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THEMATIC ISSUE

Estimation of carbon sink fluxes in the Pearl River basin (China) based on a water–rock–gas–organism interaction model

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Abstract Carbon sequestration resulting from carbonate rock weathering is closely linked to the global carbon cycle and has turned out to be important in the adjustment of atmospheric CO_2 levels. Traditional karst dynamic models based on water–rock–gas interactions underestimate carbon sink fluxes related to carbonate rock weathering because they ignore the utilization of dissolved inorganic carbon (DIC) by aquatic organisms. In this study, a new model based on water–rock–gas–organism interactions was applied in the Pearl River basin, China, to recalculate atmospheric CO_2 consumption and to develop an accurate estimation model for carbon sink fluxes at catchment scale. Stable carbon isotope ($\delta^{13}C$) and C/N ratios were used in the counting processes. Data were collected from published literature as well as through field investigation and laboratory analysis. Results show that the Pearl River carbon sink in the Pearl River is 4.31×10^9 kg/a, i.e., 15.8×10^9 kg of atmospheric CO_2 per year. Of this, the carbon sink resulting from carbonate rock weathering amounts to 2.14×10^9 kg/a, i.e., 49.7 % of the total. The three largest tributaries of Pearl River, Dongjiang, Beijiang, and Xijiang, respectively absorb 0.5×10^9, 1.19×10^9, and 2.62×10^9 kg of carbon from the atmosphere annually, accounting for 12, 28 and 60 % of the river's total carbon sink. When compared with the results of previous researches that disregarded the role of aquatic organisms, the new calculation method provides a carbon sink flux value that is 1.2–3.3 times higher, and 1.6 times higher on an average. To improve the calculation accuracy of atmospheric CO_2 consumption in global karstic rivers, further research is needed regarding carbon sequestration mechanisms that involve aquatic organisms.

Keywords Karst carbon sink · Aquatic organism · Dissolved inorganic carbon (DIC) · Pearl River basin

Introduction

Karst dynamic processes that occur in karst regions worldwide play an important role in the global carbon cycle (Baldini et al. 2006; De Montety et al. 2011; Jiang and Yuan 1999; Liu et al. 2007; Yuan 1995, 1999). This role was explored in two past research projects, IGCP 299 "Geology, Climate, Hydrology and Karst formation" (1990–1994) and IGCP 379 "Karst and Carbon Cycle" (1995–1999), and since implementation of these projects, these has been further advancement in research (Zhang 2012; Larson 2011). Many scholars argue that carbonate dissolution can take up atmospheric CO_2 and contribute toward the regulation of global climate change (Liu et al. 2007; Yuan 1995, 1999). However, some scientists (e.g., Curl) are now questioning the stability of the karst carbon sink, believing that the associated CO_2 would be re-released to the atmosphere through deposition of calcite in rivers or lakes and in shells or reefs in oceans. This would therefore lead to the conclusion that there is no net carbon

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sequestration resulting from karst dynamic processes (Curl 2012).

Groves et al. (2012) emphasized in Science that over millennia, the carbon sink related to carbonate rock weathering forms an important part of the global "missing carbon". Even over a multi-million year time scale, soluble bicarbonate (HCO_3^-) or dissolved inorganic carbon (DIC) can be sequestered and transferred to organic carbon (OC) through the actions of aquatic organisms such as *Chlorella vulgaris* and *Cyanophycin*. OC can enter the lithosphere through deposition and burial processes (Liu 2012) and then become a permanent carbon sink (Cole et al. 2007; Dean and Gorham 1998; Einsele et al. 2001; Parrick and Jerry 1982).

In previous research, high-resolution monitoring was applied to karst river of the Guancun surface stream, in southern China. This showed a significant decrease in HCO_3^- along the stream, with a loss of HCO_3^- of 94.9 kg per day, i.e., 1,152 mmol/m per day along a 1.35-km long surface river (Jiang et al. 2012; Zhang 2011). In the Ichetucknee surface river supplied by a karst spring in Florida (southeast USA), the recorded decrease was of 130 mmol/m per day, with 88 % of missing DIC consumed by the photosynthesis of aquatic plants (De Montety et al. 2011). Autochthonous particulate organic carbon (POC), coming from river plankton and river sediment releasing (Tao et al. 1997), accounts for more than 70 % of total riverine carbon in the Yuanjiang and Zengjiang Rivers (Tao et al. 2009). Furthermore, Dean and Gorham (1998), Cassar et al. (2004) and Waterson and Canuel (2008) have indicated that HCO_3^- provides important nutrition for phytoplankton in lakes, oceans, and rivers.

