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Source and flux of POC in two subtropical karstic tributaries with contrasting land use practice in the Yangtze River Basin

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ABSTRACT

Elemental (C/N ratio) and C isotope composition ($\delta^{13}C$) of particulate organic C (POC) and organic C content (OC) of total suspended solids (TSS) were determined for two subtropical karstic tributaries of the Yangtze River, the Wujiang (the eighth largest tributary) and Yuanjiang (the third largest tributary). For the latter, two headwaters, the karstic Wuyanghe and non-karstic Qingshuijiang were studied. The Wujiang catchment is subject to intensive land use, has low forest coverage and high soil erosion rate. The $\delta^{13}C$ of POC covered a range from −30.6‰ to −24.9‰, from −27.6‰ to −24.7‰, and from −26.2‰ to −23.3‰ at the low-water stage, while at the high-water stage varied in a span between −28.6‰ and −24.4‰, between −27.7‰ and −24.5‰, and between −27.6‰ and −24.2‰ for the Wujiang, Wuyanghe, and Qingshuijiang, respectively. The combined application of C isotopes, C/N ratio, OC, and TSS analyses indicated that catchment soil was the predominant source of POC for the Wujiang while for the Wuyanghe and Qingshuijiang, in-stream processes supplied the main part of POC in winter and summer. A significant increase in $\delta^{13}C$ value (1.4‰) of POC was found in the Wujiang during summer, and was attributed to the enhanced soil erosion of the dry arable uplands close to the riverbanks of the main channel. Based on a conservative estimate, POC fluxes were 3.123×10^{10}, 0.084×10^{10}, and 0.372×10^{10} g a^{-1} while export rates of POC were 466, 129, and 218 mg m^{-2} a^{-1} for the Wujiang, Wuyanghe, and Qingshuijiang, respectively. The POC export rate for the karstic Wujiang, with intensive land use, was 2–3 higher than that of the karstic Wuyanghe or of the non-karstic Qingshuijiang where soil erosion was minor. Such high values imply rapid degradation of related karstic ecosystems impacted by intensive land use activities, and pose a potential threat to the health of the Three Gorges Reservoir.

1. Introduction

Riverine particulate organic C (POC) is a main component of the global C cycle, and is important in freshwater and ocean ecology (Meybeck, 1982; Doucett et al., 1996; Humborg et al., 1997; Ludwig and Probst, 1998; Benner et al., 2005; Bianchi et al., 2007). Entry of POC into rivers through hydrological cycles is one of the main pathways for nutrient loss from soil systems. Among the seven continents, Asia supplies the major part (50%) of the global POC flux from land to ocean (197×10^{12} g C a^{-1}) (Beusen et al., 2005). However, the origin of POC in Asian tropical and subtropical rivers has not been well constrained (Ludwig and Probst, 1998; Balakrishna and Probst, 2005). The rivers originating from the Tibetan Plateau and contiguous regions (e.g., the Yun-Gui Plateau in SW China) generally have high POC fluxes due to steep uplands and high soil erosion (France-Lanord and Derry, 1997; Aucour et al., 2006). Hence, land use changes in these regions, such as from forest to agriculture, will lead to a rapid response of soil erosion rate and associated riverine POC source changes. In this respect, they are well suited for study on the association between riverine C cycles and land use changes.

The ultimate source of riverine POC is catchment soil (Bird et al., 1998; Martinelli et al., 1999) and in-stream photosynthesis (Wang and Veizer, 2000; Finlay, 2003). If the soil-supplied POC can be distinguished from the in-stream-produced POC, then the biogeochemistry of riverine POC can be related to catchment land use activities. Carbon isotope ($\delta^{13}C$) chemistry has been successfully used as a robust tool for identifying riverine POC sources (Barth et al., 1998; Otero et al., 2000; Kendall et al., 2001; Guo and Macdonald, 2006). This method is based on two observations. One is that, due to different fractionation mechanisms, aquatic plants are generally enriched in the light C isotope (^{12}C), compared with their terrestrial counterparts (Mook and Tan, 1991). Another one is that terrestrial C_4 plants have higher C isotope ratios than C_3 plants because of differential discrimination of photosynthetic enzymes (ribulose-1, 5-biphosphate carboxylase or phophoenolpyruvate carboxylase) against $^{13}CO_2$ (Farquhar et al., 1982). These

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isotopic differences can be stamped on different molecules in the river-load. However, the C isotope technique might be of limited use for those rivers in which the C isotope composition of aquatic plants overlaps with that of their terrestrial counterparts (Deegan and Garritt, 1997; Wang et al., 2004). Such being the case, this technique will be more powerful if coupled with other geochemical parameters (e.g., C/N ratio, organic C content (OC), Total Suspended Solids (TSS), etc.) (Hellings et al., 1999; Balakrishna and Probst, 2005).

In this work, the Wujiang and Yuanjiang tributaries of the Yangtze were compared in terms of POC source and export rate, based on an integration of C isotopes, C/N ratio, OC and TSS analyses. The differences in source and export rate were associated with disparate land use practices in their catchments. The potential impacts of high POC exports in the Wujiang catchment on the health of the Three Gorges Reservoir were also evaluated.

2. Site description

The Wujiang is the eighth largest tributary of the Yangtze in terms of discharge, and originates from the western part of Guizhou in the Yun(nan)-Gui(zhou) Plateau conterminous with the eastern part of the Tibetan Plateau (Fig. 1a). It is 1037 km long, with a drainage area of 8.8×10^4 km^2. The Wujiang has a discharge of 5.2×10^{10} m^3 a^{-1}, close to the discharge of 5.9×10^{10} m^3 a^{-1} for the second largest Chinese river, i.e. the Yellow River (CCGPC, 1988). Within Guizhou, these parameters are 874.2 km, 6.7×10^4 km^2 and 3.76×10^{10} m^3 a^{-1}, respectively (Table 1). The Wujiang flows into the Three Gorges Reservoir in Chongqing (Fig. 1a). It ranks first in discharge and TSS (1.1×10^8 t a^{-1}) among the tributaries in the south of this reservoir (FDGP, 2001). It supplies less than 1/8 of the total discharge (45×10^{10} m^3 a^{-1}), but it transports 1/5 of the TSS (5.3×10^8 t a^{-1}) (MEP, 2001). The catchment is underlain mainly by Permian and Triassic carbonates (Fig. 1b) (CCGPC, 1988). Guizhou extends horizontally from E103°36′ to E109°33′, and longitudinally from N24°38′ to N29°14′ (CCGPC, 1988). Its total area is 176,128 km^2, with a mean altitude of 1100 m. Moreover, Guizhou is the only Chinese province with no plains, and 92.5% of its total area is mountainous (SDG, 2006).

The Yuanjiang is the third largest tributary of the Yangtze in terms of discharge. Its origin is in the middle part of Guizhou (Fig. 1a). It flows 1022 km, and collects runoff within an area of 8.9×10^4 km^2, with a discharge of 6.67×10^{10} m^3 a^{-1} (CWRC, 2007). The Yuanjiang is composed of two headwaters in Guizhou, i.e. the Wuyanghe and Qingshuijiang. After they converge in Hunan the river becomes the Yuanjiang, which subsequently enters the Dongting Lake, which flows into the Yangtze in Hunan (Fig. 1a). The Dongting is the second largest freshwater lake in China, with an area of 2623 km^2 and a volume of 1.67×10^{10} m^3 in 1995 (CWRC, 2007). The discharges of the Wuyanghe and Qingshuijiang in Guizhou are 0.36×10^{10} m^3 a^{-1} and 1.11×10^{10} m^3 a^{-1}, respectively (Table 1). They have a combined catchment area of 2.36×10^4 km^2 (0.65×10^4 plus 1.71×10^4 km^2) inside Guizhou. The catchment of the Wuyanghe is underlain mainly by carbonates while that of the Qingshuijiang by carbonates (area above sampling site 4) or detrital rocks (area lower than sampling site 4) (CCGPC, 1988; Mao, 1992).

The precipitation patterns in the two catchments are determined by the East Asian monsoon systems. The rainfall during the summer monsoon season (May to September) accounts for about 65% of the annual total precipitation.

The Wujiang catchment is characterised by major agricultural land use (high percentage of dry arable uplands and maize plantation in summer), very low forest coverage, and severe soil erosion, compared with the Yuanjiang catchment (Table 2).

3. Methods

3.1. Field sampling

River water was collected during the low-water stage (January 18–February 8, 2002) and high-water stage (July 15–August 4, 2002). The total number of samples for each sampling period was 49 (34 for the Wujiang plus 15 for the Yuanjiang) (Fig. 1b), including 18 mainstream samples in the Wujiang (e.g., 1, 2, 6, 8, 9, 12, 14, 16, 18, 20, 22, 24, 26, 28, 29, 31, 32, 34 in Fig. 1b). The sampling order was arranged from the upper to lower streams. In the Wujiang, sampling sites 2, 6, 8, and 19 were reservoirs for power generation. In the Yuanjiang, samples 1–8 and samples 9–14 belonged to the Qingshuijiang and the Wuyanghe, respectively (Fig. 1b). At each sampling site, water in the centre of a river was collected at 0.5 m depth for mainstream and large tributaries or near the bottom for shallow streams. The water was stored in two high-density polyethylene bottles with screw caps (1500 mL, leak-poof). Bottles were rinsed three times prior to collection of the samples. Samples were poisoned in situ with 1.5 mL of saturated $HgCl_2$ solution. No space was left for air in each bottle. Water (one bottle for POC and one for C/N ratio) samples were filtered within 8 h through pre-ashed (500 °C, 5 h) 47 mm Whatman GF/F glass fibre filters (0.65 μm). Terrestrial plant samples and soils were randomly collected along the sides of the rivers.

