An assessment of the riverine carbon flux of the Xijiang River during the past 50 years

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Abstract

Most Chinese rivers have experienced great changes in discharge and sediment during the past 50 years. This study attempts to examine the long-term dynamics of riverine carbon flux in the Xijiang River by applying the relationships between riverine carbon concentrations and discharge or sediment to the historical discharge and sediment records. Results show that POC (particulate organic carbon) flux in the Xijiang has experienced a decreasing trend, caused by reduced sediment supply. However, DOC (dissolved organic carbon) shows an increasing trend. Human activities including reservoir/dam construction and domestic/agricultural effluents may intensify the upward trend of DOC. DIC (dissolved inorganic carbon) shows a declining trend with a very small slope. Variation of DIC accords well with discharge/precipitation. For total carbon flux, a more or less constant, or very small decreasing trend is displayed.

1. Introduction

Riverine carbon flux plays an important role in the carbon cycle on Earth because it links the terrestrial and ocean reservoirs of carbon. About 1015 g of carbon is exported by rivers each year from the land to the ocean (Degens et al., 1991), which is similar in magnitude to the anthropogenic fluxes of fossil fuel combustion and forest fires and the global net flux between the oceans and the atmosphere (Rotty, 1983; Meybeck and Vorosmarty, 1999). Riverine carbon transport is directly affected by rainfall, stream flow and sediment load, which have experienced great changes during the past decades. Rainfall showed a global upward trend through the 20th century caused by climate change, although large areas were characterized by decreasing trends (Hulme et al., 1998; Trenberth, 1998; Osborn et al., 2000; IPCC, 2001; Pasquini and Depetris, 2007). In most Chinese river basins, recent trends in hydrological changes related to climate factors and human activities have been reported (Lu, 2004). For example, sediment in the Yangtze basin declined significantly with obvious increasing trends in discharge and precipitation (Ren et al., 2002; Ye et al., 2004; Qin et al., 2005). In particular, completion of the Three Gorges Dam in the 1990s, the world largest dam, has caused significant decrease in sediment discharge (Yang et al., 2003, 2006; Chu and Zhai, 2006). In the Huanghe basin, there is a progressive decrease in both water and sediment discharges, partly due to the decreased precipitation and human activities including reservoir construction, water abstraction, and soil conservation (Milliman, 1997; Yang et al., 1998; Xu, 2003; Walling, 2006; Wang et al., 2006). Similarly in the Zhujiang basin, an obvious decrease in sediment flux has been found during the last 50 years, particularly since the 1990s (Zhang et al., 2008) with slight upward trends in precipitation and water discharge.

Great attention has been paid to detect long-term patterns of rainfall, water discharge and sediment load (Walling, 1995, 1997; Lu et al., 2003; Lu, 2004; Zhang et al., 2008), but very few studies have investigated how the hydrological changes further affect the riverine carbon transport. Information on historical variations of riverine carbon is scarce due to lack of available long-term data. This study attempts to examine the long-term dynamics of riverine carbon flux in the Xijiang river, the largest branch of the Zhujiang. First, the relationships of riverine carbon, including particulate organic carbon (POC), dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC), with water discharge or sediment demonstrated by a set of measured data from the lower Xijiang basin are described. Then, these relationships and detailed historical records of discharge and sediment are applied in an assessment of long-term variations of the riverine carbon flux of the Xijiang basin.
2. Background

The Zhujiang river is the second largest river in China and the 13th largest river in the world in terms of annual water discharge (336 km³/year), and is the largest contributor of dissolved materials and sediment to South China Sea (SCS). The Zhujiang basin is located south of 24° N and stretches for 2200 km with a catchment area of 0.45 × 10⁶ km² (PRWRC, 1991), entirely in a region of subtropical to tropical monsoon climate zones (Fig. 1). It is one of few evergreen forest areas in the mid-lower latitudes of the northern hemisphere. The mean annual temperature and precipitation are 14–22 °C and 1200–2200 mm, respectively. Heavy rainfall occurs mainly in June–August, accounting for 50–60% of the annual water discharge.

