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Coupled effects of hydrology and temperature on temporal dynamics of dissolved carbon in the Min River, Tibetan Plateau

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ABSTRACT

Studying the temporal dynamics and fluxes of riverine dissolved carbon is crucial in understanding the regional and global carbon cycles under various climatic conditions. Here, we studied the behaviors and fluxes of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) responding to various hydrologic conditions in the Min River, originated from Tibetan Plateau. The DIC concentrations decreased with increasing runoff, partially reflecting dilution effect, which may be ascribed to the shortened fluid transit time and then the reduced contact time with rocks. Nevertheless, DOC concentrations were positively correlated with runoff, which can be attributed to that a large amount of soil organic carbon flowed into the river as a result of the strong flushing effect. The negative relationship between $\delta^{13}C_{DIC}$ and runoff could be explained by soil CO_2 influx and organic matter degradation during the high flow season. ΔDIC (the production of DIC with changing hydrologic conditions) had a strong positive correlation with water temperature due to the accelerated DIC production rates by high temperature, which always co-varied with intense precipitation in Asian monsoonal regions. The mean DIC/DOC ratio in the Min River was 15.09, and the DOC and DIC fluxes were 1.1 and 15.2 t C km^{-2} yr^{-1}, respectively, for the studied year. And the DOC and DIC fluxes varied dramatically with runoff changes, suggesting that hydrologic conditions were critical factors for the variations in dissolved carbon export. This study shows that carbon dynamics of rivers draining from the Tibetan Plateau are greatly affected by short-term climatic variabilities, which has implications for understanding global carbon cycle under future climate change.

1. Introduction

River networks have drawn increasing attention, centered on regional and global carbon budgets (Marx et al., 2017; Schefuß et al., 2016), as the riverine carbon cycle plays a significant role in providing feedbacks on future global climate change (Cox et al., 2000; Doctor et al., 2008). Riverine carbon transportation can be affected by multiple biogeochemical processes, such as organic matter degradation, CO_2 degassing, and sediment deposition in the floodplains and continental shelf (Marwick et al., 2015). These processes have a significant effect on carbon dynamics and budgets, so the budgets of carbon from land to the inland waters are still unclear (Aufdenkampe et al., 2011; Cole et al., 2007; Marwick et al., 2015; Raymond et al., 2013). Dissolved forms of carbon include dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC), both of which have profound influences on aquatic food web processes and ecosystem sustainability (Findlay, 2010; Tank et al., 2010; Tian et al., 2015), and therefore play an important role in the global carbon cycle.

Riverine carbon dynamics are highly shifted by changing hydrologic and temperature conditions (Bengtson and Bengtsson, 2007; Romero-Mujalli et al., 2018; Tian et al., 2015; Zhong et al., 2018, 2020). For example, DIC and DOC concentrations and fluxes are closely related to hydrologic conditions and sensitive to runoff variations (Strohmeier et al., 2013; Zhong et al., 2020). The runoff is projected to increase as a result of increasing rainfall in the next few decades on the Tibetan Plateau (Li et al., 2013; Lutz et al., 2014; Su et al., 2016) as climate extremes are expected to become more frequent and intense due to global warming (Seneviratne et al., 2012). Therefore, studying the

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mechanisms and impacts of short-term climate variabilities on carbon dynamics can improve our understanding about the effects of future global climate change on the carbon budget (Reichstein et al., 2013). Using a coupled hydrological-biogeochemical model, Ren et al. (2015) reported that climate-related changes and rising atmospheric CO_2 would be responsible for more than 90% of the increase in DIC fluxes for the Mississippi River throughout the 21st Century, which is similar to the findings of Tian et al. (2015). Furthermore, Boano et al. (2014) showed that stream pCO_2 dynamics are highly influenced by the hyporheic zone across different climate zones. DOC fluxes were highly controlled by hydrologic conditions, climate patterns and episodic weather events in the South Florida estuaries (Regier et al., 2016). However, the effects of short-term climate variabilities on carbon dynamics and fluxes of Tibetan rivers were still elusive.

The annual global exports of DIC and DOC transported by river systems into the ocean were estimated to be approximately 0.41 Pg (1 Pg = 10^{15} g; Cai, 2011) and 0.17 Pg (Dai et al., 2012), respectively. Accordingly, the total dissolved carbon flux represents about 68% of the total carbon flux (0.85 Pg; Bauer et al., 2013) from rivers to estuaries, making up a significant component of global oceanic carbon budgets. As one of the most climate-sensitive areas in the world, more than 80% of the glaciers have retreated in the Tibetan Plateau, altering the water supply for billions of people and atmospheric circulation (Chen et al., 2013; Qiu, 2008), affecting hydrologic conditions and therefore change the riverine carbon export. Thus, deciphering riverine DIC and DOC dynamics in the Min River would shed a light on the dissolved carbon dynamics of the plateau rivers, although anthropogenic activities in the lower reaches may also affect the riverine carbon. Additionally, Tibetan Plateau plays an important role in global carbon cycles as a result of climate changes (Chen et al., 2013; Peng et al., 2015). And considering the importance of chemical weathering on the Tibetan Plateau for the global cooling in the Cenozoic is still in debate (Raymo and Ruddiman, 1992; Xiao et al., 2015; Wolff-Boenisch et al., 2009), the carbon budgets and dynamics should be re-evaluated in order to better understand the carbon cycles in these riverine systems (Zhang et al., 2013), especially in the Tibetan Plateau rivers.

This study presents a monthly to daily sampling dataset of DIC, DOC concentrations and isotope ratios of DIC ($\delta^{13}C_{DIC}$) in the Min River, originated from Tibetan Plateau. The main objectives of this study are: (1) to investigate temporal carbon dynamics under various hydrologic and temperature conditions; (2) to determine the factors controlling carbon dynamics in the Min River; (3) to evaluate the role of DIC fluxes from Tibetan Plateau rivers on global riverine DIC fluxes.

