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Carbon isotopic evidence for transformation of DIC to POC in the lower Xijiang River, SE China

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ABSTRACT

The sources and dynamics of riverine carbon have been discussed extensively, but the transformation from inorganic carbon into organic carbon is still poorly understood. In this study, we conducted a comprehensive investigation on the riverine carbon, stable carbon isotopic composition and POC/PN (particulate nitrogen) ratio for different seasons, including an extreme flood event, in the lower Xijiang and its three tributaries. Stable carbon isotopic analyses are also performed for soil samples across the study region. Downstream decreases in $\delta^{13}C_{POC}$ and POC/PN have been observed for all the tributaries. Meanwhile, the data obtained manifest a prominent positive shift of $\delta^{13}C_{DIC}$ and negative shifts of both $\delta^{13}C_{POC}$ and POC/PN from summer to winter. These observations suggest 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 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 3.4–20.5% in rainy season, and 12.3–22.1% in dry season. The transformation of DIC into POC implies an important sink of atmospheric CO_2 in river systems and suggests a new mechanism for the old carbon effect in ^{14}C age of aquatic-environmental sediments.

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 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 processes involved in the DIC cycling in river systems, including CO_2 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 (Ludwig et al., 1996). For less turbid rivers, however, contribution of aquatic biomass may increase significantly (Meybeck, 1993; Ludwig et al., 1996). Through interim processes such as microbial utilization, primary production and respiration, inorganic and organic carbon in the river may transform to each other (Dagg et al., 2004; Raymond et al., 2004; Liu et al., 2010). The sources, fates and dynamics of riverine carbon have been extensively discussed using $\delta^{13}C$ or $\Delta^{14}C$ constraints, but they are still topics of debate. Some studies show that riverine organic carbon is mainly composed of young terrestrial carbon originating 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 (Hwang et al., 2005; Drenzek et al., 2009; Loh et al., 2012). There are studies showing that the petrogenic carbon discharged from rivers is highly recalcitrant and can be reburied in floodplain or coastal oceans (Blair et al., 2003; Dickens et al., 2004; Goñi et al., 2005;

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Komada et al., 2005), but some studies argue that petrogenic carbon during river transport can be significantly oxidized and become the source of atmospheric CO_2 (Berner, 2004; Bouchez et al., 2010; McCallister and del Giorgio, 2012). These arguments may be resulted from the complicated interactions and mechanisms between climatic, hydrological, and biological aspects in a drainage basin during riverine transport. However, the potential influence of various in-river processes on the carbon isotopic compositions has been largely ignored, which could be a primary factor for accurate interpretation of isotopic information.

Aquatic plants such as algae can grow by directly using bicarbonate with significant isotope fractionation (Spence and Maberly, 1985; Li et al., 2005). Meanwhile, this process may introduce the ^{14}C-dead carbon from carbonate dissolution into the riverine OC. Thus, the transformation of DIC into OC by in-river photosynthesis may greatly modify both $\delta^{13}C$ and $\Delta^{14}C$ signals of the riverine organic matter, affecting the accuracy of the source and age analyses. Besides, the transformation of DIC into OC in river system may represent an important carbon sink in the global carbon budget (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 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. Study area and methods

2.1. Study area

The Zhujiang River (Pearl River) is the second largest river in China in terms of annual water discharge (336 km^3/y) 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 14–22 °C and 1200–2200 mm, respectively. Heavy rainfalls occur mainly in June, July and August, which accounts for 50–60% 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, the Guijiang, Hejiang, and Luoding (Fig. 1). These tributaries developed in various basin sizes with marked difference in carbonate/silicate ratios of the exposed bedrock. The vegetation in the study area is subtropical monsoon rainforest with a high coverage ratio (more than 50%). As