3.2. Isotopic and C/N ratio measurements

For POC and C/N ratio analyses, the filter was freeze-dried. Ground soil samples and filters were acidified with dilute HCl and oven-dried overnight at 60 °C just prior to isotope or C/N ratio determination. Cleaned plant leaves were oven-dried and ground (150 mesh).

Plant C and POC were transformed into CO_2 using the high-temperature (850 °C, 5 h) sealed-quartz tube combustion method with Cu oxide as oxidant (Buchanan and Corcoran, 1959) since the low-temperature (550 °C, 1 h) combustion method could lead to a large analytical uncertainty (Tao et al., 2001). Carbon dioxide was cryogenically separated and its pressure and temperature were measured in a sensor (Edwards Barocel® 600). The $^{13}C/^{12}C$ ratio of CO_2 was determined on a dual-inlet isotope ratio mass spectrometer (MAT 252). Carbon isotope data were reported and normalised following the "δ" denotation of Craig (1953) relative to the Vienna Pee Dee Belemnite (VPDB). The POC contents were calculated based on the above-measured mass and normalised to 1 L of water. The total precision for concentration and $\delta^{13}C$ analysis was better than 3% (1σ) and 0.1‰ (1σ), respectively.

The TSS on the acidified filter was scraped off and wrapped in a Sn capsule after weighing. The C/N molar ratio was determined in an elemental analyser (PE 2400). The TSS was determined by weight. The OC of TSS was calculated according to the following equation: OC = POC in mg L^{-1}/TSS in mg L^{-1} × 100%.

4. Results

4.1. POC contents

For the Wujiang, Wuyanghe and Qingshuijiang, the POC at the low-water stage ranged from 4.2 to 103.6 μM L^{-1}, 4.7–7.0 μM L^{-1}, and 6.2–31.9 μM L^{-1} while at the high-water stage, it varied between 8.1 and 284.8 μM L^{-1}, 27.1 and 132.1 μM L^{-1}, and 7.0 and 44.6 μM L^{-1}, respectively, (Table 3). At the low-water stage, the mean POC was 30.4 ± 21.7 μM L^{-1} (n = 21), 6.0 ± 1.2 μM L^{-1} (n = 3), and 13.5 ± 12.3 μM L^{-1} (n = 4) while at the high-water stage it was 68.6 ± 58.8 μM L^{-1} (n = 32), 59.2 ± 47.4 μM L^{-1}

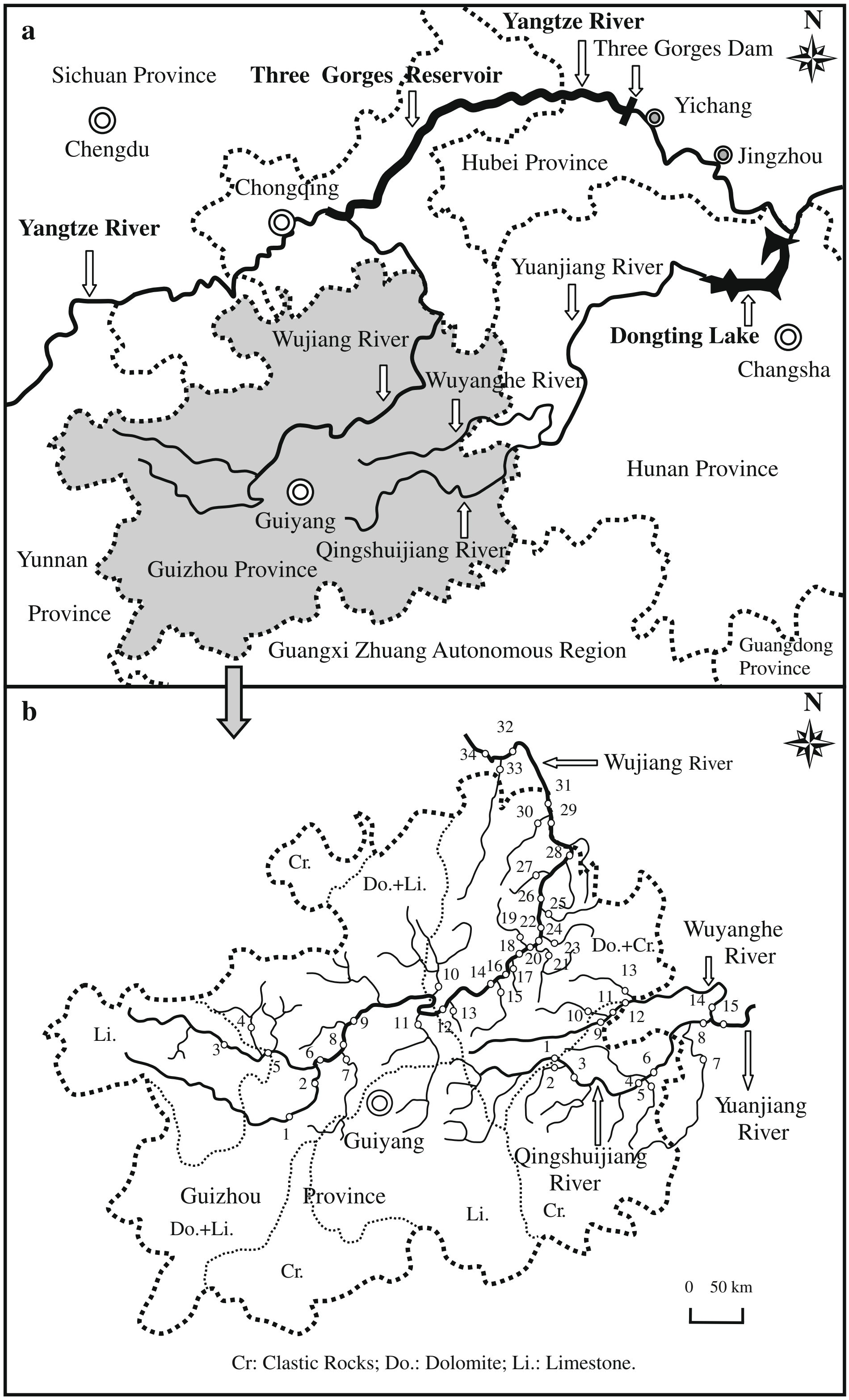

Fig. 1. Maps for the sampled river systems. (a) Showing the relationship of the Yangtze River with its two tributaries, i.e. the Wujiang River and Yuangjiang River. The Three Gorges Reservoir extends from Chongqing to Sandouping Town of Yichang in Hubei Province. The dotted line defines the provincial territory. Guizhou Province (the shadowed area) is contiguous to Sichuan Province and Chongqing in the north, to Guangxi Zhuang Autonomous Region in the south, to Yunnan Province in the west, and to Hunan Province in the east. The combination of Yunnan and Guizhou is called the Yun-Gui plateau, whose altitude is generally >1000 m. Both the Wujiang and Yuanjiang originate in Guizhou. The Wujiang confluences with the Yangtze in Chongqing, and the Yuanjiang enters the Dongting Lake in Hunan. (b) Showing the spatial distribution of water samples. The fine dotted line defines the regions with different lithology. For the Wujiang, Sampling sites 2, 6, 8, and 19 are reservoirs. The Yuanjiang inside Guizhou is composed of two tributaries, i.e. the Qingshuijiang River in the south and the Wuyanghe River in the north. During each sampling period, 34 samples were collected for the Wujiang, and 8 and 6 samples for the Qingshuijiang and Wuyanghe, respectively.

Table 1
Physical parameters for the river sections within Guizhou (CCGPC, 1988).

River	Discharge (10^8 m^3 a^{-1})	Catchment (10^4 km^2)	Unit area discharge (m^3 m^{-2} a^{-1})
Wujiang	376	6.70	0.56
Wuyanghe	36	0.65	0.55
Qingshuijiang	111	1.71	0.65

Table 2
Contrasting characteristics for the Wujiang and Yuanjiang catchments (compiled from Mao (1992), An and Zhou (2001), Wu (2001), He and Jie (2002), FDGP (2003), PGGP (2005)).

Index	Wujiang	Yuanjiang	Guizhou
Mean precipitation (mm)	1121	1246	800–1600
Forest coverage (%)	16.0	50.9	25.7
Maize acreage (%)*	6.5	0.8	4.0
Dry arable upland (%)*			
2° < slope < 15°	10.1	1.6	7.2
slope > 15°	14.8	3.5	11.8
Water and soil loss area (%)*	58.2	24.9	41.5
Soil erosion rate (t km^{-2} a^{-1})	4039	<350	1432
Lithology	Carbonate	Mainly noncarbonate	Miscellaneous

* The related area is divided by the catchment area (Table 1) inside Guizhou for the Wujiang and Yuanjiang or by the total land area (176,128 km^2) of Guizhou province, expressed in percentage.

($n = 6$), and 29.5 ± 11.5 μM L^{-1} ($n = 8$) for the three rivers, respectively. The mean POC at the high-water stage increased by a factor of 2.3 and 9.9 for the Wujiang and Wuyanghe, respectively. The mean POC at the high-water stage for the Qingshuijiang was enhanced by a factor of about 2.2, but it was less than half the Wujiang mean POC. Of all three rivers, the Wujiang had the highest mean POC.

The POC showed broad fluctuations spatially and temporally, with higher contents at the high-water stage (Fig. 2). The differences in POC content between the high-water and low-water stages were very obvious for the mainstream Wujiang (Fig. 2a and b). A linear downstream increase for the summer mainstream Wujiang (Fig. 2b) was observed ($r^2 = 0.37$, $n = 17$, $p < 0.01$), implying a significant contribution from a particular source in summer. At the low-water stage, the POC for tributaries was similar to that for mainstreams (Fig. 2a), but it was significantly lower than that for mainstreams at the high-water stage (Fig. 2b). On the other hand, a large scatter in POC was noticeable for the Wuyanghe (Fig. 2c) as opposed to the Qingshuijiang (Fig. 2d).