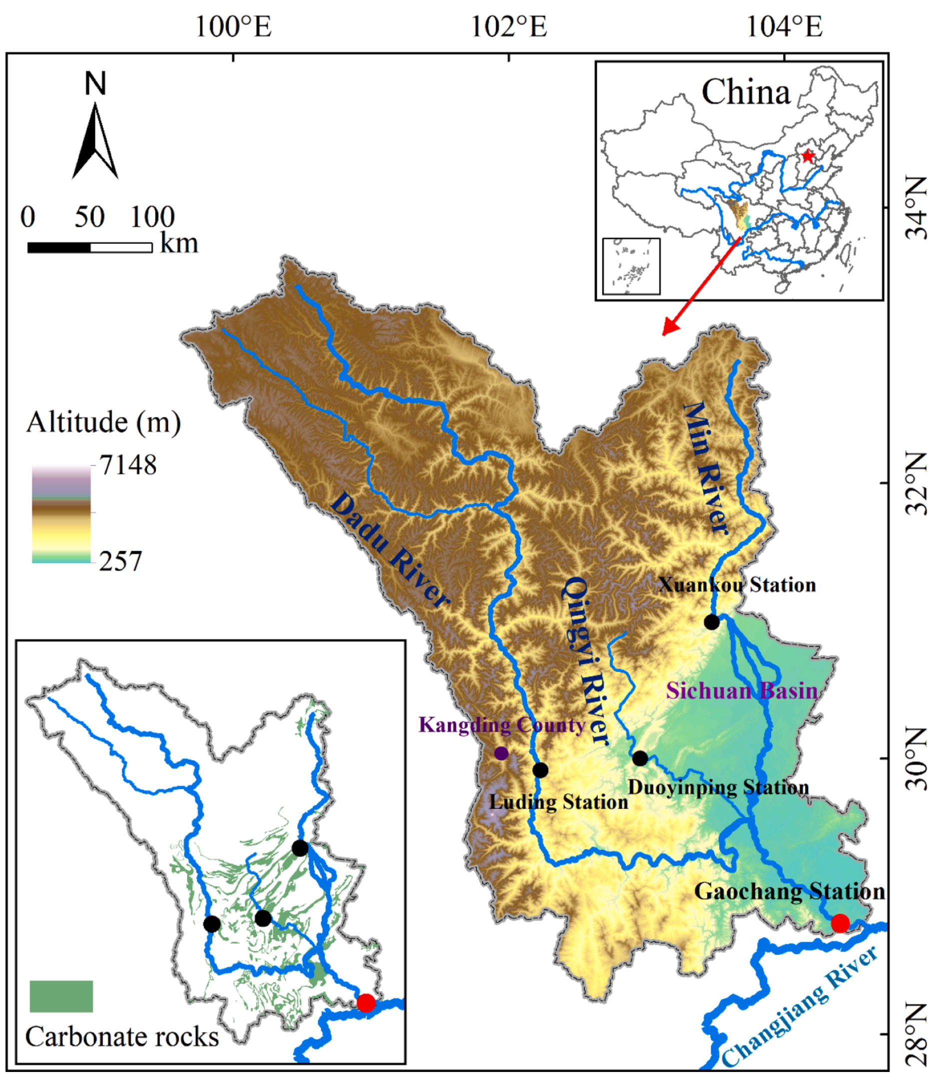

Fig. 1. Geographical map of the Min River showing the sampling site of this study (red solid circles) and the sampling sites in the study of Qin et al. (2006) (black solid circles), and a lithological map showing the distribution of carbonate rocks (lithology data from Pang et al., 2017). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Materials and methods

2.1. Study site

The Min River originates from the eastern edge of the Tibetan Plateau, with a drainage area of 133,500 km^2 (Yoon et al., 2008). The Min River has three main tributaries (Fig. 1), the Dadu River, the Qingyi River and the Min River itself, which converge at the Sichuan Basin, an industrialized and densely populated fluvial plain (Qin et al., 2006; Zhong et al., 2017a). While the upper Dadu River region has a plateau climate, the other region has a subtropical climate with mean annual precipitation of 500–800 mm on the eastern Tibetan Plateau and 1200–1500 mm in the Sichuan Basin (Yoon et al., 2008). The underlying geology of the drainage basin is mainly granite, terrigenous sediments, Quaternary fluvial deposits, volcanic rocks, high-grade metamorphic rocks, and carbonates. Carbonate rocks mainly outcrop at the source area of the Min River basin, and are scattered in the Sichuan Basin and adjacent surrounding mountainous areas. Detailed information about the topography and geology of this system is available in studies by the Bureau of Geology and Mineral Resources of Sichuan Province (1991).

2.2. Sampling and chemical analyses

Twenty-seven river water samples were collected near the Gaochang hydrological station (Fig. 1) located at the outlet of the Min River basin. The water samples were collected monthly, and additional samples were collected depending on variations in discharge, from November of 2013 to October of 2014. The pH was measured in situ, and the water samples were filtered using cellulose acetate membrane with 0.45 μm pore size for DIC and DOC analyses. Detailed information about the sampling strategies and field techniques were described in the relevant published work (Zhong et al., 2017a). Alkalinity was determined by titration with 0.02 mol L^{-1} of hydrochloric acid. Being the dominant carbon specie in mildly alkaline waters, HCO_3^- concentrations can be assumed to be equal to the concentrations of alkalinity and DIC (Clark and Fritz, 1997). $\delta^{13}C_{DIC}$ values were pretreated using a headspace analysis approach on the vacuum line, and measured by Finnigan MAT 252 mass spectrometer (Li et al., 2010, 2014; Zhong et al., 2018). The DOC concentrations were analyzed by a total organic carbon analyzer (Elemental high TOC II + N, Germany), and the partial pressure of dissolved CO_2 (pCO_2) was determined using equilibrium equations at corresponding thermodynamic constants and water temperatures (Clark and Fritz, 1997).

2.3. Methods: Load Estimator and concentration-discharge relationship

The DIC and DOC concentrations with corresponding daily discharge were used to model the daily concentrations and fluxes of DIC and DOC by Load Estimator (LOADEST; Runkel et al., 2004). The best regression model was automatically selected from nine models based on Akaike Information Criteria (AIC) in LOADEST, and the Approximate Maximum Likelihood Estimator (AMLE) was chosen for estimation and calibration of daily fluxes. The model used to estimate daily DIC loads is:

$$ln(load) = a_0 + a_1 ln(Q) + a_2 ln(Q^2) \tag{1}$$

While the model used for DOC loads estimation is:

$$ln(load) = a_0 + a_1 ln(Q) + a_2 ln(Q^2) + a_3 sin(2\pi dtime) + a_4 cos(2\pi dtime) + a_5 dtime + a_6 (dtime)^2 \tag{2}$$

where *Q* and *dtime* represent the center of discharge and decimal time, respectively, and decimal time in the LOADEST is to take seasonality into account. The *sine* and *cosine* are used for seasonality consideration, and a_0 to a_6 are the model coefficients.

Concentration-discharge (*C-Q*) relationships are often used to decipher the solutes' biogeochemical processes under different hydrologic conditions (Godsey et al., 2009; Zhong et al., 2017a). Power law function (Eq. (3)) has been widely used to model the *C-Q* (herein described as runoff (q) = Q/drainage area (A)) relationships in several rivers (Gislason et al., 2009; Godsey et al., 2009; Moquet et al., 2016; Torres et al., 2015; Zhong et al., 2017a, 2020):

$$C = a \times (q)^b \tag{3}$$

where *a* represents a constant, and *b,* being the regression coefficient, serves as the power dependence between solute concentrations and river runoff. If $b = 0$, the solute concentrations are independent of discharge. If $b = -1$, the solute concentrations are only controlled by dilution with deionized water (Godsey et al., 2009).

3. Results

The river discharge of the Gaochang hydrological station showed a significant seasonal trend, with low discharges from the late autumn to spring and a pronounced increase heading into the summer until early autumn (Fig. 2). The discharge reached the minimum value at 715 m^3 s^{-1} in May and peaked at 9560 m^3 s^{-1} in July, with an average of 2616 m^3 s^{-1} for the whole year. June to October of 2014 was defined as the high flow season, and November of 2013 to May of 2014 was defined as the low flow season, with various discharge fluctuations. The minimum water temperatures for the water samples was 9.9 °C in January of 2014 and the maximum value was 24.5 °C in August of 2014.

