (846 µatm) in the TGR, Danning and Qijiang sampled is lower than one third of global river's average (3220 µatm) (Cole and Caraco, 2001).

The higher concentrations of dissolved organic carbon (DOC) and dissolved nutrients (DTN and DTP) (Fig. S3) were observed in the TGR rivers than Qijang and Danning. Relatively higher concentrations of DOC and DTN were observed in Qijang than Daning River but mean TDP was much higher in latter than former river (Fig. S3; Table 1).

3.2. CO_2 flux using floating chambers

The calculated CO_2 areal fluxes were higher in TGR rivers (217.7 ±334.7 mmol/m^2/d, n = 35), followed by Daning (122.0 ±239.4 mmol/m^2/d, n = 28) and Qijiang rivers (50.3 ±177.2 mmol/m^2/d, n = 32) (Fig. 1). The higher CO_2 evasion

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from the TGR rivers is consistent with high riverine pCO_2 levels. The mean CO_2 emission rate was 133.1 ± 269.1 mmol/m^2/d (n = 95) in all three rivers sampled. The mean CO_2 flux differed significantly between TGR rivers and Qijiang (Fig. 1). The ratio of mean to median of CO_2 areal flux ranged between 1.4 (Qijiang) and 2.6 (TGR rivers).

3.3. k levels

Samples with ΔpCO_2 less than 110 μatm were excluded for k_{600} calculations, thus a total of 64 data were used (10 for Daning River, 33 for TGR rivers and 21 for Qijiang River) to develop k model (Table 2). No significant variability in k values were observed among the three rivers sampled (Fig. 2). The mean k (unit in cm/h) is relatively higher in Qijiang (60.2 ± 78.9), followed by Daning (50.2 ± 20.1) and TGR rivers (40.4 ± 37.6), while the median k (unit in cm/h) was higher in Daning (50.5), followed by TGR rivers (30.0) and Qijiang (25.8) (Fig. 2; Table S1). Binned k_{600} data were averaged to 48.4 ± 53.2 cm/h (95% CI: 35.1-61.7), and it is 1.5-fold higher than the median value (32.2 cm/h) (Fig. 2).

4. Discussion

We derived first-time the k values in the subtropical streams and small rivers. Our measured k_{600} levels with a 95% CI of 35.1 to 61.7 (mean: 48.4) cm/h is compared well with a compilation of data for streams and small rivers (e.g., 3-70 cm/h) (Raymond *et al.*, 2012). Our determined k values are greater than the global

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rivers' average (8 - 33 cm/h) (Butman and Raymond, 2011; Raymond *et al.*, 2013), and much higher than mean for tropical and temperate large rivers (5-31 cm/h) (Alin *et al.*, 2011). These studies evidences that k_{600} values are highly variable in streams and small rivers (Alin *et al.*, 2011; Ran *et al.*, 2015). Though the mean k in the TGR, Daning and Qijiang is higher than global mean, however, it is consistent with k values in the main stream and river networks of the turbulent Yellow River (42 ± 17 cm/h) (Ran *et al.*, 2015), and Yangtze (38 ± 40 cm/h) (Liu *et al.*, 2017).

It has been well established that k is governed by a multitude of physical factors particularly current velocity, wind speed, stream slope and water depth, of which, wind speed is the dominant factor of k in open waters such as large rivers and estuaries (Raymond and Cole, 2001; Crusius and Wanninkhof, 2003; Borges *et al.*, 2004b; Alin *et al.*, 2011). In contrast k in small rivers and streams is closely linked to flow velocity, water depth and channel slope (Alin *et al.*, 2011; Raymond *et al.*, 2012). Several studies reported that the combined contribution of flow velocity and wind speed to k is significant in the large rivers (Beaulieu *et al.*, 2012; Ran *et al.*, 2015). Thus, k values are higher in the Yellow River (ca. 0-120 cm/h) as compared to the low-gradient River Mekong (0-60 cm/h) (Alin *et al.*, 2011; Ran *et al.*, 2015), due to higher wind speed and flow velocity in the Yellow River (1.8 m/s) than Mekong river (0.9±0.4 m/s), resulting in greater surface turbulence and higher k level in the Yellow (42 ± 17 cm/h) than Mekong river (15 ± 9 cm/h). The higher k values in the TGR, Daning and Qjiang rivers are due to mountainous terrain catchment, high current velocity (10 – 150 cm/s) (Fig. 3b), bottom roughness, and shallow water depth (10 -