The Zhujiang river system is fed by the Xijiang (West river), Beijiang (North river), and Dongjiang (East river). The Xijiang is the main stem of the Zhujiang, accounting for 77.8% and 63.9% in drainage area and annual discharge of the Zhujiang, respectively. As one of the most prosperous regions in China, the Xijiang basin has been subjected to rapid industrialization and urbanization with a substantial increase in population.

3. Methods

3.1. Sampling and lab analyses

To obtain the relationships of POC, DOC and DIC with discharge and sediment, seasonal sampling was conducted on 13 sampling sites, covering the lower Xijiang trunk and its 3 major tributaries there (Fig. 1). Samples were collected in April, May (yearly-normal flow), June (flood event), July (yearly-higher flow) and December (yearly-lower flow). In each site, samples were taken from middle depth of the water column in the central stream. In addition, monthly sampling was conducted throughout 2005 at the outlet of the Xijiang basin, the Gaoyao Hydrometric Station, where depth-integrated samples were taken from 11 columns along a cross-section at each time of sampling.

On the day of sampling, the collected samples were filtered by vacuum filtration through two pieces of 0.7 um Whatman GF/F filter papers (47 mm in diameter) that were pre-weighed after combustion at 450 °C for 6 h. After filtration, one filter paper was dried at 103 °C for 24 h to calculate TSS (total suspended sediment) and the other was dried at 50 °C for 24 h and kept in plastic bag for further POC analysis. The filtrates were collected in a 100-ml amber glass bottle for DOC analysis. Prior to sampling, bottles to be used were pre-washed by immersion in acid solution for 24 h and rinsed with distilled water and rinsed again in the field with filtrates for 3 times. All the samples were kept in a refrigerator (≤4 °C) and in darkness until analysis.

HCO₃⁻ (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 was analyzed by Perkin Elmer-2400 II (Elemental Analyzer CHNS/O) with analytical errors of less than 0.3%. DOC was measured using TOC analyzer (Shimadzu TOC-Vwp) with an analytical error less than 2%.

3.2. Data analysis

The monitoring and laboratory measured results for 2005 were used to establish the quantitative relationships between carbon content of various carbon types (POC, DOC and DIC) and TSS or water discharge. For approaching the long-term variation pattern of the riverine carbon flux in the Xijiang river, the historic record at the Gaoyao hydrometric station since 1956 was used for calculation (Fig. 2). The data were obtained through daily monitoring of the water discharge and measurement of daily water samples using a strictly sampling method (the samples were synthesized at 3 different depths on 11 columns across the river). The monthly data to be used in the calculation are obtained through compounding daily data.

4. Relationships between riverine carbon and water discharge or TSS

4.1. Modern observations of riverine carbon in the lower Xijiang

Sample analyses show that suspended particulates in the lower Xijiang and its tributaries are extremely variable through a year,
varying between 0.40 and 180.90 mg/L. POC concentrations in the Xijiang river system vary between 0.03 and 2.42 mg/L. The discharge-weighted mean value calculated from monthly samples for the Gaoyao hydrometric station is 1.73 mg/L, constituting 1.0–3.0% of the TSS. POC are closely correlated with TSS concentrations (Fig. 3), suggesting the source of POC in the Xijiang is mainly terrestrial.

The mean values of DOC concentration in the lower Xijiang is 1.36 mg/L, notably below the values of most large world rivers (Spitzy and Leenheer, 1991). The maximum concentration attained in April and May, and the minimum was found in late June after a large flood event. In contrast to POC, the DOC concentrations varied spatially and temporally within a smaller range. The ratio of DOC to POC (DOC/POC) is an environmental and hydrological characteristic for a drainage basin. It varies widely in the lower Xijiang river systems with a range of 0.53–98.02. DOC/POC is extremely low in flood season (June and July).