DIC and DOC concentrations, $\delta^{13}C_{DIC}$, and pCO_2 values varied largely in the studied year (Fig. 2). The elevated DOC concentrations of the river water occurred during the high flow season, ranging from 1.3 to 2.5 mg L^{-1} (averaging 1.8 ± 0.4 mg L^{-1}), and the DOC concentrations were relatively low during the low flow season, ranging from 1.1 to 1.6 mg L^{-1} (averaging 1.3 ± 0.2 mg L^{-1}; Fig. 2b). Contrary to DOC concentrations, DIC concentrations showed higher values (127.1 mg L^{-1} to 140.4 mg L^{-1}, averaging 134.1 ± 5.1 mg L^{-1}) in the low flow season and lower values (107.3 mg L^{-1} to 128.6 mg L^{-1}, averaging 117.1 ± 3.9 mg L^{-1}) in the high flow season (Fig. 2a). The $\delta^{13}C_{DIC}$ values ranged from −10.4‰ to − 6.0‰ in the Min River, with an average of −8.3‰ for the studied year (Fig. 2c). The DIC showed a relatively ^{13}C-enriched state between −7.8‰ to −6.0‰ (averaging − 6.6‰ ± 0.6) in the low flow season, after which it showed ^{13}C-depleted state in the high flow season, with a range of −10.4‰ to −7.6‰ (averaging −8.9 ± 0.7‰). In addition, the mean pCO_2 value was (0.97 ± 0.37) × 10^{-3} atm, with a much higher value in the low flow season ((1.45 ± 0.15) × 10^{-3} atm) than that in the high flow season ((0.80 ± 0.25) × 10^{-3} atm) (Fig. 2d).

4. Discussion

4.1. Hydrologic regulations of DIC, DOC, pCO_2 and $\delta^{13}C_{DIC}$

Significant negative correlations were observed for DIC, $\delta^{13}C_{DIC}$ and pCO_2 versus runoff changes (Fig. 3). Riverine DIC behaviors are influenced by multiple biogeochemical processes including soil CO_2 influxes, water–atmosphere exchange, carbonate mineral dissolution/precipitation and aquatic photosynthesis or respiration (McClanahan et al., 2016; Shin et al., 2011). The Min River showed high DIC concentrations and pCO_2 values during the low flow season (Fig. 2), which could be ascribed

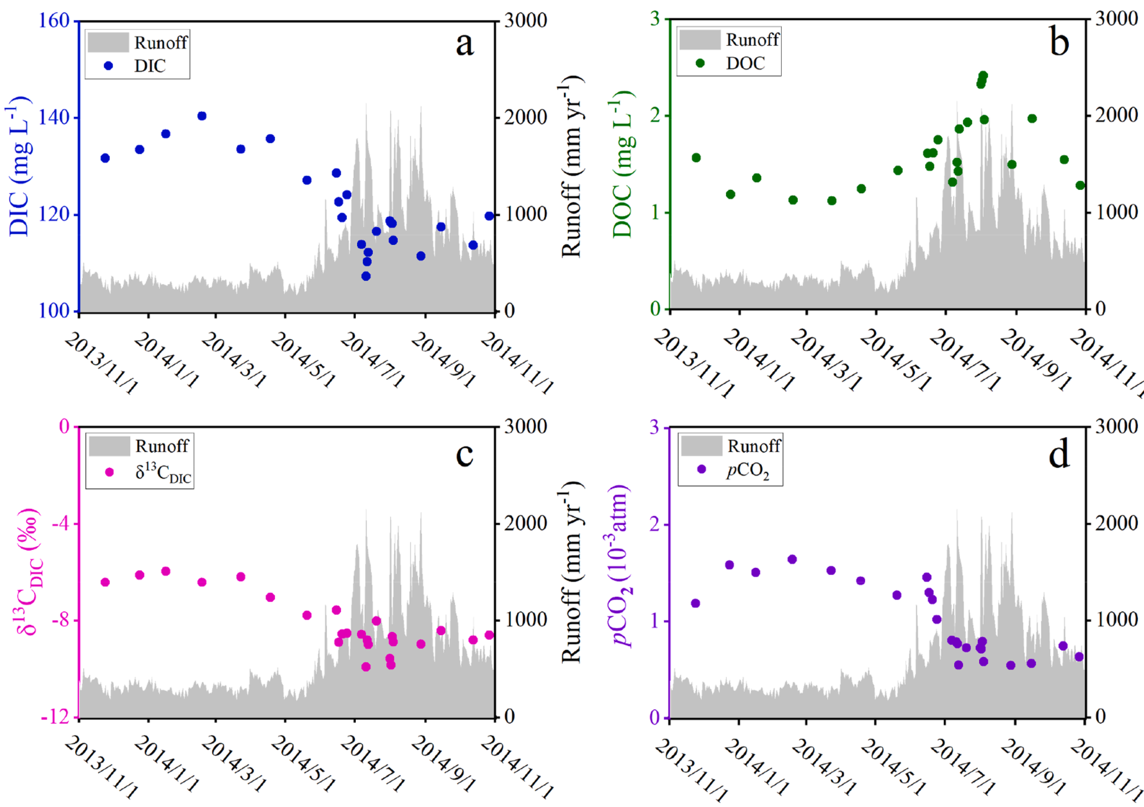

Fig. 2. Temporal variations of runoff and carbon species and isotopic composition in the Min River for (a) DIC, (b) DOC, (c) $\delta^{13}C_{DIC}$, and (d) pCO_2.

