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Transformation of dissolved inorganic carbon (DIC) into particulate organic carbon (POC) in the lower Xijiang River, SE China: an isotopic approach

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Abstract

The sources and dynamics of riverine carbon have been discussed extensively, but knowledge about the transformation from DIC into organic carbon (OC) is still poorly understood. In this study, we conducted a comprehensive investigation on the riverine carbon, stable carbon isotopic components and C/N ratios for different seasons, including an extreme flood event, in the lower Xijiang and its three tributaries. Detailed analyses are also performed for soil samples across the study region. Downstream increase in $\delta^{13}\text{C}_{\text{DIC}}$ and downstream decrease in both $\delta^{13}\text{C}_{\text{POC}}$ and C/N have been observed for all the tributaries. Meanwhile, positive shift of $\delta^{13}\text{C}_{\text{DIC}}$ and negative shift of $\delta^{13}\text{C}_{\text{POC}}$ are also observed from summer to winter. These observations likely indicate that the isotopic compositions of both DIC and POC are significantly affected by in-river primary production that converts DIC into organic matter through photosynthesis. It is estimated that the percentage contribution of the riverine aquatic primary production to the riverine POC in the Xijiang and three tributaries of Guijiang, Hejiang and Luoding is respectively 7.1 %, 43.2 %, 36.4 % and 9.9 % in rainy season, and 35.6 %, 47.3 %, 50.3 % and 40.1 % in dry season. Based on the stoichiometry involved in chemical weathering of the bedrocks, the transformation of the carbonate-sourced DIC to POC is further quantified to be 3.4–20.5 % in rainy season, and 12.3–22.1 % in dry season. This may suggest an important sink of atmospheric CO_2 in river systems that was largely ignored previously.

1 Introduction

Riverine input of dissolved and particulate carbon to oceans is an important component of global carbon cycle (Meybeck, 1982; Degens et al., 1991), which can be sourced from watershed inputs and can be influenced by fluvial processes. For most rivers, the dominant form of dissolved inorganic carbon (DIC) is bicarbonate, mainly from chemical weathering of carbonates and silicates in the drainage basin. There are complex

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processes involved in the DIC cycling in river systems, including CO₂ exchange with atmosphere, precipitation or dissolution of carbonates, photosynthesis, oxidation of organic matter in rivers (Buhl et al., 1991; Aucour et al., 1999). Riverine dissolved organic carbon (DOC) and particulate organic carbon (POC) are mainly derived from soil erosion, particularly for highly turbid rivers. For lower turbid rivers, however, contribution of aquatic biomass may increase significantly (Meybeck, 1993; Ludwig et al., 1996; Komada et al., 2004). Through interim processes such as microbial utilization, primary production and respiration, inorganic and organic carbon in the river may transform to each other.

Because of complicated interactions between climatic, hydrological, and biological aspects during riverine transport, the origin and fate of riverine carbon are still debating topics. Some studies show that riverine organic carbon is mainly composed of young terrestrial carbon originated to POC in Xijiang river from modern biosphere (Hedges et al., 1986; Druffel et al., 1992. Opsahl and Benner, 1997; Mayorga et al., 2005), and the opposing view is that organic carbon transported in rivers mostly consists of aged carbon coming from sedimentary rocks (Kao and Liu, 1996; Leithold and Blair, 2001; Raymond and Bauer, 2001; Hwang et al., 2005), which has a large contribution of vascular plant material to the aged carbon (Drenzek et al., 2009). Besides, some studies have suggested that the petrogenic carbon discharged from rivers is highly recalcitrant and can be reburied in floodplain or coastal ocean (Blair et al., 2003; Dickens et al., 2004; Goñi et al., 2005; Komada et al., 2005), but there are also studies showing that oxidation of the petrogenic carbon during river transport is a significant source of atmospheric CO₂ (Petsch et al., 2001, 2003; Berner, 2004; Bouchez et al., 2010). Although the sources and dynamics of riverine carbon have been extensively discussed using isotopic constraints, the potential influence of the in-river transformation of DIC to OC (organic carbon) on the carbon isotopic composition has been largely ignored (Mook and Tan, 1991; Raymond et al., 2004; Liu et al., 2010).

Here we conducted a comprehensive investigation on the seasonal and spatial variations of riverine carbon and soil organic carbon in the lower Xijiang area. Through

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stable carbon isotopic analysis combined with hydrochemical data, this study attempts to specify the carbon sources and processes involved in the riverine carbon cycle, and to quantitatively estimate the transformation of DIC into POC in the river.

2 Methods

2.1 Study area

The Zhujiang river (Pearl river) is the second largest river in China in terms of annual water discharge ($336 \text{ km}^3 \text{ yr}^{-1}$) and the largest contributor of dissolved materials and sediment to South China Sea (SCS) (PRWRC, 1991). It passes entirely through an evergreen forest area in the subtropical to tropical climate zones (Fig. 1). The mean annual temperature and precipitation are $14\text{--}22^\circ$ and $1200\text{--}2200 \text{ mm}$, respectively. Heavy rainfalls occur mainly in June, July and August, which accounts for $50\text{--}60\%$ of the annual water discharge (Sun et al., 2007).

The Zhujiang river system includes three branches, the Xijiang (West river), Beijiang (North river), and Dongjiang (East river) (Fig. 1). The Xijiang is the largest branch of the Zhujiang, accounting for 77.8% in total drainage area and 64% in water discharge of the entire Zhujiang. Carbonates are widely distributed in the Zhujiang Basin, especially in the headwater region of the Xijiang (see Fig. 1) with typically developed karst landscape, and covers 39% of the total drainage area (PRWRC, 1991).

This study focused on the lower part of the Xijiang river, where 3 tributaries join the main channel of the Xijiang, named as Guijiang, Hejiang, and Luoding. These tributaries developed in various basin sizes with marked difference in carbonate/silicate ratios of exposed bedrock. The vegetation in the study area is a typical subtropical monsoon rainforest with a high coverage (more than 50%). As a typical monsoon region, the air temperature and precipitation (or discharge) in the Xijiang basin vary in a simultaneous fashion; both high in summer and low in winter. For the Luoding, a large number of dams are constructed along the river, which significantly reduce both flow

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velocity and total suspended sediment (TSS) concentration. Additional characteristics of the Xijiang, Guijiang, Hejiang and Luoding are listed in Table 1.

2.2 Sampling

The river water samples were collected in April (yearly-normal flow), June (flood event), July (yearly-higher flow) and December (yearly-lower flow) in 2005. Based on spatial distributions of bedrock, vegetation, residential locality and confluent position, 13 sampling sites were assigned on the tributaries of Guijiang, Hejiang, Luoding and the main stream of Xijiang (Fig. 1). Water samples were also collected during an extreme flood process occurred in June 2005 at the Gaoyao Hydrometric Station transect in the lower Xijiang River. All samples were taken at 1m under water surface on the central line of the rivers.