4.2. Carbon isotope compositions of POC

At the low-water stage for the Wujiang, Wuyanghe and Qingshuijiang, the $\delta^{13}C_{POC}$ ranged from −30.6‰ to −24.9‰, −27.6‰ to −24.7‰, and −26.2‰ to −23.3‰ while at the high-water stage, the $\delta^{13}C_{POC}$ varied between −28.6‰ and −24.4‰, −27.7‰ and −24.5‰, and −27.6‰ and −24.2‰, respectively (Table 3). The mean $\delta^{13}C_{POC}$ at the low-water stage was −27.2 ± 1.3‰ ($n = 21$) and −26.5 ± 1.6‰ ($n = 3$) for the Wujiang and Wuyanghe, respectively. Meanwhile, the mean $\delta^{13}C_{POC}$ for the Qingshuijiang was higher than for the other two rivers, with a mean value of −24.9 ± 1.5‰ ($n = 4$). The mean $\delta^{13}C_{POC}$ (−25.8 ± 1.1‰, $n = 31$) for the Wujiang was higher at the high-water stage than at the low-water stage (−27.2 ± 1.3‰, $n = 21$) while for the Qingshuijiang the case was inverted (−26.0 ± 1.5‰, $n = 8$ at the high-water stage versus −24.9 ± 1.55‰, $n = 4$ at the low-water stage). The mean $\delta^{13}C_{POC}$ (−26.6 ± 1.4‰, $n = 6$) at the high-water stage for the Wuyanghe was close to that (−26.5 ± 1.6‰, $n = 3$) at the low-water stage.

The $\delta^{13}C_{POC}$ also displayed a distinct inter-sample variation (Fig. 3). Although the tributary $\delta^{13}C_{POC}$ was scattered for the Wujiang (Fig. 3a), yet the $\delta^{13}C_{POC}$ at the high-water stage displayed a significant downstream increase ($r^2 = 0.43$, $n = 17$, $p < 0.01$) (Fig. 3b), implying a source with a relatively higher $\delta^{13}C$.

4.3. POC content – $\delta^{13}C_{POC}$ relations

The $\delta^{13}C_{POC}$ was found to increase linearly in relation to POC for the main channel summer samples of the Wujiang ($r^2 = 0.25$, $n = 17$, $p < 0.05$) (Fig. 4a), but no significant patterns existed for the main channel winter samples (Fig. 4a) or for all samples of the Wuyanghe (Fig. 4b) and Qingshuijiang (Fig. 4b).

4.4. C/N ratios and OC

Variations in C/N ratios for the three rivers demonstrated different patterns although their $\delta^{13}C_{POC}$ were all inside the range for land plants (higher than −30‰). The C/N ratios for the Wujiang were generally >20 at the low-water stage, and >13.5 at the high-water stage but with a distinct decrease (Table 3). For the Qingshuijiang they were >10 at the low-water stage, and <10 at the high-water stage. For the Wuyanghe, they were greater than or close to 10 at the low-water stage, or <7 at the high-water stage.

The OC showed opposite patterns. For the Wujiang, the OC at the high-water stage was lower than at the low-water stage while for the Wuyanghe and Qingshuijiang, the direction was reversed, e.g., the OC at the high-water stage was higher than at the low-water stage (Table 3).

4.5. POC–TSS relations

At the low-water stage, all three rivers had low TSS, with a mean value of 4.1 ± 2.6 mg L^{-1} ($n = 34$) and a range from 0.3 to 10.8 mg L^{-1} for the Wujiang, a mean value of 3.6 ± 2.2 mg L^{-1} ($n = 6$) and a range from 0.5 to 6.1 mg L^{-1} for the Wuyanghe, and a mean value of 6.4 ± 2.8 mg L^{-1} ($n = 8$) and a range from 1.1 to 10.7 mg L^{-1} for the Qingshuijiang (Table 3). However, at the high-water stage, the Wujiang displayed a distinct increase in TSS, with a mean value of 47.9 ± 58.5 mg L^{-1} ($n = 34$) and a range from 1.0 to 239.1 mg L^{-1} (Table 3). In contrast, the Wuyanghe and Qingshuijiang TSS remained low, 4.8 ± 2.7 mg L^{-1} ($n = 6$) with a range from 1.0 to 8.4 mg L^{-1}, and 3.5 ± 1.8 mg L^{-1} ($n = 8$) spanning a range from 1.8 to 7.3 mg L^{-1}, respectively (Table 3).

At the low-water stage, a positive correlation ($r^2 = 0.25$, $n = 17$, $p < 0.05$) between TSS and POC was found for the Wujiang, but not for the Wuyanghe or Qingshuijiang (Fig. 5a). At the high-water stage, a positive correlation ($r^2 = 0.86$, $n = 32$, $p < 0.001$) between TSS and POC was present only for the Wujiang (Fig. 5b), not for the Wuyanghe (Fig. 5c) or Qingshuijiang (Fig. 5c).

Overall, the Wujiang showed different patterns in spatial and temporal variations of POC, $\delta^{13}C_{POC}$, C/N ratio, OC and TSS.

5. Discussion

5.1. Variations of POC

Within each sampling period, the inter-sample difference in POC was large (Fig. 2). POC always tends to be present in the upper part of a soil profile, being easily removed by surface runoff (Hedges and Oades, 1997). However, dense vegetation will obstruct the movement of litterfall. When soil erosion approaches bedrock, rivers will also receive a high POC supply (Hedges and

Table 3
Isotopic (δ^{13}C) and elemental (C/N molar ratio) composition of POC, organic carbon content (OC[a]), total suspended solids (TSS) and estimated terrestrial fraction (f_T) of POC.

Sample no.	River name	Low-water stage						High-water stage					
		POC (μM L^{-1})	$\delta^{13}C_{POC}$ (‰)	C/N	OC (%)	TSS (mg L^{-1})	f_T (%)	POC (μM L^{-1})	$\delta^{13}C_{POC}$ (‰)	C/N	OC (%)	TSS (mg L^{-1})	f_T (%)
Wujiang													
WJW01[b]	Wujiang	28.0	−28.8	67.9	10.8	3.1	100	47.8	−28.3	44.2	5.0	11.5	100
WJW02	Wujiang			54.7		0.3	100	28.3	−27.9	38.9	18.9	1.8	100
WJW03	Mukonghe	20.2	−26.0	74.2	30.3	0.8	100	109.9	−25.5	35.9	2.1	62.1	100
WJW04	Luojiaohe					3.9		91.8	−28.1	22.7	6.8	16.1	100
WJW05	Liuchonghe	34.5	−27.4	37.2	27.6	1.5	100	53.9	−24.5	16.4	2.2	29.5	72
WJW06	Wujiang					2.2		8.1	−26.7	14.3	6.5	1.5	56
WJW07	Maotiaohe	29.3	−24.9	12.1	70.3	0.5	39	20.6	−26.0	15.6	24.7	1.0	66
WJW08	Wujiang	20.8	−27.8	30.5	27.7	0.9	100	9.4	−26.2	12.2	7.1	1.6	40
WJW09	Wujiang	13.0	−28.0		31.2	0.5		41.0	−25.3		37.8	1.3	
WJW10	Xiangjiang			45.7		2.7	100			24.4		5.0	100
WJW11	Qingshuihe	51.5	−25.4		6.9	8.9		284.8	−24.7	19.7	1.5	224.3	98
WJW12	Wujiang	21.8	−27.8	73.2	21.8	1.2	100	65.1	−26.5	14.6	3.2	24.4	58
WJW13	Wenganhe	11.7	−27.7		7.0	2.0		127.1			1.4	112.4	
WJW14	Wujiang					3.7		77.7	−25.9	13.2	6.2	15.0	48
WJW15	Yuqingjiang	66.3	−26.8	20.7	22.7	3.5	100	17.0	−26.3	13.4	2.3	9.0	49
WJW16	Wujiang					4.0		84.1	−25.1		1.9	51.8	
WJW17	Sandaoshui	26.8	−25.9		5.6	5.7		21.4	−25.7	17.5	2.9	8.9	81
WJW18	Wujiang	10.7	−27.1	58.6	3.0	4.3	100	24.6	−25.4	13.7	0.6	45.7	52
WJW19	Liuchihe	20.5	−26.8	14.5	5.2	4.7	58	33.8	−24.7		1.1	35.5	
WJW20	Wujiang					4.1		75.5	−25.0		3.0	30.4	
WJW21	Shiqianhe	30.3	−27.8	17.9	10.7	3.4	84	34.6	−28.6	18.4	6.2	6.7	88
WJW22	Wujiang	31.0	−28.1	123.7	7.6	4.9	100	57.3	−26.5	13.4	2.2	30.8	49
WJW23	Qingduhe	28.6	−28.0	23.9	11.8	2.9	100	16.1	−25.6	15.5	2.7	7.1	65
WJW24	Wujiang	35.0	−27.1	34.4	8.6	4.9	100	95.8	−25.2	14.7	1.3	85.5	59
WJW25	Yinjianghe	26.6	−27.7		5.1	6.3		31.2	−24.8		2.2	17.3	
WJW26	Wujiang	38.0	−30.6	29.2	7.2	6.3	100	214.6	−24.9	12.1	1.7	151.5	39
WJW27	Daxiaohe	4.2	−28.0	10.1	1.2	4.1	24	45.4	−24.4	7.9	1.5	36.9	7
WJW28	Wujiang			26.0		8.2	100			16.8		239.1	75
WJW29	Wujiang					5.9		108.5	−24.9	10.7	1.4	91.1	28
WJW30	Hongduhe			33.4		1.9	100	62.6	−25.4	23.7	2.1	35.0	100
WJW31	Wujiang	103.6	−25.9	16.5	20.1	6.2	73	105.0	−26.0	18.0	1.5	85.7	85
WJW32	Wujiang	20.0			3.6	6.6		90.5	−26.0	11.5	1.9	55.8	35
WJW33	Furongjiang	17.5	−27.5	27.6	1.9	10.8	100	25.5	−24.7	10.2	0.7	46.7	25
WJW34	Wujiang	36.2	−27.0	8.1	5.4	8.0	8	87.0	−25.1	13.5	2.1	50.6	50
Yuanjiang (Qingshuijiang)													
YJW01[c]	Qingshuijiang	15.6	−25.9	14.8	3.5	5.3	60	44.6	−25.8		29.7	1.8	
YJW02	Balahe			15.5		5.7	65	40.2	−24.3	10.3	12.1	4.0	25
YJW03	Qingshuijiang			10.8		4.7	29	27.7	−24.6	12.2	10.7	3.1	40
YJW04	Qingshuijiang	7.7	−23.8	7.7	1.4	6.7	5	7.0	−24.2	8.2	3.8	2.2	9
YJW05	Liangjiang	8.2	−26.2	19.7	8.9	1.1	98	24.5	−27.6	9.6	14.0	2.1	20
YJW06	Qingshuijiang	31.9	−26.2		8.1	4.7		30.9	−26.7	7.4		4.7	3
YJW07	Qujiang	6.2	−23.3	10.5	1.0	7.1	27	35.3	−27.4	8.0	5.8	7.3	8
YJW08	Qingshuijiang					6.1		25.8	−27.4	7.3		3.2	2
Yuanjiang (Wuyanghe)													
YJW09	Wuyanghe	6.4	−27.1	9.5	1.9	4.1	19	29.2	−27.3	6.4	5.9	5.9	0
YJW10	Longjianghe	7.0	−27.6	13.6	3.4	2.5	51	27.1	−27.2	6.9	32.5	1.0	0
YJW11	Wuyanghe			11.6		2.3	35	32.6	−27.7	5.9	4.7	8.4	0
YJW12	Wuyanghe			9.9		5.9	22	106.7	−25.4	6.1	38.8	3.3	0
YJW13	Chebahe			15.4		0.5	65	132.1	−24.5		44.0	3.6	
YJW14	Wuyanghe	4.7	−24.7	11.5	0.9	6.1	35	27.4	−27.7	8.2	5.0	6.6	9
Yuanjiang													
YJW15	Yuanjiang	21.7	−25.9		4.4	5.9		31.0	−26.8	7.3	8.3	4.5	2