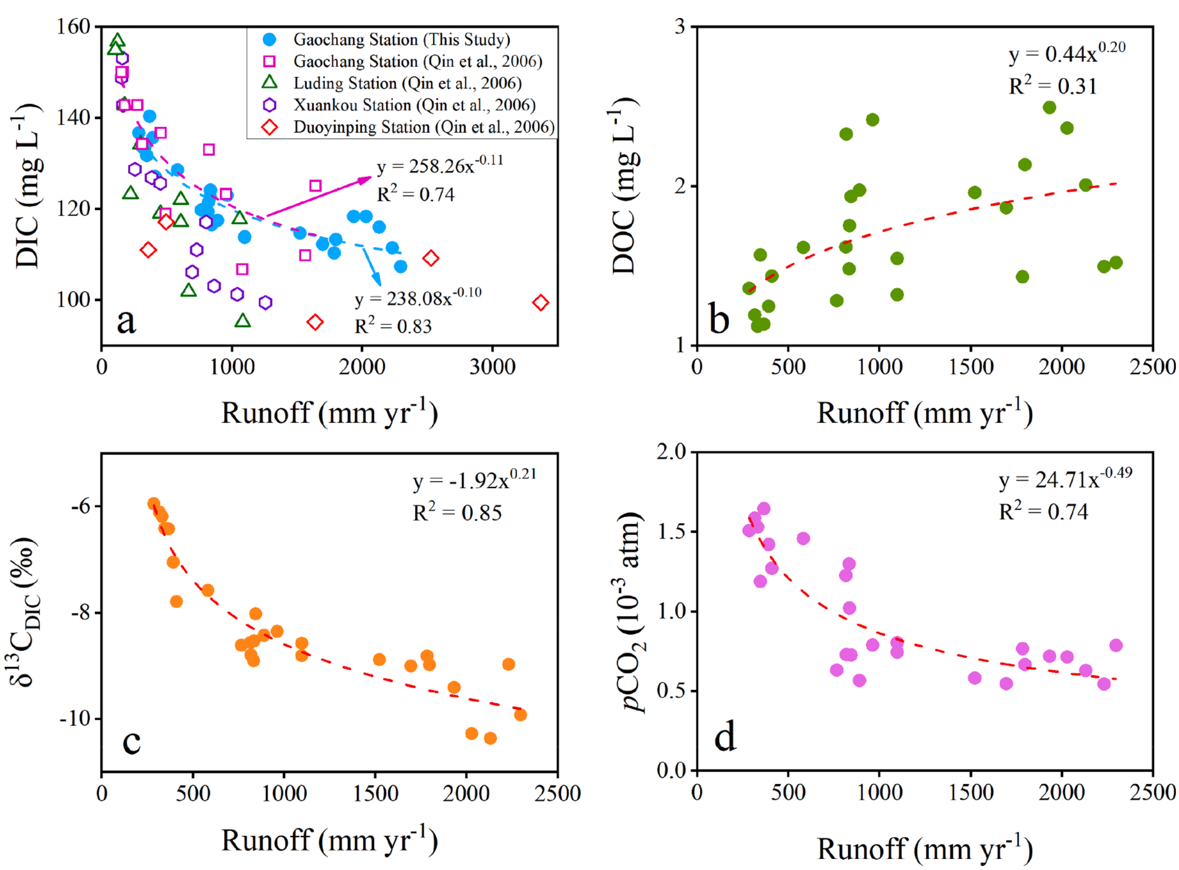

Fig. 3. Relationships between dissolved carbon species, $\delta^{13}C_{DIC}$ and runoff in the Min River for (a) DIC, including data of the Gaochang, Luding, Xuankou, Duoyinping hydrological stations from Qin et al. (2006), (b) DOC, (c) $\delta^{13}C_{DIC}$, and (d) pCO_2.

to the higher portions of subsurface flow water influx, with higher DIC and pCO_2 values (Atkins et al., 2013; Li et al., 2010; Zhong et al., 2018) than those in the surface flow water. With the arrival of high flow season, the intense precipitation would cause high runoff and be responsible for the decrease of both DIC concentrations (Fig. 3a), ascribed to the shortened fluid transit time (Tipper et al., 2006; Torres et al., 2015; Zhong et al., 2017b and 2020). Although high amounts of soil CO_2 were produced in the high flow season, accelerated chemical weathering reduced the pCO_2 in the river water. In addition, the proportion of surface flow water would increase under high runoff conditions, which has low DIC and pCO_2 values, showing dilution effects of DIC and pCO_2. However, the reactive mineral surface area could increase with the increasing runoff (Eiriksdottir et al., 2013), also resulting in the near-chemostatic behaviors of DIC under high runoff conditions (Zhong et al., 2017a). Similar *C-q* relationships of DIC were also observed in the three main tributaries of the Min River (located at Luding, Xuankou and Duoyinping; Qin et al., 2006). The three tributaries had lower DIC concentrations than those in the Gaochang hydrological station under the same runoff conditions, which could be mainly ascribed to the high temperature conditions and intense anthropogenic activities in the downstream (Qin et al., 2006). The other possible reason was the rapid weathering kinetic of sporadic carbonate rocks in and around the Sichuan Basin under warm climatic conditions (Fig. 1). Although carbonate rocks only account for a small proportion of the drainage area, water chemistry in the Min River is significantly affected by carbonate weathering (Zhong et al., 2017a). Other studies have also highlighted the importance of carbonate contribution to DIC in rivers such that even trace amounts of carbonate minerals can bear responsibility for the remarkable effects of carbonate weathering (Barth et al., 2003). Carbonate weathering is proved to be a significant source of DIC in the Min River as a result of the relatively rapid dissolution kinetics (Zhong et al., 2017a).

The DOC concentrations are positively correlated with runoff in the Min River (Fig. 3b), matching the global patterns (Wolfgang et al., 1996). During high flow conditions, rapid runoff preferentially flows through surface soil horizons and brings soil organic matter into river (Eimers et al., 2008; McClain et al., 2003; Mei et al., 2014; Shih et al., 2018). This can be confirmed by a strong flushing effect in most rivers, consistent with increasing DOC concentrations under increasing runoff conditions (Atkins et al., 2013; Clark and Fritz, 1997; Lloret et al., 2013). In addition, the average concentration of soil organic carbon is 3.24 kg m^{-2} at the lower reaches of the Min River (Lai et al., 2016). According to study of Gao et al. (2011), the soil organic carbon contribution, caused by water erosion in the Min River basin, is high in China and therefore explain the relative high DOC concentrations in high flow season. Similar to the Min River, DOC in the Jialing River also showed characteristics of terrestrial sources in the high flow season (Yan et al., 2015). While in the low flow season, deep groundwater may be the main contributor of baseflow and result in lower DOC concentrations (Mei et al., 2014; Shih et al., 2018). It should be noticed that anthropogenic activities changed the concentrations and chemical characteristics of DOC, which has been reported in previous studies (e.g., Molinero and Burke, 2009). As industrial and agricultural activities are active in the Sichuan Basin, which may lead to the high amounts of DOC in the rivers because of high fluxes of anthropogenic nutrients and sewage inputs, atmospheric deposition and land use changes (Fu et al., 2012; Monteith et al., 2007). Moreover, isotopic evidence showed that the groundwater of Min River was polluted (Li et al., 2006), which further supports that part of the anthropogenic DOC may input to the Min River. However, human-induced DOC inputs into rivers would be strengthened in the high flow season when surface runoff largely increase and soil organic carbon export also increase. The extent of anthropogenic activities effects on DOC export needs to be further studied in the future.