On the day of sampling, the collected samples were filtered by vacuum filtration through two pieces of 0.7 μm Whatman GF/F filter papers (47 mm in diameter) that were pre-weighed after combustion at 450° for 6 h. Once returned to the laboratory, one filter paper was dried at 103° for 24 h to calculate TSS. The other one was dried at 50° for 24 h and then scraped into an agate mortar for pulverization, and was acidified to remove carbonate for determining POC and particular nitrogen (PN) contents as well as carbon isotope composition. All samples were stored at 4 °C until analysis.

Samples for $\delta^{13}\text{C}_{\text{DIC}}$ analysis were prepared following the direct precipitation method (Bishop, 1990). About 1000 ml filtrate in a glass vessel was treated with $\text{SrCl}_2\text{-NH}_4\text{OH}$ solution at $\text{pH} > 10$ and sealed for 24 h. Then, the SrCO_3 precipitate in the vessel was transferred to a vacuum filtration for filtering and rinsed with boiling distilled water until the pH value of the filtrate less than 7. After drying at 80 °C for 24 h in the laboratory, the SrCO_3 precipitate was stored in plastic bags.

In addition, the soil sampling was carried out in July (summer) and December (winter) 2008 to investigate the POC, C/N, and isotopic characteristics. Eight soil profiles were selected around the riverbank which can represent the prevalent land use categories of the area (Fig. 1). Characteristics of the selected soil profiles are shown in Table 3.

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For each soil profile, 3 samples were taken from horizons of 0–5 cm, 15–20 cm and 30–50 cm, respectively. After collection, samples were dried at 50°, sieved through a 2 mm mesh, and then pulverized and acidified to remove carbonate.

2.3 Laboratory analysis

DIC concentration in the water was determined by titration with 0.01 M HCl within 24 h after sampling. The measurement of each sample was repeated for 2 or 3 times and the analytical error is less than 5%. TSS was calculated by weight difference before and after filtering. POC and PN were analyzed by Perkin Elmer-2400 II (Elemental Analyzer CHNS/O) with analytical errors of less than 0.3%. $\delta^{13}\text{C}$ of the POC and DIC were determined on a MAT-252 mass spectrometer with dual inlet. The results are reported relative to the V-PDB standard with an uncertainty less than $\pm 0.1\text{‰}$.

3 Results

3.1 Riverine DIC and $\delta^{13}\text{C}_{\text{DIC}}$

Riverine DIC is composed of HCO_3^- , CO_3^{2-} , and dissolved CO_2 . In general, the HCO_3^- is the dominant component when pH value of the river water is 6.4–10.3 (Dreydrodt, 1988). Based on historical monitoring data at the Gaoyao Hydrometric Station (1962–2002), pH values of the Xijiang River are between 6.7 and 8.4, CO_3^{2-} is nearly undetectable, dissolved CO_2 ranges from 0.004 to 0.05 mmol l^{-1} with a mean value of 0.03 mmol l^{-1} , and HCO_3^- is between 0.71 and 2.59 mmol l^{-1} with a mean value of 1.87 mmol l^{-1} . Hence, HCO_3^- is used as an approximation of the DIC in this study.

The mean DIC concentration of the Xijiang is higher than in most large rivers of the world (cf. Degens et al., 1991), characteristic of the drainage developed on typical carbonate region. The highest concentrations of DIC occur in winter (December) and the lowest in summer (June, particularly during the flood event). Compared with

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the change in water discharge, however, DIC concentration changed with smaller amplitude, suggesting that the extensive outcrop of carbonate rocks in the Xijiang River Basin could provide large amount of DIC during rainy season.

DIC concentrations in the tributaries show an order of Xijiang > Guijiang > Hejiang \geq Luoding (Table 2), generally in agreement with the order of the area ratios of carbonate/silicate in these subbasins (Sun et al., 2008). In the Guijiang and Hejiang rivers, DIC shows a decline trend from upstream to downstream, consistent with the fact that carbonate is mainly exposed in the upper reaches, indicating the dominate impact of carbonate weathering on the riverine DIC concentration of the region. More importantly, this downstream decreasing trend can be affected by the processes including (1) carbonate mineral precipitation, (2) CO₂ outgassing and (3) aquatic photosynthesis (Dreybrodt, 1988; Kanduč et al., 2007), which will be discussed later.

Stable carbon isotope signature of DIC ($\delta^{13}\text{C}_{\text{DIC}}$) in the Xijiang river system is averaged -11.2‰ in July (summer), -12.8‰ during the extreme flood and -9.3‰ in December (winter), showing a distinct seasonal difference. Largely, $\delta^{13}\text{C}_{\text{DIC}}$ in the Xijiang river system becomes more negative downstream (Fig. 2) except for the Guijiang in winter. Among the selected four tributaries, Luoding has the lowest $\delta^{13}\text{C}_{\text{DIC}}$ value as it is developed on a typically silicate-dominated area.

3.2 Riverine POC, $\delta^{13}\text{C}_{\text{POC}}$, and C/N

In the Xijiang river system, POC is positively correlated with TSS (Sun et al., 2007). TSS varied dramatically through the year, ranging from 0.4 to 180.90 mg l⁻¹ during the 4 sampling seasons (Table 2). Particularly, it reached a peak value of 802.2 mg l⁻¹ during the 05'06 flood (June 2005). Among these studied sub-basins, TSS is lower in the Guijiang and Hejiang than in the Xijiang and the Luoding, possibly due to better developed vegetation cover and lower slope of the river channel (Table 1) that greatly reduced soil erosion in the former.

In average, the stable carbon isotope composition of the POC ($\delta^{13}\text{C}_{\text{POC}}$) is -24.7‰ in July, -23.0‰ during the flood event and -25.9‰ in December (Table 2). As seen in Fig. 3, $\delta^{13}\text{C}_{\text{POC}}$ in all the three tributaries shows a consistent decreasing trend from

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upper to lower stream in both summer and winter seasons. In the Xijiang it displays a sharper downstream decrease in winter but a smaller decrease in summer. In the Hejiang, however, a notable increase of $\delta^{13}\text{C}_{\text{POC}}$ from sample HJ-3 to HJ-2 (in downstream direction) is observed. This could be agreed with the fact that a remarkably wide river shoal with abundant phytoplankton in the upper reaches of the sampling site HJ-3, because the phytoplankton has more negative $\delta^{13}\text{C}$ values (around -30‰).

C/N ratio in the Xijiang river system covers a range between 5.2 and 12.6 (Table 2). It is higher in rainy season than in dry season, and relatively higher (11.1) during the flood process, reflecting the variations in the proportion of terrestrial/aquatic origins because of higher C/N ratios of terrestrial plants, and thus reflecting variations of soil erosion intensity with the change in hydrological conditions. In the mainstream of the Xijiang, C/N ratio (9.45 on average) is higher than in its tributaries. The low C/N ratios of the riverine POC relatively to that of terrestrial plants (Cifuentes et al., 1991) imply a significant contribution of aquatic sources, for example, phytoplankton growing in the river. Similar to $\delta^{13}\text{C}_{\text{POC}}$, C/N ratio in the Xijiang river system also shows a downstream decreasing trend in both summer and winter seasons, suggesting a downstream increase of aquatic source in the riverine POC (Fig. 4).