[a] OC = POC in mg L^{-1}/TSS in mg L^{-1} × 100%.
[b] WJW = Wujiang Water.
[c] YJW = Yuanjiang Water.

Oades, 1997). That is why the Wujiang was characterised by high POC (Fig. 2a and b). But, in-stream photosynthesis can also produce high POC at the summer high-water stage. For example, the high POC contents for the high-water stage of the Wuyanghe (Fig. 2c) are probably attributable to in-stream photosynthesis as discussed in the next section.

The precipitation pattern is a major factor regulating POC variations in a river system, especially in tropical and subtropical mountainous areas (Kao and Liu, 1996). The whole of Guizhou is affected by the East Asian and South Asian monsoon systems, under which it is cold and dry in winter (mean temperature: 2–10 °C in January) while it is warm and moist in summer (mean temperature: 20–26 °C in July) (CCGPC, 1988). The summer monsoons carry copious rains with some regional heterogeneity in the amount of precipitation. Rain mainly occurs during the period from May to September, in which it can account for more than 65% of the mean annual rainfall (1000–1400 mm) (CCGPC, 1988).

Given this background, it is thus expected that at the summer high-water stage, a river in mountainous areas will have a rapid increase in POC. This is clearly shown on the plot of the ratio (R_{POC}) of the summer high-water stage POC to the winter low-water stage POC against downstream distance (Fig. 6). For the Wujiang, the increase in POC was more distinct. Most R_{POC} values (15 out of 20, Fig. 6a) were >1. Samples with R_{POC} values <1 were from tributaries

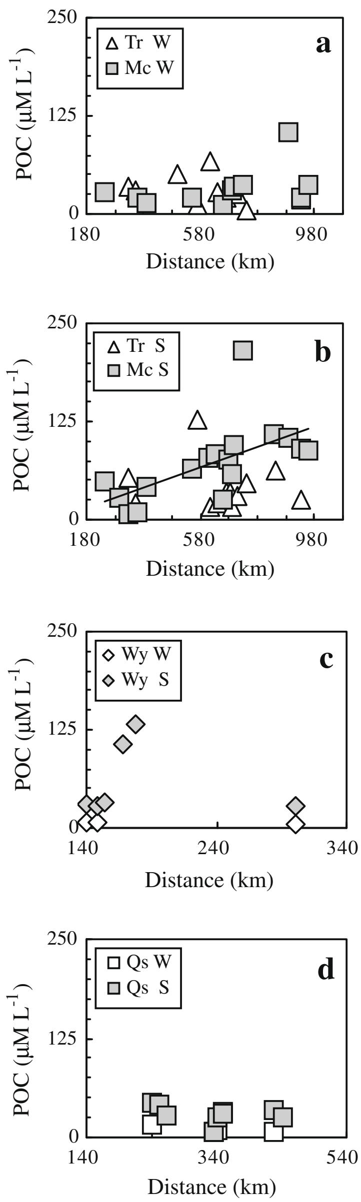

Fig. 2. POC content against downstream distance for the winter Wujiang (a), summer Wujiang (b), Wuyanghe (c), and Qingshuijiang (d). The regression line ($r^2 = 0.37$, $n = 17$, $p < 0.01$) is obtained from the summer mainstream Wujiang samples. The point for WJW11 (Qingshuihe) is outside Fig. 2b since its POC content (284.8 μM L^{-1}) is higher than the maximum on the *y*-axis (250 μM L^{-1}). Tr = Tributary. Mc = Main Channel. Wy = Wuyanghe. Qs = Qingshuijiang. W = Winter. S = Summer.

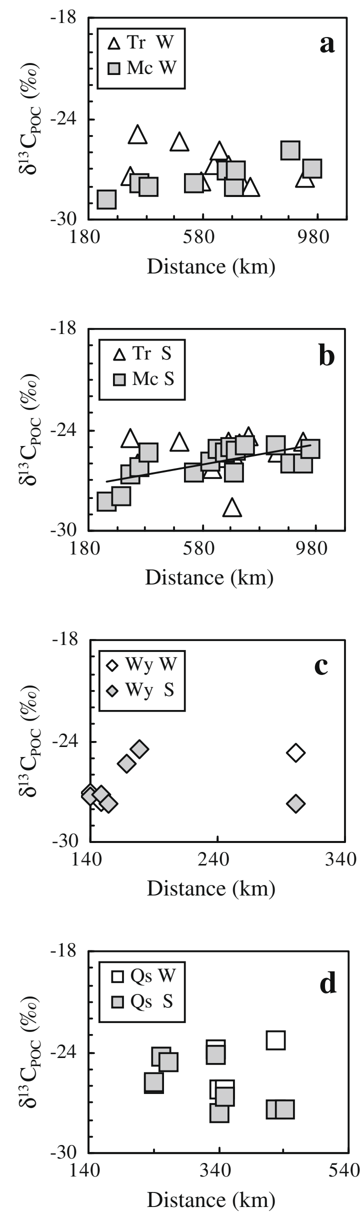

Fig. 3. $\delta^{13}C_{POC}$ value against downstream distance for the winter Wujiang (a), summer Wujiang (b), Wuyanghe (c), and Qingshuijiang (d). The regression line ($r^2 = 0.43$, $n = 17$, $p < 0.01$) is obtained from the summer mainstream Wujiang samples. The definitions of abbreviations are the same as in Fig. 2.

or reservoirs of its mainstreams. As discussed in the following section, soil (not the river ecosystem itself) was the main supplier of POC. Hence, these high R_{POC} values indicate that soil erosion mainly took place on uplands near the main channel. On the other hand, the Wuyanghe and Qingshuijiang with minor soil erosion also had high R_{POC} values (Fig 6b), which was caused by in-stream photosynthesis.

5.2. Sources of POC

5.2.1. Carbon isotope compositions of soils, and terrestrial and aquatic plants

Leaves from 21 land plant samples (11 C_3 plants and 10 C_4 plants) were separated for $^{13}C/^{12}C$ analysis. These data were pooled with another 72 for land plants in the same catchment (65 C_3 plants and 7 C_4 plants) (Zhu, 2006). Finally, a mean $\delta^{13}C$ value of $-28.5 \pm 1.4‰$ ($n = 76$) and a mean $\delta^{13}C$ value of $-13.4 \pm 1.7‰$ ($n = 18$) were obtained for terrestrial C_3 and C_4 plants, respectively. They spanned a range from $-32.7‰$ to $-25.6‰$, and from $-17.8‰$ to $-11.7‰$, respectively. These values were comparable with the range of $-34‰$ to $-24‰$ for C_3 plants, and $-19‰$ to $-6‰$ for C_4 plants, respectively, reported by Smith and Epstein (1971). Soil organic matter (including litterfall) is eventually a mixture of residues from the overlying vegetation, which is composed of C_3 and C_4 plants. The above-mentioned $\delta^{13}C$ values of C_3 and C_4 plants can be used to delimit the upper and lower limits of the mean C isotope composition of soil organic matter.