$\delta^{13}C_{DIC}$ has been widely and successfully used to investigate the riverine DIC origin and biogeochemical processes (Brunet et al., 2005; Khadka et al., 2014). The $\delta^{13}C$ value of carbonate bedrock is ~ 0‰, typically for marine limestone (McClanahan et al., 2016). Soil CO_2 originated from the plant root respiration and heterotrophic respiration of soil organic matter, with $\delta^{13}C$ values from − 34‰ to − 24‰ (averaging − 28‰; Khadka et al., 2014), and a + 4.4‰ enrichment would be produced for diffusion of soil CO_2 compared with organic matter (Cerling et al., 1991). During the CO_2 dissolution and succeeding formation of dissolved carbon species, ^{13}C fractionation would produce $\delta^{13}C_{DIC}$ values of soil water ranging from − 23‰ to − 13‰ (averaging − 17‰; Telmer and Veizer, 1999). In this way, the $\delta^{13}C_{DIC}$ value derived from silicate weathering by soil CO_2 would be close to − 17‰, and carbonate weathering by soil CO_2 would produce a $\delta^{13}C_{DIC}$ value of − 8.5‰, because half of the DIC originates from the dissolution of carbonate minerals, and the other half derives from the soil CO_2 (Li et al., 2014). The mean $\delta^{13}C_{DIC}$ value of the Min River was − 8.3‰, which was close to the $\delta^{13}C_{DIC}$ value of carbonate weathering by soil CO_2, but was much heavier than the $\delta^{13}C$ value of silicate weathering-derived DIC and dissolved soil CO_2 sourced from organic matter respiration. There are four main reasons for the enrichment of ^{13}C: aquatic photosynthesis, sulfuric acid participation in carbonate weathering, CO_2 degassing and metamorphic CO_2 influx. (1) Aquatic photosynthesis may be much stronger in the high flow season (mainly in summer) than in the low flow season (mainly in winter) due to high water temperature and strong solar radiation in the high flow season, which will shift ^{13}C-riched values. But photosynthesis can be weakened by shortened residence time (He and Xu, 2017) and the reduced water clarity (Sun et al., 2011) because of high suspended matter (i.e., more than 90% of river sediments are concentrated in the high flow season in the Min River, calculated from International Research and Training Center on Erosion and Sedimentation (2014)). Therefore, photosynthesis played a less important role for $\delta^{13}C_{DIC}$ changes, evidences from the ^{13}C-depleted values in the high flow season. (2) The $\delta^{13}C_{DIC}$ produced by carbonate weathering using sulfuric acid are consistent with the previous work in southwestern China (Li et al., 2008). Sulfur and oxygen isotopes of dissolved sulfate analyses in the Min River indicated that dissolved sulfate mainly originates from burning coal (Yoon et al., 2008; Zhao et al., 2015). Therefore, sulfuric acid participation in carbonate weathering played an important role in ^{13}C-enriched values in the low flow season for the Min River. (3) Another explanation of the enrichment of ^{13}C in river water DIC could be attributed to CO_2 degassing, which would cause ^{13}C enrichment downstream as a result of isotopic fractionation of DIC in the low flow season (Doctor et al., 2008; Polsenaere and Abril, 2012; Shin et al., 2011). CO_2 will diffuse out of water when the pCO_2 of the surface water is higher than that of the ambient atmosphere (Ran et al., 2017), which is the case of the Min River, because pCO_2 of river water samples exceeds twice the atmospheric CO_2 concentration in the low flow season. CO_2 emission rate can be reduced in the high flow season due to the shortened transit time in the river channel, inducing light $\delta^{13}C_{DIC}$ in the high flow season. (4) The last possible reason is metamorphic carbon input due to Himalayan orogenic movement (Becker et al., 2008; Evans et al., 2008; Gaillardet and Galy, 2008), which have ^{13}C-enriched values (Galy and France-Lanord, 1999), and these springs can shift ^{13}C-enriched values when they discharge into rivers. The $\delta^{13}C_{DIC}$ values of thermal springs varied from − 3.6‰ to + 2.8‰ in the Kangding county (Fig. 1), with up to 60% of the CO_2 from the springs discharged into the hydrosphere (Yang et al., 1999). However, considering that the low proportion of thermal springs discharge in the total discharge of Min River and the long distance between locations of these thermal springs (Luo, 1994) and the Gaochang hydrological station, metamorphic carbon contribution may not be important for the ^{13}C enrichment, which is consistent with Li et al. (2014).

In this study, a significant negative relationship between $\delta^{13}C_{DIC}$ and runoff was observed in the Min River (Fig. 2c). With increasing runoff, carbonate weathering was accelerated by the increased reaction surface area (Eiriksdottir et al., 2013; Zhong et al., 2020). In addition, large amounts of soil CO_2 were produced in the high flow season because of the high temperature and intense precipitation (Li et al., 2010; Zhong et al., 2018). The water with soil CO_2 of ^{13}C-depleted values flushed into the river during rain events, shifting ^{13}C-depleted values with the increase of runoff.

4.2. Temperature regulations of dissolved carbon species

The increasing temperature accelerated riverine DIC production as a result of enhanced weathering rates (Zhong et al., 2018). ΔDIC was used in this study, which was calculated as the measured DIC value subtracting the theoretical DIC value (i.e., the value when DIC concentration is diluted by deionized water, which refers to $b = -1$ in the power law function), to represent the production of DIC with changing hydrologic conditions and constrain the exogenous sources of DIC (Zhong et al., 2018). Similar to the Xijiang River, ΔDIC has a strong positive correlation with water temperature (Fig. 4a) which is highly affected by air temperature, consistent with that high temperatures accelerated the dissolution rate of minerals. With high temperature in the warm season, large amounts of soil CO_2 were produced, accelerating the chemical weathering rates (Zhong et al., 2018). In addition, large amounts of soil organic matter within the surface flow flowed into the river induced by intense rainfall during the high flow season (Li et al., 2010), which caused high DOC concentrations in the high flow season (Fig. 4b). The degradation of both soil organic matter and in-river organic carbon would increase caused by warming (Freeman et al., 2001), also producing DIC. Therefore, carbonate weathering and biological carbon influx should be responsible for the DIC dynamics.

Taking water temperature into account is important when working with isotopes, because isotope fractionation is inversely proportional to water temperature (Zhang et al., 1995). Both water temperature and ΔDIC were negatively correlated with $\delta^{13}C_{DIC}$ in the Min River (Fig. 5a and b). As highlighted above, ΔDIC derived mainly from carbonate dissolution and biological CO_2 influxes (i.e., soil CO_2 and CO_2 produced in the river). Considering that the DOC concentrations in the Min River were low, soil CO_2 influx can be identified as one of the main reasons for the ^{13}C-depleted values. Therefore, water temperature plays an important role in dissolved carbon dynamics in the Min River, because of the increased biological CO_2 and accelerated chemical weathering.

4.3. The response of DIC/DOC ratios to hydrologic conditions

Investigating the DIC/DOC ratios could improve the understanding of carbon biogeochemical processes in rivers (Brunet et al., 2009; Lloret et al., 2013; Shih et al., 2018). The mean DIC/DOC ratio in large rivers worldwide is about 1.86, which implies that DIC averagely accounts for 2/3 of the total dissolved carbon in global rivers (Shih et al., 2018). The mean DIC/DOC ratio in the Min River was 15.09, which is much higher than the global mean DIC/DOC ratio, similar to the subtropical mountainous rivers in Taiwan (14.08; Shih et al., 2018), but much lower than the Wujiang River with karst landscapes in Southwest China (27.30; Zhong et al., 2017b). The DIC export fluxes constitute a high proportion of the total dissolved carbon fluxes in the Asian monsoon rivers. Possible reasons are: (1) limited DIC consumption or a large DIC supply in the carbonate-rich catchment, and (2) fast rates of dissolved organic matter degradation (Shih et al., 2018).

The DIC/DOC ratio in the Min River decreased as runoff increased (Fig. 6a), which was mainly due to the decreased DIC concentrations and increased DOC concentrations with increasing runoff. A negative correlation was also observed between DIC/DOC ratios and water temperature (Fig. 6b). High temperature usually co-varies with high precipitation in the Asian monsoon regions, causing large amounts of DOC to be flushed into the river from the soil. Meanwhile, although DIC was diluted, large amounts of DIC were produced as a result of the increased reactive surface area between fluid and mineral surface with increasing runoff conditions, producing high contents of ΔDIC. Importantly, ΔDIC increased with runoff, ascribing to the rapid dissolution of carbonate minerals under high flow conditions. In addition, the increases of DOC and runoff were also synchronous. Therefore, ΔDIC and DOC showed a positive correlation (Fig. 6d). The DIC/DOC ratios and $\delta^{13}C_{DIC}$ were also positively correlated in the Min River (Fig. 6c), which was expected because of the biological carbon influx in the high flow season.