3.3 Soil POC, $\delta^{13}\text{C}_{\text{POC-soil}}$, and C/N

As shown in Table 3, weight percentage of POC in soil ranges between 0.21% and 2.10% with a mean of 0.85%. POC content displays a decreasing trend from the top to the bottom of the soil profile without significant seasonal variation. The soil POC content also shows a slight variation among these selected soil profiles due likely to different types of the land cover.

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The $\delta^{13}\text{C}$ value of soil POC ($\delta^{13}\text{C}_{\text{POC-soil}}$) in the Xijiang basin ranges from -25.5‰ to -19.6‰ , most of which are between about -22 and -24‰ . In average, it is -22.6‰ , consistent with previous studies (Pan et al., 2002; Chen et al., 2005) and the observed riverine $\delta^{13}\text{C}_{\text{POC}}$ values of the extreme flood. The $\delta^{13}\text{C}_{\text{POC-soil}}$ is slightly higher in December (winter) than in July (summer) by 0.6‰ in average. Basically, the $\delta^{13}\text{C}_{\text{POC-soil}}$ is lighter in the upper than in the lower of the soil profile, which can be explained by increased decomposition degree of organic matter along soil depth (Agren et al., 1996; Pan and Guo, 1999).

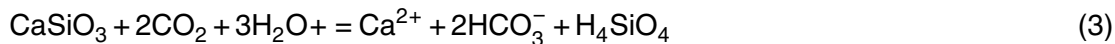
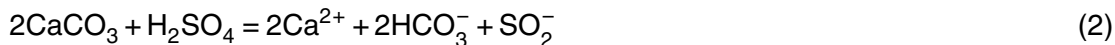
C/N ratio of the soil POC ranges from 7.3 to 12.5, with a mean of 10.2, and no prominent trend in both seasonal and spatial variations across the lower Xijiang Basin.

4 Discussions

4.1 $\delta^{13}\text{C}$ signature of riverine DIC and influence of in-river photosynthesis

4.1.1 Calculated $\delta^{13}\text{C}_{\text{DIC}}$ for rock weathering and observed riverine $\delta^{13}\text{C}_{\text{DIC}}$

The influence of carbonate and silicate weathering on the Xijiang hydrochemistry has been intensely investigated (Xu et al., 2007; Li et al., 2008; Sun et al., 2010). The rock chemical weathering processes can be represented in a simplified form as shown below.



CO_2 involved in the reactions is mainly from soil zone where $p\text{CO}_2$ values are 2–3 orders of magnitude higher than the atmosphere (Berner and Berner, 1996). Carbonate

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weathering via CO₂ is the most significant process in rock weathering (Eq. 1), producing equal contributions of both carbonate and soil CO₂ to the DIC, resulting in a mid δ¹³C value of the DIC between the two sources. Carbonate dissolution with sulfuric acid (Eq. 2) is also an important source of DIC for the Xijiang river system (Xu et al., 2007; Li et al., 2008), in which all the DIC is derived from carbonate, thus has identical δ¹³C values to the carbonate minerals. DIC from silicate rock weathering (Eq. 3) will have the same δ¹³C value as soil CO₂.

δ¹³C value of DIC from carbonate and silicate weathering can be calculated using the following end-member mixing model.

$$\delta^{13}\text{C}_{\text{DIC}} = f_{\text{cc}} \cdot \delta_{\text{cc}} + f_{\text{cs}} \cdot \delta_{\text{cs}} + f_{\text{sc}} \cdot \delta_{\text{sc}} \quad (4)$$

$$f_{\text{cc}} + f_{\text{cs}} + f_{\text{sc}} = 1 \quad (5)$$

where f represents fraction, subscripts cc, cs and sc denote the chemical weathering of carbonate with CO₂, carbonate with H₂SO₄, and silicate with CO₂ respectively.

In general, soil CO₂ converted from soil POC by microbial activities will nearly have no isotope fractionation (Cerling et al., 1995). For the Xijiang basin, the fractionation by this process has been accurately assessed to be -0.5~-1.5‰ (Pan and Guo, 1999). Using the soil POC δ¹³C signatures (-22.6‰, Table 3) and a mean fractionation value (-1‰), the δ¹³C of soil CO₂ in the Xijiang basin can be determined as -23.6‰. Given the δ¹³C of carbonate rocks in this region to be 0.4‰ (Li, 1994), the δ¹³C values of DIC from chemical weathering of carbonate with CO₂, carbonate with H₂SO₄, and silicate with CO₂ (δ_{cc}, δ_{cs} and δ_{sc}) are estimated to be -11.3‰, 0.4‰ and -23.6‰, respectively.

The percentage contributions of the three sources (processes) to DIC (f_{cc} , f_{cs} and f_{sc}) are listed in Table 2, which have been obtained from an earlier study using a widely employed mass balance approach with major ion chemistry data (Sun et al., 2010). The mean f_{cc} , f_{cs} and f_{sc} are respectively 62.1%, 15.5% and 22.4% for the wet season, and 53.0%, 17.3% and 29.7% for the dry season.

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With all the end-members evaluated, the $\delta^{13}\text{C}_{\text{DIC}}$ for the Xijiang river system can be quantitatively estimated using Eqs. (4) and (5). As shown in Table 2, it is averaged to be -12.4‰ in July (summer) and -13.1‰ in December (winter). According to a quantitative study of the same region (Sun et al., 2010), carbonate weathering contributes a greater fraction to DIC (with higher $\delta^{13}\text{C}_{\text{DIC}}$) in summer than in winter, thus leading to a negative $\delta^{13}\text{C}_{\text{DIC}}$ shift from summer to winter.

Compared to the measured $\delta^{13}\text{C}_{\text{DIC}}$ (see Table 2), the calculated value is 3.8‰ lower for winter (-13.1‰ vs. -9.3‰), 1.2‰ lower for summer (-12.4‰ vs. -11.2‰), and nearly identical for flood samples (-12.9‰ in mean). Moreover, the measured $\delta^{13}\text{C}_{\text{DIC}}$ shows an opposite seasonal trend to the calculated. All of these discrepancies may suggest that other in-river processes must be involved.

4.1.2 The influence of in-river photosynthetic POC on $\delta^{13}\text{C}_{\text{DIC}}$

The possible processes other than rock weathering influencing the $\delta^{13}\text{C}_{\text{DIC}}$ in rivers may include (1) carbonate precipitation; (2) exchange with atmospheric CO_2 ; (3) CO_2 directly comes from soil; and (4) in-river photosynthesis and respiration. Carbonate precipitation only causes 1‰ isotopic fractionation (Zhang et al., 1995) and is not a major process in the Xijiang river system (Li, 2009; Li et al., 2010). Due to higher $p\text{CO}_2$ in the river (Table 2), outgassing will dominate the CO_2 balance between atmosphere and river water, and the atmospheric invasion to the river water would be largely reduced. This may reduce DIC content in the water but has nearly no effect on isotopic composition of DIC (Palmer et al., 2001; Li et al., 2008). Under natural condition, DIC directly come from soil CO_2 is a minor fraction and can be neglected during carbonate and silicate weathering (Dreybrodt, 1988). Therefore, the possible major process is the in-river photosynthesis and respiration.