Riverine transportation of carbon, especially in the large rivers is an important process within the global carbon cycle. Previous research on the carbon cycle at catchment scale has only considered inorganic carbon, with little research focusing on the formation and transformation of OC in large rivers. In this study, a new karst dynamic model based on water–rock–gas–organism interactions was selected and the Pearl River was chosen as a case to illustrate the role of aquatic organisms in karst dynamic processes of large karst rivers and to estimate the riverine carbon sequestration, providing an available model for the precise calculation of karst carbon sink.

Materials and methods

Site description

The Pearl River is the second largest river in China. It is located in the subtropical monsoon zone of southern China (102°15′–115°35′E, 21°50′–26°48′N) (Fig. 1) and flows through the four provinces of Yunnan, Guizhou, Guangxi, and Guangdong (Cao et al. 2011). The drainage area is 452,600 km^2, accounting for 4.71 % of Chinese territory (Wang and Chen 2006) and the annual precipitation is approximately 350×10^9 m^3 (Zhang et al. 1999).

There are three major tributaries of the Pearl River, namely Xijiang, Beijiang, and Dongjiang. The river's total length is of 2,214 km, with a 2,800 m drop in altitude drop from west to east (Callahan et al. 2004). Carbonate rocks cover 158,400 km^2, accounting for 35 % of the total basin area (Cao et al. 2011). Several relevant features converge in this catchment area, including lush vegetation, abundant precipitation, high temperatures, and strong supergene geochemical processes.

Chemical analysis

Sampling points were selected along the cross section of tributaries (Fig. 1). These three control points (outlet of tributaries) were located at both the upper tidal limit and at the outlet of the basin. Three vertical lines (left, middle, and right) were selected, with three sampling points along each vertical line. A fixed-depth sampler was used at each sampling point to collect water at 0.5 m below the water surface, from the middle of the vertical line, and at 0.5 m above the bed. Samples were collected during April 2012, July 2012, and October 2012. Dissolved organic carbon (DOC) and DIC samples were injected into 500 mL polyethylene bottles, and POC samples were injected into 5,000 mL plastic buckets. Stable carbon isotopes ($\delta^{13}C_{POC}$ and $\delta^{13}C_{DIC}$) were collected in 500 mL brown glass bottles, with the addition of 1 mL of saturated mercuric chloride solution. All samples were stored in a car refrigerator at 4 °C and then brought back to the laboratory immediately for chemical analysis.

DOC and DIC were measured using a multifunction nitrogen and carbon analyzer (MultiN/C3100, Jena, Germany). POC samples were first filtered through 0.45 μm glass fiber membrane, and then dried at 50 °C in an oven. A TOC analyzer (Fusion Total Organic Carbon Analyzer, Tekmar, USA) was used to measure carbon concentration in particulate matter. The values of $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$ were determined using a continuous flow gas isotope mass spectrometer (MAT253, Finnigan, Germany), with the instrument having analytical precision of less than 0.2 ‰.

Runoff data were gathered from the Pearl River Water Resources Commission website (PRWRC, http://www.pearlwater.gov.cn/).

Water–rock–gas–organism interactions model

The traditional conceptual model of the karst dynamic systems is based on the three-phase interaction of carbonate–water–CO_2 (Yuan 1993), as per the following equation:

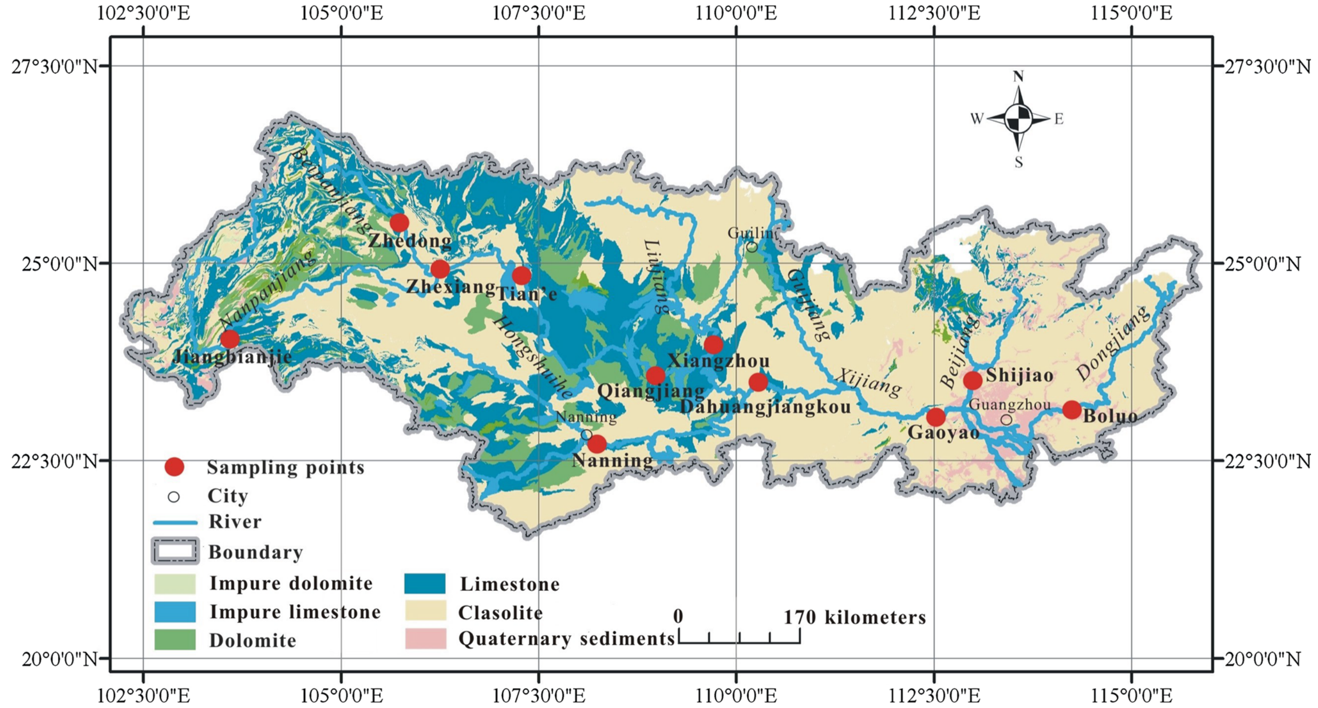

Fig. 1 Geology of the Pearl River basin and sampling point locations

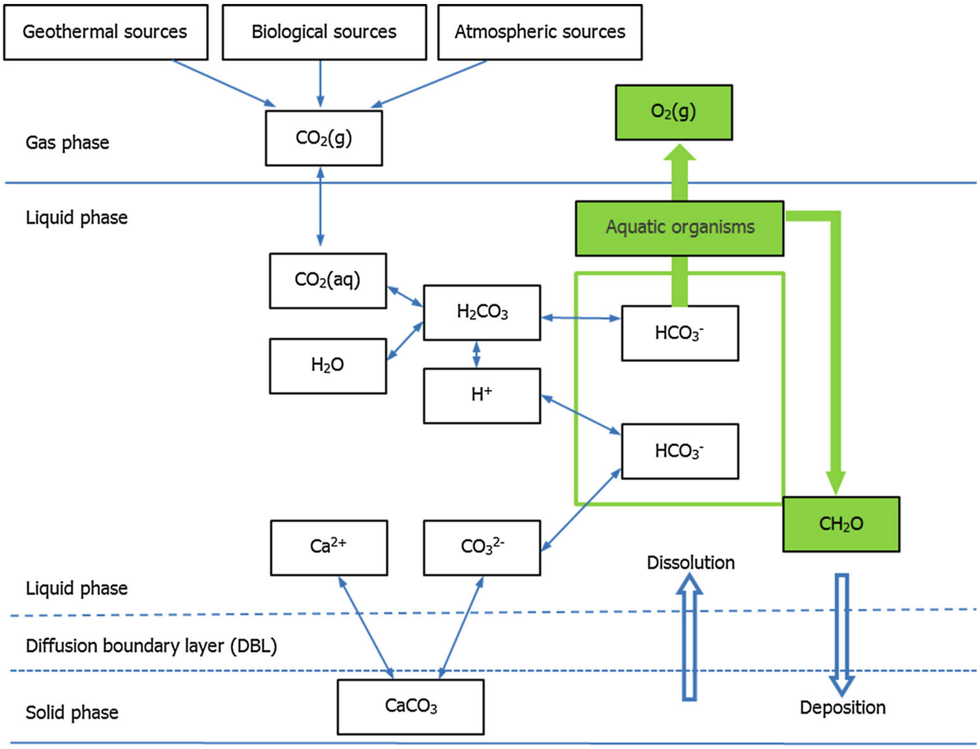

Fig. 2 Conceptual model of karst dynamic systems with the consideration of aquatic organisms (Liu et al. 2010)

$$MeCO_3(s) + H_2O(aq) + CO_2(g) = 2HCO_3^-(aq) + Me^{2+}(aq) \quad (1)$$

where $MeCO_3$ represents $CaCO_3$ or $MgCa\,(CO_3)_2$.

Riverine carbon sink estimation as per Eq. (1) is based on the concentration of inorganic carbon. Recently, a new model has been proposed based on water–rock–gas–organism interactions, which considers aquatic organisms' biological actions and OC synthesis processes (Fig. 2).

The new model, as expressed by Smith and Gattuso (2011), is therefore as follows:

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 \downarrow + A\,(CO_2 \uparrow + H_2O) + (1 - A)(CH_2O \downarrow + O_2) \quad (2)$$

where A is the percentage of CO_2 released through degasification, A is generally less than 1 (Liu et al. 2010). CH_2O represents aquatic biological organisms.

According to Eq. (2), riverine consumption of atmospheric CO_2 can be calculated as follows (Liu et al. 2010):

$$CSF = F_{DIC} + F_{ATOC} + F_{ASOC} \quad (3)$$

where CSF is the riverine carbon sink flux with the addition of the role of quatic organisms, F_{DIC} is DIC transported into the sea, F_{ATOC} is autochthonous organic carbon in the river, and F_{ASOC} is autochthonous OC deposited in sediment. F_{ATOC} and F_{ASOC} are all converted from DIC through the actions of aquatic organisms. To obtain the CSF value, we need to caculate F_{DIC}, F_{ATOC}, and F_{ASOC}.

Source of DIC