The study rivers have high flow rates, rocky beds and banks as well as deep waters, which limit the growth of submersed, emergent and floating plants (Zhu et al., 2008). Therefore, the major forms of aquatic plants are planktonic algae. $\delta^{13}C$ values of aquatic plants are dependant on photosynthesis pathways and available

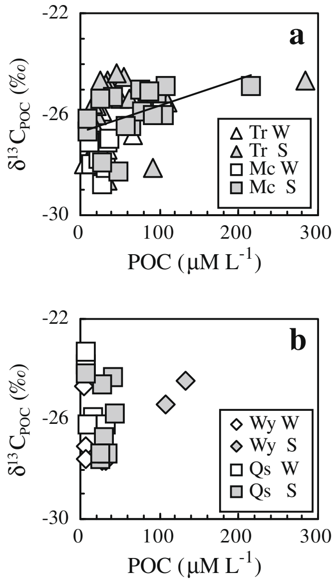

Fig. 4. A plot of $\delta^{13}C_{POC}$ value versus POC content for the Wujiang (a), Wuyanghe (b) and Qingshuijiang (b). The regression line ($r^2 = 0.25$, $n = 17$, $p < 0.05$) is obtained from the summer mainstream Wujiang samples. The definitions of abbreviations are the same as in Fig. 2.

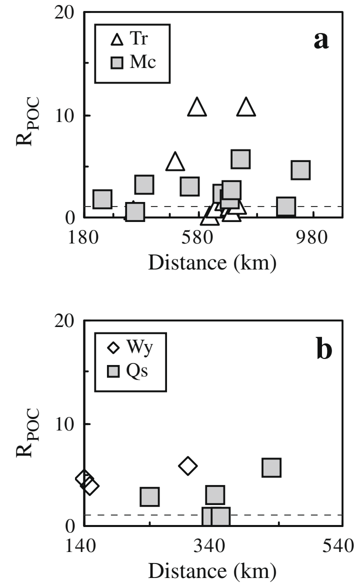

Fig. 6. Ratios (R_{POC}) of the high-water stage POC to the low-water stage POC against downstream distance for the Wujiang (a), Wuyanghe (b) and Qingshuijiang (b). The dotted line denotes $R_{POC} = 1$. The definitions of abbreviations (Tr, Mc, Wy, and Qs) are the same as in Fig. 2.

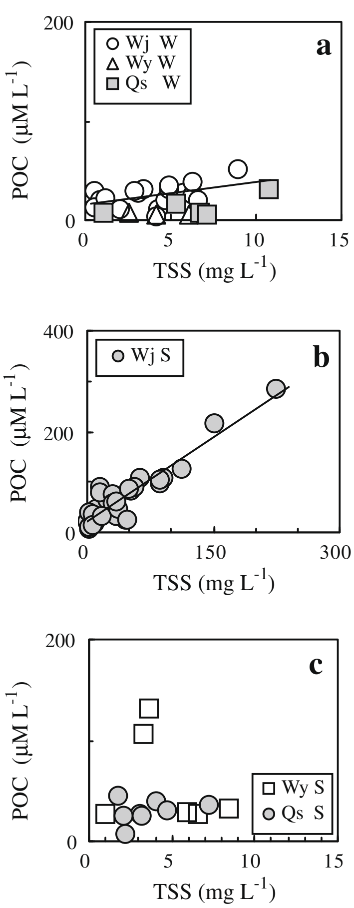

Fig. 5. TSS versus POC content for the winter Wujiang, winter Wuyanghe and winter Qingshuijiang (a), summer Wujiang (b), summer Wuyanghe (c), and summer Qingshuijiang (c). The regression lines in (a) ($r^2 = 0.25$, $n = 17$, $p < 0.05$) and (b) ($r^2 = 0.86$, $n = 32$, $p < 0.001$) are obtained from the winter and summer mainstream Wujiang samples, respectively. The definitions of abbreviations are the same as in Fig. 2.

DIC forms (dissolved CO_2 or HCO_3^-). In previous studies, a C isotope enrichment factor (ε) of about −23‰ between plant organic matter and HCO_3^- and about −13.5‰ between plant organic matter and dissolved CO_2 at 20 °C has been found for aquatic C_3 plants (LaZerte, 1983; Mook and Tan, 1991). Therefore, $\delta^{13}C$ values lower than −30‰ for aquatic plants are to be expected (Mook and Tan, 1991; Palmer et al., 2001). However, in waters with high primary production, the aquatic plants have higher $\delta^{13}C$ value (−22.5‰ or so). For example, a freshwater algal mat with a $\delta^{13}C$ value of −20.2‰ and epilithic algae in productive rivers with a $\delta^{13}C$ range from −21.7‰ to −20.4‰ were reported by Schell (1983) and Finlay et al. (1999), respectively. In this case, the C isotope measurements could not give unambiguous evidence for the POC origins.

5.2.2. C/N ratios of soils, and terrestrial and aquatic plants

The C/N ratio can be used as another useful indicator for the provenance of POC (Wang et al., 2004; Balakrishna and Probst, 2005). Vascular land plants have a high cellulose content while nonvascular aquatic plants contain no woody tissues. Thus, the former have C/N ratios generally equal to or larger than 20, and the latter have low C/N ratios, typically between 4 and 10 (Meyers and Ishiwatari, 1993).

An evaluation for the C/N ratio of plants and soils has to be made in order to calculate the relative contributions of terrestrial (allochthonous) versus aquatic (autochthonous) organic matter. Leaves of 21 land plants collected in the study watersheds had a mean C/N ratio of 26.4 ± 10.0 and a range from 9.4 to 44.2 while 21 soil samples (0–20 cm) showed a mean C/N ratio of 12.3 ± 2.9 and a range from 8.4 to 19.5. For the latter, four samples were analysed in this study and the rest were determined by Zhu (2006). Plant samples included wood, shrubs and grasses while soil samples covered a wide range of landscapes including forests, shrublands and grasslands. The agricultural soils with a wide geographical distribution also displayed a similar mean value and range of C/N ratio as reported by Tu (2007). Thus, the terrestrial part (plant plus soil) will have a mean C/N ratio of about 20 (26.4/2 + 12.3/2). The aquatic part (planktonic algae) has a low C/N ratio of about seven (Sterner and Elser, 2002). The C/N ratio of 13.5 (20/2 + 7/2) can be regarded as a threshold for judging the origin of organic matter. In general, a C/N ratio greater than or less than 13.5 means a predominance of terrestrial or aquatic contributions, respectively. Woody parts of a plant (such as stems and shoots) may have very high C/N ratios, such as between 50 and 1550 due to high C and low N contents (Cross et al., 2005). Therefore, in this study a C/N ratio >20 or <7 was simply considered as a complete contribution of terrestrial or aquatic, respectively. Using a two-endmember mass balance calculation, the terrestrially contributed POC fraction for each sample was determined (see f_T in Table 3).

Since most of the C/N ratios for the Wuyanghe and Qingshuijiang were less than the 13.5 threshold at both water stages (Table 3), a threshold higher than 13.5 will only influence judgment of the POC source for the Wujiang. The higher the C/N ratio for the terrestrial part, the higher the threshold. As a result, the POC in many samples for the Wujiang are inferred to be mainly contributed by in-stream processes. However, the threshold (13.5) is likely to be very close to the reality, considering that it is based on real measurements of soil and plant samples in the Wujiang catchment. Recently, more data have been accumulated to show that the C/N ratios for the surface soils in the Wujiang catchment are generally less than 20 (Zhu, 2006; Tu, 2007). Low vegetation coverage and intensive agricultural land use as well as high soil erosion in the Wujiang catchment (Table 2) make the authors wary of selecting a higher threshold.

5.2.3. Low-water stage

Aquatic photosynthesis at the low-water stage was restricted due to low-temperature (about 11 °C), as verified by a low content of chlorophyll-α (less than 2 μg L^{-1} during the period from November to February) in a reservoir, i.e., sampling site 9 of the Wujiang (Zhu et al., 2006). Thus, terrestrial ecosystems were the main source of POC.

The $\delta^{13}C_{POC}$ at the low-water stage for the Wujiang was generally higher than but very close to −30‰ (Table 3), implying a possible terrestrial litterfall origin. The C/N ratios further confirmed this judgement since the terrestrial contributions to POC were larger than 50% for most rivers (19 out of 22 samples) (see f_T in Table 3). In autumn and winter, litterfall mass will increase with the cessation of plant photosynthesis and the decrease of rainfall. Litterfall has a high C/N ratio, high organic C content and more negative $\delta^{13}C$ values (Zhu, 2006), compared with underlying soils. If this part is transported into rivers through hydrological cycles or by wind, then high C/N ratios for riverine organic matter might be expected. The Wujiang was typical of this case as most samples at the low-water stage had C/N ratios higher than 20 (Table 3). As a whole, low $\delta^{13}C$ value, high organic C content, high C/N ratio and low TSS for the Wujiang (Table 3) suggested that relatively more litterfall than soil passed into rivers at the low-water stage.

For the Wuyanghe and Qingshuijiang, high terrestrial contributions of POC were only found in their tributaries (see f_T in Table 3). The mainstreams displayed a main contribution from the aquatic part (see f_T in Table 3). Thus, a significant amount of POC for these two rivers can be attributed to an aquatic origin.