Respiration (decomposition) of organic matter produces ^{13}C -depleted CO_2 with a $\delta^{13}\text{C}$ close to that of organic matter, whereas photosynthetic uptake of DIC preferentially removes ^{12}C , leading to an enrichment of ^{13}C for the DIC (Yang et al., 1996). The

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relative efficiency of these two simultaneous actions depends on the hydrology and residence time of water in river (Mook and Tan, 1991). In winter (dry season), the riverine primary production plays a greater role due to lower TSS concentration and lower flow velocity, both of which favor the in-river photosynthesis. In summer (rainy season), particularly during flood, in-river photosynthesis is restricted by high turbidity and less residence time of river water. Therefore, this mechanism could explain the observed variation that $\delta^{13}\text{C}_{\text{DIC}}$ in the Xijiang river system is higher in winter than in summer.

The calculated $\delta^{13}\text{C}_{\text{DIC}}$ using the ion-based mass balance approach can imply only the initial carbon isotopic signature from chemical weathering. It will subject to in-river processes during transport, and change into the measured $\delta^{13}\text{C}_{\text{DIC}}$. Our data shows that all the measured $\delta^{13}\text{C}_{\text{DIC}}$ values for the four selected tributaries are higher than the calculated results (Table 2, Fig. 5), indicating the significance of the in-river processes for the modification of the $\delta^{13}\text{C}_{\text{DIC}}$.

4.2 Riverine $\delta^{13}\text{C}_{\text{POC}}$ and influence of in-river photosynthetic organic matter

Organic matter transported by rivers comprises a complex mixture of allochthonous and autochthonous sources. For most rivers, allochthonous fraction dominates the POC in amount and isotopic characteristics. Autochthonous source, however, may be overwhelming in some clean and slowly flowing waters (Ludwig et al., 1996; Gao et al., 2007). In previous discussion, a significant contribution of organic carbon from in-river aquatic plants to POC in the Xijiang river system has been suggested to be responsible for the seasonal and spatial variations in isotopic signature of DIC. It can be further examined from C/N ratios and carbon isotopes of POC.

Slow flowing speed and good clarity are favorable conditions for in-situ phytoplankton production and high proportion of autochthonous POC with lower values of $\delta^{13}\text{C}_{\text{POC}}$ and C/N ratio. River flow is commonly slower in lower stream than in the upper, and slower in dry season than in rainy season, coincident with the observed facts in the Xijiang river system that both $\delta^{13}\text{C}_{\text{POC}}$ and C/N decrease downstream and show prominent negative shift from summer to winter (Figs. 3 and 4).

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Generally, riverine transport of POC is complicated by multiple processes that occur within fluvial systems. In particular, it is hard to accurately determine the proportions of terrestrial or aquatic source in isotopic signature of the POC. Nevertheless, an extreme flood event occurred in the Xijiang basin provided a good reference for such an estimation. Due to drastically increased discharge and TSS concentrations (two orders higher than that in winter) in the flood event, the influence of riverine primary production can be neglected. The $\delta^{13}\text{C}_{\text{POC}}$ value for the extreme flood event ranges from -23.8‰ to -22.2‰ with a mean value of -23.0‰ , which is very close to the $\delta^{13}\text{C}$ of the soil profiles (-22.6‰ in average). Therefore, it can be considered as a typical $\delta^{13}\text{C}$ value of the regional terrestrial-sourced fraction in the riverine POC.

Riverine POC in the Xijiang river system is all depleted in ^{13}C with respect to $\delta^{13}\text{C}$ of soil organic matter, about 3.3‰ in winter, 2.1‰ in summer, and 0.1‰ for the flood event. This implies an all-year excess of production over respiration in the Xijiang river system, but close to zero during the flood event.

It is interesting that the seasonal variation trend of the difference between $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{13}\text{C}_{\text{POC-soil}}$ is totally in the opposite direction, but similar in amplitude, to that between the observed $\delta^{13}\text{C}_{\text{DIC}}$ and the calculated $\delta^{13}\text{C}_{\text{DIC}}$ (Fig. 5). This finding may indicate that the isotopic component of both DIC and POC pools is synchronously affected by riverine primary production, and suggests an important mechanism for carbon transformation in the river from DIC to POC.

As aquatic organisms such as algae and bacteria can grow by directly using bicarbonate (Spence and Maberly, 1985; Li et al., 2005) and the DIC contains large amount of old carbon derived from dissolution of old carbonates, it is reasonable for the modern riverine POC to have a much older apparent ^{14}C age as observed in the Xijiang (Wei et al., 2010), which will be discussed further in later section.

4.3 Evaluation of DIC-transformed organic carbon in riverine POC

The autochthonous and allochthonous proportions of carbon in the river can be quantitatively estimated by considering their $\delta^{13}\text{C}$ values as end-members in the following isotopic mass balance:

$$\delta_{\text{POC}} = f_{\text{au}} \cdot \delta_{\text{au}} + f_{\text{al}} \cdot \delta_{\text{al}} \quad (6)$$

$$f_{\text{au}} + f_{\text{al}} = 1 \quad (7)$$

where δ_{POC} , δ_{au} , δ_{al} are $\delta^{13}\text{C}$ values of the bulk sample, aquatic and terrestrial carbon end-members, respectively. f_{au} and f_{al} are fractional abundance of each of the two sources, respectively.

The data from sampling sites at the outlets of the Xijiang and its tributaries (XJ-1, GJ-1, HJ-1 and LD) are adopted for end-member δ_{POC} . As discussed previously, the observed $\delta^{13}\text{C}_{\text{POC}}$ (-23.0% in average) during the extreme flood event represents the terrestrial carbon with little riverine primary production, and can be used here for δ_{al} . Aquatic plants taking up DIC can impose ^{13}C fractionations of about 20–23‰ (Zhang et al., 1995; Clark and Fritz, 1997; Palmer et al., 2001). As $\delta^{13}\text{C}_{\text{DIC}}$ of the Xijiang river system ranges from -11.1% in summer to -9.3% in winter, the $\delta^{13}\text{C}$ value of primary production should be within the ranges between -29.3% and -34.1% . This is comparable to the measured $\delta^{13}\text{C}$ value of primary production in the headwater region of the Xijiang, which is -29.7% in average (Li, 2009). Because of higher percentage of carbonate area thus about 2‰ higher of $\delta^{13}\text{C}_{\text{DIC}}$ (-8%) in the upper Xijiang region, the $\delta^{13}\text{C}$ value of primary production (δ_{au}) in the lower Xijiang river system can be accordingly corrected to -32% .