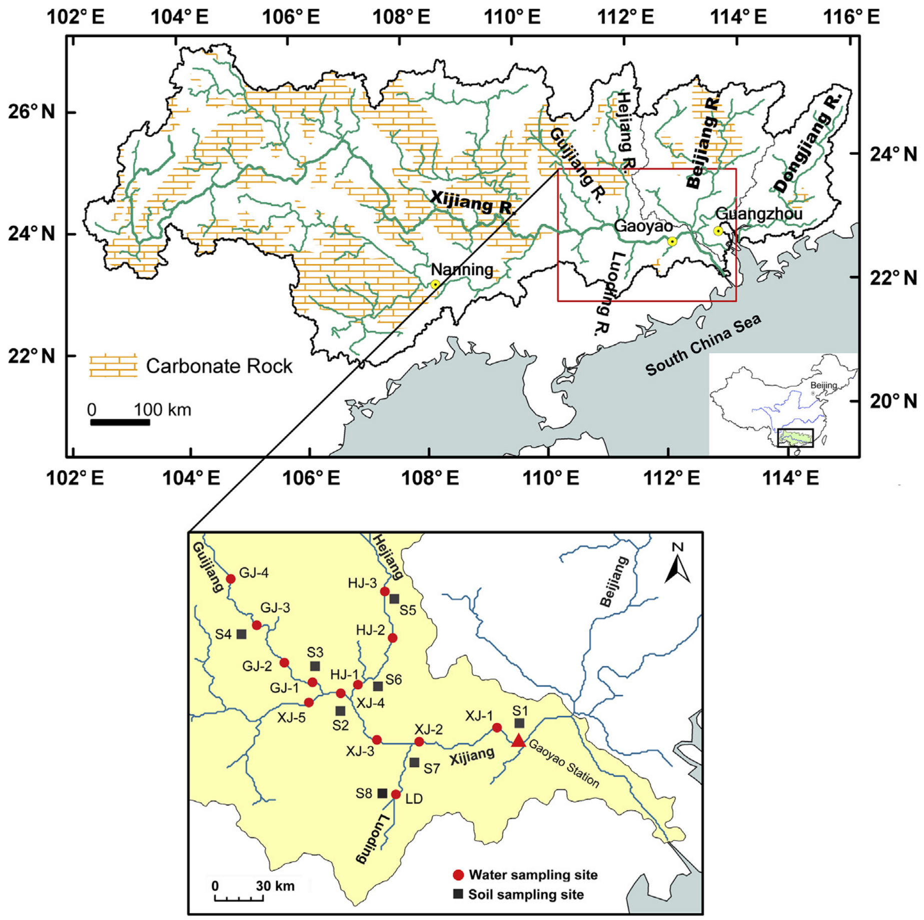

Fig. 1. The Zhujiang River system and sampling sites. The Zhujiang River is a joint river system including the branches of Xijiang (West river), Beijiang (North river), and Dongjiang (East river). All these branches flow into the joint delta and then into South China Sea via multi-outlets. The upper panel shows the entire Zhujiang catchment and these three subcatchments (delineated by grey lines). This study focuses on the lower Xijiang River before reaching the delta area (the lower panel).

a typical monsoon region, the seasonal variations of air temperature and precipitation (or discharge) in the Xijiang basin show an in-phase fashion; both high in summer and low in winter. On the Luoding River, a large number of dams were constructed, which significantly reduced the flow 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 the 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). Eleven water samples were also collected during an extreme flood event occurred in June 2005 at the Gaoyao Hydrometric Station in the lower Xijiang River. All samples were taken at 1 m in depth below water surface on the central line of the river.

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

Samples for $\delta^{13}C_{DIC}$ analysis were prepared following the direct precipitation method (Bishop, 1990). About 1000 ml filtrate in a glass vessel was treated with $SrCl_2$–NH_4OH solution at $pH > 10$ 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 laboratory, the $SrCO_3$ precipitate was stored in plastic bags.

Soil sampling was carried out in July (summer) and December (winter) 2008 to investigate the POC, POC/PN, and isotopic characteristics. Eight soil profiles were selected around the riverbank to represent the prevalent land use categories of the area (Fig. 1). Characteristics of the selected soil profiles are shown in Table 3. For each soil profile, 3 samples were taken from depths of 0–5 cm, 15–20 cm and 30–50 cm, respectively. After collection, samples were dried at 50 °C, sieved through a 2 mm mesh to remove stones, and then pulverized and acidified to remove carbonate.

2.3. Laboratory analysis

The pH and water temperature were measured on site with a Hanna HI 8424 pH/Temp meter. The precision was 0.01 unit for pH and 0.1 C° for temperature. Calibration was conducted before each measurement using two standard buffers of pH-7 and pH-10. HCl titration and Gran's method were used in the field for determination of the total alkalinity with 0.01 M HCl within 24 h after sampling. Each sample was repeated for two or three times and the standard deviation ($\pm 1\sigma$) of replicate measurements was ±0.3%. DIC and partial pressure of CO_2 in water (pCO_2) are determined based on measured alkalinity, pH and water temperature using a program CO2SYS (Lewis and Wallace, 1998). 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%. Although inorganic nitrogen, for example, NH_4^+ ion absorbed by clays may exist in the PN, it is a rather small fraction (Meybeck, 1982). Therefore, the POC/PN ratio is used for the POC/PON in this study for an attempt to explore its variations. $\delta^{13}C$ 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 analytical errors of less than ±0.1‰.