150 cm) (Fig. 3a). It has been suggested that shallow water enhances bottom shear, and the resultant turbulence increases k values (Alin *et al.*, 2011; Raymond *et al.*, 2012). These physical controls are highly variable across environmental types (Figs. 3a and 3b), hence, k values are expected to vary widely (Fig. 2). The k values in the TGR rivers showed wider range (1-177 cm/h; Fig. 2; Table S1), spanning more than 2 orders of magnitude across the region, and it is consistent with the considerable variability in the physical processes on water turbulence across environmental settings. Similar broad range of k_{600} levels was also observed in the China's Yellow basin (ca. 0-123 cm/h) (Ran *et al.*, 2015; Ran *et al.*, 2017).

Contrary to our expectations, no significant relationship was observed between k_{600} and water depth, and current velocity using the entire data in the TGR, Danning and Qjiang rivers (Fig. S5). There were not statistically significant relationships between k and wind speed and it is consistent with earlier studies (Alin *et al.*, 2011; Raymond *et al.*, 2012). Flow velocity showed linear relation with k, and the extremely high value of k was observed during the periods of higher flow velocity (Fig. S5a). Similar trend was also observed between water depth and k values (Fig. S5b). The lack of strong correlation between k and physical factors are probably due to combined effect of both flow velocity and water depth, as well as large diversity of channel morphology, both across and within river networks in the entire catchment (60, 000 km^2). This is further collaborated by weak correlations between k and flow velocity in TGR rivers (Fig. 3), where one or two samples were taken for a large scale examination. k_{600} as a function of water depth was obtained in TGR rivers, but it

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explained only 30% of the variance in k_{600}. However, model using data from Qijiang could explain 68% of the variance in k_{600} (Fig. 3b), and it was in line with general theory. Nonetheless, k from our flow velocity based model (Fig. 3b) is largely overestimated with consideration of other measurements (Alin *et al.*, 2015; Ran *et al.*, 2015; Ran *et al.*, 2017). When several extremely values are removed, k_{600} (cm/h) is parameterized as follows (k_{600} = 62.879FV + 6.8357, R^2= 0.52, p=0.019, FV-flow velocity with a unit of m/s), and this revised model is in good agreement with the model in the river networks of the Yellow River (Ran *et al.*, 2017), but much lower than the model developed in the Yangtze system (Liu *et al.*, 2017) (Fig. 3c). This is reasonable because of k values in the Yangtze system are from large rivers with higher turbulence than Yellow and our studied rivers. Furthermore, the measured k using FCs was, on average, consistent with the revised model (Table 2).

The subtropical streams and small rivers are biologically more active and are recognized to exert higher CO_2 areal flux to the atmosphere, however, their contribution to riverine carbon cycling is still poorly quantified because of data paucity and the absence of k in particular. Larger uncertainty of riverine CO_2 emission in China was anticipated by use of k_{600} from other continents or climate zones. For instance, k_{600} for CO_2 emission from tributaries in the Yellow River and karst rivers was originated from the model in the Mekong (Zhang *et al.*, 2017), and Pearl (Yao *et al.*, 2007), Longchuan (Li *et al.*, 2012), and Metropolitan rivers (Wang *et al.*, 2017), which are mostly from temperate regions. Our k values will therefore largely improve the estimation of CO_2 evasion from subtropical streams and small rivers, and improve to refine riverine carbon budget. More studies, however, are clearly needed to build the model, based on flow velocity and slope/water depth given the difficulty in k quantification on a large scale.

We compared CO_2 areal flux by FCs and models developed here (Fig. 3) and other studies (Alin *et al.*, 2011) (Tables 2 and 3). CO_2 evasion was estimated for rivers in China with k values ranged between 8 and 15 cm/h (Yao *et al.*, 2007; Wang *et al.*, 2011; Li *et al.*, 2012) (Table S2). These estimates of CO_2 evasion rate were considerably lower than using present k values (48.4±53.2 cm/h). For instance, CO_2 emission rates in the Longchuan River (e.g., k=8 cm/h) and Pearl River tributaries (e.g., k=8-15 cm/h) were 3 to 6 times higher using present k values compared to earlier. We found that the determined k average was marginally beyond the levels from water depth based model and the model developed by Alin et al (Alin *et al.*, 2011), while equivalent to the flow velocity based revised model, resulting in similar patterns of CO_2 emission rates (Table 2). Hence selection of k values would significantly hamper the accuracy of the flux estimation. Therefore k must be estimated along with pCO_2 measurements to accurate flux estimations.