The values of $\delta^{13}C$ are different in different carbon pools. The carbon isotope can therefore be used to deduce sources and evolutionary processes (Fritz et al. 1989). Researches have found that DIC in terrestrial water mainly originates from: (1) dissolution of CO_2 in soil; (2) carbonate rock weathering; (3) rainfall input; (4) exchange of soluble bicarbonate and atmospheric CO_2; (5) photosynthesis and respiration of aquatic plants; and (6) silicate rock weathering (Li et al. 2004, 2007; Liu et al. 2011).

However, according to Grossman (1997) and Telmer and Veizer (1999), riverine DIC originating from precipitation is negligible. In addition, the proportion of DIC derived from silicate rock weathering is also very low compared to DIC from carbonate rock weathering; HCO_3^- from silicate rock weathering is only about 1/15 that from carbonate rock weathering (Liu et al. 2011). According to Zhang et al. (1992a), the proportions of DIC derived from exchange of atmospheric CO_2 and HCO_3^- (aq), and from hydrophyte respiration are also very small. This means that the above-mentioned sources (3), (4), (5), and (6) can be ignored in the analysis of water DIC sources. For ease of calculation, in this study soil CO_2 and carbonate weathering were therefore considered to be the two main DIC sources.

The value of $\delta^{13}C$ in soil CO_2 is −3 to −19 ‰, with an average of −23 ‰, while $\delta^{13}C$ in atmospheric CO_2 is −6 to −8 ‰, and average −7 ‰ (Amiotte-Suchet et al. 1999; Cerling et al. 1991; Staddon 2004). Generally, CO_2 in soil is a mixture derived from these two sources (Telmer and Veizer 1999). Calculation results of the two mixed end-members had $\delta^{13}C$ ranges from −23 to −13 ‰, with an average of −17 ‰.