3. Results

3.1. Riverine DIC and $\delta^{13}C_{DIC}$

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 (Dreybrodt, 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 with a mean value of 0.03 mmol/L, and HCO_3^- is between 0.71 and 2.59 mmol/L with a mean value of 1.87 mmol/L.

Our measurements show that DIC at the sampling site XJ-1, close to the Gaoyao Hydrometric Station, ranges from 1.48 to 2.21 mmol/L with a mean value of 1.89 mmol/L. These numbers are well consistent with the historical record and the results from a previous study (Yao et al., 2007) at this station. DIC concentrations in the tributaries show an order of Xijiang > Guijiang > Hejiang ≥ Luoding (Table 2), in agreement with the order of the area ratios of carbonate/silicate in these subbasins (Sun et al., 2010). DIC concentrations in the Xijiang are higher than in most large rivers of the world (Degens et al., 1991), characteristic of the drainages developed on typical carbonate regions.

The highest concentrations of DIC occur in winter (December) and the lowest in summer (June, particularly during the flood event). Compared with 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 amounts of DIC during rainy season.

Stable carbon isotope signature of DIC ($\delta^{13}C_{DIC}$) in the Xijiang River system is averaged −11.2‰ in July (summer), −12.8‰ during the extreme flood and −9.3‰ in December (winter). A consistent and positive shift from summer to winter is clearly displayed for all the individual sites (Fig. 2). Except for the Guijiang in winter, $\delta^{13}C_{DIC}$ decreased downstream in all the tributaries for both summer and winter seasons (Fig. 2). It is interesting that among the selected four tributaries, Luoding has the lowest $\delta^{13}C_{DIC}$ value.

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

Basin	Area km^2	Flow km^3/yr	Slope (‰)	Carb	Sil	Forest	Grass	Farmland	Population people/km^2
				(%)					
Xijiang	351535	218	0.86	43	58	56	12	19	228
Guijiang	18210	17	0.43	51	49	58	33	7	262
Hejiang	11590	8	0.58	23	77	65	17	13	179
Luoding	3164	3	0.87	8	92	51	17	12	254