We used our measured CO_2 emission rates by FCs for upscaling flux estimates and it was found to be 1.39 TgCO_2/y for all rivers sampled in our study (Table 3a). The estimated emission was close to that of the revised model (1.40 ±1.31 (95% confidence interval: 0.91-1.87) Tg CO_2/y), and using the determined k average, i.e., 1.37 ±1.28 (95% confidence interval: 0.89-1.84) Tg CO_2/y, but slightly higher than the estimation using water-depth based model (1.08 ±1.01 Tg CO_2/y) and Alin's model (1.06 ± 1.00 Tg CO_2/y) (Table 3b). The estimate was within the range of our earlier work using TBL on the TGR river networks (0.64-2.33 Tg CO_2/y) (Li *et al.*, 2018). The higher emission, i.e., 3.29 ± 3.08 (2.15-4.43) Tg CO_2/y, using flow velocity based model may be over-estimated (Table 3b). Therefore, this study suggests that CO_2 emissions from rivers and streams in this area may be underestimated, i.e., 0.03 Tg CO_2/y (Li *et al.*, 2017) and 0.37-0.44 Tg CO_2/y (Yang *et al.*, 2013) as the former used TBL model with a lower k level, and the latter employed floating chambers, but they both sampled very limited tributaries (i.e., 2-3 rivers). Therefore, measurements of k must be made mandatory along with pCO2 measurement in the river and stream studies.

5. Conclusion

We provided first determination of gas transfer velocity (k) in the subtropical streams and small rivers. High variability in k values (mean 48.4 ± 53.2 cm/h) was observed, reflecting the variability of morphological characteristics on water turbulence both within and across river networks. The determined k using floating chambers (FCs) was comparable to our newly water depth based model, while substantially lower than flow velocity based model. We highlighted that k estimate from empirical model should be pursued with caution and the significance of incorporating k measurements along with extensive pCO_2 investigation is highly essential for upscaling to watershed/regional scale carbon (C) budget.

Riverine pCO_2 and CO_2 areal flux showed pronounced spatial variability with much higher levels in the TGR rivers. The CO_2 areal flux was averaged at 133.1 ± 269.1 mmol/m^2/d using FCs, the resulting emission was around 1.39 Tg CO_2/y, similar to the scaling up emission with the determined k, and the revised flow velocity based model, while marginally above the water depth based model. More work is clearly needed to refine the k modeling for evaluating regional C budgets.

Acknowledgements

This study was funded by "the Hundred-Talent Program" of the Chinese Academy of Sciences (R53A362Z10; granted to Dr. Li), and the National Natural Science Foundation of China (Grant No. 31670473). We are grateful to Mrs. Maofei Ni and Tianyang Li, and Miss Jing Zhang for their assistance in the field works. Users can access the original data from an Appendix.

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Table 1. Statistics of all the data from rivers.

		Water T (^{0}C)	pH	Alkalinity (μeq/l)	pCO$_2$ (μatm)	DO%	DOC (mg/L)	TDN (mg/L)	TDP (μg/L)
Number		115	115	115	115	56	114	114	113
Mean		22.5	8.39	2589.1	846.4	91.5	6.67	2.42	65.9
Median		22.8	8.46	2560	588.4	88.8	2.51	1.56	50.7
Std. Deviation		6.3	0.29	640.7	818.5	8.7	7.62	2.38	56.3
Minimum		11.7	7.47	600	50.1	79.9	0.33	0.01	5.0
Maximum		34	9.38	4488	4830.4	115.9	37.48	10.54	298.5
Percentiles	25	16.3	8.24	2240	389.8	84.0	1.33	0.62	25.1
	75	29	8.56	2920	920.4	99.1	9.96	3.61	88.1
95% CI for Mean	Lower Bound	21.4	8.33	2470.8	695.2	89.1	5.26	1.98	55.4
	Upper Bound	23.7	8.44	2707.5	997.6	93.8	8.09	2.86	76.4

CI-Confidence Interval.

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Table 2. Comparison of different model for CO_2 areal flux estimation (unit is mmol/m^2/d for CO_2 areal flux and cm/h for k_{600}).