Shao et al. (1996) reported that the sedimentary facies of carbonate rocks in the study area are derived from marine deposition, with strata spanning from Carboniferous to Triassic periods. Measurements of $\delta^{13}C$ isotopic composition in Latest Permian carbonate rocks, based on 98 samples from 19 sites in Guangxi, Guizhou, Yunnan, Sichuan, and Chongqing, detected a fall in values of between 5.03 and 3.25 ‰, with an average of −0.72 ‰.

Carbon isotopes were calculated according to ^{13}C mass balance between the $\delta^{13}C$ eigenvalue of carbonate rocks and soil CO_2, as shown in the following equation:

$$\delta^{13}C_{DIC} = B\delta^{13}C_{car} + (1 - B)\delta^{13}C_{soil} \quad (4)$$

where B means the proportion of carbonate rock weathering contribution to riverine $\delta^{13}C_{DIC}$ $\delta^{13}C_{car}$ and $\delta^{13}C_{soil}$ illustrate the $\delta^{13}C$ values of carbonate rock and soil CO_2, respectively.

The $\delta^{13}C_{DIC}$ value of Pearl River is shown in Table 1. The average values of $\delta^{13}C_{DIC}$ in Dongjiang, Beijiang, and Xijiang were −4.54, −4.87, and −7.18 ‰, respectively. According to Table 1, the $\delta^{13}C_{DIC}$ value appears significant temporal variations, especially in Dongjiang and Beijiang. Biological activities, intensified in July and October because the high temperature in southern China, enhance plants growth and reduce the $\delta^{13}C_{DIC}$ that derived from terrestrial vegetation (Liu et al. 2010).

Based on the values of $\delta^{13}C_{DIC}$, $\delta^{13}C_{car}$, and $\delta^{13}C_{soil}$, the contribution ratios of carbonate rock weathering to DIC in Dongjiang, Beijiang, and Xijiang are 77, 75, and 60 %, indicating that soil CO_2 in these three tributaries is 23, 25 and 40 %, respectively.

In the course of F_{DIC} calculation, HCO_3^- (replaced by DIC in the calculation) from carbonate rock weathering is considered to be half that from atmospheric CO_2, while HCO_3^- from soil is all derived from the atmosphere. F_{DIC} can therefore be described as follows:

$$F_{DIC} = 0.5F_{DICcar} + F_{DICsoil} \quad (5)$$

where F_{DICcar} is DIC from carbonate rock weathering and $F_{DICsoil}$ is DIC from soil.

Table 1 $\delta^{13}C$ value of major tributaries in the Pearl River basin

Tributaries	$\delta^{13}C_{DIC(V\text{-}PDB)}$ (‰)			
	April 2012	July 2012	October 2012	Average
Dongjiang	−0.69	−4.64	−8.29	−4.54
Beijiang	−2.3	−3.98	−8.32	−4.87
Xijiang	−4.01	−8.71	−8.83	−7.18

Sources of OC in water and sediment

There are two types of organic carbon, namely allochthonous and autochthonous types (Zhang et al. 1992b).On land, low aquatic plants and high terrestrial plants possess different C/N ratios, which would directly impact riverine suspended solid C/N ratios. In this study, riverine organic carbon was assumed to stem from soil erosion and aquatic plants. In this case, the sources of riverine organic carbon can be calculated as follows:

$$(\mathrm{C/N})_{\mathrm{sus.}} = X(\mathrm{C/N})_{\mathrm{soil}} + (1 - X)(\mathrm{C/N})_{\mathrm{plant}} \quad (6)$$

where $(\mathrm{C/N})_{\mathrm{sus.}}$ indicates the C/N ratio in suspended solids of water samples, $(\mathrm{C/N})_{\mathrm{soil}}$ is the C/N ratio of soil carried into the river, $(\mathrm{C/N})_{\mathrm{plant}}$ refers to the C/N ratio of aquatic plants, and X is the percentage of POC of soil erosion.