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

Sample	Date	pH	Tem	Flow	TSS	POC	POC/PN	Alkalinity	DIC	pCO_2	f_{cc}[a]	f_{cs}	f_{sc}	$\delta^{13}C_{DIC}$	$\delta^{13}C_{POC}$
	dd-mm		(°C)	(m^3/s)	(mg/L)			(umol/L)		(uatm)	(%)			(‰)	
XJ-1	17-Apr	7.57	21.9	2020	3.69	0.05	7.56	1566	1661	2661					
XJ-2	17-Apr	7.83	21.7	2020	2.33	0.03	9.13	1515	1563	1408					
XJ-3	17-Apr	7.79	21.6	2020	7.12	0.10	8.87	1414	1463	1436					
XJ-4	17-Apr	7.86	21.5	2020	8.9	0.12	8.22	1586	1631	1367					
XJ-5	17-Apr	7.82	21.8	2020	7.28	0.10	9.39	1667	1720	1583					
GJ-1	14-Apr	7.41	17.8	80	8.57	0.10	7.70	1465	1605	3404					
GJ-2	14-Apr	7.53	18.6	80	1.36	0.03	8.04	1515	1622	2696					
GJ-3	14-Apr	7.89	18.5	80	1.78	0.04	8.06	1535	1578	1187					
GJ-4	14-Apr	8.04	18.7	80	1.66	0.03	8.08	1667	1696	912					
HJ-1	16-Apr	7.02	21.5	117	1.18	0.03	8.65	859	1051	5151					
HJ-2	16-Apr	7.07	20.8	117	4.50	0.08	7.95	1141	1372	6059					
HJ-3	16-Apr	7.13	20.6	117	1.31	0.03	8.64	1162	1366	5355					
LD	18-Apr	7.64	22.0	26	9.31	0.15	6.93	1566	1646	2267					
XJ-1	2-Jul	7.35	25.0	26050	172.09	2.13	11.63	1350	1484	3981					
XJ-2	2-Jul	7.33	25.1	26050	174.33	2.37	12.00	1420	1567	4391					
XJ-3	2-Jul	7.22	25.0	26050	146.75	1.88	11.29	1350	1484	3981					
XJ-4	2-Jul	7.21	25.0	26050	153.72	1.86	11.34	1390	1581	5662					
XJ-5	2-Jul	7.22	25.1	26050	180.90	2.42	12.56	1500	1701	5979					
GJ-1	1-Jul	7.14	24.4	809	50.42	0.83	11.18	930	1082	4414					
GJ-2	1-Jul	7.14	24.4	809	48.20	0.90	10.73	900	1047	4272					
GJ-3	1-Jul	7.16	24.4	809	28.94	0.52	10.44	930	1075	4215					
HJ-1	30-Jun	6.94	24.9	97	15.93	0.23	8.93	680	855	5154					
HJ-2	30-Jun	7.37	25.1	97	11.89	0.20	9.92	980	1072	2763					
HJ-3	30-Jun	7.32	24.5	97	6.70	0.17	9.89	980	1085	3075					
LD	27-Jun	7.38	25.0	76	52.32	0.55	8.75	930	1016	2559					
XJ-1	13-Jul	7.09	26.0	7920	39.60	0.57	10.88	1872	2209	10199	68.9	16.6	14.5	−11.1	−23.4
XJ-2	13-Jul	7.28	26.0	7920	48.74	0.81	10.38	1922	2144	6756	62.9	20.6	16.4	−10.9	−23.3
XJ-3	13-Jul	7.39	25.8	7920	47.88	0.81	10.20	1996	2174	5429	68.3	17.6	14.1	−11.4	−23.4
XJ-4	13-Jul	7.65	25.7	7920	44.61	0.69	10.50	2058	2156	3066	69.1	16.0	14.9	−11.1	−23.0
XJ-5	13-Jul	7.98	26.7	7920	41.82	0.73	10.50	2306	2347	1621	75.8	10.5	13.7	−10.9	−22.9
GJ-1	15-Jul	7.57	25.8	415	7.15	0.41	7.73	1240	1311	2225	63.1	14.7	22.2	−11.2	−26.9
GJ-2	15-Jul	7.96	26.0	415	9.27	0.36	8.48	1277	1302	931	71.3	9.2	19.5	−11.3	−26.7
GJ-3	15-Jul	7.96	25.5	415	5.42	0.22	8.09	1438	1466	1041	73.7	9.3	17.0	−11.1	−25.8
GJ-4	15-Jul	7.96	25.2	415	5.26	0.23	9.08	1451	1479	1046	50.2	27.6	22.2	−10.9	−25.3
HJ-1	14-Jul	7.95	25.8	204	5.98	0.22	7.38	967	986	719	48.6	15.6	35.8	−11.2	−26.3
HJ-2	14-Jul	7.72	25.3	204	5.33	0.21	8.29	1240	1289	1561	59.2	15.0	25.8	−10.8	−25.1
HJ-3	14-Jul	7.89	25.5	204	1.67	0.14	8.20	1277	1308	1087	58.6	17.1	24.3	−10.0	−25.8
LD	19-Jul	6.93	24.3	20	19.01	0.26	6.73	1240	1570	9537	39.2	15.9	44.9	−13.1	−23.9
XJ-1	13-Dec	7.68	20.2	1610	5.55	0.12	6.08	2071	2170	2669	51.0	22.3	26.7	−9.0	−26.2
XJ-2	13-Dec	7.8	19.8	1610	3.71	0.12	7.43	2180	2257	2117	56.7	20.2	23.0	−9.0	−24.9
XJ-3	13-Dec	7.74	19.5	1610	6.21	0.15	6.76	2235	2327	2483	56.7	21.0	22.4	−9.5	−25.0
XJ-4	13-Dec	7.83	19.6	1610	5.81	0.17	6.84	2104	2173	1901	60.8	16.8	22.4	−9.1	−24.1
XJ-5	13-Dec	7.84	19.0	1610	8.72	0.18	7.39	2256	2329	1976	57.8	20.8	21.4	−8.5	−23.5
GJ-1	16-Dec	7.92	19.2	18	14.73	0.22	5.96	1526	1565	1113	58.4	11.2	30.4	−9.4	−27.3
GJ-2	16-Dec	8.03	19.2	18	1.85	0.05	7.74	1744	1775	986	61.0	10.7	28.3	−9.4	−27.1
GJ-3	16-Dec	8.19	19.2	18	2.64	0.07	8.01	1744	1759	679	68.9	9.9	21.1	−9.6	−26.3
GJ-4	16-Dec	8.04	19.6	18	1.87	0.05	8.63	1766	1796	980	63.5	10.9	25.7	−10.0	−26.3
HJ-1	14-Dec	7.97	19.2	167	0.40	0.01	9.16	1145	1169	743	42.8	22.4	34.7	−9.3	−27.5
HJ-2	14-Dec	8.06	18.6	167	2.87	0.09	8.17	1581	1606	827	38.2	25.3	36.5	−9.4	−25.9
HJ-3	14-Dec	8.02	18.7	167	1.17	0.04	9.54	1363	1388	783	47.9	19.4	32.7	−8.3	−26.7
LD	19-Dec	7.41	14.8	40	6.84	0.15	5.20	948	1045	2127	30.7	15.1	54.2	−11.1	−26.6
F1[b]	22-Jun		25.3	49300	360.77	6.60	10.67	1453						−13.2	−23.5
F2	22-Jun		25.3	51800	802.02	13.31	11.62	1331							
F3	23-Jun		25.2	54600	502.33	7.13	11.04	1248						−13.0	−23.0
F4	23-Jun		25.2	55000	380.55	5.29	10.24	1476							
F5	24-Jun		25.3	51700	554.86	8.32	11.66	1532						−12.8	−22.6
F6	24-Jun		25.3	50500	581.14	8.54	11.43	1607							
F7	25-Jun		25.7	47950	319.06	4.28	11.05	1453						−13.9	−23.2
F8	25-Jun		25.7	45400	307.47	4.37	9.95	1331							
F9	27-Jun		25.8	33800	235.8	2.97	11.02	1248						−12.1	−22.2
F10	28-Jun		25.3	27900	195.64	3.09	11.06	1476							
F11	28-Jun		25.1	27200	161.32	2.44	10.59	1532						−12.0	−23.8