CO_2 areal flux[a]		From FC	Flow velocity-based model (Fig. 3b)	Water depth-based model (Fig.3a)	Alin's model
k_{600}		48.4[b]	116.5[c]	38.3	37.6
Mean		198.1	476.7	156.6	154.0
S.D.		185.5	446.2	146.6	144.2
95% CI for Mean	Lower Bound	129.5	311.5	102.3	100.6
	Upper Bound	266.8	641.8	210.8	207.4

CI-Confidence Interval
a-CO_2 areal flux is based on TBL model.
b-mean level that is determined using floating chambers (FC).
c-This figure is revised to be 49.6 cm/h if the model (k_{600} = 62.879FV + 6.8357, R^2= 0.52, p=0.019) is used (Fig. 3c), and the corresponding CO_2 areal flux is 203±190 mmol/m^2/d.

Table 3. CO_2 emission from total rivers sampled in the study.

(a) Upscaling using CO_2 areal flux by FC.

	Catchment Area km^2	Water surface km^2	CO_2 areal flux $mmol/m^2/d$	CO_2 emission Tg CO_2/y
Daning	4200	21.42	122.0 ±239.4	0.042
Qijiang	4400	30.8	50.3 ±177.2	0.025
TGR river	50000	377.78	217.7 ±334.7	1.321
Total				1.39

(b) Upscaling using determined k average and models (whole dataset are used here).

		From determined k mean	Flow velocity-based model (Fig. 3b) (numbers in bracket is from the revised model; Fig. 3c)	Water depth-based model (Fig.3a)	Alin's model
Mean		1.37	3.29 (1.40)	1.08	1.06
S.D.		1.28	3.08 (1.31)	1.01	1.00
95% CI for Mean	Lower Bound	0.89	2.15 (0.91)	0.71	0.69
	Upper Bound	1.84	4.43 (1.81)	1.46	1.43

A total water area of approx. 430 km^2 for all tributaries (water area is from Landsat ETM+ in 2015).

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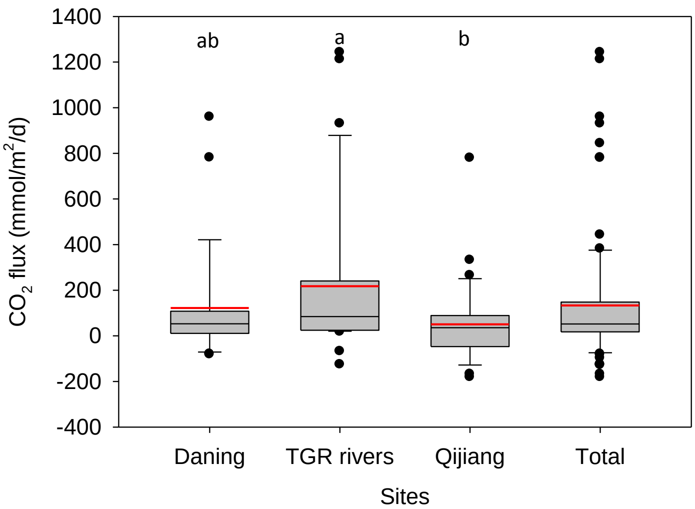

Fig. 1. Boxplots of CO_2 emission rates by floating chambers in the subtropical rivers (different letters represent statistical differences at $p<0.05$ by **Mann-Whitney Rank Sum Test**). (the black and red lines, lower and upper edges, bars and dots in or outside the boxes demonstrate median and mean values, 25th and 75th, 5th and 95th, and <5th and >95th percentiles of all data, respectively). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

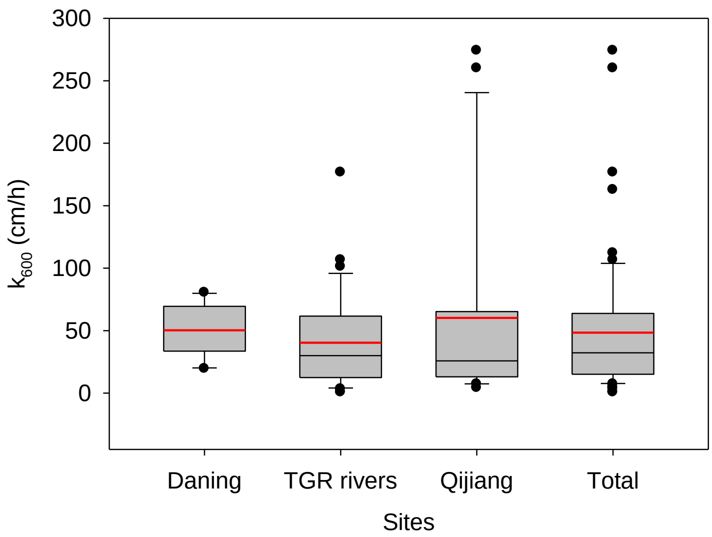

Fig. 2. Boxplots of k_{600} levels in the subtropical rivers (there is not a statistically significant difference in k among sites by Mann-Whitney Rank Sum Test). (the black and red lines, lower and upper edges, bars and dots in or outside the boxes demonstrate median and mean values, 25th and 75th, 5th and 95th, and <5th and >95^{th} percentiles of all data, respectively). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