The calculated results show that the percentage contribution of in-river primary production to riverine POC in the Xijiang, Guijiang, Hejiang and Luoding is respectively 7.1 %, 43.2 %, 36.4 %, 9.9 % in July, and 35.6 %, 47.3 %, 50.3 % and 40.1 % in December. It should be pointed out that some uncertainties may exist, because the $\delta^{13}\text{C}$ of

primary production is also affected by the changes in DIC concentration, $\delta^{13}\text{C}_{\text{DIC}}$ and the productivity of aquatic plants (Farquhar et al., 1982; Hayes, 1993).

4.4 Contributions of carbonate-sourced DIC to the riverine POC

The riverine autochthonous POC, which is assumingly derived from DIC, comes from carbonate source and soil CO_2 source through rock weathering. If all the major chemical reactions associated with their contributions (in percentage) have been evaluated (see Table 2) during carbonate rock weathering, we can quantitatively estimate how much carbonate-sourced carbon in the riverine POC.

For a first order estimation, we assume all the carbon of primary production is derived from carbonate and silicate weathering, but only carbonate weathering can introduce rock carbon into DIC. As discussed earlier, carbonate weathering includes two major processes. (1) Carbonate dissolution by carbonic acid: half amount of DIC is from soil CO_2 , and the other half is from carbonate mineral. (2) Carbonate dissolution by sulfuric acid: the DIC produced is all from carbonate mineral. Therefore, the proportion of DIC released from carbonate mineral (f_{carb}) in all the DIC produced by chemical weathering can be expressed as the following equation:

$$f_{\text{carb}} = 0.5f_{\text{cc}} + f_{\text{cs}} \quad (8)$$

Using the data of f_{cc} and f_{cs} listed in Table 2, the corresponding f_{carb} can be calculated. Further, the fraction of carbon from carbonate mineral in the riverine POC ($f_{\text{carb/POC}}$) can be obtained using the following equation.

$$f_{\text{carb/POC}} = f_{\text{carb}} \cdot f_{\text{au}} \quad (9)$$

Results show that the contribution of carbon from carbonate mineral to riverine POC in Xijiang, Guijiang, Hejiang and Luoding is 3.6%, 20.5%, 15.9% and 3.4% in rainy season, and 17.3%, 19.9%, 22.1% and 12.3% in dry season, respectively.

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4.5 Influence of carbonate-sourced DIC on apparent ^{14}C age of riverine POC

DIC from carbonate rock is ^{14}C -free ($\Delta^{14}\text{C} = -1000\text{‰}$), so the involvement of rock-sourced DIC in riverine POC will exert a great influence on the ^{14}C age information of POC. If assuming the riverine POC is composed of two parts, one from carbonate rock with proportions as the above computed results for the dry season, and the other from modern carbon with $\Delta^{14}\text{C} = 80\text{‰}$, then the mixing value of $\Delta^{14}\text{C}$ should be -107‰ , -135‰ , -159‰ and -53‰ for the Xijiang, Guijiang, Hejiang and Luoding, respectively. This implies that even the POC transported by river is totally formed in modern time, it may exhibit a notably older ^{14}C age.

The ^{14}C values of monthly POC in the Xijiang have been reported ranging from -425‰ to -201‰ with lower value (older ^{14}C age) in dry season and higher value (younger ^{14}C age) in rainy season (Wei et al., 2010). Some studies suggested that the aged carbon in rivers is considered to be mainly from sedimentary rocks or vascular plant material stably preserved in deep soil (Petsch et al., 2001, 2003; Berner, 2004; Bouchez et al., 2010). We argue that such a mechanism can hardly explain the fact of older ^{14}C age of POC in dry/winter season than in rainy/summer season observed in the Xijiang river system, because deep soil erosion is much weaker thus less old organic carbon being incorporated into riverine POC in dry season and the POC would have a younger ^{14}C age. Nevertheless, such observed seasonal pattern is consistent with the seasonal pattern of carbonate-sourced DIC in the POC; carbonate-sourced DIC contributes a larger proportion in dry season than rainy season. Therefore, our study argues that carbonate derived DIC may be highly responsible to the older ^{14}C age effect of riverine POC, especially for carbonate dominated rivers. Furthermore, this could also provide some reason for the “old carbon reservoir” effect in lake sediment and ocean floor sediment.

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4.6 Contributions of DIC-POC transformation of Xijiang to the sink of atmospheric CO₂

The annual flux of POC in the Xijiang is estimated to be $4.27 \times 10^5 \text{ tyr}^{-1}$ ($1.21 \text{ t km}^{-2} \text{ yr}^{-1}$) (Sun et al., 2007), and 82 % of this flux is transported during June and July (rainy season). Based on the proportion of carbon from carbonate rock in POC, 3.6 % in rainy season and 17.3 % in dry season, the annual flux of DIC from carbonate rock transformed into POC can be then estimated to be $2.59 \times 10^4 \text{ tyr}^{-1}$ ($0.073 \text{ t km}^{-2} \text{ yr}^{-1}$), accounting for 3 % of the annual flux of CO₂ consumed by silicate weathering in the region (Sun et al., 2010). The CO₂ consumed by carbonate weathering will return to the atmosphere by carbonate precipitation in the oceans, so the carbonate weathering has no effect in regulating the atmospheric CO₂ at a long-term scale. However, this study reveals that a considerable part of carbonate rock-sourced DIC has been transformed into POC by riverine primary production. Since this kind of POC, at least partly, will be ultimately buried, it forms a riverine “biological pump” (Longhursta and Harrison, 1989; Tortell et al., 2008) and a significant sink of the atmospheric CO₂ in the global carbon cycle, that is largely ignored (Liu et al., 2010).

5 Conclusions

DIC and POC, the two carbon pools in the Xijiang river system are dominated respectively by rock chemical weathering and soil erosion, and are also significantly affected by in-river primary production. This study employed an isotopic method with observed data and distinguished the aquatic and terrestrial fractions in the riverine POC. The percentage contribution of the riverine primary production to riverine POC in the Xijiang, Guijiang, Hejiang and Luoding is respectively 7.1 %, 43.2 %, 36.4 %, 9.9 % in rainy season (July), and 35.6 %, 47.3 %, 50.3 % and 40.1 % in dry season (December). Based on the stoichiometry of carbonate rock weathering processes, we quantitatively estimated the contribution of carbonate-sourced carbon to the riverine POC in Xijiang and its tributaries. In the riverine POC, the fractions transformed from carbonate-sourced

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DIC through photosynthesis of aquatic organisms range from 3.4% to 20.5% in rainy season, and 12.3% to 22.1% in dry season, which implies an important sink of atmospheric CO₂ in river systems and should be taken into account in global carbon cycle. In addition, the riverine DIC transformed into POC by aquatic photosynthesis may introduce a great portion of old carbon into aquatic organic matter, thus is another factor responsible for abnormally older ¹⁴C age of the sediments deposited in aquatic environments.