[a] f_{cc}, f_{cs} and f_{sc} represent the proportions of chemical weathering of carbonate with CO_2, carbonate with H_2SO_4, and silicate with CO_2, respectively. See the text for detail.
[b] F1-F11 are samples taken during the flood event.

3.2. Riverine POC, $\delta^{13}C_{POC}$, and POC/PN

In the Xijiang River system, POC concentration is positively correlated with TSS (Sun et al., 2007; also see Table 2), varying between 0.03 and 2.42 mg/L, and up to 13.31 mg/L during the flood event. TSS varied dramatically through the year, ranging from 0.4 to 180.90 mg/L during the 4 sampling seasons (Table 2). Particularly, it reached a peak value of 802.2 mg/L during the 2005–6 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

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

Sample[a]	Month	Catchment	POC (%)	POC/PN	$\delta^{13}C$ (‰)	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		0.99	8.6	−23.7	
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		1.85	9.3	−23.8	
S3-M	Dec		1.03	9.1	−22.1	
S3-B	Dec		0.26	12.3	−20.5	
S4-T	July	Guiiang	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		0.74	9.8	−23.1	
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		0.57	10.0	−22.0	
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	

[a] 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.

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 ($\delta^{13}C_{POC}$) is −24.7‰ in July, −23.0‰ during the flood event and −25.9‰ in December (Table 2). As seen in Fig. 3, $\delta^{13}C_{POC}$ in all the three tributaries shows a consistent decreasing trend from upper to lower stream in both summer and winter seasons, and a negative shift from summer to winter, which is opposite to the seasonal change showed in $\delta^{13}C_{DIC}$. In the Xijiang it displays downstream a sharper decrease in winter but a smaller decrease in summer. In contrast, a notable increase of $\delta^{13}C_{POC}$ from sample HJ-3 to HJ-2 (in downstream direction) is observed (Fig. 3). This is coincident with the fact that there is a remarkably wide and shallow riverbed with abundant phytoplankton/submerged aquatic plants and green algae in the upper reaches of the sampling site HJ-3, which may contribute a greater portion to the POC with more negative $\delta^{13}C$ values.

POC/PN 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 ratio of terrestrial/aquatic components due to higher POC/PN ratios of terrestrial plants, and thus reflecting seasonal variations in soil erosion intensity. In the mainstream of the Xijiang, POC/PN ratio is higher than in its tributaries. The low riverine POC/PN ratios relatively to C/N ratios of terrestrial plants (Cifuentes, 1991) imply a significant contribution of aquatic sources, for example, phytoplankton as a component of the riverine organic matter. Similar to $\delta^{13}C_{POC}$, POC/PN ratio in the Xijiang River system also shows a downstream decreasing trend in both summer and winter seasons, suggesting a downstream increase of aquatic fraction in the riverine POC (Fig. 4).

3.3. Soil POC, $\delta^{13}C_{POC\text{-}soil}$, and POC/PN

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 top to bottom in the soil profile