5.2.4. High-water stage

The $\delta^{13}C_{POC}$ for all three rivers at the high-water stage was much higher than −30‰, but this did not necessarily mean a terrestrial provenance. The possible interpretation is given as follows. If defining $\Delta\,\delta^{13}C_{POC}$ as the difference in $\delta^{13}C_{POC}$ between the summer high-water stage and the winter low-water stage, then this parameter had different patterns for three rivers (Fig. 7). For the Wujiang, $\Delta\delta^{13}C_{POC}$ was generally >0 (Fig. 7a) while for the Qingshuijiang it was generally <0 (Fig. 7b). The Wuyanghe is omitted because of the limited $\delta^{13}C_{POC}$ data available (Fig. 7b). The difference in $\delta^{13}C$ between soil (0–20 cm) and litterfall is generally >0.

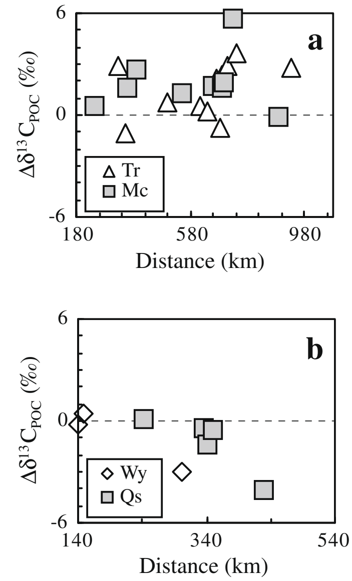

Fig. 7. Differences ($\Delta\delta^{13}C_{POC}$) in C isotope ratios of POC between the high-water stage and the low-water stage against downstream distance for the Wujiang (a), Wuyanghe (b) and Qingshuijiang (b). The definitions of abbreviations (Tr, Mc, Wy, and Qs) are the same as in Fig. 2.

For example, all 19 soil samples in the Wujiang catchment had higher $\delta^{13}C$ values than the related litterfall (Zhu, 2006). The difference ranged from 0.5‰ to 5.0‰, with 16 out of 19 samples >2‰ (Zhu, 2006). Hence, positive or negative $\Delta\delta^{13}C_{POC}$ may indicate an increased contribution of soil with respect to litterfall or an increased contribution from in-stream processes, respectively. The C/N ratios of POC for the summer Wujiang were generally greater than or close to 13.5 (19 out of 28 samples), indicating a major POC fraction being of terrestrial origin (Table 3). Six out of the remaining nine samples with C/N ratios lesser than 13.5, however, had high TSS (> 30 mg L^{-1}) and low OC (<3%), implying a terrestrial soil POC origin (WJW22, 26, 27, 29, 32 33 in Table 3). This formed a contrast to the low TSS (<8 mg L^{-1}) of the Wuyanghe and Qingshuijiang (Table 3). It was observed during the sampling period that the summer mainstream Wujiang had high contents of TSS. The turbid water has low light penetration, which greatly limits the primary production in a river ecosystem (Hough and Fornwall, 1988).

Forest and agricultural dry arable uplands can be the sources of POC. So, the question "Which source is predominant?" remains unsolved. The authors suggest the latter. The initial evidence was that the POC showed a significant downstream increase (Fig. 2b). Most of R_{POC} values larger than 1 belonged to main channel samples (Fig. 6a). Comparing the out-of-phase matching patterns of R_{POC} or $\Delta\delta^{13}C_{POC}$ between tributary and mainstream samples (Figs 6a and 7a), it could be postulated that the increase in POC in the mainstream of the Wujiang was not contributed by tributaries, and should be from the mainstream areas. Another line of evidence is that the POC for tributaries at the high-water stage was lower than for the mainstream, demonstrating that the increase in POC in mainstreams was not caused by tributaries (Fig. 2b). Secondly, a positive correlation ($r^2 = 0.24$, $n = 19$, $p < 0.05$) was found between R_{POC} and $\Delta\delta^{13}C_{POC}$ (Fig. 8a), implying that some source (agricultural uplands) with higher $\delta^{13}C$ values is regulating the C isotope composition of POC. The agricultural uplands in the riparian zones are used to plant maize, sugarcane and sorghum (Table 2), which are C_4 plants with higher $\delta^{13}C$ values. These uplands had low ratios of litterfall to soil organic matter, and hence low C/N ratios. This could be the main factor leading to decreased C/N ratios of the

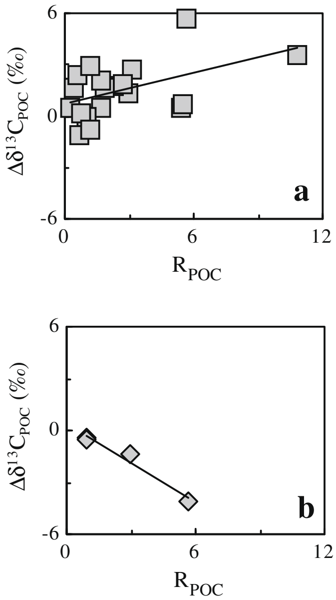

Fig. 8. A plot of $\Delta\delta^{13}C_{POC}$ versus R_{POC} for the Wujiang (a) and Qingshuijiang (b). The linear regression lines are significant in (a) ($r^2 = 0.24$, $n = 19$, $p < 0.05$) and (b) ($r^2 = 0.96$, $n = 4$, $p < 0.05$). The definitions for R_{POC} and $\Delta\delta^{13}C_{POC}$ are the same as in Figs. 6 and 7.

mainstream across the transition from the low-water stage to the high-water stage. Comparing $\delta^{13}C_{POC}$ and C/N ratios at the high-water stage with those at the low-water stage, it was found that an increase in $\delta^{13}C_{POC}$ was generally accompanied by a decrease in C/N ratio (Table 3). This further verified the enhanced soil erosion in summer. On the other hand, the increased soil erosion for the Wujiang in summer was also testified by the fact that from the low-water stage to the high-water stage, TSS increased while OC decreased greatly (Table 3). Lastly, some previous field experiments for soil erosion have demonstrated that dry arable uplands were the main source of TSS (Lin et al., 2004; FIT, 2006). The total eroded soil for the Wujiang catchment was 1.96×10^8 t a^{-1}, of which 62.1% was supplied by dry arable uplands (FIT, 2006), regardless that these uplands just accounted for 24.9% of the total drainage area (Table 2). The linear relationship between TSS and POC (Fig. 5b) is also a strong support to this argument. Lands with high vegetation coverage are generally located in the tributary watersheds of the Wujiang and far away from the main channel areas (FCRG, 1985). Compared with those lands, the agricultural uplands are easier to denude.

A positive $\delta^{13}C_{POC}$ shift ($p < 0.001$) of 1.4‰ from winter to summer was observed for the Wujiang, which could be also interpreted as due to more soils from the agricultural dry arable uplands being denuded relative to tributary lands with high vegetation coverage at the high-water stage. Soil organic matter in dry arable uplands was more enriched in ^{13}C due to plantation of C_4 plants. Moreover, the following evidence further supports this argument. From the low-water stage to the high-water stage, the C/N ratios decreased rapidly (Table 3), which is consistent with the fact that soil organic matter has a low C/N ratio, compared with litterfall. On the other hand, the distinctly increased POC (Fig. 2a) and a positive correlation ($r^2 = 0.86$, $n = 32$, $p < 0.001$) between POC and TSS (Fig. 5b) at the summer high-water stage also corroborated increased soil erosion. This interpretation is in line with the postulation mentioned in the last paragraph that the high TSS for the Wujiang should be attributed to agricultural dry arable uplands.

Although the mean $\delta^{13}C_{POC}$ in the Wuyanghe at the high-water stage was close to that at the low-water stage, its POC could be only attributed to the contribution of in-stream processes (see f_T in Table 3) because of very low C/N ratios (typically lower than 7), low TSS and increased OC at the high-water stage (Table 3).

For the Qingshuijiang, the mean $\delta^{13}C_{POC}$ at the high-water stage was lowered by 1.1‰, compared with that at the low-water stage. The Qingshuijiang was productive due to high light penetration, and hence the contribution of aquatic plants to POC could not be ruled out. The negative C isotope shift was not triggered by agricultural vegetation (e.g., rice) since the POC for the Qingshuijiang had a low C/N ratio (Table 3). A negative correlation between R_{POC} and $\Delta\delta^{13}C_{POC}$ ($r^2 = 0.96$, $n = 4$, $p < 0.05$) (Fig. 8b) existed after discarding sample 1 (which was from the karstic carbonate river, see Fig. 1b), indicating the presence of a C source with relatively lower $\delta^{13}C$ values. Thus, aquatic plants are a possible POC source (see f_T in Table 3). When TSS was mainly produced by in-stream processes, then low TSS and high OC (Table 3) for the Qingshuijiang at the high-water stage could be reasonably expected.

5.3. Conservative estimations of annual fluxes and export rates for POC

It is important to calculate the annual flux of POC transported to the Three Gorges Reservoir and to the Dongting Lake from the karstic ecosystems of Guizhou. The low-water stage (October–April) represented 35% of the total yearly discharge and the high-water stage (May–September) 65%. It is known that the POC may be inhomogeneous laterally and vertically due to gravitational and hydrodynamic effects. For the best approximation to reality, the POC flux can be derived from a depth-integrated concentration, as done by Richey et al. (1990) for the Amazon River. However, the authors' efforts to collect the depth-integrated samples were not successful since the studied rivers had high flow rates. The high flow rate for the Wujiang was produced due to large altitude differences between the origin (2260 m) and the outlet (136.5 m) (CCGPC, 1988). Therefore, in this study the concentration of the main channel sampling sites close to the outlet was used for the flux estimation. This method has frequently been used in previous studies (Balakrishna and Probst, 2005; Aucour et al., 2006). This strategy was justified, based on the following analysis. For the Wujiang, the POC at site 34 in winter was close to most of the other samples (Fig. 2a) while it was located slightly below the regression line in summer so as not to overestimate the flux (Fig. 2b). As mentioned above, several reservoirs have been constructed in the Wujiang (2, 6, 8, and 19). The terrestrial matter will have settled in these reservoirs, which will also lead to the underestimation of the POC flux. Similar logistics were also applicable to the Wuyanghe (site 14 in Fig. 2c). The same method was used for the Qingshuijiang (site 8 in summer in Fig. 2d), but at the low-water stage site 6 was used. Hence, there was an underestimated flux for the Wujiang. Overall, even if the flux estimation had some error, it did not affect the conclusions mentioned below pertaining to the POC export characteristics for all three rivers.