The $(\mathrm{C/N})_{\mathrm{sus.}}$ values of Beijiang and Xijiang were derived from literature (Gao et al. 2003). The values, as reported in July 1997 and February 1998, were 14.44 at the Sanshui hydrological station in Beijiang and 15.22 at the Makou hydrological station in Xijiang. Based on coarse and fine particle C/N research conducted by Tao et al. (2004) at Zengjiang (the main tributary of Dongjiang), the $(\mathrm{C/N})_{\mathrm{sus.}}$ value of Dongjiang is 9.99. The average C/N ratio of 50 soil profiles in the Dinghuashan nature reserve within the study area, as indicated by Xing (1998), was 17.73, and we use this figure for $(\mathrm{C/N})_{\mathrm{soil}}$ values in Eq. (6). Tao et al. (2004) also tested the C/N ratio of algae in the Pearl River basin, obtaining a result of 6.13. When considering the above, one can conclude that autochthonous OC in Dongjiang, Beijiang, and Xijiang accounts for 74, 28, and 22 % of total organic carbon (TOC) in each of these cases, respectively. This therefore means that F_{ATOC} accounts for 74, 28, and 22 % of TOC in these three tributaries.

With regard to organic matter sources in sediment of the Pearl River, Niu et al. (2008) reported that organic matter and nutrients in the Pearl River (reaches of Guangzhou) are mainly derived from the surrounding environment, with a small amount sourced from algae, zooplankton, and phytoplankton. The large slope gradient and high flow velocity in the Pearl River further increase the difficulty of organic matter depositing onto the riverbed. The average slope gradient of the Pearl River basin is greater than 1.26 ‰ in an east–west direction, much higher than that of the two longest rivers in China, i.e., the Yellow River (0.88 ‰) and the Yangtze River (0.84 ‰). This high river drop is not conducive to the deposition of allochthonous particulate matter. Consequently, F_{ASOC} in Eq. (3) is not considered to be a significant factor and Eq. (3) can therefore be simplified as follows:

$$\mathrm{CSF} = F_{\mathrm{DIC}} + F_{\mathrm{ATOC}} \quad (7)$$

Estimation of carbon sink fluxes

Based on monsoon and runoff characteristics, the hydrological year of the Pearl River can be divided into four seasons: the normal season (March–May), the rainy season (June–August), the transitional season (September–November), and the dry season (December–February). Table 2 shows the proportion of discharge in each hydrological season in Dongjiang, Beijiang, and Xijiang.

The estimation of F_{DIC} and F_{ATOC} should take into account discharge percentages in different hydrological seasons. The flux of DIC or ATOC can be written as:

$$F = \frac{1}{np}\sum_{i=1}^{n} C_i Q_i \quad (8)$$

where F is F_{DIC} or F_{ATOC} in Eq. (7), p is discharge percentage in different hydrological seasons, n is sampling frequency ($n = 2$), C_i is mass concentration (in mg/L), and Q_i is river runoff (in m^3/s). The concentrations of DIC, DOC, and POC in the Pearl River basin are shown in Table 3.

Based on the proportionate contribution of carbon sources discussed in "Source of DIC" and "Sources of OC in water and sediment", Table 3 shows the total carbon sink of Pearl River and its tributaries. The total carbon sink flux in the Pearl River basin is 4.31×10^9 kg/a, i.e., 15.8×10^9 kg of atmospheric CO_2 per year, when factoring in the role of aquatic organisms. The carbon sink caused by carbonate rock weathering is 2.14×10^9 kg/a, accounting for 49.7 % of the total. The carbon sinks of the three major tributaries, Dongjiang, Beijiang, Xijiang, comprise 0.5×10^9, 1.19×10^9, and 2.62×10^9 kg/a, accounting for 12, 28, and 60 % of the total carbon sink in the Pearl River basin, respectively.

CSF values calculated based on the traditional hydrochemical model and using this research data are 3.6×10^9, 0.27×10^9, 1.06×10^9, and 2.27×10^9 kg/a, for the main stream, Dongjiang, Beijiang, and Xijiang, respectively. According to Cao et al. (2011), the total output of DIC

Table 2 Discharge percentage of the main tributaries of the Pearl River (%) in different hydrological seasons