Riverine DIC in the Xijiang is predominated by HCO₃⁻/CO₂, and thus HCO₃⁻ can be used as an approximation of the DIC in this study. The HCO₃⁻ concentrations in the lower Xijiang river system range from 41 to 141 mg/L with a mean value of 91 mg/L. As has been discussed previously (Gao et al., 2001), HCO₃⁻ accounts for more than 40% of the TDS in the Xijiang river, and more than 80% is derived from carbonate weathering. Seasonally, the highest concentrations of HCO₃⁻ occur in December and the lowest in June. In December, the regional precipitation is at the lowest level of a year. Spatially, DIC contents are the highest in the Xijiang stem, followed by its tributaries of Guijiang and Hejiang, and the lowest in Luoding, well consistent with the order of exposed carbonate area in the subbasins (Fig. 1), demonstrating that DIC in the Xijiang is dominated by chemical weathering.

4.2. Quantitative relationships between riverine carbon and discharge/sediment

As shown in Figs. 3–5, the following equations have been obtained from the data of 2005 for the Xijiang river.

\[
P_{OC} = 0.0136 \times \text{TSS} + 0.0627 \quad (R^2 = 0.969, \ n = 64) \quad (1)
\]

\[
\frac{\text{DOC}}{\text{POC}} = 43.727 \times \text{TSS}^{-0.815} \quad (R^2 = 0.864, \ n = 64) \quad (2)
\]

\[
C_{DIC} = 3.1515 \times Q_i^{-0.059} \quad (R^2 = 0.102, \ n = 436) \quad (3)
\]

As mentioned earlier, the Gaoyao hydrometric station has monitored the discharge, sediment and other water quality data since 1956 (Fig. 2). This allows examination of the long-term dynamics of riverine carbon flux by using the relationships between riverine carbon contents and discharge or sediment. According to Eq. (1), Eq. (4) can be derived and is used to estimate the POC annual flux.
5. Results and discussion

The annual fluxes of POC, DOC and DIC for each year during 1954–2005 for the Xijiang river are calculated using the above equations and the monthly discharge and sediment data monitored at the Gaoyao hydrometric station. It is estimated that POC flux ranges from $1.65 \times 10^8$ kg (1963) to $10.0 \times 10^8$ kg (1968) with a mean of $5.83 \times 10^8$ kg during the 1957–2004. From Fig. 6a, POC flux has experienced a decrease trend with a slight upward trend in discharge. Due to the human disturbances including reforestation project and reservoir/dam construction (Zhang et al., 2008), sediment transport of the Xijiang has dramatically decreased during this period, particularly in the 1990s. Since POC in the Xijiang is mainly terrestrial origin, there should be also a reduced quantity of particulate organic matter with reduced sediment supply.

DOC flux shows an increasing trend through the past 50 years (Fig. 6b). The averaged annual DOC flux for 1957–2004 is $2.81 \times 10^8$ kg, with a maximum value of $4.74 \times 10^8$ kg occurred in 1994 and the minimum value of $1.55 \times 10^8$ kg occurred in 1963. According to Eq. (3), the increased DOC is directly caused by the dramatically decreased TSS and POC. As well, some other human disturbances may also affect the DOC transport. By 2005, more than 200 large and medium reservoirs with a total capacity of 20.6 billion m$^3$ have been constructed in the Xijiang basin (PRWRC website http://www.pearlwater.gov.cn). Reservoir building can result in lower turbidity and velocity of river water, which will improve the conditions for photosynthesis and thus contribute more DOC to the water (Spitzly and Leenheer, 1991). In addition, the increasing nutrient loading from the domestic and agricultural effluents may also lead to increased contribution of DOC. From the above discussion, with the human activities becoming large and intensive in the future, they should further intensify the increased trend of the DOC in the Xijiang as estimated using the modeling method.

DIC flux displays a slowly decreasing trend (Fig. 6c), ranging from $22.6 \times 10^8$ kg (1963) to $78.6 \times 10^8$ kg (1997) with a mean of $45.0 \times 10^8$ kg. In general, DIC flux in the Xijiang varies in accord well with discharge, suggesting it was controlled by the natural processes, while reservoir/dam construction that induced the dramatic decrease of TSS should not have much impact. DIC in the Xijiang is dominantly sourced from chemical weathering, which is highly sensitive to environmental change, as the drainage basin is a typical carbonate region.