4.4. Dissolved carbon fluxes of the Min River and comparisons with other rivers originating from the Tibetan Plateau

The discharge-weighted average concentrations of DIC and DOC were estimated by LOADEST, and the results are shown in Fig. 7. The estimated annual DOC and DIC fluxes were 1.1 ± 0.03 and 15.2 ± 0.09 t C km^{-2} yr^{-1}, respectively. The DOC flux is slightly lower than the global average (1.4 t C km^{-2} yr^{-1}), but the DIC flux is approximately six times higher than the global average (2.6 t C km^{-2} yr^{-1}; Shih et al., 2018). The DOC and DIC fluxes reached the highest values during the high flow season, indicating that changing runoff and temperature conditions were critical factors in the variations of dissolved carbon export in northern temperate rivers (Huntington and Aiken, 2013; Shih et al., 2018).

The Tibetan Plateau region is the origin of many Asian large rivers (Table 1), such as the Yellow, Changjiang, Mekong, Salween, Brahmaputra, Ganges, and Indus rivers, known as the Asian water tower. Riverine DIC fluxes of these rivers can provide information which helps

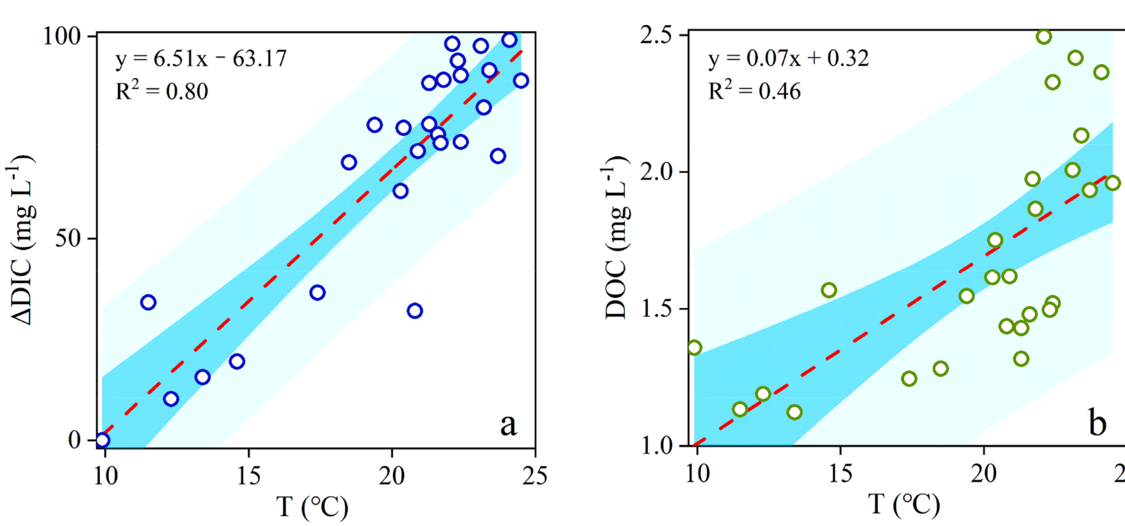

Fig. 4. (a) Relationships between water temperature and ΔDIC, and (b) relationships between water temperature and DOC.

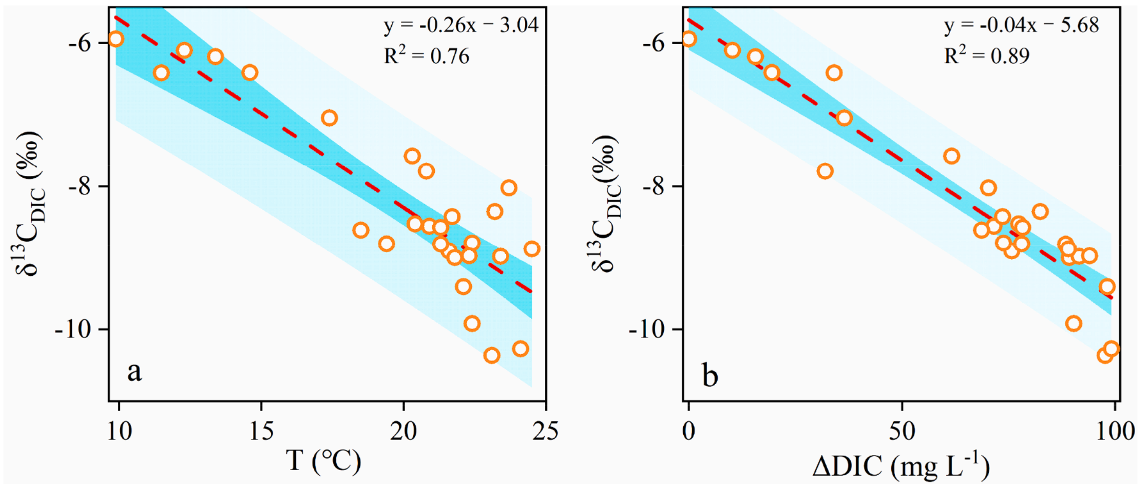

Fig. 5. (a) Relationships between water temperature and $\delta^{13}C_{DIC}$, and (b) relationships between ΔDIC and $\delta^{13}C_{DIC}$.