Tributaries	Normal season	Rainy season	Transitional season	Dry season	References
Dongjiang	28	43	19	10	Wang et al. (2010)
Beijiang	37	40	14	9	Liu (2007)
Xijiang	23	48	21	8	You et al. (2005)

transported to the sea from the Pearl River during the hydrological years 2000 and 2001 was 5.50 × 10^9 kg/a, and according to Wei (2003), the value in 1997–1998 was 7.01 × 10^9 kg/a; this implies that the carbon sink fluxes in the two hydrological year periods were 2.75 × 10^9 and 3.51 × 10^9 kg/a (half of the DIC output flux), respectively. DIC erosion fluxes in Xijiang and Beijiang, as calculated by Gao et al. (2001), were 1,103 × 10^3 and 1,289 × 10^3 mol/km^2 a, equal to 2.33 × 10^9 and 0.36 × 10^9 kg/a. Carbon sink fluxes that take the role of aquatic organisms into account in the Pearl River basin are 1.2–3.3 times higher (1.6 times higher on average) than those which do not take this factor into consideration.

Table 3 Riverine carbon fluxes of the Pearl River basin

Basin	Area (km^2)	Flow Q (April/July) (m^3/s)	DIC (April/July) (mg/L)	DOC (April/July) (mg/L)	POC (April/July) (mg/L)	TOC (April/July) (mg/L)	F_{DIC} (×10^9 kg/a)	F_{TOC} (×10^9 kg/a)
Dongjiang	27,040	886/1,995	9.23/5.91	2.45/2.97	4.2/5.71	6.65/8.68	0.44	0.51
Beijiang	46,710	2,260/3,390	18.28/12.49	2.53/2.73	2.03/4.11	4.56/6.84	1.71	0.69
Xijiang	353,120	4,030/9,260	22.69/16.72	1.67/2.07	5.26/5.85	6.93/7.92	3.25	2.25
Total							5.40	3.45

Basin	F_{ATOC} (×10^9 kg/a)	Carbonate weathering (×10^9 kg/a)	Soil CO_2 dissolution (×10^9 kg/a)	Total carbon sink (×10^9 kg/a)	Erosion modulus of carbonate weathering (×10^3 kg/km a)	Erosion modulus of soil CO_2 dissolution (×10^3 kg/km^2 a)	Erosion modulus of the total carbon sink (×10^3 kg/km^2 a)	Traditional value (×10^9 kg/a)
Dongjiang	0.38	0.32	0.19	0.51	11.46	7.03	18.49	0.27
Beijiang	0.19	0.71	0.48	1.19	15.20	10.28	25.48	1.06
Xijiang	0.50	1.13	1.50	2.63	3.17	4.25	7.42	2.27
Total		2.14	2.17	4.31	29.84	21.55	51.39	3.60

Conclusions

Carbon sink calculations that take into account the role of aquatic organisms have been recognized and endorsed by a majority of scholars as providing a more accurate reflection of reality. Effective pathways to promote the consumption of atmospheric CO_2 through human intervention can take into account in situ carbon sequestration through the actions of aquatic organisms and enhance carbon sink capacities through vegetation restoration. Such actions could play an important role in global carbon reduction. This study investigated carbon sink fluxes, taking into account the role of aquatic organisms. Results show that the carbon sink flux is 1.2–3.3 times greater (1.6 times greater on average) than when calculated without considering the role of aquatic organisms. Although there are limited data on this aspect, there is no doubt that previous calculations likely underestimated the role of the karst carbon sink.

Notwithstanding the above, it should be noted that there are still several problems to be solved in the application of this new carbon sink estimation model. The first involves the need for further improvements in understanding the mechanisms of carbon sequestration involving aquatic organisms. The carbon sequestration capacity of different aquatic organisms, such as emergent plants, submerged plants, and floating plants, varies; according to Zhang (2012), this variation can be of up to a factor of seven. For this reason, dominant plants with high carbon sequestration efficiency can be selected to restore vegetation through laboratory-scale or pilot-scale experiments. The second problem is that long-term and systematic observations in this field are needed. As carbon sinks involve various dynamic processes, it is difficult to obtain satisfactory results only on the basis of several samples. Dynamic monitoring should be strengthened to monitor dynamic carbon processes. The third problem is that impact factors were simplified in this study, as described in "Sources of

DIC" and "Sources of OC in water and sediment". In fact, hydrodynamic conditions, rainfall, and human activities are also factors that can affect carbon stability and carbon conversion processes to a certain extent. Karst carbon sink fluxes estimation using this new model that includes aquatic organic organisms therefore needs to be further improved, with advancement of estimation accuracy.

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