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Table 1. Catchment characteristics of the Xijiang, Guijiang, Hejiang and Luoding rivers.

Basin	Area km ²	Flow km ³ yr ⁻¹	Slope (‰)	Carb (%)	Sil (%)	Forest	Grass	Farmland	Population people km ⁻²
Xijiang	351 535	218	0.86	43	58	56	12	19	228
Guijiang	18 210	17	0.43	51	49	58	33	7	262
Hejiang	11 590	8	0.58	23	77	65	17	13	179
Luoding	3164	3	0.87	8	92	51	17	12	254

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Table 2. Measured and calculated results of water geochemistry in the lower Xijiang river and its tributaries.

Sample	Date dd-mm	pH	Tem (°)	Flow (m ³ s ⁻¹)	TSS (mg l ⁻¹)	POC	C/N	DIC (mmol l ⁻¹)	pCO ₂	f _{cc} (%)	f _{cs}	f _{sc}	δ ¹³ C _{DIC} (‰)	δ ¹³ C _{DIC-C}	δ ¹³ C _{POC}
XJ-1	17-Apr	7.57	21.9	2020	3.69	0.05	7.56	1.57	2.60						
XJ-2	17-Apr	7.83	21.7	2020	2.33	0.03	9.13	1.52	2.89						
XJ-3	17-Apr	7.79	21.6	2020	7.12	0.10	8.87	1.41	2.88						
XJ-4	17-Apr	7.86	21.5	2020	8.90	0.12	8.22	1.59	2.90						
XJ-5	17-Apr	7.82	21.8	2020	7.28	0.10	9.39	1.67	2.84						
GJ-1	14-Apr	7.41	17.8	80	8.57	0.10	7.70	1.46	2.50						
GJ-2	14-Apr	7.53	18.6	80	1.36	0.03	8.04	1.51	2.59						
GJ-3	14-Apr	7.89	18.5	80	1.78	0.04	8.06	1.54	2.92						
GJ-4	14-Apr	8.04	18.7	80	1.66	0.03	8.08	1.67	3.05						
HJ-1	16-Apr	7.02	21.5	117	1.18	0.03	8.65	0.86	2.31						
HJ-2	16-Apr	7.07	20.8	117	4.50	0.08	7.95	1.14	2.25						
HJ-3	16-Apr	7.13	20.6	117	1.31	0.03	8.64	1.16	2.30						
LD	18-Apr	7.64	22	26	9.31	0.15	6.93	1.57	2.66						
XJ-1	2-Jul	7.35	25	26 050	172.09	2.13	11.63	1.35	2.44						
XJ-2	2-Jul	7.33	25.1	26 050	174.33	2.37	12.00	1.42	2.39						
XJ-3	2-Jul	7.22	25	26 050	146.75	1.88	11.29	1.35	2.31						
XJ-4	2-Jul	7.21	25	26 050	153.72	1.86	11.34	1.39	2.28						
XJ-5	2-Jul	7.22	25.1	26 050	180.90	2.42	12.56	1.50	2.26						
GJ-1	1-Jul	7.14	24.4	809	50.42	0.83	11.18	0.93	2.38						
GJ-2	1-Jul	7.14	24.4	809	48.20	0.90	10.73	0.90	2.40						
GJ-3	1-Jul	7.16	24.4	809	28.94	0.52	10.44	0.93	2.41						
HJ-1	30-Jun	6.94	24.9	97	15.93	0.23	8.93	0.68	2.31						
HJ-2	30-Jun	7.37	25.1	97	11.89	0.20	9.92	0.98	2.59						
HJ-3	30-Jun	7.32	24.5	97	6.70	0.17	9.89	0.98	2.54						
LD	27-Jun	7.38	25	76	52.32	0.55	8.75	0.93	2.62						
XJ-1	13-Jul	7.09	26	7920	39.60	0.57	10.88	1.87	2.03	68.9	16.6	14.5	-11.1	-11.4	-23.4
XJ-2	13-Jul	7.28	26	7920	48.74	0.81	10.38	1.92	2.21	62.9	20.6	16.4	-10.9	-11.1	-23.3
XJ-3	13-Jul	7.39	25.8	7920	47.88	0.81	10.20	2.00	2.31	68.3	17.6	14.1	-11.4	-11.2	-23.4
XJ-4	13-Jul	7.65	25.7	7920	44.61	0.69	10.50	2.06	2.56	69.1	16.0	14.9	-11.1	-11.5	-23.0
XJ-5	13-Jul	7.98	26.7	7920	41.82	0.73	10.50	2.31	2.84	75.8	10.5	13.7	-10.9	-12.0	-22.9
GJ-1	15-Jul	7.57	25.8	415	7.15	0.41	7.73	1.24	2.69	63.1	14.7	22.2	-11.2	-12.5	-26.9
GJ-2	15-Jul	7.96	26	415	9.27	0.36	8.48	1.28	3.07	71.3	9.2	19.5	-11.3	-12.8	-26.7
GJ-3	15-Jul	7.96	25.5	415	5.42	0.22	8.09	1.44	3.02	73.7	9.3	17.0	-11.1	-12.5	-25.8
GJ-4	15-Jul	7.96	25.2	415	5.26	0.23	9.08	1.45	3.02	50.2	27.6	22.2	-10.9	-11.0	-25.3
HJ-1	14-Jul	7.95	25.8	204	5.98	0.22	7.38	0.97	3.17	48.6	15.6	35.8	-11.2	-14.0	-26.3
HJ-2	14-Jul	7.72	25.3	204	5.33	0.21	8.29	1.24	2.84	59.2	15.0	25.8	-10.8	-12.9	-25.1
HJ-3	14-Jul	7.89	25.5	204	1.67	0.14	8.20	1.28	3.00	58.6	17.1	24.3	-10.0	-12.5	-25.8
LD	19-Jul	6.93	24.3	20	19.01	0.26	6.73	1.24	2.05	39.2	15.9	44.9	-13.1	-15.1	-23.9
XJ-1	13-Dec	7.68	20.2	1610	5.55	0.12	6.08	2.07	2.62	51.0	22.3	26.7	-9.0	-12.1	-26.2
XJ-2	13-Dec	7.8	19.8	1610	3.71	0.12	7.43	2.18	2.72	56.7	20.2	23.0	-9.0	-11.9	-24.9
XJ-3	13-Dec	7.74	19.5	1610	6.21	0.15	6.76	2.23	2.65	56.7	21.0	22.4	-9.5	-11.8	-25.0
XJ-4	13-Dec	7.83	19.6	1610	5.81	0.17	6.84	2.10	2.76	60.8	16.8	22.4	-9.1	-12.3	-24.1
XJ-5	13-Dec	7.84	19	1610	8.72	0.18	7.39	2.26	2.75	57.8	20.8	21.4	-8.5	-11.7	-23.5

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Table 2. Continued.