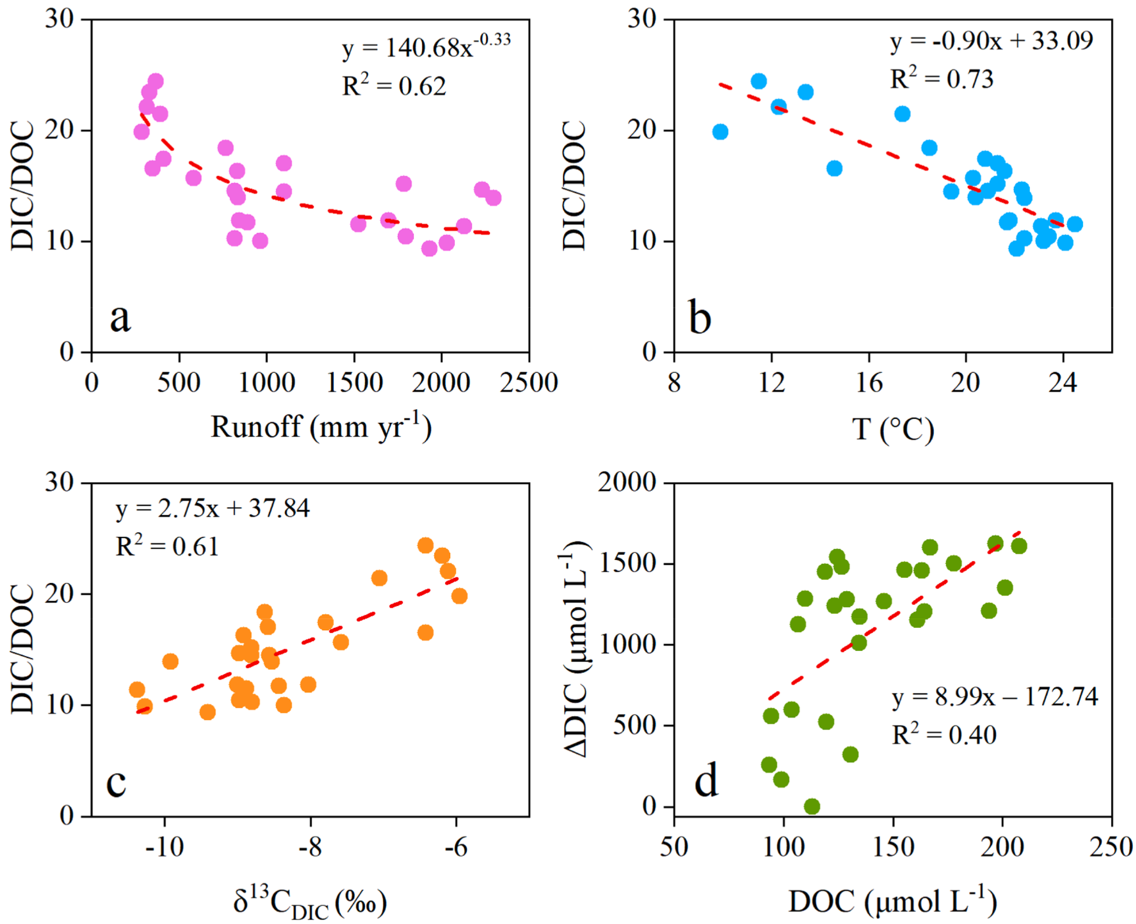

Fig. 6. The change of DIC/DOC ratio with (a) runoff, (b) water temperature and (c) $\delta^{13}C_{DIC}$, and (d) the relationship of DOC versus ΔDIC.

us to understand the role of the Tibetan Plateau region in global weathering, affecting the water quality and ecosystem stability downstream. Therefore, the DIC fluxes of large rivers derived from the Tibetan Plateau region are summarized in Table 1, and the annual DIC flux is 1.39 Tmol yr^{-1} (Tmol = 10^{12} mol). Cai (2011) have reported that global DIC flux is 33.9 Tmol yr^{-1}, which means that riverine DIC flux from the Tibetan Plateau region accounts for 4.1% of the global riverine DIC fluxes. The DIC flux is not high, because it was only the riverine DIC that just flows through the Tibetan Plateau region, not those points at the estuary. The DIC fluxes of this study is underestimated, because there are no data reported from the western part of the Tibetan Plateau. With regard to these compiled rivers in the Tibetan Plateau, the Yellow River, Jinsha Jiang, and Nu Jiang (Salween) show high DIC concentrations. However, the highest riverine DIC flux occurs in the Ganges and Brahmaputra system because of their high runoff. In contrast, the Irrawaddy and the Tarim Rivers have low DIC fluxes because of their relatively low DIC concentrations and low discharge, respectively.

The DIC concentrations in the rivers from the Tibetan Plateau show

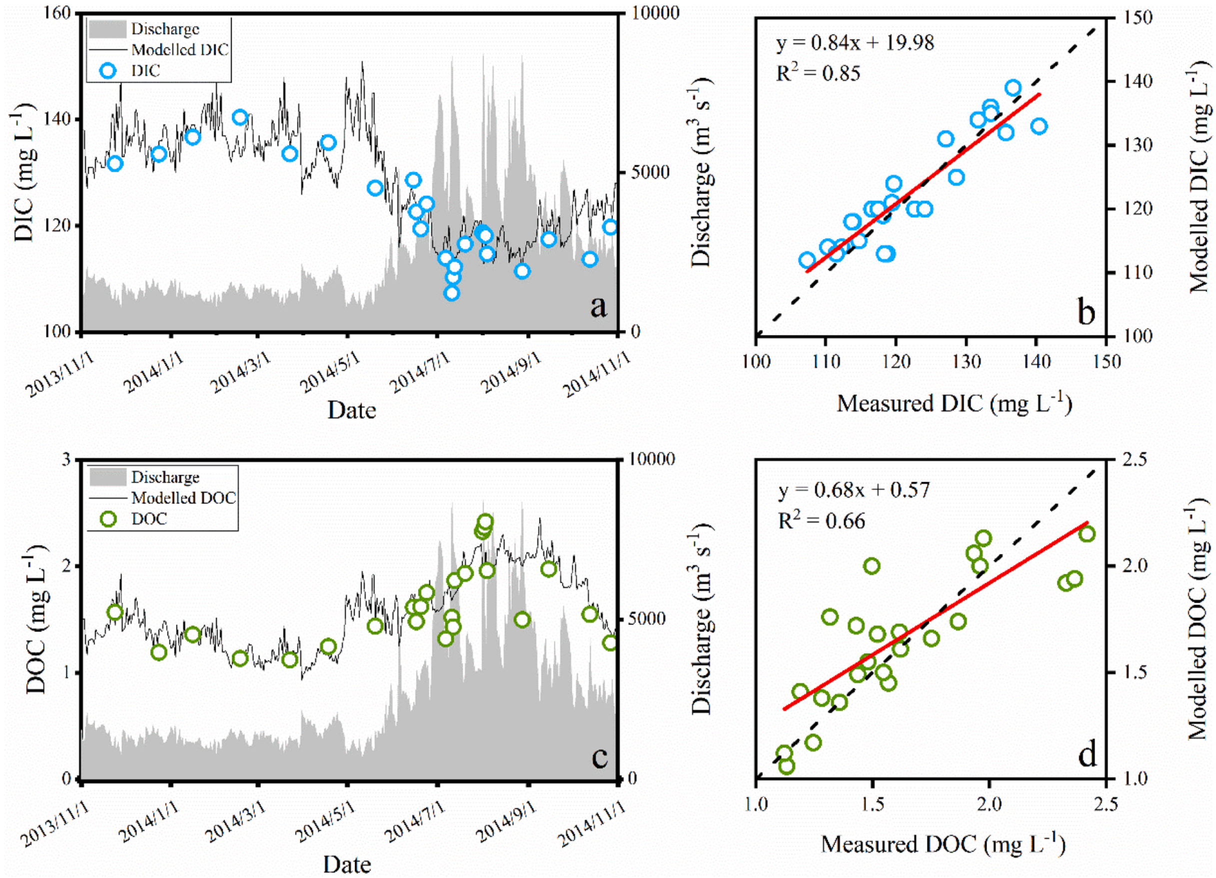

Fig. 7. Modelled daily DIC and DOC concentrations (a, c) using LOADEST (Runkel et al., 2004) and their relationships with the measured DIC and DOC concentrations (b, d). Discharge-weighted average concentrations for the Min River were calculated from time series measurements and discharge data at the Gaochang station.

Table 1
Dissolved inorganic carbon fluxes of the large rivers derived from the Plateau region.