Aucour et al. (2006) and Galy et al. (2007) found a very good positive linear relationship of OC with Al/Si ratios of sediments in the Ganges and Brahmaputra Rivers in the Himalayas. As clay sediments with high OC tend to be suspended in the upper waters of a river, a collection of surface waters may lead to a large error for the estimation of POC fluxes. However, in the studied rivers this effect may be absent or negligible. The main reasons include: (1) the studied rivers drain mainly carbonate terrains while the Himalayan rivers have silicate-rich uplands. The major minerals in the suspended matter of the studied rivers are quartz, calcite and dolomite; clay minerals are of minor importance (Liu, 2007). (2) From Aucour et al. (2006) and Galy et al. (2007), it can be observed that there is no significant relationship between OC and Al/Si ratios when the latter are below 0.2. This means that under or below this ratio, the clay content in suspended matter does not significantly affect the estimation of POC fluxes. Thus, low contents of clay

Table 4
Fluxes and export rates for POC of three rivers.

River	Carbon flux (10^{10} g a^{-1})	Export rate (mg m^{-2} a^{-1})
Wujiang	3.123	466
Wuyanghe	0.084	129
Qingshuijiang	0.372	218

minerals in suspended matter in the studied rivers prevent a significant bias against the estimation of POC fluxes.

Flux (F) is related to concentration (C) and discharge (D) through the equation:

$$F = C \times D$$

In this case, F should be the sum of the fluxes at the low-water stage (F_L) and high-water stage (F_H), then,

$$F = F_L + F_H = C_L \times D_L + C_H \times D_H = C_L \times D \times 35\% + C_H \times D \times 65\%$$

Combining the discharge (Table 1) and concentration data (Table 3), the POC fluxes were obtained (Table 4).

The C export rate was obtained from the C flux divided by the catchment area (Table 4). Of the three rivers, the Wujiang ranked first for POC export rate (Table 4). Its rate was twice as high as those for the other two rivers. On the other hand, the Qingshuijiang did not show a significant increase in POC export rate, despite its higher ratio of discharge to catchment area (Table 1). Since the POC for the Wuyanghe and Qingshuijiang was mainly contributed by aquatic photosynthesis, the true POC export rate contributed by terrestrial ecosystems would be much less than the above values. Meanwhile, due to the settling of TSS in several reservoirs, the true POC flux and POC export rate for the Wujiang would be much higher than the estimations. For example, it has been estimated that the Wujiang annually transports 1.1×10^8 t TSS into the Three Gorges Reservoir (FDGP, 2003). Given a mean POC content of 0.1% in TSS, the POC flux will be 11×10^{10} g a^{-1}. This value is three times higher than the authors' estimation (Table 4), which further amplifies the severity of ecosystem degradation in the Wujiang catchment.

To some extent, the Three Gorges Reservoir is like an ocean. It collects the POC transported by its tributaries. The fate and transformation of POC and other C species will essentially exert influences on the structure and function of this large aquatic ecosystem, and in the long term will affect the related estuaries. Increased riverine N load from agricultural and industrial activities and high light penetration created by man-made impoundments expose reservoirs and lakes to a high risk of eutrophication. Hence, much work pertaining to C cycles in tributaries of the Three Gorges Reservoir should be undertaken in the near future.

6. Conclusions

This is the first report on POC biogeochemistry within the catchments of the Three Gorges Reservoir. It presents an approach on the association between watershed soil erosion caused by contrasting land use and riverine POC cycles, based on the combined use of C isotopes, C/N ratio, OC, and TSS analyses. The disparity in land use, forest coverage and soil erosion rate between two basins is so distinct as to show a sensitive response of riverine POC sources to land use activities. By comparing the source difference and spatio-temporal variations of POC transported by the karstic Wujiang, karstic Wuyanghe, and non-karstic Qingshuijiang, the following conclusions were drawn:

(1) The Wujiang, Wuyanghe, and Qingshuijiang were all characterised by increased POC at the summer high-water stage. A distinct difference in terms of POC source was present for the Wujiang and Yuanjiang. The POC for the Wujiang was supplied by terrestrial ecosystems while the POC for the Wuyanghe and Qingshuijiang was from aquatic photosynthesis. It was inferred that soil erosion occurred in the agricultural ecosystems located along the main channel riparian zones of the Wujiang, which should be the target areas for ecological remediation.

(2) As the POC export rates indicated, the soil erosion rate of the Wujiang catchment was three times as high as that of the Wuyanghe or twice as high as that of the Qingshuijiang (Table 4), showing the rapid degradation of the terrestrial ecosystems in the Wujiang catchment.

(3) The Wujiang supplied about 1/8 of the discharge to the Three Gorges Reservoir, but it provided more than 1/5 of the total suspended solids. Of all three rivers, the Wujiang had the highest POC export rate (Table 4), giving rise to concern that the severe soil erosion in the Wujiang catchment poses a potential threat (decreased discharge and increased TSS load) to the health of this large artificial aquatic ecosystem, i.e., the Three Gorges Reservoir. It should be noted that the high TSS for the Wujiang may be an effective inhibitor for eutrophication as its POC in summer had a predominant terrestrial provenance.

(4) The $\delta^{13}C_{POC}$ values for the three rivers were $>-30‰$, within the range for terrestrial plants. Since the $\delta^{13}C$ values for planktonic algae were not known (though a value $>-30‰$ can be inferred from this dataset), the C isotope composition alone in this study was not a useful indicator for POC origins, but its combination with C/N ratio, OC and TSS is an effective tool for the characterisation of riverine POC provenance. High $\delta^{13}C$ values, high C/N ratios, low OC and high TSS may correspond to a terrestrial soil origin (such as the summer Wujiang) while low $\delta^{13}C$ values, low C/N ratios, high OC and low TSS may hint at a predominant contribution of in-stream processes (such as the summer Wuyanghe).

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References

An, H.P., Zhou, J.W., 2001. Dry arable uplands in karstic mountainous areas of Guizhou Province: current status and countermeasures during the period from farmland to forest. Bull. Soil Water Conserv. 21, 77–80 (in Chinese with an English abstract).

Aucour, A.M., France-Lanord, C., Pedoja, K., Pierson-Wickmann, A.C., Sheppard, S.M.F., 2006. Fluxes and sources of particulate organic carbon in the Ganga–Brahmaputra river system. Global Biogeochem. Cycles 20. doi:10.1029/2004GB002324 (GB2006).

Balakrishna, K., Probst, J.L., 2005. Organic carbon transport and C/N ratio variations in a large tropical river: Godavari as a case study, India. Biogeochemistry 73, 457–473.

Barth, J.A.C., Veizer, J., Mayer, B., 1998. Origin of particulate organic carbon in the upper St. Lawrence: isotopic constraints. Earth Planet. Sci. Lett. 162, 111–121.

Benner, R., Luochouarn, P., Amon, R.M.W., 2005. Terrigenous dissolved organic matter in the Arctic Ocean and its transport to surface and deep waters of the North Atlantic. Global Biogeochem. Cycles 19. doi:10.1029/2004GB002398 (GB2025).

Beusen, A.H.W., Dekkers, A.L.M., Bouwman, A.F., Ludwig, W., Harrison, J., 2005. Estimation of global river transport of sediments and associated particulate C, N, P. Global Biogeochem. Cycles 19. doi:10.1029/2005GB002453 (GB4S05).

Bianchi, T.S., Wysocki, L.A., Steward, M., Filley, T.R., McKee, B.A., 2007. Temporal variability in terrestrially-derived sources of particulate organic carbon in the lower Mississippi River and its upper tributaries. Geochim. Cosmochim. Acta 71, 4425–4437.

Bird, M.I., Giresse, P., Ngos, S., 1998. A seasonal cycle in the carbon-isotope composition of organic carbon in the Sanaga River, Cameron. Limnol. Oceanogr. 43, 143–146.

Buchanan, D.L., Corcoran, B.J., 1959. Sealed tube combustions for the determination of carbon-14 and total carbon. Anal. Chem. 31, 1635–1638.

CCGPC (Compilation Commission for Guizhou Province Chorography), 1988. Guizhou Province Chorography: Geography. Guizhou People's Press, Guiyang 595-1131 (in Chinese).

Craig, H., 1953. The geochemistry of stable carbon isotopes. Geochim. Cosmochim. Acta 3, 53–92.

Cross, W.F., Benstead, J.P., Frost, P.C., Thomas, S.A., 2005. Ecological stoichiometry in freshwater benthic systems: recent progress and perspectives. Freshwater Biol. 50, 1895–1912.

CWRC (Changjiang Water Resources Commission), 2007. An Introduction to the Changjiang River Systems. <http://www.cjw.com.cn> (in Chinese).

Deegan, L.A., Garritt, R.H., 1997. Evidence for spatial variability in estuarine food webs. Marine Ecol.-Progress Ser. 147, 31–47.

Doucett, R.R., Power, G., Barton, D.R., Drimmie, R.J., Cunjak, R.A., 1996. Stable isotope analysis of nutrient pathways leading to Atlantic salmon. Can. J. Fish. Aquat. Sci. 53, 2058–2066.