Sample	Date dd-mm	pH	Tem (°)	Flow (m ³ s ⁻¹)	TSS (mg l ⁻¹)	POC	C/N	DIC (mmol l ⁻¹)	pCO ₂	f _{cc} (%)	f _{cs}	f _{sc}	δ ¹³ C _{DIC} (‰)	δ ¹³ C _{DIC-C}	δ ¹³ C _{POC}
GJ-1	16-Dec	7.92	19.2	18	14.73	0.22	5.96	1.53	2.99	58.4	11.2	30.4	-9.4	-13.9	-27.3
GJ-2	16-Dec	8.03	19.2	18	1.85	0.05	7.74	1.74	3.05	61.0	10.7	28.3	-9.4	-13.7	-27.1
GJ-3	16-Dec	8.19	19.2	18	2.64	0.07	8.01	1.74	3.21	68.9	9.9	21.1	-9.6	-12.9	-26.3
GJ-4	16-Dec	8.04	19.6	18	1.87	0.05	8.63	1.77	3.05	63.5	10.9	25.7	-10.0	-13.4	-26.3
HJ-1	14-Dec	7.97	19.2	167	0.40	0.01	9.16	1.14	3.16	42.8	22.4	34.7	-9.3	-13.1	-27.5
HJ-2	14-Dec	8.06	18.6	167	2.87	0.09	8.17	1.58	3.12	38.2	25.3	36.5	-9.4	-12.9	-25.9
HJ-3	14-Dec	8.02	18.7	167	1.17	0.04	9.54	1.36	3.15	47.9	19.4	32.7	-8.3	-13.2	-26.7
LD	19-Dec	7.41	14.8	40	6.84	0.15	5.20	0.95	2.70	30.7	15.1	54.2	-11.1	-16.3	-26.6
F1	22-Jun		25.3	49 300	360.77	6.60	10.67	1.45					-13.2		-23.5
F2	22-Jun		25.3	51 800	802.02	13.31	11.62	1.42							
F3	23-Jun		25.2	54 600	502.33	7.13	11.04	1.33					-13.0		-23.0
F4	23-Jun		25.2	55 000	380.55	5.29	10.24	1.26							
F5	24-Jun		25.3	51 700	554.86	8.32	11.66	1.25					-12.8		-22.6
F6	24-Jun		25.3	50 500	581.14	8.54	11.43	1.41							
F7	25-Jun		25.7	47 950	319.06	4.28	11.05	1.48					-13.9		-23.2
F8	25-Jun		25.7	45 400	307.47	4.37	9.95	1.51							
F9	27-Jun		25.8	33 800	235.8	2.97	11.02	1.53					-12.1		-22.2
F10	28-Jun		25.3	27 900	195.64	3.09	11.06	1.58							
F11	28-Jun		25.1	27 200	161.32	2.44	10.59	1.60					-12.0		-23.8

F1–F11 are samples taken during the flood event.

pCO₂ is the negative logarithm of the partial pressure of CO₂ in water calculated using PHREEQC.

f_{cc}, f_{cs} and f_{sc} represent the proportions of chemical weathering of carbonate with CO₂, carbonate with H₂SO₄, and silicate with CO₂, respectively. See the text for detail.

δ¹³C_{DIC-C} is the theoretically calculated δ¹³C value of DIC using an ion-based mass balance model.

Table 3. POC, $\delta^{13}\text{C}$ and C/N in the soil profiles in the lower Xijiang basin.

Sample*	Month	Catchment	POC (%)	C/N	$\delta^{13}\text{C}$ (‰)	Land cover
S1-T	July	Xijiang	1.11	8.0	-23.5	Shrub, grass
S1-M	July		0.36	9.1	-21.7	
S1-B	July		0.41	8.6	-20.7	
S1-T	Dec	Xijiang	0.99	8.6	-23.7	Forest, shrub
S1-M	Dec		0.39	11.0	-22.2	
S1-B	Dec		0.36	9.5	-21.9	
S2-T	July	Xijiang	1.69	11.1	-24.6	Forest, shrub
S2-M	July		1.10	12.4	-22.3	
S2-B	July		0.74	10.3	-22.1	
S3-T	July	Guijiang	1.45	8.2	-24.4	Shrub, grass
S3-M	July		0.91	10.0	-21.8	
S3-B	July		0.21	12.5	-22.0	
S3-T	Dec	Guijiang	1.85	9.3	-23.8	Forest, shrub, grass
S3-M	Dec		1.03	9.1	-22.1	
S3-B	Dec		0.26	12.3	-20.5	
S4-T	July	Guijiang	1.91	8.7	-24.9	Forest, shrub, grass
S4-M	July		1.40	11.7	-24.4	
S4-B	July		0.99	10.8	-22.8	
S5-T	July	Hejiang	1.07	10.3	-24.3	Forest, shrub, grass
S5-M	July		0.71	9.9	-24.9	
S5-B	July		0.63	12.1	-21.9	
S5-T	Dec	Hejiang	0.74	9.8	-23.1	Shrub, grass
S5-M	Dec		0.53	10.4	-23.2	
S5-B	Dec		0.23	11.5	-21.1	
S6-T	July	Hejiang	2.10	10.6	-23.1	Shrub, grass
S6-M	July		1.62	11.5	-23.5	
S6-B	July		0.93	11.1	-19.8	
S7-T	July	Luoding	0.64	10.0	-22.4	Grass
S7-M	July		0.45	8.3	-21.8	
S7-B	July		0.24	11.2	-19.7	
S7-T	Dec	Luoding	0.57	10.0	-22.0	Forest, grass
S7-M	Dec		0.45	8.1	-22.4	
S7-B	Dec		0.33	11.9	-19.8	
S8-T	July	Luoding	1.10	9.9	-25.5	Forest, grass
S8-M	July		0.76	7.3	-22.7	
S8-B	July		0.39	10.6	-21.5	

* Letters T, M, B denote samples are taken from the top (0–5 cm), middle (15–20 cm) and bottom (30–50 cm) of the soil profile, respectively.