River name	Location	Area (10^6 km^2)	Discharge (10^9 m^3 yr^{-1})	Concentration (μmol L^{-1})	DIC flux (10^9 mol yr^{-1})	Study period	Reference
Jinsha Jiang[a]	Shigu	0.233	39.4	3847	151.55	2005	Wu et al. (2008)
Min River	Gaochang	0.131	82.4	2017	166.14	2013–2014	This study
Nu Jiang[a] (Salween)	Daojie	0.110	53.1	2761	146.58	2005	Wu et al. (2008)
Yellow[b] River	Lanzhou	0.223	36.2	3035	109.84	2007 and 2009	Wang et al. (2016)
Ganges and Brahmaputra[c]	/	0.176	206	1879	387.00	1996–1997	Galy and France-Lanord (1999)
Mekong	Chiang Saen	0.189	80	1649	131.93	1972–1998	Li et al. (2014)
Irrawaddy	Myitkyina	/	185	453	83.89	2004–2007	Chapman et al. (2015)
Indus	Thatta	0.916	90	2130	191.70	1992	Pande et al. (1994)
The Tarim River[d]	/	0.185	15.5	1737	24.19	2012	Wu (2016)

[a] The DIC concentration and flux are calculated from summer and winter averages.
[b] The discharge, DIC concentration and flux are calculated from 2007 and 2009 averages.
[c] The DIC concentration and flux are calculated from the sum of each main river that crosses the Main frontal thrust (MFT) region.
[d] Data are calculated from the nine rivers which originated from the Plateau.

higher values, varying over a wide range, than those in most rivers worldwide (Fig. 8a). The uplift of the Tibetan Plateau leads to the increased surface reactivity of minerals, which can accelerate chemical weathering rates and thus produce high DIC concentrations in Tibetan Plateau rivers. However, the DIC generation rates, defined as DIC × Runoff (the dashed lines in Fig. 8a and b), in Tibetan Plateau rivers were not significantly higher than the global average (Fig. 8a and b). The highest DIC generation rate was observed in the Ganges and Brahmaputra, because of the high runoff (Fig. 8a), as a result of the heavy precipitation caused by the Asian monsoon climate. The lowest DIC generation rate was found in the Indus river, which was mainly affected by the subtropical desert climate with inadequate rain throughout the year, causing low runoff and low DIC generation rate. In general, rivers with high runoff have high DIC generation rates (R^2 = 0.77 for linear regression analysis; Fig. 8a), supporting the hypothesis that hydrology and temperature associated with climate conditions regulate global carbon dynamics. However, the DIC generation rate of a large-flux river is also closely related to the drainage area (R^2 = 0.63 for power

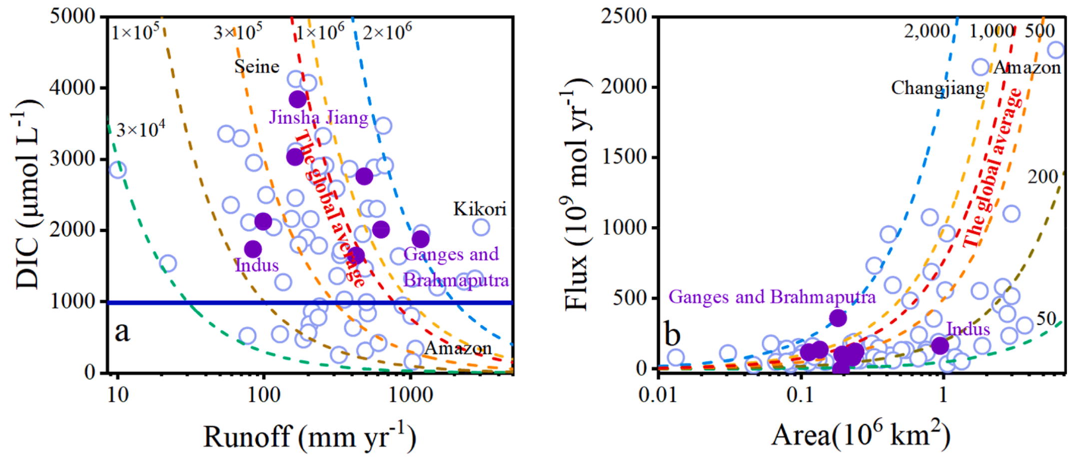

Fig. 8. The relationships between (a) DIC and runoff, (b) DIC flux and catchment area for global rivers (light blue hollow circle) and the Plateau rivers (violet solid circle). The global data were from Gaillardet et al. (1999), and the data of the Plateau rivers were from Table 1. The dashed lines represent the DIC generation rate, which is defined as (a) DIC × Runoff or (b) Flux/Area, respectively. The solid line in Fig. 8a represents the discharge weighted global average DIC. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

regression analysis; Fig. 8b), with larger drainage area but producing lower DIC generation rates, which may be the result of increasing difficulties on exports of weathering products in lager basins because of their complicated terrain and longer average distance between souce regions of weathering products and outlet of basins.

4.5. Ecosystem implications for rivers, originating from Tibetan Plateau

The Tibetan Plateau region is sensitive to global climate change, following runoff and temperature changes (Chen et al., 2013; Su et al., 2016), which would affect the carbon production and transport. The DOC and DIC fluxes in the Min River and other Tibetan Plateau rivers may increase because of the discharge in the Min River which may further increase as a result of increasing precipitation in the next few decades in the Tibetan Plateau (Li et al., 2013; Lutz et al., 2014; Su et al., 2016). Therefore, it is proposed that long-term work on different forms of carbon and climate variabilities is needed to further investigate the riverine carbon dynamics in the Tibetan Plateau.

As shown in this study, carbon dynamics are sensitive to changing runoff and temperature conditions, and carbon behaviors would have profound implications for future climate change. DIC production and transport in the Tibetan Plateau rivers would affect the ecosystem stability in downstream and the ocean, providing nutrients for gross primary production in aquatic systems. As high amounts of DIC were produced in the Tibetan river systems under high flow conditions, the Tibetan rivers play an increasing important role in global carbon cycle. The carbon dynamics would be more complicated in the future, so researchers should pay more attention to the temporal carbon dynamics in the Tibetan rivers under monsoon climate.

5. Conclusions

This study highlighted the significance of dissolved carbon dynamics in response to various runoff and temperature conditions, by investigating temporal variations of DIC and DOC concentrations and $\delta^{13}C_{DIC}$ values in the Min River, originating from Tibetan Plateau. There were distinct temporal variations in concentrations and fluxes of DIC and DOC, which was mainly controlled by changing runoff and temperature conditions. The negative *C-q* relationships indicated that DIC concentrations showed a dilution effect with increasing runoff, while DOC concentrations were positively related to changing runoff. Moreover, intense meteorological events in the high flow season also played an important role in DIC and DOC dynamics, which increased soil organic carbon and soil CO_2 influx because of the strong flushing effect and decreased fluid transit time. The primary source of DIC was carbonate weathering, but soil CO_2 influx and organic matter degradation in the river significantly affect the $\delta^{13}C_{DIC}$ values in the high flow season. Sulfuric acid participation in carbonate weathering and the CO_2 degassing could be responsible for ^{13}C enrichment in the low flow season. Temperature is also an essential factor in controlling riverine dissolved carbon dynamics, which can increase riverine DIC production by accelerating the dissolution rates of minerals and organic matter degradation. The mean DIC/DOC ratio in the Min River is 15.09, much higher than the global mean DIC/DOC ratio, suggesting that DIC is the main component in the dissolved carbon exported from the Min River. The carbon exports of DOC and DIC were 1.1 ± 0.03 and 15.2 ± 0.09 t C km^{-2} yr^{-1}, respectively. And DIC flux in the Min River showed much higher values than global average. Furthermore, to better estimate dissolved carbon export in river systems, the effects of hydrology and temperature on the carbon dynamics should be considered carefully, especially for the Tibetan Plateau region.

CRediT authorship contribution statement

Shuai Chen: Formal analysis, Writing - original draft, Writing - review & editing. **Jun Zhong:** Investigation, Conceptualization, Writing - original draft, Writing - review & editing. **Cai Li:** Writing - review & editing. **Jing Liu:** Investigation. **Wanfa Wang:** Writing - review & editing. **Sen Xu:** Writing - review & editing. **Si-Liang Li:** Supervision, Funding acquisition, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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