Farquhar, G.D., O'Leary, M.H., Berry, J.A., 1982. On the relationship between carbon isotope discrimination and the intercellular carbon dioxide concentration in leaves. Aust. J. Plant Physiol. 9, 121–137.

FCRG (Forecasting and Countermeasure-taking Research Group for Environmental Changes of Guizhou Province), 1985. Forecasting Year 2000 Environmental Changes of Guizhou Province, vol. I: Forecasting and Countermeasure-taking Research for Environmental Changes of Guizhou Province. Environmental Protection Bureau of Guizhou Province, Guizhou. pp. 1–28 (in Chinese).

FDGP (Forestry Department of Guizhou Province), 2003. A Project for Protecting Natural Forest Resources: Action Plans of Guizhou Province (in Chinese).

Finlay, J.C., 2003. Controls of streamwater dissolved inorganic carbon dynamics in a forested watershed. Biogeochemistry 62, 231–252.

Finlay, J.C., Power, M.E., Cabana, G., 1999. Effects of water velocity on algal carbon isotope ratios: implications for river food web studies. Limnol. Oceanogr. 44, 1198–1203.

FIT (Field Investigation Team for the Upper Reaches of the Yangtze River and Rivers in Southwestern China), 2006. Dry arable uplands are the main source places for water and soil erosion in the upper reaches of the Yangze River. Scientific Investigation Briefing (14), <http://www.mwr.gov.cn/ztbd/sbkkzt/20061015/79923.asp> (in Chinese).

France-Lanord, C., Derry, L.A., 1997. Organic carbon burial forcing of the carbon cycle from the Himalayan erosion. Nature 390, 65–67.

Galy, V., France-Lanord, C., Beyssac, O., Faure, P., Kudrass, H., Palhol, F., 2007. Efficient organic carbon burial in the Bengal fan sustained by the Himalayan erosional system. Nature 450, 407–410.

Guo, L., Macdonald, R.W., 2006. Source and transport of terrigenous organic matter in the upper Yukon River: evidence from isotope (δ^{13}C, Δ^{14}C, and δ^{15}N) composition of dissolved, colloidal, and particulate phases. Global Biogeochem. Cycles 20. doi:10.1029/2005GB002593 (GB2011).

He, T.B., Jie, D.Y., 2002. Water and soil loss in dry arable uplands of Guizhou Province: Current status and renovation measures. J. Guizhou Univ. (Agri. Biol. Sci.) 21, 280–286 (in Chinese with an English abstract).

Hedges, J.I., Oades, J.M., 1997. Comparative organic geochemistries of soils and marine sediments. Org. Geochem. 27, 319–361.

Hellings, L., Dehairs, F., Tackx, M., Keppens, E., Baeyens, W., 1999. Origin and fate of organic carbon in the freshwater part of the Scheldt Estuary as traced by stable carbon isotope composition. Biogeochemistry 47, 167–186.

Hough, R.A., Fornwall, M.D., 1988. Interactions of inorganic carbon and light availability as controlling factors in aquatic macrophyte distribution and productivity. Limnol. Oceanogr. 33, 1202–1208.

Humborg, C., Ittekkot, V., Cociasu, A., Bodungen, B.V., 1997. Effect of Danube River dam on Black Sea biogeochemistry and ecosystem structure. Nature 386, 385–388.

Kao, S.J., Liu, K.K., 1996. Particulate organic carbon export from a subtropical mountainous river (Lanyang Hsi) in Taiwan. Limnol. Oceanogr. 41, 1749–1757.

Kendall, C., Silva, S., Kelly, V.J., 2001. Carbon and nitrogen isotopic compositions of particulate organic matter in four large river systems across the United States. Hydrol. Process. 15, 1301–1346.

LaZerte, B.D., 1983. Stable carbon isotope ratios: Implications for the source of sediment carbon and for phytoplankton carbon assimilation in Lake Memphremagog, Quebec. Can. J. Fish. Aquat. Sci. 40, 1658–1666.

Lin, C.H., Xie, D.Y., Tu, C.L., Zhang, X.M., He, T.B., Zhang, H.L., Ji, S., He, F.F., 2004. Comprehensive use and renovation of dry arable uplands in mountainous areas of Guizhou. Res. Soil Water Conserv. 11, 211–213 (in Chinese with an English abstract).

Liu, C.Q., 2007. Earth Surface Biogeochemical Processes and Mass Cycles: Karstic Catchment Erosions and Bioelements Cycles in Southwest China. Science Press, Beijing. pp. 166–169 (in Chinese).

Ludwig, W., Probst, J.-L., 1998. River sediment discharge to the oceans: present-day controls and global budgets. Am. J. Sci. 298, 265–295.

Mao, Z.Z., 1992. Ecological and geological environments for the Wujiang drainage. Geol. Guizhou 9, 224–233 (in Chinese with an English abstract).

Martinelli, L.A., Ballester, M.V., Krusche, A.V., Victoria, R.L., De Camargo, P.B., Bernardes, M., Ometto, J.P.H.B., 1999. Land cover changes and δ^{13}C composition of riverine particulate organic matter in the Piracicaba River Basin (southeast region of Brazil). Limnol. Oceanogr. 44, 1826–1833.

MEP (Ministry of Environmental Protection of the People's Republic of China), 2001. Water Pollution Control Program for the Three Gorges Reservoir: 2001–2010 (in Chinese).

Meybeck, M., 1982. Carbon, nitrogen, and phosphorus transport by world rivers. Am. J. Sci. 282, 401–450.

Meyers, P.A., Ishiwatari, R., 1993. Lacustrine organic geochemistry – an overview of indicators of organic matter sources and diagenesis in lake sediments. Org. Geochem. 20, 867–900.

Mook, W.G., Tan, F.C., 1991. Stable carbon isotopes in rivers and estuaries. In: Degens, E.T., Kempe, S., Richey, J.E. (Eds.), Biogeochemistry of Major World Rivers. John Wiley, New York, pp. 345–364.

Otero, E., Culp, R., Noakes, J.E., Hodson, R.E., 2000. Allocation of particulate organic carbon from different sources in two contrasting estuaries of southeastern USA. Limnol. Oceanogr. 45, 1753–1763.

Palmer, S.M., Hope, D., Billeft, M.F., Dawson, J.J.C., Bryant, C.L., 2001. Sources of organic and inorganic carbon in a headwater stream: evidence from carbon isotope studies. Biogeochemistry 52, 321–338.

PGGP (People's Government of Guizhou Province), 2005. The Proclamation for Soil and Water Loss in Guizhou Province. Department of Water Resources of Guizhou Province, Guizhou (in Chinese).

Richey, J.E., Hedges, J.I., Devol, A.H., Quay, P.D., Victoria, R., Martinelli, L., Forsberg, B.R., 1990. Biogeochemistry of carbon in the Amazon River. Limnol. Oceanogr. 35, 352–371.

Schell, D.M., 1983. Carbon-13 and carbon-14 abundances in Alaskan aquatic organisms: delayed production from peat in Arctic food webs. Science 219, 1068–1071.

SDG (Science and Technology Department of Guizhou Province, Development and Reforming Commission of Guizhou Province, and Guizhou Normal University), 2006. Atlas for Degradation Control of Karstic Ecosystems in Guizhou Province (2006–2050). Guizhou People's Press, Guiyang. 1–198 (in Chinese).

Smith, B.N., Epstein, S., 1971. Categories of ^{13}C/^{12}C ratios for higher plants. Plant Physiol. 47, 380–384.

Sterner, R.W., Elser, J.J., 2002. Ecological Stoichiometry: The Biology of Elements From Molecules to the Biosphere. Princeton University Press, Princeton.

Tao, F.X., Aucour, A.M., Sheppard, S.M.F., Liu, C.Q., Leng, X.T., Wang, S.L., Liu, G.S., Xu, W.B., 2001. Evaluation of the sealed-tube low temperature combustion method for the ^{13}C/^{12}C and ^{2}H/^{1}H ratio determinations of cellulose nitrate. Chin. J. Chem. 19, 1089–1096.

Tu, C.L., 2007. Geochemical studies of soil organic carbon under different land use practices in Guiyang, Southwest China. Unpublished Ph.D. Dissertation, Institute of Geochemistry of the Chinese Academy of Sciences (in Chinese with an English abstract).

Wang, X.C., Chen, R.F., Gardner, G.B., 2004. Sources and transport of dissolved and particulate organic carbon in the Mississippi River estuary and adjacent coastal waters of the northern Gulf of Mexico. Mar. Chem. 89, 241–256.

Wang, X.F., Veizer, J., 2000. Respiration–photosynthesis balance of terrestrial aquatic ecosystems, Ottawa area, Canada. Geochim. Cosmochim. Acta 64, 3775–3786.

Wu, Z.J., 2001. Water and soil loss in the Qiandongnan prefecture: Current status, causes and control strategies. Forest Invent. Plan. 26, 60–63 (in Chinese with an English abstract).

Zhu, J., Liu, C.Q., Wang, Y.C., Li, S.L., Li, J., 2006. Temporal and spatial variations of dissolved silicon in the Wujiangdu Reservoir. Adv. Water Sci. 17, 330–333 (in Chinese with an English abstract).

Zhu, J.Y., Li, M.J., Fang, C.Z., 2008. Wetlands in Guizhou Province. <http://www.ecdc.net.cn/newindex/chinese/page/tumen/shidi_baohu/02_17.htm> (in Chinese).

Zhu, S.F., 2006. Contents and isotopic compositions of soil organic carbon in typical terrestrial ecosystems of Guizhou, Southwest China. Unpublished Ph.D. Dissertation, Institute of Geochemistry of the Chinese Academy of Sciences (in Chinese with an English abstract).