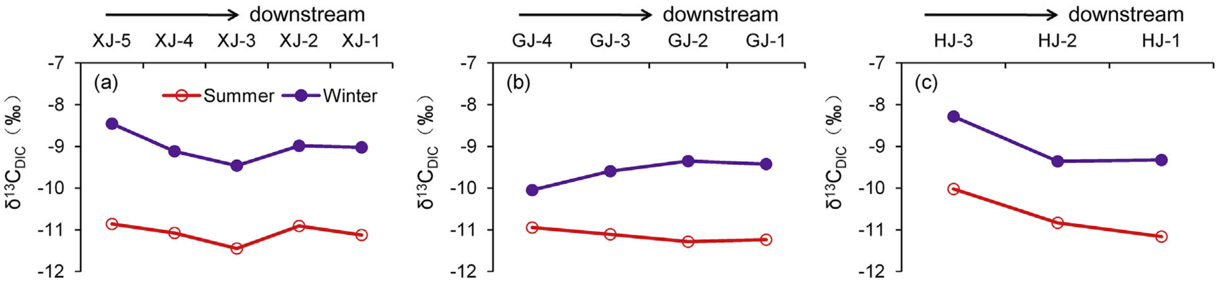

Fig. 2. Variations of $\delta^{13}C_{DIC}$ along the Xijiang (a), Guijiang (b) and Hejiang (c) rivers.

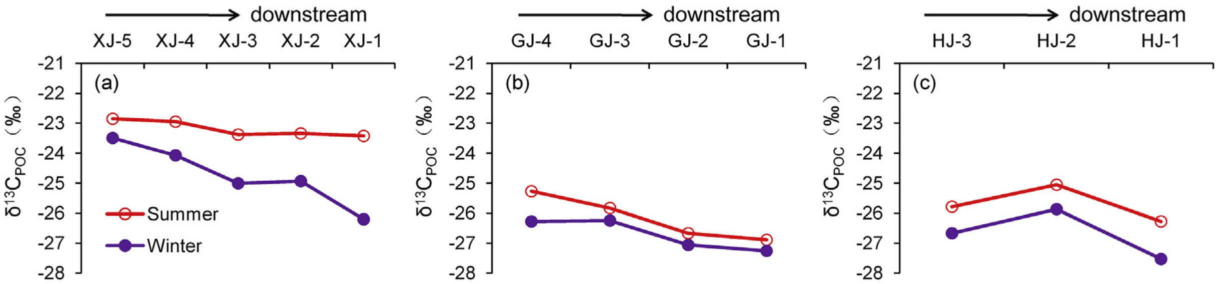

Fig. 3. Variations of $\delta^{13}C_{POC}$ along the Xijiang (a), Guijiang (b) and Hejiang (c) rivers.

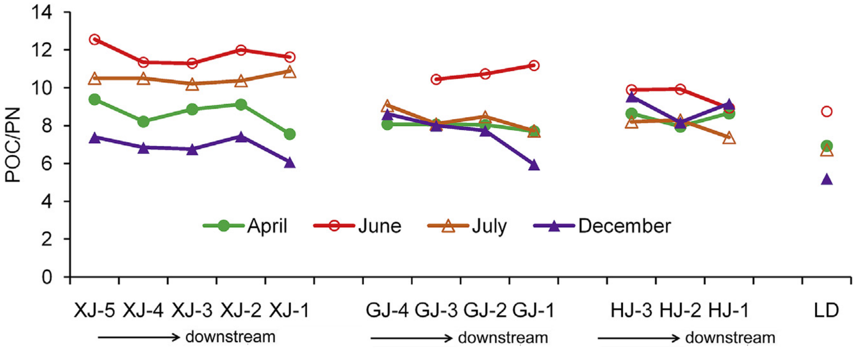

Fig. 4. Variations of POC/PN ratio along the Xijiang (XJ), Guijiang (GJ), Hejiang (HJ)and Luoding (LD) rivers.

without significant seasonal variation. The soil POC content slightly varies among the selected soil profiles due to their different land cover.

The δ^{13}C value of soil POC ($\delta^{13}C_{POC\text{-}soil}$) in the Xijiang basin ranges from −25.5‰ to −19.6‰ with an average of −22.6‰, in good accord with previous studies (Pan et al., 2002; Chen et al., 2005) and the riverine $\delta^{13}C_{POC}$ values of the extreme flood. Basically, the $\delta^{13}C_{POC\text{-}soil}$ 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). POC/PN ratio of the soil ranges from 7.3 to 12.5, with a mean of 10.2, with no prominent trend in both seasonal and spatial variations across the lower Xijiang Basin.

4. Discussion

4.1. δ^{13}C signature of riverine DIC and influencing factors

It has been demonstrated by many studies that the Xijiang hydrochemistry including DIC is dominated by carbonate and silicate weathering (Xu and Liu, 2007; Li et al., 2008; Sun et al., 2010). The rock chemical weathering processes can be represented in a simplified form as shown below.