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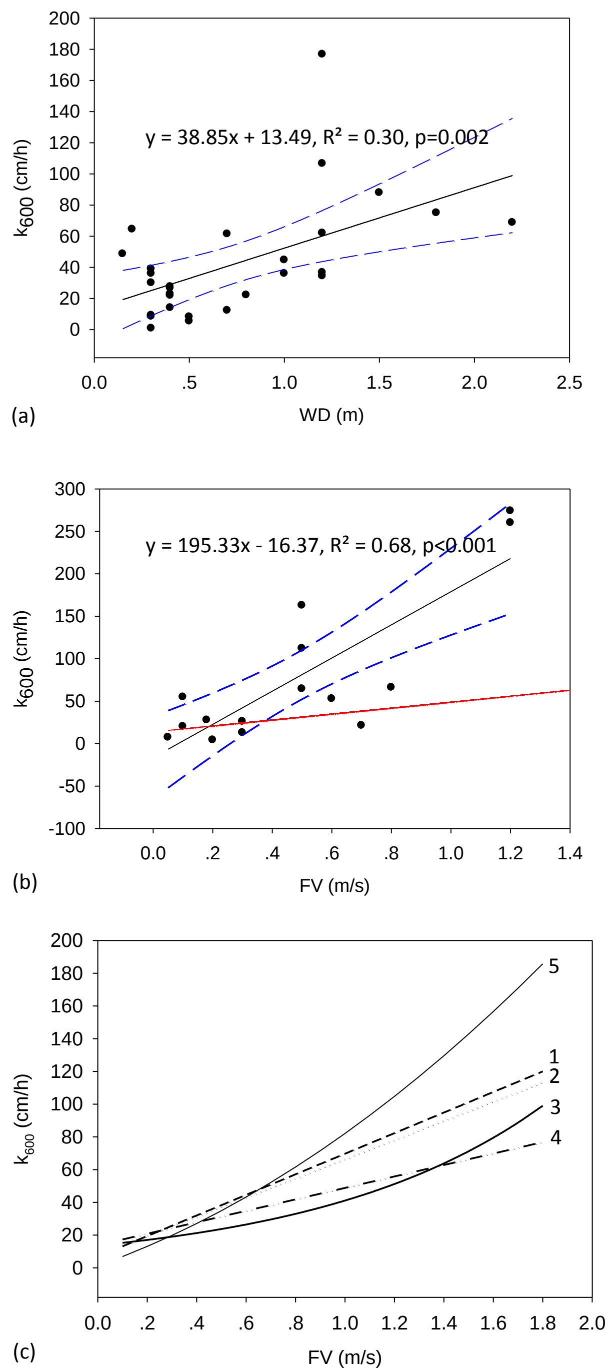

Fig. 3. The k_{600} as a function of water depth (WD) in TGR rivers (a), flow velocity (FV)

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in Qijiang (b), and comparison of the developed model with other models (c) (others without significant relationships between k and physical factors are not shown). The solid lines show regression, the dashed lines represent 95% confidence band, and the red dash-dotted line represents the model developed by Alin et al (2011) (in panel b, if several extremely values are removed, the revised model would be k_{600} = 62.879FV + 6.8357, R^2 = 0.52, p=0.019) (in panel c, 1-the revised model, 2-model from Ran et al., 2017, 3-model from Ran et al., 2015, 4-model from Alin et al,, 2011, 5-model from Liu et al., 2017) (1- k_{600} = 62.879FV + 6.8357; 2- k_{600} = 58.47FV+7.99; 3- k_{600} = 13.677exp (1.1FV); 4- k_{600} = 35 FV + 13.82; 5- k_{600} = 6.5FV^2 + 12.9FV+0.3) (unit of k in models 1-4 is cm/h, and unit of m/d for model 5 is transferred to cm/h).