DIC is the predominant component of the riverine carbon in the Xijiang, and thus dominates the TC variation over the history. It shows a very slight decline through the past 50 years (Fig. 6d). The maximum TC flux is $90.8 \times 10^8$ kg (1997) and the minimum is $25.8 \times 10^8$ kg (1963), having a mean of $53.5 \times 10^8$ kg. During the period of 1957–2004, DIC, POC and DOC account for 70.7% (mean: 90.7%), 18.9% (mean: 10.9%) and 2.4% (mean: 5.5%) of TC respectively.

As the relationships between carbon and discharge/TSS are established from the modern observations, they may not be precisely suitable for the past 50 years and require further refinement. However, these estimations and the long-term variation trends displayed can be matched to the significant changes in the history of the Xijiang river. In addition, DIC is the dominant component of the riveric TC (total carbon) in the Xijiang, which is mainly affected by carbonate weathering and thus rainfall/water discharge (rather than other factors such as long-term suffering under acid rain). Furthermore, the DIC flux is calculated from direct measurement results rather than the DIC-discharge relationship-based calculation for most years. Also, the strong POC-TSS relationship expressed by Fig. 3 and Eq. (1) involves samples of three subcatchments that largely differ in environmental conditions, implying that the second major component, POC, in the Xijiang is highly correlated with TSS and other factors might not be so significant. Such a good POC-TSS relationship has been observed by many other studies (e.g., Kempe et al., 1991; Gao et al., 2007; Ni et al., 2008; Zhang et al., 2005). As POC and DIC components account for over 90% of TC in the Xijiang river, and are basically constrained, the estimate of the carbon flux over history could be fairly a reliable approach, although DOC, a minor component (accounting for less than 10%) of TC, is difficult to constrain.

\[ F_{\text{POC}} = \sum_{i=1}^{12} Q_i \times C_{\text{POC}} = \sum_{i=1}^{12} Q_i \times (0.0136 C_{\text{TSS}} + 0.0627) \]  
(4)

Where, \( F_{\text{POC}} \) represents the annual flux of POC. \( Q_i \) is the total water discharge of the \( i \)th month through a specific year. \( C_{\text{POC}} \) and \( C_{\text{TSS}} \) are the monthly mean concentrations of POC and TSS for the \( i \)th month, respectively.

\[ F_{\text{DOC}} = \sum_{i=1}^{12} Q_i \times C_{\text{DOC}} = \sum_{i=1}^{12} Q_i \times \left(43.727 \times C_{\text{TSS}}^{0.815} \times C_{\text{POC}}\right) 
= \sum_{i=1}^{12} Q_i \times \left(43.727 \times C_{\text{TSS}}^{0.815} \times (0.0136 C_{\text{TSS}} + 0.0627)\right) \]  
(5)

Where, \( F_{\text{DOC}} \) represents the annual flux of DOC. \( Q_i \) is the total water discharge of the \( i \)th month through a year. \( C_{\text{DOC}} \) and \( C_{\text{TSS}} \) are the monthly mean concentrations of DOC and TSS for the \( i \)th month through a year, respectively.

\[ F_{\text{DIC}} = \sum_{i=1}^{12} Q_i \times C_{\text{DIC}} \]  
(6)

Where, \( F_{\text{DIC}} \) represents the annual flux of DIC. \( Q_i \) is the total water discharge of the \( i \)th month through a year. \( C_{\text{DIC}} \) is the concentration of HCO$_3^-$ measured for the \( i \)th month through a specific year.

For the years of 1968–1979 and after 1999 in which monitoring data of DIC are not available, Eq. (3) is used to estimate the DIC.

Fig. 5. Relationship between discharge and DIC in the Xijiang.
6. Conclusions

The quantitative relationships between various components of riverine carbon and discharge or sediment are developed based on the data from a systematic sampling program over the lower Xijiang basin. These relationships are then applied to the historic records of water discharge or sediment for estimation of long-term dynamics of the riverine carbon fluxes. Results show that POC flux varied with a notable decreasing trend, but DOC shows an increasing trend. DIC shows a decrease trend with a very small slope. In total carbon flux, a more or less constant or very small decreasing trend is demonstrated. These long-term changes may be related to human activities, such as reservoir/dam construction and reforestation projects, as well as input from industrial agricultural discharges.

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References