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^- \tag{1}$$

$$2CaCO_3 + H_2SO_4 = 2Ca^{2+} + 2HCO_3^- + SO_4^{2-} \tag{2}$$

$$CaSiO_3 + 2CO_2 + 3H_2O = Ca^{2+} + 2HCO_3^- + H_4SiO_4 \tag{3}$$

Accordingly, for chemical weathering of carbonate with CO_2, half amount of bicarbonate ions is from the carbonate rock with higher δ^{13}C value (commonly ~0‰), and half is from soil CO_2 with lower δ^{13}C value. For carbonate dissolution by H_2SO_4, all bicarbonate ions are produced from the rock, while all bicarbonate is from soil CO_2 during silicate weathering. As bicarbonate is the dominant component of DIC in the Xijiang River, the sources of bicarbonate must influence the δ^{13}C signature of riverine DIC, that is, higher area ratios of carbonate/silicate in the catchments results in higher $\delta^{13}C_{DIC}$ value. Therefore, it is not difficult to understand that the Luoding River has the lowest $\delta^{13}C_{DIC}$ value among the selected four tributaries because it developed on an area with the lowest carbonate/silicate ratio. It may also explain the downstream decrease of the $\delta^{13}C_{DIC}$ mentioned above because carbonate is mainly exposed in the upper reaches (Fig. 1). However, this mechanism cannot account for the positive shift of $\delta^{13}C_{DIC}$ from summer to winter, as carbonate weathering contributes a greater portion to the DIC in summer than in winter (Sun et al., 2010), and there must be other processes influencing the isotopic composition of the riverine DIC.

The possible processes other than rock weathering that influence the riverine $\delta^{13}C_{DIC}$ may include (1) carbonate precipitation; (2) exchange with atmospheric CO_2; (3) CO_2 directly comes from soil (i.e. dissolved by surface and rain water and discharged into river); 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 pCO_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. Outgassing 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 conditions, the fraction of DIC directly coming from soil CO_2 dissolution is minor and can be neglected during carbonate and silicate weathering (Dreybrodt, 1988; Aucour et al., 1999). 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 δ^{13}C value close to that of organic matter, whereas photosynthetic uptake of DIC preferentially removes ^{12}C, leading to an enrichment of ^{13}C in the DIC (Yang et al., 1996). The relative efficiency of these two processes 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 shorter residence time of river water. Therefore, in-river primary production is responsible for the positive shift of $\delta^{13}C_{DIC}$ from summer to winter in the Xijiang River system.

4.2. Riverine $\delta^{13}C_{poc}$ and influence of in-river photosynthetic organic matter

In the previous discussion, the significant process of in-river primary production has been inferred from the isotopic signature of DIC. As an important source of riverine POC, primary production must synchronously affect its isotopic signature and POC/PN ratio.

Organic matter transported by rivers comprises a complex mixture of allochthonous and autochthonous sources. As mentioned earlier, slow flow and lower turbidity are favorable conditions for in-situ phytoplankton production, and thus a higher proportion of autochthonous organic matter with lower values of both δ^{13}C and POC/PN ratio. River flow is commonly slower in lower reaches than in the upper and slower in dry season than in rainy season, coincident with the observed facts that both $\delta^{13}C_{poc}$ and

POC/PN decrease downstream and negatively shift from summer to winter (Figs. 3 and 4). It is interesting that the seasonal variation trend of $\delta^{13}C_{POC}$ and $\delta^{13}C_{DIC}$ is totally in the opposite direction. The conjoined and reversed seasonal variations of the riverine POC and DIC suggest that they are both affected by in-river photosynthetic production which transformed DIC into organic matter.

Generally, riverine transport of POC is complicated by multiple sources and processes that occur within the basins. 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, as demonstrated by the $\delta^{13}C_{poc}$ values of the extreme flood (−23.0‰ in mean) and the soil profiles (−22.6‰ in average) (Tables 2 and 3). Therefore, it can be considered as a typical $\delta^{13}C$ value of the regional terrestrial-sourced fraction in the riverine POC.

Riverine POC in the Xijiang River system is all depleted in $\delta^{13}C$ with respect to soil organic matter, in average, by 3.3‰ in winter, 2.1‰ in summer, and only 0.1‰ for the flood event (see Table 2). This implies an input of in-river primary production with more negative $\delta^{13}C$ than soil organic matter in the riverine POC.