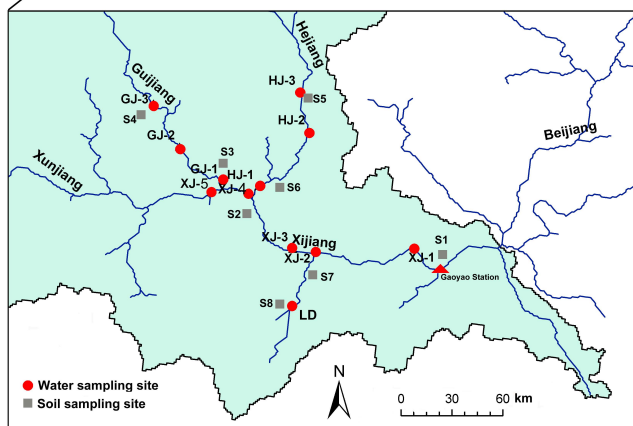
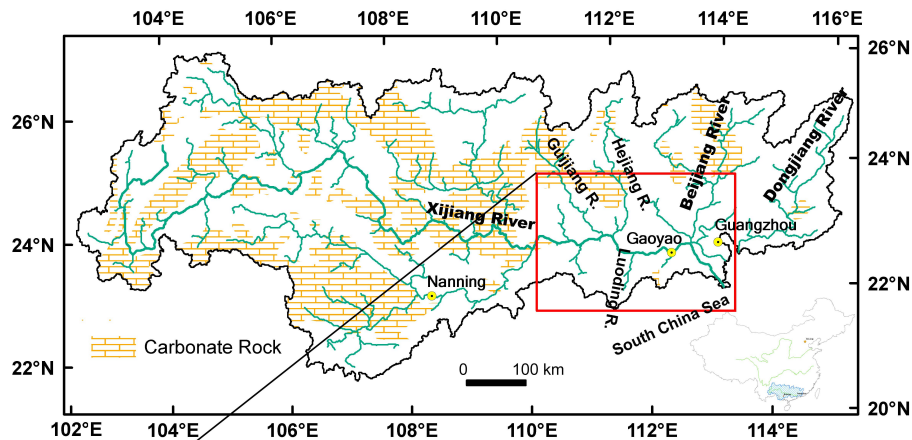


Fig. 1. Map showing the Zhujiang basin and sampling sites.

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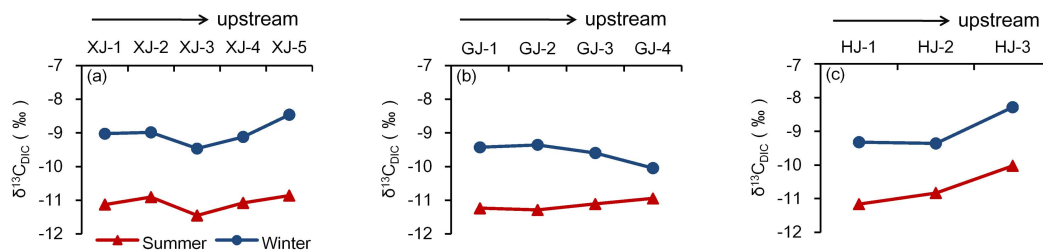


Fig. 2. Variations of $\delta^{13}\text{C}_{\text{DIC}}$ along the Xijiang (a), Guijiang (b) and Hejiang (c) rivers.

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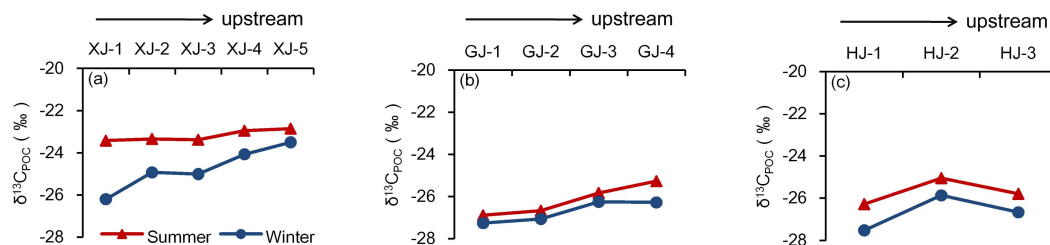


Fig. 3. Variations in $\delta^{13}\text{C}_{\text{POC}}$ along the Xijiang (a), Guijiang (b) and Hejiang (c) rivers.

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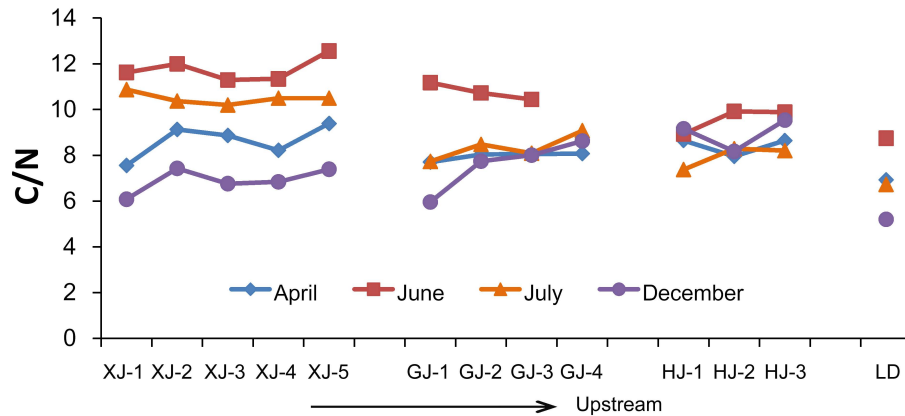


Fig. 4. Variations in C/N ratios along the Xijiang (XJ), Guijiang (GJ), Hejiang (HJ) and Luoding (LD) rivers.

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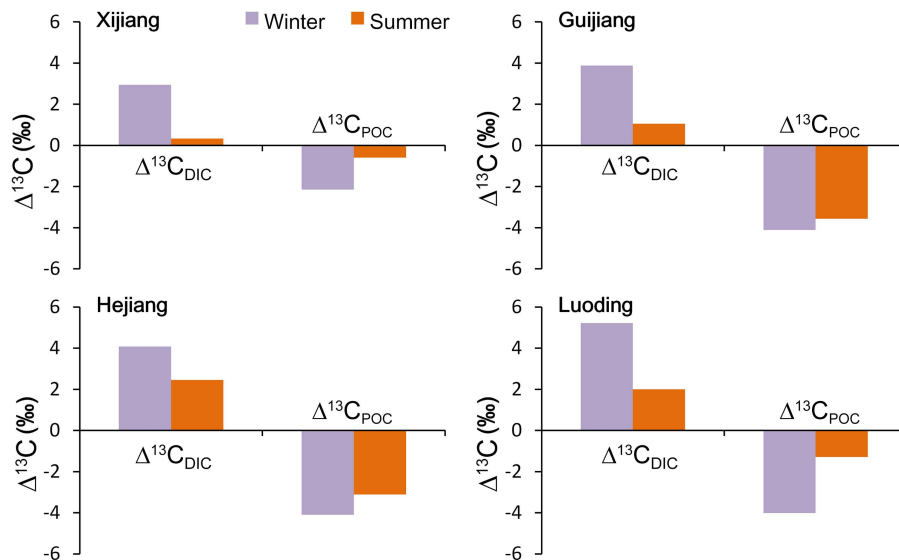


Fig. 5. Difference between the measured and the calculated $\delta^{13}\text{C}_{\text{DIC}}$ ($\Delta^{13}\text{C}_{\text{DIC}} = \delta^{13}\text{C}_{\text{DIC}} - \delta^{13}\text{C}_{\text{DIC-C}}$) and difference between riverine $\delta^{13}\text{C}_{\text{POC}}$ and soil $\delta^{13}\text{C}_{\text{POC}}$ ($\Delta^{13}\text{C}_{\text{POC}} = \delta^{13}\text{C}_{\text{POC}} - \delta^{13}\text{C}_{\text{POC-soil}}$).

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