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 $\delta^{13}C$ values as end-members in the following isotopic mass balance:

$$\delta_{POC} = f_{au} * \delta_{au} + f_{al} * \delta_{al} \tag{4}$$

$$f_{au} + f_{al} = 1 \tag{5}$$

where δ_{POC}, δ_{au}, δ_{al} are $\delta^{13}C$ 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 as the end-member δ_{POC}. As discussed previously, the observed $\delta^{13}C_{POC}$ (−23.0‰ in average) of the extreme flood represents the terrestrial carbon, i.e. δ_{al}. Aquatic plants taking up DIC can impose ^{13}C fractionations of about 20–23‰ (Zhang et al., 1995; Palmer et al., 2001). As $\delta^{13}C_{DIC}$ of the Xijiang River system ranges −11.1‰ in summer to −9.3‰ in winter, the $\delta^{13}C$ value of primary production should be within the ranges between −29.3‰ and −34.1‰. This is comparable to the measured $\delta^{13}C$ value of primary production in the headwater region of the Xijiang (−29.7‰ in average, cf., Li, 2009). Because of higher percentage of carbonate area thus about 2‰ higher of $\delta^{13}C_{DIC}$ (−8‰) in the upper Xijiang region, the $\delta^{13}C$ value of primary production (δ_{au}) in the lower Xjiang river system can be accordingly corrected to −32‰. The calculated results show that the percentage contribution of in-river primary production to the riverine POC of 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.

4.4. Impact of riverine DIC-POC transformation on apparent ^{14}C age and CO_2 sequestration

The riverine autochthonous POC, which is assumingly derived from DIC, comes from carbonate and soil CO_2 through rock weathering. Given the percentage contributions (see Table 2) of the three major types of weathering processes (Equations (1)–(3)) to the DIC, which have been obtained from an earlier study (Sun et al., 2010) using a mass balance approach with major ion chemistry data, we can calculate the contributions of carbonate-sourced carbon in the riverine POC.

For a first order estimation, we assume that all the carbon of primary production is derived from carbonate and silicate weathering, but only carbonate weathering can introduce rock carbon into DIC through the two following 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}) can be expressed as the following equation:

$$f_{carb} = 0.5f_{cc} + f_{cs} \tag{6}$$

where f_{cc} and f_{cs} represent the proportions of chemical weathering of carbonate with CO_2 and carbonate with H_2SO_4, respectively. 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 ($f_{carb/POC}$) can be obtained using the following equation.

$$f_{carb/POC} = f_{carb} * f_{au} \tag{7}$$

Results show that the contribution of carbonate-rock carbon 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.

Transformation of DIC into POC may introduce large amount of old carbon from dissolution of old carbonate ($\Delta^{14}C$ = −1000‰). Assuming that 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 $\Delta^{14}C$ = 80‰, then the mixing value of $\Delta^{14}C$ should be −107‰, −135‰, −159‰ and −53‰ for the Xijiang, Guijiang, Hejiang and Luoding, respectively. This implies that even though the POC transported by river is totally formed in modern time, it may exhibit a very ancient ^{14}C age.

The ^{14}C values of monthly POC in the Xijiang have been reported ranging from −425‰ to −201‰ (Wei et al., 2010). Some studies suggested that the aged carbon in rivers, or even in the coastal regions, is considered to be mainly from sedimentary rocks or vascular plant material preserved in deep soil (Berner, 2004; Bouchez et al., 2010; Loh et al., 2012). Our study argues that carbonate rock-derived DIC may be also responsible to the older ^{14}C age of riverine POC, especially for carbonate dominated rivers. Meanwhile, this transformation of DIC to OC could also provide a mechanism for the “old carbon reservoir” effect on the ^{14}C age of marine and lacustrine sediments that contain aquatic biogenic materials.

Our calculation is based on the assumption that all the carbon of primary production is derived from a DIC purely by chemical weathering, but other processes can also affect the carbon isotope composition. For example, respired CO_2 from riverine organic carbon may interchange with the DIC, making the DIC a younger ^{14}C age, thus reducing the old carbon effect.

The transformation of DIC by aquatic photosynthesis in river systems contributes not only to POC, but also DOC. The latter deserves to be examined in a future study. Nevertheless, this study is calling for a reconsideration on the traditional belief that carbonate weathering has “no effect” in regulating the atmospheric CO_2 at a long-term scale. The carbonate rock-sourced DIC transformed into OC by riverine primary production, at least partly, will be ultimately buried, constituting a riverine ‘biological pump’ (Longhurst and Glen Harrison, 1989; Tortell et al., 2008; Liu et al., 2010).

5. Conclusions

This study employed an isotopic method with observed data and identified the aquatic and terrestrial fractions in the riverine POC. Based on the stoichiometry of carbonate rock weathering, we further estimated the contribution of carbonate-sourced carbon to the riverine POC in the Xijiang and its tributaries. In the riverine POC, the fractions transformed from carbonate-sourced 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 CO_2 in river systems. The transformation of DIC into POC may introduce a notable portion of old carbon derived from carbonate dissolution into aquatic organic matter, thus providing a new mechanism for explaining abnormally older ^{14}C age of the sediments deposited in aquatic environments.

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